Title:
Reducing Antiblock and Polymer Processing Additive Interactions for Improved Blown Film Melt Fracture Elimination

Abstract:

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Reducing Antiblock and Polymer Processing Additive Interactions for Improved Blown Film Melt Fracture Elimination

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ABSTRACT

Combinations of antiblock and polymer processing additive (PPA) can result in interactions that reduce the PPA effectiveness. This is typically characterized by the need for higher concentrations of PPA to eliminate melt fracture compared to formulations not containing antiblock. New technology can reduce the potential for negative interactions between antiblock and PPA and allow for improved LLDPE film optical properties.

INTRODUCTION

Antiblock additives are often used in high clarity polyolefin films. Antiblock additives are non-melting solid, which can diminish clarity and increase haze. The need for efficient film separation and slip competes with the need for acceptable optical properties such as haze. Antiblock additive research has caused a shift in technology away from more expensive silica based materials to talcs[1-2]. This is especially true for conventional LLDPE and the newer, high clarity, metallocene catalyzed LLDPE grades.

Fluoropolymer based polymer processing additives (PPAs) have been used for many years in LLDPE, HDPE and other polyolefin extrusion processes to eliminate melt fracture[3], reduce melt pressure[4-5], eliminate die build-up[6] and most recently to reduce gel formation[7]. The trends for polyethylene films moving to lower melt index, narrower molecular weight distributions and narrower die gaps for thinner films–all favor the use of processing additives.

The combination of antiblock and processing additive can reduce the effectiveness of the PPA[8]. This interaction may be caused by two different mechanisms: adsorption of the PPA by the antiblock component or by removal of the PPA coating from the die surface by the antiblock additive. Fluoropolymers have an affinity for metal and metal oxide surfaces and can be readily attracted to the aluminum and magnesium oxide particles composing talc. The adsorption mechanism can be even stronger when the PPA and antiblock are compounded together at high concentrations as in a combined masterbatch. Additionally, the solid talc particles can interfere with the coating of the visco-elastic PPA fluid on the die surface.

Results from our experiments demonstrated that a new, high clarity antiblock interacts less with different PPAs in terms of melt fracture elimination and extruder pressure drop. Also, a new experimental antiblock showed almost no interaction with PPA, even when added via a combined masterbatch. This information can help processors choose the most effective PPA/antiblock combinations for clear film applications.

EXPERIMENTAL AND MATERIALS

Polymers

1.0 MI LLDPE = butene comonomer, stabilized (Escorene™ 1001.32 from Exxon Chemicals)
2.0 MI LLDPE = butene comonomer, stabilized as masterbatch base (DFDA 7042 from UCC)

Processing Additives

PPA-1 = (Dynamar™ FX 9613)
PPA-2 = (Dynamar™ FX 5920A)

Antiblocks

AB-1 = Current industry standard talc (ABT®-2500 from Specialty Minerals)
AB-2 = Clarity antiblock (OPTIBLOC™-10 Clarity Antiblock from Specialty Minerals)
AB-3 = Clarity antiblock with experimental coating (based on AB-2)
AB-4 = Clarity antiblock with experimental coating (based on AB-2)
AB-5 = Current industry standard Diatomaceous Earth (Superfloss™ from Celite)

Equipment and Sample Preparation

Masterbatches of PPA, antiblock or combinations of the two were made with DFDA 7042 on a Haake counter rotating, intermeshing, conical twin screw extruder. The extrudate was water quenched and pelletized. The melt temperature of the extrudate was approximately 200°C. Masterbatches were tumble blended with the pelletized 1001.32 base resin for 30 minutes prior to extruding on the film line. The formulations were blown into film on a Kiefel blown film line. The film line consisted of a 40 mm diameter extruder and die, 0.6 mm die gap, 24/1 L/D, spiral die design, 18/35/60 mesh screen pack and a single lip air ring. Throughput of the film line was maintained at 12.5 kg/hr ($614 s^{-1}$ shear rate). The temperature profile is shown below in Table I.

Table I: Temperature Settings for the 40 mm Kiefel Blown Film Line

Temperature Zone	Set Temperature (°C)
Zone 1 (Feed)	182
Zone 2 (Metering/Mixing)	199
Zone 3 (Mixing)	199
Die Zone 1	199
Die Zone 2	199
Die Zone 3	199
Actual Melt (Average)	**193**

Melt fracture was measured as a percent of the width of the film. To better view the melt fracture, the film image was projected on an overhead projector. Clarity/transparency, haze and gloss testing on the film samples were done in keeping with appropriate ASTM test methods (D1746-92 and D1003-92 respectively). Blocking tests were done according to ASTM D3354-96.

RESULTS AND DISCUSSION

Melt Fracture Elimination; Separate Masterbatches of PPA and Antiblock

Processing additives function by coating the metal surface of a die, effectively changing the interfacial properties between the metal and the polyolefin melt. Since polyolefins have a low surface energy they can interact (stick to) with the higher energy metal surface. The PPA has an even lower surface energy than a polyolefin so it preferentially coats the metal surfaces of the processing equipment and provides a slip interface for the polyolefin. Figure I shows the PPA coating the film die, reducing the stick and slip of the polyethylene on the die surface and eventually eliminating melt fracture. The control remained 100% melt fractured, and obviously would not be commercially viable at this shear rate without the presence of PPA to eliminate melt fracture.

The PPA coating mechanism is dependent on several physical characteristics such as base resin polymer viscosity, dispersion and concentration of the PPA. The time for the PPA coating to form on the die surface is commonly called the "conditioning time." The conditioning time is dependent on the mass flow of the processing additive over the metal surface. This flow can be interrupted by other additives in several ways: Adsorption, abrasion, chemical reactivity with the PPA components and interference at the metal surface. A good measure of additive interaction is obtained by comparing the melt fracture elimination time for the PPA by itself (Figure 1) to the melt fracture elimination time for PPA combined with the potentially interfering additive. Figure 2 shows this comparison for PPA-1 and PPA-2 when combined with AB-I by separate masterbatches. In this base resin the AB-I interfered slightly less with PPA-2 than with PPA-1. Very little interference between either PPA and AB-2 is shown in Figure 3.

