Polymer Processing Additives to Enlarge the Process Window for Polyolefins Extrusion

Greet Dewitte
Dyneon N.V.

Abstract:

Fluoropolymer based polymer processing additives (PPA) are frequently used in the plastics industry for the processing of polyethylene and polypropylene.

The use of PPA is not anymore limited to blown film extrusion exclusively: nowadays fluoropolymers are widely used in film production, pipe extrusion, blow molding, wire and cable production, co-extrusion, fiber spinning... using LLDPE, MDPE, HDPE, and PP. Recently this list is even extended to non-polyolefins.

Besides for the problem solving of phenomena as melt fracture and die build-up, PPAs are widely used to optimise the process conditions in a wide range of applications without having to make compromises on the properties of the final products.

The objective of this paper is to give some insight to the mechanism of fluoropolymer-based polymer processing additives (PPA), the benefits that PPA users will experience. This paper explores technical experiments showing how Dynamar™ PPAs will improve the various aspects of polyethylene extrusion, which results in a broader processing window for the plastic converter and a higher productivity.

Introduction

The biggest challenge for designing a new plastic is finding the right combination of the desired mechanical properties and the possibility to process this resin in a technical and economical acceptable way. A link between the relatively good processability of LDPE and the toughness of LLDPE has been the key subject for many since the introduction of the LLDPE on the market. The use of fluoropolymer-based additives provides that link today.

Originally, fluoropolymer based PPAs were designed to eliminate the melt fracture (the so called ‘shark-skin’) during blown film extrusion. Figure 1 shows typical examples of LLDPE films made with and without PPA under the same conditions, the latter resulting in a film with sharkskin.
Over the past decade, the use of PPA has greatly expanded its utility. In addition to the improvement of the surface quality other benefits have been realized e.g. reduction of head pressure in the extruder, increased output, reduction in processing temperature, reduction in die deposits, or in general terms, a broadening of the process window.

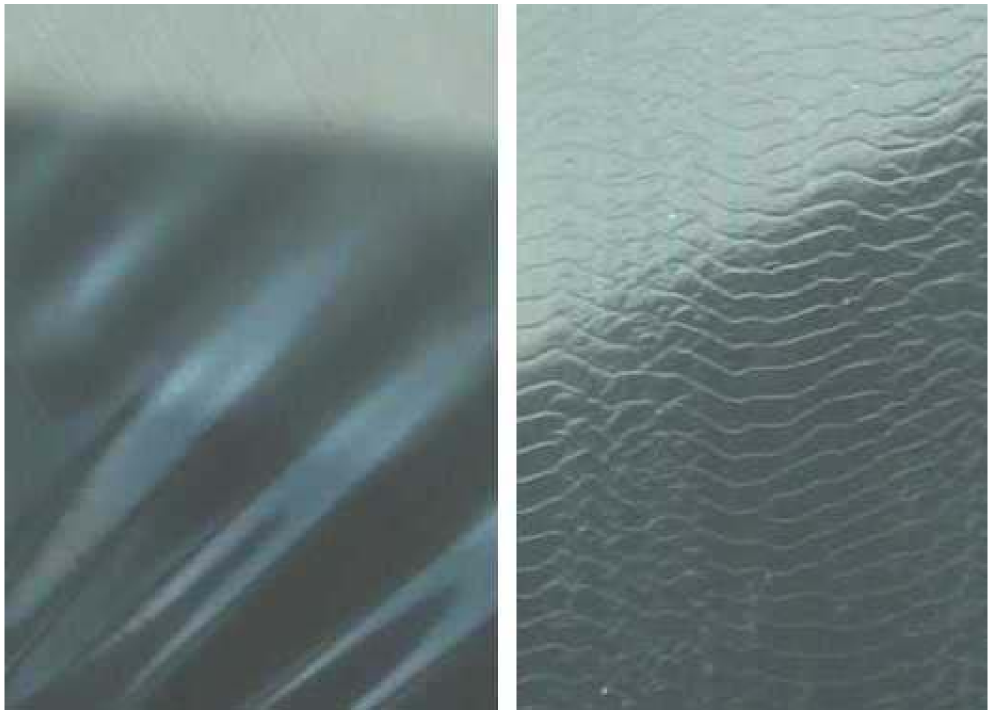


Figure 1: Photographs of LLDPE films
(left: with PPA; right: without PPA)

Materials

The PPAs used in this study were based on fluorocarbon polymers. The products used are commercially available as free-flowing powders from Dyneon:

PPA-1: Dynamar™ PPA FX 9613
PPA-2: Dynamar™ PPA FX 5920A
PPA-3: Dynamar™ PPA FX 5911

Mechanism

Fluoropolymers by nature are quite inert to chemical reactions and thermal degradation. They have a low surface energy and are generally incompatible with other polymers. Microscopic examination of a polyethylene (PE) that contains PPA, reveals discrete micron-sized droplet shaped particles of the fluoropolymer [1]. Typical PPA use levels vary from 100 to 1000 ppm depending on the application.

When extruded, the applied shear-field allows the PPA to phase separate from the PE matrix and form a thin, persistent coating on the metal surfaces of the extrusion equipment. Once this coating is established, the differential

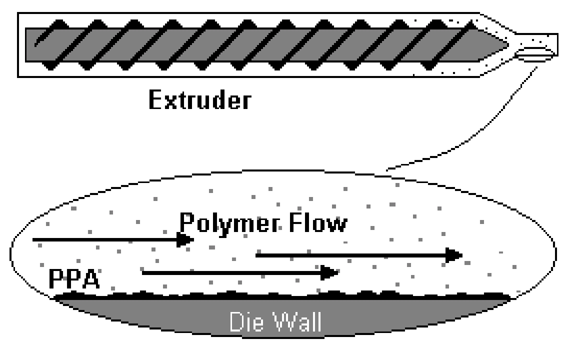


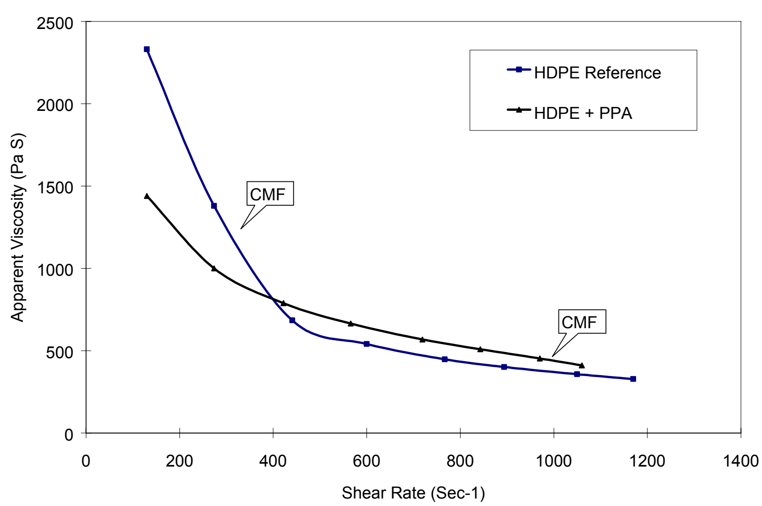
Figure 2: Schematic representation of the mechanism of PPA

between the surface energies of the two polymers allows for reduced friction during extrusion of the PE (Figure 2).

Evaluation of a PE containing PPA by capillary rheometry results in a decrease in extrusion pressure as this coating is formed. Eventually an equilibrium is reached and the host polymer appears of lower viscosity than expected. Reduced gate pressure, lower torque, and by consequence more efficient power consumption are recorded during actual processing. The reduction of the apparent shear stress results in a shift of the onset of the (cyclic) melt fracture towards higher shear rates.

Figure 3 shows the curves of the apparent viscosity and apparent shear stress as a function of the shear rate for formulations of a HDPE with and without PPA. For this example a reduction of the apparent viscosity of 38% was measured upon addition of 600 ppm of PPA-3. The onset of the cyclic melt fracture was postponed from about 300 sec^{-1} to 1100 sec^{-1}.
(HDPE: MFI: 5.5 (21.6 kg) ; <O.1 (5 kg); density: 0.946)

The formation of this coating is not instantaneous. PPA use levels are often determined to allow complete coating within an acceptable time period. It has also been found that other ingredients added to the PE matrix could both help or hinder the formation and stability of the coating.



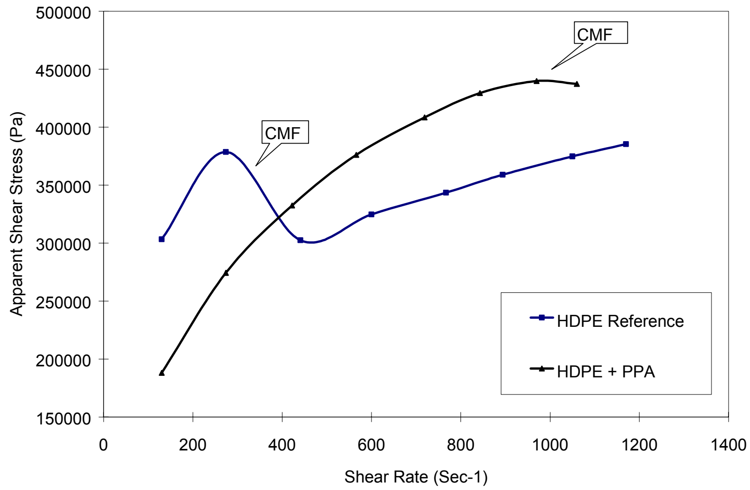


Figure 3: Apparent viscosity & apparent shear stress as a function of the apparent shear rate for a HDPE resin (with and without 600 ppm PPA-3)

Effect of PPA on the process parameters

When a fluoropolymer coating is formed at the die walls, the pressure in the extruder die will decrease because of the lower resistance of the molten plastic against the metal side. Together with this pressure reduction, the energy consumption of the motor will decrease.
When the pressure is the limiting factor of the extrusion process, this pressure reduction can be used in beneficial way to increase the output by increasing the motor speed. On the other hand, the use of PPAs will allow to process a resin through a narrow die gap, without any compromises on the choice of the resin (molecular weight and MFI) and thus on the physical properties of the extrudate. A narrow die gap allows a better control of the mechanical properties of the extruded goods (ratio machine / transverse direction) and an optimal use of the cooling capacities of the equipment.

An actual problem is the need to increase the percentage of LLDPE in a blend with LDPE. The higher viscosity of the LLDPE results in a higher die pressure. This might cause problems with extruders typically designed to process LDPE. Expensive modifications of the equipment can be made like more complex screw designs or changes to the die geometry can overcome this problem. An attractive alternative is the use of PPAs, which are very effective to reduce the apparent viscosity of high molecular weight resins. These PPAs will allow increasing the ratio of LLDPE / LDPE before the extrusion limits are reached [3].

