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Title:
The Effect Fluoropolymer Processing Additive and Stearate Additive Levels Have on Processing of HDPE Resins

Abstract:

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An experiment was performed to evaluate the effectiveness of calcium stearate and fluoropolymer to improve the extrusion processing of HDPE resin. Elimination of melt fracture, reduction in extrusion pressures and the rate of formation of die build up were measured and used for comparison.

We found that high levels are required to eliminate melt fracture, but this may lead to the formation of die build-up, generation of smoke and fumes during processing and the formation of plate out and surface deposits on secondary processing equipment. In contrast a low level of fluoropolymer has been demonstrated to provide improvements which allow the processor to operate with reductions in extrusion pressures, elimination of melt fracture, and at the same time, avoid the formation of die build up.

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The Effect Fluoropolymer Processing Additive and Stearate Additive Levels Have on Processing of HDPE Resins

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ABSTRACT

Extrusion processing of high density polyethylene (HDPE) resins can be improved by the use of various additives. This practice is widely accepted, and the specific additive selected can have measurable effects on the resin processing. These additive effects may be both positive and negative, and they may be observed simultaneously. It is the desire of the processor to minimize the negative effects and maximize the positive effects.

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INTRODUCTION

The properties and processing of polyethylene resins continues to evolve and improve. Materials with improved properties are being developed, but these materials are also characterized by higher viscosity. While these materials provide distinct advantages, they may also present processing challenges. Several techniques are employed to improve the processing characteristics. Changes in die geometry and process control settings, changing the resin molecular weight or molecular weight distribution, or incorporation of specific lubricating additives are all techniques employed to improve the material processing characteristics.

Metallic soaps have been widely recognized as lubricants for polyethylene extrusion processing. These additives are used at low levels to neutralize polymerization catalyst residues, but they are also added at higher levels for lubrication during melt processing. The low level used to neutralize catalyst residue is added by the resin producer. When used at higher levels they may be added as a component of the resin additive package or added by the resin processor through a concentrate. Zinc stearate and calcium stearate are two examples of catalyst neutralizers that are widely utilized in the polyethylene industry. During processing these additives melt and behave as a low viscosity fluid additive. They are intended to provide lubrication between the metal die surface - polymer melt interface.

Fluoropolymer based polymer processing additives (PPAs) are also recognized for their ability to improve the extrusion processing of polyethylene processing.[1] During extrusion processing, flow from the die is characterized as pressure driven flow with a shear rate gradient present. The shear rate is defined as zero at the flow centerline, and is at a maximum at the metal die surface - polymer melt interface. Without a PPA present there is a zero velocity boundary condition at this interface. When a PPA is present it can establish a low surface energy layer between the polymer melt and the metal die surface. This PPA layer induces a slip velocity of the melt at the interface.[2,3] The resistance of the extrudate to flow through the die is also reduced. Decreases in extrusion pressure, extrusion energy requirements, elimination of melt fracture, ability to reduce processing temperatures and the ability to change to narrower die gaps have been demonstrated.(4,5)

Although both stearates and fluoropolymers are thought to establish an interface layer between the polymer melt and the metal die, there are distinct differences in the performance of these two as processing additives. The experiments summarized in this paper demonstrate these two materials are providing distinctly different benefits to the polyethylene extrusion process.

To compare the performance of these two processing additives four compounds were evaluated. HDPE resin with 1000 ppm calcium stearate, 3000 ppm calcium stearate, 6000 ppm calcium stearate, and a combination of 1000 ppm calcium stearate plus 500 ppm fluoropolymer.

These compounds were extruded through a laboratory cast film extrusion die. Reductions in extrusion pressure and extrusion energy requirements, elimination of melt fracture and the formation of die build up were used as comparisons for the processing of these four compounds.

EXPERIMENTAL PROCEDURE

This experiment was performed on a laboratory scale Haake cast film extrusion line. The extrusion equipment specifications, measured variables and temperature profile are given in Table I.

The resin evaluated was a commercially available 0.9 MI (0.956 density, British Petroleum manufacturing process) HDPE, properly stabilized with primary and secondary antioxidants and a minimal level of calcium stearate for catalyst neutralization. Calcium stearate (Baerlocher 5862) and a fluoropolymer (Dynamar™ FX 5911X) were used as polymer processing additives. These materials were compounded into

3% concentrates with the HDPE base resin using a twin screw Haake compounding extruder.

