

# THE EFFECT OF COMBINING BORON NITRIDE AND FLUOROELASTOMER ON MELT FRACTURE IN EXTRUSION BLOW MOULDING\*

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## Abstract

*Boron Nitride (BN) is a new polymer processing aid, which not only eliminates surface melt fracture in the extrusion of molten polymers but it postpones the critical shear rate for the onset of gross melt fracture to significantly higher values depending on resin type and additive concentration. In this work, the influence of BN powder as a polymer processing additive is first examined in the extrusion of blow molding of high-density polyethylene (HDPE) resins in order to evaluate its usefulness and performance in operations other than simple extrusion. The equipment used includes both a Battenfeld/Fisher 50mm-extrusion blow moulding machine and parallel-plate rheometer. Two types of HDPE, which are blended with boron nitride at various concentration levels, are tested accordingly. It is found that the degree of BN dispersion, characteristics of the HDPE resins, extrusion temperature and induction time play an important role in eliminating melt fracture. Finally, the influence of combining BN with fluoroelastomer as potentially better processing aids on the melt fracture is examined. It is found that this combination is a superior processing aid allowing extrusion blow molding at very high shear rates.*

**Key words:** Boron Nitride, Fluoroelastomer, Blow Molding, Melt Fracture, Processing Aids

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\* This paper will be submitted for the next ANTEC conference (ANTEC-2001), and to the Journal of Vinyl and Additive technology.

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## Introduction

Extrusion blow moulding is one of the most important processes for polymer conversion. However, it is known that in many commercially important melt extrusion operations, including film blowing, blow molding, profile extrusion, and various coating flows, flow instabilities occur [1, 2]. In these processes, the polymeric melt emerging from the die often shows surface distortions at throughput rates above a critical value. As a result of these instabilities, the final product becomes unattractive and commercially unacceptable. 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 melt fracture or sharkskin) or severe irregular distortions at higher throughput rates (gross melt fracture) [3].

Therefore, it is obvious that the rate of production in these processes is seriously affected by the onset of these flow instabilities. To increase the process output, one must either eliminate melt fracture or postpone it to higher rates. The most common approach to achieve this objective is the use of *processing aids*. 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 masterbatch. 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 melt fracture and the so-called stick-slip (oscillating or cyclic) melt fracture. To the best of our knowledge, they do not appear to have any noticeable effect on the extrudate appearance in the gross melt fracture region. Moreover the use of polymer processing aids permit extrusion using narrower die gaps at lower melt temperatures. Note that higher temperatures minimize melt fracture and accentuate bubble instability in film blowing [4].

Recently, it was reported that compositions containing fine boron nitride (BN) particles can be successfully used as processing aids. These compositions not only may eliminate sharkskin melt fracture,

but also may substantially postpone gross melt fracture to significantly higher shear rates well within the gross melt fracture region in the extrusion of polyolefins and fluoropolymers [5-8]. Boron nitride is a solid lubricant, whose structure resembles that of graphite. 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, it initiates the nucleation of voids in polymer extrudate. During the extrusion of fluoropolymers or polyolefins with BN particles, the maximal shear rate at which the extrudate appears smooth is usually orders-of-magnitude higher than that which can ordinarily be achieved in the absence of this additive. More importantly, this maximal shear rate is usually much higher than that at which the virgin resin exhibits gross melt fracture. This means that BN, unlike fluoropolymers in the extrusion of polyethylene, can eliminate not only surface and stick-slip melt fracture but also may significantly delay the onset of gross melt fracture to much higher shear rates.

In another recent study, it has been demonstrated that the combination of BN and fluoroelastomer is a superior processing aid than either of these two used individually [6, 9, 10, 11]. Teflon<sup>®</sup> and Viton<sup>®</sup> were used in combination to a BN powder in capillary and wire coating extrusion of a m-LLDPE. It was shown that while Teflon<sup>®</sup> and Viton<sup>®</sup> cause a significant reduction in the extrusion pressure drop, BN is a superior processing aid and that the combination of BN+ Teflon<sup>®</sup> and BN+Viton<sup>®</sup> are even superior processing aids than ever conventional known ones today.

