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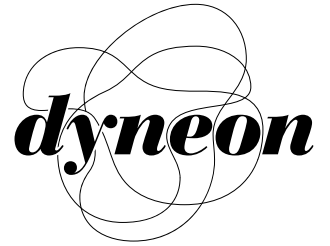
Title:

The use of Polymer Processing Additives (PPAs) to Improve Melt Processing of m-LLDPE Extrusion

Abstract:

There is a large body of work showing that the addition of polymer processing additives (PPAs) results in an improvement in the processing performance of polymers. Some of the processing improvements that have been observed include a reduction in melt fracture, pressure, die build-up, and gels along with an increased processing window and improved surface finishes. Previous experiments have shown the addition of a PPA has reduced gels that result from cross-linking, oxidization, and unmelted material. This work will investigate the reduction of unmelt gels seen with the addition of PPA to a polyolefin plastomer (POP) and will infer the mechanism of how the coating of the PPA on the extrusion barrel reduces the unmelt gels. In addition to the mechanism this paper will evaluate the different methods of adding the PPA to the extrusion system.

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**The use of Polymer Processing Additives (PPAs)
to Improve Melt Processing
of m-LLDPE Extrusion**

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ABSTRACT

There is a large body of work showing that the addition of polymer processing additives (PPAs) results in an improvement in the processing performance of polymers. Some of the processing improvements that have been observed include a reduction in melt fracture, pressure, die build-up, and gels along with an increased processing window and improved surface finishes. Previous experiments have shown the addition of a PPA has reduced gels that result from cross-linking, oxidization, and unmelted material. This work will investigate the reduction of unmelt gels seen with the addition of PPA to a polyolefin plastomer (POP) and will infer the mechanism of how the coating of the PPA on the extrusion barrel reduces the unmelt gels. In addition to the mechanism this paper will evaluate the different methods of adding the PPA to the extrusion system.

INTRODUCTION

The recent advances in metallocene catalysts have introduced a new family of materials that have unique molecular architecture as compared to that of traditional Ziegler-Natta polyethylenes. These changes cause unique physical properties, along with enhanced properties of the end products. As a result, these materials have very different processing characteristics. It has been shown that modification to either single screw design operating conditions and/or additives may be necessary in order to process these new families of resins (1,2,3).

The primary use of PPA has been the elimination of melt fracture in polyethylene films (4). Other processing additive benefits such as widening processing windows, improvement in surface properties (5), and eliminating die lip build-up (6) have also been demonstrated. A new benefit of gel reduction has been identified and several mechanisms postulated (7). This work will show that a properly designed PPA product can reduce the amount of unmelted gels by preventing premature melting of resins in the feed section of the extruder.

A properly designed PPA will move to the areas of highest shear in an extruder and form a low surface energy coating. This is typically on the metal die surfaces and where the screw flights sweep tightly across the extruder barrel. The fluoropolymer coating changes the interfacial properties between the metal surface and the host resin in preventing stick and lowering frictional forces.

Due to frictional heating, plastomers can melt too early in the feed section of an extruder. This can cause solid encapsulation and solid bed break-up in a barrier screw configuration. Adding a PPA has been postulated to reduce premature melting of the plastomer by reducing the interfacial frictional heating.

Therefore PPA can dramatically reduce unmelt gel formation. This concept was shown with empirical work published at ANTEC 2000 (11). Further work was needed to determine whether PPA was actually coating the barrel in the feed section and how this could occur without being in a polymer melt stream. This latter point was investigated by using different methods of addition for the PPA.

These experiments also examined the changes that occur, with the addition of PPA, to solids conveying, melting characteristics and process performance.

Experimental

Experimentation was conducted on a 3 MI polyolefin plastomer (POP) with a PPA (FX 5920A) added 4 different ways. The POP has been shown to have early melting behavior (1). Experiments measured the solids conveying, melt pool formation and gel level of the POP and how it is affected by different means of PPA addition.

Extrusion tests were conducted on a 63.5mm 24:1 L/D. The extruder speed was fixed at 50 RPM and the barrel profile was kept constant at: Zone #1 - 191°C, #2 - 204°C, #3 - 232°C, #4 - 260°C, while the die and adapter temperatures were kept at 260°C. The breaker plate pressure was approximately 20 MPa for all of the test runs. All of these conditions are typical of running production LLDPE cast film. Overall performance was characterized by specific output, melt temperature, power consumption, total melt temperature variation, and total pressure variation. The solids conveying, melting, and pumping processes within the extruder were monitored and interpreted by means of pressure traces which were recorded at very high sampling rates (8). The transducers were placed at approximately 6 L/D intervals starting at 3.8 L/D from the feed opening. The melt temperature was recorded at the discharge of the extruder using an exposed junction melt thermocouple immersed to the center of the melt stream. A side stream of the material was extruded into a cast film and examined for melt quality by analyzing the size, quantity and type of gels in the extrudate.