Four formulations were evaluated in this experiment and are outlined in Table 2. The first formulation (compound A) was the base resin and was extruded to determine a baseline for the evaluation. The second and third (compounds B&C) formulations were extruded to determine the effects of higher levels of calcium stearate on the extrusion characteristics of the HDPE resin. The fourth formulation (compound D) contained the Dynamar FX 5911X processing additive. Specific formulations were made by tumble blending the necessary amounts of individual concentrates into the HDPE host resin to reach the desired concentrations of additives.

The process variables monitored during the experiment were screw speed (rpm), melt pressure (MPa) and melt temperature (°C) measured both at the ‘coat hanger’ reservoir of the die and at the exit of the extruder. The output was measured by weighing film samples taken over a specified period of time. Other variables measured were percent melt fracture as a function of time and die lip build-up as a function of time. Percentage melt fracture was evaluated by estimating the percentage of surface of film that was melt fractured as a function of the entire film surface. Die lip build-up was recorded through the use of a digital camera focused at the exit of the cast film die.

The extrusion process variables, output, melt fracture and die lip build-up was monitored every 15 minutes. After a period of 90 to 120 minutes extrusion time with the PPA or calcium stearate present, a steady state extrusion condition was observed and this was defined as the equilibrium condition. This condition was used for comparison against the base line conditions.

The equipment was purged with 5 kg of a 70% calcium carbonate purge compound followed by 5 kg of an HDPE resin between formulations. The base resin was extruded after purging until the original base line was obtained prior to running each formulation.

RESULTS AND OBSERVATIONS

Extrusion pressure (PI), die pressure (P2), output increase, melt fracture elimination and time to die build-up measurements are summarized in Tables 3-7. Estimated error for the sample preparation and the recording of the extrusion variables is approximately 5%, and this should be considered when reviewing the data tables.

Extrusion Pressure (PI), Die Pressure (P2) & Output Increase: Reference Tables 3-5

Extruder pressure was measured at the exit of the extruder (PI), and these values are summarized in Table 3. A 14% reduction in PI pressures with Compound D (containing fluoropolymer) was observed. No significant reduction in die pressures with either 3000 ppm or 6000 ppm calcium stearate present was observed.

Die pressure was measured in the coat hanger of the die (P2), and these values are summarized in Table 4. A 20% reduction in P2 pressures was observed for Compound D. No significant reduction in die pressures was observed with either 3000 ppm or 6000 ppm calcium stearate.

After observing a reduction in extrusion pressure it is possible to increase the output to generate the original control pressure. This allows for a comparison to be made between the original and new outputs. A reduction in die pressure was used to determine whether a specific compound could allow for increased output. Compound D had a 20% reduction in P2 pressure at constant screw rpm. Increasing the rpm to generate the original control die pressure resulted in a 72% increase in output. Neither compound containing calcium stearate provided an extrusion or die pressure reduction during processing.

Melt Fracture Elimination: Reference Table 6

Extrusion of Compound A (1000 ppm calcium stearate) resulted in a film surface that was 100% melt fractured for the entire 120 minutes of extrusion time. Compound B (3000 ppm calcium stearate) demonstrated a quick reduction in melt fracture, with less than 5 % after 30 minutes; however, the melt fracture was never completely eliminated after 120 minutes extrusion time. Compound C (6000 ppm calcium stearate) did eliminate melt fracture after 60 minutes. Compound D (500 ppm fluoropolymer) also eliminated melt fracture after 60 minutes.

Time to Form Die Build-up: reference Table 7 and Die Pictures

Extrusion of Compound A (1000 ppm calcium stearate) showed no visible die build-up after 60 minutes run time. Compound B (3000 ppm calcium stearate) showed some die build-up after 45 minutes run time. Compound C (6000 ppm calcium stearate) showed significant die build-up formation after only 30 minutes run time. Compound D (500 ppm fluoropolymer) showed no die build-up after 450 minutes of run time.

DISCUSSION AND CONCLUSIONS

To evaluate if the extrusion processing of this HDPE resin is being affected by incorporation of these additives several empirical observations were made.

The extrusion and die pressures were reduced with a fluoropolymer present, but no reductions were observed when using high levels of calcium stearate. A reduction in extrusion pressures is a primary benefit which allows the process variables to be changed to more favorable operating conditions. Reductions in processing temperatures, changes in resin, or increases in output are all possible after a reduction in extrusion pressure is observed.

The potential to increase output was assessed in this experiment. The reduction in extrusion pressure with the fluoropolymer present allowed the output to be increased while maintaining the extrusion pressure observed in the control condition. Incorporation of calcium stearate did not provide this benefit.

