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Title:
Polymer Processing Additives and Anti-Oxidants...Extruding Under the Influence

Abstract:
Polymer Processing Additives (PPAs) are used extensively to enhance the extrusion of various thermoplastic polymers. This paper discusses various rheological aspects which affect, and ultimately control, the performance of PPAs in polyethylene. Additionally, the paper explores and outlines the influence and impact of polymer stabilization on the performance of PPAs.

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Polymer Processing Additives and Anti-Oxidants… Extruding Under the Influence

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ABSTRACT

Polymer Processing Additives (PPAs) are used extensively to enhance the extrusion of various thermoplastic polymers. This paper discusses various rheological aspects which affect, and ultimately control, the performance of PPAs in polyethylene. Additionally, the paper explores and outlines the influence and impact of polymer stabilization on the performance of PPAs.

BACKGROUND

The use of PPAs to improve various aspects of polyolefin extrusion is now common place (1). Although much has been written about the influence of other additives and modifiers on their performance (2-6), some of which has since been verified by others (7), little is available that describes the variables which affect PPA performance during the final extrusion process.

EXPERIMENTAL

Materials

The polyethylene resins studied herein were all commercially obtained. Their specifics are described in the attached figures and corresponding text. Two commercially available additives were used, Dynamar™ Polymer Processing Additives FX-9613 and FX-5920A. The latter is a proprietary, synergistic blend developed for accelerated performance and to overcome additive interactions. For the purposes of this paper, both products will simply be referred to as PPA, with no further specification. The concepts and constraints to be explained forthcoming are applicable to all processing additives.

Equipment

Melt fracture (MF) elimination trials were conducted using a Kiefel blown film line with a 40 mm, 24/1, grooved feed extruder. The die was of spiral design with a 40 mm diameter and 0.6 mm die gap. Capillary rheometry experiments were performed on an Instron 4202 frame with a 3210 rheometer barrel using a flat entry die with 0.508 mm diameter and a 40/1 : L/D ratio. Reported apparent viscosities were not corrected.

RESULTS AND DISCUSSION

Effect of Mass Throughput

For any given PPA, Figure 1 shows the typical sigmoidal-shaped curve for the elimination of MF as a function of time. Percent melt fracture is expressed as the percentage of the blown film circumference which exhibits surface defects (MF). In the first initial minutes of this curve, there is no apparent effect from addition of the PPA. This delay is simply the time it takes for PPA to travel from the hopper to lips (land) of the extrusion die. The remainder of the curve then suggests the shape of a residence time distribution as the PPA coats the die.

In Figure 2, a fractional melt index resin, containing a minimal level of PPA, is extruded under several sets of conditions. Curve A portrays MF elimination at an extrusion speed of 45 rpm. Curve B represents the same formulation extruded at 25 rpm. Interestingly, both curves have a similar appearance, with curve B simply spread out over a greater time span. Indeed, if the data of curve B is compressed by a time factor of 1.8, (the ratio of outputs from A & B), the resulting curve C nearly super-imposes itself onto curve A. This result suggests a direct relationship to MF elimination and PPA-mass throughput. Note that previous work has shown some additive interferences to be shear rate dependent (6), such interferences will negate the above stated mass throughput equality.

Figure 3 further supports this mass throughput assertion. Here, curve A represents the MF removed by a constant level of PPA. Curve B tracks the MF eliminated when the PPA is increased at hourly intervals. When the data of curve B is adjusted to the same mass per time throughput of curve A, (e.g. 700ppm @ 1 hr = 1000ppm @ 0.7 hr, etc.), the resulting curve C again superimposes with curve A.

Yet, if a PPAs performance is directly proportional to both concentration and mass throughput (shear rate), why do all of the afore mentioned MF curves display a non-linear “tailing-off” region towards the end of their performance? An explanation can be found by contemplating the flow through an extrusion die.

Effect of Die Design

Most blown film dies are now manufactured around an internal spiral manifold. This design both minimizes the severity of weld lines and, ideally, produces a uniform melt and exit velocity around the die circumference. Figure 4 displays the opening of a spiral manifold die, above which are portrayed illustrative velocity profiles. Profile A is the expected melt velocity, of relative uniformity, with slightly higher output directly above each of the spiral exit ports. If this is correct, then the teachings from Figure 2 suggest that MF will be eliminated first in these higher velocity regions. Indeed, first-hand observations have shown that the initial number of MF-free regions on a blown film bubble corresponds with the number of spirals in the manifold.