An alternative way to benefit from the reduction of apparent viscosity, is the possibility to reduce the process temperature without reaching the pressure limitations. Extruding at lower temperatures will in the first place reduce the energy consumption, but also reduce the degradation of the polyolefins during the extrusion. This is important certainly in applications that are sensitive for taste and odour problems, e.g. pipes for potable water. In case that the cooling capacity is the limiting factor, the possibility to reduce the operating temperature offers a way to optimise the productivity.

Besides the effect on the process parameters, the PPA coating can provide the additional benefit of reducing or eliminating accumulation of die build-up and internal deposits. If left unchecked, these unwanted accumulations will degrade, causing die lines or exit the extrusion process as visible contamination on the extrudate. The low surface energy coating of the PPA can minimize this problem. A study has shown that the appearance of die build-up is correlated to the die swell of the extrudate. In turn, the die swell is correlated to the stress on the molten plastic. It is known that PPAs will reduce the shear stress during extrusion. Indeed, experiments on the capillary rheometer and on cast film lines prove that the use of PPAs reduces the die swell and eliminates or postpones the appearance of die build-up [4].

Figure 4 shows photographs of the capillary die after extruding yellow pigmented HDPE (MFI: 0.17; density: 0.938) with and without adding 600 ppm of PPA-2.

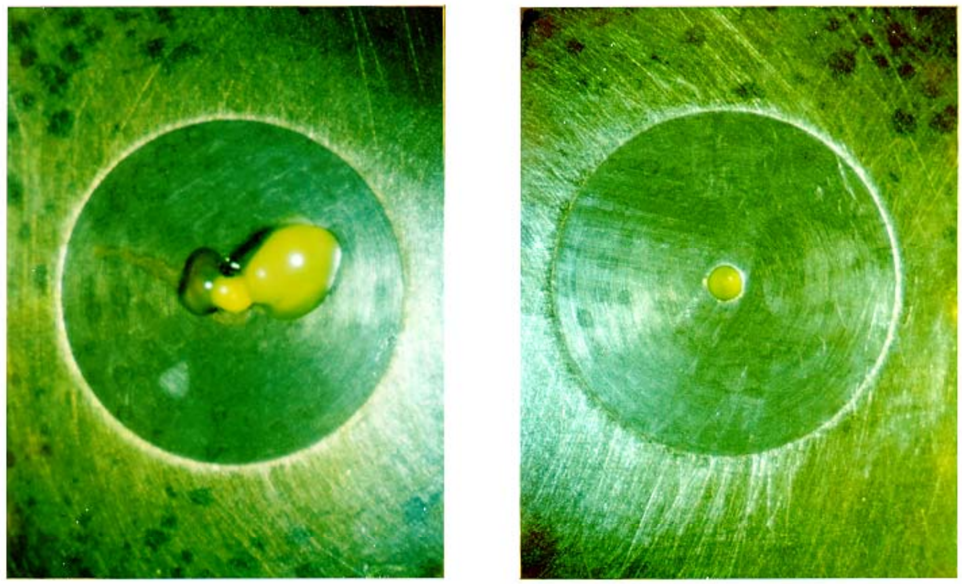


Figure 4: Photographs of the capillary die after extrusion of a yellow pigmented HDPE resin (left: without PPA right: with PPA)

Effect of PPA on properties of finished goods

After exiting an extrusion process, the inclusion of a PPA has little if any further intended purpose. The effect of its long-term presence in finished articles is an often-expressed concern.

To evaluate this concern, LLDPE blown films have been fabricated with PPA levels of 2 to 4 times the typical user levels [5]. Evaluation of mechanical properties such as tear, tensile and dart impact indicated no positive or negative effect due to the PPAs presence. Given the fluoropolymer has a density twice that of polyethylene its volumetric effect is only half of its weight contribution to the PE mixture.

Since the coating mechanism of PPAs can reduce pressure and torque during extrusion, PPAs can also be utilised to extrude under previously unattainable conditions such as higher throughput rates, through narrower die gaps and at lower temperatures. Changes in these variables allow for greater control of PE molecular orientation and hence optimization of mechanical properties. Extrusion through narrower die gaps can improve properties such as dart impact and the machine and transverse direction balance of tear properties. The effect of allowing increased cooling rates is especially noticeable with products like PPA-2. Visible reductions in haze and improvements in gloss are observed [5]. Gloss improvements have also been documented in applications in HDPE blow molded parts [6].

Finally, the components of the different PPA grades are optimized to prevent their migration from within solidified polyethylene. It is only in the melt phase under shear that the PPAs are designed to function.

To confirm this, the same films that were extruded for mechanical property measurements were evaluated over a one year period for surface changes. Surface energy and contact angle measurements, along with ESCA (Electron Spectroscopy for Chemical Analysis) and SSIMS (Static Secondary Ion Mass Spectroscopy) verified no physical or chemical presence of the PPAs at the surface of the films during a one year period, both corona treated and untreated. No effect was observed from the presence of intentionally elevated PPA levels.

Further surface studies have been completed in films formulated for outdoor packaging. PPA was added at a level of 2000 ppm to a formulation containing TiO_2 pigment, silica anti-block, HALS, UV absorber, anti-static agents, and slip agent. The films were corona treated and aged at 40 °C and 80 % humidity.
Surface wetting studies have indicated no negative effect due to the presence of PPA. No effect on the ability for, and stability of, corona treatment could be noticed.

Conclusions

Fluoropolymer-based processing additives provide a range of benefits beyond melt fracture elimination. Among these benefits are improved production capacities, and a better control of molecular orientation and final physical properties. Due to their design and low volumetric contributions, no adverse effects have been detected due to the PPAs presence.
As the needs to reduce production costs grows, so will interest for today's processor to get the most out his raw materials. The use of fluoropolymer-based processing additives will continue to meet that need.

References

1. 3M Method "Optical Microscopy Method for Dispersion Analysis in Polyolefins"

2. T. Blong, K. Fronek, B. Johnson, D. Klein, and J. Kunde, SPE Polyolefins VII Int. Conf. "Processing Additives on the Surface, Mechanical, and Optical Properties of LLDPE blown Film", 1994.

3. J. Horns TAPPI – Polymers, Laminations and Coatings Conference, Boston, MA, 1996, "The influence of Using Fluoropolymer Processing Additives to Improve the Extrusion Characteristics of LDPE/LLDPE Resin Blends".

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5. T. Blong, D. Klein, A. Pocius, and M. Strobel, SPE ANTEC 94 "The influence of Polymer Processing Additives on the Surface, Mechanical, and Optical Properties of LLDPE Blown Film", 1994.

6. D. Duchesne, T. Blong, and M. Brandon, SPE ANTEC 93 Conference Proceedings "Processing Additives in High Density Polyethylene Extrusion Blow Moulding Applications".

Polymer Processing Additives to Enlarge the Process Window for Polyolefin Extrusion

Presented by: Greet Dewitte

Prepared for TAPPI – May 14, 2003

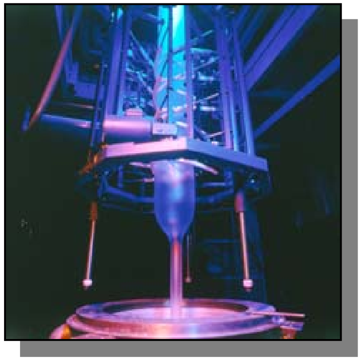
Outline

- Mechanism of fluoropolymer based Polymer Processing Additives (PPA’s)
- Performance benefits
- Influence of PPA’s on Optical, Physical and Surface Properties
- Conclusions

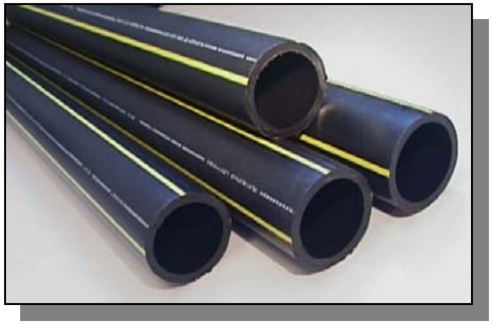
What are Polymer Processing Additives?

Dynamar™ Polymer Processing Additives are a family of Fluoropolymer based additives designed by Dyneon to improve the processing of polyolefin polymers, PA, PS, PVC and other plastics.

