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This technical paper was written and developed in 1998 when the author(s) was an employee of Dyneon LLC. Dyneon LLC was formerly a wholly-owned subsidiary of 3M Company and was fully integrated into 3M Company on January 1, 2011.

Title:
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Abstract:
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The Use of Polymer Processing Aids to Reduce Gel Formation in Polyolefin Plastomer Extrusion

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ABSTRACT

Polymer additives have long been linked to gel formation and reduction in polyolefin film extrusion. Several hypothesis about these additive/gel links have been empirically explored in a controlled blown film experiment. A study comparing gel levels in a metallocene catalyzed polyolefin plastomer was done on a lab size blown film line with a groove feed extruder. A photo imaging process was used to count gel levels, per unit area, during a significant portion of each run. Additive packages were varied to determine the effect of potential gel reducing additives. The data support the hypothesis that Dynamar™ Polymer Processing Additives can reduce the amount of gel particles in the film.

INTRODUCTION

Gel formation in polyolefin film is a phenomenon that is difficult to predict, reproduce and solve. Understanding the causes of a gel problem can be difficult since there can be several different types of gels[1] present such as unmelted, unmixed, or crosslinked polyethylene, oxidized material, fibers from packaging materials and cross contamination of other resins. Gel formation may have one or more compounding factors like humidity, polymer stabilization package, catalyst residues, polymer molecular weight distribution, the presence of oxygen, extruder and die design, and dispersion of inorganic additives to name a few.

The use of polymer processing additives (PPA) to eliminate melt fracture and die build-up in LLDPE is well known[2-4], and the same mechanism should make this additive useful for unmixed, crosslinked and oxidized gel reduction. Fluoropolymer processing aids function by coating metal surfaces, effectively changing the interface between metal and molten polyolefin to that of metal to fluoropolymer to polyolefin. We postulate that the low-energy surface provided by the fluoropolymer coating prevents the accumulation of low molecular weight species and oxidized polyethylene, and may also (in grooved feed extruders) help prevent gels caused by premature melting of lower density POP's.

The reduction of gels through a processing aid coating mechanism may be enhanced by stabilizers and other additives. Several patents describe the use of polyalkelene glycol as a gel reducer in polyethylene film extrusion[5-7]. Phosphite stabilizers can reduce polymer oxidation, but, if these stabilizers are hydrolytically unstable that may cause black specs and gel formation[8]. Phosphorous and phosphoric acids are produced from phosphite hydrolysis and are effective in cleaning oxidized, carbonaceous material from the extruder and die. Processing aid can also have a cleaning effect: if it is added to an unclean extruder, it may purge out black specs as it coats the metal surface displacing these charred particles. After the system is clean, and coated with fluoropolymer, fewer particles should be seen.

This study was a range finding study conducted in order to point us in the right direction as far as the effect PPAs have on gel reduction.

EXPERIMENTAL

Materials

PPA's: **PPA-1** = Dynamar™ FX 9613

PPA-2 = Dynamar™ FX 5920A

PPA-3 = Dynamar™ FX 5911X

Additive: **AO-I** = tetrakis [2,4-di-tert-butylphenyl] 4,4'-biphenylylenediphosphonite

Polymers: **Base Resin** = Single site catalyzed, Polyolefin Plastomer (POP), 0.9 MI, 0.910 density, storage stabilizer package (very low levels of primary and secondary antioxidant).

Masterbatch Resin = POP, 6 MI, 0.911 density

Equipment and Sample Preparation:

Masterbatches of the various processing aids and/or other additives were made in a 6 MI POP base resin on a single screw extruder with a flat 210°C temperature profile. The target concentration for masterbatches was 5 %. The target letdown concentration from the masterbatch was in all cases, except one, 1000ppm.

The formulations were blown into film on a Kiefel blown film line. The film line consisted of a 40 mm grooved feed extruder, 24/1 L/D, 18/35/60 mesh screen pack, 40mm die, 2 mm die gap, and a single lip air ring. Throughput of the film line was 8 – 9 KG/hr. The temperature profile is shown on the following page in Table I.