The PPA's elimination of MF from these port-regions also results in a reduction of internal melt pressure at those points. As a result, the velocity profile will become further accentuated as in Profile B. External markings on blown film bubbles have shown that melt velocity is greater in the regions where PPAs have first coated. As a result, the velocity in the yet-to-be coated regions must decrease to maintain the overall mass balance. And thus, if the velocity decreases, so must the PPA conditioning rate at those points. Fortunately, as the PPA completes its coating process, these events subside, and the velocity profile returns to normal. Accordingly, the "tailing-off" effect towards the end of the MF elimination process is a direct result of a combination of die-design and the coating function of the PPA.

Rheological Influences

Figure 5 shows a schematic of a typical shear stress versus shear rate curve for a linear polyethylene, both with and without PPA. Note, that at very low and high output rates, the rheological behavior of the base polymer is unaffected by the addition of PPA. Curiously, the PPA first begins to show benefit around the point at which visible surface defects first occur. At high shear rates, the shear stress of extrusion fully exceeds the work of adhesion for the polymer to the metal die, and the resin "slips" through the die in a plug-flow fashion. At this point, the polymer has lost all contact with the die-wall interface and it no longer matters whether the polymer is flowing past bare metal or over a PPA coated die.

The maximum difference between the two curves in Figure 5 occurs near the point where the PPA-free LLDPE enters CMF, (cyclic melt fracture). CMF is a rapid alternation between sharkskin MF and slip MF that occurs when the shear stress begins to exceed the work of adhesion for the polymer to the metal die. By taking advantage of this shear stress differential, optimal PPA performance can be obtained by operating at conditions near the CMF onset. However, experimentation has also shown it can become difficult for a PPA to initiate and/or finish its coating process when extruded at conditions above the CMF onset. The critical shear stress for the CMF onset of linear polyolefins varies with molecular weight and to a lesser extent temperature (8). Knowledge of this onset allows for selection of extrusion conditions thereby permitting improved PPA performance.

In Figure 6, a resin with a fixed level of PPA was extruded at conditions both above and below its CMF onset. Even though the mass throughput had been decreased at the lower shear rate of 600 s^{-1}, by operating below the CMF onset, the PPA was more effective at coating the die. Note however, that a further lowering of the shear rate will decrease the PPA conditioning rate as taught earlier in this text.

Alternatively, Figure 7 shows how changes in melt temperature can be used to shift the extrusion shear regime into closer proximity of the CMF onset. While extruding at a constant shear rate of 500 s^{-1}, decreasing the melt temperature from 230 °C to 215 °C, lowered the CMF onset from 800 s^{-1} to about 500 s^{-1}, thereby allowing for faster action of the PPA. Note however, that further lowering of the melt temperature will eventually shift the CMF onset below the extrusion shear rate resulting in poorer PPA performance.

Although the visual appearance, (severity), of MF increases with either an increase in output or a decrease in melt temperature, so does the driving force for effective PPA coating, (shear stress). The effectiveness of PPAs increase with increasing shear stress, up to the point of CMF onset. Benefits from PPAs are possible both during and beyond the CMF region, but only after the extrusion die is adequately coated.

Effect of Stabilization

Figure 8 shows the MF elimination for a common level and type of PPA in two separate commercial LLDPEs. Although both resins have the same melt index, density and comonomer, and both were made by the same manufacturing process, the performance of a PPA in these two resins is quite different. Resin B was completely free of MF within one hour, while resin C was re-tested several times but never was able to attain the same performance. Although it would be assumed that these two resins are quite similar, the PPAs performance was not. Interestingly, neither resin contains slip or anti-block, or other additives that are known to interfere with the performance of PPAs (2-6). All that was known of the two resins was that each contained different levels and types of stabilizing agents. Studies were therefore carried out to research the effect of stabilization on PPA performance.

Using capillary rheometry, the flow behavior of LLDPE with and without anti-oxidants (AO) was studied. In Figure 9, resin A contained a bare minimum level of a phenolic AO, while resin B was the same base polymer, but with a high level of phenolic and phosphite AOs. In the absence of PPA, both resins appear to have the same rheological profile over the range of shear rates tested. However, with the addition of PPA, the performance was quite different. The PPA in the stabilized resin B was much more effective at lowering the apparent viscosity.

Evidence of synergy from both primary & secondary AOs with PPAs has been previously reported (2), but without explanation as to possible mechanisms. To confirm this apparent synergistic AO effect, resin A was supplemented with a higher level of a phenolic AO and re-tested with PPA. Figure 9 shows that this blend (A+AO) now matches the performance provided by the PPA in the well-stabilized resin B.

