Process Efficiency and Long-Term Performance of *α*-Tocopherol in Film-Blown Linear Low-Density Polyethylene

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ABSTRACT: *α*-Tocopherol was compared with a commercial phenolic antioxidant (Irganox 1076) as a long-term and process antioxidant in film-blown and compression-molded linear low-density polyethylene. The antioxidant function of *α*-tocopherol was high in the film-blown material, especially in the processing, according to oxygen induction time measurements with differential scanning calorimetry. The residual content of *α*-tocopherol after processing, determined with chromatographic techniques, was less than that of the commercial phenolic antioxidant in both the film-blown and compression-molded materials. The process stabilizing efficiency was nevertheless higher for the material containing *α*-tocopherol. During the long-term stabilization, the efficiency of *α*-tocopherol was less than that of the commercial phenolic stabilizer Irganox 1076 in the thin films, according to chemiluminescence and infrared measurements. The long-term efficiency in the compression-molded samples stabilized with *α*-tocopherol or Irganox 1076 was equally good because of the low loss of both *α*-tocopherol and Irganox 1076 from the thicker films. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2427–2439, 2005

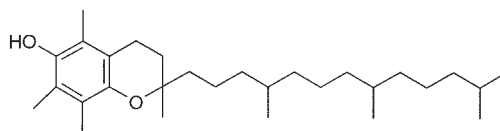**Key words:** ageing; antioxidants; polyethylene (PE)

INTRODUCTION

Natural antioxidants are of great interest as stabilizers for polymers, and the fact that natural antioxidants are biologically degradable in nature and in vivo makes them attractive for use in the stabilization of food and medical packaging. In nature, antioxidants play an important role in protecting plants, animals, and humans against free radicals. Vitamins such as vitamin C, vitamin E, and bioflavonoids acts as antioxidants and lengthen the lifetimes of all living species. Most are in general more sensitive to higher temperatures than synthetic antioxidants. *α*-Tocopherol is the most biologically active form of vitamin E (Fig. 1).

Antioxidants are used in polymeric materials both for processing and for long-term stabilization to prevent degradation and aging of the materials. In process stabilization, the antioxidant must tolerate high temperature and shear. During the processing, the carbon–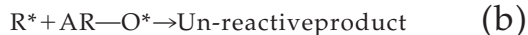carbon bonds in the polymer break because of shear stresses, and mechanically induced chain scission and initiation of alkyl radicals and alkyl peroxyl radicals take place.[1] Film-blown and compression-molded materials have different properties as a result of their different processing conditions. The film-blown material is exposed to a higher stress in the processing step. It is first extruded at a high temperature and then film-blown; during this step, it is outstretched and blown. In compression molding, solvents are often used.

α-Tocopherol is a suitable natural antioxidant for use in polymers because of its lower sensitivity for high temperatures and its higher molecular weight in comparison with, for example, ascorbic acid. The general chain-breaking mechanism of phenolic antioxidants is shown in Scheme 1. The phenol *α*-tocopherol is an efficient alkyl radical trap according to rate-constant studies of its antioxidant activity, and it reacts with peroxyl radicals via a chain-breaking donor mechanism [Scheme 1(a)] and forms *α*-tocopherol radicals, which can then react via a chain-breaking accep-

Figure 1 Structure of *α*-tocopherol.

$$ROO* + AR{-}OH \rightarrow ROOH + Ar{-}O* \quad (a)$$

$$R* + AR{-}O* \rightarrow Un\text{-}reactive\,product \quad (b)$$

Scheme 1 Chain-breaking mechanism of a phenolic antioxidant (Ar—OH; e.g., α-tocopherol), peroxyl radical (ROO*), hydroperoxide (ROOH), phenolic (α-tocopherol) radical (Ar—O*), and carbon-centered radical (R*).

tor mechanism [Scheme 2(b)] with carbon-centered radicals.[2,3] Intensive research on the stabilizing properties of α-tocopherol in polymeric materials has been reported during the last 15 years. In addition to its biological antioxidant function, α-tocopherol works well for process stabilization in polyolefins and also is more efficient than synthetic antioxidants in the melt.[4,5] Equivalent performance has been achieved with less antioxidant than in the traditional stabilization system used in processing. The consumption of the antioxidant leads to oxidation of the antioxidant, and oxidation products are formed. Al-Malaika and Issenhuth[4] studied the amounts of oxidation products from α-tocopherol and their contribution to the stabi-

lization efficiency in polypropylene. Several oxidation products were formed with antioxidant properties: quinonoids (**I**), trimers (**V**), dimers (**III** and **IV**), and aldehydes (**II**; Fig. 2). These are chain-breaking antioxidants, and they deactivate both alkyl peroxyl and alkyl radicals. The aldehyde has an even greater efficiency as a stabilizer than α-tocopherol.[4]