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

Temperature Zone	Set Temperature (°C)
Zone 1 (Feed)	121
Zone 2 (Metering/Mixing)	190.6
Zone 3 (Mixing)	190.6
Die Zone 1	190.6
Die Zone 2	190.6
Die Zone 3	204.4
Actual Melt (Average)	198.9

The gel counter consisted of a digital camera mounted just after the nip roll connected to a Model FT4 Optical Control Systems gel counter. The system takes 3 "line" photographs of the web per second. Once a given number of line photos are assembled into a picture a gray scale image analysis is performed to detect and measure the size of defects in the film. The size range is programmable, but for this analysis we looked at gels above 207 microns in size. The number of defects was summed for I hour, after the line reached equilibrium. Different moments of distribution, such as number of gels, diameter, area, or volume were calculated and recorded by the OCS computer. The data we have reported is the gel area per film area. This is referred to as the "Gel Count Weighted Average". This parameter weights the average toward larger particles, compared to gel number or diameter.

To ensure a baseline condition for each film extrusion experiment a purge procedure, consisting of running 10 KG of 70% calcium carbonate masterbatch was followed by running a standard LLDPE resin with no processing aid. This standard 1.0 MI, 0.920 density LLDPE is well characterized for melt fracture and die pressure response on the Kiefel film line. Deviations of 5% from standard pressure readings required an additional purge cycle. The baseline POP was also run briefly before each formulation was run in order to ensure the baseline count was within the expected range.

RESULTS

A summary of the results can be seen in Table II and are plotted in Figures 1 - 4.

DISCUSSION

Gels can form in many places on the path from resin producer to finished film product. Resin is made by the producer, shipped to a converter, and extruded. It is stored and transferred along the way. Potential gel sources can be identified at each location on this path. Improper handling during transfer, contamination in shipping and storage, processing temperature, residence time and shear rates can all play a role in gel formation. Because of the complexities in gel formation and in order to properly handle gel reduction, resin producer, additive supplier, and converter should work together to address gel concerns.

While the additives studied in this evaluation had a significant impact on gel reduction - none totally eliminated gels. All three of the PPAs evaluated were effective in suppressing gels. We would like to emphasize that PPAs decreased, but did not totally eliminate, gels.

Selection of Experimental Parameters

Experimental parameters were selected in order to generate gels in a short period of time. Typically, one would expect gel counts to be conducted over long periods of time – like days - to give more accurate levels than counts conducted over the short term - like hours - as in this study. However, one can see by looking at the data in Table II that we were able to generate representative data in a relatively short period of time.

The relative standard deviations are in the 25-35% range which is typical for what the OCS equipment gives even over a period of days. The resin we selected contained a minimal stabilization package in order to generate a relatively high gel count as a baseline and to more clearly see the effects of the additives evaluated. We used a grooved feed extruder with a decompression screw that had a pineapple mixing section. These extrusion variables have been shown by industry experience to pose a gel reduction challenge with the particular type of polymer we used in our evaluation. In addition, as discussed below, we were careful to purge very well (with one exception) between formulation changes.

The Importance of Purging

Since this was the first attempt to quantify gel formation in our laboratory we had a few learning experiences while conducting the experiment. One such lesson was that purging well was vital to demonstrate effective gel reduction. Figure 2 is a plot of the baseline POP and the POP+ PPA-2 both with and without proper purging. By improper purging we mean we did not follow our established procedure and rushed through the purge step and did not check our baseline. The baseline for the POP was 152 gel count weighted average. The POP+PPA-2 gave a gel count of 287 without proper purging. Our theory is that without proper purging, as the PPA coated out, it displaced material that had hung up on the metal surfaces in the extruder. The validity of this theory was demonstrated when we shut down and purged well, then started up again on POP + PPA-2. The gel counts dropped to 52. This value is consistent with our PPA-1 evaluation of 73 and PPA-3 of 61.