In this study, we use BN powder and the combination of BN+Viton<sup>®</sup> in extrusion blow molding of three types of HDPE, in order to evaluate the performance of these processing aids in operations other than profile extrusion. The objective of the work is to study the effect of the boron nitride concentration on the rheology and processability of two types HDPE as they can be assessed by means of a parallel plate rheometer and a blow molding machine respectively.

## Experimental

**Materials.** BN having an average particle size of 5-10  $\mu\text{m}$ , is used in our blow moulding extrusion experiments. CTF5 has unique properties and its effect on melt fracture in profile extrusion has been discussed elsewhere [8]. Three resins are studied, namely a high molecular weight high-density polyethylene (Resin A) and two intermediate molecular weight high-density polyethylene (Resin B and C). Resin A is a high molecular weight high-density polyethylene resin with a broad molecular weight distribution. This resin is designed for use in the blow moulding of large parts such as shipping containers in sizes from 5 to 50 gallons. Resin B and C are a high-density polyethylene resin with an intermediate molecular weight distribution. These resins are intended primarily for use in intermittent high shear rate blow moulding equipment designed for high-speed production of blow moulded containers. Some of the chemical and physical properties of both resins are listed in Table 1. Note that the melt index and the flow index of Resin A are much lower than that of Resins B and C.

A twin screw preparation mixer was employed to introduce BN into the resins. A masterbatch of 5-wt % BN with virgin HDPE was prepared by using a preparation mixer. A desired final concentration of the materials was obtained by mixing the pure HDPE with the masterbatch directly inside the extruder of the blow molding unit during the experiments. Table 2 summarizes all the blends prepared and studied. Resins A and B are used to study the effect of BN on the melt fracture behavior in extrusion blow molding and Resin C is used to study the effect of combining BN and Viton<sup>®</sup> on its melt fracture behavior again in extrusion blow molding.

**Measurements.** A Battenfeld/Fisher 50mm extrusion blow moulding machine was used in this study. Compositions with BN at various concentrations of each type of HDPE were tested in a wide range of die gaps, extrusion temperatures and induction times. In order to assess the effect of BN and the combination of BN+Viton<sup>®</sup> on the rheology of the polymers, linear viscoelastic measurements were per-

formed. This type of experiments usually serves as a measure of possible structure formation at certain time scales. The parallel-plate rheometer for these linear viscoelastic experiments was Rheometrics System V with plates of diameter equal to 25 mm. Frequency sweep experiments were performed in a frequency range from 0.02 to 100 rad/s. The working temperature was 190°C for Resin A and 185°C for Resins B and C. Processing below these temperatures may cause damage of the extrusion screw inside the extruder. Pictures of the extrudate (bottle) surface of each type resin with and without BN were also taken by using a 35mm camera.

## Results and Discussion

**Linear viscoelastic measurements.** To study possible effects of the BN addition to the resin on its rheology, linear oscillatory shear experiments were carried out for Resins A, B and C using a Rheometrics System IV rheometer equipped with the parallel-plate geometry. Frequency sweep experiments for Resin A and Resin B with and without BN were carried out at 190°C and 185°C respectively. Figure 1 plot the storage and loss moduli of Resins A at the corresponding processing temperatures. No significant difference was found in the linear viscoelastic behavior of the pure and BN-filled and BN+Viton<sup>®</sup>-filled resins. This is exactly what has been observed for most other BN powders reported previously.

**Extrusion blow moulding.** Experiments were first carried out with pure resin in order to prevent any accumulation of BN inside the unit. The BN filled resin were then evaluated. Equilibrium extrusion condition were ensured by using the same die that were reserved for BN and operating for at least 10 minutes with a given compound before the readings were taken. The extruder was purge and the die was cleaned carefully before a different compound was tested.