Applications in which PPAs are used



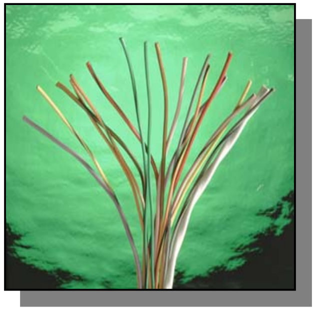
Blown Film



Pipe Extrusion

Cast Film

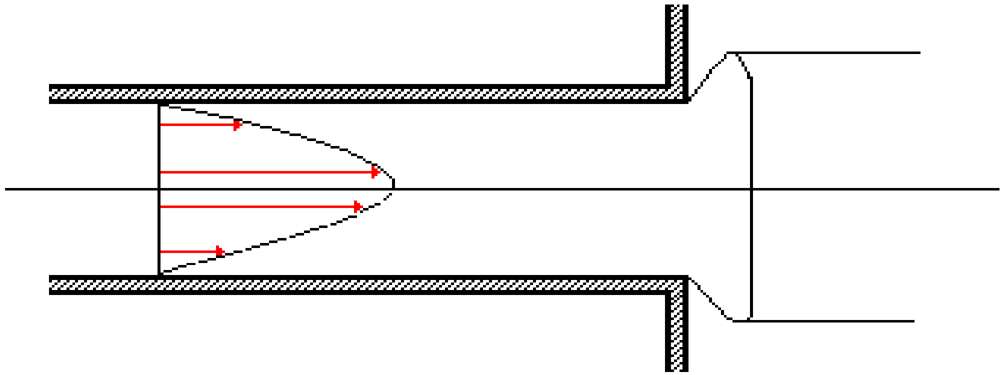
Pigment Dispersion



Wire & Cable

Blow Molding

Mechanism



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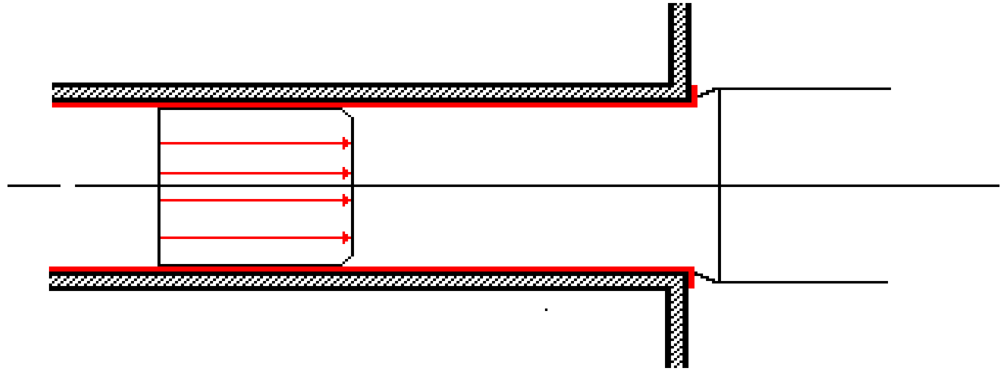
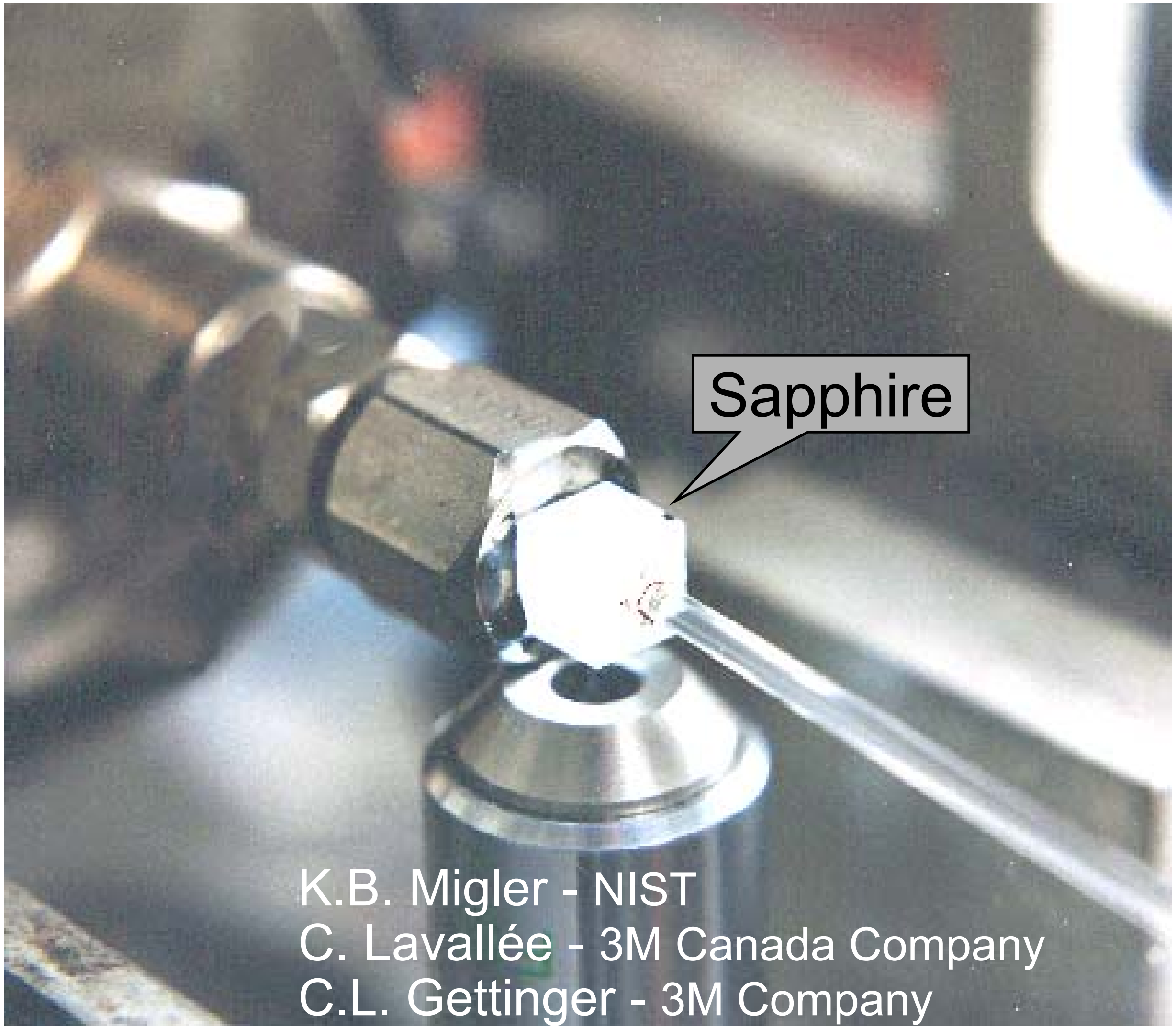
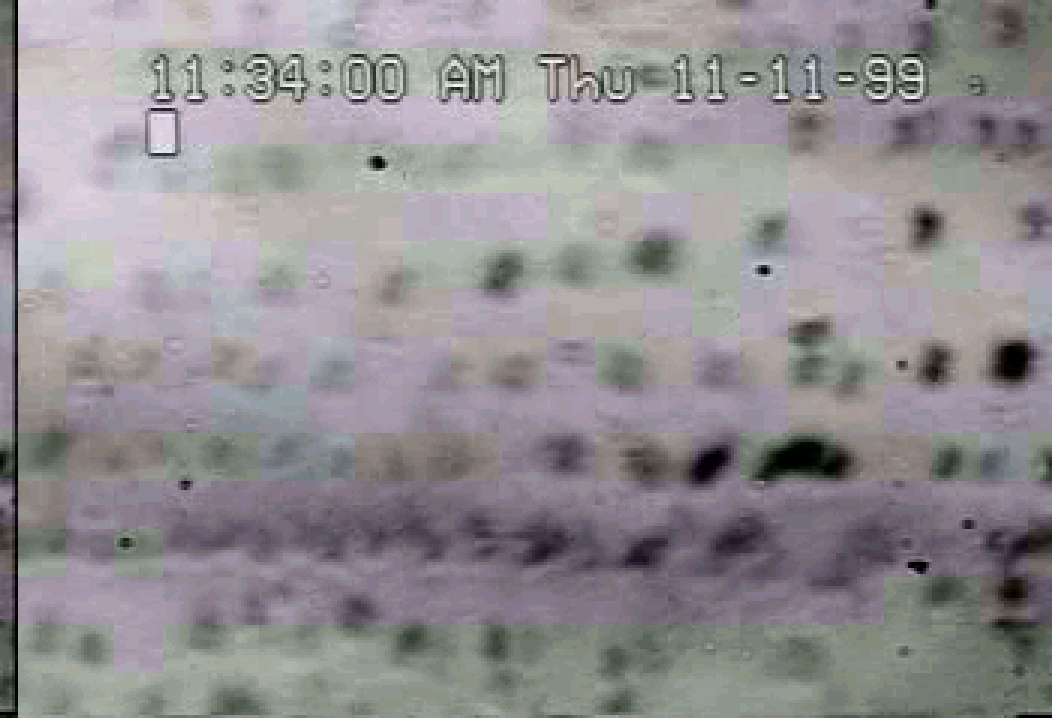