Although the presence of AO showed no apparent effect on the extrusion nature of the base LLDPE (curves A vs B, without PPA, in Figure 9), there should be some effect from the AOs absence. Further analysis was conducted using a Rheometrics Mechanical Spectrometer.

Figure 10 shows the results of a frequency (shear rate) sweep at 190 °C for resins A, B & C. Note that all the curves converge between 10 & 10^2 rad/s. This region corresponds to the lowest shear rate tested in the capillary rheometer (Figure 9) and indicates why no differences were noted. Furthermore, melt index measurements usually occur in the range of 10^0 & 10^1 rad/s, indicating why no significant differences would be observed with this common test.

However, at lower frequencies, Figure 10 does reveal significant differences in the viscosities of these materials. Resin A initially has a higher viscosity than the other materials, but then shear thins with frequency as expected. Resin B, which allowed for the best PPA performance (Fig. 8), has the lowest overall viscosity curve. Resin C, which gave variable MF performance (Fig. 8), shows an initial increase in viscosity with increasing frequency. This increase is assumed to be due to cross-linking of the resin as it is exposed to the time & temperature of the test. The frequency sweeps of these tests were from low to high.

To confirm the suspicion of cross-linking of the polymer, Resin A with the additional AO was also tested. Its viscosity curve in Figure 10 is nearly identical to that of the well-stabilized resin B.

An alternate way of running the above rheological test is to scan at a fixed frequency with time. Figure 11 shows the change in storage modulus, G’, with time. Note that the addition of phenolic AO postpones the increase in modulus, with the assumption that as it is consumed, the resin then begins to cross-link and build molecular weight. The same figure also shows that the addition of PPA has no apparent effect on the stability of the base resin.

Given the observed viscoelastic changes due to the presence or absence of AO, an explanation for the underlying mechanism of how this affects the PPA is still needed. Field experience has long held that contamination of metal die surfaces can impede the action of a PPA. Experiments were devised to see if the “higher” molecular weight degradation products of the PE could be fouling the die surface and preventing the PPA from coating.

Using the capillary rheometer, resin B (well stabilized) was extruded three separate times with a fixed PPA level. The only difference in each test was that, just prior to each extrusion, the rheometer was purged with a resin having a differing degree of stabilization. Figure 12 shows the results; when the die was purged with the minimally stabilized resin (resin A), the ability of the PPA to decrease pressure in the die was dramatically lowered. In contrast, when the die was purged with well-stabilized resin B, the PPA in the ensuing test gave the best overall performance. Finally, purging with a resin of intermediate stability allowed for a pressure drop between the two extremes.

Final confirmation for the proposed outcome of insufficient stabilization leading to the creation of higher molecular weight species that can persist at the die wall, is found in the following test simulation.

The well-stabilized resin B (1MI) was extruded through a blown film line for a one hour period. Without interruption, a PPA was then introduced; the MF elimination rate is shown in Figure 13. After a thorough cleaning to remove all PPA, a well stabilized 0.5 MI LLDPE, without PPA, was extruded for a one hour period under the same conditions. The extruder feed was then switched back to resin B along with the original level of PPA. The second MF curve in Figure 13 shows a significant delay in both the initial and the final elimination of MF. This delay is assumed to be the time it takes to remove the higher molecular weight resin from the die surface before the PPA can begin coating. MF can not be removed until resin containing PPA reaches the metal surface.

Commercial Examples and Implications

Figure 14 shows the MF elimination curves for three commercial LLDPEs obtained from different vendors. All are of the same melt index, co-monomer, and density. All were manufactured by the same polymerization. The only apparent difference was in the amount of talc anti-blocking agent present. Conventional wisdom of additive interferences would predict that the formulation with the least amount of talc would allow for the best PPA performance.

However, in Figure 14, we see that the formulation with the most talc, resin X, required the least amount of PPA for MF elimination. In resin Z, which contained no talc, over twice the level of PPA was still ineffective at eliminating the MF, even after six hours of testing. Analysis of these materials found that resin X had the highest overall level of AOs; resin Y had a lower level of AOs, and in resin Z, no active AOs, or their residuals, could be extracted!

The creation of “higher” molecular weight competitive (persistent) materials is not instantaneous, but rather, will occur over a period of time. It will be dependent on any factor that affects the consumption of AOs, including extrusion conditions such as: the residence time, temperature profile, and shearing/mixing in a given piece of equipment. Also, the other additives in a given formulation, including recycled polymer, can influence AO consumption. All of this may explain why, for a given resin formulation, varying degrees of PPA performance have been observed at different customer locations. Given this myriad of variables, the combined teachings of this text urges for the use of higher extrusion rates (to generate higher shear stresses) in order to form a stable PPA coating before significant degradation products can accumulate.

