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Efficiency of curcumin, a natural antioxidant, in the processing stabilization of PE: Concentration effects

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The stabilising efficiency of curcumin was studied in polyethylene during processing and under oxygen at high temperature. The effect of the natural antioxidant was investigated at concentrations of 0–1000 ppm in combination with a phosphonite secondary antioxidant (Sandostab P-EPQ) of 1000 and 2000 ppm, respectively. The polymer was homogenized with the additives then processed by six consecutive extrusions taking samples after each processing step. The samples were characterized by FT-IR spectroscopy, melt flow index, colour, and OIT measurements. Compared to the effect of pure phosphorous antioxidant, the melt stability of PE is increased already at 5 ppm curcumin content. The melt as well as the high temperature oxidative stability (OIT) of the polymer are controlled by both types of antioxidants. Curcumin hinders the oxidation of polyethylene and the formation of long chain branches during processing, which can be attributed to the fact that curcumin is not only a hydrogen donor but its unsaturated linear moiety can also scavenge alkyl and oxygen centred macroradicals. Curcumin discolours polyethylene already at small concentrations but the colour fades with increasing number of extrusions.

1. Introduction

Stabilisation of polyolefins with natural antioxidants got into the focus of attention recently because of the unknown effects of the reaction products of synthetic phenolic antioxidants on human health [1]. Health safety has vital importance in many application areas, like food contacting objects (e.g., packaging materials, water pipes), medical applications, toys, etc. The small molecular mass additives used in polyolefins for stabilisation, colouring, or anti-blocking are generally polar compounds, therefore their solubility is small and migrate onto the surface of the polymer during application [2]. Their dissolution into contacting substances cannot be avoided but any harmful effect must be prevented.

Among the natural antioxidants, first α-tocopherol was studied extensively for the stabilisation of polyolefins [e.g., [3–9]]. Intensive research resulted in the application of α-tocopherol for the stabilisation of ultra high molecular mass polyethylene (UHMWPE) used as total joint implant [e.g., [10–15]]. Even an ASTM standard specification was implemented for medical grade UHMWPE blended with vitamin E [16]. The study of different natural antioxidants in polymers has been widely extended lately. The goals of the investigations are mainly the improvement of the safety of packaging materials and the development of functional packaging [e.g., [17–25]].

Curcumin, 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione, is the principal curcuminoid of *Curcuma longa* rhizomes (turmeric). The powdered root is used as a spice, food colourant, and food preservative. The effects and reactions of curcumin have been the subject of investigation in the fields of biology, medicine, pharmacology, and in the food industry yielding a large number of publications for many years. The medical activity of curcumin has been known since ancient times. The beneficial effects can be attributed to its antioxidant activity which involve radical and peroxide scavenging, as well as metal chelating effect [e.g., [26–32]]. The actual reaction site and the mechanism of free radical scavenging have not been clarified unambiguously yet. According to some

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authors the OH groups on the two phenyl rings participate in the reactions [e.g., [29,33,34]], others claim that the β-diketone moiety is responsible for the antioxidant action [35], while other publications [36–38] indicate that the strong antioxidant activity of curcumin originates mainly from the phenolic OH groups, but the central methylene group of the heptadione link plays also a role. However, the site of double bond in the β-diketone moiety participating in addition reactions depends also the chemical nature of the reaction partner [39].

The effect of curcumin on the processing and high temperature oxidative stability of polyethylene (PE) was studied first in our laboratory [40]. The efficiency of 1000 ppm curcumin was compared to that of the same amount of the commercial phenolic antioxidant Irganox 1010 without and in combination with 2000 ppm phosphonite secondary antioxidant (Sandostab P-EPQ) during multiple extrusions. We concluded that curcumin is an efficient melt stabiliser of PE, and similarly to synthetic phenolic antioxidants, its efficiency is enhanced by the addition of a phosphorous secondary antioxidant. The effects of curcumin and the synthetic phenolic antioxidant on the characteristics of polyethylene during multiple extrusions are compared in Table 1. The number of the reactions of vinyl groups is not affected by the type of the phenolic antioxidant and the consumption rate of the phosphorous secondary antioxidant is reduced by both phenolic antioxidants. On the other hand, melt flow index increases and yellowness index decreases as a function of the number of extrusions in the presence of curcumin, while just the opposite occurs in the presence of the synthetic phenolic antioxidant. Curcumin protects the polymer from oxidation more efficiently than Irganox 1010. These results indicate different stabilizing mechanisms for the two phenols. The aim of the present work was the determination of the effect of antioxidant concentration on the melt stabilising efficiency of curcumin/phosphonite additive pairs in polyethylene.

