Enhancing Productivity in Blown Film: a New Perspective on Additive Interactions and Optimizing Polymer Processing Additive Efficiency through Process Parameters

Paul Neumann  
Dyneon, L.L.C. – a 3M Company  
6744 33rd St. N., Oakdale, MN  55128

ABSTRACT

To understand the impact on polymer processing additive (PPA) performance, the effects of interactions from hindered amine light stabilizers (HALS) and antiblock and the combined effects of extrusion temperature and shear rate were investigated. PPA performance was significantly affected by both temperature and shear rate, and also depended on the type of HALS present in the formulation. The effect of temperature was more significant than the effect of shear rate with respect to interactions involving antiblock. A new perspective concerning the temperature dependence of PPA performance in formulations containing antiblock is presented.

INTRODUCTION

Fluorinated polymer processing additives (PPAs) are widely used to improve the extrusion characteristics of polyolefins. One well known processing limitation of polymers is the occurrence of melt fracture commonly referred to as sharkskin. PPAs are frequently used to enable film processors to extrude otherwise difficult-to-process polymers without encountering the rate-limiting effects caused by sharkskin melt fracture.

The general mechanism by which fluoropolymer based PPAs function to eliminate or reduce sharkskin melt fracture is through a coating, or “conditioning”, process on the metal surface of the die wall, creating a layer of reduced friction at the polymer-metal interface and thus allowing the polymer to slip past the die under reduced stress. The PPA coating at the die wall also results in a lessened differential of the velocity profile in the melt (i.e., “plug flow”). This mitigates the slip-stick phenomenon inside the die land and acceleration rate of the extrudate surface upon exit of the die, thereby delaying the onset of melt fracture to higher shear stresses and shear rates. The change in velocity profile along the die due to a PPA coating has been observed recently.

This work revisits the effect of extrusion temperature and shear rate as it relates to the ability of PPAs to coat dies effectively. It uses a temperature – shear rate dependence model for PPA performance as a framework to investigate the interactive effects of other additives (antiblock and HALS). Additionally, this study offers new insight towards the combinative effects of extrusion temperature and antiblock interactions, which advances our understanding of important underlying factors that control the PPA coating kinetics.

Numerous studies have been conducted to investigate how PPA performance is affected in formulations that contain antiblock. Particle size, surface area, and surface treatment of the antiblock can affect PPA performance. It is generally accepted that antiblocks interfere with PPA performance by two primary mechanisms: 1) adsorption of the fluoropolymer to the inorganic antiblock particulate, thus preventing the PPA from coating the die effectively; and 2) abrasion of the fluoropolymer coating by the inorganic particulates. Several studies have also investigated the effects of HALS on PPA performance. The modes of PPA interference with HALS have been identified as: 1) potential chemical reactivity between HALS and PPA; and 2) competition between HALS and PPA to adhere to the die wall. These studies have shown that the effects of interference on the PPA coating process can be reduced through careful selection of additive package and optimization of processing conditions.

The effect of extrusion processing conditions, such as mass flow rate and shear rate, on the PPA conditioning has been studied extensively as well. Increasing the mass flow rate during extrusion reduces the time required for the PPA to condition the die, as does increasing the shear rate via increasing the mass flow or reducing the die gap width. It is thought that migration of PPA droplets from the melt to the die surface occurs more rapidly due to the greater velocity gradients associated with higher shear rates.
This paper consists of three parts. Part I investigates PPA performance with HALS; Part II systematically explores the temperature – shear rate dependence of PPA performance with antiblock; and Part III focuses on the abrasion effect from antiblock.

**METHODOLOGY**

**Equipment**

Melt fracture elimination trials were conducted on a 40 mm blown film extruder with a grooved feed section. The screw had a 24:1 L/D and an Egan mixer. The die was a 6-port spiral feed mandrel die. The die pins used in this study resulted in either a 1.22 mm (0.048”), 0.91 mm (0.036”), or 0.61 mm (0.024”) die gap width, depending on the desired shear rate for each particular experiment (specified later in the text).

**Procedure**

Prior to each experiment on the blown film extruder, it was necessary to ensure that no residual fluoropolymer remained on the die surfaces or elsewhere in the extruder from previous trials. A thorough cleaning procedure involved the extrusion of several extruder volumes full of an abrasive silica-containing purging compound, followed by an equal amount of base LLDPE resin. After this material was extruded, the die was removed and wiped clean with a 3M Scotch-Brite® pad. The die was then reinserted, and a thorough purge was evident when the subsequent extruded blown film exhibited a uniform and fully melt fractured surface, in addition to attaining melt pressures that were expected for that particular formulation and processing conditions.