CONCLUSION

It has been shown that the conditioning rate of a PPA is directly related to not only concentration, but to the shear rate (shear stress) at which it is extruded. Also, knowledge of the viscoelastic parameters for a polymer, particularly the CMF onset, can be used to minimize the conditioning time. However, the conditioning rate of a PPA is still ultimately limited by the residence time distribution of the extruder and die design.

Furthermore, it has been demonstrated that the degree of stabilization of the polymer matrix being tested can have a profound impact on the PPA. Low levels of anti-oxidants can lead to formation of persistent, higher molecular weight, species that can interfere with the PPA coating process. Adequate polymer stabilization can allow for more efficient usage of PPAs, “freeing” them to contend with interactions from other additives.

Finally, all of this insight, helps explain why PPAs in seemingly similar resin formulations can have vastly different performance in supposedly similar extrusion situations.

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Figure 1: Blown Film Data
Melt Fracture Elimination

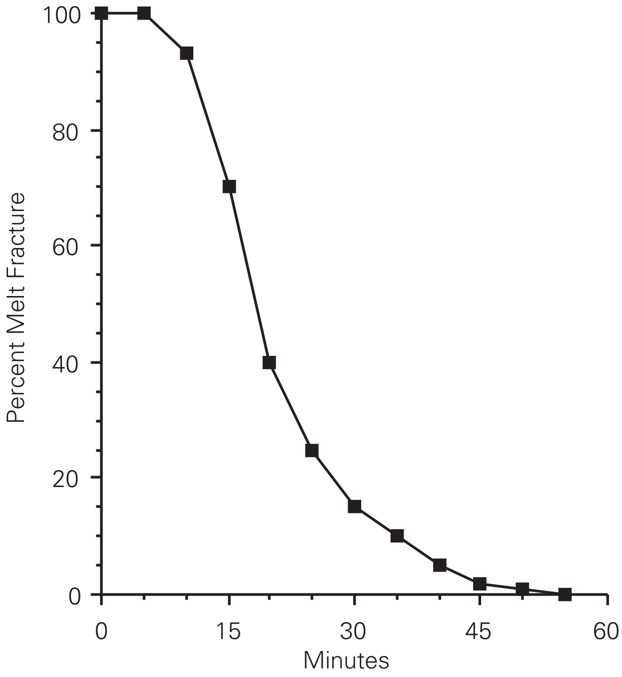


Figure 2: Blown Film Data
Effect of Mass Throughput on
Melt Fracture Elimination
0.3 MI, C-6, LLDPE, 300ppm PPA

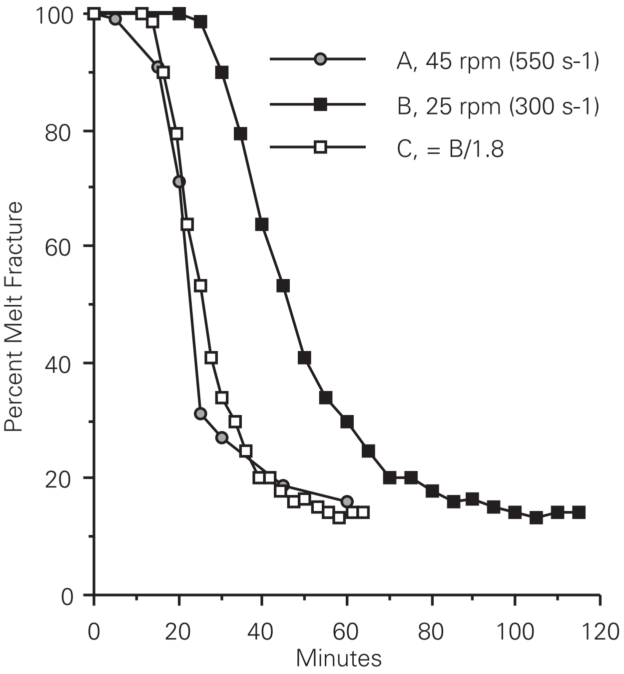


Figure 3: Blown Film Data
Effect of PPA Concentration on
Melt Fracture Elimination
0.5 MI, C-4, LLDPE, 5000ppm Talc