Figures 2 and 3 show the effect of shear rate at the die exit on the head pressure of Resins A and B at the die gap of 0.5mm respectively. The screw speed was 30 rpm. The shear rate in the blow moulding

unit can be calculated as:

$$\dot{\gamma}_A = \frac{6Q}{\pi(R_o + R_i)(R_o - R_i)^2} \quad (1)$$

where  $Q$  is the volumetric flow rate,  $R_o$  is the radius of the mandrel and  $R_i$  is the radius of the die. It can be seen from Figure 2 and 3 that the addition of BN shifts the flow curve to lower head pressure values. In other words, higher shear rates (flow rates) can be obtained at the same head pressure in the presence of BN. Furthermore, this means that the head pressure can be reduced at certain shear rates with the addition of BN for both resins. The reduction in pressure drop with the addition of 1000ppm BN is of the order of 3 to 10 %. The data points in Figures 2 and 3 represent averages of two runs. It should be noted that this reduction was not due to the experimental error as reproducibility was checked to be within 1% ( $\pm 20$ psia).

**Effect of induction time and extrusion temperature.** Figure 4 plots transient extrusion experiments for resin A with and without BN. The head pressure is plotted as a function of time for pure Resin A and Resin A containing 250ppm and 1000ppm of BN. It can be seen that the final steady-state head pressure is different depending on the used BN concentration. Higher BN concentration reduces further the steady-state pressure. It should be noted that there is a finite time to attain steady-state (induction time) in each case. While for the case of pure resin A, steady-state is attained fast, it takes about 3 minutes for resin A containing 250ppm BN and about 8 minutes for resin A containing 1000ppm of BN. It is apparent that as polymer flows through the die, BN diffuses to the wall and provides some kind of conditioning (lubrication) to the die that allows melt slippage at the wall. As a result, a gradual reduction in the head pressure is observed. Figure 5 shows the same experimental result for Resin B at 185°C and 1.6mm die gap. The screw speed was also 30 rpm. The pressure curve for 0.025% and 0.1% BN filled resin are almost coincide. However, both pressure curves for 0.025% and 0.1% BN-filled resins are lower than

that of the pure resin. The observation of the induction time is also seen here and conforms with the result obtained for Resin A (Figure 4).

Visual observation also conducted on the filled resins in order to check the quality of the BN dispersion in the two resins. It was found that the resulted dispersion is more uniform in Resin B i.e. the parison was uniform in color with Resin B containing 250 and 1000 ppm of BN. However, Resin A containing BN had a white-colored streamlines running along the parison. This indicated that BN was not distributed quite uniformly in the case of Resin A, mainly due to its high viscosity. This dispersion quality observation is related directly to the performance of BN in eliminating melt fracture. In order to examine the appearance of the extrudate surface visually i.e., surface of the bottle, pictures were taken. Select photos are shown in Figures 6-7. Figure 6 shows the effect of BN on the bottle surface made by Resin B at 185°C. It can be seen that the surface exhibits melt fracture for the pure resin case. However, the surface of 0.025% and 0.1% BN filled resin remains smooth, clearly showing that BN may eliminate melt fracture.

In Figure 5, it was seen that the pressure during a transient extrusion experiment decreased with time and that it became stable only after about 8 minutes for resin containing BN. In order to investigate the effect of the induction time on the surface appearance of the bottle, samples were collected at two different times; i.e., after 1 and 10 minutes from the start-up of the extrusion process. Figure 7 shows the surface appearance of the bottle at 1 and 10 minutes respectively. It can clearly be seen that the bottle surface was smooth at the time instant of 10 minutes compared to the sample that exhibits melt fracture at 1 minute. This observation implies that BN requires a finite period of time (induction time) in order to migrate to the die wall, to promote slip and thus to eliminate melt fracture.

