STUDY OF THE THE POSITIVE EFFECTS SEEN WHEN USING FLUORINATED POLYMER PROCESSING & RECYCLING AIDS (PPRA) IN REPROCESSED LLDPE

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Abstract

Compared to other technologies, plastic products bring tremendous benefits to many consumer and industrial uses. Plastics can be: ultra-durable and puncture proof; insulators from heat or cold; energy saving light weight; abrasion resistant; post-bendable to form around surfaces to protect or cover; easily heat sealed for safe containment; pure and non-rusting; chemically resistant; soft and safe to the touch; a great barrier to keep food fresh; easily cleanable & reusable. There is an additional major advantage of plastics that has yet to be fully realized, and this is the ability to "easily" recycle. At this time, the amount of plastic that is readily recyclable but not currently converted, is giving this great technology a bad name, when in fact, plastics are one of the easiest materials to reprocess into safe and easy to use final products. Our society needs to do better focusing on the sustainability of recycled products, and in conjunction with that mindset, manufacturers need to take more care to give proper focus to making as many high quality products from recycled materials as they can. The photos you can find on the internet of piles of plastics laying in public areas, floating in the ocean, or filling up landfills are very real, but this does not need to be the case. Given the proper attention, these materials discarded as trash, offer the potential to make the same product over-and-over without consuming additional resources. Many plastics are recyclable and reprocessible, and this paper will focus specifically on improving the reprocessing of polyethylene (PE), the number one plastic family produced in the world (FN-1).

Introduction

Polyethylene is a wonderful polymer commonly processed into films, sheets, containers, pipe/tubing, fittings, fibers, cable jacketing, toys, houseware and more. What makes this material attractive is the light weight, low cost, toughness & durability, and ease of melt processing and post fabrication. Final products made with polyethylene can be distinguished by appearance and/or physical properties that are enhanced or degraded depending on the processing conditions during manufacture. To gain an edge over the competition a manufacturer may request the addition of certain additives that enhance the end performance of the product. One such additive is termed polymer processing aid (PPA). For polyethylene a PPA is often a fluorinated polymer or elastomer called PVDF, PVDF copolymer or FKM. Using extruded film as an example, PPAs provide:

Aesthetics

- improved surface finish with the elimination of sharkskin, orange peel or melt fracture
- improved clarity of film
- improved gloss of film

Performance

- Improved physical and mechanical properties by allowing lower melt index materials to easily process
- Reduction of gels and weak spots
- Reduction of die build up that can cause surface irregularity

Energy and Material Savings

- Lower pressure and torque on the machine, thus extending the life of equipment
- Improved gauge control to reduce material waste
- Faster line speeds for improved productivity without investing in extra equipment and space
- Allow option to use lower processing temperatures thus saving energy

Other Applications

The positive effects of a PPA are not limited to film. When used in injection molding, cycle times can be decreased, flow length can be increased, processing temperatures can be decreased, and lower melt index materials can be effectively processed where otherwise they would not fill properly, or when filling they would be subject to poor surface condition.

When used in pipe, monofilament, wire & cable, and profiles, a PPA can: help with production; improve gloss of a final product; and reduce gels and imperfections caused by die build up.

Concept of PPRA

It has been known for some time that fluorinated polymer processing aids are very effective in providing the performance described above (FN-2). It has only recently been established and studied by Arkema that the use of these PPA polymers and elastomers have very positive effects in the reprocessing of polyolefin resin mixtures. It may not be well known until this publication that the Kynar Flex® brand of PVDF copolymers are manufactured without the use of PFAS surfactants. The combination of these 3 points; 1) the PPA effect to assist in melt fracture reduction and pressure reduction in the processing of PE, 2) the knowing use of a PPA in a PE that is intended to be recycled, and 3) the use of a fluorinated PPA that is manufactured without any use of PFAS surfactants in that process, gives a new name recognition to the PPA in this case. Such a product will be termed as a Polymer Processing and Recycling Aid (PPRA) throughout the rest of this paper.

Experimental Procedure

A previous study presented by Lowrie, et al (FN-3), examined commercially available recycled PE materials of various color and additive formulations on a flat die film line, and controls were compared to recycled polymer with the addition of fluorinated PPRA. The below picture shows the before and after effect on the recycled film after the addition of the PPRA. The addition of the fluorinated PPRA eliminated melt fracture, reduced die build up, and reduced extruder pressure in each recycled LLDPE sample tested.