Each blown film evaluation began by extruding the LLDPE resin at the desired output rate until the pressure and melt temperature had reached and maintained equilibrium. After extruding the LLDPE resin for approximately 30 minutes under this steady-state condition, the formulation was changed to include a dry blend of the LLDPE resin containing the desired level of PPA and other additives, such as slip, HALS, or antiblock. Formulations were prepared by tumble blending the desired ratios of additive masterbatches with LLDPE resin for 30 minutes. Once the formulation was changed to include the PPA, the amount of time required to completely eliminate melt fracture on the film surface was measured. The percent melt fracture was quantified by obtaining a film sample, and measuring the amount of melt fracture along the layflat width of the film. During each evaluation, samples were taken at 10-minute intervals to measure the percent of melt fracture remaining. Time to zero percent melt fracture was measured to the nearest minute, beginning with the time the PPA-containing formulation was added to the hopper (i.e., “time zero”) and ending when the film was melt fracture free. During the evaluation, the screw speed and melt temperature were continuously monitored and adjusted as necessary to ensure constant throughput and melt temperature. The line speed on the winder was adjusted as necessary for each throughput condition in order to maintain a nominal thickness of 1 mil on all films.

Data were collected for the PPA coating time, the gate melt pressure, and the total amount of PPA required to eliminate melt fracture. The total amount of PPA required to eliminate melt fracture, reported in grams, is referred to as PPA efficiency. The PPA efficiency was calculated by subtracting the residence time of material in the extruder from the overall time to eliminate melt fracture, and multiplying this time by the weight fraction of PPA in the formulation and the output rate. This performance metric is particularly useful involving comparisons between experiments with varying PPA concentrations or output rates since the PPA coating kinetics are largely driven by the mass flow of PPA particles\(^{12}\). For example, if doubling the output at a given PPA concentration results in reducing the melt fracture elimination time in half, the overall PPA consumed is still the same. Thus comparing performance as the amount of PPA consumed provides a good indicator of PPA efficiency.

**PART I: The Effect of HALS, Temperature and Shear Rate**

**Materials / Methodology**

The base resin used for blown film fabrication was a 0.9 melt index (g/10 min, 190°C / 2.16 kg), 0.918 density (g/cc), hexene copolymer linear low density polyethylene (LLDPE). All film formulations also contained 4000 ppm of antiblock (coated talc) added via a 50% masterbatch in LLDPE.
Three HALS from three different suppliers were tested: Chimmassorb ® 944, Cyasorb ® UV 3529, and Uvinul ® 5050H, hereinafter referred to as HALS-A, HALS-B, and HALS-C respectively. HALS-A is a secondary hindered amine and is a benchmark standard for previously published additive interaction studies from Dyneon. HALS-B and HALS-C have been promoted as less interfering HALS. HALS were incorporated in the film formulation at 2000 ppm, added via 10% concentrate in 2 MI LLDPE. The selected level of 2000 ppm HALS is useful in comparing the degree of interference with PPA performance, but is not suggestive of the recommended use levels to impart a desired degree of UV resistance.

The polymer processing additive used in PART I blown film experiments was Dynamar™ FX 9614. The PPA was added to the LLDPE as a 3% concentrate in a 2.0 MI, 1-butene, 0.918 LLDPE.

Each evaluation began with an FX 9614 level of 100 ppm. If melt fracture remained after the first 60 minutes of film extrusion, the FX 9614 level was increased to 200 ppm. If melt fracture still remained after an additional 60 minutes of extrusion, the level was increased to 300 ppm. The evaluation stopped when melt fracture was eliminated. These types of PPA blown film evaluations - where the PPA concentration is incrementally increased on an hourly basis until melt fracture is eliminated - are referred to as minimum level studies.

In addition to evaluating the effect on PPA performance with respect to the type of HALS that was present in the formulation, the effects of temperature and shear rate were also investigated. Each HALS formulation was evaluated separately at a shear rate of 150 s⁻¹ and 400 s⁻¹, and at melt temperatures of 193°C (380°F) and 232°C (450°F). Table 1 summarizes the experimental design that was used to investigate the effect of HALS, temperature, and shear rate on PPA performance.

<table>
<thead>
<tr>
<th>HALS</th>
<th>Apparent Shear Rate (s⁻¹)</th>
<th>Temperature (°C / °F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>150</td>
<td>193 / 380</td>
</tr>
<tr>
<td>None</td>
<td>150</td>
<td>232 / 450</td>
</tr>
<tr>
<td>None</td>
<td>400</td>
<td>193 / 380</td>
</tr>
<tr>
<td>None</td>
<td>400</td>
<td>232 / 450</td>
</tr>
<tr>
<td>HALS-A</td>
<td>150</td>
<td>193 / 380</td>
</tr>
<tr>
<td>HALS-A</td>
<td>150</td>
<td>232 / 450</td>
</tr>
<tr>
<td>HALS-A</td>
<td>400</td>
<td>193 / 380</td>
</tr>
<tr>
<td>HALS-A</td>
<td>400</td>
<td>232 / 450</td>
</tr>
<tr>
<td>HALS-B</td>
<td>150</td>
<td>193 / 380</td>
</tr>
<tr>
<td>HALS-B</td>
<td>150</td>
<td>232 / 450</td>
</tr>
<tr>
<td>HALS-B</td>
<td>400</td>
<td>193 / 380</td>
</tr>
<tr>
<td>HALS-B</td>
<td>400</td>
<td>232 / 450</td>
</tr>
<tr>
<td>HALS-C</td>
<td>150</td>
<td>193 / 380</td>
</tr>
<tr>
<td>HALS-C</td>
<td>150</td>
<td>232 / 450</td>
</tr>
<tr>
<td>HALS-C</td>
<td>400</td>
<td>193 / 380</td>
</tr>
<tr>
<td>HALS-C</td>
<td>400</td>
<td>232 / 450</td>
</tr>
</tbody>
</table>
Results and Discussion

