



Role of phenol and phosphite antioxidant combinations in the thermal stabilisation of metallocene LLDPE (mLLDPE): Optimisation and performance and influence of metal stearates on multiple extrusions

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ABSTRACT

This study progresses our earlier studies and takes the performance characteristics of a 1:1 Irganox 1010: Irgafos 168 combination at 1000 ppm each through multiple extrusion processes in a metallocene LLDPE (mLLDPE) investigating for the first time the role of a broad range of calcium and zinc stearates based on animal vs vegetable origins of the stearine function. In this case performance was assessed using Melt Flow Rate (MFR) coupled with HPLC to determine not only the additive depletions after processing but also the rate of production of the phosphite to phosphonate. Comparative control studies were also undertaken on the single use of the separate antioxidants. Both stearates influenced the activity of the antioxidants in particular their consumption. A greater consumption after the third and fifth extrusion was observed with metal stearates produced from the vegetable stearine. Moreover, zinc stearates seemed to provide a greater detrimental effect than calcium stearates. Hydroperoxide analysis on the stearates confirmed the animal stearine to contain higher levels of peroxides which may contribute toward the higher activity. The optimisation of the thermal stabilisation of the metallocene polyethylene (mLLDPE) has also been investigated in this study. Several conditions of stability were determined for the determination of the optimal antioxidant (phenol:phosphite) ratio. The main parameter was high melt stability for a maximum processing stability of the final package via DSC analysis (OIT) coupled with assessments of embrittlement time (oven ageing) and yellowness index. Long-term stability against thermo-oxidation was considered coupled with a consideration of their hydrolytic stability as a complicating factor. In this work the (phenol/phosphite) antioxidant formulations with two different phenolic antioxidants (Irganox 1010, Irganox 1076) and six different phosphite antioxidants (Irgafos 168, Irgafos P-EPQ, Adekastab PEP-8, Adekastab PEP-36, Adekastab PEP-24G, Adekastab HP-10) were assessed at different levels taking into account the various criteria for optimal performance providing hitherto useful information than many prior studies on 1:1% ratios i.e. how much phosphite is required for optimal activity. A question often posed in the field with the results concluding an interesting unified optimum ratio of 4:1 (for most antioxidants studied) taking into account all the critical parameters.

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1. Introduction

Metallocene polyethylene are notable for their narrow molecular weight distribution ($M_w/M_n = 2$ to 3) and in particular for the

uniformity of the comonomer distribution along the chain length. Indeed, modern metallocene catalysts only have one type of catalytically active site (single-site catalysts); the homogenous metallocenes produce then much more homogeneous polyolefins with narrower MMDs. On the other hand, conventional Ziegler-Natta (ZN) catalysts consist of a variety of centers with differing catalytic activity, resulting in complex product mixes; Polymers produced in this way are characterised by their broad molar mass distributions (MMD), whereas copolymers additionally have high chemical in-homogeneities, i.e. the comonomer is predominantly

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incorporated in the wax-like, low-molar mass fractions. With metallocene copolymers, the comonomers are distributed evenly over the chain lengths. This means that metallocene polyolefins and metallocene olefin copolymers have significantly lower contents of low-molar mass, wax-like fractions. This guarantees excellent organoleptic properties. These molecular characteristics leads also to superior mechanical and optical properties. However, the narrow molecular weight distribution also has certain implications for processing.

Metal stearates are commonly used as acid scavengers in combination with sterically hindered phenolic antioxidants and phosphite processing stabilisers for the stabilisation of polyolefins. Indeed, the use of such antacid co-additives is essential in the stabilisation of Ziegler-Natta polyolefins; such polymers contain acidic catalyst residues such as chlorine from TiCl_3 , AlR_2Cl or MgCl_2 that can cause corrosion of the processing equipment and catalyse peroxide decomposition, hence affecting polymer oxidative stability. Such acidic residues are also known to promote dealkylation of phenolic antioxidants, and therefore enhance the discoloration in the polymer [1]. Early studies [1] showed that metallic stearates could prevent colour formation in Ziegler-Natta polyolefins stabilised with hindered phenolic antioxidants. Indeed, it has been demonstrated that titanium catalyst residues ($>\text{Ti-Cl}$) could interact with sterically hindered phenolic antioxidants and result in the formation of coloured species [2].

In the case of chromium-based polyethylenes, the benefits of antacid agents are more variable since remnant chromium oxide catalyst residues are neutral and do not require the addition of acid neutraliser. However, the presence of acid scavenger such as zinc stearate did improve colour performance in Phillips-type HDPE, while slight antagonism was observed with calcium stearate [1]. The development of the latest metallocene catalyst technology has introduced polyolefins with unique properties and low catalyst residues content. However, the use of zirconocene chloride catalyst may require the need of acid scavengers like in Ziegler-type polymers.