Random white recycled PE film and after 10 minutes of using fluorinated PPRA

Random clear recycled PE film and after 20 minutes of using fluorinated PPRA

Random Grey recycled PE film and after 30 minutes of using fluorinated PPRA

Photo 1: Various colored and natural recycled LLDPE resins appearance from the die before and after the addition of Kynar Flex® PPRA

Arkema decided to study a similar processing method, but using a highly controlled method of making the reprocessed material. The idea of controlling the reprocessed material in this case allowed a new type of study that compared a reprocessed PE that did not originally use a PPRA, a reprocessed material that was certain to have contained a PPA, as well as combinations of each of these reprocessed materials.

The study consisted of a 1 MI LLDPE polymer that was known to have few additives and no PPA added into the polymer. The LLDPE was then extruded into a monofilament, ground as recycle, and then extruded again into a pellet. Photo 2 shows the production of the monofilament used to make the reprocessed LLDPE. The pellet generated from this action was termed LLDPE 1.

Photo 2: Generation of extruded polymer to be used as the reprocessed polymer in the study

The same initial LLDPE was combined with a 2.5% masterbatch of Kynar Flex® 5300 PPRA and let down to 500 ppm final PPRA level, and extruded into a monofilament. This monofilament was then reground and processed into a pellet. The pellet generated from this action was termed LLDPE 2.

As a control, LLDPE 1 was then extruded on a 1.25 inch extruder with a 50 mm flat die with a 0.5 mm die gap, at a range of temperatures from 155C to 177C, and a shear rate of 300s-1. Photo 3 shows the apparatus used to develop the data for the testing described later in the report. The LLDPE 1 control extrusion was checked for processing pressure and melt fracture.

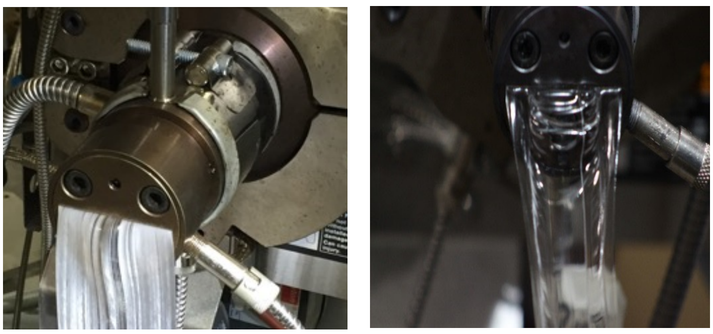
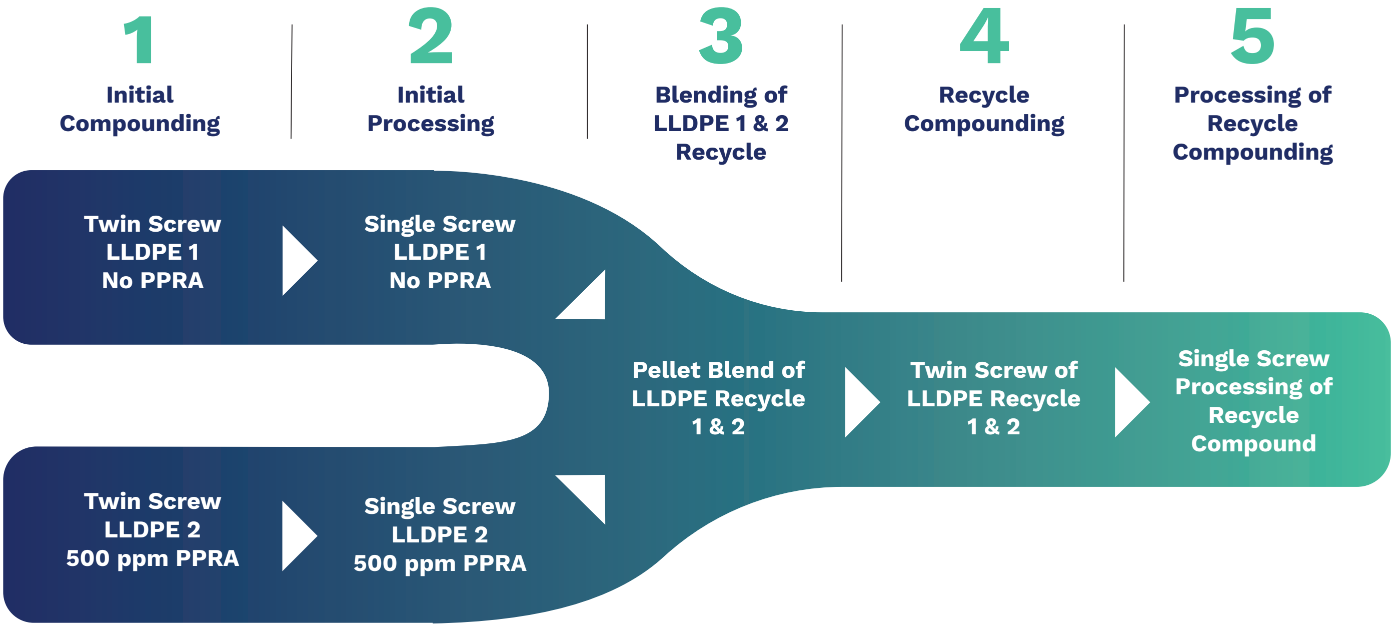