The Effect Of Process Aids

We believe that the mechanism of PPAs (or process modifiers) for gel reduction is similar to that of how they reduce die build-up[3]. It is commonly believed that PPAs are effective for die build-up reduction through a mechanism of the fluoropolymer coating the die metal surfaces which prevents polymer, oxidized material and additives from sticking and accumulating. It would follow that this same coating mechanism would be effective in reducing crosslinked and oxidized gels but not necessarily other types of gels caused by fibers or cross contamination. In this study we ran over periods of hours. It is possible that the types of gels we saw and reduced with PPA were mostly unmixed[9], as opposed to cross-linked or oxidized gels which one would typically expect to build up over longer periods of time. One theory about unmixed gel formation with grooved feed extruders and lower density POP's is as follows. The high compression in the grooved barrel section generates enough heat to cause early melting of the POP. Perhaps the PPA coats the metal surface and allows the POP pellets to slide more easily thus delaying the early onset of melting and enabling proper mixing to occur down stream in the extruder. The coating could also allow any prematurely melted material to move forward.

The effect of PPAs on gel counts can be seen in Figure 3, which shows a plot of the baseline POP with PPA-1, PPA-2 and PPA-3. All the PPAs are effective at reducing gel counts. This effect of PPA in reducing gels is supported by previous work by Butler and Pirtle[9].

The plot of PPA-3 (Figure 4) over time shows the gel count trending down - equilibrium was not reached during the gel count measurement. We assumed equilibrium had been reached, and started recording the gel counts, when the level was comparable to that obtained for PPA-I and PPA-2. It became apparent, when reviewing the plot, that this was not the case. This continuation of a downward trend was probably due to a higher effective level of fluoropolymer in PPA-3 relative to PPA- I and PPA-2.

The Effect Of Antioxidants

It is commonly accepted that antioxidants are effective gel suppressing agents. They prevent polyethylene oxidation and thus the oxidative crosslinking mechanism shown below (Equations I - 4).

Polymer Oxidation
$$P + O_2 \longrightarrow PO_2 \quad (1)$$

Crosslinking
$$2PO_2 \longrightarrow POOP + 2O_2 \quad (2)$$

Phenolic AO
$$PO_2 + AH \longrightarrow PO_2H + A \quad (3)$$

Phosphite AO
$$PO_2H + R'PhOR_2 \longrightarrow POH + R'OPhOR_2 \quad (4)$$

Phosphite Hydrolysis
$$R'PhOR_2 + H_2O \longrightarrow R'OHPhOR + ROH \quad (5)$$

Though the addition of phosphite was expected to help reduce gels there was no additive or synergistic effect seen with the PPA-A/O combination in this study. In retrospect, this is not surprising because we probably didn't provide enough phenolic antioxidant or humidity to allow the phosphite to prevent oxidation, or to undergo hydrolysis respectively. Hydrolysis causes phosphonous (equation 5) and eventually phosphoric acid to form. These acids can clean the metal surfaces of the extruder and die and allow the PPA coating to seal out the accumulation of newly oxidized material. No attempt was made to induce hydrolysis of the phosphite.

Angel Hair and Dust

Another learning experience came at the end of the trial. We were running the baseline POP and encountered a small amount of angel hair/ floss and dust at the bottom of the gayloard. The gel counter rose excessively high - to 800- 900 counts which was much above our normal baseline count of 152. Many gels were visible in the film. It is commonly accepted that excessive angel hair and dust can contribute to gels. The PPA-2 we put in at this time was not successful in significantly reducing this type of gel neither by the measured gel count or by our visual assessment. We believe this is because angel hair and dust do not form in the film extrusion process - they are present in the feedstock and transported through the extruder thus altering the polymer-metal interface did not affect an improvement.

CONCLUSIONS AND RECOMMENDATIONS

All three PPAs evaluated in this range finding study showed significant reduction in gel counts. We believe they accomplish this by coating the metal surfaces thereby changing the polymer-metal interface.

We did not see the expected cumulative effect of antioxidant and PPA in this study. This was likely due to our experimental conditions. As mentioned earlier - this was a range finding study. Further work in this area needs to be done.

There is strong evidence that process aids can actually purge out gels that have been previously formed and are 'hung up' in the extruder. One suggestion to prevent this from happening is to run consistently with PPA to prevent hang up from occurring in the first place. Another option would be to purge with a compound that contains antiblock and PPA (such purging compounds are commercially available) to clean out the extruder prior to a gel critical run and then run with PPA.

