

This technical paper was written and developed in May, 1998 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:

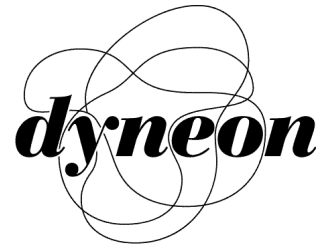
The Application of Fluoropolymer Based Processing Aids in Polypropylene and Thermoplastic Rubber

Intro:

The use of fluoropolymer based processing aids (FPA) to eliminate melt fracture in polyethylene (LLDPE and HDPE) is well known (1 - 4). For other polyolefins the use of this type of processing aid is limited to a few general statements in patents, papers and product literature with little or no supporting data. In commercial practice, the use of FPA in polypropylene and other olefin based polymers is small in comparison with polyethylene. In the case of polypropylene, shear thinning and degradation lower the polymer melt viscosity, making it less susceptible to melt fracture. Yet, the use of FPA can be effective for lowering extrusion pressure - increasing polymer throughput, and eliminating die drool (die lip build-up). As for thermoplastic rubber, the use of FPA has not been examined publicly.


To answer some of the above information gaps, experiments were performed to examine the effect of FPA on PP and styrene-ethylene-butadiene-styrene (SEBS) thermoplastic rubbers. The experiments were conducted on lab equipment (capillary rheometer) and on a lab-scale fiber extrusion line.

Date Published: May, 1998



A 3M Company

**The Application of
Fluoropolymer Based Processing
Aids in Polypropylene and
Thermoplastic Rubber**

By Stephen E. Amos 

Pro-fax is a trademark of LyondellBasell Industries Holdings, B.V.

Kraton is a trademark of the KRATON Polymers Group of Companies.

Achieve is a trademark of ExxonMobil Corporation.

The Application of Fluoropolymer Based Processing Aids in Polypropylene and Thermoplastic Rubber

INTRODUCTION

The use of fluoropolymer based processing aids (FPA) to eliminate melt fracture in polyethylene (LLDPE and HDPE) is well known (1-4). For other polyolefins the use of this type of processing aid is limited to a few general statements in patents, papers and product literature with little or no supporting data. In commercial practice, the use of FPA in polypropylene and other olefin based polymers is small in comparison with polyethylene. In the case of polypropylene, shear thinning and degradation lower the polymer melt viscosity, making it less susceptible to melt fracture. Yet, the use of FPA can be effective for lowering extrusion pressure, increasing polymer throughput, and eliminating die drool (die lip build-up). As for thermoplastic rubber, the use of FPA has not been examined publicly.

To answer some of the above information gaps, experiments were performed to examine the effect of FPA on PP and styrene-ethylene-butadiene-styrene (SEBS) thermoplastic rubbers. The experiments were conducted on lab equipment (capillary rheometer) and on a lab-scale fiber extrusion line.

EXPERIMENTAL

Materials

Processing Aids:

FPA-1 = a blend of vinylidene fluoride/hexafluoropropylene copolymer with polyethylene oxide (Dynamar™ FX 5920A).

FPA-2 = vinylidene fluoride/hexafluoropropylene copolymer ground to a 25 mesh powder (Dynamar™ FX 9613).

FPA-3 = Dynamar™ FX 5911X

Polymers:

0.5 MFR polypropylene homopolymer, unstabilized (Pro-Fax™ 6801 from Montell Polyolefins).

1.4 MFR polypropylene homopolymer, unstabilized (Pro-Fax™ 6601 from Montell Polyolefins).

35 MFR polypropylene homopolymer, stabilized pellet (Achieve™ 3825 from Exxon Polymers).

1.5 MFR polypropylene homopolymer, stabilized, mixed with a 57% green pigment MB.

2 Grades of SEBS (Kraton™ G-1657, Kraton™ G-6578 from Shell Chemical).

Equipment and Sample Preparation:

Masterbatches and final (let-down level) FPA formulations, for capillary rheometry, were prepared using a torque rheometer and mixing bowl fitted with roller blades. The mixing sequence included a three minute loading period at 210°C and 15 rpms. After the third minute the rotors were ramped up to 50 rpms with the temperature held constant. This condition was held for approximately 4.5 minutes (total of 8 minutes) and then the rotors were stopped and the material was removed from the bowl. The mass of material removed from the bowl was allowed to cool to room temperature, chopped and ground into pieces small enough to be added to the capillary barrel.

