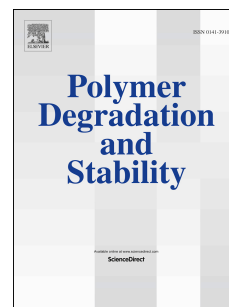


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**Efficiency of curcumin, a natural antioxidant, in the processing stabilization of PE:
concentration effects**

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Abstract

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 to 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.

Keywords: curcumin, natural antioxidant, polyethylene, stabilisation, phosphonite

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 antiblocking 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 colorant, 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 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/cm³) 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 presence of 1000 ppm P-EPQ MFI decreases with increasing number of extrusions (Fig. 4). The decrease is the most significant in the absence of curcumin. This natural antioxidant contributes to the melt stabilizing efficiency of P-EPQ already at an amount of 5 ppm and the change in the melt flow index as a function of the number of extrusions decreases with increasing curcumin concentration. At 1000 ppm curcumin content the melt flow index increases slightly in the multiple processing operations. The processing history influences the melt flow index less at 2000 ppm P-EPQ concentration than with 1000 ppm (the maximum difference among the MFI values does not exceed 0.035 g/10 min). The melt flow index does not change without curcumin, while it increases continuously with increasing number of extrusions at curcumin concentrations of ≥ 250 ppm. It is worth to note that the MFI values are larger at 250 than at 1000 ppm curcumin content.

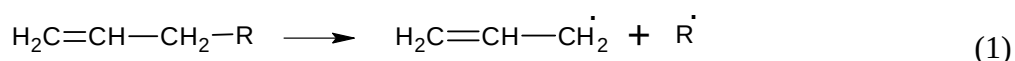
The high temperature oxidative stability (OIT) is also affected by both types of antioxidants (Fig. 5). The increase in the concentration of curcumin and P-EPQ results in the increase of OIT. At large curcumin concentrations high temperature oxidative stability increases with increasing residual concentration of the phosphonite, while at small concentrations curcumin does not contribute significantly to the effect of P-EPQ (Fig. 6).

Curcumin discolours PE strongly already at small concentrations (Fig. 7). The phosphonite does not influence discolouration, except at very small curcumin content (5 ppm), at which an insignificant effect can be observed. Yellowness index decreases with increasing number of extrusions which indicates the participation of the unsaturated linear moiety of curcumin in chemical reactions during the processing of polyethylene.

Discussion

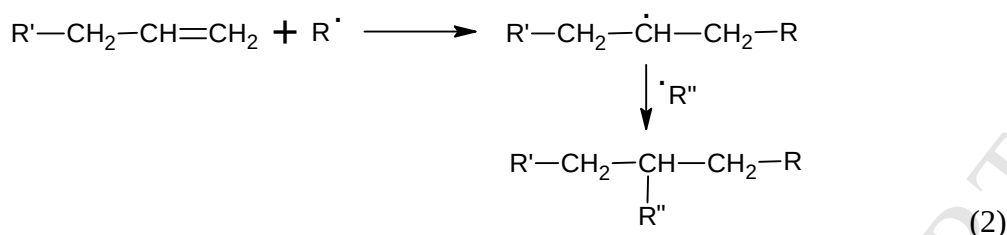
The reactions of vinyl groups are influenced by several factors. In the presence of a phosphonite secondary antioxidant the concentration of vinyl groups decreases linearly with the residual amount of P-EPQ (Fig. 8). After the complete loss of the secondary antioxidant vinyl concentration continues to decrease further. The reactions of the vinyl groups are not accompanied by a decrease in the melt flow index of polyethylene until any phosphonite stabiliser is present. Although there are some small differences in MFI values, a significant decrease of the melt flow index starts only after the complete loss of the phosphorous antioxidant (Fig. 9). The correlation between the concentration of vinyl groups and the melt flow index (Fig. 10) provides some information on the melt stabilising effect of curcumin after the complete loss of phosphonite (<0.79 vinyl/1000 C). The melt flow index of polyethylene stabilised with the phosphonite antioxidant alone is affected by the reactions of the vinyl groups more than in the presence of curcumin. In the latter case the decrease in vinyl concentration is accompanied by a smaller reduction of melt flow index. This result can be attributed to the reactions of alkyl radicals with curcumin.