In long-term stabilization, the migration and loss of the antioxidant must be avoided. The rate of loss of an antioxidant is determined by its volatility, solubility, and diffusion rate in the polymer. The solubility and rate of diffusion in the polymer depend on the molecular dimensions of the antioxidant, on the amount of free volume in the polymer, on the polymer–antioxidant interaction, on the temperature, and on the pressure.[6] Accelerated aging is often used for the long-term determination of the stabilization of polymeric materials to minimize the experimental time. The problems with accelerated aging are several. Extrapolation from a higher temperature to the final user temperature is required, and this causes problems because chemical reactions depend on activation energies that depend on the temperature. The polymer
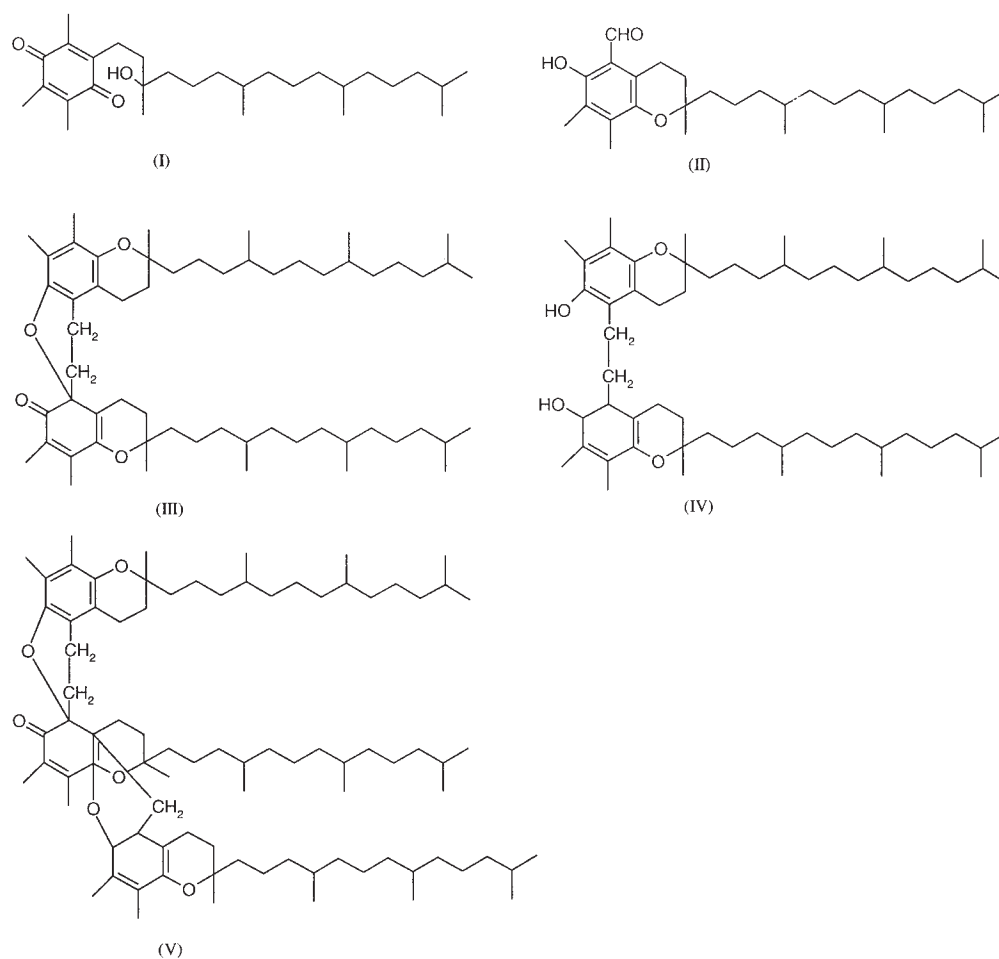
Figure 2 Oxidation products from α-tocopherol: quinonoids (**I**), aldehydes (**II**), dimers (**III** and **IV**), and trimers (**V**).

TABLE I
LLDPE Films

Antioxidant	Film-blown LLDPE		Compression moulded LLDPE	
	PE-toc	PE-lrg1076	PE-toc_CM	PE-lrg 1076_CM
α-Tocopherol (wt%)	0.1	—	0.1	—
lrganox 1076	—	0.1	—	0.1

morphology, the solubility and migration of additives, and the mechanism of antioxidant loss also depend on the temperature.[7] The efficiency of α-tocopherol in long-term stabilization has been studied but not in film-blown linear low-density polyethylene (LLDPE). It has been shown to work better than synthetic hindered phenols in high-density polyethylene (HDPE)[8] and worse than synthetic antioxidants in ultra-high-molecular-weight polyethylene (UHMWPE).[9]

The amount and type of the stabilizer determine the service life and performance for many polymers, and accurate measurements of the antioxidant content by chromatographic techniques are therefore important. Different kinds of extraction techniques can be used to extract the antioxidant from the polymer matrix. Microwave-assisted extraction (MAE) is a method that is fast with reduced solvent volumes and a high recovery rate.[10] Another widely used technique for polymer characterization is thermal analysis, that is, differential scanning calorimetry (DSC). It gives an overall assessment of the stability in a polymer. A sensitive technique for monitoring oxidation and antioxidant efficiency in polymers is chemiluminescence (CL).[11] Hydroperoxides are formed in the early stages of oxidation, and in an inert atmosphere, the emission of CL from a polymer sample is proportional to the amount of hydroperoxide formed.[12] The intensity in a typical CL graph increases up to a maximum and then decreases to the level of the background noise. The area under this curve is, in an inert atmosphere, proportional to the hydroperoxide concentration and is called the total luminescence intensity (TLI).[13] The hydroperoxides decrease in stability during oxidation, and their decomposition leads to the formation of carbonyl groups.[14] With Fourier transform infrared (FTIR) transmission spectroscopy, the analysis of a thin film (up to 100 μm) is possible, and the formation of carbonyl groups in the bulk and on the surface of the sample is measured, whereas FTIR attenuated total reflection (ATR) analysis penetrates only a thin layer of the sample and shows the carbonyl formation on the surface of the material.

This article focuses on the efficiency of α-tocopherol as a long-term and process antioxidant in film-blown LLDPE in comparison with a commercial phenolic antioxidant (Irganox 1076). Irganox 1076 was chosen because its structure is similar to the structure of α-tocopherol. The film-blown materials are also compared

with compression-molded materials. Most studies on polyethylene are made on compression-molded materials, and we want to point out the differences between film-blown and compression-molded materials, especially in long-term performance. LLDPE is often used in films, and it is anticipated that LLDPE metallocene types will take over 50% of the market from low-density polyethylene and HDPE, mainly for film applications.[15]

EXPERIMENTAL

Materials

Unstabilized LLDPE (PE) was supplied by Borealis (Stenungsund, Sweden; crystallinity = 43%, melting point = 123°C). Irganox 1076 [octadecyl 3,5-di(*tert*)-butyl-4-hydroxyhydrocinnamate] and α-tocopherol (a mixture of equal amounts of the eight possible optical isomers of α-tocopherol, DL-α-tocopherol) were obtained from Ciba Specialty Chemical Inc. (Basel, Switzerland). The solvents used for analysis were dichloromethane (DCM), chloroform, and n-hexane (99%) from Lab-Scan (Stockholm, Sweden), 2-propanol from Acros Organics (Stockholm, Sweden), ethyl acetate (EtAc) and water for chromatography from Merck, and acetonitrile from Lab-Scan.