The results from the experiments are summarized in Table 2. The PPA efficiency is measured in terms of the amount of PPA required to eliminate melt fracture throughout the duration of the test. The range in amount of PPA required to clear melt fracture provided a significant spread of the data, ranging from 0.55 grams to 2.65 grams – representing nearly an 8 times difference in PPA efficiency.

Table 2. Summary results for Part I blown film evaluations.

<table>
<thead>
<tr>
<th>HALS</th>
<th>Apparent Shear Rate (s⁻¹)</th>
<th>Temperature (°C / °F)</th>
<th>Time to Eliminate Melt Fracture (min)</th>
<th>Gate Pressure Reduction</th>
<th>Amount of PPA to Clear Melt Fracture (grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>150</td>
<td>193 / 380</td>
<td>70</td>
<td>13.8</td>
<td>1.59</td>
</tr>
<tr>
<td>None</td>
<td>150</td>
<td>232 / 450</td>
<td>74</td>
<td>5.4</td>
<td>1.72</td>
</tr>
<tr>
<td>None</td>
<td>400</td>
<td>193 / 380</td>
<td>42</td>
<td>23.1</td>
<td>0.55</td>
</tr>
<tr>
<td>None</td>
<td>400</td>
<td>232 / 450</td>
<td>54</td>
<td>18.7</td>
<td>0.70</td>
</tr>
<tr>
<td>HALS-A</td>
<td>150</td>
<td>193 / 380</td>
<td>96</td>
<td>4.7</td>
<td>2.59</td>
</tr>
<tr>
<td>HALS-A</td>
<td>150</td>
<td>232 / 450</td>
<td>177</td>
<td>0.8</td>
<td>6.77</td>
</tr>
<tr>
<td>HALS-A</td>
<td>400</td>
<td>193 / 380</td>
<td>52</td>
<td>7.6</td>
<td>0.67</td>
</tr>
<tr>
<td>HALS-A</td>
<td>400</td>
<td>232 / 450</td>
<td>88</td>
<td>7.9</td>
<td>1.48</td>
</tr>
<tr>
<td>HALS-B</td>
<td>150</td>
<td>193 / 380</td>
<td>97</td>
<td>9.1</td>
<td>2.63</td>
</tr>
<tr>
<td>HALS-B</td>
<td>150</td>
<td>232 / 450</td>
<td>97</td>
<td>9.1</td>
<td>2.63</td>
</tr>
<tr>
<td>HALS-B</td>
<td>400</td>
<td>193 / 380</td>
<td>53</td>
<td>19.6</td>
<td>0.67</td>
</tr>
<tr>
<td>HALS-B</td>
<td>400</td>
<td>232 / 450</td>
<td>68</td>
<td>19.6</td>
<td>0.98</td>
</tr>
<tr>
<td>HALS-C</td>
<td>150</td>
<td>193 / 380</td>
<td>93</td>
<td>5.8</td>
<td>2.45</td>
</tr>
<tr>
<td>HALS-C</td>
<td>150</td>
<td>232 / 450</td>
<td>79</td>
<td>2.6</td>
<td>1.90</td>
</tr>
<tr>
<td>HALS-C</td>
<td>400</td>
<td>193 / 380</td>
<td>52</td>
<td>17.1</td>
<td>0.68</td>
</tr>
<tr>
<td>HALS-C</td>
<td>400</td>
<td>232 / 450</td>
<td>56</td>
<td>12.2</td>
<td>1.09</td>
</tr>
</tbody>
</table>

A comparison of Figures 1 and 2 reveals that the shear rate had a substantial impact on the PPA performance. This is consistent with previously published data⁴⁻⁵, where higher shear rates result in faster times to eliminate melt fracture and better PPA efficiency. Thus, factors that result in higher extrusion shear rates such as increased throughput and narrower die gaps can improve the PPA performance.

Figures 1 and 2. Amount of PPA required to clear melt fracture at the low shear rate (150 s⁻¹, Figure 1) and high shear rate condition (400 s⁻¹, Figure 2). Low temp = 193°C (380°F), High temp = 232°C (450°F).

