Fluoropolymer Polymer Processing Additive - Antiblock Interactions

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Abstract

Fluoropolymer polymer processing additives (PPA) and antiblocks (AB), two components of polyolefin resin additive packages, are used in polyolefins for different reasons. They have to achieve their respective roles in the presence of the other components of the additive package. ABs and PPAs may interact by adsorption of one to the other, or by the AB abrading the dynamic PPA coating during end-use processing. These interactions may impact PPA effectiveness. To ensure that the desired PPA effect is delivered, it is important to consider PPA-AB interactions. Earlier investigations, have shown the varying influence of different ABs on PPA performance [1,2]. In this study, we quantified the influence of several ABs on the melt fracture elimination performance of three PPAs in LLDPE blown films. To increase relevance to differing use levels of different ABs, we performed this at two different AB concentrations. As polyolefins, PPAs and ABs have evolved, we have expanded our data on PPA - AB interaction investigations to include benchmark and higher performing materials particularly newer PPAs and newer commercially available ABs. We present these updated data and offer suggestions to minimize PPA-AB interactions while achieving needed PPA effectiveness by matching AB type with optimal PPA type and PPA concentration,

Introduction

PPAs and ABs are used as components of polyolefin/ polymer additive packages for film applications along with many other additives. They are found together in fully-formulated resins, MBs (MBs), powder blends, etc. ABs and PPAs provide different benefits. Plastic films tend to stick together, a phenomenon called "blocking". Anti-block additives are used in films to prevent this. ABs are generally fine particulate materials, that provide very small bumps on film surfaces. These bumps minimize film to film contact. Available ABs differ in several factors including antiblocking efficiency, clarity in film, physical properties, potential interaction with other additives, and cost. PPAs provide processing advantages such as elimination of melt fracture, reduction of operating pressures, and elimination of die build up, without impacting end use film properties. PPAs form a dynamic layer on metal surfaces in contact with flowing molten polymer as on die surfaces. This PPA layer is central to providing the desired processing advantages. Factors reducing the formation or integrity of the PPA layer, would reduce PPA performance. Such factors include process conditions, apparent PPA concentration ,

and the presence of other additives that reduce PPA layer integrity.

ABs and PPAs may interact and these interactions can affect PPA performance. Decades of commercial use have shown that PPAs do not impact the blocking efficiency of ABs. However, there are situations where the AB additive can negatively impact the performance of the PPA [2]. PPA-AB interaction is expected to happen in two primary ways. First, adsorption between PPAs and ABs can make less of the PPA available to coat metal surfaces. PPA-AB adsorption is expected to be influenced by factors including AB surface area, AB surface treatment, synergist present in the PPA and PPA/AB addition method. Second, ABs may also abrade the PPA layer formed on the die surface and reduce PPA effectiveness. Abrasion by ABs is expected to be influenced by factors including AB & PPA type and concentration. Both types of PPA-AB interactions would reduce apparent performance of the PPA and would require either higher concentration of PPA in the additive package, a different mode of addition of the PPA and AB to the resin, or longer time for the PPA to be able to perform as expected. In this study, we address impact of AB type on PPA performance, and present data and suggestions for optimizing PPA performance in the presence of various ABs.

Materials

All materials were used as received. "AB-*" and "PPA-*" are the labels we use. These AB materials were supplied by the manufacturers listed.

Talc ABs (® or ™ of Specialty Minerals Inc.)
- ABT® 2500 (AB-1)
- Optibloc® 8 (AB-2)
- Optibloc® 10 (AB-3)
- Polybloc™ (AB-4)
- Microbloc® (AB-5)

Talc AB (® of CIMBAR Performance Minerals)
- Clear-Bloc® 80 (AB-6)

Nepheline syenite ABs (® of Unimin Specialty Minerals)
- Minbloc® HC1400 (AB-7)
- Minex® 7 (AB-8)

Synthetic silica ABs (® of Evonik Degussa Corporation)
- Sipernat® 44 MS (AB-9)
- Sipernat® 310 (AB-10)