100% melt fracture was observed in the control extrudate under the process conditions of this study. After 1 hour of extrusion, 3000 ppm calcium stearate resulted in partial elimination of melt fracture, and 6000 ppm calcium stearate resulted in complete elimination of melt fracture. Using 500 ppm fluoropolymer resulted in complete elimination of melt fracture after 1 hour of extrusion. These results suggest that the fluoropolymer is more effective. At lower usage levels it establishes an interfacial layer between the polymer melt and metal die surface. The fluoropolymer has a greater effect on reducing the interface shear stress which may be generating melt fracture.

Possible concerns when using high levels of stearates in a resin compound is the potential for die build up and smoke generation as a result of additive degradation during processing. Both compounds with 3000 ppm calcium stearate and 6000 ppm calcium stearate displayed die build up. With 3000 ppm calcium stearate present die build up was observed after 60 minutes. With 6000 ppm calcium stearate present die build-up was observed after 30 minutes. The rate of formation appears to be concentration dependent. Reference photographs of these phenomena are included in this paper. Smoke generation was observed when processing these calcium stearate containing compounds.

Another effect of high stearate levels is build-up of these materials on take off equipment or other secondary processes. During this evaluation, film roll slippage was observed when processing Compound C (6000 ppm calcium stearate). The slippage resulted in flow lines on the film surfaces and a build-up of white residue on the take-off rollers. Stearates are believed to be partially mobile after the extrudate profile has solidified. They may build up on take off equipment and printing rollers, and can negatively affect film printing properties. This phenomena has not been observed when using a PPA.(6,7)

The results of these experiments suggest that the resin processor may have a difficult time to define an acceptable level of calcium stearate.

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Table 1: Extrusion Conditions

Extruder Details:	Haake single screw cast film extrusion line	
	25 mm diameter barrel	
	24:1 Length/diameter ratio	
	5 HP Drive motor	
	15 cm die width	
	0.6 mm die gap	
Extrusion Temperature Profile:	Extruder zone #1	120°C
	Extruder zone #2	200°C
	Extruder zone #3	200°C
	Die	190°C
Output:	3-4 kg/hr for the HDPE resin	
Pressure Sensors:	P1: Pressure monitored at the exit of the extruder	
	P2: Pressure monitored at the “coat hanger” reservoir of the die	

Table 2: Resin Formulation

Compound	**A**	**B**	**C**	**D**
Calcium Stearate (CaSt)	0.1	0.3	0.6	0.10
Dynamar™ FX 5911X	—	—	—	0.05
HDPE resin	99.9	99.7	99.4	99.85

Table 3: **Extruder Pressure (P1)** **unit = Megapascals**

Time (minutes)	**Compound A**	**Compound B**	**Compound C**	**Compound D**
0	16.36	16.13	15.89	16.18
15	16.36	16.07	15.57	16.08
30	16.42	16.11	15.45	16.12
45	16.47	16.00	15.52	15.64
60	16.38	16.07	15.30	15.20
75		16.18	15.43	14.23
90		16.31	15.37	14.24
105		16.07	15.54	13.91
120		16.07	15.43	13.95

Table 4: **Die Pressure (P2)** **unit = Megapascals**

Time (minutes)	**Compound A**	**Compound B**	**Compound C**	**Compound D**
0	12.04	11.91	11.53	11.75
15	12.04	11.87	11.40	11.64
30	12.04	11.67	11.20	11.60
45	12.03	11.62	11.33	11.18
60	11.94	11.73	11.17	10.77
75		11.69	11.11	9.84
90		11.89	11.17	9.66
105		11.73	11.26	9.54
120		11.78	11.30	9.44

Table 5: **Output** **unit = kg/hr**

Extruder RPM	**Compound A**	**Compound B**	**Compound C**	**Compound D**
120	3.4	3.4	3.5	3.5
145				4.2
162				4.9
200				6.0

Table 6: **Melt Fracture** **unit = percent**

Time (minutes)	**Compound A**	**Compound B**	**Compound C**	**Compound D**
0	100	100	100	100
15	100	30	25	95
30	100	10	10	60
45	100	<5	<5	15
60	100	<5	0	0
75	100	<5	0	0
90	100	<5	0	0
105	100	<5	0	0
120	100	<5	0	0

