Title:
Dynamar™ Fluoropolymer Processing Additives (PPAs) in Applications of HDPE Pipes

Abstract:
Fluoropolymer based polymer processing additives (PPAs) are Frequently used in the polyethylene industry. Besides their ability to eliminate melt fracture and die build-up, PPAs are used to optimize the process conditions in a wide range of applications without having to make compromises on the properties of the final products. This paper explores technical experiments showing how Dynamar™ PPAs can improve the various aspects of polyethylene extrusion, which results in a broader processing window for the plastic converter, without negative effects on the mechanical properties of the pipes.

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Dynamar™
Polymer Processing Additives

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Dynamar™ Fluoropolymer Processing Additives (PPAs) in Applications of HDPE Pipes

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ABSTRACT

Fluoropolymer based polymer processing additives (PPAs) are frequently used in the polyethylene industry. Besides their ability to eliminate melt fracture and die build-up, PPAs are used to optimize the process conditions in a wide range of applications without having to make compromises on the properties of the final products.

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INTRODUCTION

Fluoropolymer based polymer processing additives are known to be active in polyolefins by the formation of a dynamic fluoropolymer coating on the metal surface of the die. Fluoropolymers are immiscible with polyolefins. Under high shear conditions, the dispersed droplets of the fluoropolymer will migrate to the outside of the melt flow to form a coating on the metal die wall. This coating will eliminate the zero-velocity condition near the die wall. The result is that the sharp velocity profile will change to a plug flow shaped profile by reduced shear resistance at the polymer / metal interface. During extrusion, this effect is translated into a reduction of the gate pressure and to a smooth surface of the extrudate[1].

PPAs were originally designed to solve surface defects such as sharkskin or cyclic melt fracture during polyethylene extrusion. However, when these PPAs became more widely used in the polyolefin market, their function broadened.

The use of PPAs allows a wider choice of the type of resin. For instance the pressure drop that can be observed allows the use of a resin with a lower melt index which could be beneficial for the properties of the extruded goods.

In a recent study, it was shown how the level of LLDPE could be increased in a blend with LDPE without running into a high pressure condition on extrusion equipment typically designed for LDPE[2]. Also in another study it was proven that PPAs were suitable for the reduction of die build-up[3] and the reduction of gels[4].

The aim of this work is to discuss the benefits that a plastic converter can experience on the various aspects of polyethylene extrusion when using fluoropolymer based polymer processing additives.

The Effect of PPA on the Process Parameters During HDPE Extrusion:

Compounds were prepared based on a HDPE resin
(Melt Index: 0.45 [5 kg/10 min], Density: 0.946 g/cm).
All compounds contained 2.5% carbon black.

For the experiments described in this paper, the following polymer processing additives were used:

PPA 1:	Dynamar™ PPA FX 9613
PPA 2:	Dynamar™ PPA FX 5920A
PPA 3:	Dynamar™ PPA FX 5911X
PPA 4:	Dynamar™ PPA FX 5920B

Earlier experiments using a capillary rheometer were performed for a comparison with the different types of PPAs. PPA 1, PPA 2 & PPA 3 were added at equal levels to the black compounds. PPA 3 showed the best performance in this specific HDPE resin in terms of the greatest reduction in apparent viscosity. For this reason, PPA 3 was chosen in this experiment to scale up the extrusion trials.

A reference compound contained no polymer processing additives. To one compound, 300 ppm of PPA 3 was added. A second one contained 600 ppm PPA 3. The PPA and the carbon black were added to the HDPE resin via a masterbatch containing 40% of a “P type” carbon black manufactured by Cabot Corporation.

Compound 1: HDPE + 2.5% CB + 0 ppm PPA (Reference)

Compound 2: HDPE + 2.5% CB + 600 ppm PPA 3

Tubes were produced using a Reifenhauser 45 mm single screw extruder. The extruder was equipped with a tubing die with an outside diameter of 11.8 mm and an inside diameter of 8.3 mm.