Summarizing this part of the study, one may conclude that for optimum performance of BN on the HDPE, the following requirements apply. (1) BN should be thoroughly dispersed in the resin. (2) BN must be used at its optimal concentration depending on the type of the polymer and the extrusion tem-

perature. (3) the extrusion induction time should be long enough so that it will allow the BN particles to migrate to the die wall.

**Effect of combining BN and Viton<sup>®</sup> as Processing Aid:** Figure 8 is a plot of pressure drop versus apparent shear rate for Virgin HDPE C, and HDPE C including BN and Viton<sup>®</sup>. It can be seen that a reduction in pressure is encountered in the presence of BN and Viton<sup>®</sup>. In the latter case the reduction is greater. This is due to the effect of slip.

Similar observations can be made from Figure 9. A reduction in pressure is encountered in the presence of both BN and Viton<sup>®</sup> with the reduction to be slightly higher when higher amounts of these two additives are used.

The effects of these additives on the melt fracture behavior are also very clear from the Tables 3-7. Virgin HDPE fractures at  $1096 \text{ s}^{-1}$  and exhibits gross at  $1394 \text{ s}^{-1}$  (see Table 3). When 0.1% of Viton<sup>®</sup> is added the melt fracture improves a little (see Table 4). However, when 0.1%Bn is added (Table 5) slight distortion appear at the rate of  $1840 \text{ s}^{-1}$ .

The situation further improves when combining BN and Viton<sup>®</sup>. Distortions do not appear at rates of  $2088 \text{ s}^{-1}$  that is the maximum shear rate used (see Table 6). When only 0.05% of BN and 0.05% of Viton<sup>®</sup> is used the situation does not improve much as distortions appear at a rate of  $1863 \text{ s}^{-1}$ .

## Conclusions

The effect of boron nitride as a possible processing aid in the extrusion blow moulding of two types HDPE was studied. BN can successfully reduce the head pressure in the extrusion blow moulding operation and as a result to eliminate melt fracture. While the effect of BN on the melt fracture of HDPE is significant, the rheological behavior of Resin A and B was found to change very little with the addition

of BN. The extrusion temperature and induction time found to play a key role in eliminating the melt fracture.

The combination of BN and Viton<sup>®</sup> is a better processing aid compared to either of them used individually. A better Viton<sup>®</sup> might improve the situation even further as a higher reduction in the pressure is usually encountered in the presence of fluoroelastomers.

### **Acknowledgments**

This work was financially supported by Carborundum and CRT. Materials were kindly provided by Exxon Chemical Company and Carborundum Corp.

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**Table 1:** Chemical and physical properties of Resins A, B and C.

<b>Properties</b>	<b>Typical values, Resin A</b>	<b>Typical values, Resin B</b>	<b>Typical values, Resin C</b>
<b>melt index</b>	0.08 dg/min	0.35 dg/min	0.32 dg/min
<b>flow index</b>	10 dg/min	35 dg/min	-
<b>Density</b>	0.948 g/cm <sup>3</sup>	0.953 g/cm <sup>3</sup>	0.951 g/cm <sup>3</sup>
<b>Processing temperature</b>	190 °C	185 °C	185 °C
<b>Tensile strength at yield</b>	24.1 MPa	26.9 MPa	-
<b>Melting point</b>	140 °C	130 °C	133 °C

**Table 2:** Blends prepared and studied

<b>Blend</b>	<b>Composition</b>
<b>1</b>	HDPE C
<b>2</b>	HDPE C + 0.1% Viton <sup>®</sup>
<b>3</b>	HDPE C + 0.1% BN
<b>4</b>	HDPE C + 0.1% Viton <sup>®</sup> + 0.1% BN
<b>5</b>	HDPE C + 0.05% Viton <sup>®</sup> + 0.05% BN
<b>6</b>	HDPE A, B + 0.025% BN
<b>7</b>	HDPE A, B + 0.1% BN