We used these PPAs (3M™ Dynamar™)
- FX 5927 (PPA-1)
- FX 5920A (PPA-2)
- FX 9613 (PPA-3)

A commercial granular 2.0 melt index LLDPE, and a commercial 0.9 melt index, 0.918 g/cc, C6 LLDPE were used as the carrier resin (for MBs) and the base resin (for blown film), respectively. Masterbatches (MBs) were stabilized with Irganox® B900 antioxidant (® of BASF) and zinc stearate. We also used two, commercially purchased, AB MBs to compare to our lab made MBs1) a MB containing 60 weight % talc in LDPE, and 2) a MB containing 15 weight % "natural silica" in unspecified PE carrier resin.

Experimental

We performed this controlled melt fracture elimination study, under conditions chosen to highlight PPA performance changes. These controlled conditions allow us to attribute the observed differences to PPA-AB interactions. Specifically, we set up, AB containing but PPA-free, conditions on a blown film line that resulted in the film having maximum melt fracture. As blown film production was continued, we introduced PPA along with the other additives, at a concentration that cleared melt fracture but in a long time. Film line operating conditions, including the shear rate, were industry relevant. It has been shown [3] that higher shear rates help PPAs eliminate melt fracture faster. Our chosen shear rate and low PPA concentrations, stretch out melt fracture elimination so differences in PPA performance are obvious. Actual film production operations would be run under conditions that maximize production of acceptable film. However, the influence of PPA-AB interactions would still be present and our study identifies these.

First, MBs of the various ABs and PPAs were prepared. Next, melt fracture elimination performance of the PPA MBs was evaluated in film produced on our blown film line, in the presence of the different ABs (individually), at chosen let down formulation concentrations.

AB MBs were compounded using a Haake 9000, counter-rotating, twin screw extruder. MBs contained 50 weight % AB except for MBs of AB-3 & AB-10. Other components were carrier resin, 1000 ppm antioxidant and 700 ppm zinc stearate. PPA MBs contained 3 weight % PPA, 1000 ppm antioxidant, 700 ppm zinc stearate, and carrier resin. Melt fracture elimination performance was evaluated in (0.9 MI LLDPE) film produced on a Kiefel blown film line with a 40 mm, 1/24 (L/D) grooved feed extruder and a 40 mm die with a die gap of 36 mils. Percent remaining melt fracture was quantified by measuring the actual width of melt fracture bands across the film and expressing as a percentage of the total film width. Film samples were collected every 10 minutes during the trial. Trials concluded when melt fracture was eliminated completely (0 %). Time from the start to 0% melt fracture is the "time to clear melt fracture" (TTCMF).

Film line extruder and die temperatures were set to a target melt temperature of 210 C (410F) and throughput was controlled to an apparent shear rate target (die) of $220s^{-1}$. Base resin pellets and additive MB pellets were tumble blended prior to charging to the film line hopper. Each blown film trial was preceded by an extensive purge procedure to ensure removal of any residual PPA. After this, the film was "strung up" with the resin formulation containing all additives used in the trial, except PPA. Film samples were analyzed to ensure 100 % melt fracture was present. Then "baseline" film samples were collected for a further 30 minutes (still no PPA). Next, resin dry blend containing all additives including PPA, was added to the blown film line. As the PPA established a coating on the die, melt fracture reduced from 100% (during baseline), to zero % marking the end of the trial.

Results and Discussion

We chose to use melt fracture elimination performance as the measure of PPA performance because it is relevant to blown film production. Plots of remaining % melt fracture vs. time were used to compare the effect of different ABs on PPA performance. Shorter TTCMF indicated better PPA performance. Longer TTCMF implies that more PPA has to pass through the die before melt fracture is eliminated. A longer TTCMF can be interpreted as more PPA required to clear melt fracture. By increasing PPA concentration, the TTCMF can be shortened. Observations [1,2] indicate that the shortest TTCMF is expected in the absence of AB. Both PPA-AB adsorption and PPA abrasion by AB, are expected to reduce coated PPA layer formation and/or integrity. Hence PPA-AB interactions are expected to reduce PPA performance and result in longer TTCMF.