Process conditions

Films with a thickness of 30 ± 5 μm were film-blown with a Brabender (Duisburg, Germany) DSK 35/9 D counter-rotating twin-screw extruder equipped with a film-blowing unit. During the extrusion, the temperature of the three heated zones was 175°C. The screw speed was 10 rpm. Compression-molded films with a thickness of 80 ± 20 μm were made with a Schwabenthan Polystat 300s (Berlin, Germany). The material was compression-molded at 140°C and 20 bar for 1 min, and the pressure was then increased to 200 bars. After a total time of 4 min, the material was cooled for 5 min. Compression-molded films were made with and without solvents. In the samples with a solvent, the antioxidant was dissolved in the solvent and mixed with the LLDPE powder before processing. The mixture was left at room temperature for 1 h to evaporate the solvent. The obtained films are presented in Table I. Data for the antioxidants are given in Table II,

TABLE II
Data for the Antioxidants; Weight-Average Molecular Weight (M_w), Bond Dissociation Energy (BDE), and Melting Temperature (T_m)

Antioxidant	M_w (g/mol)	BDE (kJ/mol)[a]	T_m (°C)
α-tocopherol	430.71	327.7	2
lrganox 1076	530.87	339.6	51

[a] BDE according to Denisov.[19]

and the structure for Irganox 1076 is illustrated in Figure 3.

Thermooxidation procedure

Samples (5 × 10 cm) were cut from the films. The samples were placed in a circulating air oven from Heraues (Hanau, Germany) under a load of 10 g (65.5 kN/m²) and at a temperature of 80°C. The compression-molded films were cut into pieces (1 × 1 cm), placed in sealed glass vials, and aged in air at 80°C.

MAE

The antioxidants were extracted in standard vessels with an inner diameter of 30 mm with a model MES-1000 microwave extraction system from CEM Corp (Indian Trail, NC). with a nominal power of 1000 W. The film-blown samples (0.5 g cut into 1.5 × 1.5 cm pieces) were extracted with 15 mL of acetonitrile. The extraction was carried out in three steps: (1) heating from the ambient temperature to 80°C in 6 min at 75% of the nominal power, (2) heating from 80 to 100°C in 4 min at 100% power, and (3) isothermal treatment at 100°C for 30 min at 90% power. The compression-molded film samples were extracted (0.3-g film cut into 1 × 1 cm pieces) in a mixture of 20 mL of chloroform and 2 mL of 2-propanol. The extraction was carried out in two steps: (1) heating from room temperature to 100°C in 5 min and (2) isothermal treatment at 100°C for 40 min at 50% of the nominal power. Duplicate measurements were made for each sample.

High-performance liquid chromatography (HPLC)

The film-blown samples were analyzed with a Hewlett–Packard (HP) 1100 Series Variable Wave-

length Detector and an HP 1100 Series Autosampler (Waldbronn, Germany) with a deuterium UV detector and a Shimadzu LC-10AD pump (Kyoto, Japan). The antioxidant concentration was determined by re-versed-phase HPLC, with acetonitrile–water (95/5) as the mobile phase and a Waters Symmetry C18 column (Sollentuna, Sweden) (3.9 cm × 50 mm, 5 μm). The concentration of antioxidants was estimated from the absorption at 220 nm. The compression-molded samples were analyzed with a PerkinElmer 250 binary LC pump connected to a PerkinElmer 235 diode array detector (Norwalk, CT). A Supelcosil LC-Si column (15 cm × 4.6 mm, 5 μm) was used. The mobile phase consisted of 55% hexane and 45% chloroform. The concentration of the phenolic antioxidant was esti-mated from the absorption at 280 nm. In both proce-dures, an injection volume of 10 μL and a flow rate of 1 mL/min were used, and the extraction solutions were filtered through 0.45-μm polytetrafluoroethylene filters before analysis. Duplicate measurements were made for each sample.

DSC

A Mettler–Toledo 820 DSC instrument (Greifensee, Switzerland) was used to measure the oxygen induc-tion time (OIT) and the crystallinity of the materials. Al cups (100 μL) were used with 5 ± 1 mg samples, and triplicate determinations were made for each sam-ple. OIT measurements were carried out in a dynamic oxygen atmosphere with a flow rate of 80 mL/min at 180°C. The crystallinity was calculated from the ratio of the melting enthalpy of the samples to the melting enthalpy of 100% crystalline polyethylene (293 J/g).[16] Thermograms were recorded in five steps: (1) heating from 0 to 180°C, (2) isothermal conditions at 180°C for 3 min, (3) cooling from 180 to 0°C, (4) isothermal conditions at 0°C for 3 min, and (5) a second heating from 0 to 180°C. The heating and cooling rates were 10°C/min.

CL

Changes in the amounts of the hydroperoxides in the materials were studied with a Lumipol-2 CL instru-ment (Bratislava, Slovakia). Measurements were made
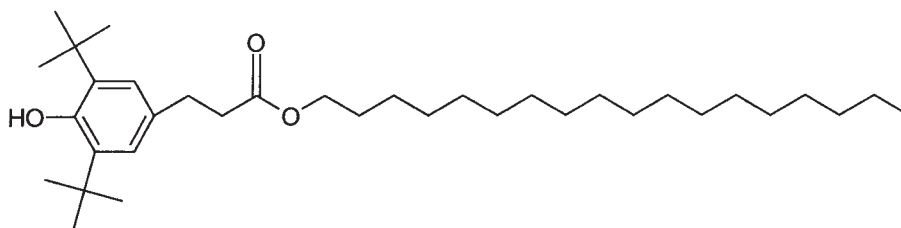
Figure 3 Structure of Irganox 1076.
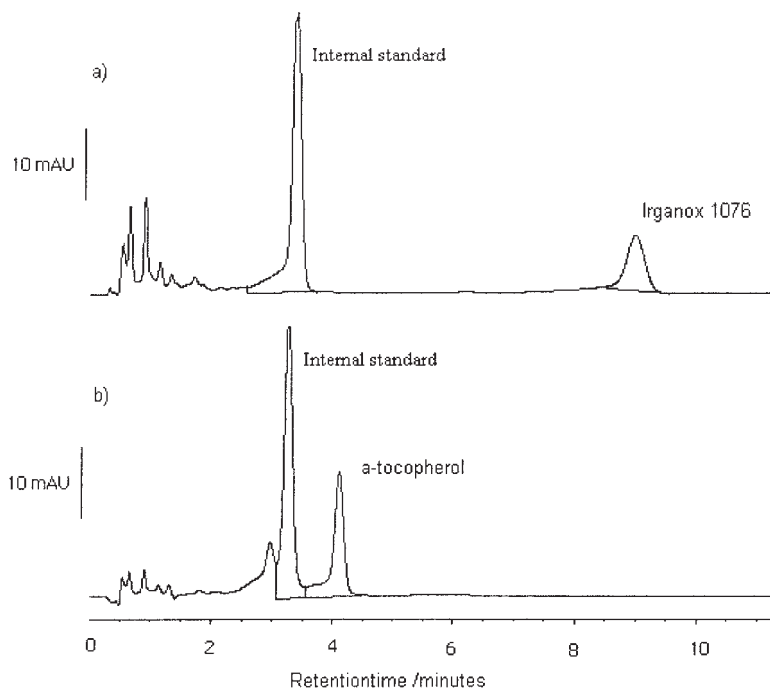
Figure 4 HPLC chromatograms of extracted solutions of film-blown LLDPE after processing: (a) PE-Irg1076) and (b) PE-toc.

under isothermal conditions at 180°C in a pure nitrogen atmosphere with a gas flow rate of 70 mL/min for 42 min. The samples were heated to 180°C at a rate of 10°C/min. TLI was calculated from the CL graphs. All CL values are the means of duplicate measurements.