The Influence of PPA on the Extrusion Pressure

The first investigation examined the effect of the PPA on the gate pressure at constant motor speed and constant temperature.

A stable reference pressure at 131 bar was established with compound 1. Subsequently, compound 2 was added into the extruder. This compound contained 600 ppm of PPA 3.

The motor speed and the temperature were kept constant while the pressure was monitored. Almost immediately the pressure started to decrease which is a typical result of PPA coating the die wall. After about 20 minutes the pressure became stable at 110 bar. This corresponds with a pressure reduction of 13%. *(Figure 1)*.

Higher PPA levels may result in faster conditioning times and greater pressure drops.

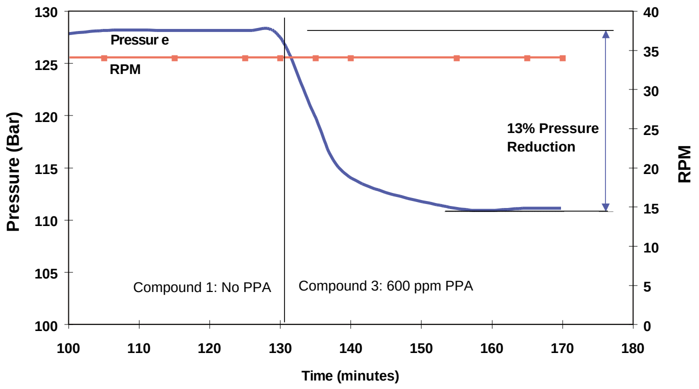


Figure 1: The influence of 600 ppm PPA 3 on the pressure during HDPE pipe extrusion

The Influence of PPA on Output

In a second test the influence of 600 ppm PPA 3 was examined to evaluate the effect on the output of the extruder when the material was processed at constant pressure and temperature. This test allows one to quantify the benefits of PPA for increasing output on a conversion process where the pressure is the limiting factor for the productivity.

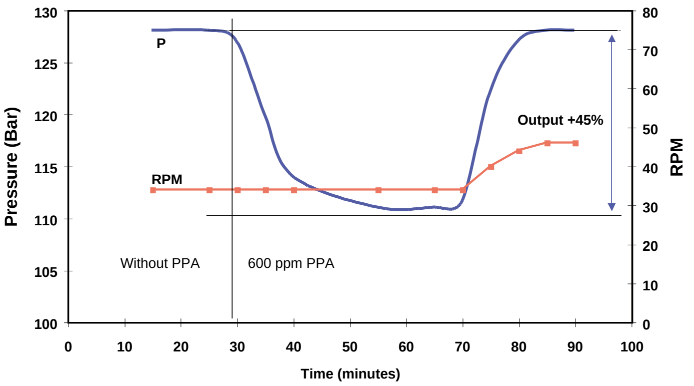


Figure 2: The additional output during HDPE pipe extrusion at constant pressure using 600 ppm PPA 3

The motor speed was increased after reaching equilibrium at the reduced pressure when extruding the compound containing 600 ppm PPA 3. Starting at 34 rpm, the motor speed was increased step by step until the pressure of the extruder reached the reference pressure at 47 rpm. The output was measured before and after the motor speed was increased. An output increase of 45% was realized *(Figure 2)*.

The effect of PPA will typically be weaker during the production of larger wall thickness and stronger for the production of thin walled pipes.

The Influence of PPA on the Temperature / Pressure Conditions

It may be beneficial to lower the extrusion temperature of the process. For critical applications less degradation of the resin will have a positive impact on the final properties. Also, lower temperatures will decrease the accumulation of die build-up. For blown film extrusion, a lower temperature will result in a more stable bubble. Pipes extruded at a lower temperature will have less taste and odor issues. For blow molding, lower temperatures will decrease the cycle time.

This experiment shows how PPA 3 allows for decreasing the temperature settings of the extruder without exceeding pressure limits.

The settings of the extruder were established, without PPA, at a motor speed of 34 rpm and at the corresponding pressure of 128 bar (Temperature settings 1).

