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## Processing Additives in High Density Polyethylene Extrusion Blow Moulding Applications

By

Denis Duchesne 3M Canada Inc.

P.O. Box 5757 London, Ontario Canada N6A 4T1

Thomas J. Blong Specialty Fluoropolymers Department

3M Company St. Paul, MN 55144-1000

and

Marc Brandon 3M Europe

P.O. Box 193 NL 2300 Ad Leiden The Netherlands

## INTRODUCTION

As the number of applications for high density polyethylene (HDPE) grows, new opportunities will arise along with new challenges in the area of processing. For instance, processing problems like melt fracture can limit the use of HDPE in applications requiring high gloss such as packaging for personal care products. Polymer processing additives (PPA), which have been described as external lubricants (1 - 4), have been shown to offer solutions to a variety of processing problems encountered with new materials and new applications. For instance, fluoropolymer-based processing additives are now widely used in linear low density polyethylene (LLDPE) and high molecular weight high density polyethylene (HMW-HDPE) film applications to eliminate melt fracture and provide significant productivity gains. The processing additives also offer advantages in wire and cable coating operations by eliminating die build-up. Finally, processing additives are also used in profile extrusion of stress crack resistant HMW-HDPE resins to eliminate die build-up and reduce the apparent viscosity of the resins.

Capillary rheometry studies conducted in our laboratories over the last few years (3, 5) have shown that 250 ppm to 1000 ppm of processing additive can significantly improve the processability of high density polyethylene resins. More specifically, tests conducted on blow moulding grade resins showed that melt fracture can be delayed and in most cases eliminated, while the apparent viscosity is noticeably reduced. However, capillary rheometry techniques do not lend themselves very well to the determination of processing additive effects on gloss. Also, benefits associated with potential reductions in processing temperature due to the impact of the processing additive on apparent melt viscosity cannot be assessed. This is of particular significance when considering the impact of processing temperature on cycle time and melt strength.

In order to better assess the effects of processing additives on the processability of blow moulding grade HDPE resins, the performance of a processing additive in three HDPE blow moulding grade resins was evaluated by capillary rheometry and on commercial scale extrusion blow moulding equipment. Data was also generated for a second type of processing additive on commercial scale equipment. Capillary rheometry techniques were used to characterize the flow behavior of the various resins under consideration; especially the shear rate for the onset of melt fracture. Extrusion blow moulding trials were conducted to investigate the effects of the additives on melt fracture, gloss, melt pressure, and processing temperature during the blow moulding extrusion of the pigmented HDPE resins.

## EXPERIMENTAL

### Materials.

Two fluoropolymer-based processing additives were used in the course of this study. One was a copolymer of vinylidene fluoride and hexafluoropropylene containing 10% inorganics as partitioning agent while the other was a proprietary formulation containing a fluoropolymer and a co-additive designed to provide specific processing improvements (6). These additives will be referred to in the text as PPA-1 and PPA-2, respectively. Both of these additives are commercially available as Dynamar™ FX-9613 (PPA-1) and Dynamar™ FX-5920 (PPA-2).

The high density polyethylene resins (HDPE-1, HDPE-2, and HDPE-3) used in laboratory and commercial scale evaluations were commercial samples and are described in Table 1.

### Equipment.

Laboratory scale compounding of both masterbatches and final let downs of the processing additive at ppm level was performed using a torque rheometer and mixing bowl fitted with roller blades. Size reduction of all compounds was done by grinding the melt mixed materials at room temperature. Final PPA concentrations in the case of both masterbatches and let downs were verified by the "Total Oxygen Combustion Method for Fluorine" (7).

Capillary extrusion studies were carried out on a capillary rheometer fitted with a flat entry die having a 0.56 mm diameter and a length to diameter ratio (L/D) of 36:1. The dwell time was ten minutes and the melt temperature 190°C (HDPE-1, HDPE-2) or 210°C (HDPE-3). All viscosities are reported uncorrected for end effects.

Commercial scale extrusion blow moulding experiments were performed on a Uniloy MS Series single parison continuous extrusion blow moulding system. The screw diameter was 80 mm and the length to diameter ratio (L/D) 24:1. The mould temperature was held constant at 5°C. One litre bottle moulds were utilized in a dual mould shuttle system. The die diameter was 44.4 mm and the die gap was 0.76 mm in the cases of HDPE-1 and HDPE-2. In the case of HDPE-3, experiments were conducted with die gaps of 1.7 mm and 2.2 mm. The parison was not programmed so that the shear rate would be constant throughout the experiment. Finally, the parison temperature was continuously monitored using an infra-red temperature sensing system.

Gloss measurements were made using a BYK-Gardner hand-held Micro TRI Gloss reflectometer on flattened bottle cross-

sections. Values reported here are the average of five measurements.

### Sample Preparation.

Capillary rheometry. Samples for capillary extrusion were made by first preparing 2% processing additive masterbatches in the HDPE resin under investigation. Each masterbatch was then analyzed for PPA content and subsequently diluted with an appropriate amount of resin to final PPA concentration.

Extrusion blow moulding. Titanium dioxide (50%), phthalocyanine blue/titanium dioxide (30%) and processing additive (3%) masterbatches were commercially available products which were used as received. The final processing additive and pigment dilution to ppm level was done by dry-blending the appropriate amounts of masterbatches in the base resin with a tumble-blender. The mixing time was about 20 minutes and was sufficient to insure uniform distribution of the masterbatches.

## RESULTS AND DISCUSSION

### Capillary Rheometry.

The impact of PPA-1 on the processability of the three HDPE resins under consideration was investigated by capillary rheometry prior to commercial scale trials. A summary of the results is given in Table 2. In general, it was found that the viscosities at  $600 \text{ s}^{-1}$  were lower for the PPA-containing resins than those for the resins without processing additives. In addition, the processing additive was found to noticeably improve the surface appearance of the extrudate by delaying and, in most cases, eliminating various types of melt fractures.

