Effect of Change in Phosphte Antioxidant Additives on Degradation Behavior of Linear Low Density Polyethylene Film Grade

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Abstract

Free radicals may form during polymerization, processing, fabrication, or final application. For most applications, a combination of a phenolic antioxidant and a phosphite melt processing stabilizer can provide the primary stabilization necessary to provide the retention of physical properties, good processability, long-term thermal stability without compromising the overall aesthetic appearance of the film product. In this research, the effects of Irgafos 168, a phosphite secondary antioxidant, and Tri-nonylphenolphosphate (TNPP), currently used phosphite antioxidant, on the degradation behavior of Linear Low Density Polyethylene (LLDPE) were compared and investigated. Our results have shown that applying an appropriate combination of Irgafos 168 and a primary antioxidant was effective enough to take TNPP place in our additives combination package.

Introduction

Plastic additives are used to either aid in the processing of the material, or to make the final product more appealing, durable or useful. Many of these compounds can be used for multiple functions, and many of them interact synergistically to provide optical, physical, or chemical behavior. Oxidation additives are used in a variety of resins to prevent oxidative degradation. Degradation is initiated by the action of highly reactive free radicals caused by heat, radiation, mechanical shear, or metallic impurities [1]. Stabilization of polyolefins is necessary to protect the polymer from degradation during melt processing and end-use conversion. Besides processing stability, primary stabilizers provide long-term thermal stability in use. Stabilizers are by nature reactive chemicals and sometimes tend to give undesired reactions and effects. Examples are blooming or die build up as well as the tendency of phenolic antioxidants to discolor when exposed to active catalyst residues and exhaust gasses from combustion processes. TNPP is a successful phosphite stabilizer for LLDPE due to its excellent price/performance ratio and its good compatibility in PE. As a response to ecological concerns surrounding some chemicals with similarities to nonylphenol, some organizations have taken cautious step of removing these stabilizers. This has created a need for resin producers to devise new environmentally friendly formulations which are able to meet the requirements of these markets without containing TNPP. Two factors are key in being able to optimally formulate base stabilization packages. One is having access to a diverse toolbox of additives from which to choose. Perhaps even more important is having the knowledge and experience to apply the use of additives to different situations. Schematic figure of autoxidation cycle for olefin polymers is shown in Figure 1. Most, if not all of these changes are unwelcome in that they can change the physical properties, melt processability and the final utility of the polymer during its life cycle[2]. A phenolic antioxidant (AO), typically in combination with a phosphite melt processing stabilizer (P), can be used at various loadings and ratios to meet most requirements of a given end-use application. The role of the phenolic antioxidant is to scavenge oxygen centered free radicals, such as allyl, hydroxyl and peroxy type species, while the role of the phosphite is to decompose the hydroperoxides into relatively inert products (before they can split back into oxygen centered free radicals) [4]. Figures 2 shows effect of utilize these antioxidants on the inhibited auto-oxidation cycle for polyolefins.[5] For improved initial color maintenance, a similar variety of approaches can be used, such as: Change the nature of phenolic antioxidant, Change the phosphite by alleviating the workload on the phenolic, Change the phenolic to phosphite ratio, Examine “hyper active” stabilizers (hydroxylamines, benzoalureones) as a booster for traditional binary blends, Change the acid acceptors and Eliminate the phenol antioxidant. In this research, the effects of utilize Irgafos 168 antioxidant instead of TNPP were investigated. In this regard, LLDPE powder was granulated and some of qualitative tests used for study of mentioned effects.

Experimental

Irgafos 168 was purchased from BASF and AO 1076 and TNPP were purchased from Richiyo. All materials were used as they were supplied. Pellets were prepared from LLDPE powder (3895S film grade) with following specifications that were produced under baseline (Sphireline technology license) (Table 1). Samples were prepared by laboratory single screw Brabender extruder (L/D=20, 60 rpm, 210°C) with formulation that provided in Table 2.

Table 1. Longitudinal samples composition without AO [L/D=20, 60 rpm, 210°C]

<table>
<thead>
<tr>
<th>Compound</th>
<th>PP (L/H)</th>
<th>AO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irgafos 168</td>
<td>0.15</td>
<td>AO 1076</td>
</tr>
<tr>
<td>TNPP</td>
<td>0.15</td>
<td></td>
</tr>
</tbody>
</table>

Samples were characterized after extruded five times. Figure 2 shows DFT results of samples that prepared according to formulation that provided in table 2. As seen in this figure, C1 has highest DFT in compared with other samples. Figure 4 shows Y1 results of samples after three and five times extrusion. As seen in this figure, most of samples preserved colors after three times extrusion, specially B1, B2 and C1 had excellent behavior than reference sample (A). Degradation mechanism for PE are either cross-linking which lead to decreasing of MFI or chain scission which lead to increasing MFI. According to MFI results, in all of samples, changes in MFI results after three and five times extrusion, for C1and C2 are less than the others (Figure 5) that indicates the performance of antioxidant combination for these two samples are acceptable.

Results and discussion

In this research the samples prepared by two types of antioxidants including phosphate-based and phenolic-based materials. These additives and their combinations were studied to eliminate TNPP as a main antioxidant that used for LLDPE film grades. Results have shown that applied combination of phosphorous-based and phenolic-based antioxidants was effective to protect samples against oxidative degradation. The sample of C1 (1500ppm in 3895S film grade) after long term exposure (2000h) and in the presence of oxygen, no color change seen.

Conclusions

In the study we found that phosphites are effective alternative to phenols to stabilize LLDPE, when are used as a booster for traditional binary blends. The antioxidant system based on phosphite and phenolic antioxidants offers a cost effective and potential alternative to the traditional phenolic antioxidant-based systems. Also it can be concluded that antioxidation mechanism for PE are either cross-linking which lead to decreasing of MFI or chain scission which lead to increasing MFI. According to MFI results, in all of samples, changes in MFI results after three and five times extrusion, for C1 and C2 are less than the others (Figure 5) that indicates the performance of antioxidant combination for these two samples are acceptable.

References