Melt Fracture Elimination; Combined Masterbatches

To look at the effect of combined versus separate masterbatches, a series of film trials were conducted keeping PPA-2 constant and varying the antiblock by use of different types of talc or diatomaceous earth. Historically, diatomaceous earth has been shown to interfere least with PPA and has not required a higher loading of PPA to eliminate melt fracture. Figure 4 shows the performance of PPA-2 with the different antiblocks, using separate masterbatches. Though the silica containing AB-5 initially showed a faster conditioning, AB-2 and AB-4 took less time to actually clear melt fracture. The end-point is more important than the conditioning time because this leads to higher productivity in commercial practice.

When the same experiment was conducted with combined masterbatches, the performance of some of the combinations was severely degraded by the PPA/antiblock interactions (figure 5). Conditioning time with the uncoated talc, AB- 1, was very long. Likewise experimental antiblock AB-4 increased the time for PPA to coat the die. The PPA-2 with AB-2 and AB-5 combined masterbatch experiments showed a slightly slower rate of conditioning than PPA-2 without antiblock. The experimental AB-3 with PPA-2 came very close to duplicating the performance of PPA-2 alone, and was certainly better than the silica containing AB-5. A direct comparison of separate versus combined masterbatches data can be seen in Figure 6.

Head Pressure with Antiblock and Processing Additive

Typically, the apparent melt viscosity of LLDPE increases with the addition of a high loading of antiblock. The loading level for these experiments was on the high side, 7500 ppm. Figure 7 shows that the addition of antiblock did not significantly change the base resin viscosity, as measured at the end of the extruder (before the die). The pressure reading was taken after 30 minutes of extrusion for equilibration.

The PPA helps to reduce the apparent viscosity of the host resin resulting in a concomitant reduction in extruder pressure. This effect is the result of the lower friction coating of PPA that forms on the extruder die. In fact, this pressure reduction is often used by processors to increase line productivity. This pressure reduction can be accompanied by an increase in RPM that brings the specific output to a higher level than the pre-PPA condition. To minimize changes in variables, the specific output in these experiments was kept constant (constant shear rate). As Figure 8 demonstrates, the head pressure dropped 15%–20% when separate PPA and AB masterbatches were used to eliminate melt fracture. Pressure reduction was slightly less for all of the PPA + AB combined masterbatches.

Blocking Data

A combination of antiblock and slip additives, such as erucamide and oleamide, gives the best performance in terms of blocking and coefficient of friction (CoF) properties[9]. The main objective of these experiments was to observe the interaction between antiblock and PPA. Slip agents may also interfere with the PPA performance[10] and were not added in order to isolate interaction. Blocking data will obviously be higher than normally accepted values due to the lack of a slip agent. Samples of film with antiblock and no PPA were not measured because under these processing conditions the film was melt fractured.

Since PPA affects the surface properties of film, it was thought that its addition may also change CofF and blocking properties, and could potentially interfere with printing. A further understanding of the PPA mechanism led to the realization that these changes are not likely. The PPA is only mobile in the molten polymer and changes surface properties by reducing the adhesion of the polyethylene to the metal surfaces of melt processing equipment. Once the LLDPE solidifies, the high molecular weight fluoropolymer constituents are frozen into the polyethylene matrix. To show that processing additive has no effect on blocking properties, we measured induced blocking for combinations of PPA-1 and PPA-2 alone and in combination with AB-1 and AB-2. It is evident in Figure 9 that there was no change in blocking properties with the addition of either PPA. It is also obvious that PPA alone does nothing to prevent blocking of the LLDPE film. Printability is often raised in the same context of surface property changes due to the presence of PPA. Addition of PPA does not affect printability as documented in previous publications[11-12].

Processing additives and antiblock performance can depend on the dispersion of the additives in the film. Often the combination of the two additives can affect dispersability of the PPA through the adsorption mechanism described earlier. On the other hand, PPA may decrease or increase the dispersion of the antiblock. The reduced antiblock dispersion, in a combined masterbatch, may be related to the fact that high levels of PPA may cause some screw slippage. The improvement in dispersion, for a combined masterbatch, may result from the PPA coating the antiblock particles, which can prevent agglomeration. Figure 10 compares the effect on blocking force for separate versus combined masterbatches. Poorer antiblocking efficiency was usually observed with combined masterbatches. The differences might be related to whether the antiblock was treated (coated), such as AB-2 through 4, and what type of treatment was applied.

Optical Properties

As mentioned in the Introduction, the addition of antiblock can cause an increase in haze and a decrease in clarity. This effect can be seen in Figures 11 and 13 compared to samples without antiblock. The controls contained PPA because the film without PPA was melt fractured (which would greatly affect the optical properties). The improved clarity of AB-2 over the more traditional product AB-1 is also evident in Figure 13.

Again the affect of separate versus combined masterbatches was mixed with respect to optical properties. The clarity and haze for AB-3 and AB-4 improved with the combined masterbatch shown in Figures 12 and 14. Conversely AB-2 had poorer haze and clarity in the combined masterbatch. The uncoated talc, AB-1 had better clarity but higher haze for the combined masterbatches.

SUMMARY AND RECOMMENDATIONS

The combination of selected processing additives (PPAs) materials and antiblock types can minimize interactions that reduce the effectiveness of the PPA in terms of melt fracture elimination. Combinations of PPA-1 or PPA-2 with AB-2, from separate masterbatches, tended to reduce the potential for interactions. Combined masterbatches would not generally be recommended except for instances where they are necessary. In such cases, combinations of PPA-2 and experimental antiblock technology (AB-3) can reduce the potential for interactions. Another, but more expensive alternative, is to use diatomaceous earth with PPA to reduce interactions.

Though the interaction of PPA and antiblock can cause significant changes in conditioning time and ultimate pressure reduction, there seemed to be little effect on antiblock efficiency. Combined masterbatches could cause better or worse blocking ability. Whether there is a positive or negative interaction is probably dependent on the coating technology.

Haze and gloss properties were improved by the use of AB-2, which was designed as an alternative for AB-1 with better optical properties. Experimental products, AB-3 and AB-4, also gave improvements in clarity compared to AB-1. Again, the effect of separate or combined masterbatches on optical properties was dependent on whether the antiblock was coated, and the composition of the coating. A combined masterbatch greatly improved the haze and clarity performance of AB-3.

To obtain the most cost-effective balance of antiblock properties, melt fracture elimination, productivity increases (pressure drop) and optical properties it is recommended that:

1) PPA-1 or PPA-2 be used with AB-2
2) Whenever possible, use separate masterbatches of PPA and antiblock
3) When combined masterbatches are necessary, combinations of PPA-2 and AB-2, AB-3 or AB-5 should be considered.