The full flow curves for melt mixed HDPE-1 and HDPE-1 with 1000 ppm PPA-1 are shown in Figure 1 while log-log plots of the dependence of the viscosity on shear rate for the same materials are shown in Figure 2. The control HDPE was subjected to a melt mixer sequence identical to that for the PPA-containing sample to insure that both materials had the same shear history. The introduction of 1000 ppm PPA-1 in HDPE-1 provided for a substantial reduction in apparent viscosity, 38% at  $600 \text{ s}^{-1}$ . As well, it eliminated the occurrence of matte surfaces and cyclic melt fracture (CMF) or slipstick. Photomicrographs of strands generated during the capillary extrusion of HDPE-1 with and without PPA-1 are shown in Figure 3. Finally, it is worthwhile noting that the flow curve generated for the PPA-containing sample does not exhibit, in the shear rate range investigated, the sigmoid shape usually associated with the occurrence of CMF or slip-stick. This

strongly suggests that processing additives could be useful not only in continuous blow moulding extrusion operations but also in intermittent blow moulding operations.

Lower shear stresses and viscosities at equivalent shear rates were also observed for both PPA-1/HDPE-2 and PPA-1/HDPE-3 combinations, as indicated in Table 2. The positive impact of PPA-1 on the surface appearance of HDPE-2 extrudates is obvious, as shown in Figure 4; the processing additive eliminating the appearance of microsharkskin or matte finish to an apparent shear rate greater than  $1600 \text{ S-I}$ . Finally, PPA-1 was found to greatly improve the surface appearance of HDPE-3. As shown in Figure 5, the processing additive eliminated the occurrence of sharkskin and postponed the onset of CMF to a higher apparent shear rate.

### Continuous Extrusion Blow Moulding.

The effects of PPA-1 on the processability of pigmented HDPE-1 was evaluated on commercial scale equipment using the conditions described in Table 3. The results, shown in Figures 6 and 7, indicate that the introduction of 400 ppm to 1000 ppm of PPA-1 in HDPE-1 provided for 8%-10% reductions in melt pressure and improved the  $60^\circ$  gloss. It is assumed that the drop in melt pressure results from the processing additive acting as an external lubricant (1 -4) and reducing the apparent viscosity of the resin while not affecting the bulk viscosity. The  $3^\circ\text{C}$  drop in parison temperature (Table 3) recorded for HDPE-1/PPA-1 combinations ) using an infra-red temperature sensing system is also believed to be related to the lubricating effect of the processing additive. The improvement in gloss is thought to be due to the processing additive ability to eliminate micro-sharkskin or matte finish on the extrudate, as observed in capillary rheometry experiments.

A series of experiments performed with PPA-1/HDPE-2 combinations, under the extrusion conditions described in Table 3, gave similar results. As can be seen in Figure 8, melt pressures were 8%-10% lower when PPA-1 had been incorporated in HDPE-2. Significantly higher  $60^\circ$  gloss values were also measured, as shown in Figure 9. The data also shows that higher gloss is obtained at PPA-1 level of 600 ppm and above. Again, in this case, the processing additive is thought to act as an external lubricant and a melt fracture suppressor. Experiments were also performed at a lower melt temperature,  $170^\circ\text{C}$ , with PPA-1/HDPE-2 and PPA-2/HDPE-2 combinations. The data, Figure 10, indicates that the lowering of the melt temperature did not reduce the effectiveness of PPA-1 at improving gloss. Finally, the performance of PPA-2 under these conditions was found to be, within experimental error, similar to that of PPA-1.

HDPE-3 was found to behave similar to a linear low density

polyethylene during capillary rheometry experiments exhibiting well defined sharkskin instead of the typical micro-sharkskin or matte finish generally observed with HDPE resins. This behavior was attributed to HDPE-3 having a narrower molecular weight distribution than what is typical for HDPE resins used in blow moulding applications. For the same reason, it was anticipated that the resin would have poor melt strength. While it was possible to extrude HDPE-3 melt fracture-free using condition A, as described in Table 4, it was not possible to mould bottles because of high parison draw. Although bottles could not be made, greater than 80% reflected light at 60. was measured on a chilled parison. In order to improve melt strength, the melt temperature was lowered by 22°C (Condition B). While the melt strength characteristics of the material were improved, the extrudate was completely melt fractured, therefore ruining the surface appearance of the molded article. The introduction of 300 ppm PPA-1 (Condition C) allowed for a further reduction in melt temperature (6.C) and resulted in an additional improvement in melt strength. More importantly, the small amount of processing additive prevented the occurrence of sharkskin melt fracture, thus permitting the manufacture of smooth, high gloss bottles. Table 5 shows the variation of the melt pressure and the melt fracture status as a function of time for the PPA-1/HDPE-3 combination. In addition, experiments at a higher shear rate ( $300 \text{ s}^{-1}$  VS  $175 \text{ s}^{-1}$ ) or smaller die gap (1.7 mm vs 2.2 mm) were performed (Conditions D and E). Again, in this case, despite nearly doubling the shear rate, melt fracture was still totally eliminated while melt pressure and shear heating were decreased as a result of incorporating 300 ppm PPA-1 in the resin.

## CONCLUSIONS

In this study, PPA-1 was found to provide a variety of benefits during continuous blow moulding extrusion of HDPE resins. For instance, significant reductions in melt pressure and melt temperature were achieved; the latter resulting in better melt strength retention. Also, the processing additive was found to greatly improve extrudate surface appearance by eliminating the occurrence of various types of melt fracture thus allowing for the manufacture of high gloss articles. PPA-2 was also found to be an effective processing additive in HDPE-2 and should be the subject of further investigation. Therefore, processing additives offer a viable means of extending the range of applications for HDPE blow moulding grade resins including those that require high gloss.

## LITERATURE CITED

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Table 1  
Resin Characteristics

Resin	Melt Flow Rate* (g/10 min)	Density (kg/m <sup>3</sup> )
HDPE-1	0.4	955
HDPE-2	0.5	951
HDPE-3	1.4	952

\* ASTM D1238 190/2.16 Method B; ISO 1133 cond 4.