Photo 3: Film line used to measure pressure drop and melt fracture reduction

As a study, LLDPE 2, a fully reprocessed LLDPE originally containing a PPRA at 500 ppm loading was extruded the same as the control and was checked for processing pressure and melt fracture throughout the experiment. A timer was set and melt pressure values were recorded throughout the experiment vs. time. Melt fracture was captured by a camera in 5 minute intervals. At the conclusion of the test, the extruder was emptied and purged to remove any remaining PPRA from the die wall. Then the next samples were added in each test in the same mannerwith the same purging procedure.

Diagram 1 shows the process of making the reprocessed LLDPE resin with and without PPRA in the initial product and then how the mixture compounds were made.

Diagram 1: Study 1 Protocol - to investigate the difference between a recycled product that already contained PPRA and one that did not originally use a PPRA



Results

The expected result of LLDPE 1 having continuous melt fracture and unchanged processing pressure, and LLDPE 2 ultimately having a declining processing pressure of almost 35%, and full elimination of melt fracture within 60 minutes, set the stage for additional tests and discovery.

Blends of LLDPE 1 and LLDPE 2 were created at ratios of 90/10 (calculated 50 ppm of PPRA); 75/25 (calculated 125 ppm of PPRA); 50/50 (calculated 250 ppm of PPRA); 25/75 (calculated 375 ppm of PPRA) were studied in the same manner, and the pressure and melt fracture reduction were recorded in Figure 1 and Figure 2 respectively.

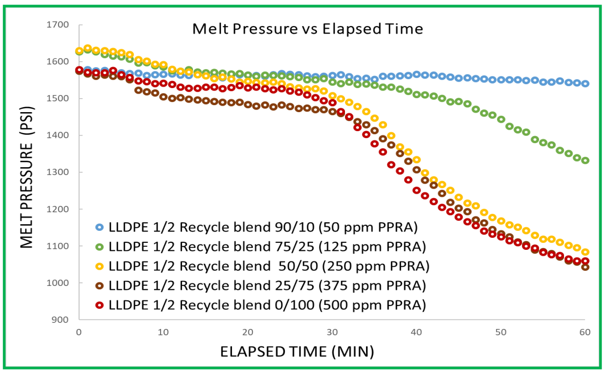


Figure 1: Melt Pressure Reduction Over Time for LLDPE Recycled Polymer Reprocessed into Film Using Various Blends of Recycle With and Without PPRA Used in the Original Product