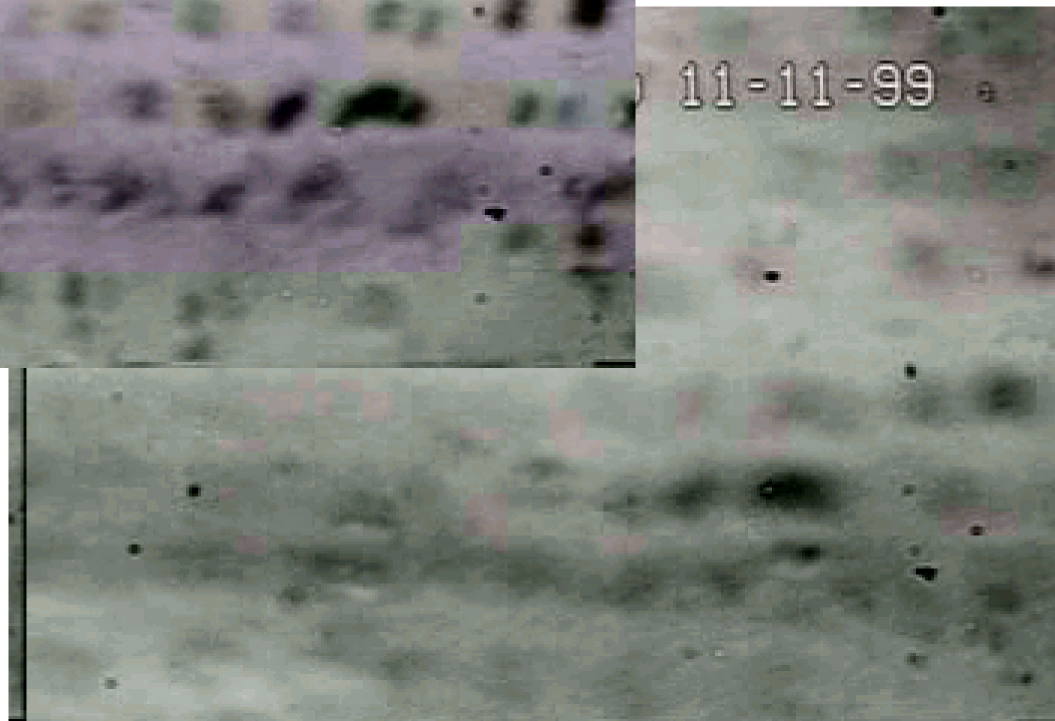
Using PPA

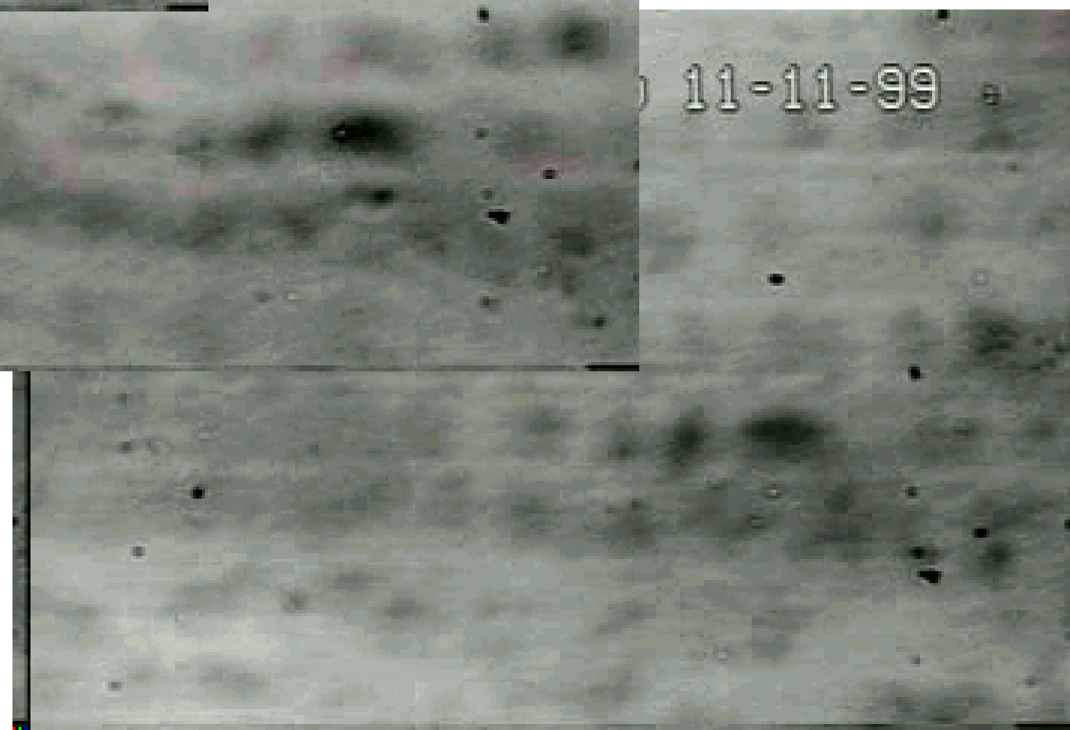
Capillary Rheo-optics





Flow Visualization





250X
Frame Width: 500μm

Dynamar™ PPA

FX 9613 (PPA 1)
- 90% fluoropolymer / 10% partitioning agent
- Free flowing powder
- Usually best choice for HDPE

FX 5920A (PPA 2)
- 97% synergistic blend / 3% partitioning agent
- Free flowing powder
- Usually best choice for LLDPE
- Usually best choice when additive interference exists

FX 5911 (PPA 3)
- 100% high temperature stable fluoroplastic
- Usually best choice for use under extreme conditions

General Benefits:

- *Eliminate melt fracture*
- **Extrusion through narrower die gaps**
  - **less machine direction drawing**
  - **better balance of properties**
  - **less cooling requirements**
  - **improved (better) gauge control**
  - **reduce production down time**
- **surface smoothness**
- **Faster color change**
- **Improve processing of lower MI resins**

Melt Fracture Elimination in BFL

Formulation: LLDPE

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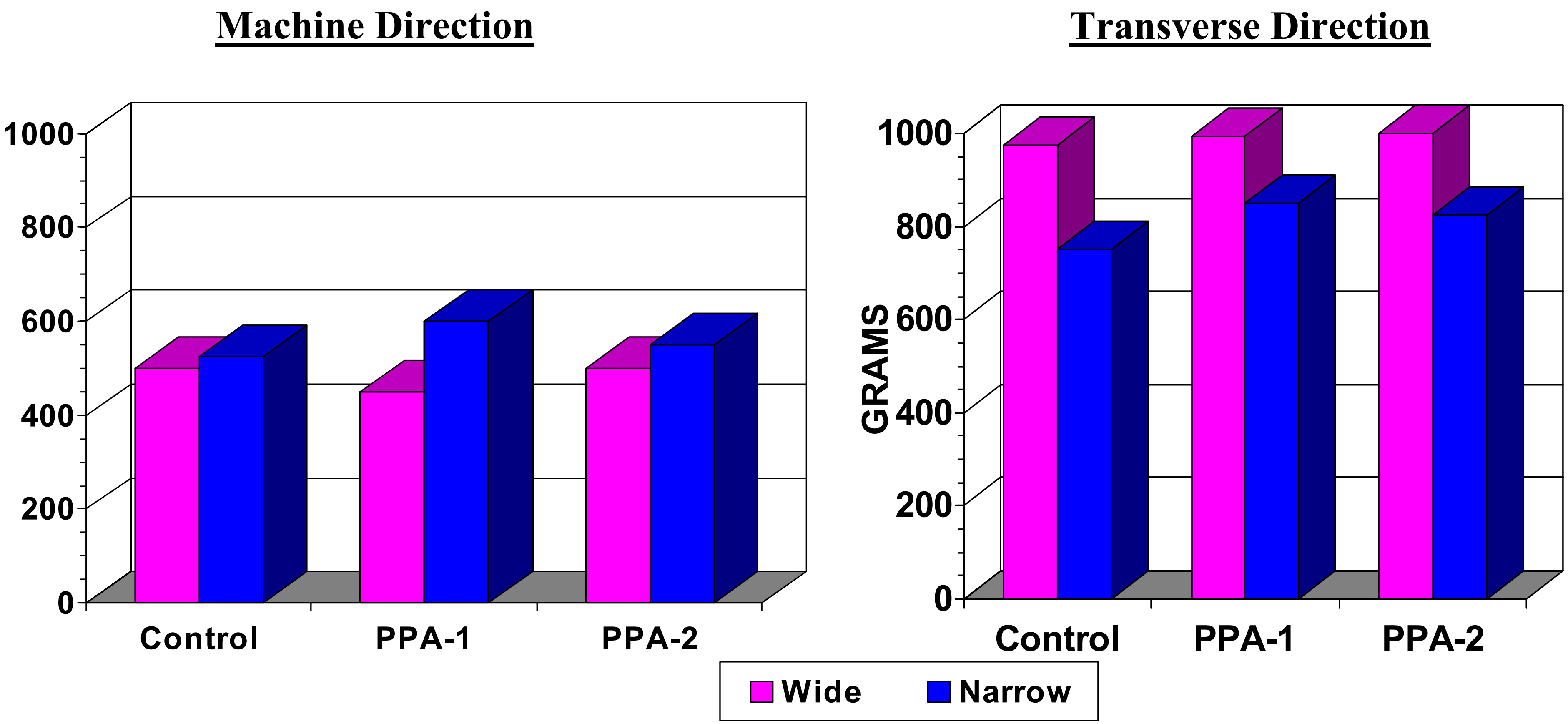
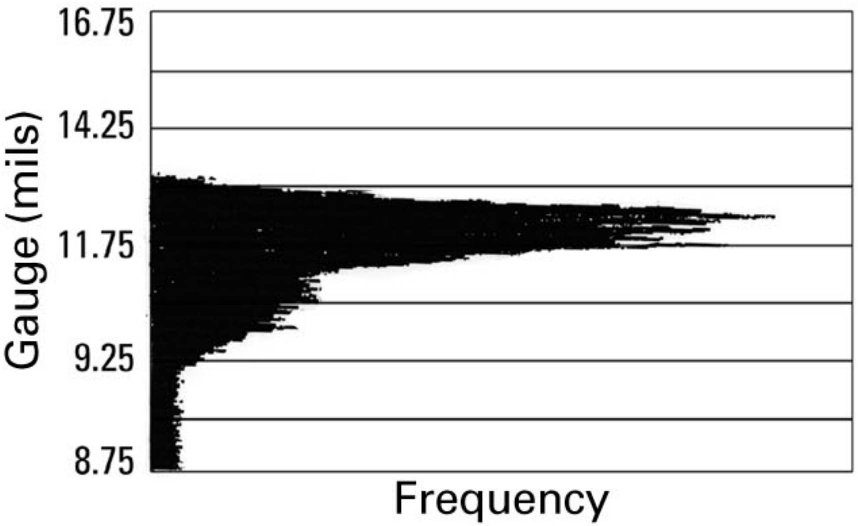
Better balance of properties
Effect of die Gap