FTIR spectroscopy

Changes in the carbonyl region during oxidation were monitored with a PerkinElmer Spectrum 2000 FTIR spectrometer. Each spectrum was taken as the average of 20 scans at a resolution of 4 cm^{-1}. The carbonyl index was calculated by a comparison of the peak at 1712–1717 cm^{-1} (chain-end and backbone ketones[17,18]) with that at 1463 cm^{-1} (—CH$_2$— scissoring peak). The instrument was equipped with a Golden Gate ATR unit with a diamond crystal. Analyses were performed both in the transmission mode and in the ATR mode for the film-blown materials, whereas the compression-molded materials were only analyzed with ATR. Triplicate measurements were made for each sample.

RESULTS

The use of natural and nontoxic antioxidants in plastics instead of synthetic ones is of great interest, especially in food and medical applications. In this study, both the process efficiency and long-term stabilizing efficiency of the natural antioxidant α-tocopherol in polyethylene, in comparison with the synthetic antioxidant, were studied with several techniques.

Chromatographic analysis of the residual antioxidant content

In Figure 4, the HPLC chromatograms of the extracted solutions of the film-blown LLDPE containing 0.1% α-tocopherol (PE-toc) and the LLDPE containing 0.1% Irganox 1076 (PE-Irg1076) after processing are shown. The differences in the retention time between the antioxidants and the internal standard can be seen. Figure 5 presents the residual antioxidant content in the film-blown and compression-molded samples after processing. The amount of Irganox 1076 left in the film-blown sample was about 39% higher than the amount of α-tocopherol. The results for the film-blown material agreed with those for the compression-molded material, although less α-tocopherol was detected in the film-blown material. Figure 6 shows the residual antioxidant content in the compression-molded materials during aging. After aging, only about 25% of the initial amount of α-tocopherol was left in the material, in comparison with about 65% of Irganox 1076. The residual content of Irganox 1076 was almost constant during the aging, whereas the amount of α-tocopherol decreased.

Crystallinity and thermal analysis

The crystallinity of the film-blown materials is presented in Table III. The crystallinity decreased by ap-
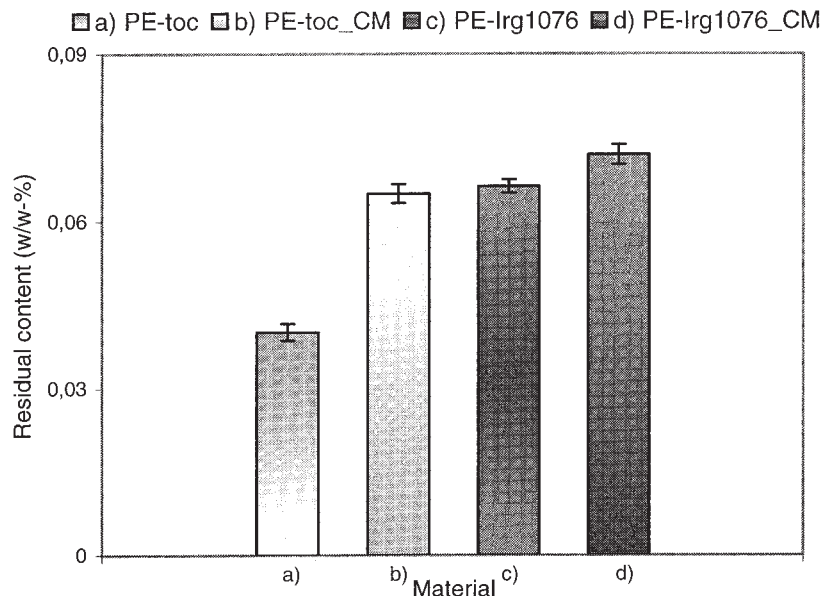
Figure 5 Residual antioxidant content of film-blown LLDPE [(a) PE-toc and (c) PE-Irg1076] and compression-molded LLDPE [(b) PE-toc_CM and (d) PE-Irg1076_CM] after processing, as determined by MAE/HPLC.

proximately 20% during the aging, with only a small difference between the materials. Figure 7 shows the OIT determined with DSC for the compression-molded samples with and without a solvent. Solvents are often used in film preparation to obtain more homogeneous samples. The polymer powder was mixed with the dissolved antioxidant before the processing step. DCM and EtAc were chosen because they are both good solvents for the antioxidants, even if EtAc might be better because of its higher polarity.

OIT was higher for the materials, especially for polyethylene stabilized with Irganox 1076 and compression-molded with a solvent (PE-Irg1076_CM). The OIT values of the materials dissolved in DCM or EtAc showed no difference. The DSC thermograms of the compression-molded materials after processing are displayed in Figure 8. A higher OIT value for the compression-molded material containing α-tocopherol (PE-toc_CM) than for PE-Irg1076_CM is visible. Figure 9 shows the OIT values for the film-blown and
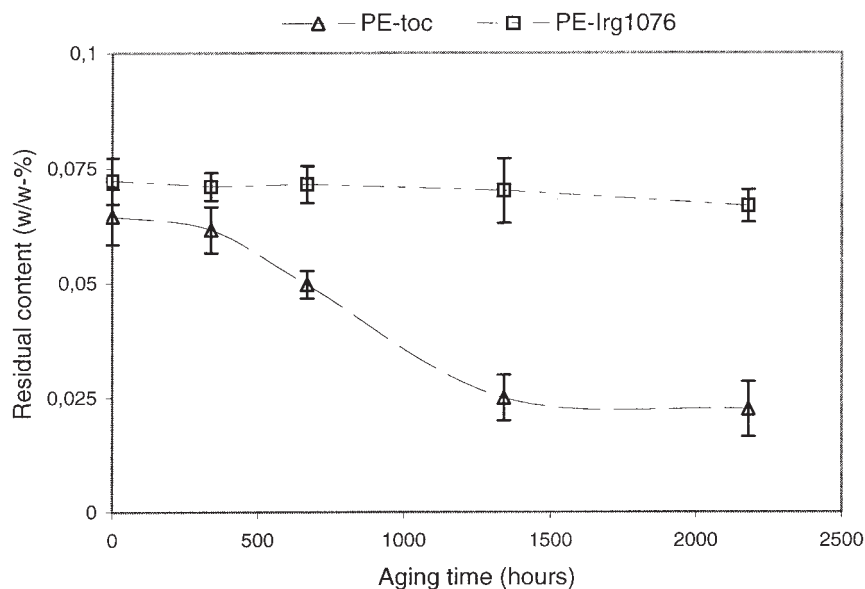
Figure 6 Residual antioxidant content of compression-molded LLDPE during aging in air at 80°C, as determined by MAE/HPLC: ($\triangle$) PE-toc_CM and ($\square$) PE-Irg1076_CM.