Figure 1: Melt Fracture Elimination in LLDPE with PPA-1 and PPA-2
(PPAs at 750 ppm)

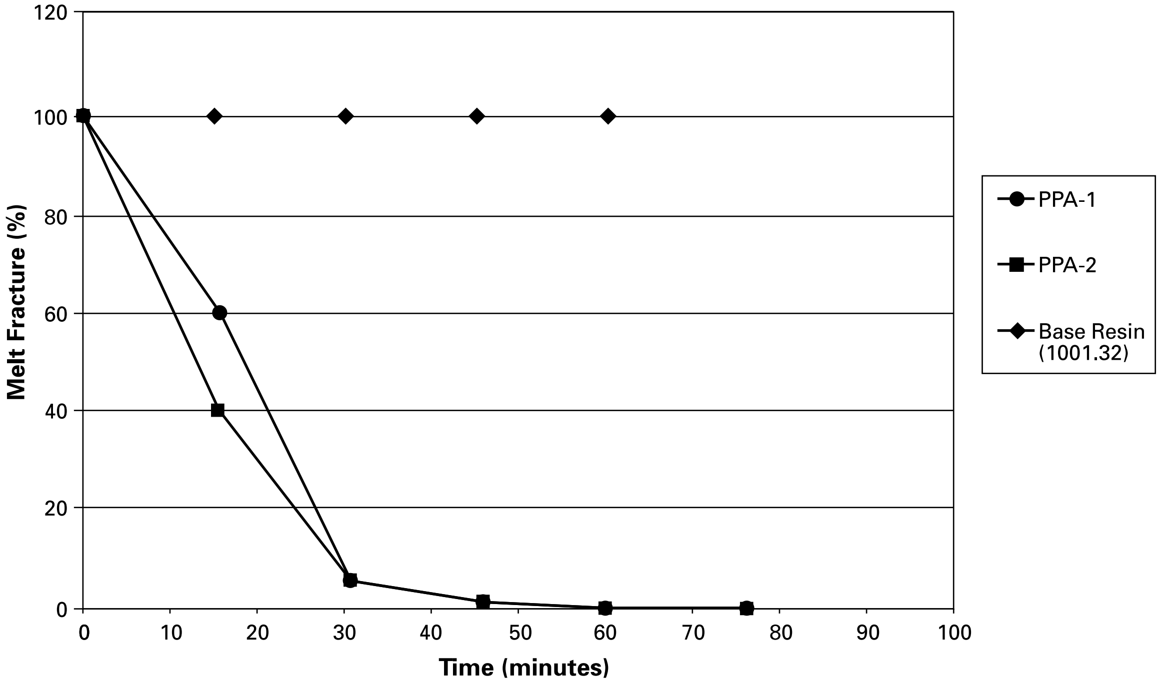


Figure 2: Melt Fracture Elimination in LLDPE with AB-1
(PPAs at 750 ppm, AB at 7500)

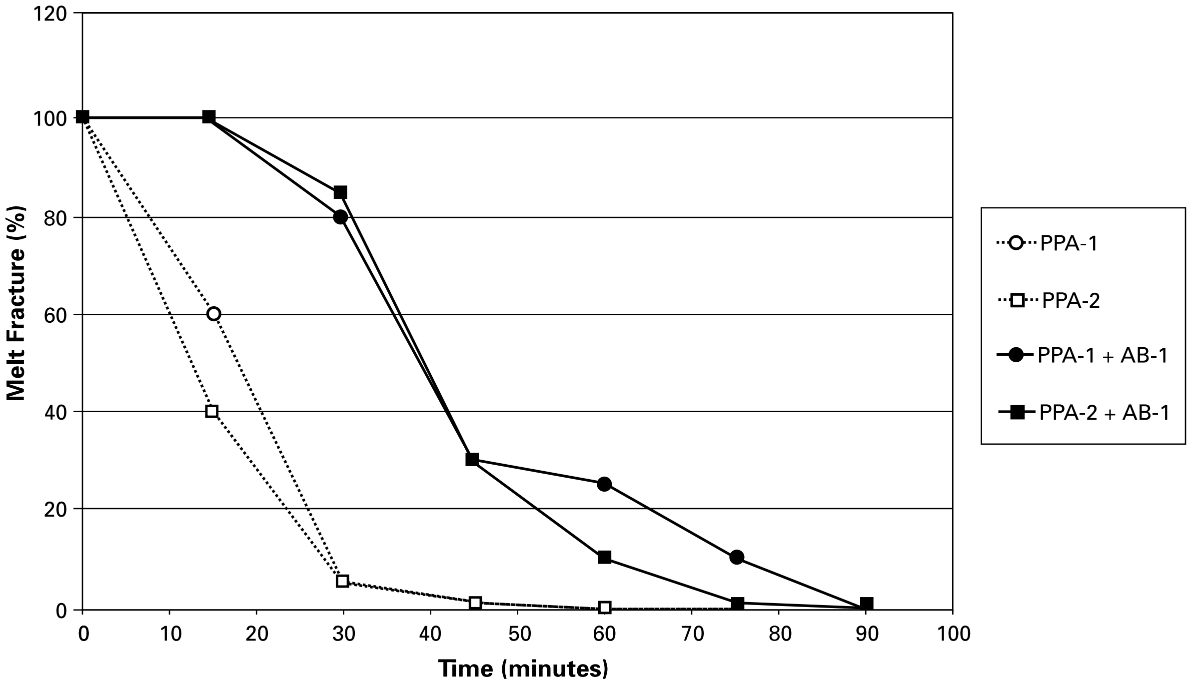


Figure 3: Melt Fracture Elimination in LLDPE with AB-2 (PPAs at 750 ppm, ABs at 7500 ppm, Separate Masterbatches)