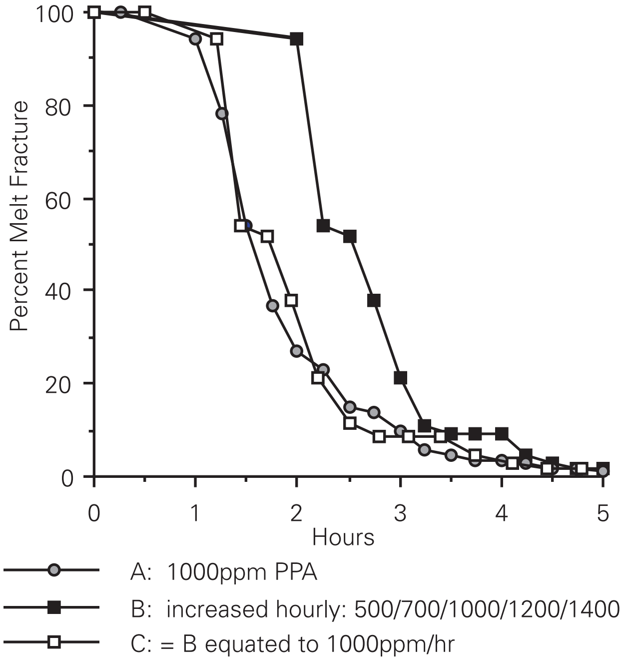
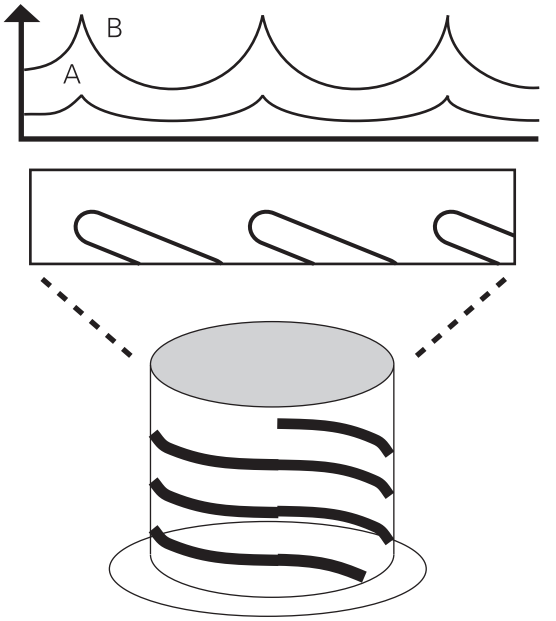


Figure 4: Spiral Design Blown Film Date
Illustrates Velocity Profiles

Profile A: Before PPA & After Coating is Finished
Profile B: Initial PPA Coating



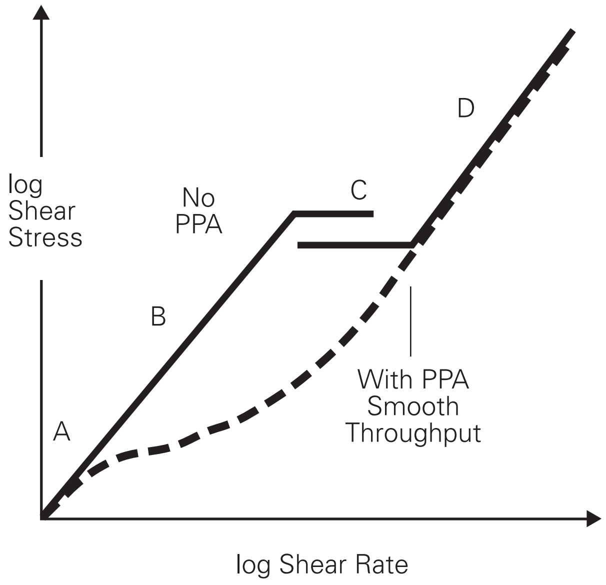


Figure 5: Viscoelastic Profile for a Linear Polyolefin
With & Without PPA
A: Matte, (faint sharkskin)
B: Sharkskin
C: “CMF”
D: “Slip”