Table 2  
Effects of PPA-1 on the Processability Characteristics of HDPE Resins  
(Capillary Rheometry, 190°C)

Resin	PPA Type (level, ppm)	Apparent Viscosity (Pa s)		Melt Fracture Behavior
		600 1/s	1000 1/s	
HDPE-1	No PPA, Melt Mixed Resin	355	278	Matte < 600 1/s CMF @ 2900 1/s
	PPA-1 (1000)	260	200	Glossy @ 3000 1/s
HDPE-2	No PPA, Melt Mixed Resin	390	272	Matte @ 600 1/s
	PPA-1 (1000)	330	250	Glossy @ 1600 1/s
HDPE-3	No PPA, Melt mixed Resin	515	378	Sharkskin < 200 1/s CMF @ 1000 1/s
	PPA-1 (800)	320	264	Glossy @ 1600 1/s

CMF = Cyclic melt fracture

Table 3

Extrusion Blow Moulding Conditions for HDPE-1 and HDPE-2  
(1% TiO<sub>2</sub>)

HDPE	Die Gap (mm)	Melt Temperature (°C)	Parison Temperature (°C)	Screw Speed (rpm)	Output Rate** (kg/hr)
1	0.76	187	197 (200*)	26	46
2	0.76	187	197 (199*)	26	46
	0.76	170	181 (182*)	26	46

\* Conditions for pigmented resins without processing additive.

\*\* Apparent shear rate = 1260 s<sup>-1</sup>

Table 4

Effects of PPA-1 on the Processability  
of HDPE-3 in Extrusion Blow Moulding\*  
(0.3% Blue Pigment)

Condition	PPA-1 (ppm)	Die Gap (mm)	Melt T. (°C)	Parison T. (°C)	Gate Pressure (MPa)	Melt Fracture (-)
A	0	2.2	202	218	19.6	No**
B	0	2.2	180	195	22.3	Yes
C	300	2.2	174	185	20.9	No
D	0	1.7	180	196	23.6	Yes
E	300	1.7	180	193	21.0	No

\* Output rate = 53- 54 kg/hr, Screw Speed = 26- 27 rpm

Apparent shear rate = 300 S<sup>-1</sup> @ 1.7 mm die gap, 175 S<sup>-1</sup> @ 2.2 mm die gap.

\*\* Very weak melt strength, not possible to make bottles.

Table 5

Gate Pressure and Melt Fracture vs Time  
for PPA -1/HDPE-3 Combination  
(Condition C\*)

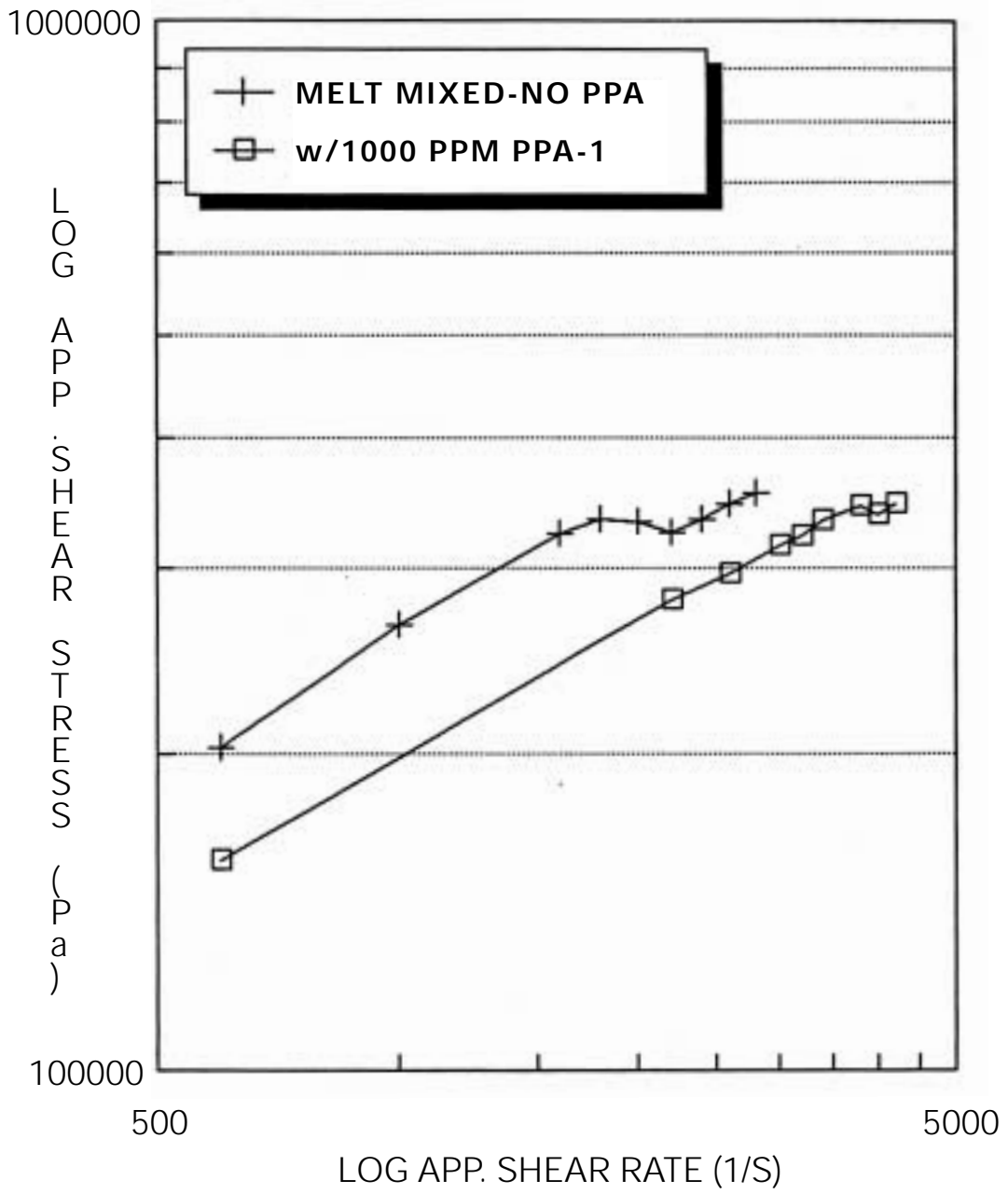
Time (Minutes)	Gate Pressure (MPa)	Melt fracture
0	22.0	Full Fracture
10	21.4	Full Fracture
20	21.1	Partial Fracture
30	21.0	Residual Fracture
40	21.0	No Fracture
50	20.9	No Fracture

\* See Table 4.