Data presented in this study were collected for commercially available ABs and PPAs in a C6 LLDPE base resin. Our list of ABs and PPAs included materials representative of various relevant categories. ABs used included uncoated talcs, specialty talcs, coated talcs, nepheline syenites, and synthetic silicas. We also tested two commercially purchased AB MBs. One of these contained natural silica AB and the other contained talc AB. In our observations, PPA performance with this commercial talc MB, was consistent PPA performance observed with lab-made uncoated talc AB MB. We included these commercially purchased AB MBs because: 1) they provided data points for comparing our lab-made AB MBs to commercial MBs, 2) provided a possible comparison point for the uncoated talc ABs we tested, and 3) provided a reference point for PPA performance in the presence of natural silica AB. The three PPAs tested represent a variety of the PPA offerings available commercially. PPA-1 is one of the newer high performance PPAs available and is a fluoropolymer/synergist combination. PPA-2 is an

established fluoropolymer/synergist combination PPA, and PPA-3 does not contain a synergist.

Use levels of different ABs would be expected to depend on many factors including AB efficiency, end use film properties such as clarity, potential interaction with other additives, and base & carrier resin systems. From previous studies and experience, we did know that high concentrations of ABs had a higher probability of affecting PPA performance. For these reasons, we chose to run trials at 7500 ppm and 2000 ppm of AB to cover the major range of end-use AB concentrations.

PPA levels were chosen based on prior testing in this particular LLDPE resin. Each PPA was evaluated at a level that would result in complete elimination of melt fracture in approximately 2 hours based on a formulation containing 7500ppm of AB-1. PPA-1was used at 400 ppm, PPA-3 at 700 ppm, and PPA-2 at 1400 ppm. Additionally, one data set was collected with PPA-1 at 125ppm, and another with PPA-1 at 350ppm.

PPA-AB interactions at 7500 ppm AB:

Figure 1 shows the effect of 7500 ppm of one of, AB-1 through AB-9 or one of the two commercial AB MBs, individually, on performance of 400 ppm PPA-1. PPA-1 was able to clear melt fracture with all these ABs although some ABs almost doubled TTCMF under these conditions.
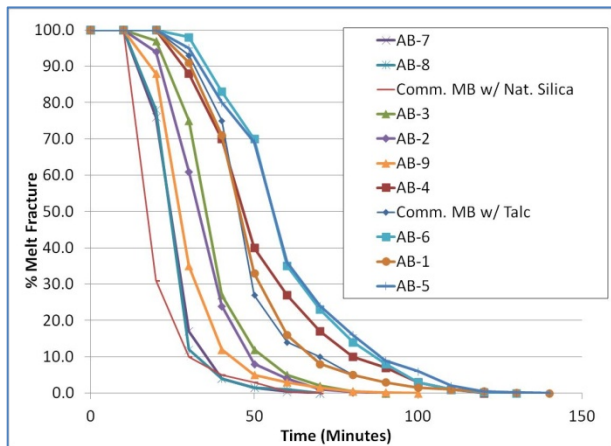

Figure 1: Effect of one of AB-1 through AB-9, or one of the two commercial AB MBs (individually) on melt fracture elimination performance of 400ppm of PPA-1 at 7500 ppm AB &1500 ppm erucamide.

TTCMF for these data (Figure 2) falls in three broad blocks. Block 1: PPA-1 performance was impacted the most by these ABs resulting in the longest TTCMFs. This group included lab-made uncoated talc AB MBs (AB-1 or AB-6), and the commercial talc MB. Also in this group were lab MBs, with one of AB-4, or AB-5 (specialty talcs, coated?). Block 2: Lab MBs of AB-2, AB-3 (specialty talcs) and AB-9 (synthetic silica) impacted PPA-1

performance less as evidenced by shorter TTCMFs. Block 3: Lab MBs of AB-7, AB-8 (nepheline syenites) and the commercial MB with natural silica, impacted PPA-1 performance the least as evidenced by the shortest TTCMF.