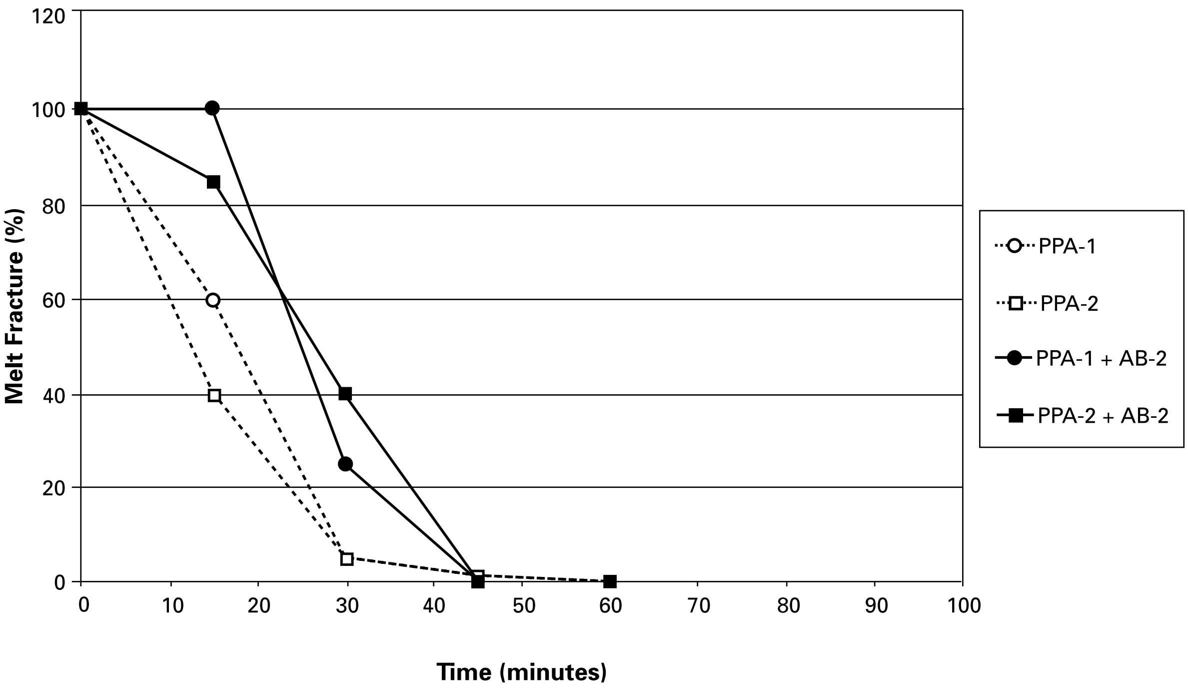


Figure 4: Melt Fracture Elimination in LLPDE with PPA-2 and Various Antiblocks (PPAs at 750 ppm, ABs at 7500 ppm, Separate Masterbatches)

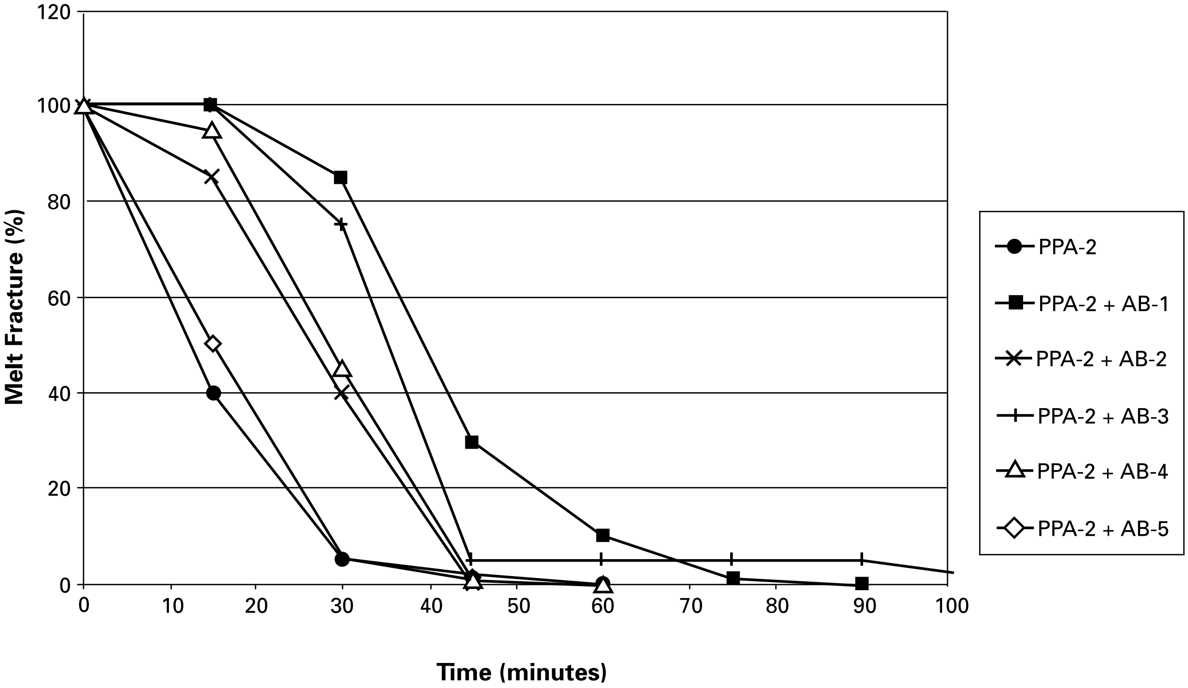


Figure 5: Melt Fracture Elimination in LLPDE with PPA-2 and Various Antiblocks (PPAs at 750 ppm, ABs at 7500 ppm, Combined Masterbatches)