The effect of HALS was most severe at the low shear rate condition (Figure 1), where more PPA was required to clear melt fracture compared to the high shear rate condition (Figure 2). At low shear rate and low temperature, all HALS-containing formulations reduced PPA efficiency compared to the control, but there was very little difference observed with HALS type. However, at the low shear rate and high temperature condition, differences with HALS type were observed. HALS-A clearly reduced PPA efficiency the most in comparison with HALS-B and HALS-C. The differences with temperature at the low shear rate condition suggest that reactivity between HALS-A and PPA
is most severe, whereas the primary mode of interference with HALS-B and HALS-C is via competition with the PPA for adhesion to the die wall.

Besides the obvious overall improvement in PPA efficiency, there are other interesting comparisons regarding the effect from HALS-type and temperature at the high shear rate condition (Figure 2). Similar to low shear rate, high shear rate and low temperature showed very little difference in PPA performance with HALS type; however, one difference was that performance was similar to the control without HALS. This observation at the low temp and high shear rate condition suggests that the higher stresses from the flowing polymer are too high for the HALS to remain at the die wall.

The observations at high shear and high temperature show similar trends: an overall improvement in PPA efficiency due the higher shear rates and slight differences in HALS types that are attributable to the higher extrusion temperatures. Consistent with before, HALS-A shows the strongest interference with elevated temperature, albeit much less compared to the low shear rate.

**PART II: Experiments with Antiblock under Equivalent Stress**

**Materials / Methodology**

PART II of this work investigated the combined effects of extrusion temperature and shear rate on PPA performance. However, shear stress is inseparable from temperature and shear rate. As the melt temperature of the polyethylene increases, the shear stress decreases. Conversely, as the shear rate increases the shear stress also increases. Since the melt temperature, shear stress and shear rate are interrelated, it was desirable to select processing conditions that would also result in experimental design points of equivalent shear stress.

The process parameters that would yield experimental design points of equivalent shear stress were determined by characterizing the rheology of the base resin. This characterization was conducted by dynamic mechanical analysis using a parallel plate rheometer. The complex viscosity was used for this purpose, since it is often closer to the apparent viscosity than the simple shear data. The output from this analysis was used to calculate the flow activation energy using the Arrhenius equation\[16\]. This equation was then used to identify processing conditions that would result in an experimental design with points of equivalent shear stress. This was convenient because it enabled the simultaneous and systematic analysis of the effects of temperature, apparent shear rate and shear stress.

<table>
<thead>
<tr>
<th>Temperature (°C / °F)</th>
<th>Apparent Shear Rate (s⁻¹)</th>
<th>Interpolated Complex Viscosity (P)</th>
<th>Calculated Stress (kPa)</th>
<th>Stress Ranking</th>
</tr>
</thead>
<tbody>
<tr>
<td>207 / 405</td>
<td>125</td>
<td>16227</td>
<td>203</td>
<td>1</td>
</tr>
<tr>
<td>232 / 450</td>
<td>180</td>
<td>11260</td>
<td>203</td>
<td>1</td>
</tr>
<tr>
<td>207 / 405</td>
<td>150</td>
<td>14414</td>
<td>216</td>
<td>2</td>
</tr>
<tr>
<td>182 / 360</td>
<td>125</td>
<td>18584</td>
<td>232</td>
<td>3</td>
</tr>
<tr>
<td>207 / 405</td>
<td>180</td>
<td>12739</td>
<td>229</td>
<td>3</td>
</tr>
<tr>
<td>232 / 450</td>
<td>275</td>
<td>8485</td>
<td>233</td>
<td>3</td>
</tr>
<tr>
<td>207 / 405</td>
<td>235</td>
<td>10547</td>
<td>248</td>
<td>4</td>
</tr>
<tr>
<td>182 / 360</td>
<td>180</td>
<td>14296</td>
<td>257</td>
<td>5</td>
</tr>
<tr>
<td>207 / 405</td>
<td>275</td>
<td>9398</td>
<td>258</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3 shows the design points and indicates where processing conditions were expected to have approximately equivalent apparent stress, or pressure, values (stress rankings of “1”, “3” and “5”). There are no replicate points for the processing conditions with stress rankings of “2” and “4”. However, these points help to fill in gaps in the design space for a more thorough analysis. A schematic view of the experimental design is shown in Figure 3.
Figure 3. Schematic representation of the experimental design. The design points in the dotted boxes highlight processing conditions that were predicted to exhibit similar stress (either low, medium, or high relative stress rankings) during blown film extrusion.

All tests were conducted using the same die geometry in order to control the shear rate by adjusting the throughput rate only, since the die gap and land length can also influence the PPA performance. The die gap width was 0.91 mm (0.036”), and length-to-gap ratio of 10. Output rates ranged from 5.5 kg/hr at the lowest shear rate to 12 kg/hr for the highest shear rate condition. Tests were conducted at one of three temperatures shown in Table 3: 182°C (360 °F), 207°C (405°F), and 232°C (450°F).