TABLE III
Crystallinity (%) of the Film-Blown Samples
During Aging in Air at 80°C

Material	Aging time (h)	
	0	840
PE	43.4 ± 1.1	35.3 ± 0.6
PE-toc	43.3 ± 0.8	33.7 ± 1.8
PE-lrg1076	45.1 ± 0.4	34.1 ± 6.4

Calculated from DSC data.

compression-molded materials after processing. PE-toc had the longest OIT. The results for the compression-molded samples with α-tocopherol and Irganox 1076 agreed with the results for the film-blown samples, even though the difference was greater between the two film-blown materials. Figure 10 shows the OIT values for the aged compression-molded materials. There were no significant differences in the OIT values for the different materials. PE-toc_CM showed the highest initial value, but it decreased more rapidly than that for PE-Irg1076_CM.

CL in an inert atmosphere

The TLI values for the different materials and the different aging times are presented in Figure 11. The CL area was highest in PE-toc, and it exhibited no suppression of CL and no induction time. TLI signals were emitted already from the processed materials. The suppression of CL was high in PE-Irg1076. After 250 h of aging, PE contained less hydroperoxide than PE-toc.

FTIR spectroscopy

Figure 12 displays the FTIR ATR spectra of the compression-molded material after processing and after aging for 2800 h. There was no visible carbonyl absorbance in the compression-molded unstabilized material (PE_CM) even after aging. Figure 13 shows the carbonyl index for the aged film-blown materials measured with FTIR in the ATR mode. There was a significant difference in the long-term stabilizing effect of the two antioxidants, Irganox 1076 and α-tocopherol. PE-Irg1076 had a longer induction time and a lower carbonyl index than PE-toc. Figure 14 presents the FTIR transmission and ATR measurements of the materials during thermal aging. The development of carbonyls was greater on the surface than in the bulk for all materials in the early stages of the aging. After aging, PE had almost the same carbonyl absorbance in the bulk and on the surface. The antioxidants were efficient during the aging, especially in the bulk of the polymer. Up to 340 h of aging, PE-Irg1076 exhibited a very low carbonyl index, whereas the carbonyl index for PE-toc increased linearly from the beginning. Irganox 1076 demonstrated superior bulk stabilization in comparison with α-tocopherol.

DISCUSSION

Process efficiency of α-tocopherol in film-blown and compression-molded LLDPE

There was no significant difference between the crystallinity of the film-blown materials, and this showed that the differences in the oxidation of the materials were not due to differences in the crystallinity. The amount of Irganox 1076 left in the film-blown sample
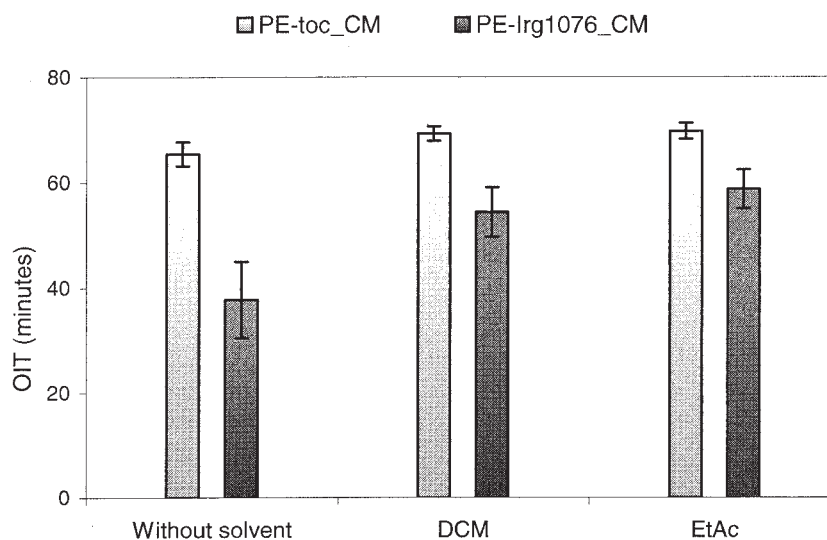
Figure 7 OIT for compression-molded LLDPE with and without the solvents DCM and EtAc: PE-toc_CM and PE-Irg1076_CM.
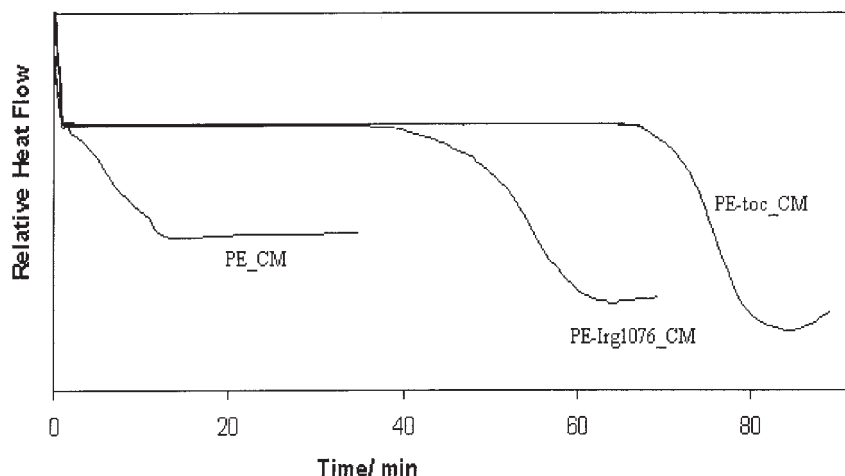
Figure 8   Thermograms of OIT of compression-molded LLDPE after processing: PE-CM, PE-toc_CM, and PE-Irg1076_CM.