All of the tests were conducted with a barrier screw that is suitable for running cast film grade LLDPE. The barrier screw had a secondary flight introduced in the transition section of the screw. This secondary flight had a clearance greater than the main flight (barrier gap). This flight separated the solid bed from the melt pool, while the barrier clearance allows the melted polymer to pass from the solids channel to the melt channel. The lead of the main flight within the barrier section was increased in order to maximize the available area for melting against the barrel wall. The barrier flight had a lead greater than the main flight, which changed part way through the barrier section. This decreased the volume of the solids channel while increasing the volume of the melt channel as

the barrier flight proceeded down the barrier section of the screw. In addition to changing the width of each channel, the channel depths were altered. The depth of the melt channel was increased, while the depth of the solids channel was decreased, as they progressed down the screw, in order to match the volume of the melted polymer. The barrier gaps and channel depths that were selected were typical of those used in production cast film screws. The screw had an overall compression ratio of 2.53:1 and incorporated a Union Carbide mixing section in the metering section of the screw to ensure melt homogeneity.

The PPA was added to the material in three different methods: i) as a masterbatch, ii) pre-compounded into the POP, and iii) direct addition of the neat, PPA powder. In all cases the PPA was added at a level of 1000 ppm with the plastomer. The PPA masterbatch was made with 2 different carrier resins to investigate whether different melting behavior would change the ability of the PPA to form a coating in the feed section. One masterbatch was made with a 2 MI LLDPE carrier resin (commercial product) and the second was compounded with the POP by a DTEX co-rotating fully intermeshing twin screw extruder. Both masterbatches incorporated the PPA at a 3% loading and were let down to 1000 ppm concentration for the study. The same twin screw extruder that produced the POP masterbatch made the pre-compounded PPA in POP. A sample of virgin POP was run through the twin screw in order to evaluate the effect of the twin screw heat history on the gel count.

Once the PPA was added to the system, the extruder was run for at least 1 hour to ensure that the PPA fully coated the extrusion barrel, screw, and downstream adapter and die system. Probes were installed along the barrel to test for the presence of PPA. The probes were 4140 steel rods that were machined such that the tip matched that of a pressure transducer and extended very close to the inner barrel surface. These probes were installed at 6, 15, and 21 L/D from the feed opening in pressure transducer ports in the barrel. After running each PPA, the extruder was abruptly stopped and the barrel probes were removed. After this "purge", probes were installed and the extrusion system was purged with virgin POP until the original steady state conditions were obtained. At this point, a new set of barrel probes were installed and the next PPA material was tested. These probes were then tested for the presence of PPA by ESCA analysis for fluorine.

RESULTS AND DISCUSSION

Process Performance

Figure #1 shows the output verses the type of PPA addition to the POP. As the figure shows, the PPA precompounded into the POP had the lowest rate reduction, followed by the

POP/PPA masterbatch. The PE/PPA masterbatch had a slightly greater reduction in rate while the direct addition of PPA powder had the greatest impact on the output rate. Figure #2 shows the melt temperature and energy change with the addition of PPA. The process stability was measured by the total pressure variation and melt temperature variation in the adapter pipe. This data is shown in Figure #3. All of the samples with the exception of powder addition showed excellent process stability, less than 0.74% total pressure variation and less than 0.3°C total temperature variation. The powder addition had significantly greater variation, 1.9% pressure variation and 0.8°C temperature variation, both of which are considered unacceptable for cast film.

Pressure Analysis

The addition of PPA to POP showed the same trend of eliminating solid bed breakup that was observed in prior work (11) regardless of the form in which the PPA was added to the POP. The PPA helped eliminate the unmelted gels by delaying the onset of melting until the introduction of the barrier section. Additionally, the PPA reduced the size of the melt pool in the solids channel, thereby preventing the solid bed from breaking up. This breakup causes unmelted material to be encapsulated in the melt creating gels in the extrudate.

When the PPA was added as a powder there was a significant increase in the pressure fluctuations observed in the feed section of the screw as compared to the other methods of PPA addition and the virgin POP. This instability can probably be attributed to the addition of powder causing slippage in the feed section.

