

Material Behaviour

The role of organic phosphite primary structure in the overall stabilization performance in polypropylene

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ABSTRACT

The role of the primary P³⁺ functionality in the phosphite overall stabilization performance was re-evaluated. Tris(2,4-di-*t*-Bu-phenyl)phosphite (P-1) and its oxidation product tris(2,4-di-*t*-Bu-phenyl)phosphate (P-1_{ox}) were tested both alone and in the presence of hindered phenol during processing in polypropylene. Efficiencies were quantified using the processing degradation index (PDI). The position of the traditional multiple extrusion curve was determined by a single parameter, describing the degree of polymer degradation. Its reciprocal allowed calculating formulations relative efficiencies. It was shown that oxidation of P³⁺ into P⁵⁺ is responsible for 75 % phosphite stabilization performance, regardless phosphite acts alone or in combination with phenol. If P³⁺ is completely oxidized, stabilizer still works. For the residual performance, the reactions of 2,4-di-*t*-Bu-phenyl substituents (secondary structure), are responsible. Besides processing, reactions of P³⁺ also contribute to the long-term stability at 150 °C. Once phosphite is oxidized, the secondary structure does not contribute to the long-term stability at all.

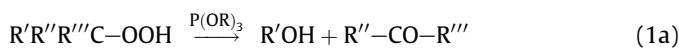
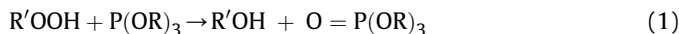
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1. Introduction

Organic phosphites belong to the class of processing stabilizers utilized in variety of synthetic polymers, most frequently polyolefins. Together with sterically hindered phenols they provide powerful protective systems, capable of efficient protection of polymer during melt processing [1–14]. High protective performance is a consequence of a synergistic effect, making the efficiency of phenol-phosphite blend higher than as if the efficiencies of both single components were purely added up. As it has been published previously, phosphites perform by means of a complex mechanism, stemming from their inherent molecular structure. In phosphite molecule, the primary and secondary structures may be defined. While the primary structure refers to P³⁺ functionality, the secondary structure refers to the substituents, that participate in phosphite's overall performance as well. The phosphite stabilization activity was described by the following mechanisms of action [15–20]:

1.1. Decomposition of hydroperoxides

Based on the reactions of phosphite functionality decomposing hydroperoxides in a non-radical way. Phosphite is simultaneously oxidized and converted into phosphate (1) or acts as a catalyst of alkyl hydroperoxide non-radical decomposition (1a). Reaction (1) is influenced by phosphite substitution, with bulky substituents its rate decreases [16,18].



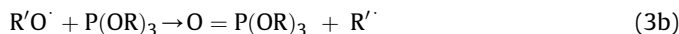
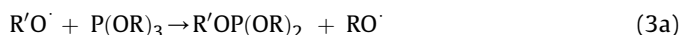
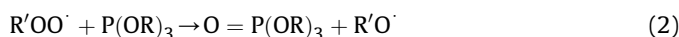
1.2. Reaction with alkyl peroxy and alkoxy radicals

Alkyl peroxy radicals oxidize the phosphite into phosphate (2). The reaction with alkoxy radicals depends on the phosphite secondary structure. If the molecule contains a suitable hindered aryloxy functionality, e.g. 2,4-di-*t*-butyl phenyl (R), it is released by substitution and provides a relatively stable radical, unable of

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further propagation (3a). Other reactions with alkoxy radicals do not contribute to the stabilization efficiency of the system.



1.3. Hydrolysis

The non-radical process, during which hindered phenol is released from the phosphite molecule, acts as a chain breaking antioxidant and contributes to the overall stabilization efficiency [11,12].



R = sterically hindered aryl, R', R'', R''' = alkyl.

1.4. Metal ions complexing

In the phosphites stabilizing mechanisms also the complexing ability should be included. The phosphites are known by their positive impact to polymer colour. This effect is explained by the ability of complexing metal ions, which may be present in polymer either as a part of additive package or as catalyst residues [20,21]. Once metal ion is complexed, it does not catalyse radical scission of hydroperoxides and/or oxidation of phenols into highly absorbing and polymer discolouring quinones.

