3M Science. Applied to Life.™



Title:
Effect of MWD on the Amount of Polymer Process Additive (PPA) Required to Suppress Sharkskin Melt Fracture in LLDPE

Abstract:
It has recently been reported1 (TAPPI-2000) that different types of High-Performance Hexene LLDPE (HPH-LLDPE) behave differently with respect to the onset of sharkskin-melt-fracture (SSMF), depending
on the breadth of the molecular weight distribution (MWD). The MWD differences were small and subtle, but the effect on the onset of melt fracture was significant. The present study is a continuation of that work, through a comparative investigation under shear rate conditions high enough to induce melt fracture in both narrow and broad-MWD LLDPEs. A polymer processing additive (PPA) was then added in stepwise increments in order to eliminate melt fracture. It was found that the narrow-MWD resin required more than twice the amount of PPA in order to eliminate SSMF.

Date Published: August, 2001

dyneon
*A 3M Company*

# Effect of MWD on the Amount of Polymer Process Additive (PPA) Required to Suppress Sharkskin Melt Fracture in LLDPE

Harry Mavridis
Equistar Chemicals, LP

Kirsten Fronek
Dyneon LLC

## ABSTRACT

It has recently been reported[1] (TAPPI-2000) that different types of High-Performance Hexene LLDPE (HPH-LLDPE) behave differently with respect to the onset of sharkskin-melt-fracture (SSMF), depending on the breadth of the molecular weight distribution (MWD). The MWD differences were small and subtle, but the effect on the onset of melt fracture was significant. The present study is a continuation of that work, through a comparative investigation under shear rate conditions high enough to induce melt fracture in both narrow and broad-MWD LLDPEs. A polymer processing additive (PPA) was then added in stepwise increments in order to eliminate melt fracture. It was found that the narrow-MWD resin required more than twice the amount of PPA in order to eliminate SSMF.

## INTRODUCTION

There have been significant developments in recent years in the area of hexene-LLDPE resins for film applications. The common characteristic of the new hexene-LLDPE resins is that they achieve significant enhancement in film strength properties. There are, however, subtle differences between the commercially available High-Performance Hexene LLDPEs that can translate to different extrusion or film performance behavior. In a recent paper[1], the relative behavior of two families of HPH-LLDPEs with respect to SSMF was investigated via blown film extrusion and capillary rheology experiments. The broader-MWD HPH showed no signs of SSMF within the range of blown film conditions studied, whereas the narrower-MWD HPH showed severe SSMF within the same range of processing conditions. Film impact strength, as measured by dart drop, was shown to be very sensitive to SSMF and was reduced drastically by SSMF, whereas capillary rheology seemed less effective in distinguishing relatively small differences in SSMF tendency The present study is a continuation of the earlier work[1], through a comparative investigation under shear rate conditions high enough to induce melt fracture in both narrow and broad-MWD LLDPEs. A PPA was then added in stepwise increments in order to eliminate melt fracture. PPAs are used in blown film extrusion to eliminate melt fracture and provide other extrusion benefits such as throughput improvement, gel reduction and die build-up reduction[2]. The objective of this study was to determine the amount of fluoropolymer PPA required to suppress SSMF and how this amount may be influenced by the breadth of the MWD.

## EXPERIMENTAL

### Materials

The LLDPE resins studied are listed in Table I. Samples A and B are commercially available, high-performance hexene-LLDPE, tradenamed *Petrothene Select*™, described elsewhere[3]. Sample A and Sample B are both of the *Petrothene Select*™-type, the only difference being in the Melt Index. Sample C is a narrower-MWD, high-performance hexene-LLDPE. The fluoropolymer PPA is Dynamar™ FX 5920A and was added as a 3% masterbatch in 2 MI LLDPE.

### Melt Fracture Evaluations

***Equipment.*** As in similar studies from the Dyneon laboratory[4], melt fracture evaluations were performed on a Kiefel blown film line, equipped with a 1.6 in (40mm) grooved feed extruder (24:1 L/D) and a 1.6 in (40mm) die with a 0.024 in (0.6mm) die gap. Target melt temperature is 204.4°C (400°F) and both extruder and die zones are set at 204.4°C (400°F). The output rate is 28 lb/hr (12.7 Kg/hr), which translates to shear rate at the die gap of approximately 600 sec-1. BUR, layflat and take-off speed are 1.6, 8.5 in and 40 ft/min (1.6, 21.6 cm and 12.2m/min), respectively.