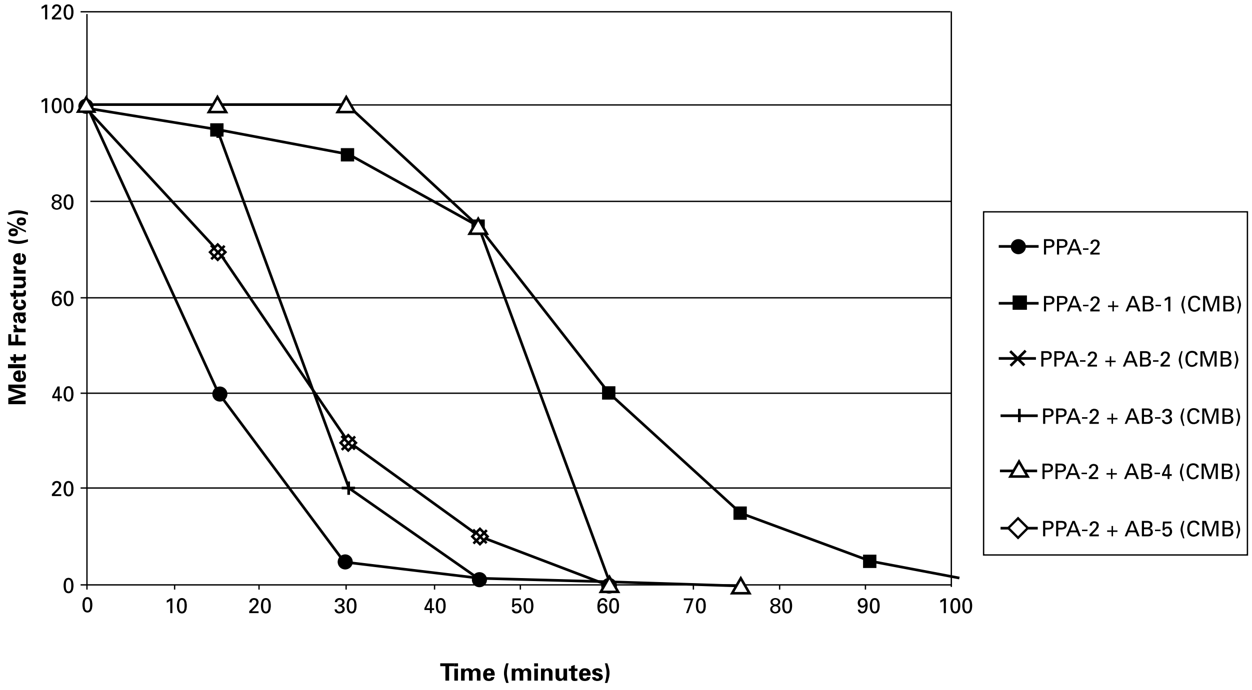


Figure 6: Melt Fracture Elimination in LLPDE with PPA-2 and Various Antiblocks (PPAs at 750 ppm, ABs at 7500 ppm, Separate Versus Combined Masterbatches)