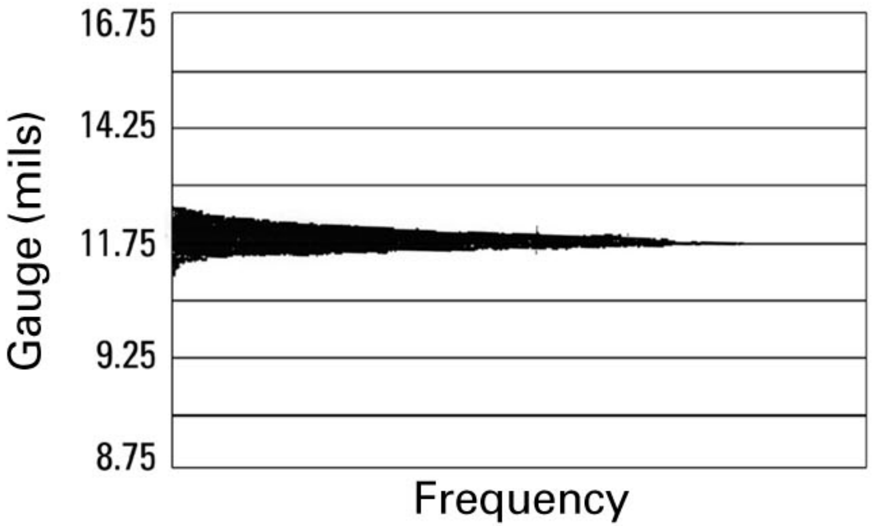
Tear Properties

film gauge for BOPP films

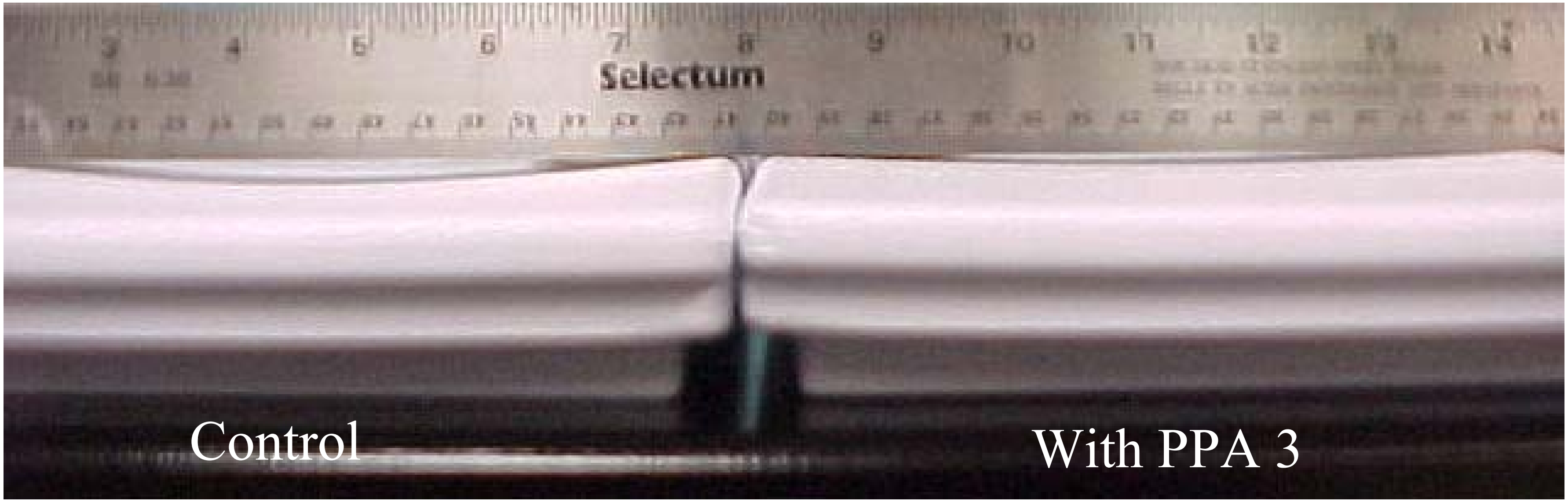
no PPA



300ppm PPA3



Less cooling requirements



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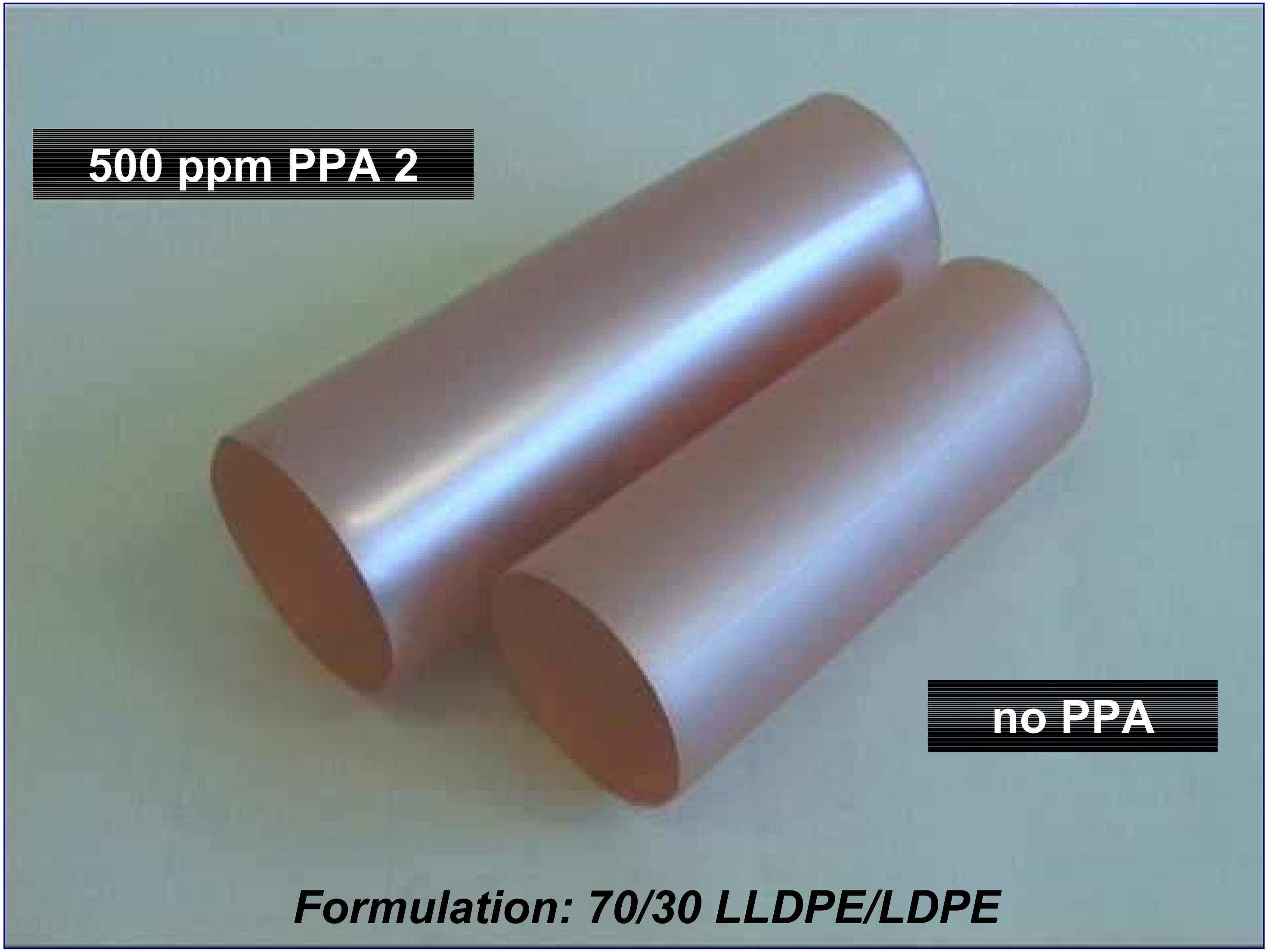
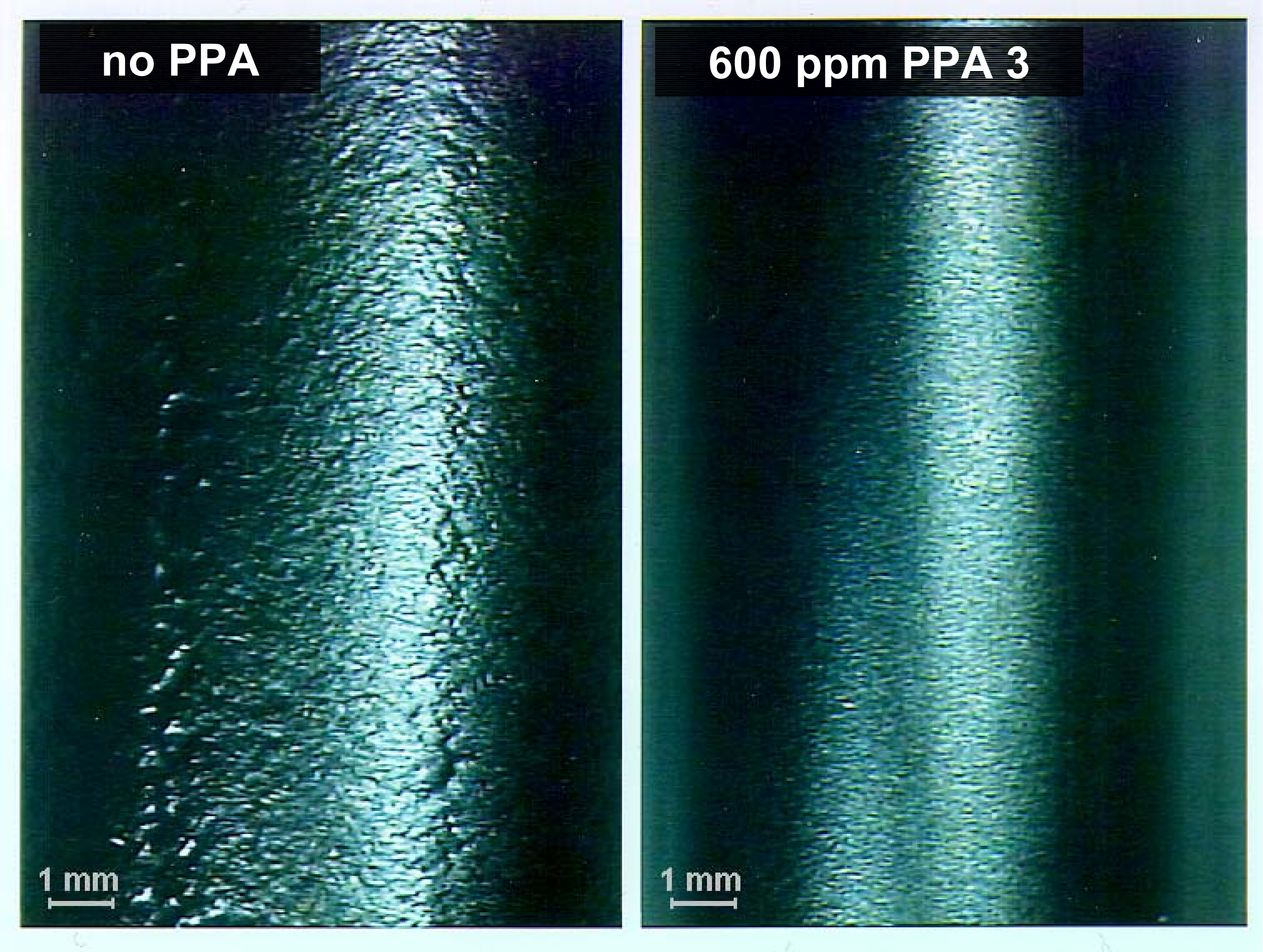
Tube for cosmetics



Photograph of inner side of pipe



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- Improve processing of lower MI resins

Color Change-over

No PPA

PPA 3

Other Color Change-over Examples

- **Semi-rigid PVC W&C Application**

  50% reduction in color changeover time.

- **PP Fiber Extrusion**

  30% reduction in color changeover time.

- **HDPE Cast Film Application**

  Color changeover time from 10 hr. to 1.25 hr.

- **Injection Molding of PET**

  20% Reduction in color changeover time.