**Table 3:** Melt Fracture behaviour of Blend 1 in Extrusion Blow Molding (Virgin HDPE)

Shear rate (s <sup>-1</sup> )	Pressure (psi)	Bottle appearance
780	3010	Smooth
930	3100	Smooth
1096	3213	Sharkskin
1254	3316	Sharkskin
1394	3460	Sharkskin+Gross
1510	3553	>>
1758	3667	>>
1873	3811	>>

**Table 4:** Melt Fracture behaviour of Blend 2 in Extrusion Blow Molding (HDPE+0.1% Viton<sup>®</sup>)

Shear rate (s <sup>-1</sup> )	Pressure (psi)	Bottle appearance
1016	3020	Smooth
1109	3100	Partial smooth
1287	3210	Smooth
1391	3310	Partial smooth
1518	3400	Sharkskin
1646	3500	>> + Gross
1829	3600	>>
1965	3720	>>
2229	3800	>>

**Table 5:** Melt Fracture behaviour of Blend 3 in Extrusion Blow Molding (HDPE + 0.1% BN)

Shear rate (s-1)	Pressure (psi)	Appearance
1031	3000	Smooth
?	3100	>>
1215	3210	>>
?	3310	>>
1476	3400	>>
1620	3500	>>
1840	3610	Slightly sharkskin
1920	3700	>>

**Table 6:** Melt Fracture behaviour of Blend 4 in Extrusion Blow Molding (HDPE + 0.1%Viton + 0.1%BN)

Shear rate (s-1)	Pressure (psi)	Appearance
?	2812	Smooth
924	2912	>>
1031	3029	>>
1234	3145	>>
1376	3271	>>
1582	3427	>>
1838	3592	>>
2088	3695	>>

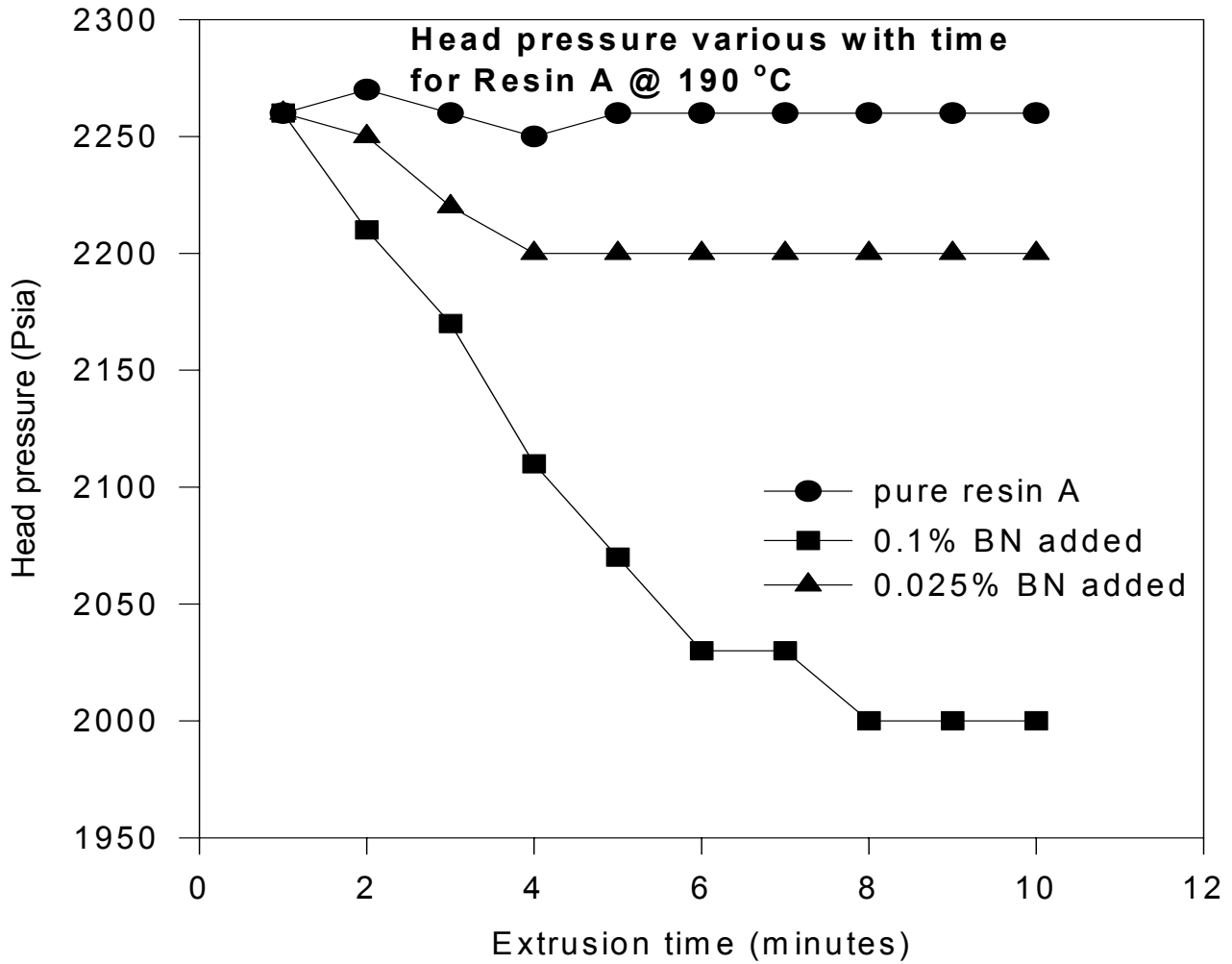
**Table 7:** Melt Fracture behaviour of Blend 5 in Extrusion Blow Molding Blend 5 (HDPE + 0.05%Viton + 0.05% BN)