FIGURE 1

LOG SHEAR STRESS VS LOG SHEAR RATE

(CAPILLARY RHEOMETRY, HDPE 1, 190 C)

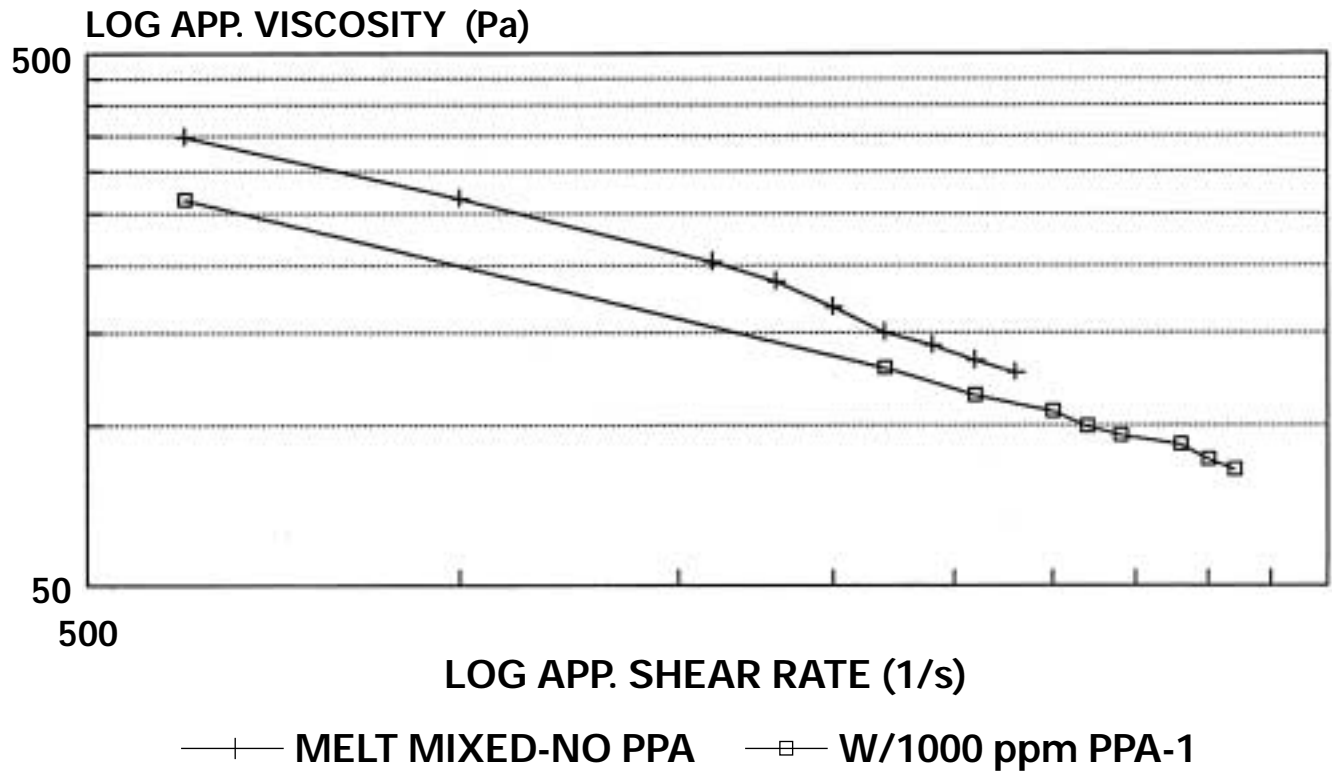


SPE-1SI

FIGURE 2

LOG SHEAR STRESS VS LOG SHEAR RATE

(CAPILLARY RHEOMETRY, HDPE 1, 190 C)



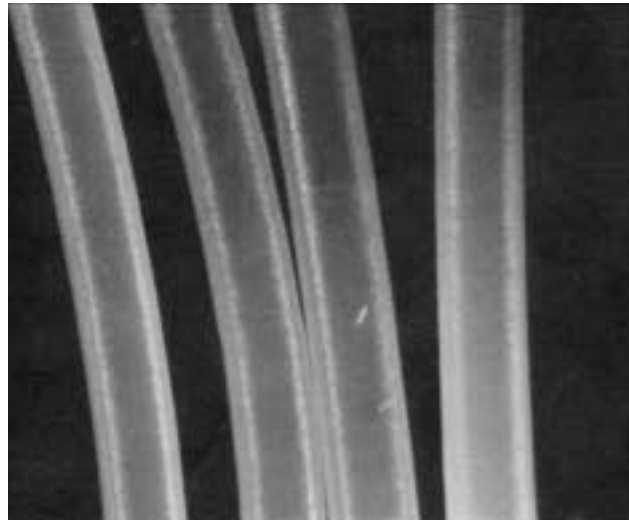
SPE-2SI



Figure 3

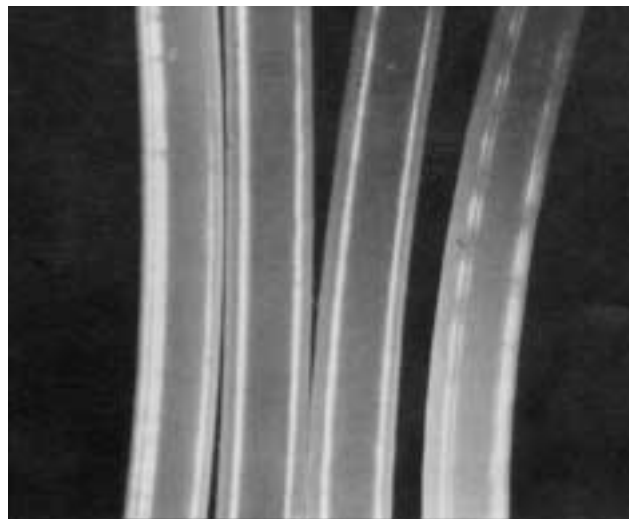
Effect of PPA-1 on HDPE-1  
Extrudate Surface Appearance