A point which should be emphasized is that this was a short term range finding study. This experiment has pointed the direction for future work. PPA levels were not optimized. It seems likely that the mechanisms for die build-up and gel reduction are similar and thus similar levels of PPA would be effective in reducing gels. In our work we did see a significant gel reduction from the baseline with as little as 330 ppm of PPA-1. The use of PPA-2 at 1000 ppm shows a benefit for the combination of fluoropolymer with polyethylene oxide. Given the downward trending data for the 1000 ppm of PPA-3, it is possible that this additive may provide the lowest gel count of the three when it reaches equilibrium. Future work should also consider longer run times and the potential positive effect PPA should have on gels one might expect to be formed more predominantly over longer run times like cross-linked and oxidized gels.

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We'd also like to acknowledge the assistance of Jim Spoon and Betsy Farkas also both of The Dow Chemical Company for setting up the gel counter; and Patti Blum-Bangen, of Dyneon, for running the blown film line.

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Table II: Summary of Results

Formulation	Gel Count – Weighted Average	Standard Deviation	% Relative Standard Deviation	Comments
Barefoot	152	45	30.6	
330 ppm PPA-1	73	32	35.6	
1000 ppm PPA-2	52	17	32.7	
1000 ppm PPA-3	61	32	52.5	Trending (downward) continuously is reason for high RSD
1000 ppm AO-1	100	39	39	
1000 ppm PPA-1+ 1000 ppm AO-1	91	21	23.1	
1000 ppm PPA-2+ 1000 ppm AO-1	98	26	26.5	
1000 ppm PPA-3+ 1000 ppm AO-1	70	22	31	

Figure 1 - Gel Counts (weighted average)

