ELIMINATING SURFACE MELT FRACTURE USING PPA: THE ROLE OF PPA DOMAIN SIZE

Mathurin G. Meillon, Dave Morgan, David Bigio University of Maryland, College Park MD 20742
Semen Kharchenko, Kalman Migler
Polymers Division, National Institute of Standards and Technology, Gaithersburg MD 20899
Steve Oriani, Dupont Dow Elastomers L.L.C, Newark DE 19711

Abstract

The investigation of the elimination of sharkskin using polymer processing aids (PPA) requires the consideration of factors such as: PPA domain size, operational shear rate and matrix/PPA viscosity ratio. In this work, the role of PPA droplet size in the elimination of surface melt fracture was investigated. The parameters monitored were the die entrance pressure, the PPA coating thickness and the extrudate appearance. We found a substantial enhancement in coating thickness and speed upon increasing the droplet size.

Introduction

The flow instabilities known as melt fracture are frequent in the polymer processing industry. Polymer processing additives (PPA) have been used successfully for years to eliminate sharkskin. However, the mechanism of PPA action is not well understood. Cogswell (1) suggested that sharkskin is caused by a tear of the extrudate at the exit of the die. Using a Linear Low Density Polyethylene (LLDPE) and fluoroelastomer blend, Migler (2) showed that PPA droplets create a coating on the die surface allowing the LLDPE to slip, thus eliminating sharkskin. In this work, we investigate the role of PPA domain size in the elimination of sharkskin by extruding blends with known different PPA domain sizes. Oriani (3) observed that bigger PPA droplets reduced sharkskin faster than smaller ones. We will also estimate such important parameters as the coating thickness.

Background

During the processing of polymers, flow instabilities occur above some critical conditions. These instabilities, most easily observed in extrusion through a die, are commonly known as melt fracture. Below a certain throughput the surface of the extrudate is smooth. At the critical throughput the surface becomes distorted. Generally, flow distortions are classified into three categories: surface melt fracture also known as sharkskin, stick-slip, and gross melt fracture. Sharkskin is characterized by a roughness on the surface of the extrudate. Stick-slip is characterized by pressure and flow rate oscillations when operating at an imposed flow rate. During these oscillations, alternating surface aspects of the extrudate are observed. During gross melt fracture, the extrudate surface distortions develop into a periodic wavy shape [Kay (4), Dealy (5)]. For linear polymers, the plot of the wall shear stress versus the apparent shear rate identifies three regions of instabilities with increasing shear rate. Sharkskin is the first instability to occur, followed by stick-slip and then finally gross melt fracture. Hence a study of melt fracture requires an understanding of the mechanism of sharkskin. Sharkskin is believed to originate near the exit of the die [Cogswell (1), Migler (2)]. Several techniques have been successfully used to eliminate surface melt fracture. They include using different die material such as brass [Ghanta (6)], and the addition of polymer processing aids [PPA, Migler (1), Migler (7)]. Both techniques aimed at changing the boundary conditions between the polymer and the die wall, but the usage of PPA is more feasible industrially. During the extrusion of polyethylene/PPA blends, PPA was observed to accumulate at the die entrance, and then migrate towards the die exit in the form of the form of streaks [Kharchenko (8)]. These streaks eventually grow to form a slippage layer on the die wall and eliminate sharkskin. Oriani (2) observed that polyethylene/PPA blends with bigger PPA domain size were more effective in eliminating sharkskin than blends with smaller. In order to better understand the mechanism of sharkskin elimination using PPA, Polyethylene/PPA blends with well-known PPA characteristics should be extruded under the sharkskin regime.

Experiment

In this work, we utilized the same apparatus used by Kharchenko (8). It consisted of a sapphire die mounted on a capillary rheometer. The cylindrical sapphire die was fitted at one end with a sapphire cube. Using the Frustrated Total Internal Reflectance (Frus-TIR) technique we measured the growth of the PPA coating in a region about 2 mm upstream from the exit of the die. The Frus-TIR is capable of measuring the thickness of the fluoropolymer coating layer in one spot as it builds up on the die wall. The coating thickness is related to the intensity of a laser reflection off of the die wall. We will not go into intricate details on the Frus-TIR technique because the above authors recently published a paper fully describing their technique.

The main goal of this experiment was to investigate the role of PPA domain size in the elimination of surface melt fracture. Three LLDPE/PPA blends with characterized PPA domain sizes were run at the same shear rate. The parameters we monitored were die entrance pressure, PPA coating thickness and extrudate appearance. These experiments were conducted at 180 °C and the die had length L = 38.2 mm and diameter d = 1.6 mm.