The base resin used for blown film fabrication was a 1.0 melt index (g/10 min, 190°C / 2.16 kg), 0.918 density (g/cc), hexene copolymer metallocene linear low density polyethylene (mLLDPE). All film formulations also contained 7500 ppm of an uncoated talc, added via a 60% masterbatch in LLDPE, and 1500 ppm of a slip additive, added via 5% masterbatch in LLDPE.

Two polymer processing additives were separately evaluated in these blown film experiments: Dynamar™ FX 5920A and Dynamar™ FX 9613, hereinafter referred to as PPA-1 and PPA-2, respectively. The PPA was added to the LLDPE as a 3% concentrate in a 2.0 MI, 1-butene, 0.918 LLDPE. The PPA was incorporated into the LLDPE according to the procedure described above, and let down to 1200 ppm for all tests.

Results were recorded for the time and amount of PPA required to clear melt fracture. The gate melt pressure was also monitored throughout the experiment, and results for gate pressure reported before PPA addition, at time zero, to check the validity of design points of equivalent stress. The results were analyzed with a regression analysis using Minitab® statistical software.
Results and Discussion

The results for the amount of PPA to eliminate melt fracture are summarized in Table 4.

Table 4. Summary data from Part II blown film evaluations.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Apparent Shear Rate (s⁻¹)</th>
<th>Gate Melt Pressure at Time Zero (psi)</th>
<th>Amount of PPA to Clear Melt Fracture (grams)</th>
<th>Time to Clear Melt Fracture (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PPA-1 1200 ppm</td>
<td>PPA-2 1200 ppm</td>
<td>PPA-1 1200 ppm</td>
</tr>
<tr>
<td>182 / 360</td>
<td>125</td>
<td>2395</td>
<td>2443</td>
<td>9.29</td>
</tr>
<tr>
<td>182 / 360</td>
<td>180</td>
<td>2819</td>
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<td>207 / 405</td>
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<td>2153</td>
<td>2201</td>
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<td>207 / 405</td>
<td>275</td>
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<td>13.85</td>
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<tr>
<td>232 / 450</td>
<td>180</td>
<td>1925</td>
<td>2022</td>
<td>22.50</td>
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<tr>
<td>232 / 450</td>
<td>275</td>
<td>2570</td>
<td>2557</td>
<td>22.26</td>
</tr>
</tbody>
</table>

Effect of processing conditions on gate melt pressure. As expected, the gate melt pressure increased with shear rate. Also as expected, the gate melt pressure decreased with increasing temperature. The gate melt pressure values in Table 4 show relative consistency at a given processing condition, regardless of PPA. This is anticipated since measurements obtained at time zero are independent of PPA type in the formulation. The variability observed between PPAs at each process condition is indicative of the typical range of measurement fluctuation observed for this particular piece of equipment (within +/- 50 psi).

Figure 4. Response surface regression for gate melt pressure at time zero ($R^2 = 99.1\%$). Note that the iso-pressure lines tend to pass through the experimental design points intended to have equivalent stress (points outlined by the dotted rectangles).
A regression analysis on the time-zero pressure data (depicted in Figure 4) shows that the iso-pressure lines closely correspond to the points with processing conditions that were expected to have equivalent shear stress values. This validates the experimental design.

**Effect of processing conditions on the time to clear melt fracture.** In this particular resin and under the experimental conditions, there was only a very small difference between the two PPAs with respect to the time to clear melt fracture. On average, the difference in performance was less than 15 minutes which is considered within the normal variation for any given PPA on this particular blown film extruder. Since there were little differences between PPAs, the data were pooled together to draw inferences based on a larger data population size.

The data presented in Table 4 shows that the time required to eliminate melt fracture can be strongly affected by the processing conditions. Within the range studied, the time to clear melt fracture ranged from 50 minutes to 147 minutes. Both temperature and mass flow (shear rate) have a substantial influence on the PPA performance. Figure 5 illustrates the combined effects of temperature and shear rate and clearly shows the effect of increasing shear rate on reducing the time to clear melt fracture. The chart also shows how lower extrusion temperatures can reduce the time to clear melt fracture. The PPA coating rate was faster at higher shear rates and lower temperatures, indicating that PPA performance is influenced by the shear stress and melt viscosity of the polymer during extrusion. Indeed, this has been a prevailing explanation to describe the PPA coating mechanism and a regression analysis on the averaged time to clear melt fracture data also shows a strong correlation of PPA performance with shear stress (Figure 6).

![Average Time to Clear Melt Fracture](image)

**Figure 5.** Plot of average time to clear melt fracture as a function of shear rate and temperature.
Figure 6. Response surface regression for time to clear melt fracture ($R^2 = 91.0\%$). Note that the contour lines tend to pass through the experimental design points intended to have equivalent shear stress (points outlined by the dotted rectangles).