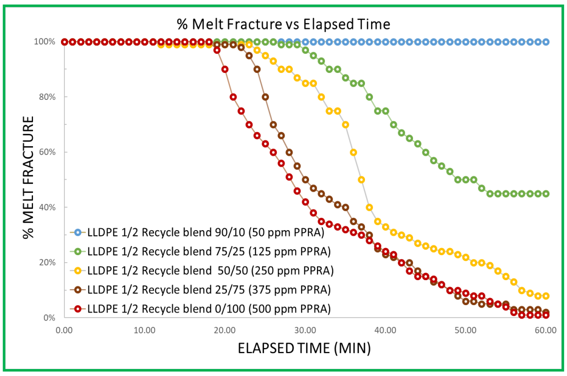


Figure 2: Melt Fracture Reduction Over Time for LLDPE Recycled Polymer Reprocessed into Film Using Various Blends of Recycle With and Without PPRA Used in the Original Product

Interesting observations of “blended recycled LLDPE”

- at the 90/10 ratio of LLDPE 1 to LLDPE 2, there was no observed benefit of having the original PPRA in the product. It should be pointed out that there was no disadvantage seen either.
- at the 75/25 ratio of LLDPE 1 to LLDPE 2, there was a significant reduction of extruder pressure (16%) and noticeable reduction of melt fracture even if it did not come close to going to zero.
- at the 50/50 ratio of LLDPE 1 to LLDPE 2, there was dramatic pressure reduction (30%) and significant melt fracture reduction, but still not all the way down to zero
- at the 25/75 ratio of LLDPE 1 to LLDPE 2, the pressure reduction was equivalent as if the product was 100% LLDPE 2 (35%) and melt fracture was fully eliminated at 60 minutes which was slightly longer than the 100% LLDPE 2 result.

The testing clearly showed that if the original LLDPE was processed using Kynar Flex® 5300 PPA at 500 ppm loading, and then recycled, it had significant processing and quality advantages to a LLDPE that was processed without any use of PPRA. Also, it is important to note that if a LLDPE was processed using Kynar Flex® 5300 PPRA at 500 ppm loading, it could be combined with another recycle faction of product that did not use PPRA, and if the calculated level of PPRA was at least 125 ppm, significant extruder pressure drop could be seen and some improvement of film surface finish could be expected. Finally, it seemed that by the time a blend ratio of a recycled LLDPE that originally contained 500 ppm of PPRA was at least 75% of the total PPA in the final product (375 ppm), the result of substantial pressure drop and full melt fracture reduction could be achieved.

Additional testing related to blending methods

In earlier work, Lowrie (FN-4) already showed that adding a masterbatch of LLDPE plus Kynar Flex® 5301 PPRA to industrial reprocessed LLDPE materials of various formulations (White, Clear, Grey) could vastly improve the processing and appearance of these materials. Building on that discovery, new LLDPE masterbatches were created with 2.5% loading of Kynar Flex® 5300 and added to pure recycled LLDPE with no PPRA. This was prepared in a controlled environment to achieve the same calculated levels of PPRA in the final product.

Diagram 2 shows the process taking reprocessed resin without use of a PPRA and blending in a masterbatch containing PPRA and then how mixture compounds were made

DIagram 2: Study 2 Protocol - Using a masterbatch to add PPRA to a recycled LLDPE that did not originally use a PPA