Materials

The carrier matrix used in this experiment was a linear low-density polyethylene (LLDPE 1001.09 produced by Exxon-Mobil Company [9], with density $\rho = 918$ kg/m^3 and molecular weight $M_w = 80$ kg/mol).

The polymer processing additive used was a fluoroelastomer (A-500 provided by Dupont Dow Elastomers). Dupont Dow Elastomers supplied blend master batches of 1%, 5% and 12% PPA mass fraction, each containing different domain sizes. The LLDPE/PPA blends used in the experiments were obtained by further diluting the master batches to a 0.1% mass fraction at various processing conditions.

Samples of the blends were optically analyzed to statistically measure the range of domain sizes used in the experiments. Table 1 summarizes the results of that analysis. The ± in the domain size represent the standard deviation in the measurements.

Procedure

The objective in the experiment was to investigate the role of PPA domain size in the sharkskin elimination process. The parameters monitored were die entrance pressure, PPA coating thickness, and extrudate appearance. The experimental design consisted of running 2.3μm, 3.4 μm and 5.6μm PPA domain sizes at a shear rate of 215 s^{-1}. At this shear sharkskin was fully developed on a LLDPE extrudate. Experiments were conducted at a temperature of 180 °C.

An experimental load consisted of extruding about 20g of blend while collecting pressure drop readings and laser reflectance intensities. Following, laser intensities were collected across about 60 μm circumference on the die (this represented about 1% of the die circumference).

We proceeded in three major steps. First, we ran loads of pure LLDPE through the capillary rheometer in order to establish the entrance pressure drop and the coating thickness baseline readings. We also observed the appearance of the extrudate and made sure that we had fully developed sharkskin, therefore insuring that we had a barrel and die not contaminated with PPA. Secondly, we ran loads of the blend until we reached steady state values in both the entrance pressure and coating thickness readings. Finally, we oven cooked the die and fittings at 650 °C and 450 °C respectively to burn off the PPA coating before running a different blend. We also scraped and wiped clean the barrel.

Results and Discussions

In this work, we conducted in-situ measurements of the die entrance pressure drop and the PPA coating thickness. The pressure drop readings were obtained directly from a pressure transducer located near the entrance of the die (see Figure 1).

Figure 2 summarizes the reduction of the entrance pressure as a function of blend volume, the amount of material that goes through the die. The standard uncertainty in our pressure measurements was estimated from extrusion of several loads of pure LLDPE. The sensitivity of the measurements was estimated to be ± 5%. Each plot was normalized by the highest pressure reading for that experimental run. As explained above, the experimental procedure not only allowed us to track the total volume of material needed to fully coat the die, but also the time it took. The normalized pressure plot shows a domain size dependence as the blend containing the smallest PPA domain size (2.3 μm) was the slowest to reduce the entrance pressure. The effect was noticeable early but this blend used 160cc to reduce the pressure to its steady state value. The mid-size blend (3.4μm), which faster needed only 100cc to reach steady state. Finally, the blend with the biggest PPA domain size (5.6μm) was the fastest to cause an entrance pressure drop, where only about 60cc were used. For all three blends the steady-state pressure value occurred at similar reduction of about (75 ± 5) %. Also we observed that sharkskin was eliminated at pressures slightly higher than the steady state ones. In addition to the pressure drop, the PPA coating thickness was measured using the Frus-TIR technique. Figure 3 summarizes those results. The ± in the coating thickness measurements represent the fluctuating nature of the values at steady state. Here again we observed a domain size effect. The smallest domain size blend (2.3 μm) was the slowest to develop a coating, beginning at 40cc and reaching a final thickness of (150 ± 33) nm. The faster mid-size blend (3.4μm) developed a coating from 20cc and reached a final thickness of (200 ± 34) nm. The largest domain size (5.6μm) was the fastest. The PPA coating using this blend continued increasing after 0% sharkskin (arrow), and then reached a steady state value of (315 ± 120) nm where the uncertainty is from the time fluctuations in the coating thickness. Similar behavior of the PPA coating was observed in all the blends we ran beyond the 0% sharkskin point.

The effectiveness of the blends in eliminating sharkskin shows the domain size effect. Figure 4 summarizes the reduction of sharkskin observed on the extrudate as a function of blend volume. Here the ± 5% is an estimate of ability to estimate the sharkskin by eye. The smallest PPA domain size blend used 160cc to fully eliminate sharkskin (0% SS). The mid-size blend was faster needing about 65 cc to reach 0% SS. The largest domain size blend was fastest to eliminate sharkskin at about 34cc.