**Effect of processing conditions on overall PPA efficiency.** Table 4 reveals that different processing conditions can result in significant differences in the amount of PPA consumed. Figure 7 averages the data from both PPAs to better illustrate how the shear rate and extrusion temperature affected the PPA efficiency. Figure 7 demonstrates that performance is strongly affected by the extrusion temperature, with lower temperatures resulting in better PPA efficiency. However, the effect of increasing the shear rate had very little effect on PPA efficiency. This is to be expected, since the amount of PPA consumed is a throughput normalized calculation.

Figure 7. Plot of average amount of PPA to clear melt fracture as a function of shear rate and temperature.
A response surface regression for the amount to clear melt fracture is shown in Figure 8. It reinforces the trend described above in that the effect of shear rate had essentially no impact on PPA efficiency, while the temperature clearly had an effect. The analysis also indicates that PPA coating efficiency is not solely due to the degree of shear stress of the LLDPE during extrusion because the contour lines in Figure 8 do not correlate with the points of equivalent shear stress. This is important because it suggests that other factors -- not just the melt rheology of the mLLDPE -- are contributing to the PPA efficiency.

**Figure 8.** Response surface regression for PPA efficiency of FX 5920A (amount of PPA to clear melt fracture) $R^2 = 91.6\%$. The contour lines do not pass through the experimental design points of equivalent shear stress (outlined by the dotted rectangles), suggesting that the melt rheology of the mLLDPE is not the only factor affecting PPA performance.

A closer inspection of the experimental parameters reveals that several other factors could explain why the melt rheology of the mLLDPE during film fabrication was not the sole contributor to affect the PPA efficiency. The first consideration is that the formulations in the experiments all contained antiblock. Secondly, the melt rheology of the polymer processing additive is different than mLLDPE. The temperature – shear rate model for PPA performance only considers the melt rheology of the host polymer (mLLDPE); it does not take into account the effects of additive interactions or the melt rheology of the PPA itself. The next set of experiments was designed to help understand the interaction between these factors and the PPA coating process.
**PART III: PPA De-conditioning Experiments**

The removal of the PPA is accelerated by the abrasive effect from the antiblock. The process of removing the PPA is called "de-conditioning" and it allows for a closer inspection of the abrasive effect of antiblock. A series of experiments were conducted with FX 5920A to gauge the effect of temperature on the removal of the PPA coating. Just as in the preceding experiments the film formulations were comprised of the same mLLDPE, 1500 ppm slip, 7500 ppm antiblock, and 1200 ppm of the PPA. Tests were conducted at constant output and shear rate (7.9 kg/hr, 180 s\(^{-1}\)), varying only the temperature. Three extrusion temperatures were tested: 182°C (360°F), 207°C (405°F), and 232°C (450°F). The difference with this set of experiments was that once all the melt fracture was completely eliminated by the PPA, the PPA was removed from the formulation and film extrusion continued until 100% of the melt fracture reappeared and the extrusion pressures returned to levels that typified the process prior to PPA addition.

Results from these tests are shown in Table 5, which shows two distinct trends: 1) the PPA conditioning time is reduced at lower temperatures; and 2) the PPA is removed most quickly at higher temperatures. The first trend simply confirms data presented earlier in this text and by the work of others. The faster conditioning time at lower temperatures follows the temperature – shear rate model for PPA performance discussed earlier. The increased stress that occurs at lower temperatures and higher shear rates provides a greater driving force to promote migration and adhesion of the PPA to the die wall. The trend observed during the de-conditioning phase may not be all that intuitive, however. Although the abrasive effect of the polyethylene is greater at lower temperatures, the time to remove the PPA at lower temperatures is much longer.

<table>
<thead>
<tr>
<th>Melt Temperature (F / C)</th>
<th>PPA Conditioning Time (minutes)</th>
<th>PPA De-conditioning Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>360 / 182</td>
<td>50</td>
<td>290</td>
</tr>
<tr>
<td>405 / 207</td>
<td>110</td>
<td>190</td>
</tr>
<tr>
<td>450 / 232</td>
<td>150</td>
<td>160</td>
</tr>
</tbody>
</table>

The observed results regarding the time to remove the PPA can be explained in view of other additives in the formulation. Although the range of extrusion temperatures has a significant effect on the rheology of the mLLDPE and PPA, it has no effect on the rheology of the inorganic antiblock particles. So although higher temperatures result in lower stress from the flowing polymer and thus lower abrasion forces, these higher temperatures also reduce the abrasion resistance of the PPA. It is likely a decrease in fluoropolymer viscosity at elevated temperatures that renders the PPA more susceptible to removal by an abrasion mechanism.

