Sioplas crosslinking of PE: The effect of ZnO on shelf life of silane-grafted polyethylene granules

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ABSTRACT

Having been processed and granuled, vinyl silane-grafted polyethylene must exhibit strong resistance against unwanted premature crosslinking until the final process of mixing with catalyst masterbatch and shaping thereafter takes place. The use of ZnO powder in this due was found to prolong the shelf life of the grafted polyethylene by absorbing the excess amount of water and acid in the surrounding reaction environment. This profoundly prevents loss of mechanical resistance and other useful material properties in the final end product.

Key words: Low density polyethylene, Sioplas, vinyl silane, crosslinking, shelf life

INTRODUCTION

The dominant trend in developing new products in the plastics industry is no longer the synthesis of new polymers. To a great extent, material properties are being improved by modifying the overall characteristics of existing polymers. One good example of this trend is crosslinking of polyethylene, which makes it more desirable by increasing its resistance against plastic yield at high temperatures, improved ageing, abrasion, and chemical resistance, as well as implementing a reinforced memory effect.

Three general methods exist for crosslinking of polyethylene: peroxide, silane, and irradiation crosslinking. In contrast to the two other processes, the silane crosslinking method makes use of a more cost-effective technology, which excludes the need for highly expensive equipment such as electron accelerators or continuous vulcanization. In the process of silane crosslinking, reactive groups are first grafted on PE molecules by addition of silane and very small amount of peroxide, whereafter shaping takes place in one-step (Monosil [1]), or two-step (Sioplas [2]) extrusion process.

The crosslinking reaction is conducted through the use of moisture or water, and accelerated by a tin catalyst [3]. In this work catalyst masterbatch and polyethylene, grafted by Sioplas technique, were prepared in both single and twin-screw extruder, procedure of which is reported elsewhere. The shelf life of Sioplas PE granules prior to mixing with catalyst masterbatch and extruding to the desired shape is of utmost importance. A minimum of six months is needed for storage of granules in practice. In this regard the effect of Zinc oxide on the stability of PE compounds in preventing a premature crosslinking during the storage period was investigated.

EXPERIMENTAL

Materials

To carry out the experiments we made use of the following materials:

1. Low density polyethylene (POLIRAN-LH0075 equal to NA-462): Sp. G.= 0.919, MFI= 0.55 g/10min.
2. Vinyltrimethoxy silane (Dynasilane VTMOS) manufactured by Hüls: B.P.= 123°C, Density = 0.97 g/cm^3
3. Dicumyl peroxide (DCP): Degree of purity = 0.98, Sp. G. = 1.02, M.P.= 49°C
4. Polymerized trimethyl-dihydro-guindine (Flectol H – as antioxidant): M.P.= 80°C
5. Dibutyl tin dilaurate (DBTDL - as catalyst): B.P.= 205°C, Density = 1.04 g/cm^3
6. Zinc oxide (ZnO)

Equipment

The compounds were mixed in a HAAKE-RC90 internal mixer. The screw was of Banbury type with a rate of 60 rpm.

To extrude the compounds a single and twin-screw extruder were used.

FTIR spectroscopic analysis was carried out in a Bruker IFS-48 FTIR instrument.

Procedure

In this work four compounds with the following formulations were prepared. Two out of four contained catalysts and one of each two groups of formulations contained 1 phr Zinc oxide.

Material	phr
PE	100
VTMOS	5
DCP	0.25
Flectol H	0.5
DBTDL	0.1

Our goal was to study the effect of ZnO on the stability of grafted polyethylene. We also had to scrutinize the effect of ZnO on the grafting and curing processes. The ascertainment of grafting reaction was done using FTIR spectroscopy. Analyzing the spectra, an absorption peak is observed around 1090 cm^{-1}, which is specific to the attached silane groups, hanging out of the PE backbone chains. The height of this peak is a direct measure of the amount of grafting having taken place. Before conducting the FTIR spectroscopy, the possible unreacted remaining silane was removed by acetone. The degree of crosslinking was measured through crushing of PE granules, and thereafter extracting the sol content by boiling Xylene in a reflux instrument for about 16 hours, and weighing the remainder as gel content.

RESULTS & DISCUSSION

To determine the effect of ZnO on the amount of grafting, two FTIR spectra were taken for two catalyst-free compounds, one with ZnO and the other without it (see figure 1). It is clearly seen that the presence of ZnO not only excludes incorporation of negative effects on grafting, but also encourages it to even higher levels. The reason to this observation lies in the strong ability of ZnO in effectively absorbing water and other present impurities to prevent their reaction with silane [4].

The main purpose of this study has been the investigation of the role of ZnO in prolonging the environmental stability of grafted PE during storage. To achieve this, two catalyst-free compounds, one with ZnO and the other without it, were prepared and examined periodically to determine their gel content. The rate of increase in the gel content or the amount of crosslinking was hereby obtained. The results are shown in figure 2.

As illustrated, the gel content for ZnO-containing PE is initially high due to the higher degree of grafting. This situation, however, levels off and finally a minor growth is observed. In order to explain this kind of behavior, we have to take into account the role of mechanisms for grafting and crosslinking reactions (see figure 3).

This figure indicates a formation of OH-groups on the tail of hanging silane groups in the initial stage of crosslinking reaction. ZnO molecules can coordinate with these groups by surrounding them. Additionally ZnO molecules can act as rather strong water molecule scavengers, which greatly prevent pre-crosslinking.