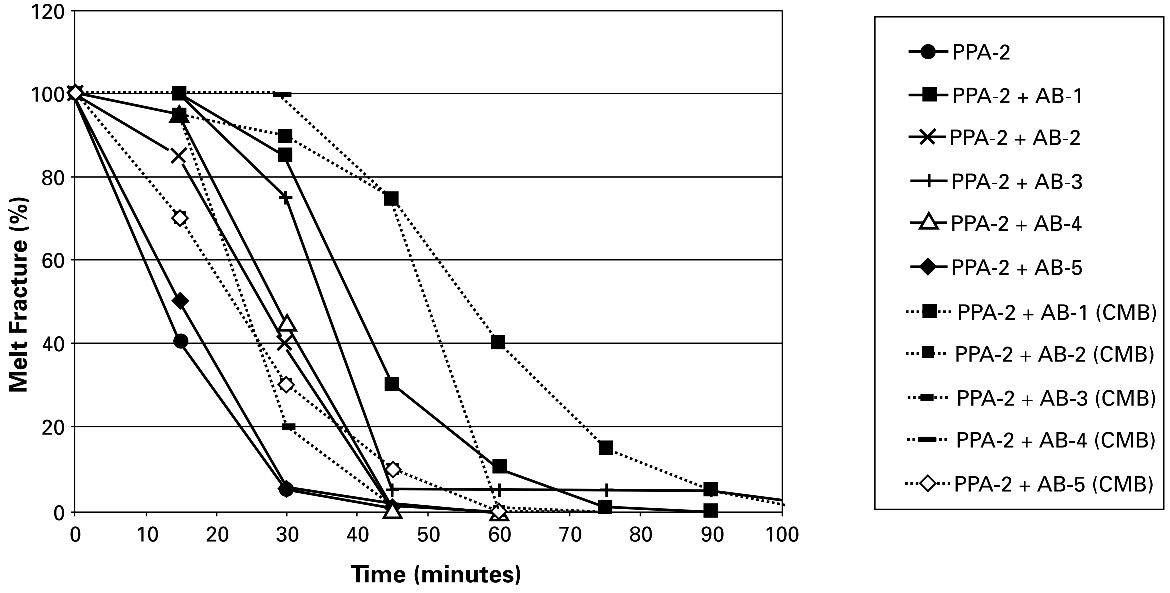


Figure 7: Head Pressure of Base LLDPE and Base Resin Various Antiblocks

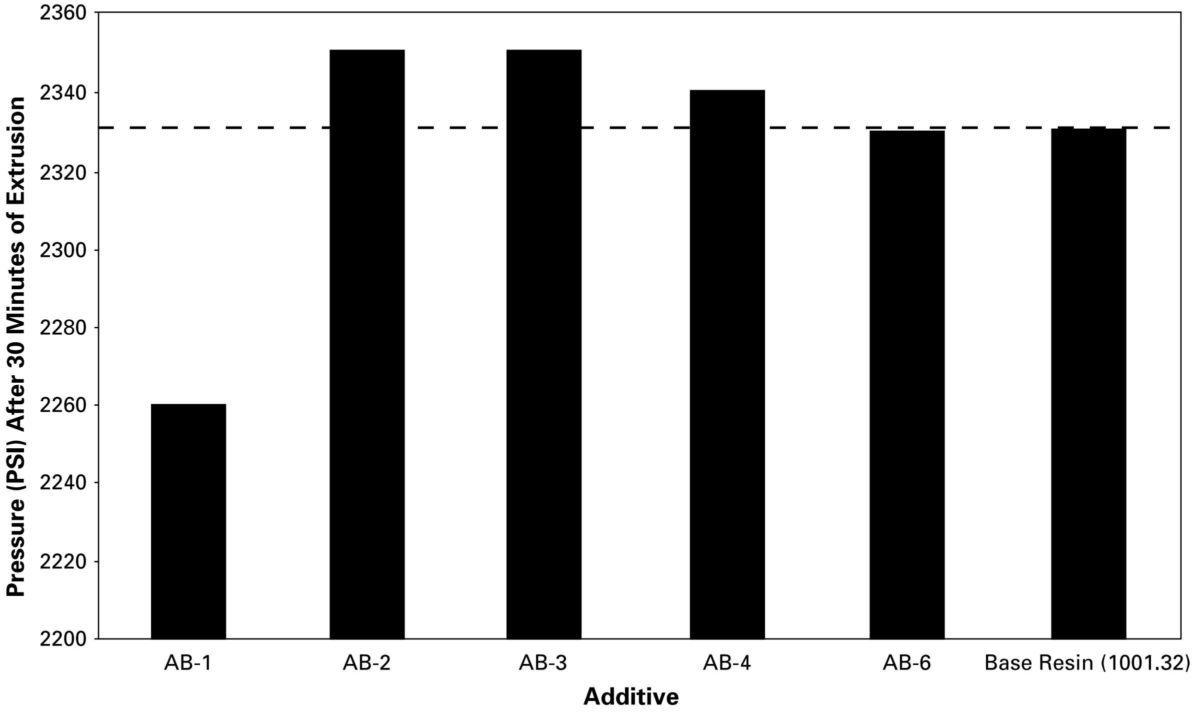


Figure 8: Head Pressure of Base LLDPE with Various Additives Combinations Made from Separate or Combined Masterbatches (PPA Containing Samples are at 0% MF Equilibrium)

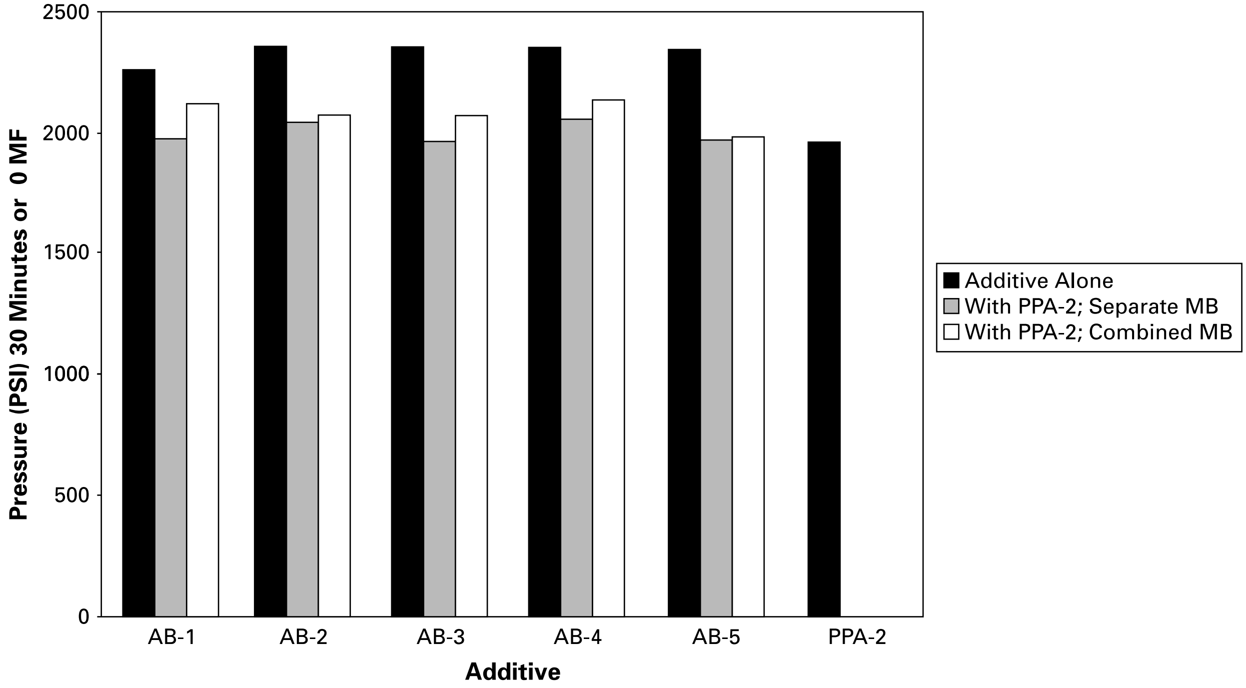


Figure 9: Induced Blocking of LLDPE Film with AB-1 and AB-2 (Separate Masterbatches)

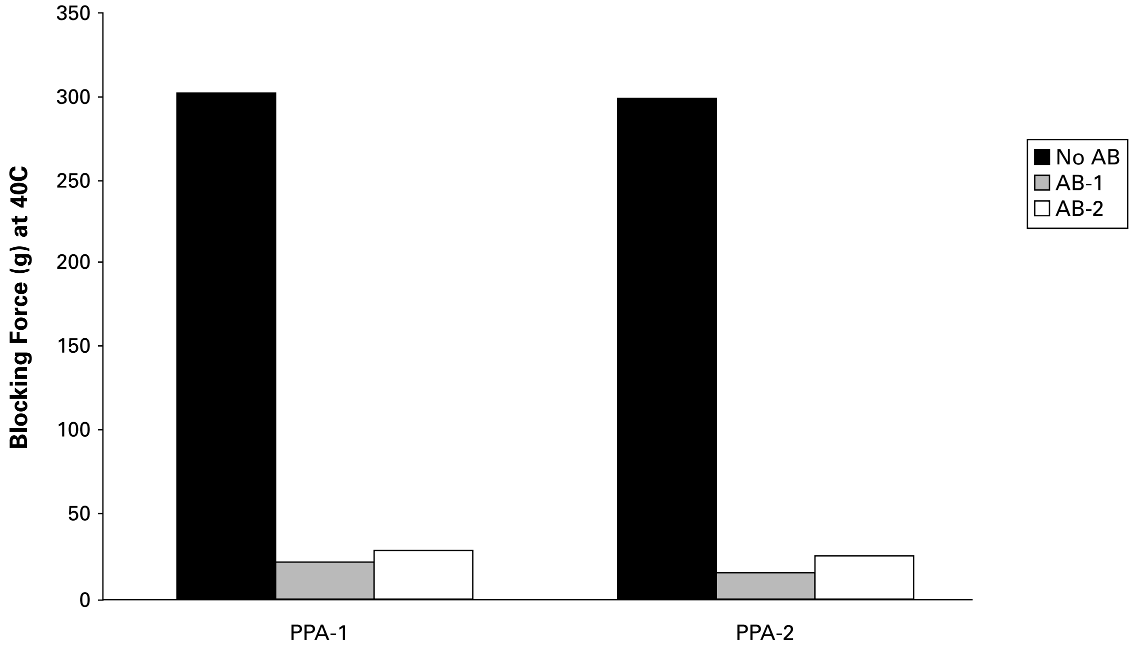


Figure 10: Induced Blocking of LLDPE Film with PPA and AB Added from Separate and Combined (CMB) Masterbatches