No PPA



600 1000 1600 2000 (s<sup>-1</sup>)

W/1000 PPM PPA - 1

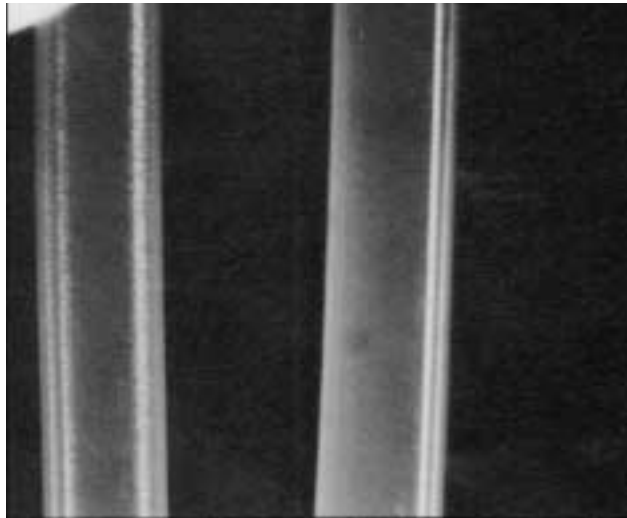


600 2200 2600 3000 (s<sup>-1</sup>)

Figure 4

Effect of PPA-1 on HDPE-2  
Extrudate Surface Appearance

600 s<sup>-1</sup>



No PPA

W/1000 PPM PPA-1

1200 s<sup>-1</sup>



No PPA

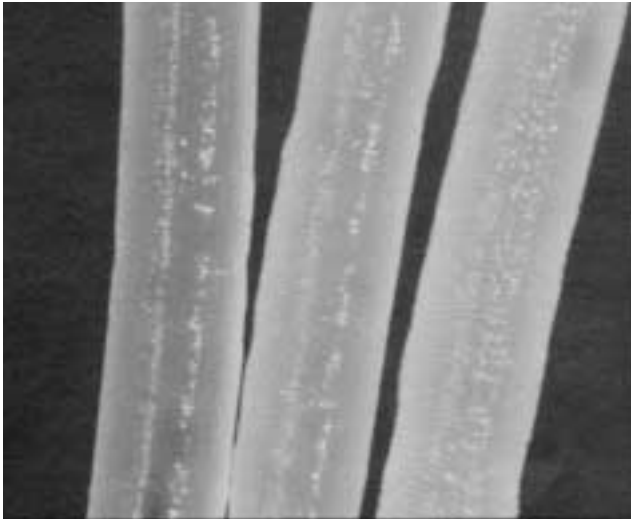


W/1000 PPM PPA-1

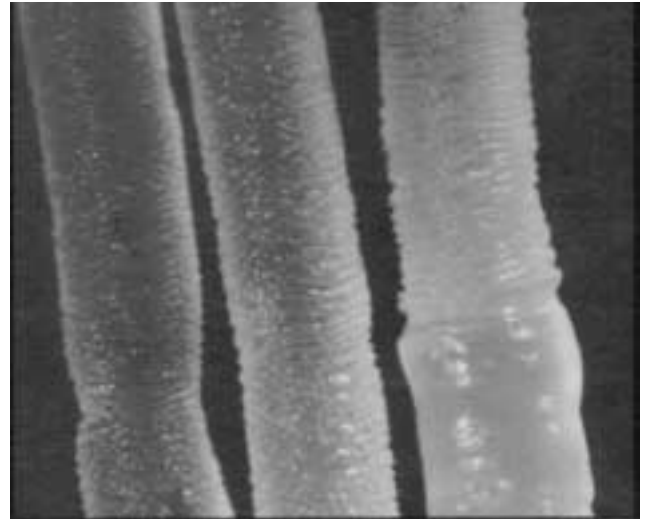
Figure 5

Effect of PPA -1 on HDPE-3  