We chose AB-1 and AB-7 to represent AB categories that caused the most and least impact to PPA-1 performance. Using only these two AB, we looked at the effect of AB on PPA-2 and PPA-3 performance.
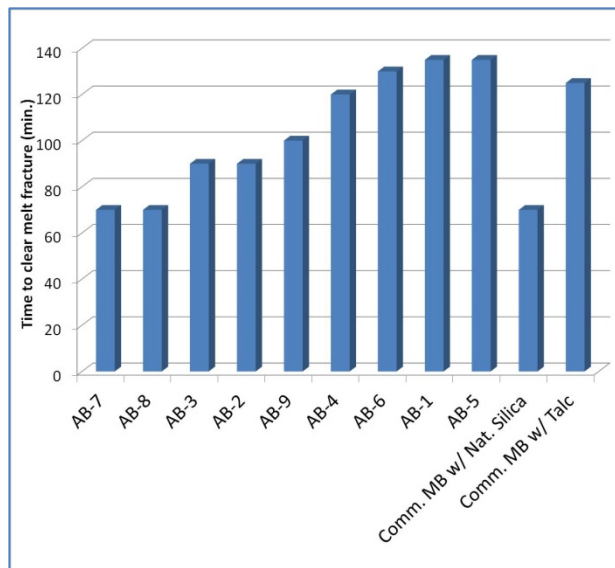

Figure 2: Time to clear melt fracture as a function of AB (individually) on 400ppm PPA-1 performance at 1500 ppm erucamide, and7500 ppm antiblock.

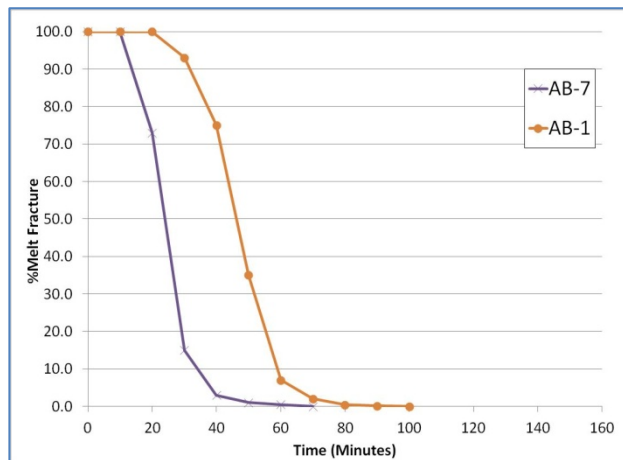## Effect of selected ABs on performance of different PPAs:

Figure 3: Effect of selected ABs (individually) on performance of 1400ppm of PPA-2 at7500 ppm AB & 1500 ppm erucamide.

Figures 3 and 4 compare the melt fracture elimination performance of, PPA-2 and PPA-3, respectively, in the presence of 7500 ppm of either AB-1 or AB-7. These data, for PPA-1, are already presented in Figure 1. All three PPAs have shorter TTCMFs in the presence of AB-7 indicating that AB-7 has lesser effect on performance on these three PPAs than AB-1.

Since the three PPAs were used at different concentrations, it is not appropriate to compare TTCMF across these data. Instead, we compare the amount (grams) of PPA that had to go through the die before melt fracture was eliminated. *Amount to clear melt fracture (g) = PPA concentration (ppm) x 10^{-6} x film line throughput (kg/h) x TTCMF (h) x 1000 (g/kg)*. "Amount (g) to clear melt fracture" (Figure 5), allows us a way to compare performance across different PPAs used at different levels.
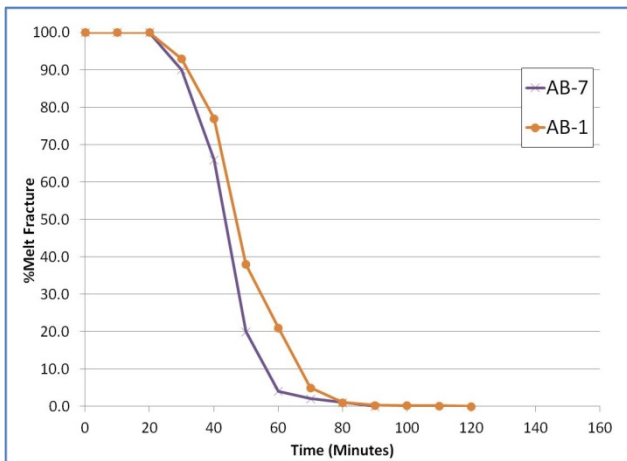