<b>Shear Rate (s-1)</b>	<b>Pressure (psi)</b>	<b>Bottle appearance</b>
1031	3079	Smooth
1111	3198	>>
1176	3267	>>
1336	3386	>>
1506	3475	>>
1604	3564	>>
1851	3663	Slight sharkskin
1996	3782	Slight sharkskin

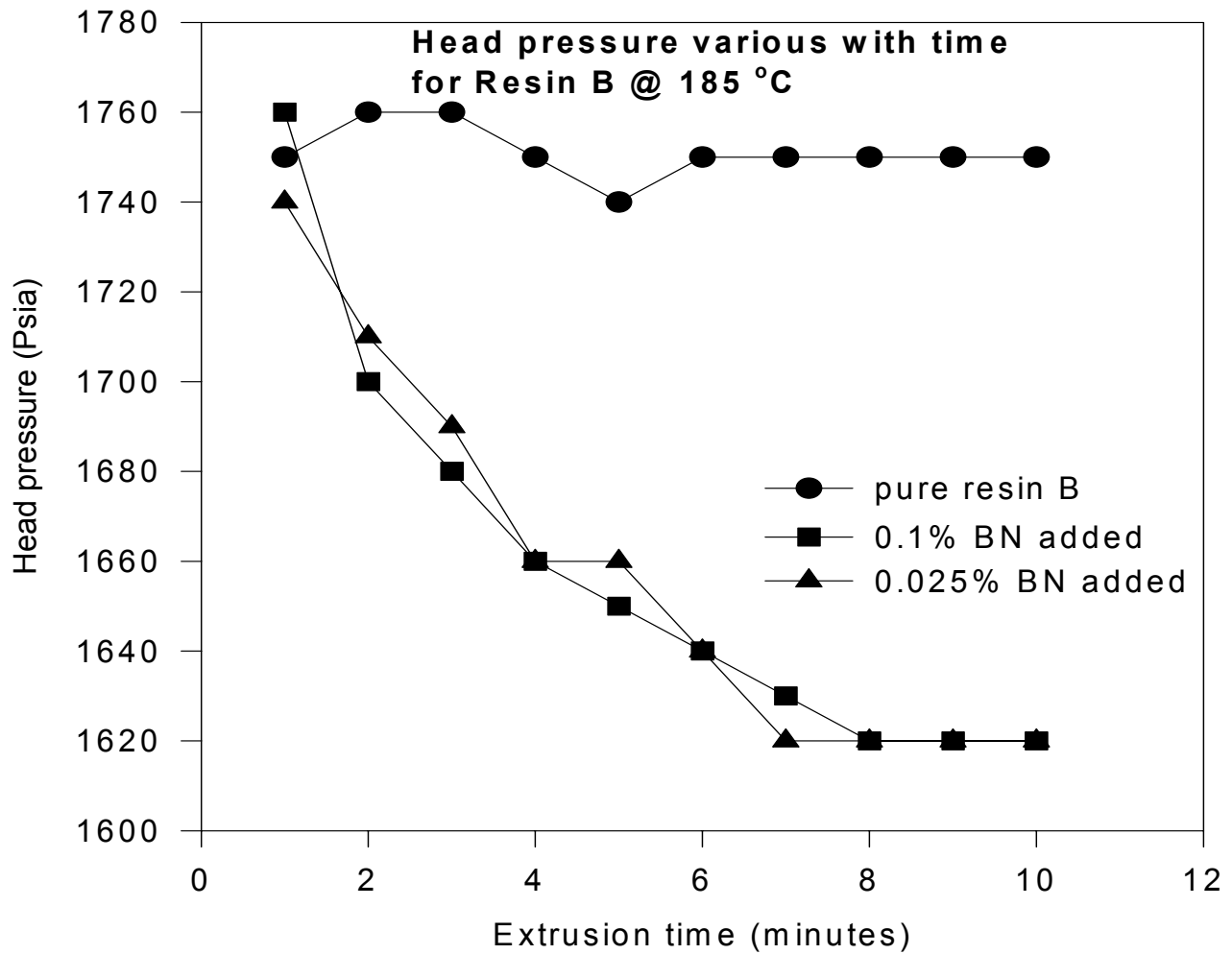
**Figure 1:** The dynamic moduli and viscosity data for