Barrel Probe Analysis

It has been postulated that PPA coating helps eliminate gels caused by thermal and/or oxidative degradation. In coating the screw and barrel the PPA prevents material from stagnating and creating gels at these surfaces. Therefore, at each steady state condition the barrel probes were tested for the presence of PPA. This was accomplished by ESCA, which would report the presence of fluorine on the face of the probe that was exposed to the polymer inside the barrel. Since the only component in the system that contains fluorine is the PPA any positive result would indicate a PPA coating. Analysis of the barrel probes showed the presence of fluorine as early as 6 L/D into the barrel for all the methods of PPA addition. This confirms that the PPA is coating the entire barrel.

Gel Analysis

Gel counts were performed on the film samples per ASTM condition D3351. Figure #4 shows the total gel count and Table #1 lists the type of gels that were observed in each sample. The data shows that the compounding of the POP in the twin screw caused an increase in the amount of gels which would be expected due to the increased heat history

which would cause crosslinking, oxidization and the increased potential for contamination. The data also show that the gel reduction was the greatest when the PPA was added by either the POP masterbatch or precompounded into the POP. The PE masterbatch also showed a reduction in the amount of gels but not as great as the POP masterbatch. The PPA powder did not reduce the amount of gels as effectively as the other two methods of PPA addition.

Conclusions

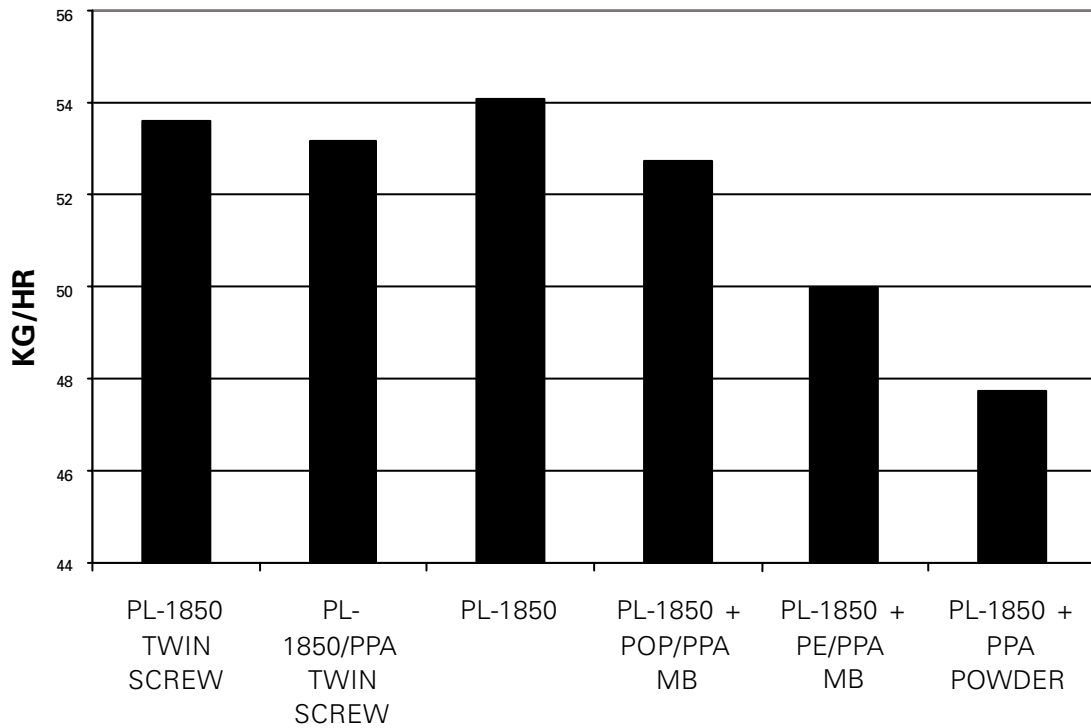
The addition of polymer processing additive to a polyolefin plastomer that exhibits early melting behavior was able to reduce the number of unmelted gels in the extrudate regardless of the form in which the PPA was added. It was shown that the addition of PPA by means of the same base material gave the best performance, while the addition via a similar material still gives good results (PE carrier). When the PPA was added as a neat powder it also reduced the unmelted gels but caused other processing problems to occur. This can be attributed to slipping in the feed section due to the powder-pellet combination, which will result in extruder surging. This was observed as an increase in process variation that was observed in the adapter pipe.