Extrudate Surface Appearance

No PPA

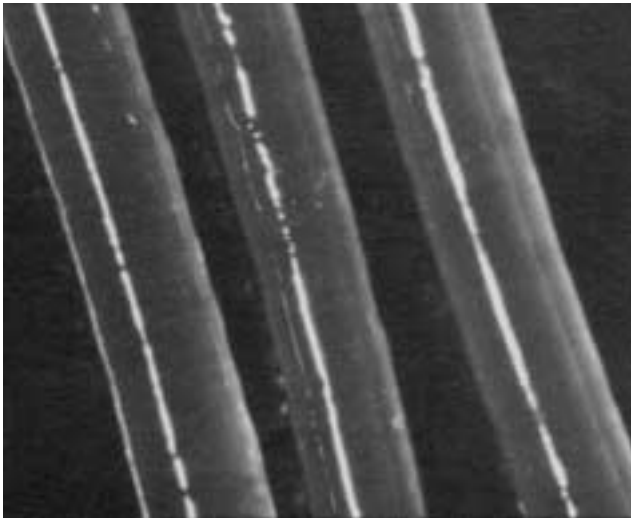


400 500 600 s<sup>-1</sup>

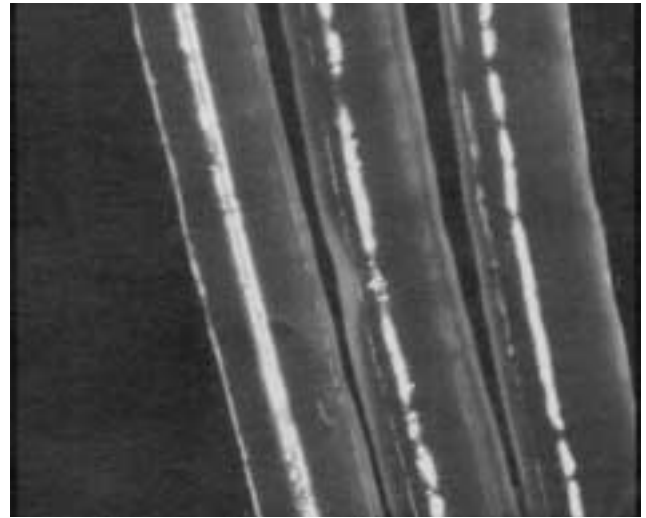


700 800 900 s<sup>-1</sup>

W/800 PPM PPA - 1



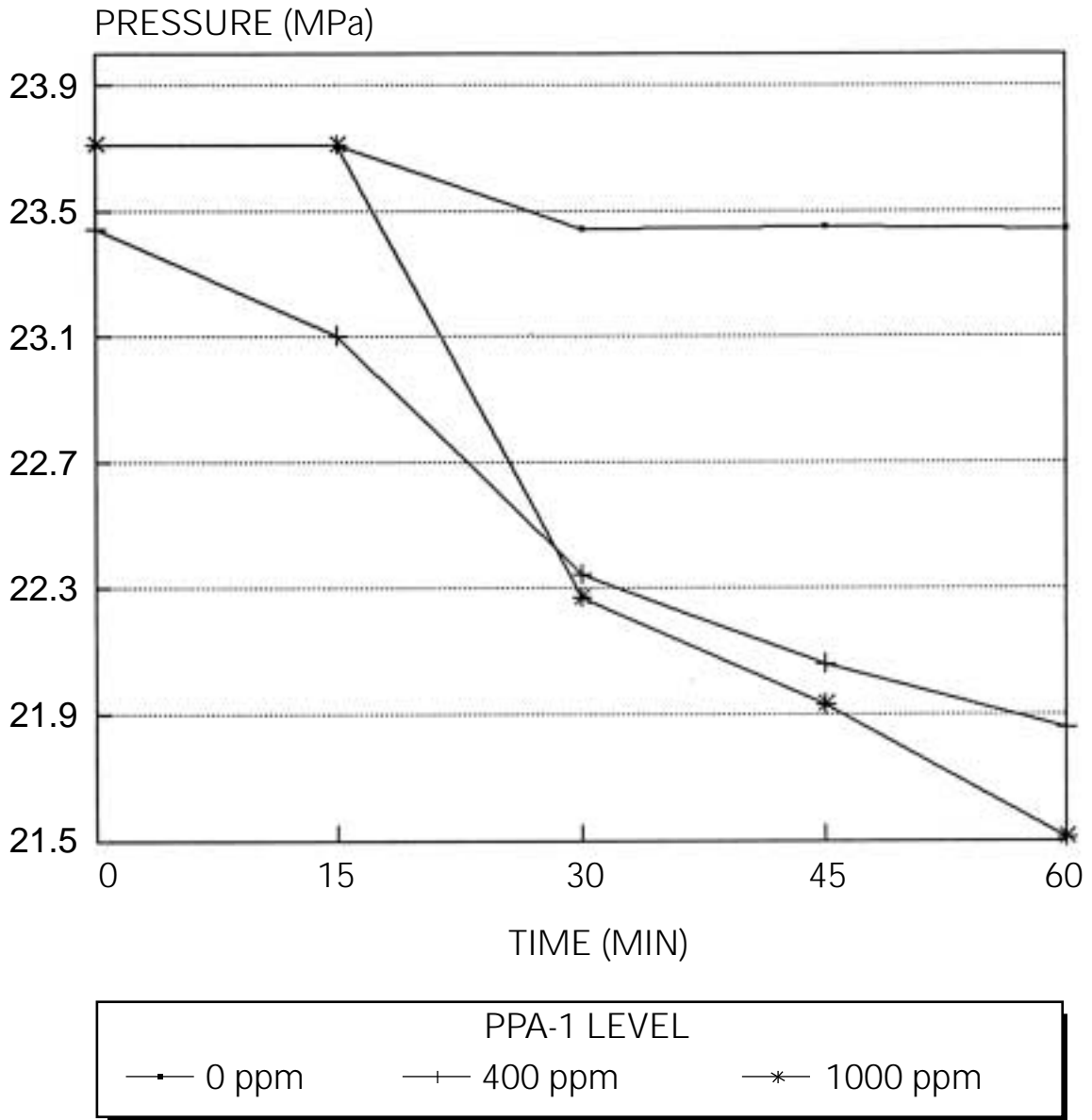
100 200 400



500 600 800 s<sup>-1</sup>

Figure 6

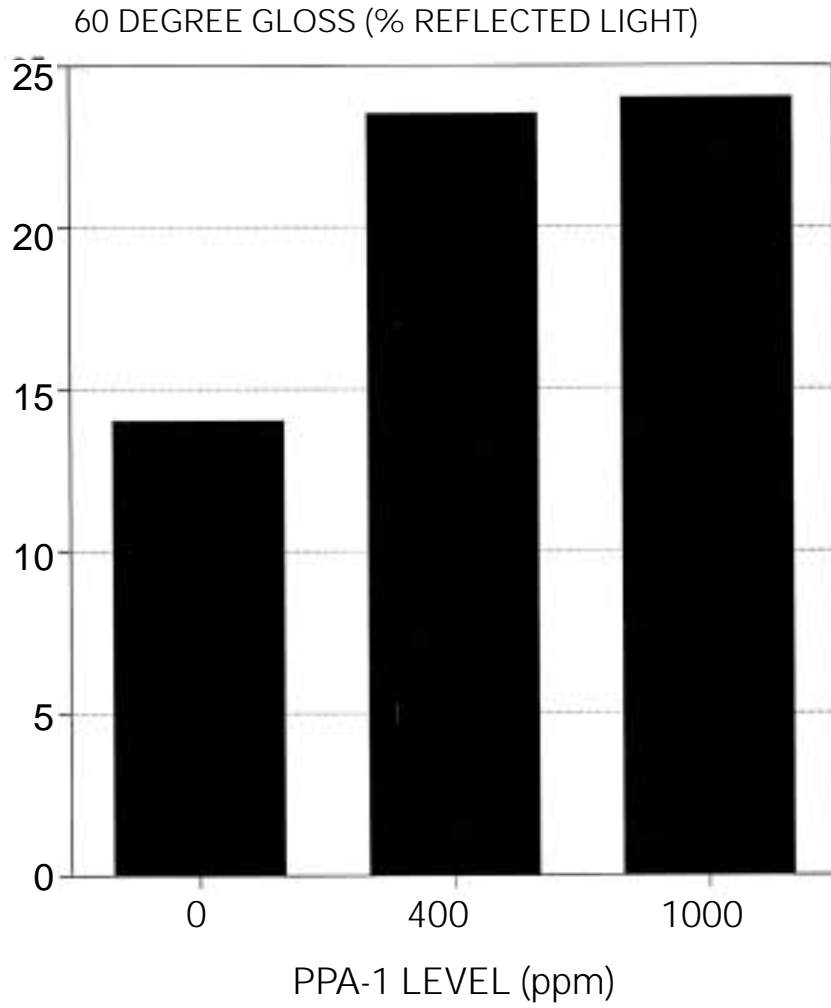
PRESSURE VS TIME  
(BLOW MOULDING, HDPE-1. 1% TiO<sub>2</sub>. 187 C)



