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The Application of Silane as a Processing Aid (PA) in High Speed Extrusion

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Summary: Silane grafting is one of the most recently used technologies in manufacturing crosslinked products due to its enormous advantages. In highspeed extrusion Polymer Processing Aid materials (PPA) additives are usually a copolymer of vinylidene fluoride and hexafluoropropylene. They are added during extrusion process to improve the process-ability and to eliminate surface meltfracture that's occurred during processing of various polyolefin's resins.

In this paper an attempt was made to investigate the application of VTEOS (Vinyltriethoxysilanes) and VTMOS (Vinyl trimethoxysilane) as a replacement of PPA and to determine its improvement in high speed extrusion of Polyethylene cable. It has been found that silane did contribute to eliminate meltfracture and improvement has been made. Nevertheless interaction phenomenon with carbon black and other additives did influencing significantly the performance of the silane and minimized its efficiency. Rheological measurements confirm this behaviour.

Factors such as chemical reaction, physical adsorption and abrasiveness are involved in many of these situations. The presence of other storage stabilizer in the polyethylene contributes in negative way as well for formulation deficiency. Special attention in selecting the ingredient to minimize adverse effect is also very important in assuring optimum effectiveness.

Keywords: additive; cable extrusion; carbon black; compounding; fluorocarbon -based processing additives; interaction; LLDPE; TAC; PPA meltfracture; silane

Introduction

The use of PPA (fluorocarbon elastomers) in combination with polyolefin's to eliminate melt fracture and improve throughput especially in narrow die gap extrusion of LLDPE such as blown film extrusion, blow molding, cable and pipe extrusion has become standard practice in the plastic's industry.[1–2] The performance of processing additives can be affected by interactions with other common storage stabilizer and other additives present in commercial resins.[2–5] The loss in the processing additive's functionality usually results in the appearance of melt fracture and consequently a loss in throughput.[6,8]

Melt fracture is sharkskin like surface of the extruded items. Another advantage of PPA materials is, it reduces the pressure in the extruder and die head, that means increasing output.[7,9]

Melt fracture problems can be related to inturbulence of the melt, and this will be influenced by, the nature of the equipment, the processing conditions as well as factors related to the LLDPE resin. When PPA is added to the resin, it coats the inner surface of the extruder's cylinder, screw and dies, so that it is acting as extrusion lubricant.[10–12] Similar behavior has been observed when using Silane in wire and cable extrusion.

Attempt to develop new resin grades for high-speed extrusion applications for the wire and cable industries were limited due to the problem of the meltfracture.

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Melt fracture was more severe especially when PPA was used in combination with Carbon Black. Interference problem between Carbon Black and PPA resulted in minimizing the efficiency of the additive package and reducing the crosslinking density of the resin. Silane crafting wasn't any more efficient. Therefore this investigation was carried out to evaluate and to determine the interference problem in the presence of carbon black and silane.

Certain resin conditions can contribute to the ineffectiveness of Silane to eliminate melt fracture at moderate to high die extrusion rates quite effectively, but experience has shown that they are not as effective at extremely high production rates. In addition, the presence of moderate to high levels of zinc stearate, which often are present in PE-additive packages, can render silane ineffectiveness as melt fracture eliminators.[9,12] Silane will be most effective when absorbed directly by the resin and not intensively compounded into a master batch and then dry blended with resin.[14]

It has been reported that die design and material selection plays a significant role in eliminating meltfracture.[14–15] Interaction between the processing additives and anti blocking agents, rutiles, UV stabilizers, and acid neutralizers such as metal stearates and hydrotalcites were found to warrant special attention. Chemical reaction, physical absorption, and abrasion were found to be most likely the major interactions.[11,12,16]

Experimental Part

Material

SABIC LLDPE -LADENE 726 N (0.7 MI 0.926 Density and contains Butene as a copolymer and LLDPE- LADENE 118N (1.0 MI 0.918 Density and contains Butene as a copolymer were chosen and used throughout this investigation. Despite storage stabilizer, the resin was obtained without any additives in powder form. The Silane used was manufactured by OSI(VTMOS – silox931). The Carbon black (free flow and combined) used was supplied by Cabot/ USA. Degussa/Germany supplied the Triallylcyanurate (TAC).

TAC was used as a co-catalyst in a very low concentration to enhance polymer processability when combined with Silane to improve crosslinking degree. The formulation used is presented in Table 1. Variation of silane concentration was applied in order to determine proper concentration of silane to be used.