Capillary rheometer experiments were performed using a flat entry die with a 0.508 mm diameter and a 40/1 L/D. The unstabilized PP samples were extruded at 230°C. The 1.5 MFR PP and the SEBS samples were extruded at 190°C. The polymer was held for 10 minutes, at extrusion temperature, to allow it to come to thermal equilibrium before extrusion. The load needed to maintain a constant shear rate was recorded and translated to apparent viscosity and apparent shear stress. Samples containing FPA coat the die with a mechanism reported in previous literature (4). Depending on the type of resin and processing conditions, a load reduction may be observed showing the efficiency of the FPA. The viscosities are reported uncorrected for entrance effects.

Formulations made from unstabilized polypropylene flake were also blended with antioxidants and an acid neutralizer to provide stabilization. The package consisted of 1000 ppm of Irganox™ 1010, 1000 ppm Irgafos™ 168, 700 ppm calcium stearate.

Formulations made for the die build-up experiments blended the 1.5 MFR polypropylene base polymer, with a green pigment masterbatch in the torque rheometer at conditions similar to those reported above.

Masterbatches of the FPA's, for use during the fiber spinning experiments, were made on a counter rotating, intermeshing, conical twin screw extruder. The extrudate was water quenched and pelletized. Base resin was tumble blended with the FPA for 30 minutes prior to extruding the material.

The fiber extrusion line consisted of a 63.5 mm extruder connected to a gear pump and then connected to the die. The spinnerette had 250 orifices. Melt temperature was kept at 315°C. Pressures were monitored in the extruder, gear pump entrance, gear pump exit and die.

RESULTS AND DISCUSSION

Processing aids function by coating the metal surface of a die, effectively changing the interfacial properties between the metal and the polyolefin melt. Since polyolefins have a low surface tension they can interact, stick, to the high surface tension metal surface. The FPA has an even lower surface tension than a polyolefin so it preferentially coats the die surface and provides a slip interface for the polyolefin.

The FPA coating mechanism is also dependent on several physical characteristics such as base resin polymer viscosity, dispersion and concentration of the FPA. Given these factors, there are some characteristics of polypropylene that have limited FPA applications. For one, the viscosity of polypropylene is generally lower compared to that of LLDPE and HDPE (these polymers broadly use processing aid technology for the elimination of melt fracture and to enhance their processing characteristics). To illustrate this viscosity difference Figures 1 & 2 compare the apparent viscosities of two polypropylene homopolymers with film grades of LLDPE and HDPE respectively. The lower viscosity of polypropylene makes the FPA less effective in coating the die surface.

The viscosity difference can become even greater if polypropylene undergoes oxidative chain scission. This chain scission/viscosity lowering mechanism is actually utilized in some commercial applications of polypropylene such as film and fiber extrusion. Unfortunately the degradation can also negatively effect the physical properties of the final product. If processing aid technology can be developed which lowers polypropylene's apparent viscosity, then the degradation mechanism can be skipped in favor of preserving the molecular weight and physical properties of the final product.

Capillary Experiments

The grades of polypropylene selected for this study were low MFR, high molecular weight materials used in extrusion processes to form PP netting, geotextiles and film. Since a polymer's melt viscosity is dependent on temperature, there is generally a temperature range or processing window at which a polymer may be processed without melt fracture. Figure 3 shows the reduction of apparent viscosity for a 0.5 MFR PP, at 200s⁻¹, over a range of temperatures. The samples containing FPA have an equal or greater response to increasing temperature in comparison with the base resin without FPA,.

The responses (apparent viscosities) of 0.5 MFR and 1.4 MFR PP resin, to the addition of 1000 ppm of FPA-1, and FPA-2 are shown in Figures 4 and 5. For FPA-2 the apparent viscosity is reduced 10.2% and 14.4% for the 0.5 MFR and 1.4 MFR PP respectively. This is at the lowest shear rate measured - 50s⁻¹. At higher shear rates the apparent viscosities of samples containing FPA-1 and FPA-2 match that of the control without FPA.