***General procedure.*** Film line formulations were prepared by tumble blending the LLDPE resin with the appropriate amount of the PPA masterbatch on a pail tumbler for a minimum of 10 minutes before charging to the film line extruder. For the PPA minimum level experiments, the initial PPA level tested was chosen so as to have the initial level too low to completely eliminate melt fracture within one hour. Before each run the film line was purged with a 70% calcium carbonate in LDPE purge compound followed by a neat LLDPE film resin. Throughout the trial the film line conditions were recorded and film samples taken every 15 minutes. To measure the amount of melt fracture in a film sample, a sample of the layflat was placed on an overhead projector to project the image onto a larger surface. The melt fracture was recorded as a percentage of the layflat.

***PPA minimum level studies.*** To determine the minimum level of PPA needed to eliminate melt fracture, the following procedure was followed in all cases:

1. Establish base line conditions with the base resin sample. Run for at least 1 hour to establish 100% melt fracture and steady baseline gate pressure.
2. Charge resin sample containing 400 ppm PPA. Run for 1 hour.
3. If melt fracture is not eliminated in the previous step, increase PPA level by 100 or 200 ppm, depending on the amount of melt fracture remaining, and run that condition for one hour.
4. Repeat step 3, increasing PPA level by at least 100 ppm until melt fracture is completely eliminated.
5. Purge the line and continue the procedure with the next sample.

A summary of the blown film trial data can be found in Table II.

## RESULTS AND DISCUSSION

### Resin Structure and Melt Fracture Tendency

Past work[1] with the resins of the present study showed a substantial difference in melt fracture tendency. Under the film fabrication conditions of Ref.[1], Samples A & B showed no melt fracture, whereas Sample C showed severe melt fracture once the shear rate exceeded ~200 $sec^{-1}$, for a die gap of 1.0 mm (0.040"). The effect of sharkskin melt fracture is most dramatically evident on the film impact strength, as measured by Dart Drop. Fig.1, taken from Ref.[1], shows a comparison of film impact data for the three resins of the present study. It is clearly evident that with Sample C there is a transition around ~200 $sec^{-1}$, at which the Dart Drop impact strength suffers a precipitous reduction. No such transition can be seen in the data of Samples A & B. A visual comparison of Samples A & C at a shear rate of 300 $sec^{-1}$ is given in Fig.2.

The difference in molecular structure responsible for the observed difference in melt fracture tendency is believed to be the breadth of MWD, as Fig.3 shows. Other additives that may interfere with melt fracture, such as antiblock or stearates[5-8], are listed in Table I and are shown to be at comparable levels for all three samples. Samples A and B have similar MWD, the only difference being a slight difference in average molecular weight (reflected in the different Melt Index). Sample C has a slightly narrower MWD and a Melt Index intermediate between that of Samples A & B.

The differences in MWD are directly reflected in the rheological properties, as Figs.4-6 show. Specifically, Fig.5 is a representation of the rheological data designed[9] to normalize out the molecular weight effect and only show MWD differences (broader MWD corresponding to higher G', also quantified in the ER value of Table I. The ER and PDR numbers listed in Table I, are measures of rheological polydispersity, as shown and discussed in Ref.[9]). As Fig.5 shows, Samples A&B are virtually indistinguishable, whereas Sample C is narrower, in agreement with Fig.3.

It is also important to examine the capillary viscosity data over the range of shear rates used in the melt fracture elimination studies (Fig.6). It can be seen that Sample A has the highest viscosity at all shear rates, followed closely by Sample C. This ranking of viscosities is relevant to the criterion of the onset of sharkskin melt fracture. It has been suggested that melt fracture sets in at a critical value of shear stress. If this critical shear stress were a universal parameter, independent of MWD, we would expect the following order in melt fracture tendency: A~ C >>B, with A having the worst melt fracture tendency. The results below are clearly in disagreement with such an order and therefore the critical shear stress must depend on MWD.