Table 7: **Die Build-up** **unit = visual observation**

Time (minutes)	**Compound A**	**Compound B**	**Compound C**	**Compound D**
0	none detected	none detected	none detected	none detected
15	none detected	none detected	none detected	none detected
30	none detected	none detected	present	none detected
45	none detected	none detected		none detected
60	none detected	Present		none detected
75				none detected
90				none detected
105				none detected
120				none detected*

*none detected after 450 minutes extrusion time

Compound A

Time = 0 minutes

Compound A

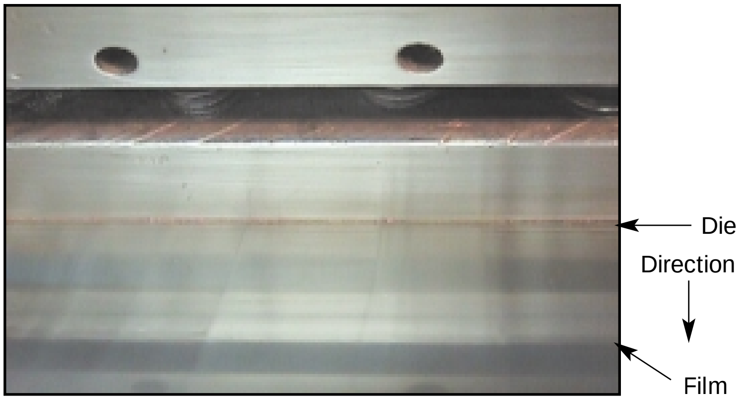
Time = 30 minutes

Compound A

Time = 60 minutes