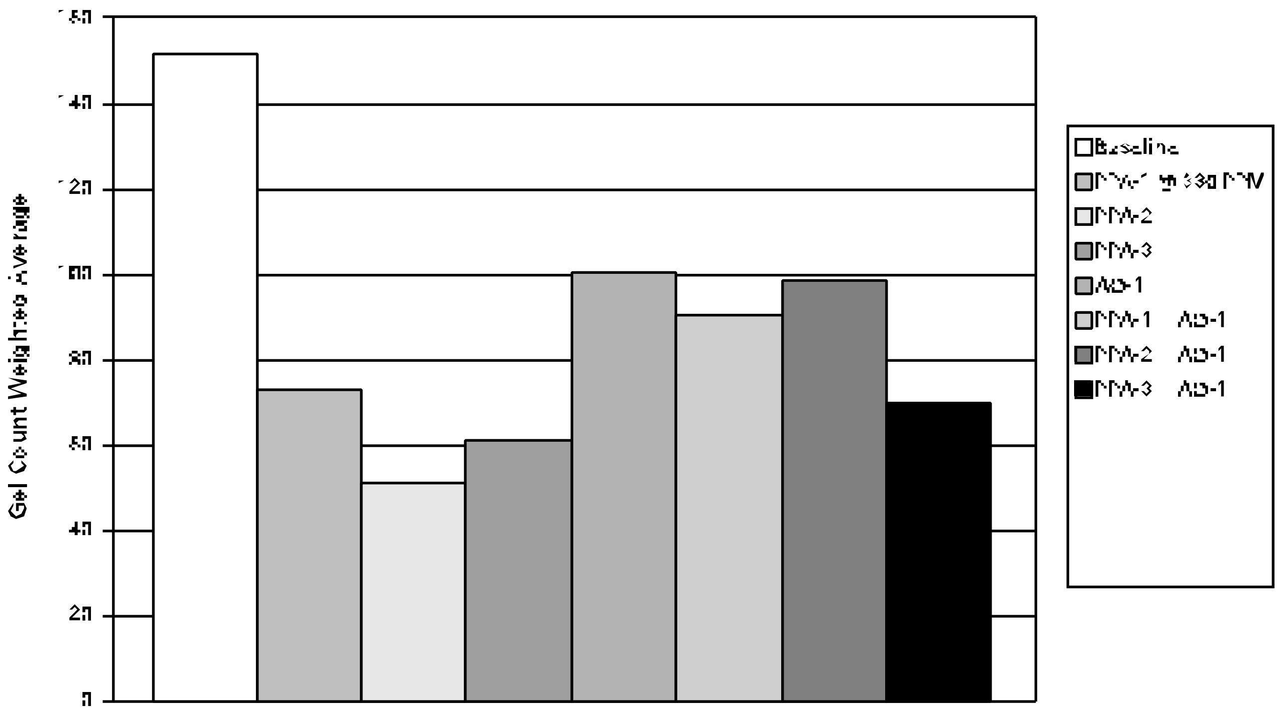


Figure 2 - Trendplot of Purging with PPA-2

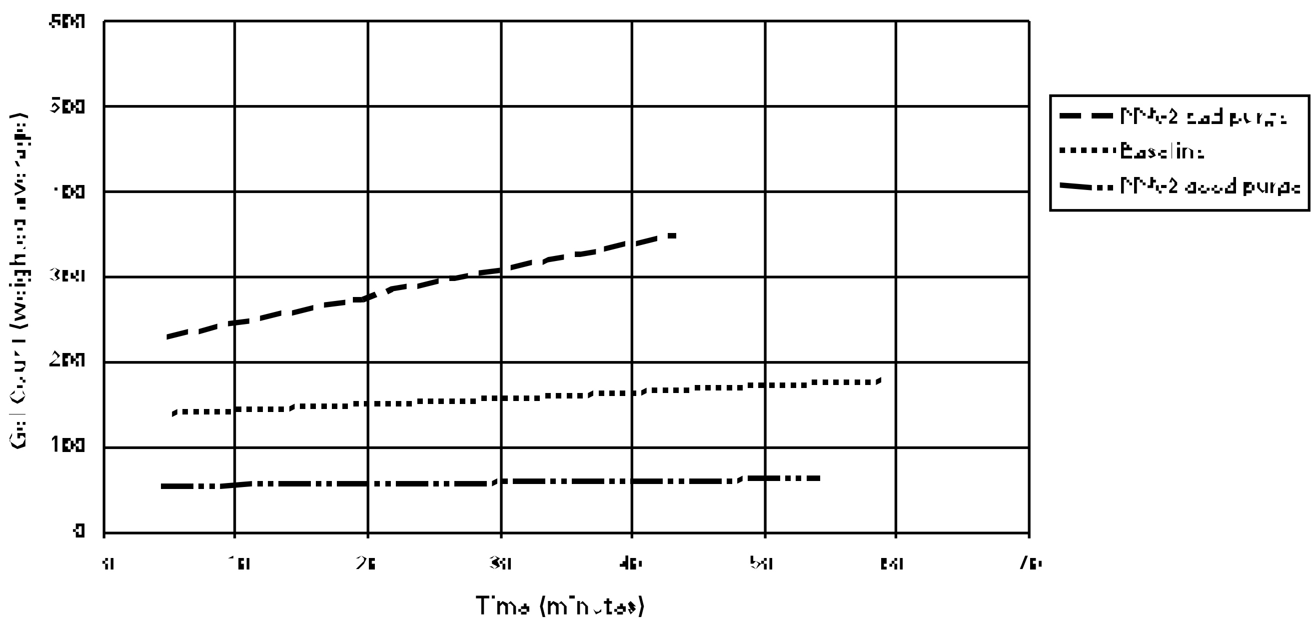


Figure 3 - Effect of PPAs on Gel Reduction