A processing additive was introduced to the system and the pressure came to equilibrium at 110 bar. At this point, the temperature settings of the different zones in the extruder were lowered by 15 - 20°C (27 - 36°F) (Temperature settings 2). The temperatures of the first zones (including the feeding zone) were kept constant. When the temperature reached the new settings, the pressure increased from 110 to 118 bar.

In a second step the temperature was reduced an additional 10°C (18°F) (Temperature settings 3).

Temperature settings :

	T1	T2	T3	T4	T5	T6	T7	T8	T9	Tdie	
1	160	200	210	220	225	225	225	230	230	230	(°C)
2	160	200	200	205	210	210	210	210	210	200	
3	160	200	200	200	200	200	200	200	200	200	

At the point where the temperature became stable, the pressure reached a value of 124 bar. This pressure is still lower than the value that was obtained during the process of the reference compound at a temperature of 25°C (45°F) higher. As a result, using PPA 3 at 600 ppm allows a reduction of the temperature settings by 25 - 30°C (45 - 54°F) without compromising the output or pressure limits.

Figure 3 shows how the pressure changes in function of the different temperatures settings of the extruder.

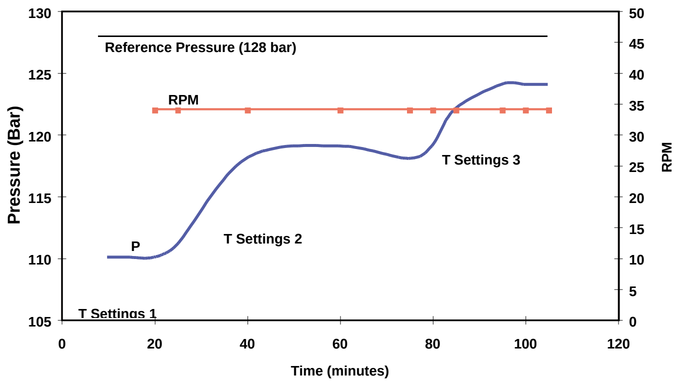


Figure 3: The pressure as a function of temperature during HDPE pipe extrusion using 600 ppm PPA 3

The Effect of PPA on Long Term Hydrostatic Strength Properties (LTHS)

Dynamar PPA's are immiscible with the HDPE resins. Upon mixing the phases separate as described above. Over a short time frame they form a thin, low surface energy layer on the die. This layer reduces the force needed to move the polymer melt across the die surface. The shear stress is reduced significantly *(Figure 4)* and hence the apparent viscosity is lower in a PPA containing formulation compared to the control resin *(Figure 5)*. Also the graph in Figure 6 shows an important feature of using Dynamar PPA: the lowest apparent viscosity was achieved at low level addition and at low temperatures. This is important for the HDPE pipe product as well; enabling the manufacturer to maintain and preserve the physical properties of the resin formulation which may benefit the life span of the pipe product.

Since PPA forms a discrete separate phase, there is concern by pipe and resin producers that these particles may concentrate stress or cause crack propagation. The following data, obtained through an independent testing organization, suggest that the LTHS property of HDPE pipe is not affected by adding a processing additive *(Figures 7-8)*.

EXPERIMENTAL

HDPE Polymers: Resin A = HDPE, density 0.947; HLMI 9
Resin B = HDPE, density 0.945; HLMI 10
Resin C = HDPE, density 0.944; HLMI 9

LTHS Testing:

Each resin was compounded with 1000 ppm of PPA and compared to a control without PPA. The high concentration was chosen in order to maximize the impact of PPA on physical properties. Pipe specimens were tested according to ASTM D2837 and ISO TR 9080.

PPA 1, 2 and 3 were tested at 23°C (73.4°F) according to ASTM D2837 in Resin A. The PPA was added from a combined masterbatch with carbon black to limit the amount of masterbatch carrier resin added to the formulation.