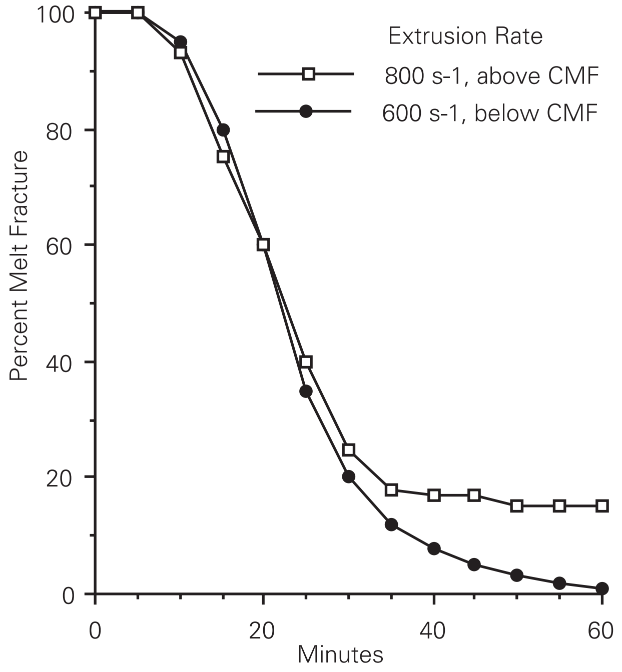


Figure 6: Blown Film Data, Extruded at 190°C
Influence of Extrusion Rate and CMF Onset
on Effect Melt Fracture Elimination
1MI, 918, LLDPE (CMF=650s-1 @ 190°C)

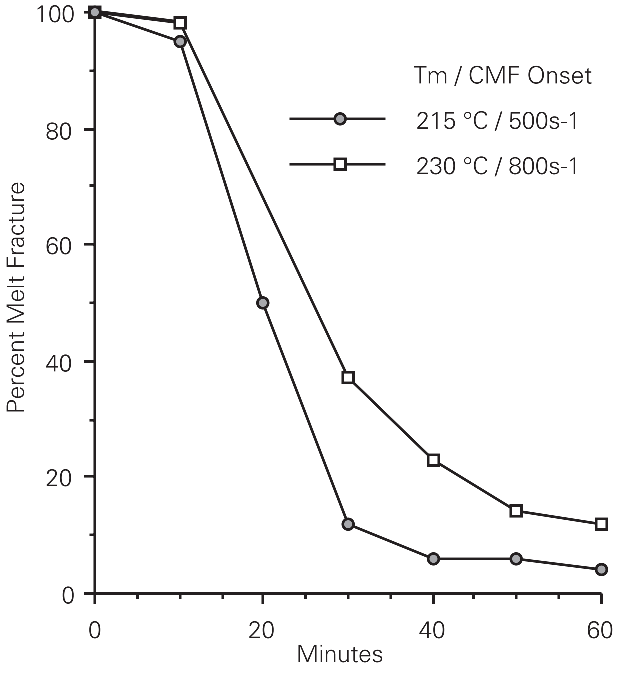


Figure 7: Blown Film Data, Extruded at 500s-1
Effect of Melt Temperature on CMF Onset
Influence on Melt Fracture Elimination
0.5 MI, C-6, LLDPE, 800ppm PPA

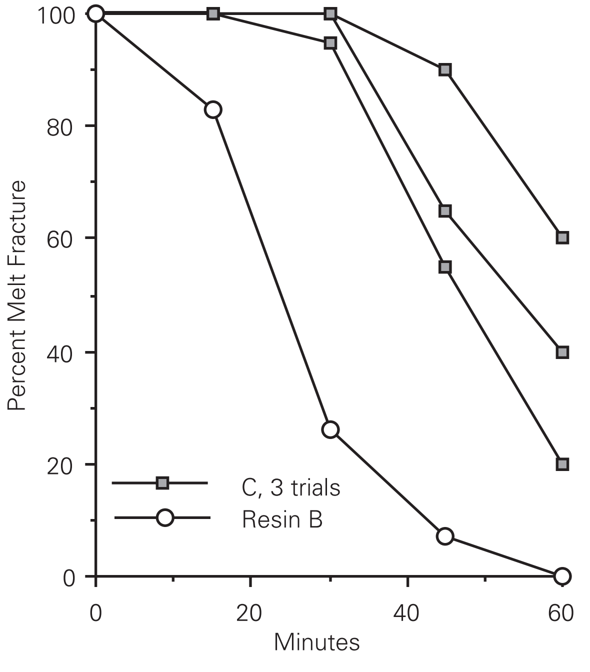
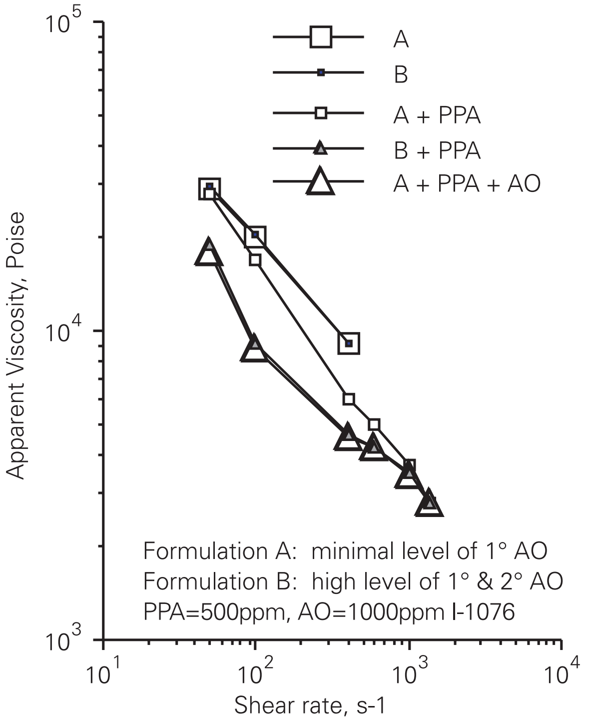