SPE-3ASI

Figure 7

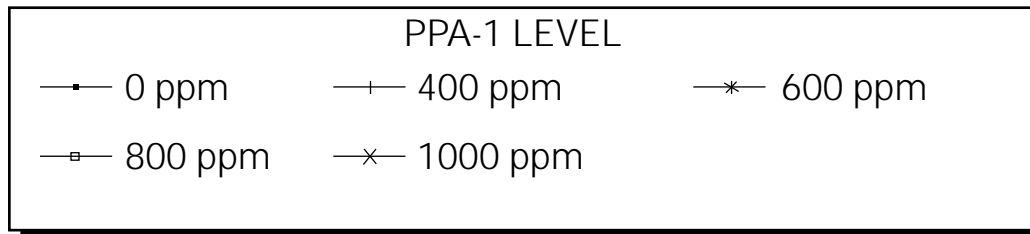
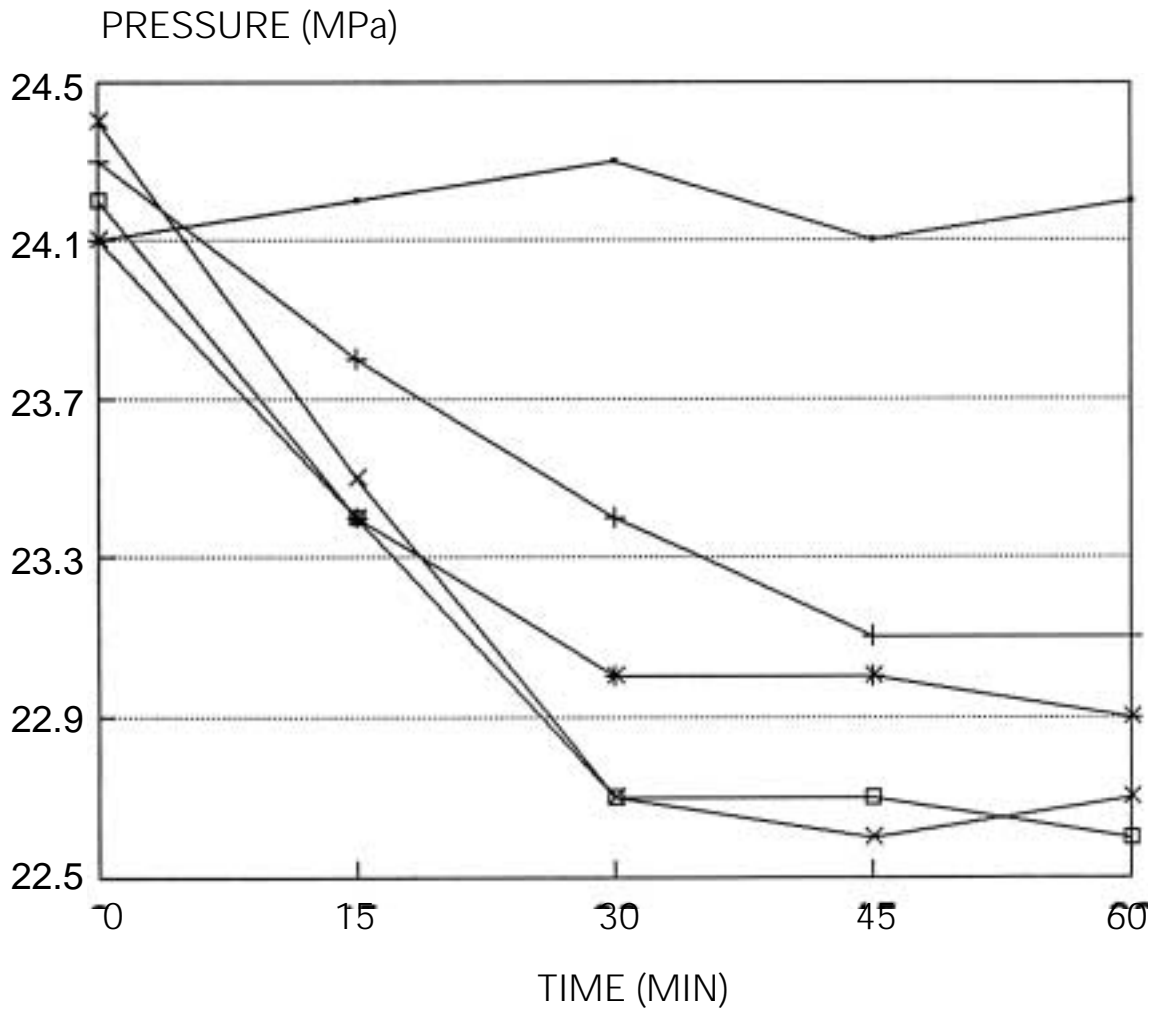
GLOSS VS. PPA LEVEL  
(BLOW MOULDING, HDPE-1. 1% TiO<sub>2</sub>. 187 C)