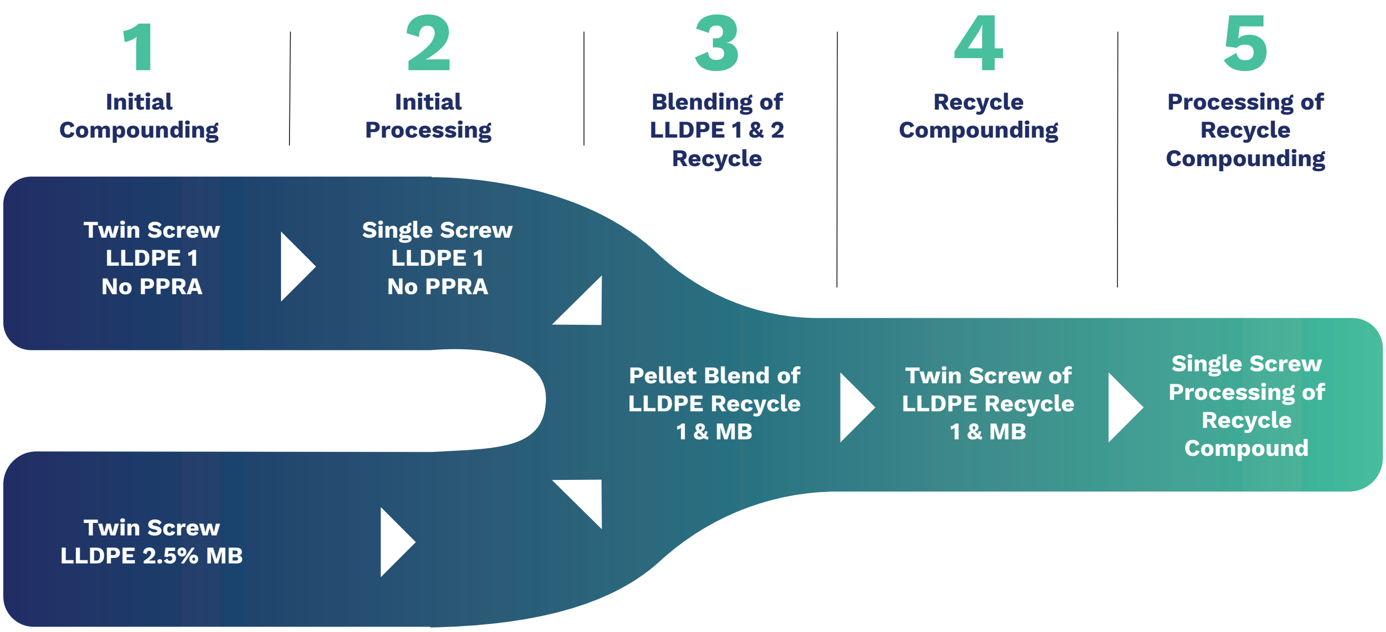


Figure 3 and Figure 4 depict the reduction of pressure during extrusion and reduction of melt fracture respectively.

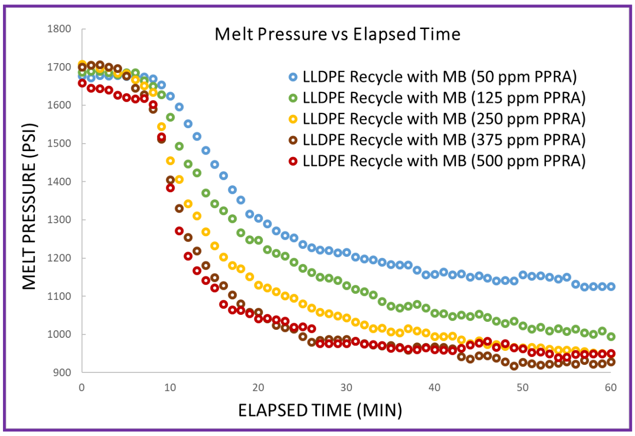


Figure 3: Melt Pressure Reduction Over Time for LLDPE Recycled Polymer With Masterbatch (MB) Addition of Kynar Flex® 5300 PPRA

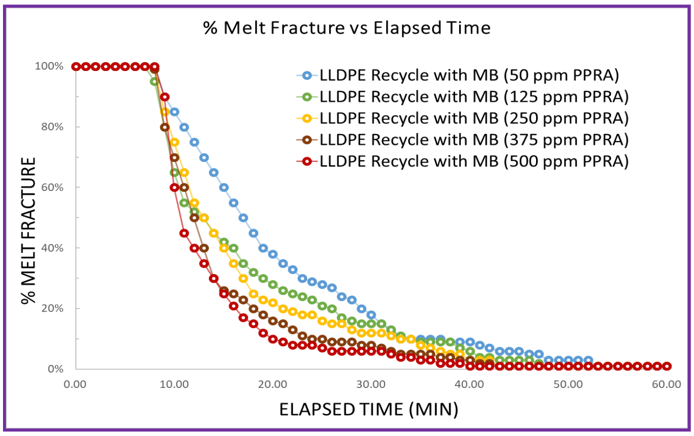


Figure 4: Melt Fracture % Reduction Over Time for LLDPE Recycled Polymer With Masterbatch (MB) Addition of Kynar Flex® 5300 PPRA