Equipment

The laboratory scale compounding line, a twin extruder ZSK 30 from Werner and Pfleidere/ Germany and extruder/pelletizer combination, Small scale blown film extrusion line made by MPM /USA -Film line, 1½ inches screw diameter (L/D = 24:1) were used in this study. The film line had a 3-inch's diameter die with a gap of 1 mm.

Instron capillary extrusion rheometer experiment were carried out on a capillary rheometer fitted with a flat entry die having a 0,51 mm diameter and a length to diameter ratio 40:1. The dwell time was 10 s.

The extrusion settings of the extruder were unchanged throughout all investigations as follow:

Sample Preparation

The first step was the preparation of PE-carbon black masterbatch. Virgin LLDPE resin was applied to prepare a masterbatch containing 30% Carbon black materials using free flow carbon black. The masterbatch were melt-blended on the Henschel mixer for 5 minutes under a very low speed (30RPM) to achieve homogenous mixing. After 5 minutes TAC and the silane were injected to the molted mass and then mixed

Table 1.
Formulation and concentration used in this study.

type	Concentration PPM
Silane	0 as ref. Sample, 500, 1000, 2000, 3000, 5000
Carbon Black	500, 1500; 3000
TAC	50 PPM

for 2 more minutes, so that proper mixing was provided. The prepared compound was then twin extruded and pelletized. The masterbatch were diluted with the base LLDPE for the blown film to achieve a final CB concentration as motioned in Table 1. MPM film line was used to produce films of 60 micron thickness for investigation of melt fracture throughout this project. Line processing conditions were remain unchanged and recorded every 15 minutes.

Line Purging Procedure

In order to compare the effectiveness of the silane, it was necessary to ensure that the blown film line was free of residual process additive from previous evaluations. This was accomplished by extruding for 20 minutes a purging resin available in the Lab. The extruder screw speed is increased to maximum and the hopper run to empty. 20 kg general purpose polystyrene is charged to the extruder and continued to run through at maximum speed until consumed. The base resin is again charged and run at full speed long enough to push out the majority of the polystyrene. The extruder gate pressure, melt temperature and conditions of the film were observed

Results and Discussion

The level of silane to eliminate melt fracture was varied and determined. A baseline condition is established by running a clear untreated virgin resin for at least 60 minutes or until full melt fracture is observed in the film. The extruder gate pressure, melt temperature, and the conditions of the film were recorded at this time. The processing conditions (Temp and pressure, motor amperage and RPM) were recorded every 15 minutes. Once the baseline for the resin to be evaluated is established, the prepared samples are charged to the extruder and the time is recorded. At 2 minute intervals a film sample is taken and all extrusion condition was recorded. The film condition in terms of percentage melt fracture is also visually measured and recorded.

Based on industrial experience melt fracture was ranked between 0 and 6. Rank 6 is the most severe one and is not allowed to be produced on commercial scale. If melt fracture is reduced to 0 percent within 60 minutes, then the test was complete. If not, the silane level is increased as mentioned in Table 1 and the process is repeated for another 60 minutes. This process is continued until melt fracture is completely eliminated within 60 minutes. The level of Silane required to achieve this point is recorded. At this point the extruder is purged and prepared for the next experimental condition.

Figure 1, indicates the effect of two different silane on melt pressure against time. Melt pressure was determined at constant RPM with time in order to

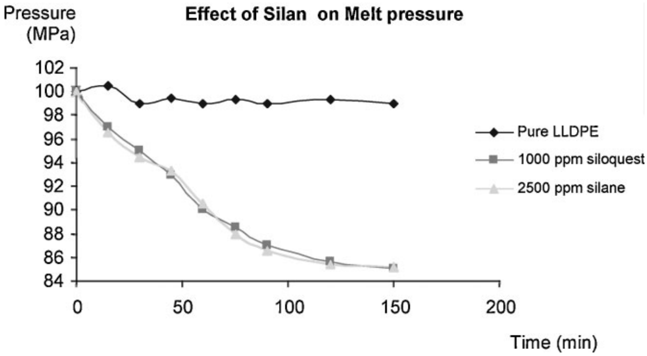

Figure 1.
Effect of silane on melt pressure in the extrusion line.

determine differences in performance of the silane. It could be seen that silane supplied by 2 different suppliers (Bayer and OSI) do not vary very much from each other. After approximately 60 minutes the pressure remains almost constant and the meltfracture was eliminated from the product. It's obvious that the percentage meltfracture decrease with time, because the silane coats the internal screw, cylinder and die surface acting as meltfracture eliminator similar to PPA.