SPE-4ASI

Figure 8

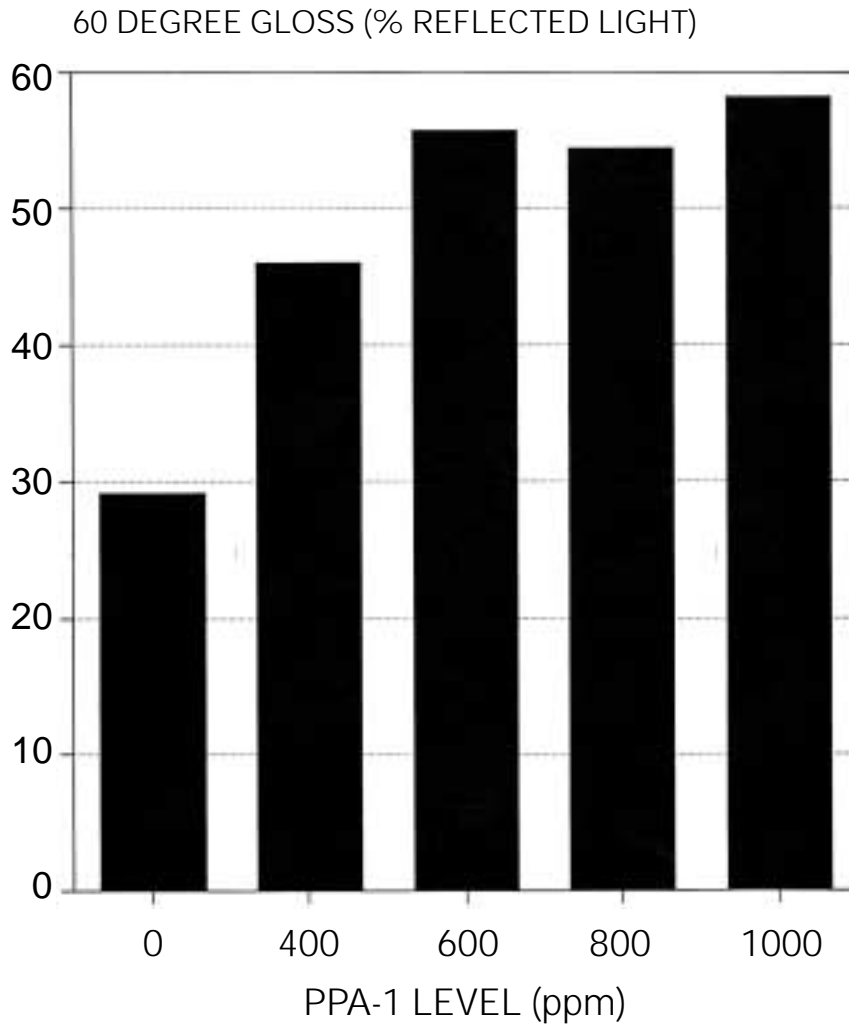
PRESSURE VS TIME  
(BLOW MOULDING, HDPE-2. 1% TiO<sub>2</sub>. 187 C)



SPE-7ASI

Figure 9

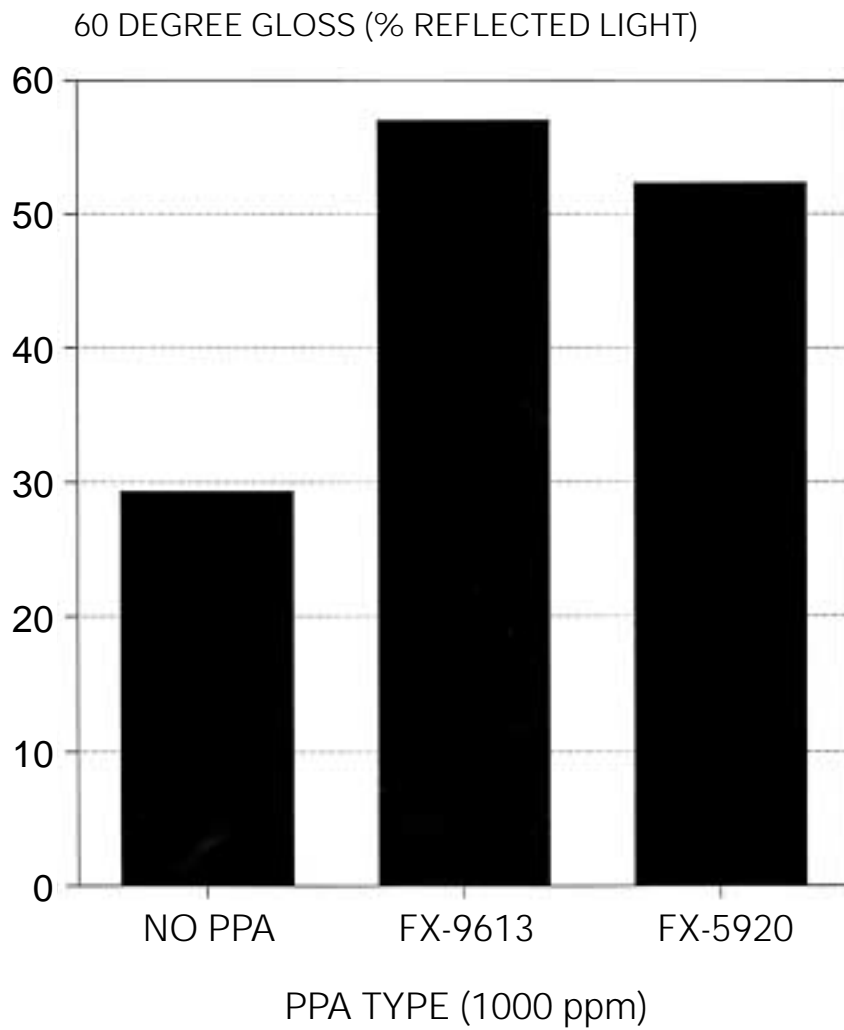
GLOSS VS. PPA LEVEL  
(BLOW MOULDING, HDPE-2. 1% TiO<sub>2</sub>. 187 C)



SPE-8ASI

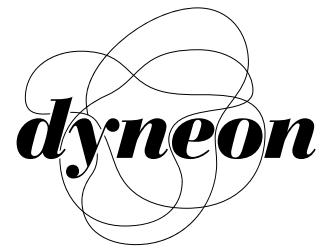
Figure 10

GLOSS VS. PPA TYPE  
(BLOW MOULDING, HDPE-2. 1% TiO<sub>2</sub>. 170 C)



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Dyneon LLC  
6744 33rd Street North  
Oakdale, MN 55128  
Phone: +1 800 723 9127  
+1 651 733 5353  
Fax: +1 651 737 7686

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