The response of the higher viscosity (0.5 MFR) PP was much greater for the experimental FPA-3, see Figure 6. Not only is the apparent viscosity reduction greater than FPA-1 and FPA-2 but it covers a wider range of shear rates (10 to 20% reduction from 50 to 800s⁻¹). In effect FPA-3 can allow a higher molecular weight polypropylene (6801) to process similarly to a lower molecular weight polymer at shear rates less than 600s⁻¹, see Figure 6. A summary of apparent viscosity reductions for these three processing aids is shown in Table 1.

Along with reducing apparent viscosity, the FPA is also able to delay the onset of melt fracture as seen in the capillary extrudate. Table 2 shows the shear rate for the onset of melt fracture for the three different FPA's. Again, FPA-3 is more effective in delaying the onset of melt fracture for the 0.5 MFR PP (300s⁻¹) as compared to FPA-1 (none) and FPA-2 (100s⁻¹).

The same type of capillary experiment was used to evaluate two SEBS polymers. These materials are being used in various extrusion applications such as nonwoven fibers and as a coextrusion layer in polyolefin films. Figure 7 shows the response of these SEBS grades to FPA -2. The apparent viscosity was reduced 23% and 15% with FPA-2 at the lowest shear rate (50s⁻¹). A reduction in apparent viscosity was evident out to 700s⁻¹. A delay in the onset of melt fracture from 200s⁻¹ (no FPA-2), to 1200s⁻¹ (1000 ppm FPA-2) was observed for grade 6578.

Die Build-Up Experiments

The final capillary experiment evaluated the die drool of a heavily pigmented PP resin used for synthetic grass carpets. The 1.5 MFR base resin was blended with a green pigment masterbatch (7% final pigment concentration). Samples with and without FPA-1, and FPA-2 were extruded at 190°C. The control sample developed die drool after 1 barrel of capillary extrusion (see Photo 1). In contrast, the samples containing 300 ppm of FPA-1 and FPA-2, had no die drool (Photos 2 & 3).

Fiber Extrusion Experiments

Another possible application for FPA technology is in polypropylene fiber extrusion. Some critical properties that depend on the polymer rheology are; the resultant fiber diameter, the efficiency of the fiber line (least amount of fiber breaks), and the extrusion pressure in the die or spinnerette. In order to obtain a small fiber diameter, low viscosity polypropylene is used. The polymer is blown or spun to a thin fiber diameter after exiting the die. The polypropylene may be low in viscosity as polymerized or oxidatively degraded to lower viscosities with high temperature, and/or with the use of relatively expensive organic peroxide additives.

An experiment was conducted to see if FPA could be used to make an as polymerized 35 MFR polypropylene (35 MFR) process on a lab-scale fiber extrusion line, with reasonable extrusion pressures, to obtain small fiber diameters. The mechanism for obtaining small diameter fibers is theorized to be related to the lack of die swell caused by the presence of FPA. Comparisons of the process data and fiber diameter are shown in Table 3. The use of FPA-2 significantly reduced the extrusion pressure and resulted in a lower fiber diameter.

CONCLUSION

Though polypropylene does not suffer from melt fracture as much as HDPE and LLDPE the use of fluoropolymer based polymer processing aids can provide the benefits of lowering apparent viscosity, lowering extruder pressure - increasing throughput, and eliminating die drool. Capillary rheometer experiments showed that depending on the choice of FPA, the apparent viscosity of low MFR PP can be lowered by 20% over a wide range of shear rate. An even greater reduction in apparent viscosity, 25%, is possible in extrusion grades of SEBS. The use of FPA was also able to eliminate die drool, in a capillary rheometer, for a heavily pigmented grade of PP. And finally, the reduction of extrusion pressure and fiber diameter was seen in a semi-commercial melt blown fiber process.

CONTRIBUTIONS

The author would like to thank Greet DeWitte, Dyneon - Belgium, for her work on the die drool experiments. Thanks also go to Glenda Brunsell for running the capillary rheometer, Scott Tuman for help with the fiber processing experiments and to Claude Lavallee for discussions concerning process aid mechanisms.