It is well recognised that the presence of such acid neutralisers can significantly affect the overall performance of the whole additive package for polyolefin stabilisation [3]. The effect of metal stearate antacids may depend strongly on the polymer used as well as the co-additives present in the stabiliser package. However, the inherent properties of those salts of fatty acids may have to be also taken into consideration. Indeed, metallic stearates are available in a broad range of grades, and the origin of the stearine sources used for the formation of such acid scavengers has never been considered in the literature as a factor influencing the response of such additive in terms of processing colour and stability in polyolefin stabilisation.

Recent studies on the influence of zinc stearate in the long-term thermal stabilisation of a chromium-based HDPE with phenol/phosphite stabiliser blends also showed antagonistic effect of such antacid [4]. Interesting results were observed in terms of interactions between phenolic antioxidant (Irganox 1010) and zinc or calcium stearate. Indeed, second derivative UV evaluation of stabilised HDPE films showed that a higher decomposition rate of the phenolic antioxidant during oven ageing at 110°C was observed in the presence of both acid scavengers. Furthermore, a single pass extrusion experiment also emphasised the antagonistic effect of zinc stearate when added to the phenolic antioxidant alone or with the phenol/phosphite blend. Antagonistic effects have also been recorded in HDPE for antioxidant blends in the presence of calcium stearate [5]. In some formulations complexation and exchange by the phosphite with the stearate ligand was identified. These interesting observations led to the investigation of the consumption of both antioxidants, i.e. Irganox 1010 and Irgafos 168, during

the multiple extrusion experiments proposed here.

The purpose of this study was to examine the influence of metal stearates further (calcium and zinc stearates) on the melt stabilisation performance in combinations with a hindered phenolic antioxidant (Irganox[®] 1010) and a phosphite processing antioxidant (Irgafos[®] 168) in a standard metallocene LLDPE using melt flow rate (MFR) and HPLC. This work investigates particularly the influence of both the origin of the stearine blend (i.e., animal or vegetable) used for the production of the metal stearates and the type of metallic stearate, i.e., zinc and calcium stearate. Peroxide levels in the stearates have also been assessed. The phenolic antioxidant, the phosphite antioxidant and the metal stearate were all used at a concentration of 1000 ppm each for suitable analysis by HPLC for detection purposes. Lower concentration values at long processing times (x5) would inevitably result in zero levels of detection. A control formulation containing only the phenolic and phosphite antioxidants, but no metal stearate, was also used as a reference. This investigation following our previous investigation [6] provides a useful and more detailed analysis of the complexities of stabilising interactions over five extrusions with a wide range of types of metal-based ant-acid stearines of different origins.

Although there have been numerous investigations into the complexities and stabilising performance of additives in polyolefins [4–15] many have dealt with earlier non-metallocene type polymers, light stabilisation or antioxidant combinations usually at single ratios and often at 1:1. Thus, many have provided useful stability data and interactions but in most cases do not provide the complete picture where for example either mole ratios or percentage ratios can exhibit major performance characteristics and in some cases abnormalities. To provide a useful follow-up of the study here we have also investigated a detailed analysis of the stabilisation of mLLDPE of two phenolic antioxidants (namely Irganox 1010 and 1076) coupled with a range of phosphite antioxidants of varying hydrolytic stability at different percentage ratios. In this analysis a whole range of methodologies have been utilised, compared and cross-analysed to determine optimum performance through carbonyl index, DSC (OIT) and Yellowness Index. Overall, all the data provides a very useful technological outcome in verifying the maximum stabilising ratio at 4:1 in order to satisfy most of the criteria used with the phenolic playing the major role and the phosphite acting as an initial protector at a much lower level.

2. Experimental

2.1. Materials

The polymer mLLDPE (Repsol) was analysed for a range of metal catalyst residues (aluminium, titanium, chromium and zirconium) using an inductively-coupled plasma (ICP) emission spectrophotometry via VARIAN Vista AX CCD Simultaneous ICP-AES instrument. Only 0.1 ppm of Zr was found—no other metals were present.

2.1.1. Antioxidants chemical names

The antioxidants and ant-acids were as follows:

Irgafos 168 (Clariant): Tris(2,4-di-*tert*-butylphenyl) phosphite
 Irgafos PEP-Q (Clariant): Tetrakis(2,4-di-*tert*-butylphenyl) [1,1'-biphenyl]-4,4'-diylbis(phosphonite)
 Adekastab PEP-8 (Asahi Denka Kogyo K.K.): distearyl pentaerythritol diphosphite
 Adekastab PEP-36 (Asahi Denka Logyo K.K.): bis(2,6-di-*t*-butyl-4-methylphenyl) pentaerythritol diphosphite
 Adekastab HP-10 (Asahi Denka Kogyo K.K.): 2,2-methylenebis(4,6-di-*tert*-butylphenyl)octylphosphite

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