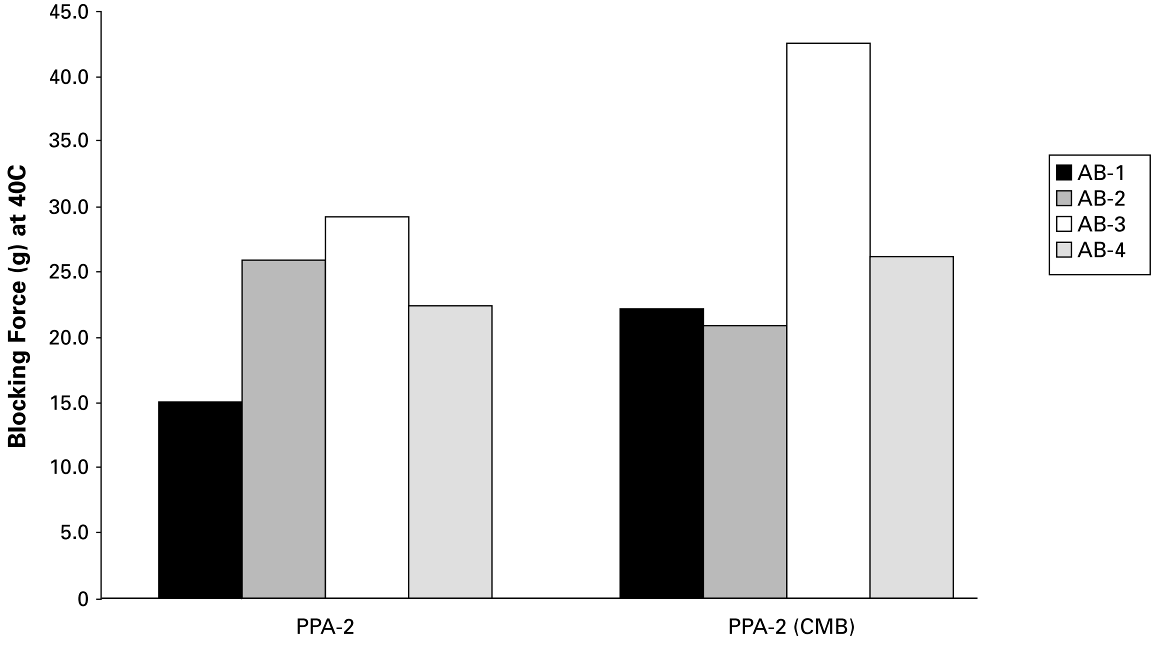


Figure 11: % Haze of LLDPE Film with and without AB-1 & AB-2 (Separate Masterbatches)

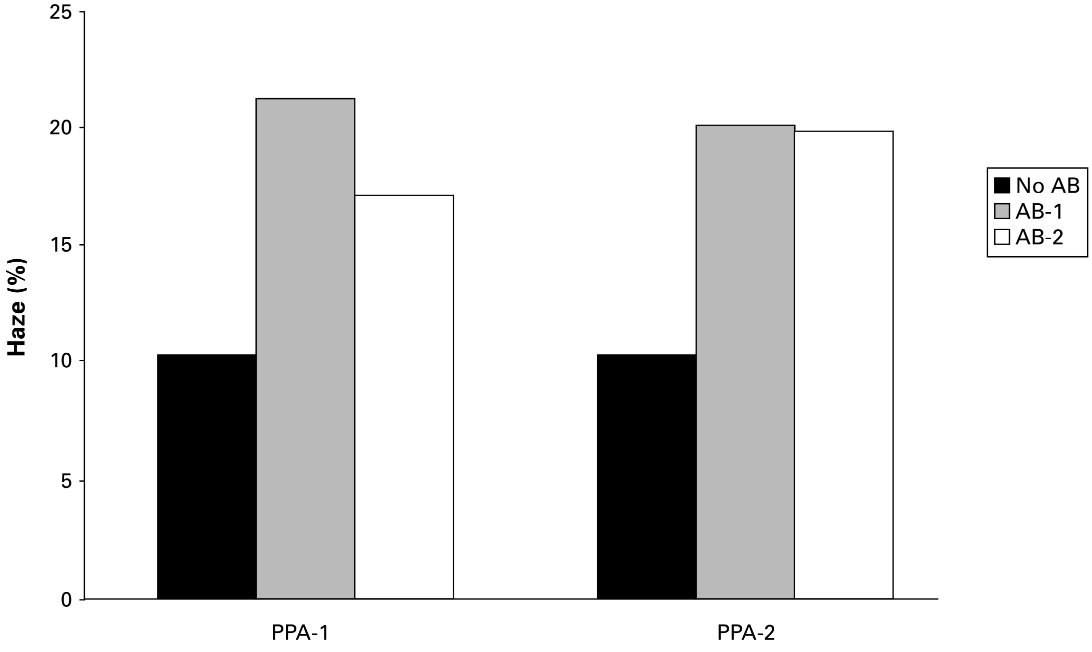


Figure 12: Haze of LLDPE Film with PPA and AB Added from Separate and Combined (CMB) Masterbatches