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- ***Improve processing of lower MI resins***

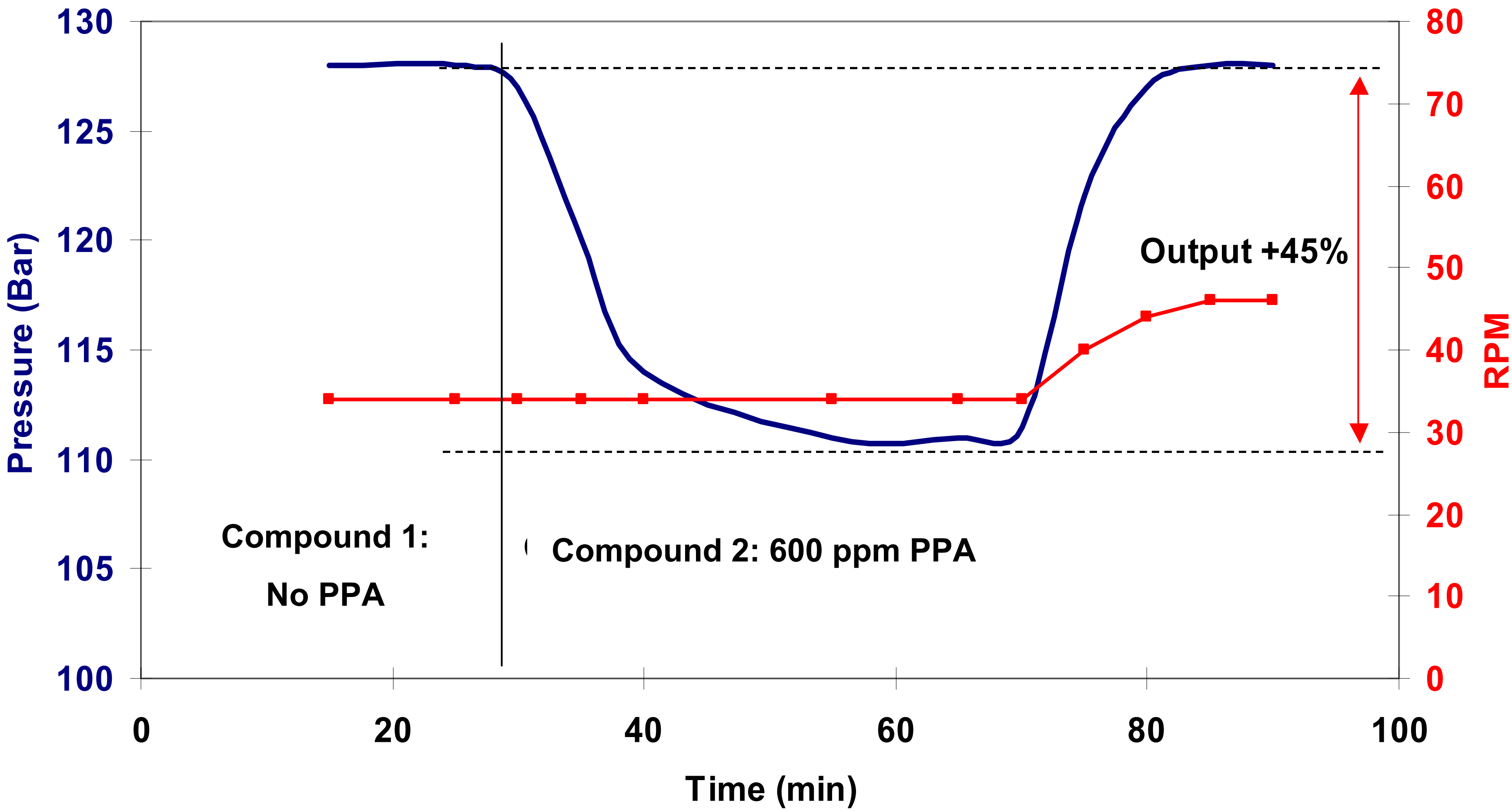
General Benefits:

- ***Reduce operating pressures and amperage draw***
  - increase output / energy savings
- **Operate at lower processing temperature**
  - decrease degradation / energy savings
- **Alleviate die build up**
  - reduce production down time
- **Reduction in gel formation**
- **Reduce (or eliminate) LDPE blending**

Effect of 600 ppm PPA on Output

Pressure & RPM

(Temp Constant)



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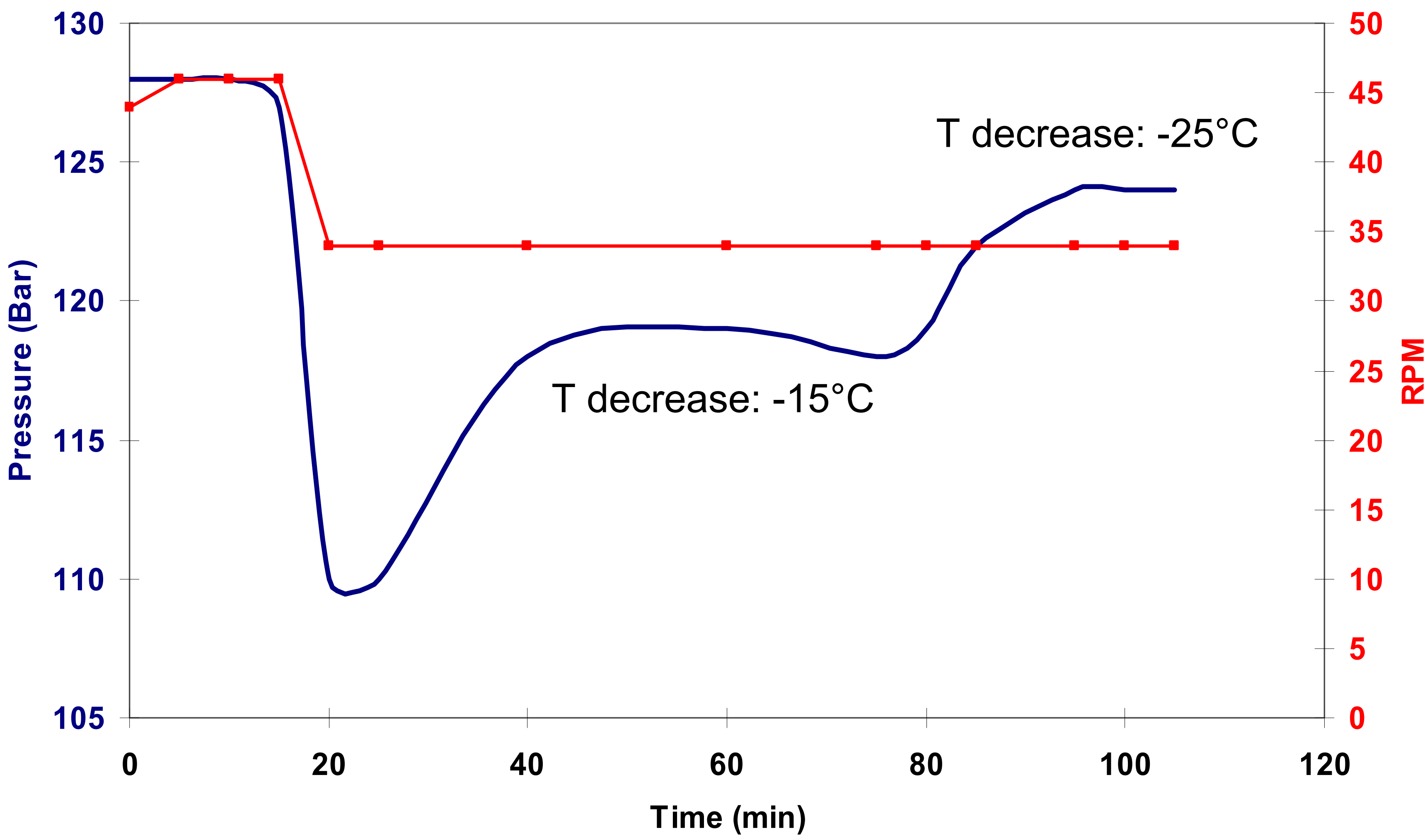
Effect of Temp decrease on Pressure

RPM Constant



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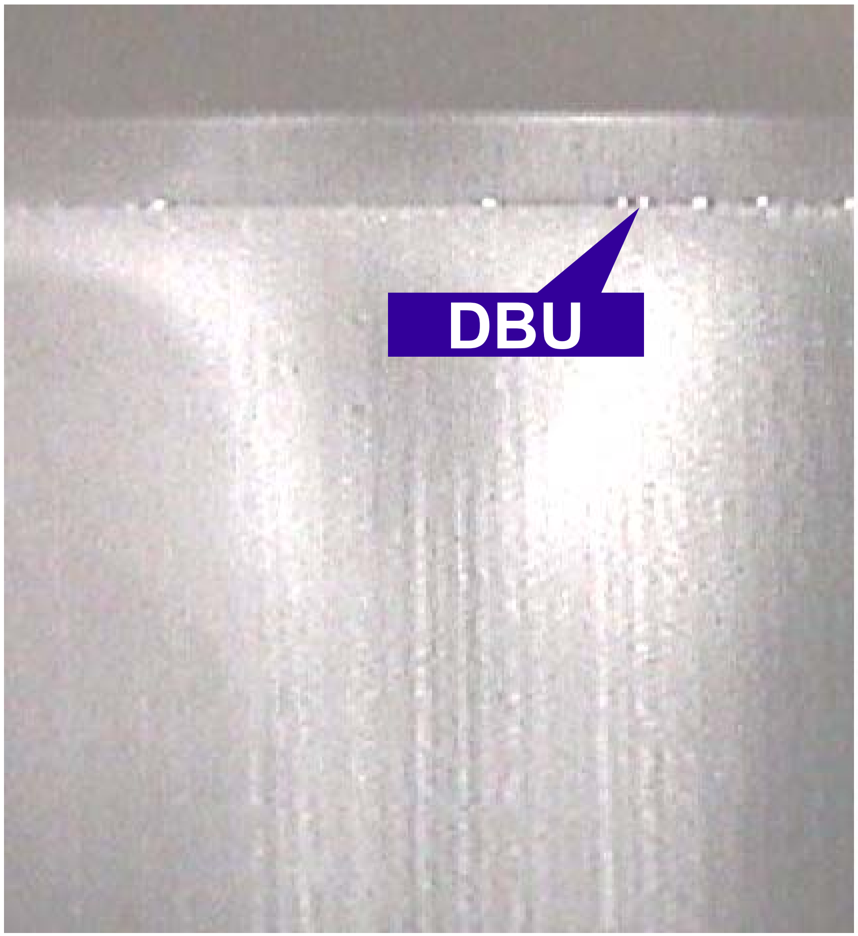
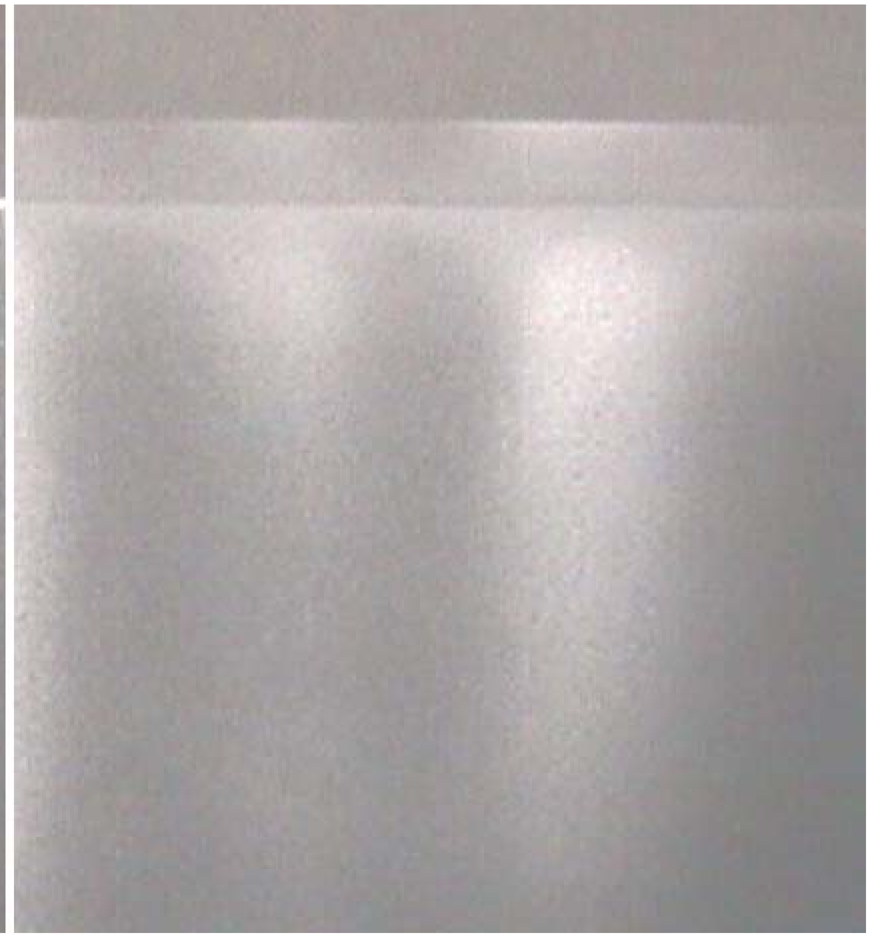
Die Build-Up Monitoring: Cast Film Line