The addition of PPA delayed the onset of melting, lowered the pressure profile, and improved melt quality (less gels) of the POP when processed on an LLDPE barrier type screw. The PPA gives the processor the ability to alter the melting characteristics of POP in order to utilize a more general purpose screw design. Screw design changes can yield similar benefits (1), this could reduce or eliminating the need for PPA addition when trying to eliminate unmelted gels, however it could also result in the need for a dedicated screw for each different material that has unique melting characteristics.

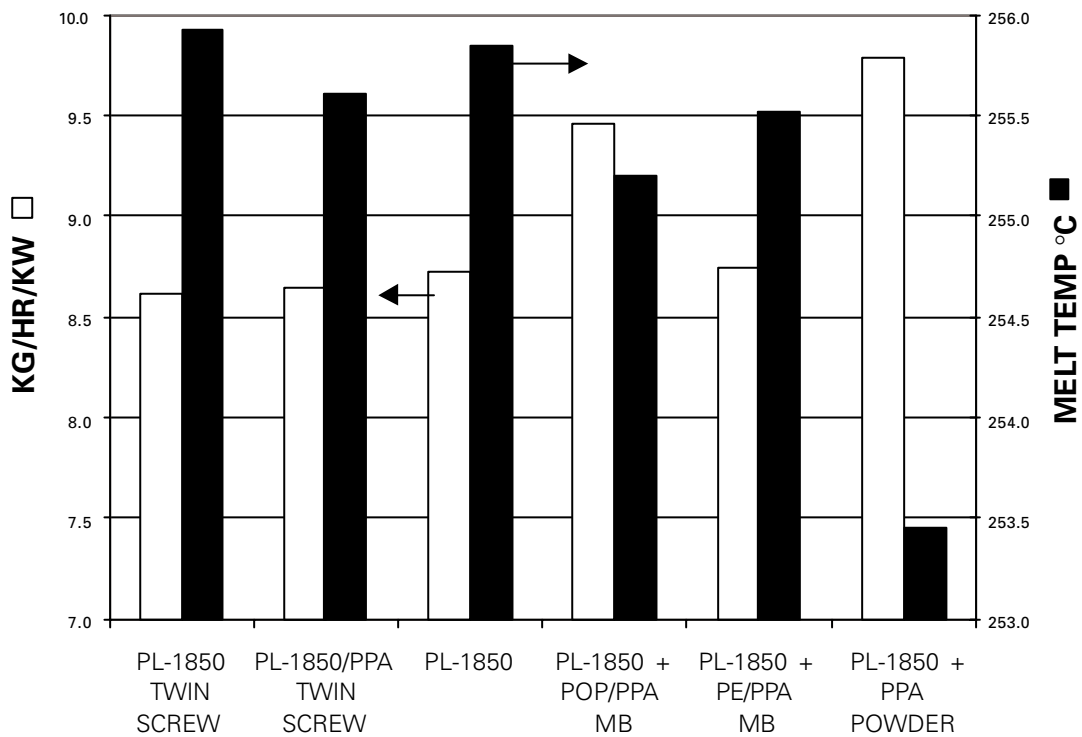
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Tables & Figures