Figure 4: Effect of selected ABs (individually) on performance of PPA-3 at 700 ppm with 7500 ppm AB & 1500 ppm erucamide.
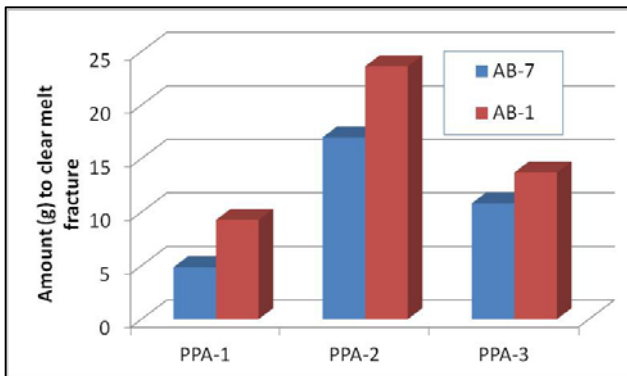

Figure 5: Effect of selected AB-1 or AB-7 (individually) on performance of one of PPA-1(@400ppm), PPA-2 (@1400 ppm), or PPA-3 (@700 ppm), all at 7500 ppm AB & 1500 ppm erucamide.

For all three PPAs, it takes less (g) PPA to clear melt fracture in the presence of AB-7 than AB-1. In addition,

PPA-1 was able to clear melt fracture with the least amount of PPA for either AB. If the goal were to minimize the amount of PPA in the additive package, these data suggest that PPA-1 would be the best candidate for melt fracture elimination in this resin, for these ABs under these specific conditions. Combining these data with pricing information would allow cost-in-use comparisons of the additive package (e.g. PPA, AB, etc.).

PPA-AB interactions at 2000ppm AB:

ABs are used at different levels in films for many reasons including different anti-blocking requirements and resin differences. Since we did not set up our trials for a particular level of anti-blocking effectiveness, we evaluated influence of PPA-AB interactions on PPA-1 performance at a lower AB concentration (2000 ppm AB).
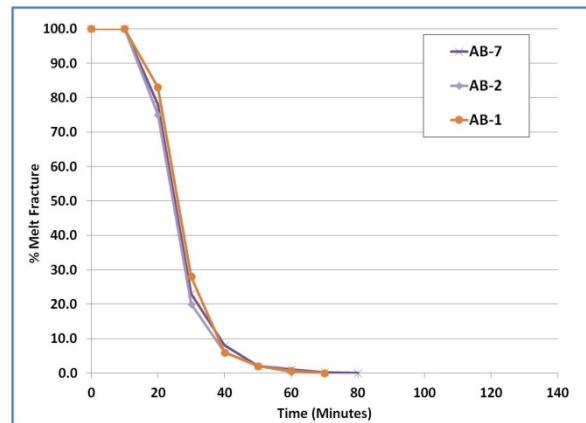

Figure 6: Effect of ABs (individually) on performance of 350ppm PPA-1 (2000 ppm AB &750 ppm erucamide).

At 2000 ppm AB and 350 ppm PPA-1, AB-1, AB-2 and AB-7, did not seem to affect PPA performance (Figure 6). When tested at 7500 ppm AB and 350 ppm PPA-1, AB-1, AB-2, AB-7, and AB-10, affected PPA-1 performance to different degrees (Figure 7).

To verify if our observations at 2000 ppm AB (Figure 6) were due to too much PPA, we repeated the study at 125 ppm PPA-1. At 125 ppm PPA-1, AB-1, AB-2, AB-7, and AB-10, affect PPA-1 performance to different degrees (Figure 8). Further, the ranking of AB affecting PPA-1 performance was the same at 7500 ppm AB (Figure 7) and at 2000 ppm AB (Figure 8).