### Melt Fracture Elimination Studies

Following the procedure outlined in the experimental section, we were able to establish 100% melt fracture with all three (A, B and C) base resins at the run conditions selected; 204.4°C (400°F) and 600 $s^{-1}$. The resin samples did vary however in the degree of melt fracture. At the baseline conditions, without processing additive, Sample C had the sharpest, most well defined melt fracture pattern, followed by A and then B which showed the softest melt fracture even though it covered 100% of the layflat. Sample A run at a melt temperature of 221.1°C (430°F) had a slightly softer melt fracture pattern than when run at 204.4°C (400°F).

Once the PPA processing additive was added to the resin, it appeared to clear melt fracture slightly faster in Sample A than in Sample B although total elimination of melt fracture occurred essentially at the same time and level of processing additive, clearing between 3 and 3 1/2 hours and at 600 ppm PPA (Fig.7). The response to processing additive was significantly different in Sample C. Although 600 ppm PPA was sufficient to clear Samples A and B, at 600 ppm PPA the Sample C film still had 90% melt fracture remaining at the end of the hour. At 1000 ppm the film still had 4% melt fracture remaining. After running the 1000 ppm condition, we had only enough Sample C to run one more level of processing additive, so we increased the PPA level to 1600 ppm. At 1600 ppm PPA the melt fracture was quickly eliminated so the actual minimum level to clear melt fracture is probably between 1000 and 1600 ppm PPA (Fig.8).

Gate pressures of the resins were also recorded. Sample A had the highest baseline gate pressure followed by C, whereas Sample B had the lowest gate pressure (see Figs.9-10). Therefore the average wall shear stress for Sample C is intermediate to that of Samples A and B and yet Sample C had the worst melt fracture. It would appear that the criterion of a critical shear stress for onset of melt fracture is not universally valid, or at least that it shows a MWD-dependence.

Finally, melt temperature appeared to have little effect on PPA performance in Sample A. Although the baseline melt fracture was slightly softer at 221.1°C (430°F) than at 204.4°C (400°F) the rate of melt fracture elimination was not significantly different (Fig.11). In other resin systems evaluated at Dyneon we have observed that by running at lower temperatures the processing additive sometimes provides larger pressure reduction over the base condition than running with processing additive at higher temperatures[2]. That was not evident in this trial as indicated by the overall pressure reductions at 204.4°C (400°F) and 221.1°C (430°F), Fig.12.

## CONCLUDING REMARKS

The onset of sharkskin-melt-fracture (SSMF) in LLDPE shows a dependence on the breadth of the molecular weight distribution (MWD), with narrow-MWD showing SSMF earlier (lower shear rate). At sufficiently high shear rates, both narrow and broad MWD LLDPEs show SSMF. Addition of a PPA can eliminate SSMF. The results of the present work show that the PPA amount required to eliminate SSMF also depends on the breadth of the MWD. For the polymers studied in the present work, the narrower-MWD LLDPE required more than twice the amount of PPA, even though the differences in MWD were relatively small. Capillary viscosity measurements showed that the level of shear stress was comparable, or slightly higher, for the broader-MWD LLDPE. It would therefore appear that the critical shear stress for the onset SSMF is not a universal constant but depends on the breadth of MWD , with higher critical shear stress for broader-MWD.

## REFERENCES


1. H. Mavridis & R. Shroff, *TAPPI PLC Conf. Proc.*, (2000)
2. S. Amos, G. Giacoletto, J. Horns, C. Lavallee, S. Woods, "Polymer Processing Aids" in Plastics Additives Handbook, Hanser (2000) 553-584
3. H. Mavridis, *SPE ANTEC Tech Papers*, 41-45 (1999)
4. S. Woods, R.E. King and C. Lavallee, *TAPPI PLC Conf. Proc.*, 1115-1124 (2000)
5. B. Johnson & J. Kunde, *SPE ANTEC Tech Papers*, 1425(1988).
6. B. Johnson, T. Blong, J. Kunde & D. Duchesne, *TAPPI PLC Conf. Proc.*, (1988)
7. T. Blong, & D. Duchesne, *SPE ANTEC Tech Papers*, 1336 (1989).
8. T. Blong, K. Fronek, B. Johnson, D. Klein & J. Kunde, *SPE Polyolefins VII Int Conf. Proc.*, 593-613 (1991)
9. H. Mavridis & R. Shroff, *J. Appl. Polym. Sci..*, 57, 1605-1626 (1995)


## ACKNOWLEDGMENTS


We gratefully acknowledge the contributions of S. Woods of Dyneon who set up the PPA testing protocol at the early stages of this work.