Resin A with and without BN obtained by using a parallel plate-rheometer.

**Figure 2:** The effect of BN on the flow curve of resin A at 190°C. The die gap was 1.6mm.

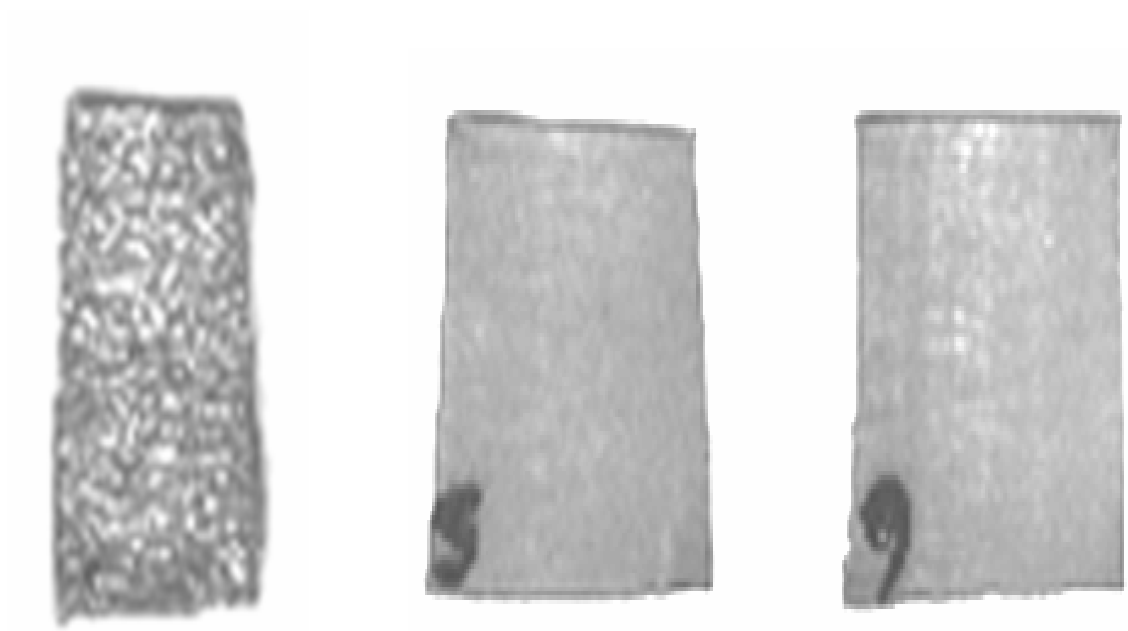
**Figure 3:** The effect of BN on the flow curve of resin B at 185°C. The die gap was 1.6mm.