PPA 4 was tested at all test temperatures of ISO TR 9080 (20, 60 and 80°C) (68, 140 and 176°F) in Resin B. PPA 4 was directly compounded into the granular resin after the polymerization process.

The actual testing of the pipe specimens was contracted to an independent testing site used by the pipe industry.[5]

Capillary Rheometer Testing:

Capillary rheometer samples containing the desired levels of fluoropolymer processing additives were produced by adding the Dynamar FX 5911X directly to the host resin at three concentrations: 500, 1000 and 1500 ppm. The formulations under evaluation did not contain carbon black.

The capillary (446°F) evaluation was done at two temperatures of 190°C (374°F) and 230°C. A 0.51 mm diameter (D) flat entry die of 2 cm in length (L), an L/D = 40, was used. A sample containing PPA 3 was allowed to condition the capillary die. After conditioning, the sample was evaluated for responses through a shear rate range of 50 – 1100s^{-1}.

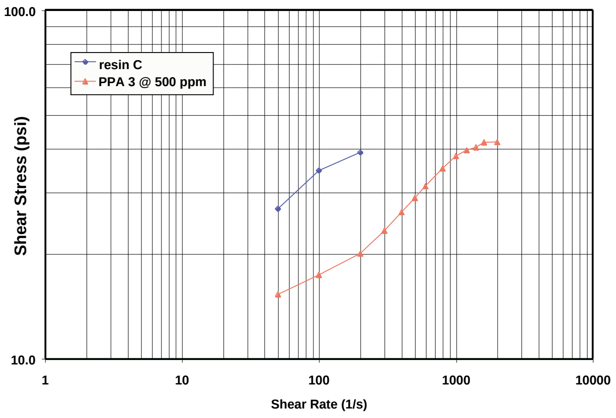


Figure 4: Capillary evaluation at 190°C (374°F): reduction in shear stress

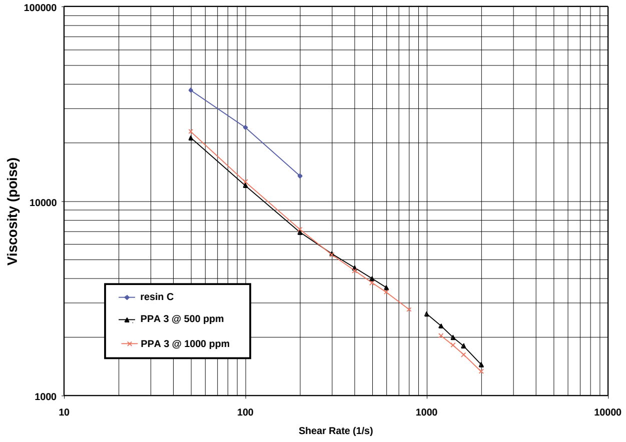


Figure 5: Capillary evaluation at 190°C (374°F): lower apparent viscosity

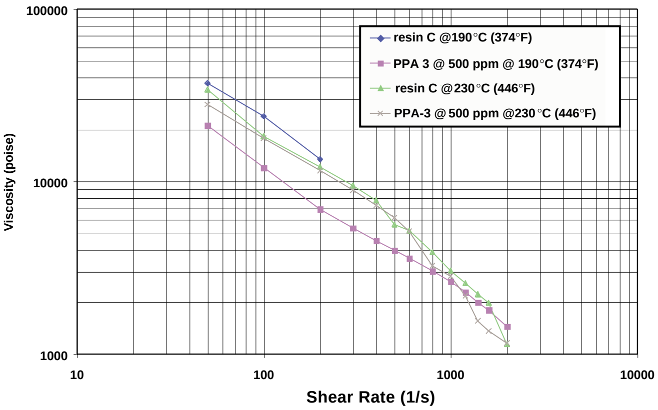


Figure 6: Capillary evaluation at 190°C (374°F): lowest viscosity at low temperature