LLDPE + 6% TiO_2



LLDPE + 6% TiO_2 + PPA 1

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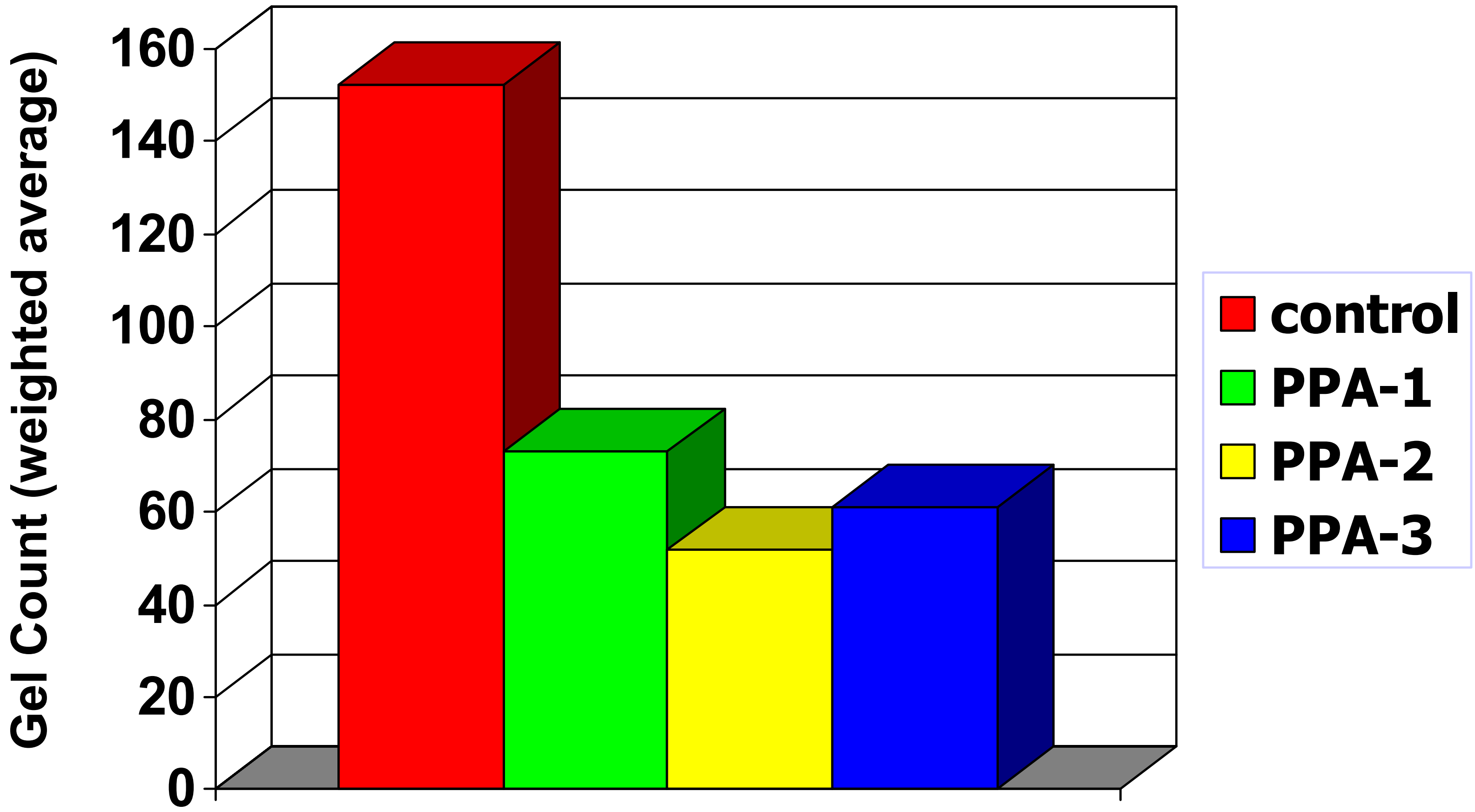
PPA Reduces Gels

Results Summary:



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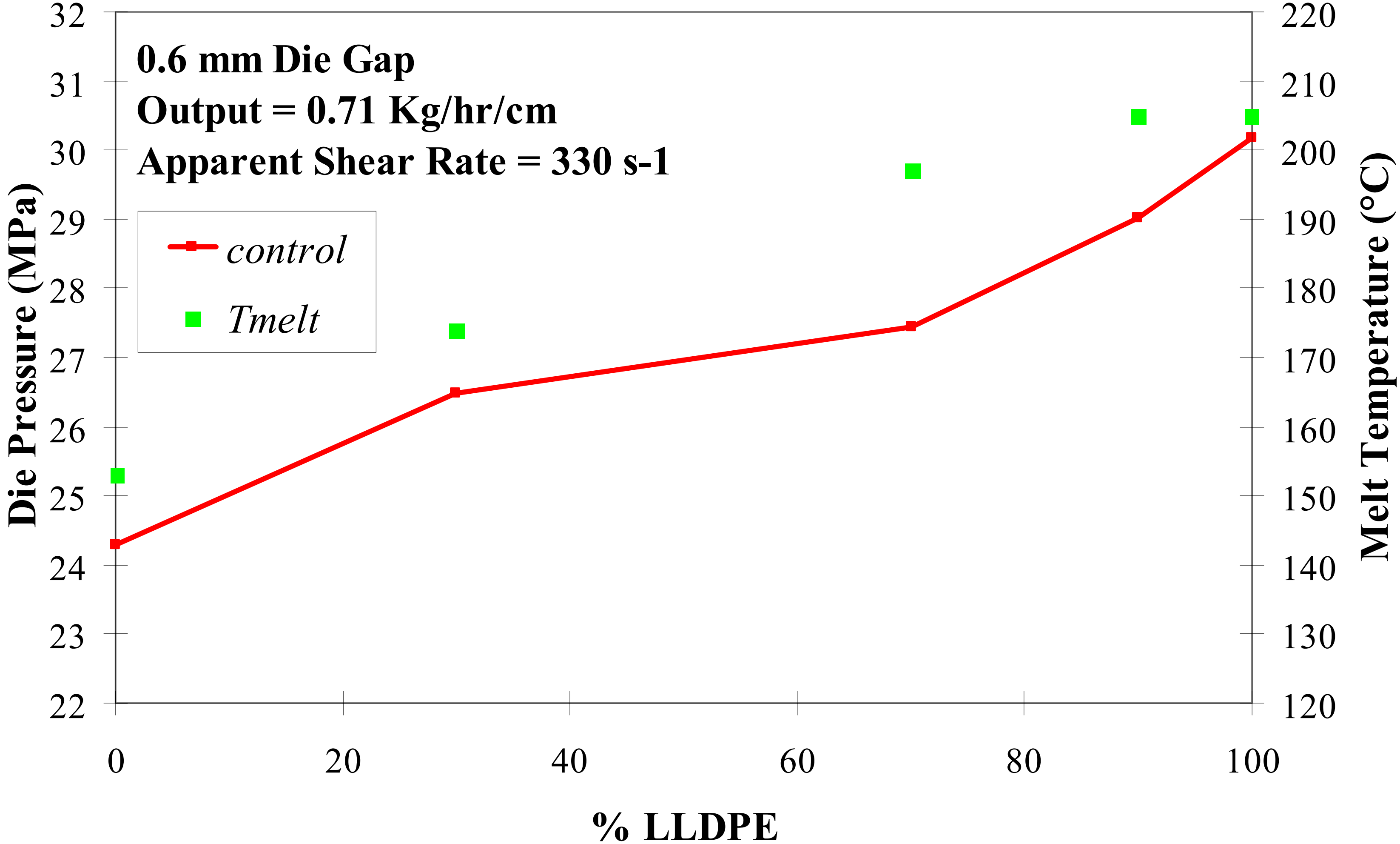
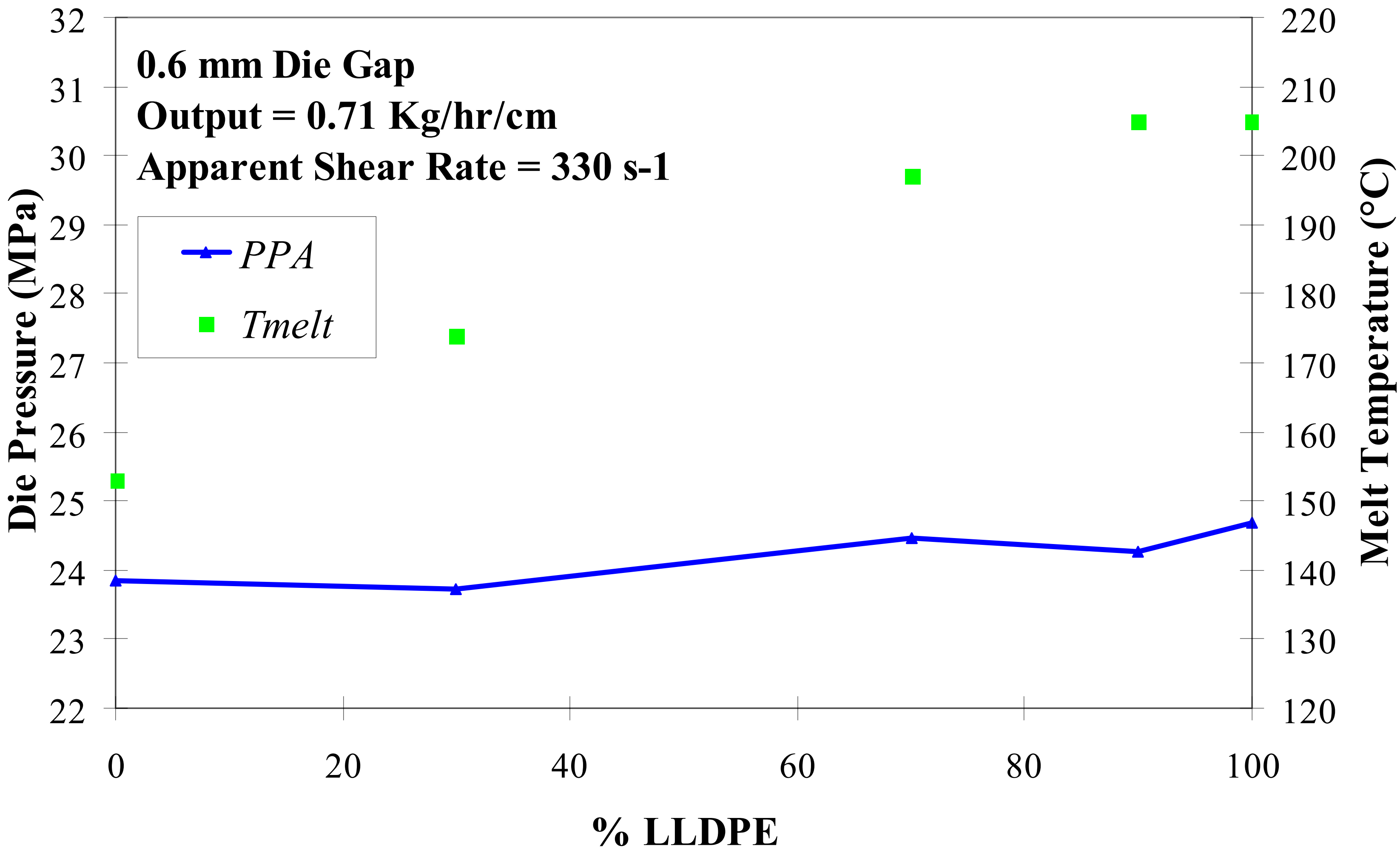
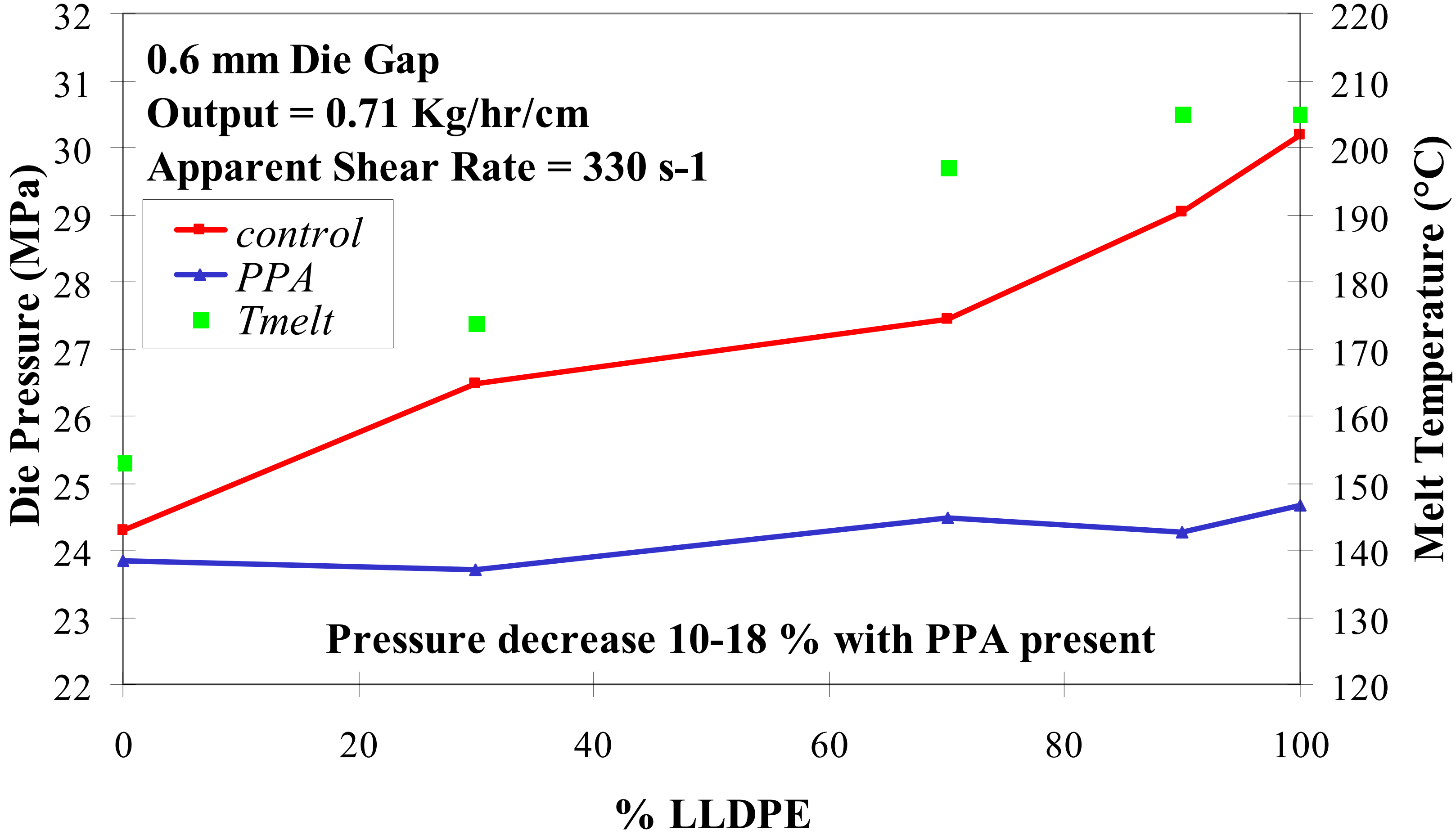
Die Pressure versus %LLDPE



Die Pressure versus %LLDPE



Die Pressure versus %LLDPE



The Influence of Dynamar™ Polymer Processing Additives On the Surface, Mechanical & Optical Properties of Extruded Articles

Influence on Optical Properties

Blown LLDPE Settings

- Materials
  - LLDPE 1
    - MFI 1,0
    - Dens. 0,918
    - C6
  - LLDPE 2 (mb carrier)
    - MFI 2,0
    - Dens. 0,918
    - C4

	Minimum Level	Test Level
PPA-1	400 ppm	**1500 ppm**
PPA-2	300 ppm	**1500 ppm**
Control:	95% LLDPE-1 5% LLDPE-2	

Minimum Level: PPA required to eliminate melt fracture in one hour

Extruder	Die	
89 mm (3.5 in)	Diameter:	20.3 cm (8 in)
24 L/D barrier screw	Gaps	2.3 mm (90 mils)
30-35 RPM		1.0 mm (40 mils)
86 kg/hr (190 lbs/hr)	BUR	2.5/1
Zones 1-5: 180 °C	Temp.	210 °C
	Film Gauge:	38 µm (1.5 mil)

Influence on Optical Properties

Property	Sample	Wide	Narrow
% Transmission	Control	93.6	93.6
	PPA-1	93.6	93.6
	PPA-2	93.5	93.5

% Haze	Control	15.9	14.6
	PPA-1	18.6	16.9
	PPA-2	16.2	9.5

% Gloss	Control	42.6	45.4
	PPA-1	40.8	45.3
	PPA-2	44.7	64.9

Influence on Mechanical Properties

Tensile Properties Wide Die Gap

ASTM D-822 Property		Control	1500 ppm	
		No PPA	PPA-1	PPA-2
Yield Stress, MPa	MD	12.6	12.6	12.6
	TD	13.0	12.9	13.3
Break Stress, MPa	MD	48.9	47.2	48.4
	TD	37.3	36.6	38.2
Break Elongation, %	MD	632	622	640
	TD	741	736	740

No Melt Fracture

Influence on Mechanical Properties

Seal Strength wide Die Gap

Property	Sealing Temp	Control No PPA	1500 ppm	
			PPA-1	PPA-2
Seal Strength, N	110 ^{o}C	1.58	1.57	1.67
	120 ^{o}C	11.18	11.50	11.10

Influence on Surface Properties

Wetability of Film Water Drop Contact Angle

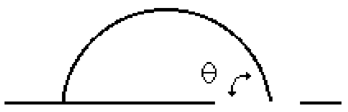
		Not Treated		**Corona Treated**	
		θ a	θ r	**θ a**	**θ r**
GAP	Film Sample	Degrees		**Degrees**	
WIDE	CONTROL	106	91	**69**	**25**
	PPA-1	107	91	**70**	**26**
	PPA-2	107	91	**70**	**27**
NARROW	CONTROL*	108	90	**72**	**24**
	PPA-1	107	90	**70**	**26**
	PPA-2	107	91	**69**	**24**

* Melt fracture present

Water contact angles

θa: Advancing Contact Angle

θr: Receding Contact Angle



Influence on Surface Properties

ESCA Results Corona Treated LLDPE film

		Day One			12 Month		
Gap	Film Sample	C %	O %	F %	**C %**	**O %**	**F %**
WIDE	**CONTROL**	86.9	12.2	-	**91.0**	**8.6**	**-**
	PPA-1	88.4	11.6	-	**91.5**	**8.5**	**-**
	PPA-2	87.8	12.2	-	**92.0**	**8.0**	**-**
NARROW	**CONTROL***	88.3	11.7	-	**91.3**	**8.7**	**-**
	PPA-1	88.4	11.6	-	**90.9**	**9.1**	**-**
	PPA-2	88.5	11.5	-	**91.2**	**8.5**	**-**

* Melt fracture present

Conclusions

Dynamar™ PPA provide processing benefits to a wide range of polyolefin applications that result in an overall increase in productivity.