Figure 8: Blown Film Data, Melt Fracture Elimination
Resin B versus C, Both 1MI, 918, C-4
Both From Same Polymerization Process
Same Level and Type of PPA

Figure 9: Capillary Rheometer Data @ 190°C
Base Resin: 1MI, 918, C-4, LLDPE



Formulation A: minimal level of 1° AO
Formulation B: high level of 1° & 2° AO
PPA=500ppm, AO=1000ppm I-1076

Figure 10: Parallel Plate Rheometry Data
Frequency Sweep, 1% Strain, 190°C

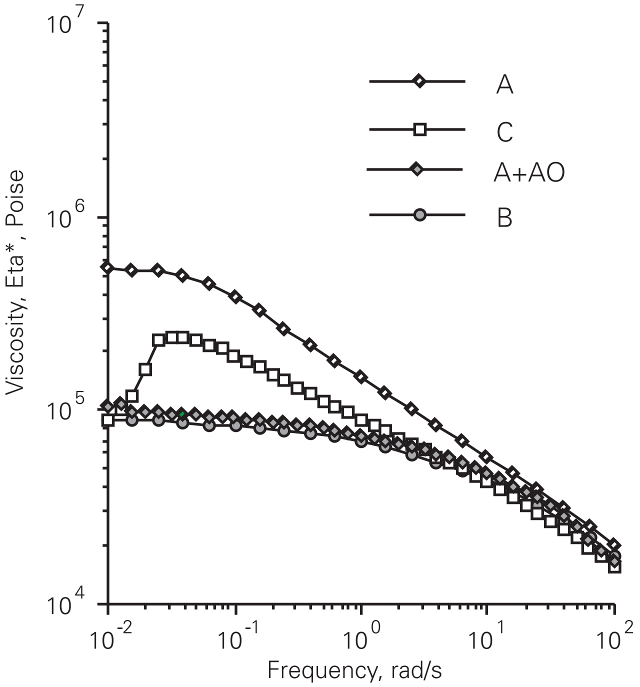


Figure 11: Parallel Plate Rheometry Data
Time Sweep @ 210°C, Frequency = 1 Hz
0.5 MI LLDPE

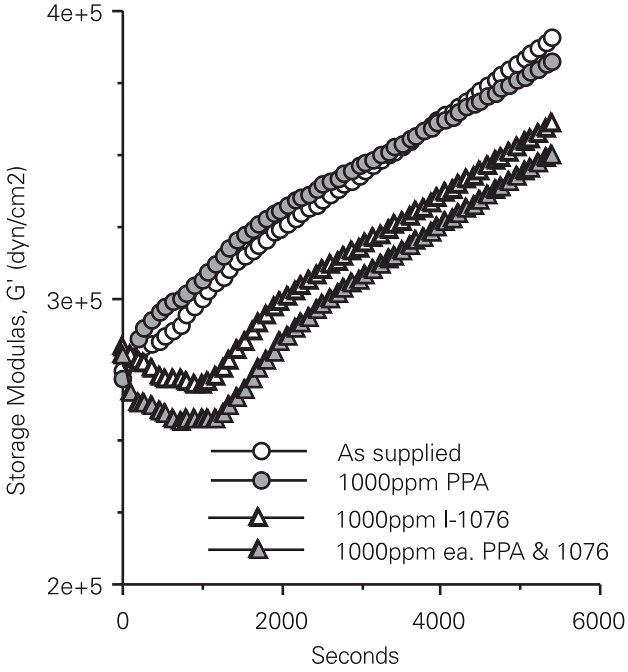


Figure 12: Capillary Rheometry Data, 190°C
Effect of Purge Resin Stability
500ppm PPA in Resin B (High AO)
Tested Immediately Following Purge