was higher than the amount of α-tocopherol after processing according to the chromatographic analysis. This was a result of the fact that α-tocopherol is more volatile and less soluble in the polymer matrix than Irganox 1076 because of its lower molecular weight, shorter aliphatic tail, and lower melting temperature. TLI signals were emitted already from the processed materials according to the CL measurements (Fig. 11), and this showed that the hydroperoxide formation started during the processing. PE-toc had better performance than PE-Irg1076 during the film blowing according to the OIT measurements. Our results agreed with earlier studies in which α-tocopherol was shown to have higher efficiency than synthetic antioxidants in the melt.[4,5] The high OIT value of PE-toc, despite the low residual content, presumably depends on a higher diffusion rate and mobility in the polymer

matrix of α-tocopherol due to the small size and on its low bond dissociation energy for H-donation [19] (Table II). Another possible explanation for the high efficiency of α-tocopherol is its oxidation products, which are chain-breaking antioxidants and deactivate both alkyl peroxyl and alkyl radicals (Scheme 1 and Fig. 2).[4] The oxidation products are said to have an even higher efficiency as stabilizers than α-tocopherol.[4]

The OIT values for the compression-molded samples with a solvent were higher than those for the samples without a solvent (Fig. 7). This demonstrated that the solvent changed the properties of the material and increased the long-term stability. Film blowing will therefore give materials with a greater reliability than compression-molding. There was a larger concentration of antioxidants in the compression-molded material after processing according to the chromato-
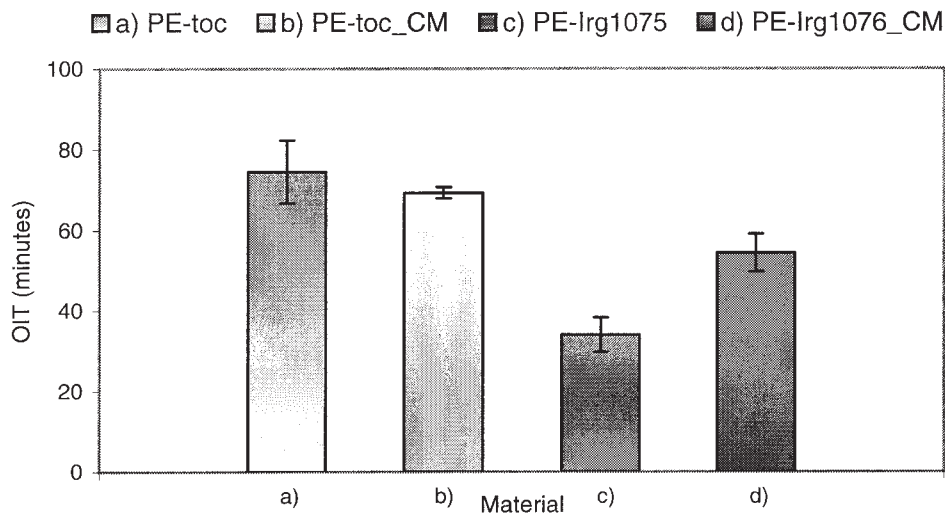
Figure 9   OIT for film-blown LLDPE [(a) PE-toc and (c) PE-Irg1076] and compression-molded LLDPE [(b) PE-toc_CM and (d) PE-Irg1076_CM] after processing.
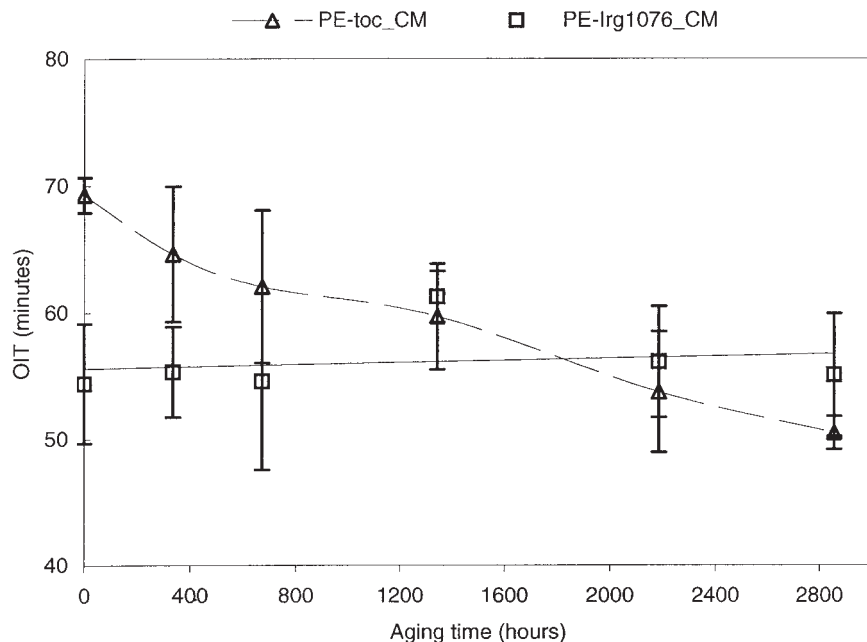
Figure 10 OIT for compression-molded LLDPE during aging in air at 80°C: (△) PE-toc_CM and (□) PE-Irg1076_CM.

graphic analysis. This was due to the gentler processing conditions in the compression molding. The antioxidants were consumed to a greater extent in film blowing, and they evaporated from the thinner film-blown material during the cooling stage. The antioxidants were homogeneously distributed in the melt during processing, but during cooling, polar antioxidants were seen as defects in the semicrystalline polymer. They were excluded from the crystalline phase and were retained in the amorphous phase.[20]