REFERENCES

1. A. Rudin, A. Worm and J. Blacklock, J. Plast. Film Sheet, "Fluorocarbon Elastomer Processing Aid in Film Extrusion of LLDPE's" 1(3): 189(1985).
2. A. Valenza, F. P. La Mantia, Intern. Polymer Processing - 2, 3/4:220 (1988).
3. K. Fronek, B. Johnson, T. Blong, J. Kunde, D. Duchesne, SPE ANTEC 1990 Conference Proceedings, "Tailoring Processing Additives for High Density Polyethylene Applications", 1172 (1990).
4. Blong, T. J., Klein D. F., Pocius A. V., Strobel M. A., TAPPI Polymer Laminations and Coatings Conference Proceedings, The Influence of Polymer Processing Additives on the Surface, Mechanical, and Optical Properties of LLDPE Blown Film, (1993).

Figure 1: PP Viscosity Compared to PE at 230°C

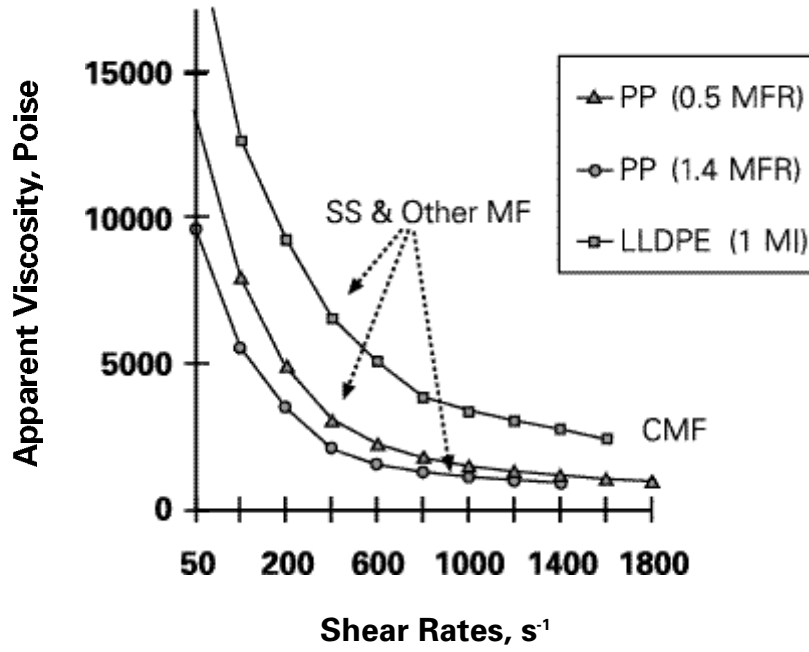


Figure 2: PP Viscosity Compared to PE at 210°C

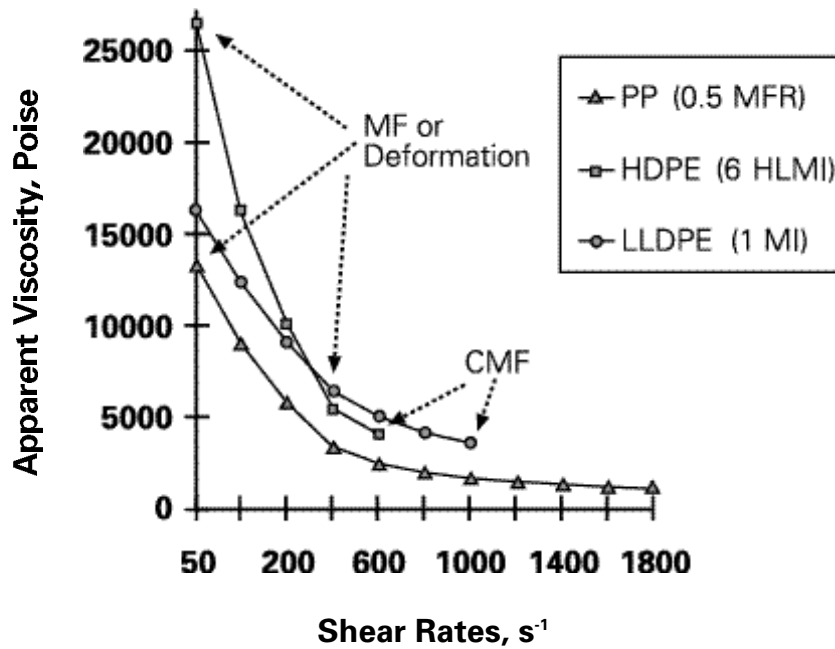


Figure 3: Effect of FPA's on PP at Different Temperatures 0.5 MFR PP at 200s⁻¹

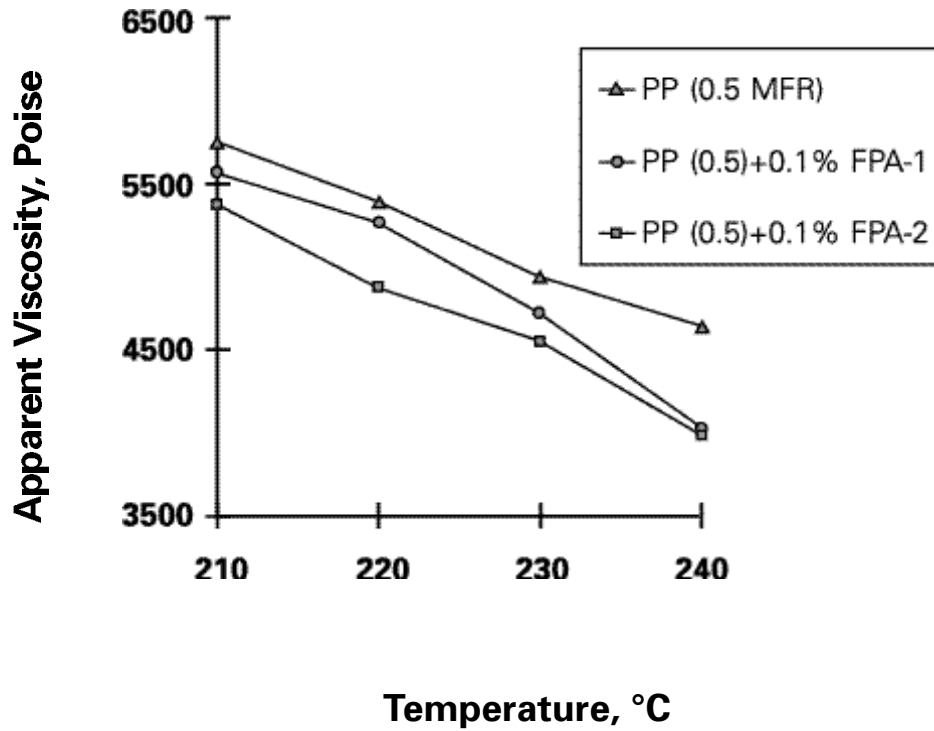