## KEYWORDS


Blown Film, High Performance Hexene-LLDPE, Sharkskin Melt Fracture, Polymer Process Aid


**Table I. List of hexene-LLDPE resins studied**

| | Sample A | Sample B | Sample C |
|---|---|---|---|
| Type | hexene-LLDPE | hexene-LLDPE | hexene-LLDPE |
| Melt Index | 0.7 | 1.0 | 0.9 |
| Density | 0.916 | 0.916 | 0.917 |
| Slip (Erucamide),ppm | 1300 | 1350 | 1500 |
| Antiblock (Talc), ppm | 7900 | 6000 | 7800 |
| Zn-Stearate, ppm | 450 | 640 | 470 |
| GPC | | | |
| Mw | 147,000 | 133,000 | 137,000 |
| Mw/Mn | 4.8 | 5.4 | 3.8 |
| Mz/Mw | 2.7 | 2.8 | 2.6 |
| Rheology 200°C (392°F) | | | |
| ER (Ref.3) | 0.83 | 0.82 | 0.59 |
| PDR (Ref.3) | 3.6 | 3.9 | 3.1 |

**Table II. Blown Film Trial Data Summary**

| Sample A + PPA at 204.4°C (400°F) | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time (hrs)(1) | PPA Level (ppm) | Melt Temp. °C (°F) | Screw rpm | Output (lb/hr) | Gate Press. (psi) | Drive Motor Amps | Melt Fracture % |
| 1 | 0 | 205 (401) | 42 | 29.3 | 2470 | 37 | 100 |
| 2 | 400 | 204.4 (400) | 39 | 28 | 2420 | 35 | 25 |
| 3 | 500 | 205 (401) | 39 | 28.4 | 2380 | 35 | <1 |
| 3.5 | 600 | 205 (401) | 39 | 28.2 | 2350 | 34 | 0 |

| Sample B + PPA at 204.4°C (400°F) | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time (hrs)(1) | PPA Level (ppm) | Melt Temp. °C (°F) | Screw rpm | Output (lb/hr) | Gate Press. (psi) | Drive Motor Amps | Melt Fracture % |
| 1 | 0 | 202.22 (396) | 42 | 28.7 | 1950 | 32 | 100 |
| 2 | 400 | 203.33 (398) | 41 | 28.6 | 1980 | 32 | 60 |
| 3 | 500 | 204.4 (400) | 40 | 28.2 | 1900 | 31 | 1 |
| 3.25 | 600 | 204.4 (400) | 40 | 28.3 | 1900 | 31 | 0 |

| Sample C + PPA at 204.4°C (400°F) | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time (hrs)(1) | PPA Level (ppm) | Melt Temp. °C (°F) | Screw rpm | Output (lb/hr) | Gate Press. (psi) | Drive Motor Amps | Melt Fracture % |
| 1 | 0 | 203.33 (398) | 39 | 28.6 | 2280 | 39 | 100 |
| 2 | 400 | 205 (401) | 37 | 28.5 | 2250 | 37 | 100 |
| 3 | 600 | 204.4 (400) | 37 | 28.2 | 2210 | 36 | 90 |
| 4 | 1000 | 204.4 (400) | 37 | 28.5 | 2180 | 35 | 4 |
| 4.5 | 1600 | 205 (401) | 38 | 28.2 | 2120 | 31 | 0 |

| Sample A + PPA at 221.1°C (430°F) | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time (hrs)(1) | PPA Level (ppm) | Melt Temp. °C (°F) | Screw rpm | Output (lb/hr) | Gate Press. (psi) | Drive Motor Amps | Melt Fracture % |
| 0.5 -1 | 0 | 220.55 (429) | 43 | 29.4 | 2150 | 37 | 100 |
| 2 | 400 | 221.66 (431) | 39 | 28.2 | 2090 | 34 | 15 |
| 3 | 500 | 221.66 (431) | 39 | 28.3 | 2040 | 32 | 0 |

(1) Data shown was taken at the end of the hour indicated. The baseline condition, no PPA, was only run for 1/2 hr for Sample A at 221.1°C (430°F).