Long-term performance of α-tocopherol in film-blown and compression-molded LLDPE

A reliable study with accelerated aging has to be performed at a temperature as near as possible to the
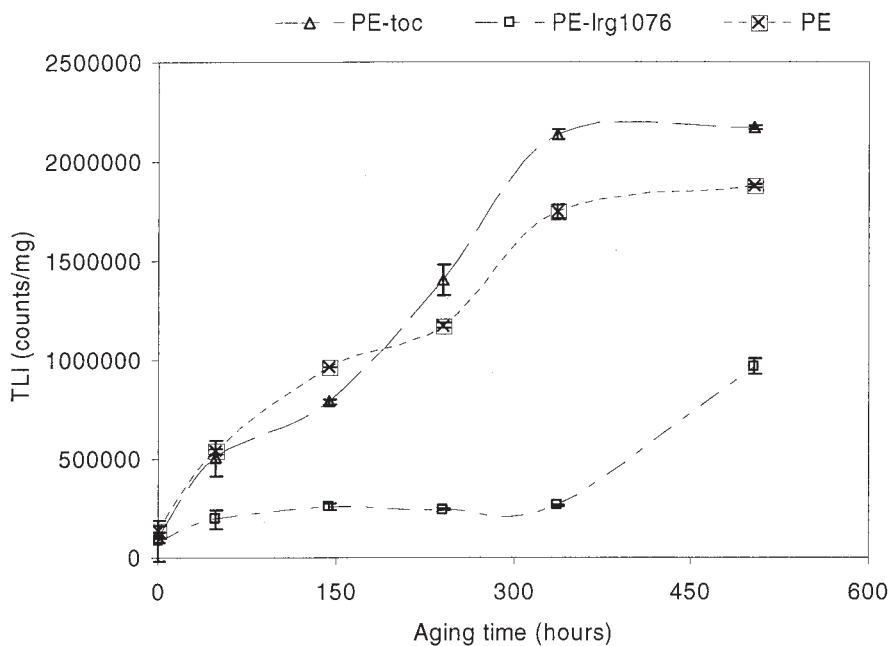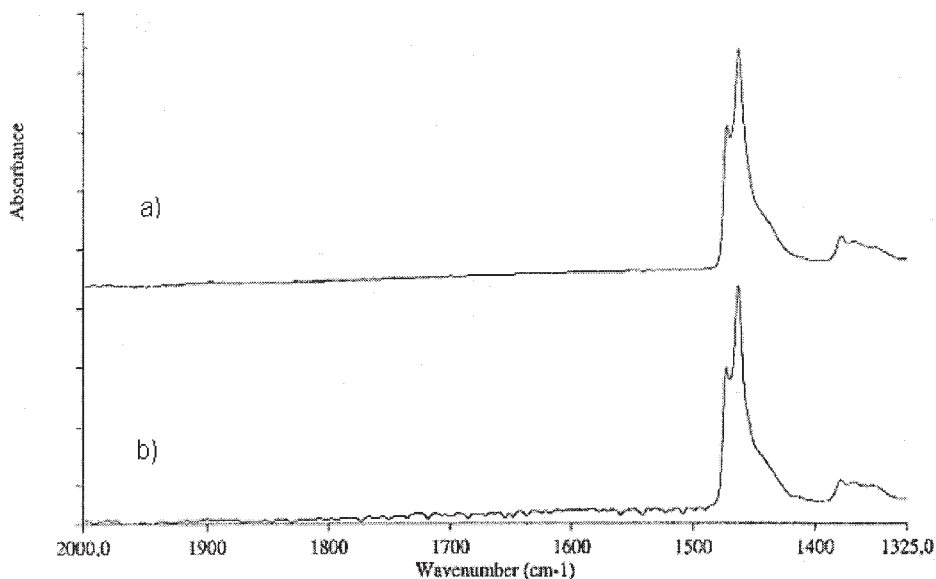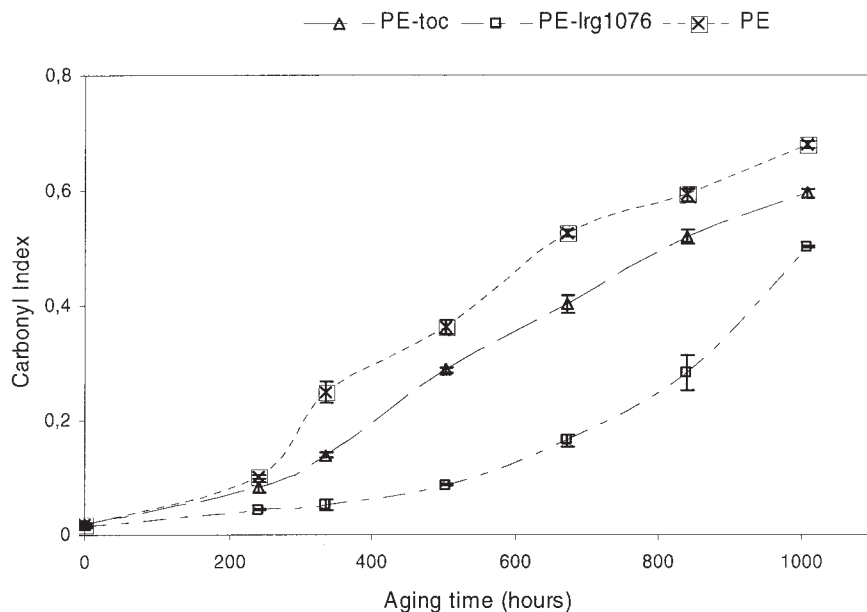

Figure 11 TLI for film-blown LLDPE during aging in air at 80°C: (×) PE, (△) PE-toc, and (□) PE-Irg1076.

Figure 12 FTIR ATR spectra of compression-molded unstabilized LLDPE (a) after processing and (b) after aging in air at 80°C for 2800 h.

intended service temperature. In this study, a quite low temperature for accelerated aging was chosen (80°C). There was a significant difference in the long-term stabilizing effect of the two antioxidants according to the FTIR ATR analysis; PE-Irg1076 had a longer induction time and a lower carbonyl index than PE-toc (Fig. 13). After only a short time of aging, there was a sharp decrease in the performance of α-tocopherol in both the FTIR measurements and TLI (Fig. 11) of the film-blown PE-toc. The fact that less residual content

was extracted from PE-toc after film blowing affected the long-term stability. The prevention of oxidation decreased when fewer antioxidant molecules were present. The crystallinity decreased during the aging in all the materials because of chain scission and oxidative degradation of the crystalline regions[21] (Table III). The oxidation products from α-tocopherol act as process stabilizers,[4] but they are presumably inferior in long-term stabilization because of their high ability to scavenge alkyl radicals but not peroxyl radicals.