Figure 4: Effect of FPA-1 on PP Viscosity at 230°C

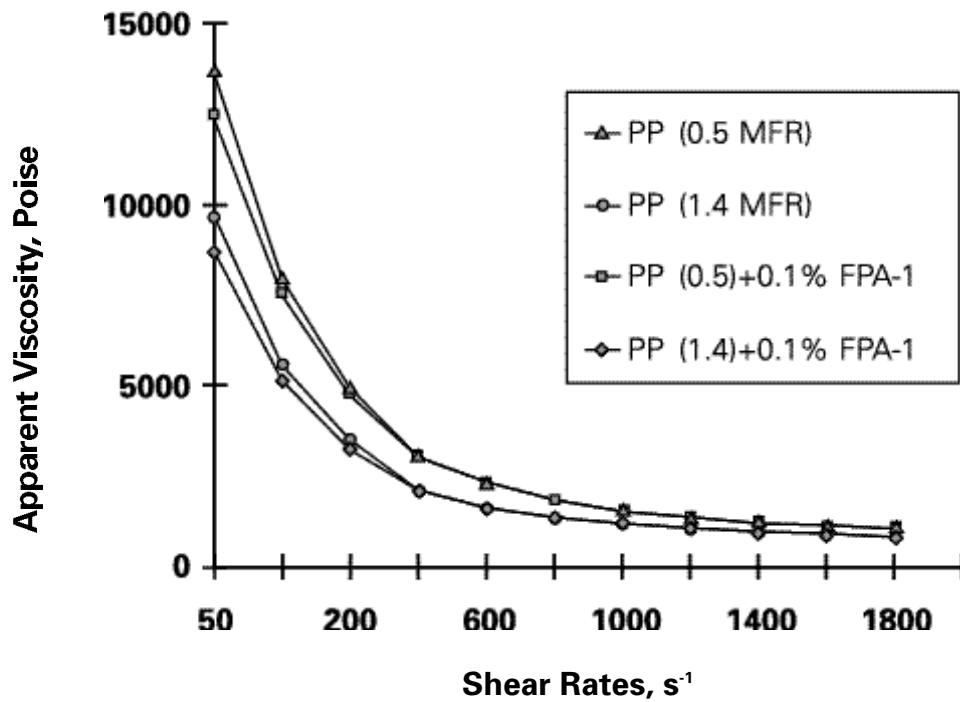


Figure 5: Effect of FPA-2 on PP Viscosity at 230°C

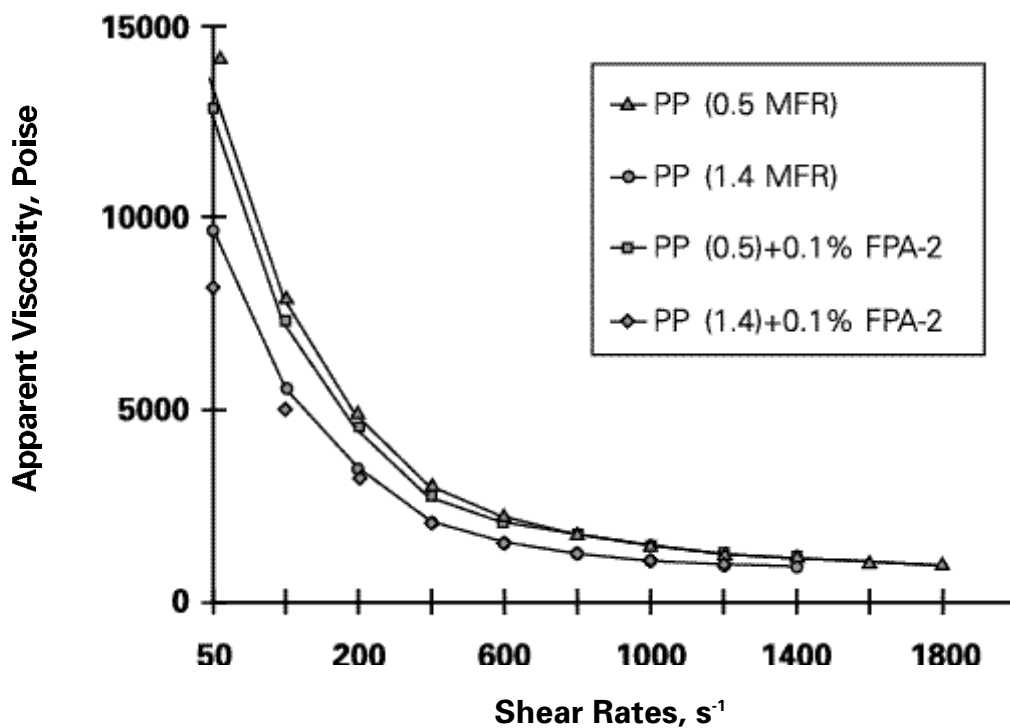


Figure 6: Effect of FPA-3 on PP Viscosity at 230°C

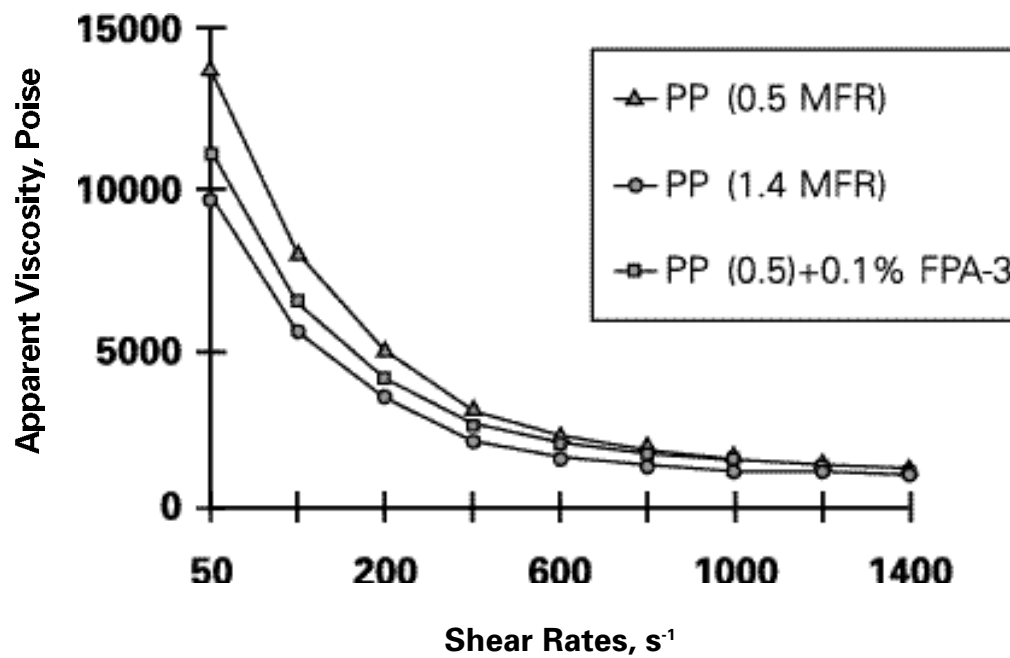


Figure 7: Effect of FPA's on SEBS Viscosity at 190°C

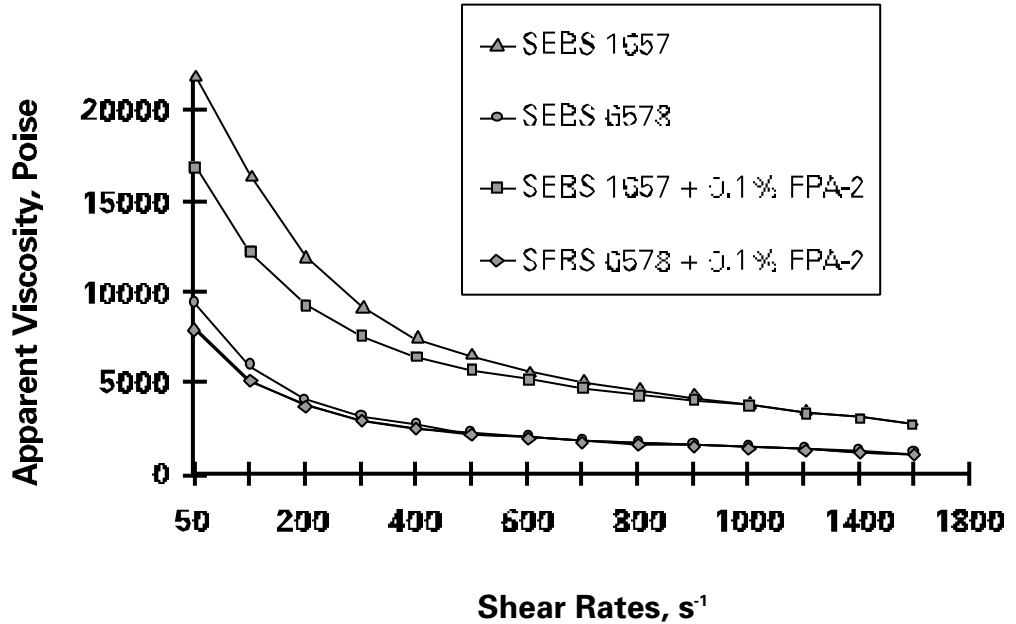


Table 1: Summary of Viscosity Reduction for FPA's in PP

PP MFR/FPA	% Change of Visc. (50s ⁻¹)	% Change of Visc. (500s ⁻¹)
0.5 w/FPA-1	9.5	0
0.5 w/FPA-2	10.2	0
0.5 w/FPA-3	19.7	9.6
1.4 w/FPA-1	6.7	0
1.4 w/FPA-2	14.4	0

Table 2: Shear Rate (s⁻¹) for the Onset of Melt Fracture with FPA's in PP at 230°C

	No PPA	FPA-1	FPA-2	FPA-3
0.5 MFR PP	300	300	400	600
1.4 MFR PP	900	1000	1200	-
1 MI LLDPE	400	>1400	>1400	-

Table 3: FPA Pressure Drop In Nonwoven PP (35 MFR)

	No PPA	FPA-1	FPA-2
Inlet Pressure (PSI)	39	36	14
Outlet Pressure (PSI)	108	105	68
Fiber Diameter (Microns)	17.8	18.1	12.1