There were dramatic differences in the results when 50 ppm, 125 ppm, 250 ppm, 375 ppm and 500 ppm levels of PPRA were in the recycled films and processed in the same manner as described in the experimental procedure section of this document. First of all, even at just 50 ppm of PPRA added to the recycled LLDPE manufactured without any original PPRA, there was large and immediate improvement in pressure drop (32%) and almost complete elimination of melt fracture after 50 minutes. As the level of Kynar Flex® 5300 PPRA was increased to 125 ppm, 250 ppm, 375 ppm and 500 ppm, the pressure drop continued to fall to as low as 45% of the original number. Interestingly enough, while the induction period (initial period of rapid reduction) of the 500 ppm sample was the fastest, after 60 minutes the 375 ppm sample had the lowest pressure by a slight margin. Our belief is that the values could be considered equal within limits of error of the test and equipment gauges. Melt fracture reduction when using a masterbatch to gain the concentration was much faster than in the first blends tested where recycled material already containing the PPRA were used. Full melt fracture elimination occurred within 45 minutes for the 250 ppm, 375 ppm and 500 ppm masterbatch addition samples. See Figure 5 for the full comparison.

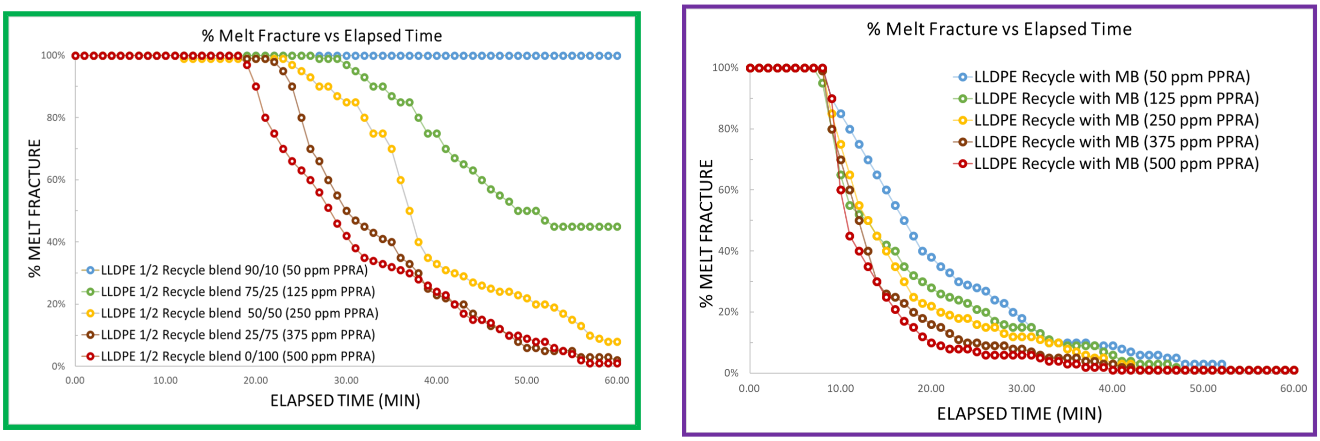


Figure 5: Side by side comparison of melt fracture reduction depending on the method that the PPRA is introduced into the LLDPE film production (PPRA already contained in the reprocessed LLDPE vs. PPRA added by masterbatch to a recycled LLDPE without PPRA in the original extrusion)

Conclusions

- We all need to work together to recycle more materials for the good of the environment. Plastics as a class of materials offer low hanging fruit in the area of recycling that our society needs to give more focus to.
- Using a Fluoropolymer PPRA in the original processing of a polyethylene product will significantly aid in any future recycling steps.
- Up to a certain amount, the more PPRA that is used originally, the easier the recycled material may process.
- Even if some of the recycled material does not contain a PPRA, if it is combined with another portion of recycled material that did contain a PPRA, that blend will likely process better
- Adding a PPRA via a masterbatch method to recycled materials helps improve the processibility; if PPRA already exists in the recycled polymer, then the amount of PPRA needed to give good processing performance could be less than what is standardly used for virgin resins.

References

1. https://en.wikipedia.org/wiki/Polyethylene
2. Blatz, P.S., US Patent 3,125,547 (March 1964)
3,4 Lowrie, R; Henry, J; DeAngelo, M; Cavalier, C; Seiler, D., “The Effect of Fluorinated Thermoplastic Processing Aids in Film Processing of Recycled Polyethylene Resins”, Compounding World Expo, Cleveland, OH, November 2021.

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