Table 2 to 5 indicates results obtained for the film quality by varying silane concentration in the film produced, whereby the CB concentration of 2500 PPM and TAC concentration of 50 PPM remains unchanged for all samples.

Throughout the investigation, samples were taken at constant RPM for physical mechanical and analytical tests.

It was observed if increasing the silane concentration more than 3000 PPM, the effect on output or melt fracture elimina-

Table 2.
Processing condition during extrusion.

Extrusion Setting:	Die Setting:	Take off Settings:
Zone #1: 204 C	Zone #1: 207 C	Winding speed 12.2 m/min.
Zone #2: 209 C	Zone #2: 207 C	Lay Flat Width 240 mm
Zone #3: 215 C	Zone #3: 207 C	Film gauge 35–40 microns
Zone #4: 210 C		Blow up ration4.1
		R.P.M: 25 min.; 35; 40; 45; 50; 55; 60

Table 3.
Influence of silane on meltfracture elimination after 60 minutes.

RPM	Output g/min	Extrudate description	Film Ranking	Silane level
25	10.5	Smooth, glossy	0	500 PPM
30	15.2	Rough	2	
35	18.2	Very rough	4	
40	21.6	Melt fracture (mf)	5	
50	27.8	Severe mf.	6	

Table 4.
Influence of silane on meltfracture elimination after 60 minutes.

RPM	Output (118 N) g/min	Extrudate description	Film Ranking	Silane level
25	10.5	Smooth, glossy	0	1000 PPM
30	15.2	Rough	1	
35	18.2	Very rough	3	
40	21.6	Melt fracture (mf)	5	
50	27.8	Severe mf.	6	

Table 5.
Influence of silane on meltfracture elimination after 60 minutes.

RPM	Output (118N) g/min	Extrudate description	Film Ranking	Silane level
25	10.5	Smooth, glossy	0	2000 PPM
30	15.2	Rough	1	
35	18.2	Very rough	3	
40	21.6	Melt fracture (mf)	5	
50	27.8	Severe mf.	5	

Ranking: 0 = smoothest, 6 = most melt fracture.

Table 6.
Influence of silane on meltfracture elimination after 60 minutes.

RPM	Output (118N) g/min	Extrudate description	Film Ranking	Silane level
25	10.5	Smooth, glossy	0	3000 PPM
30	15.2	Rough	1	
35	18.2	Very rough	2	
40	21.6	Melt fracture (mf)	4	
50	27.8	Severe mf.	5	

Ranking: 0 = smoothest, 6 = most melt fracture.

tion was not changed. Therefore tests with the concentration of higher than 3000 PPM concentrations were neglected.

Figure 2 indicates the gate pressure for different carbonblack concentrations, whereby the silane concentrations kept constant at 1500 PPM. Pressure readings were recorded every 15 minutes until meltfracture was eliminated and head pressure remains const.

Similar behavior was observed for both resins the LLDPE 118 resins.

And the LLDPE 726 N resin. It's obvious that the pressure decreases with extrusion time up to a minimum after 60 minutes and after that the pressure remains constant. Significant differences between both resins could not be determined.

Figure 3 Indicates the Meltfracture determined in blown film of 60 micron thickness for three different CB concentration, whereby silane concentration was kept constant at a level of 1500 PPM. Its obvious that meltfracture decreases with time for all three CB concentrations. After 60 extrusion meltfracture was completely eliminated. As may be noticed 1500 PPM of either product did not succeed in eliminating meltfracture completely within short time. A level of 500 PPM however resulted in a meltfracture free film within one hour. This behaviour is similar to the application of standard processing aid.

The melt pressure and the percent meltfracture for the various Silane/CB combination are shown in Figure 2 and 3 respectively. It is obvious from those figures that the pressure and melt fracture decrease gradually with extrusion time until the silane is effectively coating out the die, after which the pressure levels of and remain constant.

Carbon Black/Silane -Interactions

As it could be seen in Figure 3, interaction between carbon black and different silane concentrations was taken place, especially at begins of the runs. From said figure sever meltfracture depending on CB concentration was obvious.