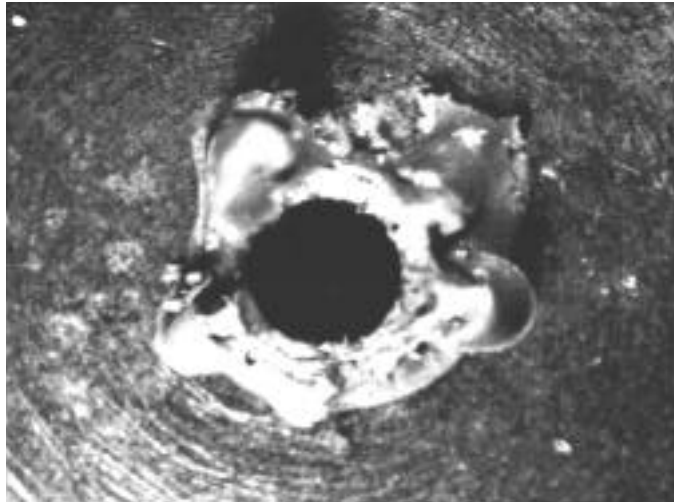


Photo 1: Die Build-up, no Dynamar PPA

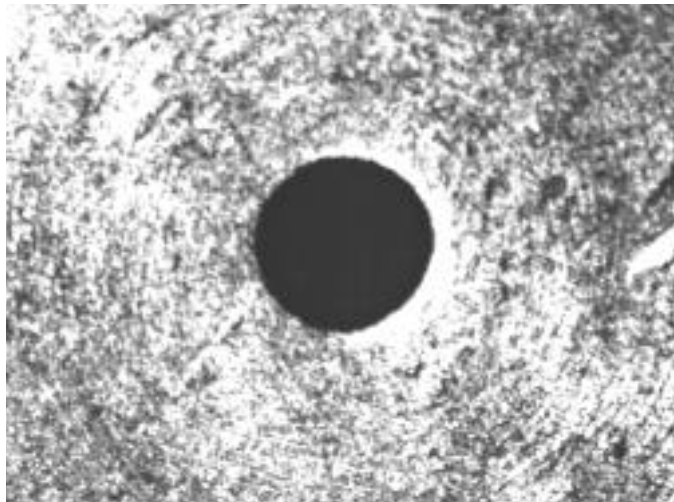


Photo 2: 300 PPM PPA-1

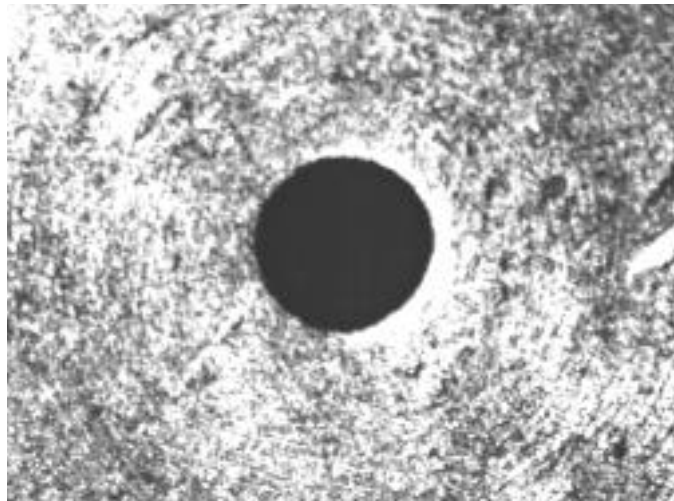
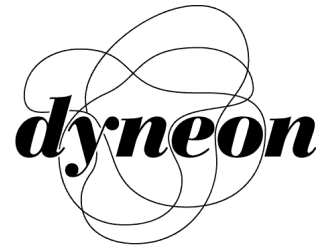


Photo 3: 300 PPM PPA-2



A 3M Company

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 2000
Issued: 5/98,10/00

Printed in USA
98-0504-1103-6
All Rights Reserved

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

Product Information:

+ 1 651 733 5353
+ 1 800 723 9127

Dyneon and Dynamar are
trademarks of Dyneon

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.



3M Center
St. Paul, MN 55144-1000
1-800-810-8499
www.3M.com/fluoropolymers

Please recycle. Printed in USA.
© 3M 2014. All rights reserved.
98-0504-1103-6

3M is a trademark of 3M.
Used under license.