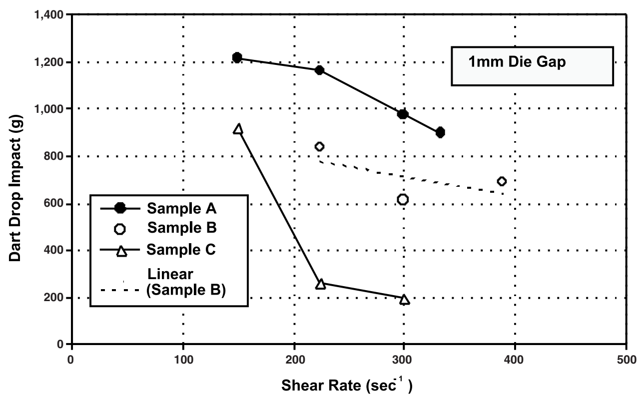


**Figure 1.** Effect of output rate on film impact strength (shear rate is proportional to output rate). Sharkskin melt fracture appears on Sample C at ~200 sec$^{-1}$ and causes a precipitous reduction in film impact strength. Samples A and B show no melt fracture at all shear rates examined.

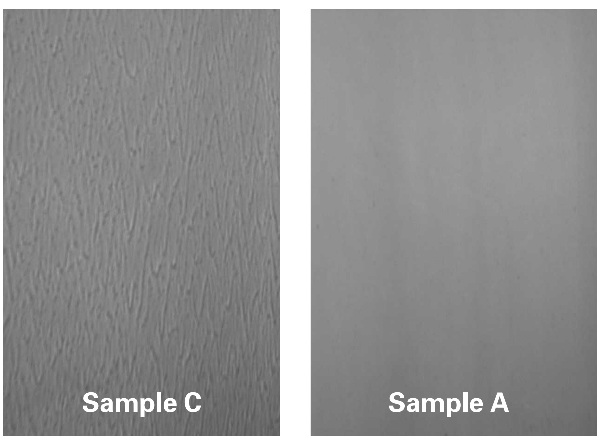


**Figure 2.** Illustration of the difference in sharkskin melt fracture of blown films with Sample A and Sample C (1.0 mm die gap, Shear Rate~300 sec$^{-1}$). MD- and TD-direction are vertical and horizontal, respectively.