These data show that the effects of ABs on PPA performance may not be apparent if the level of PPA is high enough for the given level(s) of AB. Desired PPA performance can be obtained, even in the presence of interfering ABs at high PPA concentration.
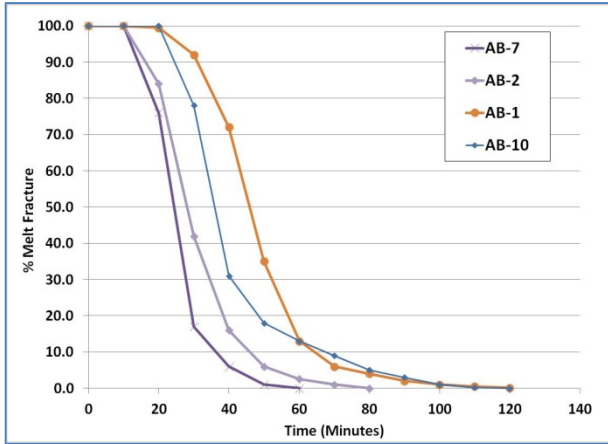
Figure 7: Effect of antiblocks (individually) on melt fracture elimination performance of 350ppm PPA-1 at 7500 ppm antiblock & 750 ppm erucamide.
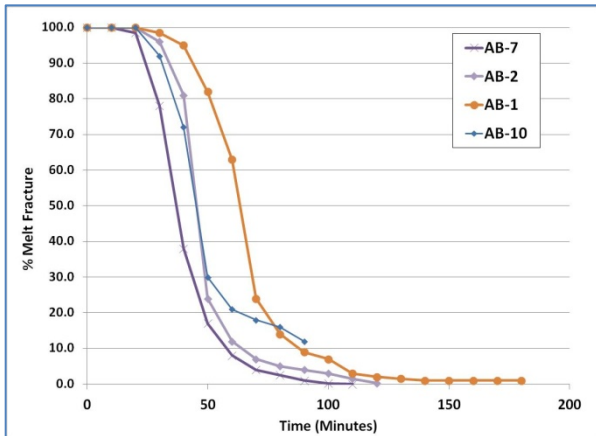

Figure 8: Effect of ABs (individually) on performance of 125 ppm PPA-1 (2000 ppm AB &750 ppm erucamide). The curve for AB-10 could not be completed as the blown film line bubble was not stable.

Conclusions

Ten different ABs, two AB MBs, and three PPAs were examined in this work. We present evidence that all three PPAs, individually, can eliminate melt fracture, albeit at different PPA levels, even in the presence of high concentrations of these ABs, individually. These ABs affect PPA-1 performance to different degrees in three broad categories. The nepheline syenite ABs and commercial natural silica MB affected PPA performance the least. Films made with these ABs, required the least PPA to clear melt fracture. The specialized (perhaps coated) talcs & synthetic silica ABs interfered with PPAs a little more. Films made with these ABs, required slightly more PPA to clear melt fracture. Finally the uncoated talcs, some specialty & coated talcs, and the commercial talc MB, affected PPA performance the most. Films made with these ABs, required the most PPA to clear melt

fracture. The relative degree to which the, least and most interfering, ABs affect PPA performance, is the same for all three PPAs studied. We demonstrate a method to compare the cost in use of various PPAs, in the presence of chosen ABs, using the amount (g) of PPA to clear melt fracture. By extension, this method can be used to optimize AB & PPA components of polyolefin additive packages. Our data show that PPA-1 is the best option for minimizing PPA use levels, for this resin and additive package, in comparison to established, PPAs (PPA-2 and PPA-3) that also achieve the desired PPA benefits but at higher use levels. We ranked the effect of various ABs on PPA performance and show that this ranking is similar at two different AB concentrations. We also show PPA performance reduction, due the presence of specific ABs can be overcome by a higher PPA concentration. Our results were obtained in one industry relevant resin system. We expect this relative ranking of PPA-AB interactions to be a good starting point for PPA-AB interactions in other resin systems. Our work provides a basis for planning and optimizing PPA levels for use in various resin systems, in the presence of different ABs.

Acknowledgements

References

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