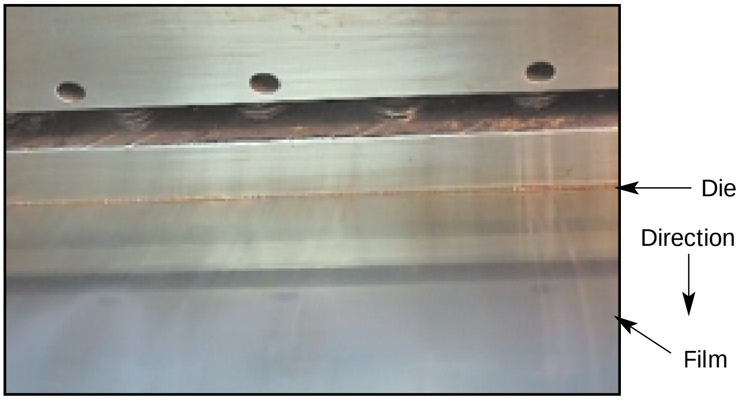
Compound B

Time = 0 minutes



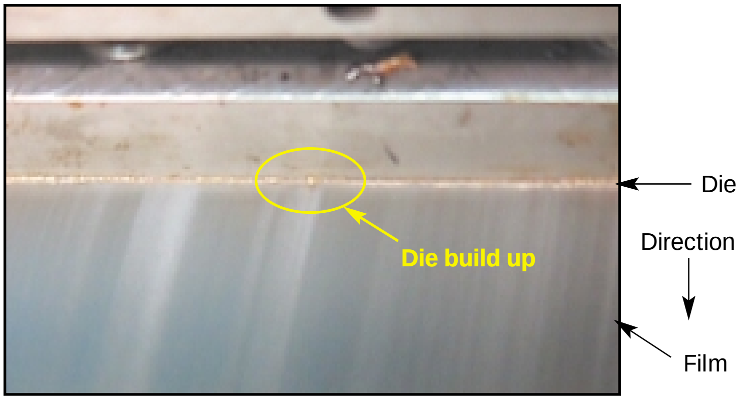
Compound B

Time = 30 minutes



Compound B

Time = 60 minutes



Compound C

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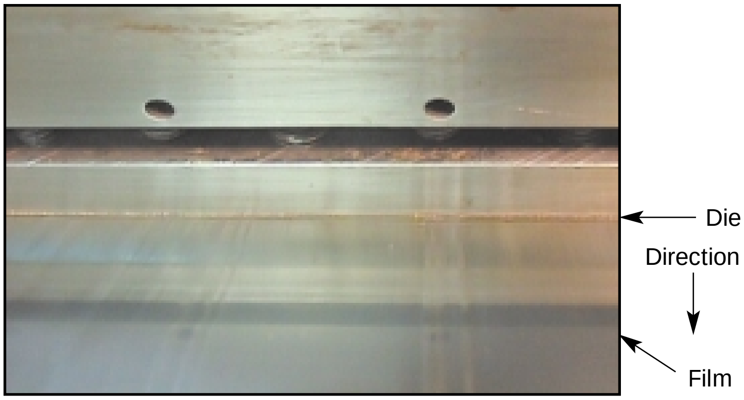
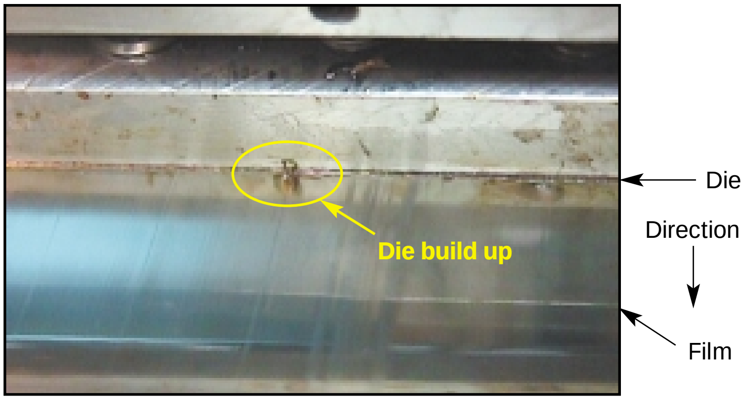


Compound C

Time = 30 minutes



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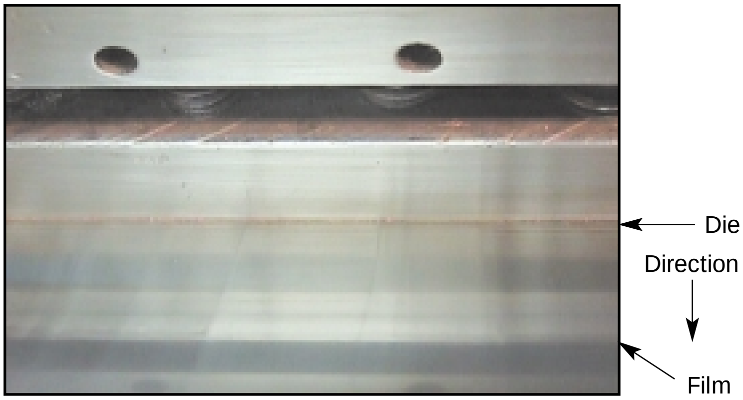
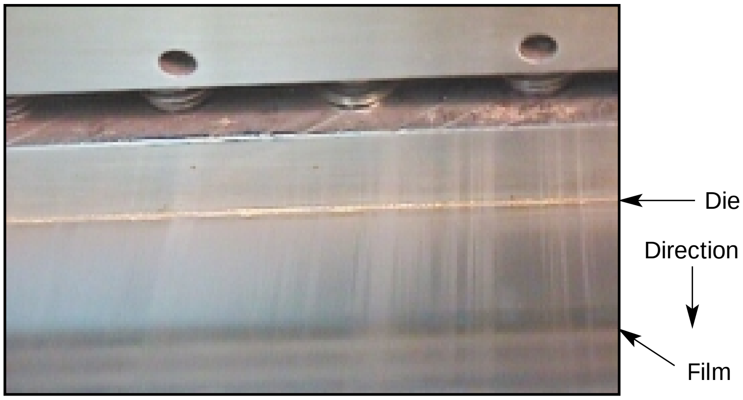


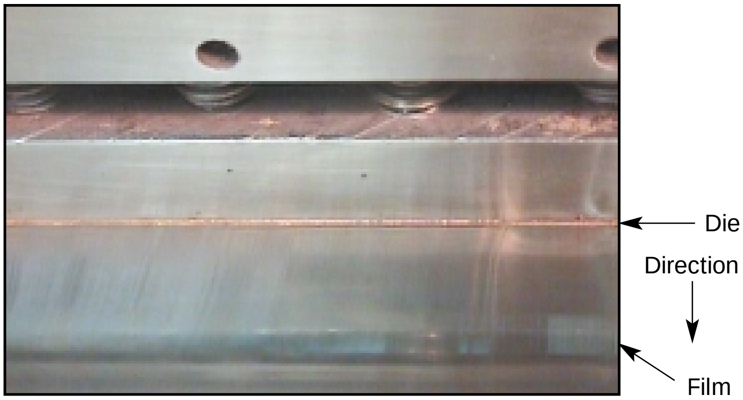
Compound D

Time = 30 minutes



Compound D

Time = 60 minutes



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