These results indicate that while the steady state pressure reduction is independent of domain size; the steady state coating thickness is a function of PPA domain size. Kharchenko (8) proposed a model for the steady state coating thickness based on the balance between the mass flow rate of the PPA that coats the die and the mass flow rate of the PPA leaving the die downstream. They expressed the steady state coating thickness as:

$$d = \left(\frac{2CV_s S}{\rho \dot{\gamma}_{ppa}} \right)^{0.5} \qquad (1)$$

Where C is the bulk concentration of the PPA in the PPA/PE blend, V_s is the PPA/PE interface slippage velocity, S is the radius of the PPA droplet, ρ is the density of the PPA, and γ-dot its shear rate.

Note that the thickness scales as the square root of droplet size. Their model yielded coating thickness values in the same order of magnitude as their experimental results. This model was used to predict the steady state coating thickness for this set of experiments, and then we compare the outputs to our experimental values. Figure 5 summarizes the results. The model proved to be a good qualitative prediction of the steady state PPA coating thickness. Although the size of the PPA coating was overestimated, the model yielded values in the same order of magnitude as the experiments.

Conclusions

The extrusion of PE/PPA blends with known PPA domain size elucidated the role that domain size plays in the elimination of surface melt fracture. The parameters monitored were the reduction die entrance pressure, the coating thickness, and the extrudate appearance. These measurements indicate that bigger droplets establish thicker coatings and are more effective in eliminating sharkskin than smaller ones. Overall an entrance pressure reduction of (77 ± 5) % was recorded when sharkskin was totally eliminated. Final coating thicknesses ranged from (150 to 300) nm with increasing PPA domain sizes. Larger PPA drop blends reached a smooth extrudate in 3 to 4 times less volume than blends with smaller PPA drops. These results are consistent with the observations reported by Oriani (2).

Acknowledgements

The authors would like to thank C. Macosko for helping facilitate this work.

References

[1] Cogswell, F. N. “Stretching flow instabilities at the exit of extrusion dies”. J. Non-Newtonian Fluid Mech. **2**, 37-47, (1977).

[2] Migler, K. B., Y. Son, F. Qiao, and K. Flynn. “Extensional deformation, cohesive failure, and boundary conditions during sharkskin melt fracture”, J. Rheol. **46**, 383-400, (2002).

[3] Oriani, S. R. and G. R. Chapman. “Fundamentals of melt fracture elimination using fluoropolymer process aids”, SPE ANTEC Tech. Papers **49**, 22-26, (2003).

[4] Kay D., P. J. Carreau, and P. G. Lafleur. “A study of the stick-slip phenomenon in single-screw extrusion of linear polyethylene”. Polym. Eng. Sci. **43**, 78-90, (2003).

[5] Kim S, J.M. Dealy. **“** Gross melt fracture of polyethylene. II: Effects of molecular structure”. Polym. Eng Sci. **42** (3), 495-503 (2002).

[6] Ghanta, V. G., L. Riise, M. M. Denn. “Disappearance of extrusion instabilities in brass capillary dies”, J. Rheol. **43**, 435-442, (1999).

[7] Migler, K. B., C. Lavallee, M. P. Dillon, S. S. Woods, and C. L. Gettinger. “Visualizing the elimination of sharkskin through fluoropolymer additives: Coating and polymer-polymer slippage”, J. Rheol. **45**, 565-581, (2001b).

[8] Kharchenko, S. B., P. M. McGuiggan, and K. B. Migler. “Flow induced coating of fluoropolymer additives: development of frustrated total internal reflection imaging”, J. Rheol. **46**, 1523-1545, (2003).

[9] Certain equipment, instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.

Table 1 Range of PPA domain sizes used in the experiments

Blend Origin	% Concentration	DDE Original Batch	Number of Droplets	Average Diameter (µm)
NIST	.1	1	162	**2.3 ± .4**
NIST	.1	12	107	**3.4 ± .7**
NIST	.1	5	120	**5.6 ± .5**