2. Experimental

2.1. Materials

The experiments were carried out with the Tipelin FS 471 grade ethylene/1-hexene copolymer (melt flow index of the powder: 0.32 g/10 min, nominal density: 0.947 g/cm^3) polymerized by Phillips catalyst. The additive-free polymer powder was provided by Tisza Chemical Ltd. (*TVK*), Hungary. The polymer was stabilised with various amounts of curcumin from curcuma longa (*Sigma–Aldrich*; 65% curcumin with 35% demethoxycurcumin and bisdemethoxycurcumin) ranging from 0 to 1000 ppm in combination with the Sandostab P-EPQ (*Clariant*) phosphonite secondary antioxidant added at 1000 and 2000 ppm, respectively. The chemical structure of the antioxidants used is compiled in Table 2.

2.2. Sample preparation

The polymer and the additives were homogenized in a high speed mixer (Henschel FM/A10) at a rate of 500 rpm for 10 min then pelletized by six consecutive extrusions using a Rheomex S ¾″ type single screw extruder attached to a Haake Rheocord EU 10V driving unit at 50 rpm and barrel temperatures of 180, 220, 260 and 260 °C. Samples were taken after each extrusion step. Films of about 100 μm were compression moulded at 190 °C for FT-IR measurements using a Fontijne SRA 100 machine.

2.3. Methods

The concentration of the functional groups (unsaturated and carbonyl) of polyethylene and the residual concentration of the phosphorous antioxidant were determined by FT-IR spectroscopy using a Tensor 27 (*Bruker*) spectrophotometer [41]. Five parallel measurements were carried out on each sample. The melt flow index (MFI) of the polymer was measured according to the ASTM D 1238-79 standard at 190 °C with 2.16 kg load using a Göttfert MPS-D MFI tester. Five parallel measurements were done on each sample. The high temperature oxidative stability of the polymer was characterised by the oxidation induction time (OIT) measured at 200 °C using a Perkin Elmer DSC-2 apparatus under oxygen in five parallel experiments. The colour of the samples was determined on a Hunterlab Colourquest 45/0 apparatus with three parallel measurements. Yellowness index (YI) was calculated as the characteristic parameter.

3. Results

The concentration of vinyl groups of the polymer powder decreases significantly (from 1.15 to 0.82–0.84 vinyl/1000 C) in the first extrusion step. Changing the concentration of curcumin from 0 to 1000 ppm and that of P-EPQ from 1000 to 2000 ppm does not affect significantly the vinyl group concentration measured after the first extrusion. Considering that <1000 ppm P-EPQ is consumed in the first extrusion even in the absence of curcumin, this result confirms the essential role of the secondary antioxidant in the melt stabilisation of polyethylene [41,42]. However, vinyl group concentration decreases in a slightly lesser extent with increasing curcumin concentration (Fig. 1). In further extrusion steps the vinyl groups participate in more reactions leading to a gradual decrease in their concentration. Changing the amount of P-EPQ from 1000 ppm to 2000 ppm does not affect these processes, while increasing curcumin concentration leads to a somewhat slower decrease in the number of vinyl groups with increasing number of extrusions.

The polymer oxidizes in some extent during processing especially in the first extrusion step (Fig. 2). Curcumin protects polyethylene against oxidation, the concentration of carbonyl groups formed decreases with increasing concentration of the antioxidant. Curcumin slows down the consumption of phosphonite in each processing step. 5 ppm of curcumin is already effective in this process, and the increase in its concentration results in a continuous decrease in the consumption rate of P-EPQ, as shown in Fig. 3.

The changes in the melt flow index of polyethylene are influenced by the concentration of both types of antioxidants. In the

Table 1
Effect of 1000 ppm phenolic antioxidant (Irganox 1010 and curcumin) combined with 2000 ppm phosphonite (Sandostab P-EPQ) on the characteristics of polyethylene during multiple extrusions.

Synthetic phenolic antioxidant	Curcumin
Similar number of vinyl group reactions	
Long chain branching	Reduced long chain branching
Oxidation of polymer chains	Restricted oxidation of polymer chains
Rate of phosphonite consumption is slower than without a phenol derivative	
Small discolouring effect; increase of YI with increasing processing steps	Strong discolouring effect; decrease of YI with increasing processing steps