The graph in Figure 9 illustrates this concept. Rheological data on the mLLDPE and on the PPA fluoroelastomer were acquired using a parallel plate rheometer. Because the polymer flow at the die wall is mostly simple shear, the simple shear viscosity data was used. Figure 9 shows the shear viscosity (interpolated values) of the materials as a function of test temperature at 180 rad/sec, which is essentially the same shear rate condition used in the PPA de-conditioning experiments. The change in PPA fluoroelastomer viscosity over the range of temperatures studied in the blown film experiments (182°C -232°C) represents an approximate twofold reduction in viscosity, while the shear viscosity of the mLLDPE remains relatively constant. A similar trend was observed over the shear rates investigated in Part II: the shear viscosity of the mLLDPE changes very little over the typical blown film processing window compared to the change in the shear viscosity of the fluoropolymer of the PPA.

These results reinforce the importance of matching the viscosity of the processing aid with the viscosity of the host resin. These findings may also help explain why higher viscosity fluoroelastomers show better efficiency, as these fluoroelastomers likely have better cohesion properties that would render them less susceptible to removal.
Shear Viscosity at Constant Shear Rate (180 rad/s)

![Graph showing shear viscosity at constant shear rate](image)

**Figure 9.** Comparison of the shear viscosity of the polyethylene (mLLDPE) and the PPA fluoroelastomer at constant shear rate. The shear viscosity of the fluoroelastomer is affected more by temperature than the mLLDPE, which could affect the adhesion properties of the PPA to the metal surface.

**CONCLUSIONS**

Results from this work show that temperature, shear rate, and type of additive interactions can significantly affect the PPA coating process. The role of temperature becomes particularly important in formulations that contain additives that interfere with the PPA coating, such as hindered amine light stabilizers and antiblock, due to the temperature effects towards the degree of reactivity (in the case of HALS – PPA interactions) and the rate of PPA abrasion (in the case of antiblock interactions). The role of shear rate on PPA performance becomes especially evident in conditions where the mode of interference is through competition for adhesion at the die wall, as was observed with HALS.

The melt viscosity of the LLDPE host resin factors into the PPA coating kinetics, as the PPA coating time was reduced at higher stresses. The melt rheology of the PPA also contributes to the coating process. A new perspective on PPA-antiblock interactions is presented in this context. Results from PPA de-conditioning experiments with antiblock support the idea that changes in PPA viscosity with extrusion temperature can influence the PPA resistance to abrasion and overall PPA efficiency. This concept also provides new insight that may help explain why higher viscosity fluoroelastomer based PPAs exhibit improved efficiency. To explore this further, future de-conditioning experiments should be conducted comparing the removal effect by antiblock with respect to the PPA fluoroelastomer viscosity.

This work demonstrates that film processors can get the most efficiency from the polymer processing additive through careful selection of processing conditions and additive package. As a general rule, reduced extrusion temperatures and increased throughput rates will maximize PPA efficiency.
ACKNOWLEDGEMENTS

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REFERENCES

Polymer Processing Additives: The Effect of Extrusion Parameters and Additive Interactions in Blown Film

Presented by:
Paul Neumann
*Dyneon, LLC* - A 3M Company
Presentation Overview

- Introduction of Polymer Processing Additives
- Common Additive Interactions
- Extrusion Processing Parameters that affect PPA Performance
- Summary of recent studies by Dyneon
- Conclusions
What is a Polymer Processing Additive?

- Improves processability of high molecular weight polymers
- Fluoropolymer – based chemistry
- Effective during the extrusion process
- Effective at low use levels (<1500 ppm)
PPA Benefits

- Elimination of Melt Fracture
- Reduction in Operating Pressure
- Alleviation of Die Build-Up
- Reduction in Gel Formation
- Faster Color Transitions
PPAs: Mode of Action

PPA exists as immiscible droplets in polyolefin matrix

PPA has high affinity for metal die wall

Forms low surface energy, dynamic coating

Allows melt to slip through
Shear Rate (velocity gradient)

Controlled by:
- Output rate
- Die geometry

Low Shear Rate

High Shear Rate

Polymer flow

Polymer flow
To improve production rate, film manufacturers often run at high extrusion temperatures.

- This reduces the melt pressure and the severity of melt fracture.

- However, this limits the efficacy of Polymer Processing Additives because:
  - It reduces the stress from the flowing polymer that assists in formation of the PPA coating.
  - It increases interference from other additives in the formulation (i.e., HALS).
Melt Fracture is Melt Fracture

• Increasing processing temperature lessens the severity of melt fracture, but may not eliminate MF altogether.