Figure#1 – Output Rate vs. PPA Addition at 50 RPM



Figure#2 – Melt Temperature and Energy vs. PPA Addition at 50 RPM

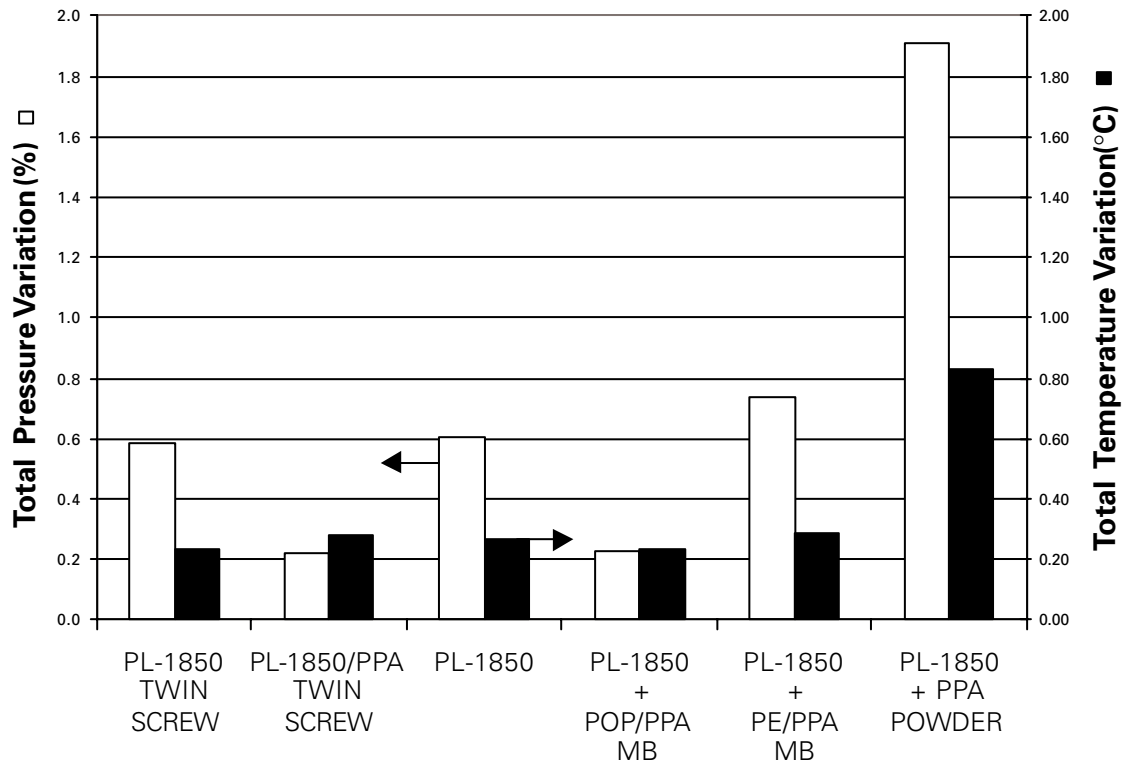


Figure #3 – Process stability

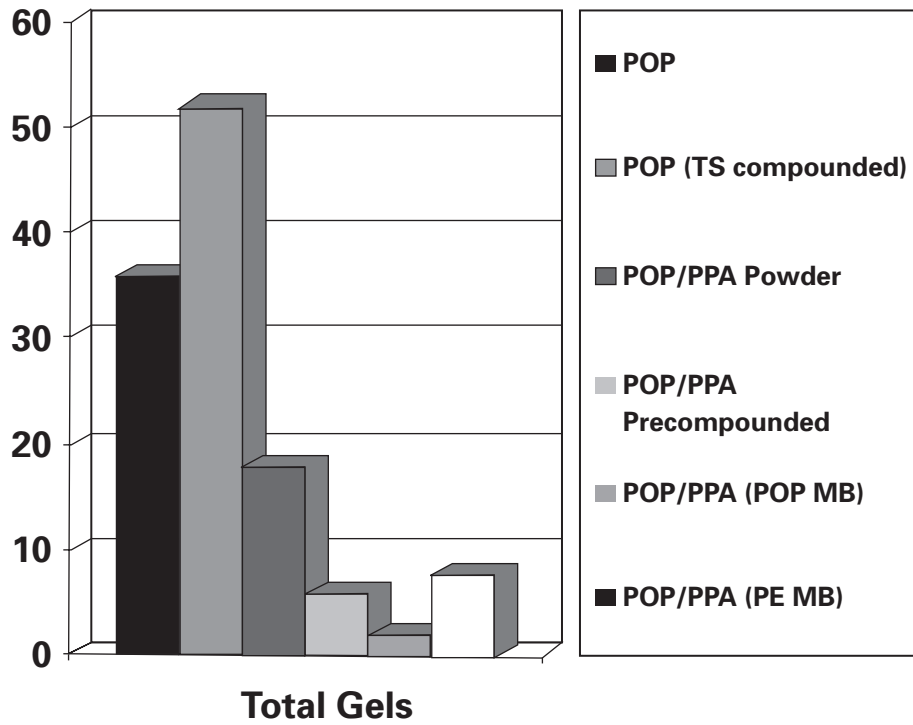
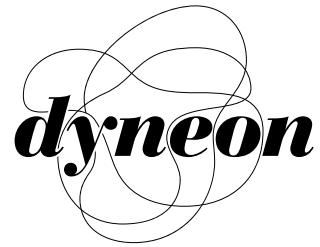


Figure #4 – Gel Count by ASTM D3351

Sample	Gel Type
POP	Unmelt Gels
POP Twin Screw	Unmelt Gels, Black Specs
PPA Precompound	Unmelt Gels
PPA Powder	Unmelt Gels
POP/PPA MB	Unmelt Gels
PE/PPA MB	Unmelt Gels, Fiber Contaminates

Keywords: Gel, Barrier Screw Design, Film, Polymer Processing Additives, PPA, polyolefin plastomer, POP

Table #1 – Gel Type



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