The decrease in vinyl concentration can be attributed to two reactions: a) elimination and b) addition reactions. Although the formation of alkyl radicals during processing is still controversial [43], Holström and Sörvik concluded [44-47] that the thermal degradation of polyethylene starts with the scission of C–C bonds in allylic position to a double bond. The scission at the carbon atom next to a vinyl group results in the formation of an allyl and an alkyl radical without an essential change in the molecular mass of the polymer:



The allyl radical can further react and/or leave the system by evaporation at the high temperatures of polyethylene processing resulting in a decrease in vinyl group concentration without any significant change in MFI. The addition of an alkyl radical to the vinyl group

leads to the formation of a secondary radical [48,49] which can react with a further alkyl radical resulting in long chain branching [43] and an increase in the viscosity of the polymer:



The results presented above reveal that the dominating reaction of vinyl groups during processing is reaction (1) in the presence of the phosphonite secondary antioxidant. The alkyl radicals formed in the first degradation step react with the small amount of oxygen present in the processing machine. Peroxy radicals are scavenged by hydrogen atoms donated by the OH groups of curcumin. The resultant hydroperoxide groups are decomposed by the phosphonite to stable products. After the oxidation of all phosphonite molecules, the addition reaction (2) becomes predominant resulting in the formation of long chain branches accompanied by a decrease in MFI.

The beneficial effect of curcumin on the melt stability of polyethylene is twofold. The reaction of curcumin with alkyl radicals hinders the oxidation of the polymer (Fig. 2) and the formation of long chain branches (Fig. 10). The observed increase in the melt flow index of polyethylene with increasing number of extrusions at large antioxidant contents (Fig. 4) may be explained by the chain scission of the polymer at α -position to vinylidene and vinylene groups and/or β -scission of secondary radicals [44,45,47], and their subsequent addition to a double bond in the linear linkage of curcumin molecules. This leads to a decrease of the number of conjugated double bonds of curcumin and to a lighter colour, which seems to be confirmed by Fig. 7. The reaction mechanism of curcumin at high temperatures is under further investigation by model experiments.

The melt flow index of polyethylene measured after the first extrusion depends on the concentration of curcumin. Fig. 11 shows that MFI decreases with increasing amount of the

natural antioxidant. The effect is the most significant at small curcumin contents and differences in MFI do not exceed -0.02 g/10 min even at 1000 ppm. The small decrease in the stabilising efficiency of the phosphonite secondary stabiliser can be attributed to the specific interaction of the two antioxidants. This phenomenon is typical for partially and unhindered phenols. These antioxidants are efficient stabilisers already at small concentrations even when used alone, but their efficiency is often limited by the interaction of their functional groups [50,51].

Conclusions

The study of the stabilizing effect of curcumin in polyethylene under processing conditions revealed that the melt stability of PE is increased already at 5 ppm curcumin content, compared to the effect of phosphonite used as a single antioxidant. The consumption of the secondary antioxidant reduces gradually with increasing curcumin concentration. Curcumin hinders the oxidation of the polymer and the formation of long chain branches. The melt and the high temperature oxidative stabilising efficiencies are controlled by both types of antioxidants. Curcumin colours polyethylene even at small amounts. The decrease in yellowness index with increasing number of extrusions, as well as the correlation between the concentration of vinyl groups and the melt flow index of the polymer indicate that besides the reactions of the phenolic OH groups, the double bonds in the linear linkage between the two methoxyphenyl rings also takes part in addition reactions with the alkyl macroradicals formed during processing. Model reactions are in progress to determine the exact reaction mechanism of curcumin.

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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