Photographs of melt fracture from blown film extrusion

- 360 °F Melt Temp
- 450 °F Melt Temp
PPAs do not adversely affect the performance of other additives.
Hindered Amine Light Stabilizers (HALS)

- Two potential modes of PPA interference:
  - 1) Chemical reaction between the PPA and HALS
    - Acid / Base reaction
    - Prevents PPA bonding to the die wall
  - 2) Competition for adhesion to the die wall ("die site competition")
    - HALS, like PPA, also has affinity for metal surface
    - Blocks PPA from coating the die
Potential Interactions with HALS

(Via Hydrogen Bonding Mechanism)

Fluoroelastomer
PPA

Oxides and Hydroxides

Metal Oxide Layer
2-20 microns

Metal

HALS
Antiblocks

• Two potential modes of PPA interference:
  
  – 1) Adsorption of the PPA fluoropolymer to the antiblock particulate
    • Prevents PPA bonding to the die wall
  
  – 2) Abrasion of the PPA coating
    • Influenced by AB particle size, surface area, hardness and surface treatment
Abrasive Interference with Antiblock

Fluoroelastomer PPA Coating on a Metal Surface

Without Antiblock

With Antiblock

10 μm/div
Process Parameters and the Effect of HALS
Experimental Conditions

40 mm blown film extruder, 24/1 L/D, grooved feed extruder

- C6 LLDPE (0.9 MI, 0.918d)
- 3 different HALS tested (2000 ppm each)
- 2 shear rates
  - 150 s\(^{-1}\) & 400 s\(^{-1}\)
- 2 extrusion melt temperatures
  - 380 °F (193 °C) & 450 °F (232 °C)
- PPA: Dynamar™ FX 9614
- Measured: Total amount of PPA required to clear melt fracture
Materials - HALS

Chimassorb® 944
“HALS-A”

Uvinul® 5050 H
“HALS-B”

Cyasorb® UV-3529
“HALS-C”

- Chimassorb is a registered trademark of Ciba Specialty Chemicals
- Cyasorb is a registered trademark of Cytec
- Uvinul is a registered trademark of BASF Aktiengesellschaft
• High shear rate reduces the interaction and improves PPA performance

• Evidence of increased interference at high temperature suggests chemical interactions
Summary with HALS

- Low Shear / Low Temp
  - HALS reduced PPA Efficiency

- Low Shear / High Temp
  - HALS reduced PPA Efficiency
  - Notable differences observed between type of HALS used
    - This effect from temperature suggests additional interference via chemical reactivity
Summary with HALS (Cont’d)

• High Shear / Low Temp
  – Very little effect from HALS observed
  – Suggests that high shear conditions can overcome interference via HALS competition for adhesion to metal surface

• High Shear / High Temp
  – Slight reduction in PPA efficiency
  – Interference from chemical reactivity observed even at high shear rates
Process Parameters and the Effect of Antiblock
Experimental Conditions

- C6 mLLDPE (1.0 MI, 0.918d)
- 7500 ppm of antiblock (uncoated talc)
- 5 shear rates
  - 125, 150, 180, 235, and 275 s\(^{-1}\)
- 3 extrusion melt temperatures
  - 360 °F (182 °C), 405 °F (207 °C), and 450 °F (232 °C)
- PPAs
  - Dynamar™ FX 5920A (PPA-1)
  - Dynamar™ FX 9613 (PPA-2)
- Processing parameters predetermined to yield points that would have equivalent stress

40 mm blown film extruder, 24/1 L/D, grooved feed extruder
Experimental Design

Experimental Design Resulting in Low, Medium & High Shear Stress Conditions

Temperature (F)

App. Shear Rate (s⁻¹), controlled by throughput

ΔT : change in temperature
Δγ : change in shear rate
σ : constant shear stress

\[ \Delta \gamma = \Delta \tau \]

\[ \Delta T = \sigma \]

\[ \Delta \tau = \sigma \Delta \gamma \]

Low

Med

High
Average Gate Melt Pressure at Time Zero

Response Surface for Average Baseline Pressure:  \( R^2 = 99.3 \% \)

C6 mLLDPE, 1.0 MI, 0.918d, 7500 ppm AB, 1500 ppm SLIP, 36 mil die gap, 10 L/G, Cr plated
Effect of Temperature and Shear Rate

- **Time to clear melt fracture** was improved with:
  - reduced extrusion temperature
  - increased shear rate

- **PPA Efficiency** was improved with:
  - reduced extrusion temperature
Effect of Stress

- PPA coating rate correlated with shear stress
- PPA efficiency did not correlate with shear stress
PPA “De-conditioning” Experiments

• PPA coating is a dynamic process
  – Consists both of PPA deposition and removal

• PPA de-conditioning experiments
  – 1200 ppm PPA-1, constant shear rate (180 s\(^{-1}\))
  – PPA was considered removed when 100% melt fracture returned and the gate melt pressure returned to baseline
  – Concerned only with the effect of temperature on PPA removal
Effect of Temperature on PPA Coating Dynamics

Conditioning / De-conditioning Curves
Approximately twofold reduction in PPA viscosity across the processing window.
Conclusions

• PPA performance is better at lower extrusion temperatures and higher shear rates

• Physical and chemical additive interactions are reduced at lower temperatures

• To optimize PPA performance, the general rule is to “Extrude More and Heat Less”
Thank You

PRESENTED BY
Paul Neumann
*Dyneon, LLC - A 3M Company*

*Please remember to turn in your evaluation sheet...*