This technical paper was written and developed in October, 2001 when the author(s) was an employee of Dyneon LLC. Dyneon LLC was formerly a wholly-owned subsidiary of 3M Company and was fully integrated into 3M Company on January 1, 2011.

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.

Date Published: October, 2001
Dynamar™ Fluoropolymer Processing Additives (PPA's) in Applications of HDPE Pipes

Siegmund Papp
Dyneon LLC

Steve E. Amos
Dyneon LLC

Joris Briers
Dyneon LLC
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.

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 extrudate1.

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 LDPE². Also in another study it was proven that PPAs were suitable for the reduction of die build-up³ and the reduction of gels⁴.

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.
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.

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).

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 (77°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.

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
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.

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.
REFERENCES:


5. Springborn Testing and Research, 10 Water Street, Enfield, CT, 060682
Technical Information and Test Data
Technical information, test data, and advice provided by Dyneon personnel are based on information and tests we believe are reliable and are intended for persons with knowledge and technical skills sufficient to analyze test types and conditions, and to handle and use raw polymers and related compounding ingredients. No license under any Dyneon or third party intellectual rights is granted or implied by virtue of this information.

Important Notice:
Because conditions of product use are outside Dyneon’s control and vary widely, user must evaluate and determine whether a Dyneon product will be suitable for user’s intended application before using it. The following is made in lieu of all express and implied warranties (including warranties of merchantability and fitness for a particular purpose): If a Dyneon product is proved to be defective, Dyneon’s only obligation, and user’s only remedy, will be, at Dyneon’s option, to replace the quantity of product shown to be defective when user received it or to refund user’s purchase price. In no event will Dyneon be liable for any direct, indirect, special, incidental, or consequential loss or damage, regardless of legal theory, such as breach of warranty or contract, negligence, or strict liability.

© Dyneon 2001
Issued: 10/01
Printed in USA
98-0504-1403-0
All Rights Reserved

Product Information:
+1 651 733 5353   +1 800 723 9127

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

Dyneon GmbH & Co. KG
Hammfelddamm 11
D-41460 Neuss, Germany
Phone: +49 2131 14 2227
Fax: +49 2131 14 3857

Dyneon GmbH & Co. KG
Werk Kelsterbach
D-65444 Kelsterbach, Germany
Phone: +49 6107 772 516
Fax: +49 6107 772 517

Dyneon N.V.
Canadestraat 11, Haven 1005
B-2070 Zwijndrecht, Belgium
Phone: +32 3 250 7537
Fax: +32 3 250 7905

Dyneon GmbH & Co. KG
Succursale France
Boulevard de l’Oise, Tour 3M F-95506 Cergy France
Phone: +33 1 3031 6611
Fax: +33 1 3031 6613

Dyneon GmbH & Co. KG
Sede Secondaria Italia
Via San Bovio, 3
Milano San Felice
I-20090 Segrate (MI) Italy
Phone: +39 02 7035 3206-7
Fax: +39 2 7035 3208

www.dyneon.com
Dynanar and Dyneon are trademarks of Dyneon

Dyneon GmbH & Co. KG
UK Branch House
3M House
P.O. Box 1, Market Place
Bracknell, Berkshire, RG12 1J U
United Kingdom
Phone: +44 1344 429675
Fax: +44 1344 429484

Sumitomo 3M Limited
33-1 Tamagawadai 2-chome
Setagaya-ku, Tokyo
158 Japan
Phone: +81 03 3709 8111
Fax: +81 33709 8743

3M China Limited
10/F, New Town Mansion
55 Liu Shan Guan Road
Shanghai 200035
P.R.C.
Phone: +86 21 6725 3553
Fax: +86 21 6725 2343

3M Singapore Pte. Ltd.
9, Tagore Lane
Singapore 787472
Phone: +65 450 8822
Fax: +65 552 2119

3M Australia Pty., Ltd.
950 Pacific Highway
Pymble, N.S.W. 2073
Australia
Phone: +61 2 9498 9333
Fax: +61 2 9498 9666

3M Canada Inc.
P.O. Box 5757
London, Ontario NGA 4T1
Phone: +519 451 2500
Fax: +519 452 6262

3M Brazil
Via Anhanguera, km. 110
Sorocaba, Sao Paulo
CEP 13181-900
Phone: +55 13984 7000
Fax: +55 1338 606

www.dyneon.com
Warranty, Limited Remedy, and Disclaimer: Many factors beyond 3M's control and uniquely within user's knowledge and control can affect the use and performance of a 3M product in a particular application. User is solely responsible for evaluating the 3M product and determining whether it is fit for a particular purpose and suitable for user's method of application. Unless a different warranty is specifically stated in the applicable product literature or packaging insert, 3M warrants that each 3M product meets the applicable 3M product specification at the time 3M ships the product. 3M MAKES NO OTHER WARRANTIES OR CONDITIONS, EXPRESS OR IMPLIED, INCLUDING, BUT NOT LIMITED TO, ANY IMPLIED WARRANTY OR CONDITION OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE OR ANY IMPLIED WARRANTY OR CONDITION ARISING OUT OF A COURSE OF DEALING, CUSTOM OR USAGE OF TRADE. If the 3M product does not conform to this warranty, then the sole and exclusive remedy is, at 3M's option, replacement of the 3M product or refund of the purchase price.

Limitation of Liability: Except where prohibited by law, 3M will not be liable for any loss or damages arising from the 3M product, whether direct, indirect, special, incidental or consequential, regardless of the legal theory asserted, including warranty, contract, negligence or strict liability.

Technical Information: Technical information, recommendations, and other statements contained in this document or provided by 3M personnel are based on tests or experience that 3M believes are reliable, but the accuracy or completeness of such information is not guaranteed. Such information is intended for persons with knowledge and technical skills sufficient to assess and apply their own informed judgment to the information. No license under any 3M or third party intellectual property rights is granted or implied with this information.