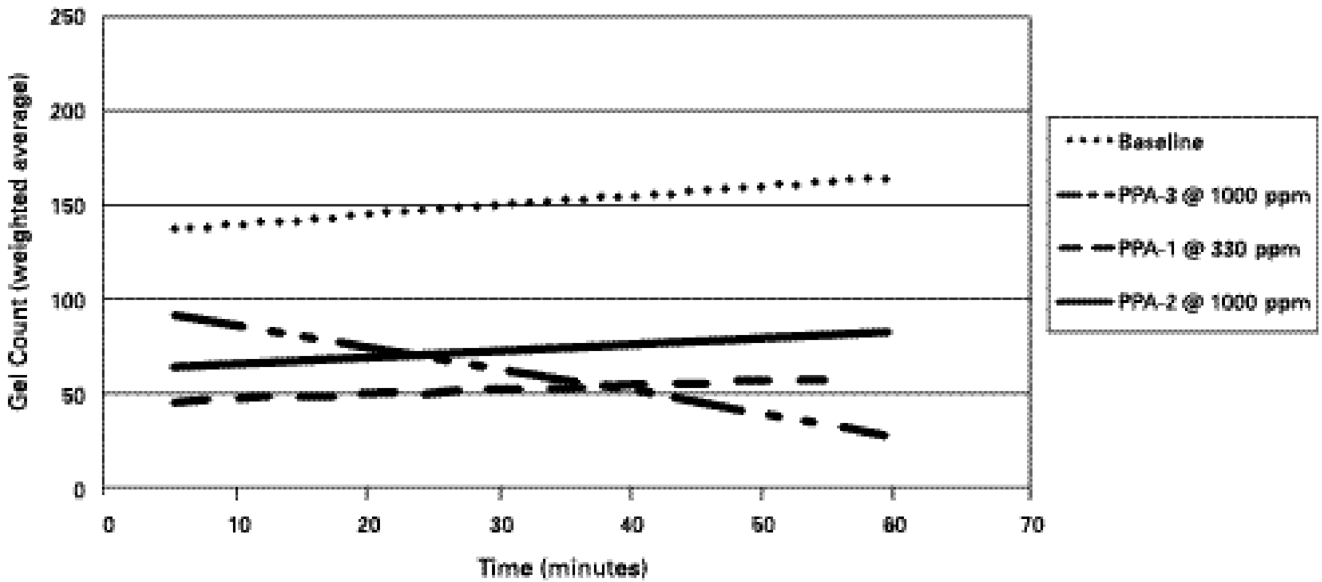
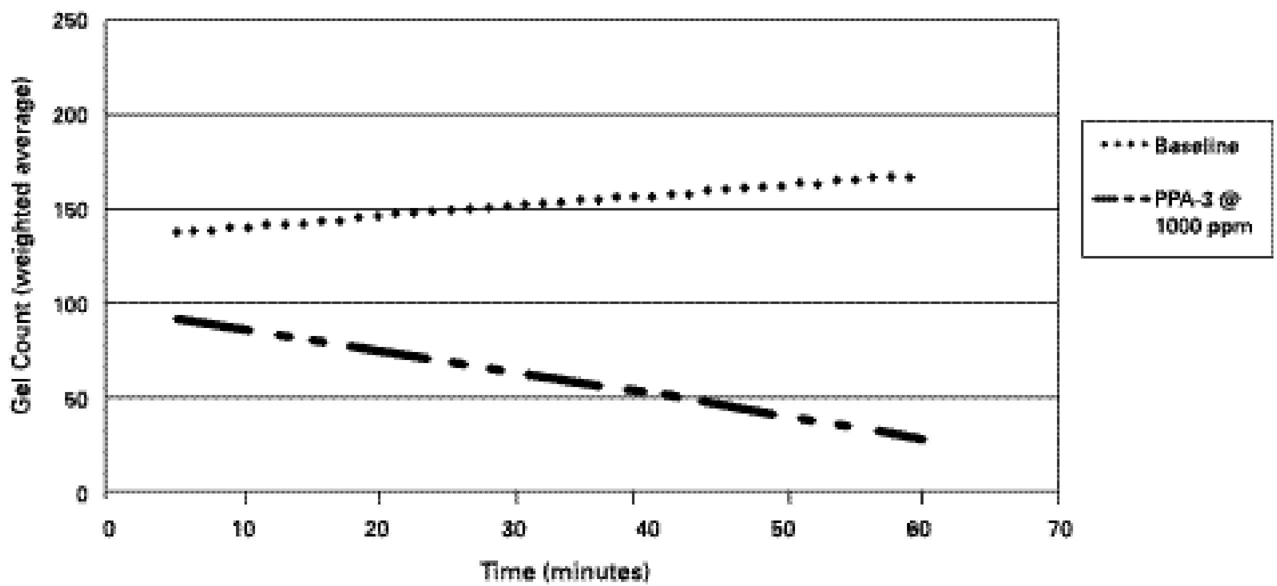


Figure 4 - 1000 ppm PPA-3



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