The last effect studied in this work was the likelihood of negative effect of ZnO on curing reaction after completion of the shaping process. Long curing time is understandably undesirable from the economical point of view. To investigate this, two catalyst-added compounds, one with ZnO and the other without it, were left in 90°C water to cure. Their gel content was measured with time (see figure 4). According to the figure, the presence of ZnO has no remarkable effect on the curing reaction. The reason to this observation can be associated with the weakening of attraction between ZnO and water molecules or OH-groups at elevated temperatures.

CONCLUSION

While increasing the amount of grafting through inhibitive effect on occurrence of unwanted reactions between water, or other impurities, and silane, Zinc oxide affects the silane-grafted polyethylene in such a way that the shelf life is prolonged. Furthermore, in experiments conducted no negative effect on curing rate of the shaped samples was observed using catalyst-rich, ZnO-added compounds.

REFERENCES

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4. U.S. Patent 4,822,857 (Shell Oil Company)

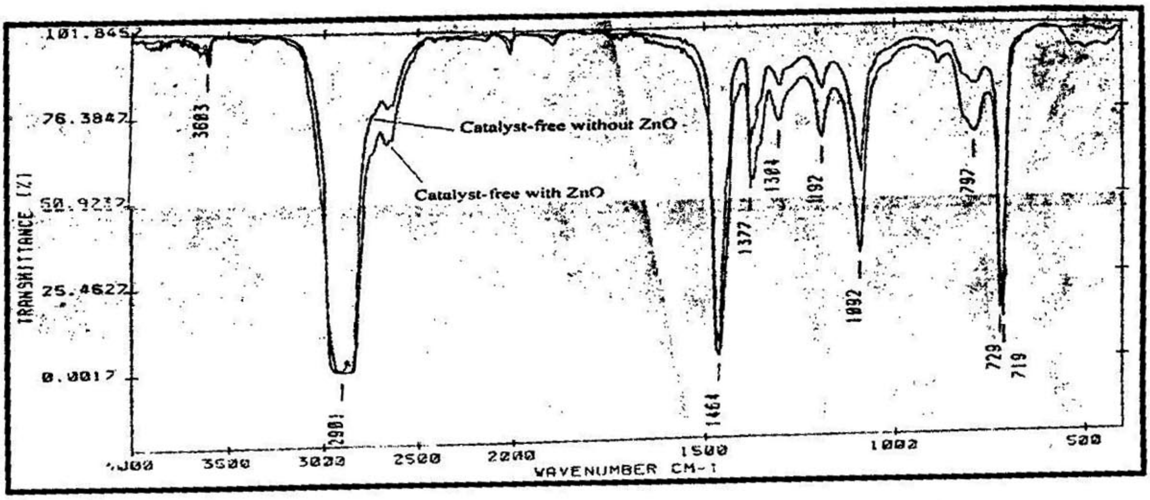

Figure 1. FTIR spectra for two catalyst-free compounds (with ZnO and without it)

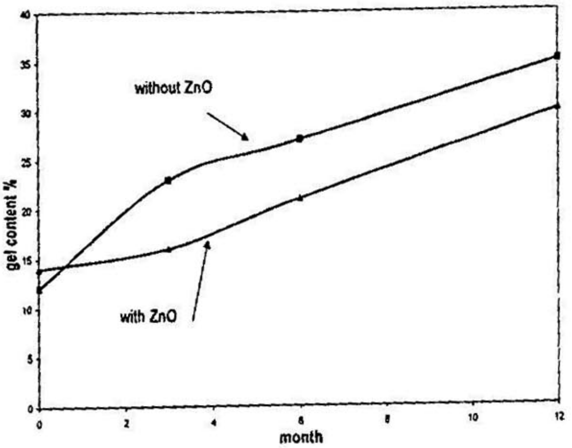

Figure 2. Effect of ZnO on Shelf life of silane-grafted PE

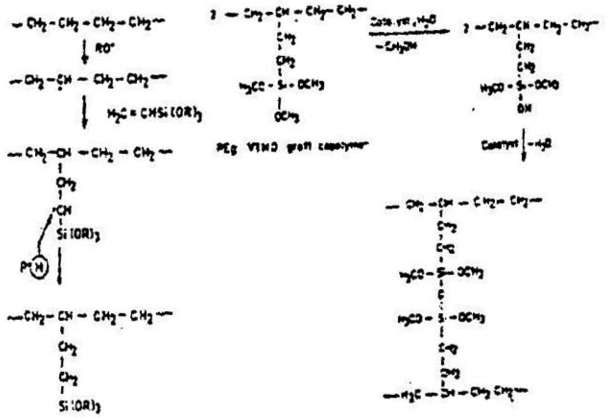

Figure 3. Grafting and crosslinking mechanisms

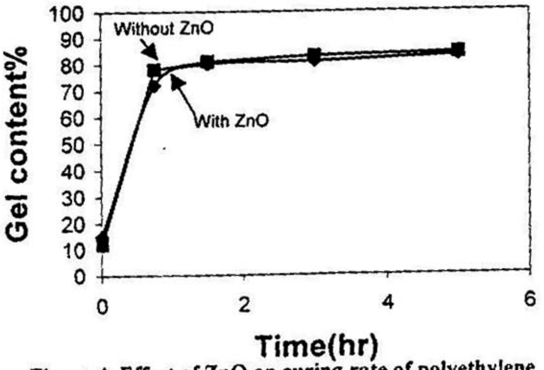

Figure 4. Effect of ZnO on curing rate of polyethylene