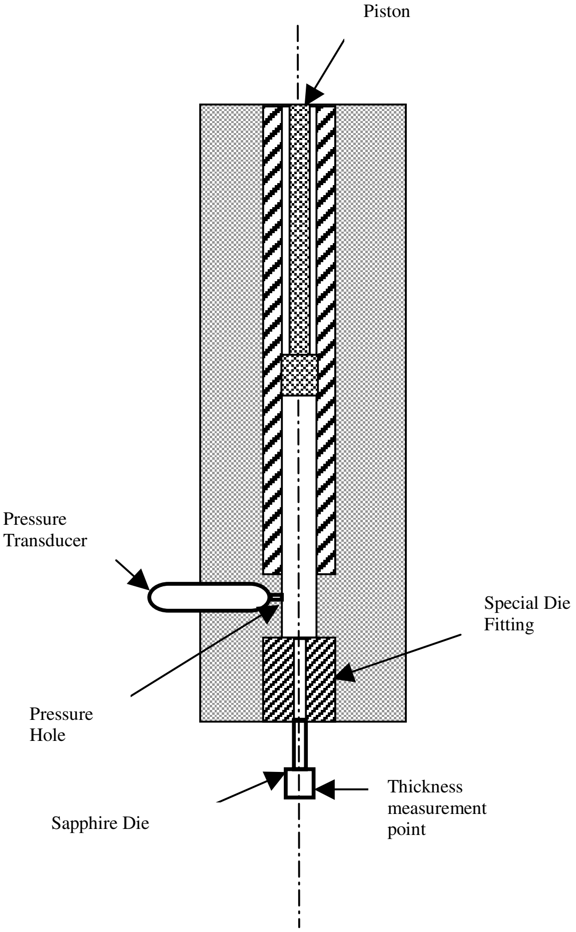

Figure 1. Capillary Rheometer Schematic

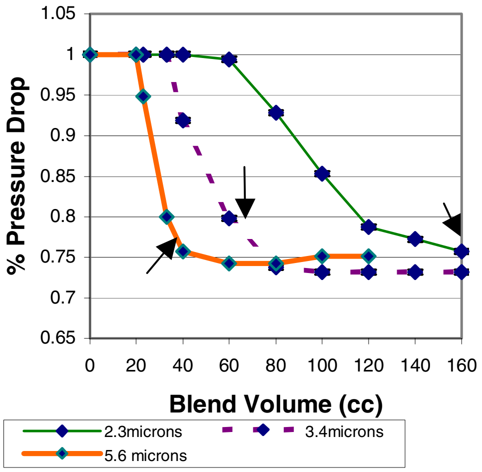

Figure 2. Normalized pressure drop vs. blend volume at shear rate of 215 s^{-1}; Arrows mark 0% sharkskin

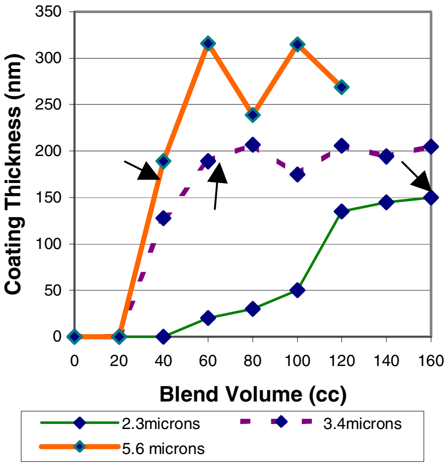

Figure 3. Coating Thickness vs. blend volume at shear rate of 215 s^{-1}; Arrows mark 0% sharkskin

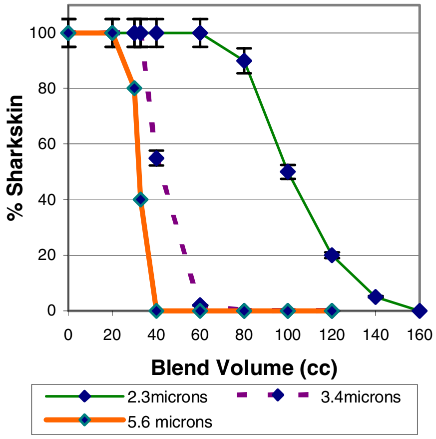

Figure 4. Percent sharkskin vs. blend volume at shear rate of 215 s^{-1}

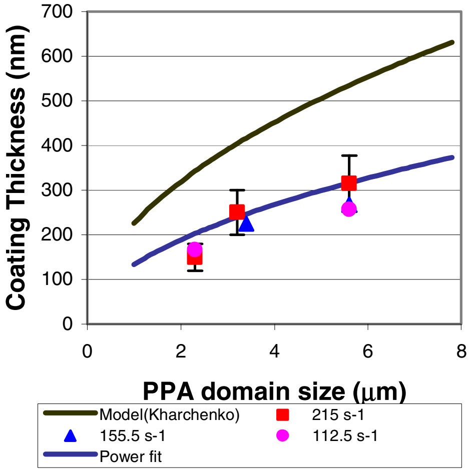

Figure 5. Steady State Coating Thickness vs. PPA Domain Size. Comparing experimental results to model prediction from Kharchenko (2003).

Phrase Index

Sharkskin
Polymer processing aid
Domain size