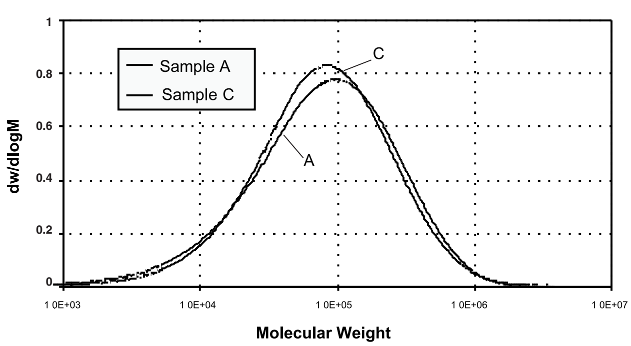


**Figure 3.** Comparison of Molecular Weight Distributions.

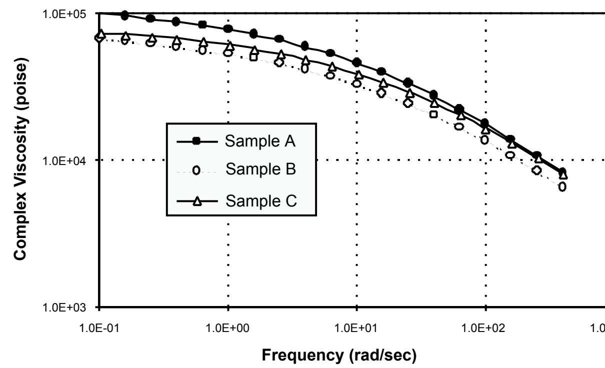


**Figure 4.** Comparison of dynamic viscosity data at 200°C (392°F).

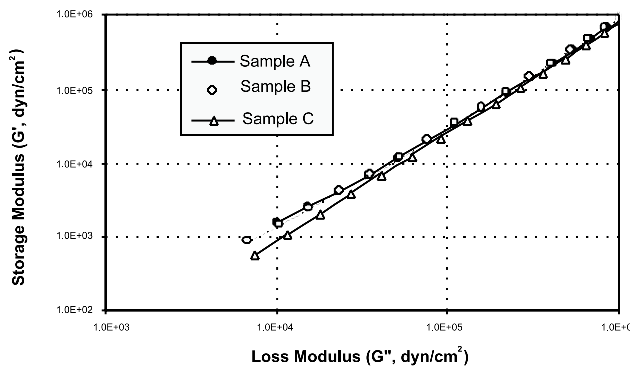


**Figure 5.** Dynamic viscoelastic data in a form suitable for identifying rheological polydispersity: Samples A and B have indistinguishable polydispersity and are both broader than Sample C.

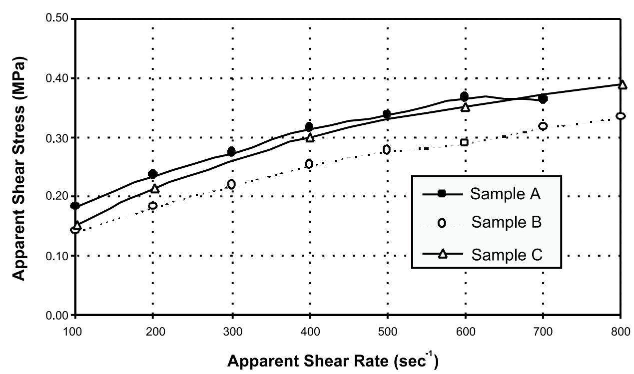


**Figure 6.** Capillary viscosity data 210°C (410°F). Instron Capillary Rheometer. Flat entry die, 0.5 mm diameter, 40/1 L/D.

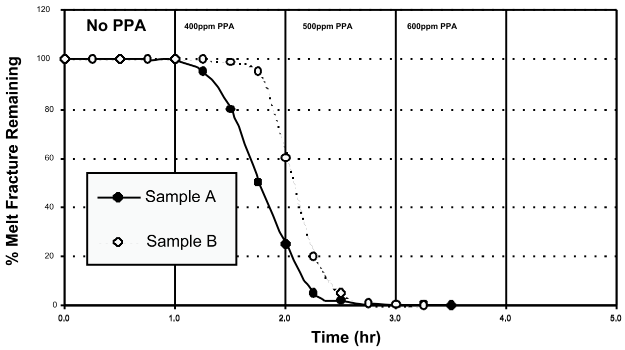


**Figure 7.** Kinetics of melt fracture elimination and PPA concentration required to eliminate melt fracture completely, for Samples A and B.

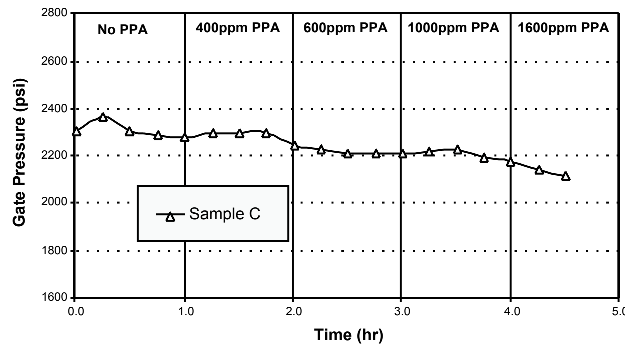


**Figure 10.** Pressure traces in the melt fracture elimination test of Fig.8, for Sample C. Note that the pressure level is intermediate to that of Samples A and B in Fig.9.