Based on the above mechanisms, in the course of stabilization, the P³⁺ primary structure is oxidized due to reactions (1), (2) and (3b), where only (1) and (2) may lead to the protection of polymer. Besides this, the phosphites overall performance in polymer is strongly influenced by the secondary structure. Depending on the type and number of substituents, one, two or more of the above mechanisms may be involved. That is why, despite having the same P³⁺ functionality, individual phosphites may considerably differ in performance. Since the main reaction on primary structure - non-radical decomposition of hydroperoxides - was proven to be typical for all of the organic phosphites, it became the subject of our interest. The issue of this work was to identify its role and quantify its share in the overall stabilization performance during polymer processing and long-term heat ageing. The investigations were carried out with tris(2,4-di-*t*-Bu-phenyl)phosphite (P-1) and its oxidized form tris(2,4-di-*t*-Bu-phenyl)phosphate (P-1_{ox}). While the first represents the typical and most used phosphite, the latter provides the same structure with blocked P atom, unable of performing as oxidizable substrate. The performance of both structures was investigated both alone and in blends with phenolic antioxidant AO-1. The measurements were carried out in isotactic polypropylene during the multiple extrusion [22–25] on a laboratory single-screw extruder.

2. Experimental

2.1. Materials

Polypropylene homopolymer (h-PP; MFR = 3 dg/min 230°C/2.16 kg; Unipetrol RPA, gas-phase process) was used for experiments. Polymer was acquired from the producer without additives, in the fluffy form. Tris(2,4-di-*t*-Bu-phenyl)phosphite (P-1) was provided by BASF under the commercial name Irgafos 168, Tris(2,4-

di-*t*-Bu-phenyl)phosphate (P-1_{ox}) was provided by Ratiochem, Brno (CZ), pentaerythrityl tetrakis[3-(3,5-di-*tert*-Bu-4-hydroxyphenyl)propionate] (AO-1) was provided by BASF as Irganox 1010. The additives were dry-blended with fluffy polymer and compounded on a single-screw extruder at 220 °C/100 rpm. This step was denoted as zero extrusion.

2.2. Methods and measurement

Processing stability experiments were carried out using a laboratory Brabender single-screw extruder, D = 19 mm, L/D = 30, at 260 °C (all barrel zones)/100 rpm; nozzle diameter 3 mm.

Extruded polymer melt was water quenched, pelletized and dried. Pellets produced in this way were used for the following extrusion. Melt-flow rate (MFR) after each extrusion was measured at 230 °C/2.16 kg (EN ISO 1133).

Yellowness index (YI) according to ASTM D 1925 was determined on pellets, using the Spectra Flash SF 650 (Datacolor) under the light/observer D65/10° conditions.

Residual contents of stabilizers were determined in pellets after 0, 1, 3 and 5th extrusion. The pellets were ground on a laboratory mill, extracted with boiling dichloromethane-cyclohexane (3:1) blend and analyzed using HPLC/DAD technique (C18 column, acetonitrile-water gradient as a mobile phase, Tinuvin P was used as an internal standard).

Long-term heat ageing (LTHA) stability at 150 °C was measured with test specimens 2 × 40 mm cut of 0.5 mm compression moulded films. Samples were exposed in the open test tubes, LTHA stability was given as the time to sample embrittlement. A brittle failure as a criterion of degradation was observed after pulling the sample out and flexing by 90°.

A stress-controlled rotational rheometer (AR-G2, TA instruments) was used to measure the rheological properties of the selected samples at 170 °C. Polymer plates were placed inside the environmental test chamber. Parallel-plate geometry with diameter of 25 mm at a gap of 1 mm was used for all shear tests. Strain sweeps were carried out to identify the linear viscoelastic region during the test (typically less than 1% strain over the whole frequency range). Angular frequency sweeps were subsequently performed in the range of 0.0628–628.0 rad/s at a constant strain of 0.8%. From these measurements, storage modulus G', loss modulus G'', were obtained at different angular frequencies.

3. Results and discussion

3.1. Multiple extrusion

Processing performance of phosphite P-1 was investigated both alone and in combination with AO-1. Phosphate P-1_{ox} was followed as the main conversion product of P-1 and/or it was used as a reference. The formulations investigated are shown in Table 1.

Processing stability was evaluated by 5-fold extrusion on a single-screw extruder at 260 °C/100 rpm, MFR was measured after each extrusion, Fig. 1. Multiple extrusion primarily confirmed the known fact, that P-1 exhibits only average performance when used alone but a strong effect in blend with AO-1. However, it has also shown that oxidized phosphite represented by P-1_{ox}, did not exhibit zero performance as expected, but some not negligible stabilization effect could be seen when P-1_{ox} was used both alone and with AO-1. Processing records allowed to calculate processing degradation index (PDI) [26], quantifying the extent of processing degradation and inversely providing information on the strength of stabilizer formulation. PDI was calculated based on equation (5) using the MFRs after individual extrusions, Table 2.

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