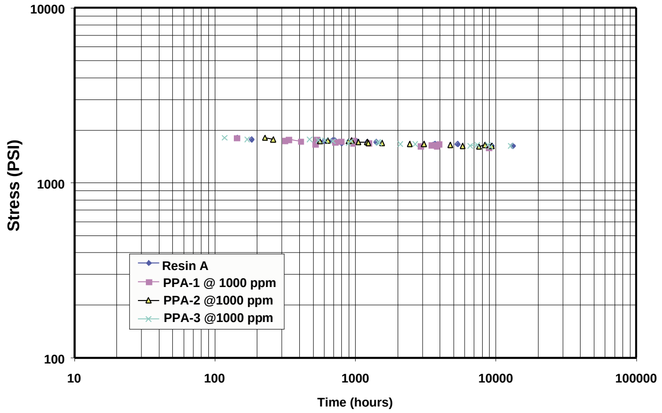


Figure 7: LTHS data in resin A at 23°C (73.4°F)(ASTM D2837)

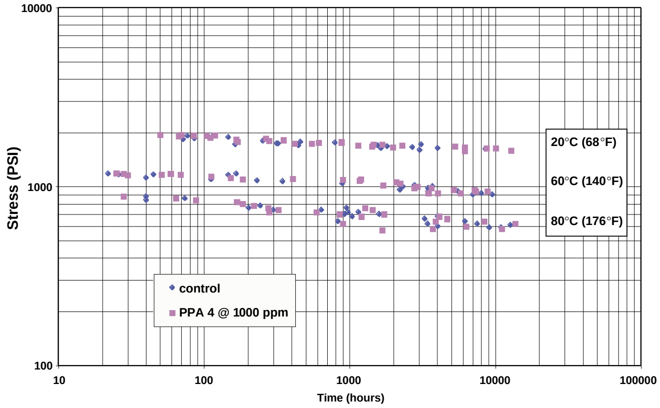
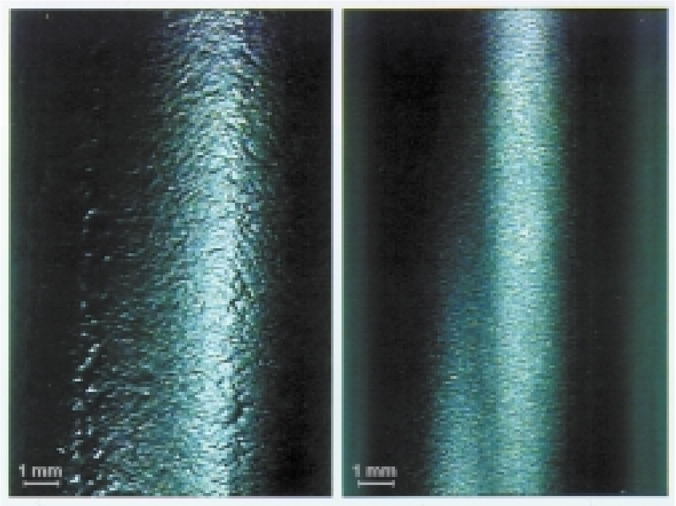


Figure 8: LTHS Data in resin B at 20°C (68°F), 60°C (140°F) & 80°C (176°F) (ISO TR9080)

The Surface Appearance

The surface conditions of the pipes were visually observed after extrusion. Figure 9 shows photographs of the surfaces of the inside of a pipe sample without PPA (left) and a sample with 600 ppm PPA 3.



Without PPA

With 600 ppm Dynamar™ FX 5911X

Figure 9: Photographs of the surface of the inside pipe wall

CONCLUSIONS:

Using PPA during HDPE extrusion results in a significant pressure reduction in the extruder. A reduction in torque will reduce the energy consumption of the extruder.

When the pressure in the extruder is the limiting factor, addition of PPAs can increase the output significantly when the equipment has the capability and the cooling capacity to handle this additional output.

Using PPA allows a reduction in temperature settings without compromising the output or pressure limits.

Compounds containing PPA lead to a smoother surface. Long-term mechanical tests give no indication that the use of PPA has a negative effect on the long-term mechanical properties of HDPE pipes.

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