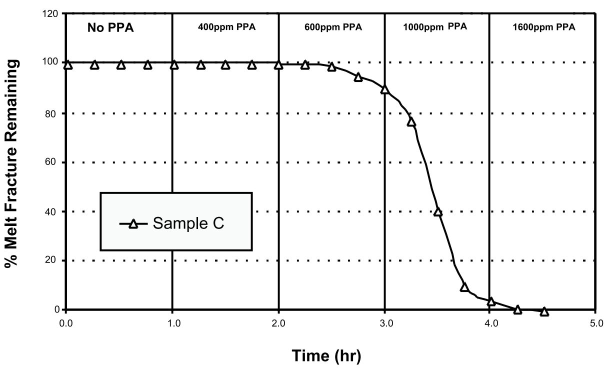


**Figure 8.** Kinetics of melt fracture elimination and PPA concentration required to eliminate melt fracture completely, for Sample C. Note higher PPA concentration required, compared to Samples A and B in Fig.7.

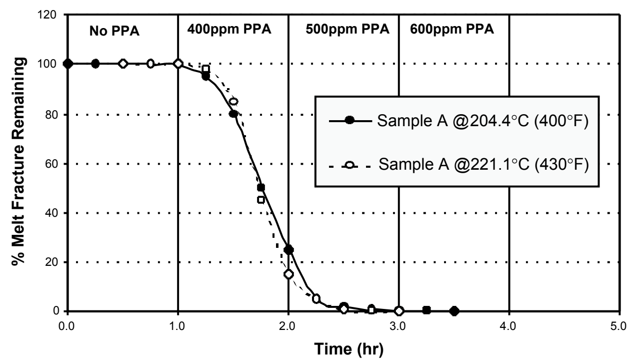


**Figure 11.** Effect of melt temperature on the kinetics of melt fracture elimination and PPA concentration required to eliminate melt fracture completely, for Sample A.

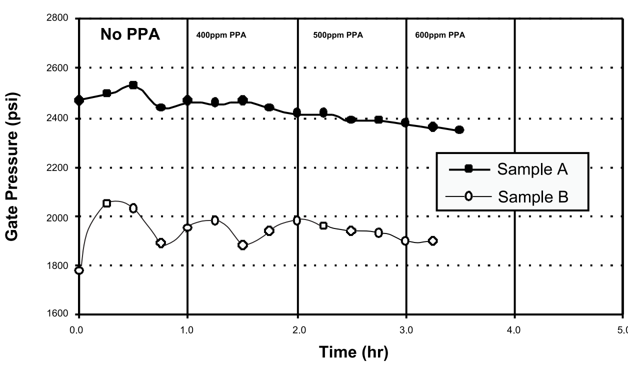


**Figure 9**. Pressure traces in the melt fracture elimination test of Fig.7, for Samples A and B.

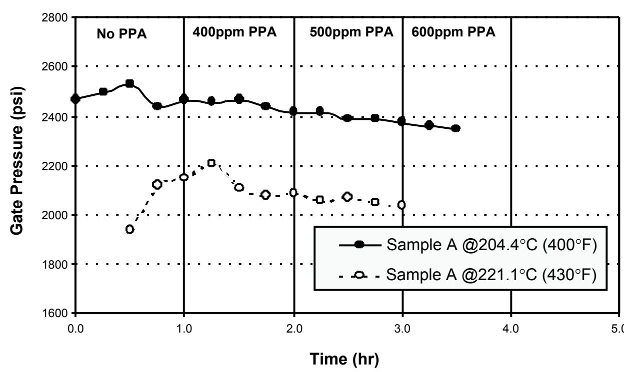


**Figure 12.** Pressure traces in the melt fracture elimination test of Fig.11, for Sample A (effect of melt temperature).

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.

Presented at TAPPI PLC 2001
Polymers, Laminations and Coatings Conference
August 2001 San Diego, California

**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.**


Issued: 08/01

Printed in USA
98-0504-1396-6


**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.
Canadastraat 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-95006 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

Dyneon GmbH & Co. KG
UK Branch House
3M House
P.O. Box 1, Market Place
Bracknell, Berkshire, RG121JU
United Kingdom
Phone: +44 1344 429675
Fax:+44 1344 427904

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 Lou Shan Guan Road
Shanghai 200335
P.R.C.
Phone: +86 21 6275 3535
Fax: +86 21 6275 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
Sumare, San Paulo
CEP 13181-900
Phone: +55 19864 7000
Fax:+55 3838 6606

**www.dyneon.com**

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


98-0504-1396-6