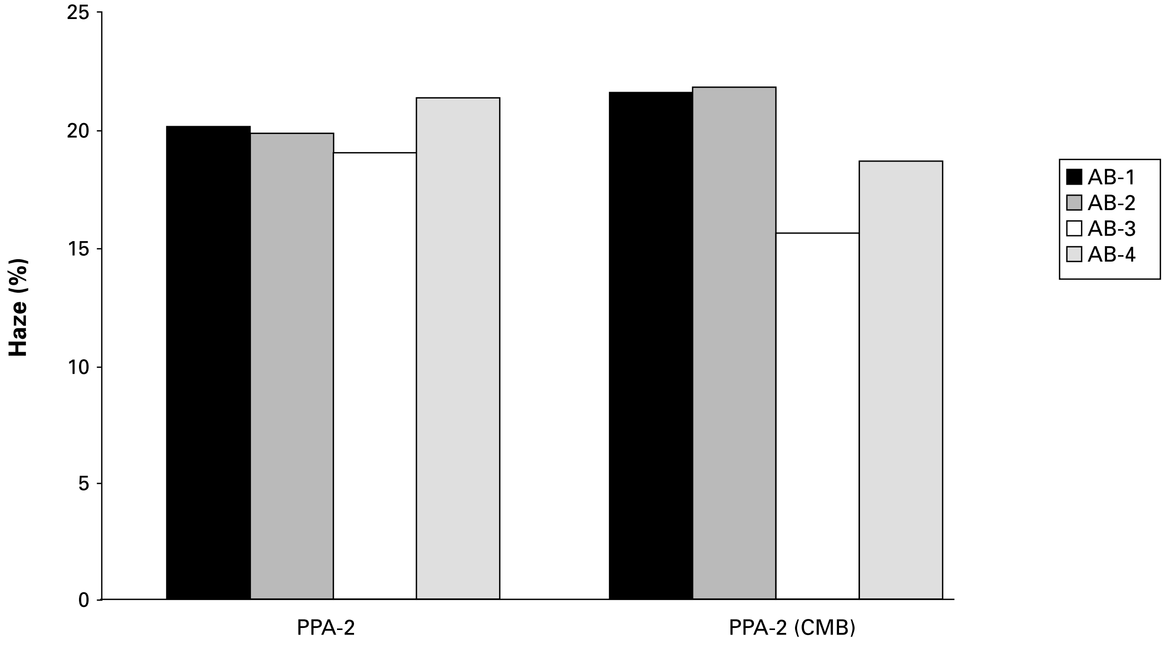


Figure 13: Clarity of LLDPE Film with and without AB-1 & AB-2 (Separate Masterbatches)

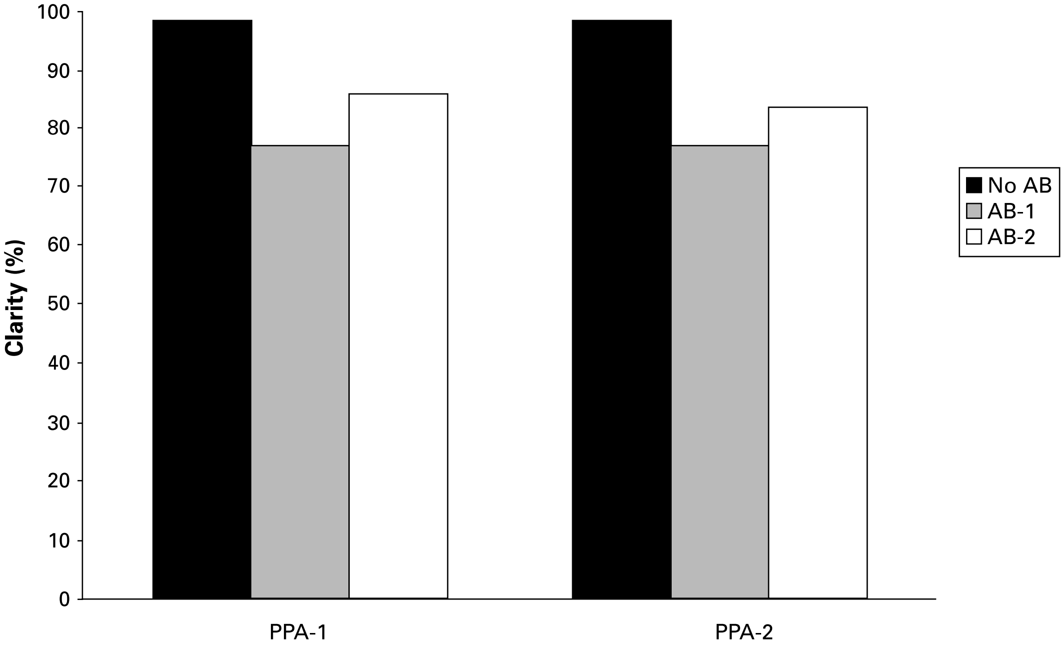
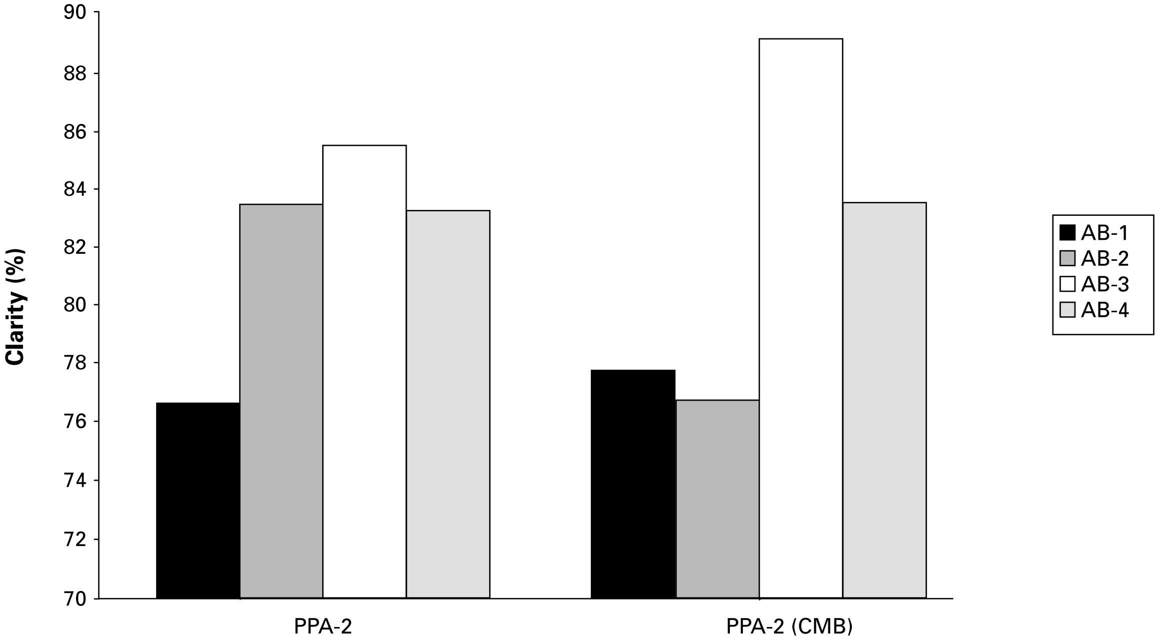


Figure 14: Clarity of LLDPE Film with PPA and AB Added from Separate and Combined (CMB) Masterbatches



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