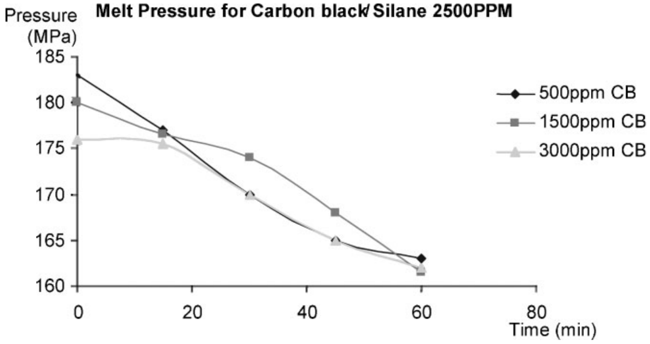

Figure 2.
Indicates the melt pressure as a function of extrusion time for different carbon black concentrations at a constant silane concentration to indicate interaction mechanism.

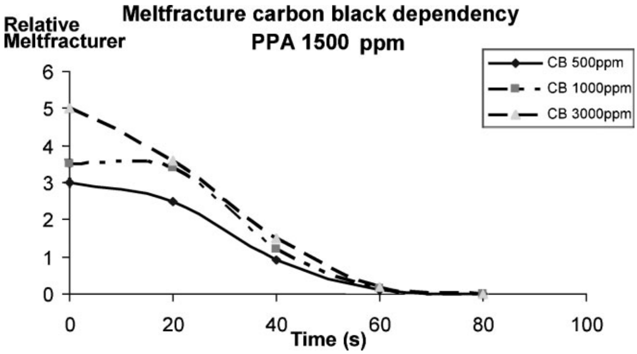

Figure 3.
The influence of carbon black on the generation of meltfracture in film samples.

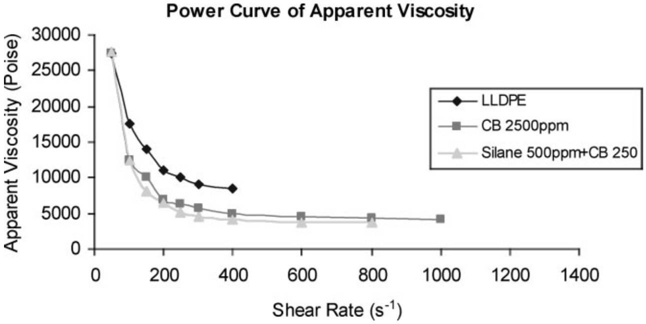

Figure 4.
influence of carbon black on silane efficiency.

Similar tendency was observed for the viscosity measurements. In order to correlate the results of chemical reactivity with the behavior of the reactive additive silane at PPM level, rheological measurement on these systems were also performed using capillary extrusion techniques. Figure 4 shows that the silane apparent viscosity exhibits higher values for the combination SILANE + CB more than that for the resin containing silane only. This suggests that the CB in this study interfered with to some extent with the processing additive. These results also indicate that the uses of masterbatches tend to amplify the magnitude of the interaction between the silane and any other additives might present in the resin. The results shows that increase in carbon black concentration while keeping the silane level constant has a profound impact on the ability of the later to lower resin viscosity. Indeed the data in figure 5 indicates that at a SILANE/CB ratio greater than 2:1 affects the efficiency of the silane significantly and there is a little difference between the silane apparent viscosity and that for the resin containing no silane.

Overall the data indicates that consideration should be given to additive ratios and processing temperatures when dealing with resin containing both silane and carbon black as these parameters have a strong influence on the extent of interaction between these type of additives. Addition of carbon black at levels up to 3000 PPM in the presence of silane resulted in increasing melt pressure and silane apparent viscosity.

Conclusion

Investigation presented in this paper has shown that silane is acting similar to processing aid in eliminating meltfracture in LLDPE-film. To many applications requiring the adding of carbon black either in pipe, cable of film applications. The presence of carbon black influences the performance of silane additives minimizing its efficiency. Though there is some evidence of chemical reaction between the carbon black and the silane, no big differences could be observed between different types of Silane. It was obvious that Interactions between silane additives and other polyolefin's additives are not common but do occur in cases involving fillers, rutile, amine-based additives, certain types of acid neutralizer and carbon black. While these interactions have the potential for reducing silane performance, other additives might contribute to improve the performance of the silane additive combination. In any case strategies such as the use of: separate masterbatches; appropriate extrusion temperature profiles, and synergistic processing additive systems can bring these interactions to a manageable level. Direct translation of the results presented to specific commercial operation is advised although differences in extrusion system, resin characteristic and processing conditions do exist.

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