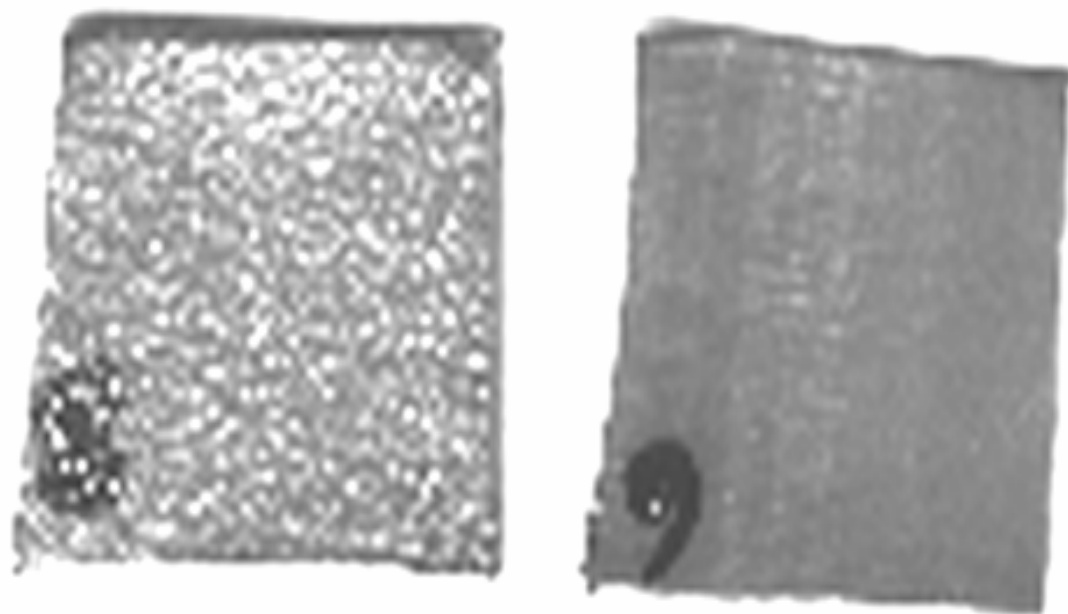
**Figure 4:** Transient extrusion runs showing the head pressure versus extrusion time for Resin A with and without BN at 190°C. Note that the final equilibrium pressure and the time to reach steady-state vary with BN levels.



**Figure 5:** Transient extrusion runs showing the head pressure versus extrusion time for Resin B with and without BN at 185°C. Note that the final equilibrium pressure and the time to reach steady-state vary with BN levels.



**Figure 6:** Surface appearance of extrudate (part of bottle) made by using Resin B at  $2800s^{-1}$   
Left: pure virgin Resin B  
Middle: 0.025% BN added  
Right: 0.1% BN added



**Figure 7:** The effect of the induction time on surface appearance of Resin A at 190°C.  
A) Sample collected at time = 1 minute (left) and  
B) Time =10 minutes (right)

**Figure 8:** The Effect of Boron Nitride and the effect of fluoropolymer (Viton) on the flow curve of HDPE C.

**Figure 9:** The Effect of combined Boron Nitride and fluoropolymer (Viton) on the flow curve of HDPE  
C.