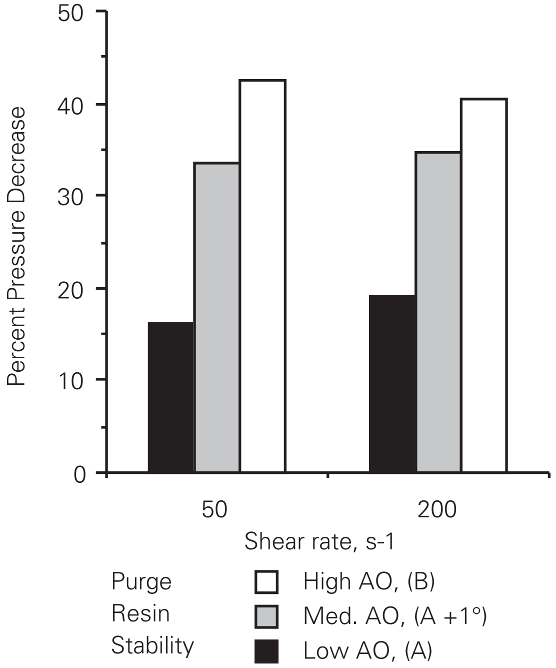


Figure 13: Blown Film Data
Effect of Previously Extruded Resin
on Melt Fracture Elimination
Test Resin: 1MI LLDPE, 500ppm PPA

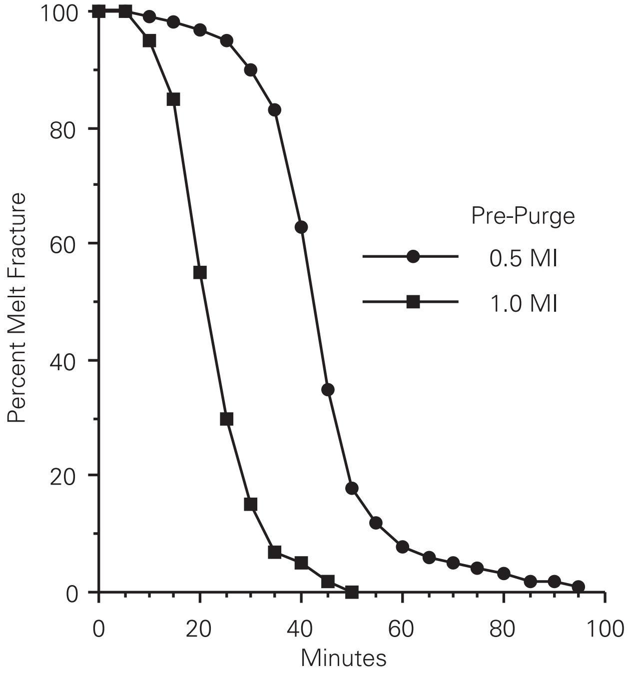
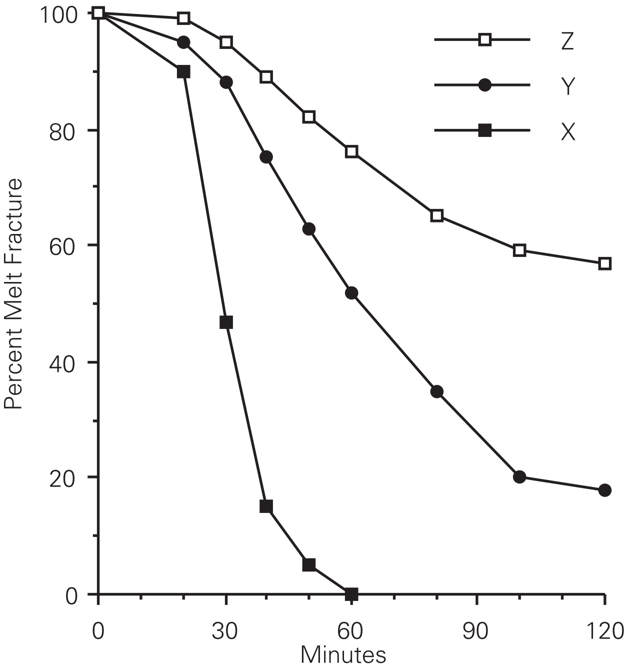


Figure 14: Blown Film Data
Melt Fracture Elimination
Commercial Examples, Resins
From Same Polymerization Process



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