Table 2

Antioxidants investigated

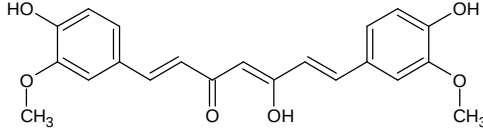
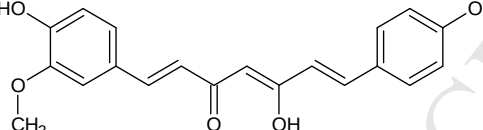
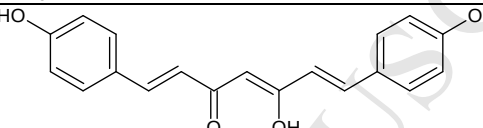
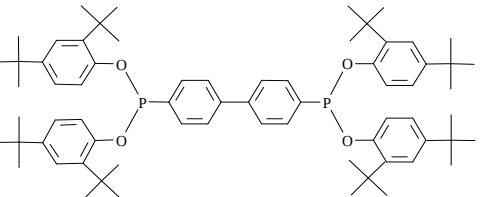
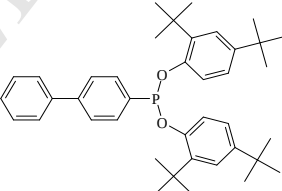
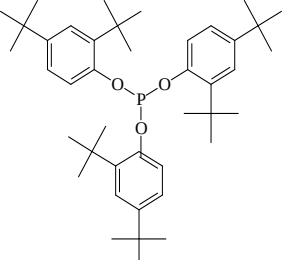
Chemical name	Chemical composition	Molecular mass (g/mol)
Curcumin from curcuma longa (<i>Sigma-Aldrich</i>)		
Curcumin (~65 %)		368
Demethoxycurcumin		338
Bisdemethoxycurcumin		308
Sandostab P-EPQ (<i>Clariant</i>)		
Diphosphonite (>70 %)		1035
Monophosphonite (~20 %)		595
Phosphite (<10 %)		647

Figure captions

Fig. 1 Effect of additive concentration and processing history on the vinyl group content of polyethylene stabilised with 0 ($\square$), 5 ($\circ$), 25 ($\triangleleft$), 50 ($\triangle$), 100 ($\triangleright$), 500 ($\diamond$), and 1000 (∇) ppm curcumin in combination with 1000 ppm P-EPQ.

Fig. 2 Effect of additive concentration and processing history on the carbonyl group content of polyethylene stabilised with 0 ($\square$), 5 ($\circ$), 25 ($\triangleleft$), 250 ($\ast$), and 1000 (∇) ppm curcumin in combination with 2000 ppm P-EPQ.

Fig. 3 Effect of additive concentration and processing history on the residual amount of phosphonite antioxidant in polyethylene stabilised with 0 ($\square$), 5 ($\circ$), 25 ($\triangleleft$), 50 ($\triangle$), 100 ($\triangleright$), 500 ($\diamond$), and 1000 (∇) ppm curcumin in combination with 1000 ppm P-EPQ.

Fig. 4 Effect of processing history on the melt flow index of polyethylene stabilised with 0 ($\square$), 5 ($\circ$), 25 ($\triangleleft$), 50 ($\triangle$), 100 ($\triangleright$), 250 ($\ast$), 500 ($\diamond$), and 1000 (∇) ppm curcumin in combination with 1000 ppm P-EPQ.

Fig. 5 Effect of additive concentration and processing history on the high temperature oxidative stability of polyethylene stabilised with different amounts of curcumin in combination with 1000 ($\triangle$) and 2000 ($\square$) ppm P-EPQ, respectively.

Fig. 6 Correlation between the residual amount of phosphonite antioxidant and the high temperature oxidative stability of polyethylene stabilised with different amounts of curcumin in combination with 1000 ppm P-EPQ, processed by multiple extrusions.

Fig. 7 Effect of additive concentration and processing history on the yellowness index of polyethylene stabilised with different amounts of curcumin in combination with 1000 ($\triangle$) and 2000 ($\square$) ppm P-EPQ, respectively.

Fig. 8 Correlation between the residual amount of phosphonite antioxidant and the vinyl group concentration of polyethylene stabilised with different amounts of curcumin in combination with 1000 ppm P-EPQ, processed by multiple extrusions.

Fig. 9 Correlation between the residual concentration of the phosphonite antioxidant and the melt flow index of polyethylene stabilised with 0 ($\square$), 5 ($\circ$), 25 ($\triangleleft$), 50 ($\triangle$), 100 ($\triangleright$), 500 ($\diamond$), and 1000 (∇) ppm curcumin in combination with 1000 ppm P-EPQ, processed by multiple extrusions.

Fig. 10 Correlation between the vinyl group concentration and the melt flow index of polyethylene stabilised with 0 ($\square$), 5 ($\circ$), 25 ($\triangleleft$), 50 ($\triangle$), 100 ($\triangleright$), 500 ($\diamond$), and 1000 (∇) ppm curcumin in combination with 1000 ppm P-EPQ, processed by multiple extrusions.

Fig. 11 Correlation between the amount of curcumin and the melt flow index of polyethylene measured after the first extrusion. P-EPQ contents: 1000 ($\circ$) and 2000 ppm ($\triangle$).