Figure 13 Carbonyl index measured with FTIR in the ATR mode during aging in air at 80°C for film-blown LLDPE: ($\times$) PE, ($\triangle$) PE-toc, and ($\square$) PE-Irg1076.
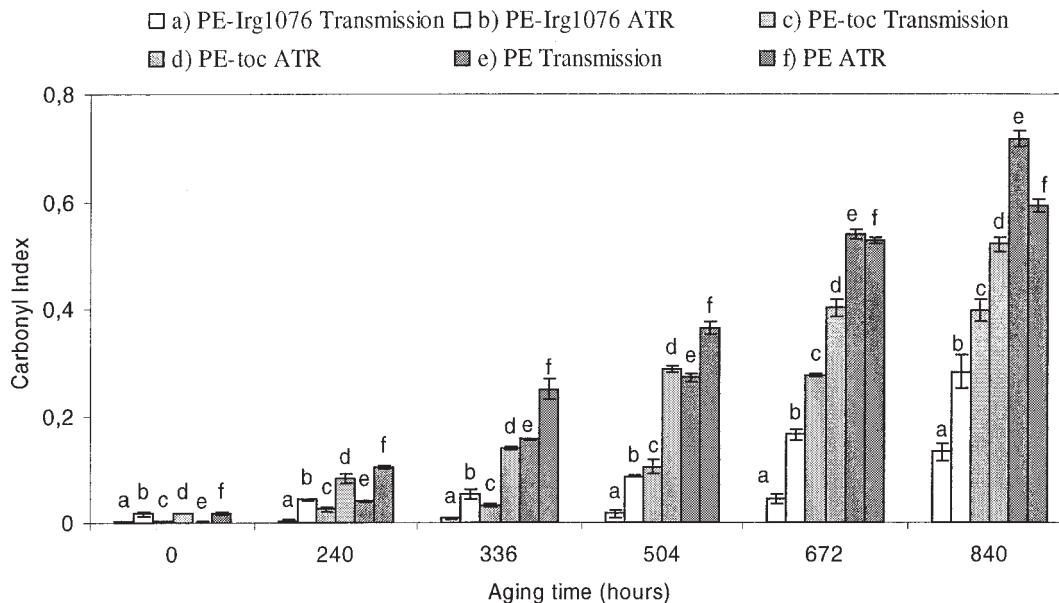
Figure 14 Carbonyl index for film-blown LLDPE during aging in air at 80°: (a) PE-Irg1076 measured in the transmission mode, (b) PE-Irg1076 measured in the ATR mode, (c) PE-toc measured in the transmission mode, (d) PE-toc measured in the ATR mode, (e) PE measured in the transmission mode, and (f) PE measured in the ATR mode C.

The efficiency of α-tocopherol in the long-term stabilization of polymers has been studied, and some reports have postulated that it works better than synthetic hindered phenols,[8] whereas others have reported the opposite.[9] Mallegol et al.[9] studied α-tocopherol in γ-radiated HDPE with FTIR, and Wolf et al.[8] used FTIR, DSC, and mechanical testing to analyze 0.05 and 0.2% α-tocopherol in UHMWPE. The results from this study are difficult to compare with the results of those other studies because of the characterization of another polymer under different conditions and with different amounts of α-tocopherol. For irradiated materials, faster oxidation is usually observed than for only thermally degraded materials. LLDPE is more easily oxidized than HDPE and UH-MWPE and has a higher need for stabilization. The crystallinity is also lower in LLDPE. Early oxidation of the film-blown material was detected in this study with the sensitive CL technique in comparison with the FTIR measurements, without the need for irradiation. We have previously shown that CL under inert conditions is a tool for the early detection of oxidation in a material.[22] The interpretation of a CL graph is often complex because CL light emitters might be quenched or photons can be absorbed in the sample.[23] In this study, the differences in the antioxidant efficiency between samples of the same geometry and history have been compared with CL,[13] and this makes the interpretation easier. After 250 h of aging, PE contained less hydroperoxide than PE-toc. This
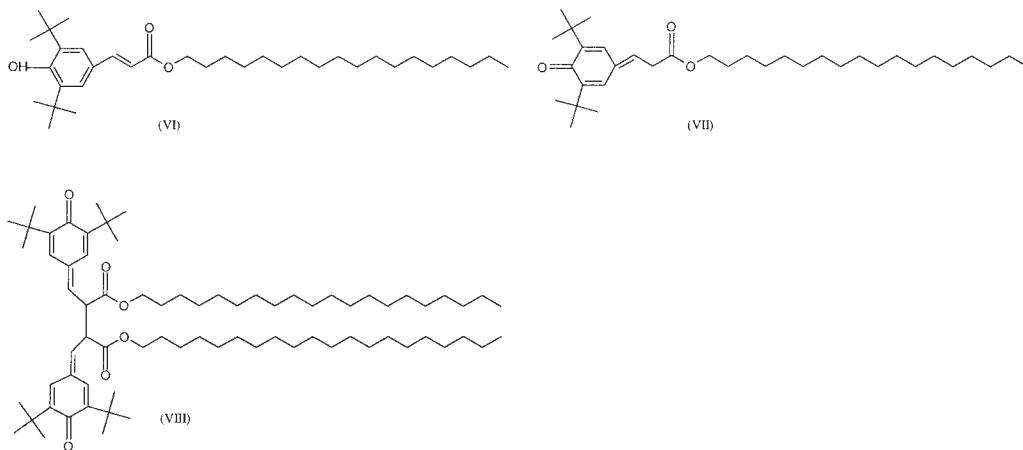
Figure 15 Oxidation products from Irganox 1076: quinone methides (**VI** and **VII**) and dimers (**VIII**).

additive CL was most probably due to the oxidation of α-tocopherol.[24,25] The suppression of CL was high in PE-Irg1076 (Fig. 11). Irganox 1076 had higher long-term efficiency than α-tocopherol because of its longer carbonyl chain, which gave it better solubility and less loss from the polymer matrix. The oxidation products of Irganox 1076 may also improve the efficiency. The propionate group in Irganox 1076 gives oxidation products, and quinone methides (**VI** and **VII**) and dimers (**VIII**) are formed (Fig. 15).[26,27] The quinone methides scavenge carbon-centered free radicals,[28] and their aromatization can subsequently regenerate the phenolic function.[26]

The FTIR transmission and ATR study revealed that the development of carbonyls was much higher on the surface than in the bulk for all the film-blown materials before aging. This was due to surface-limited oxidation. Impurities on the surface gave initially higher oxidation, and in the processing step, there was diffusion-limited oxidation with a depth of approximately 10 μm, which produced a thin layer of oxidation products in the surface of the polymer.[29] The oxidation is said to be more homogeneous in a thin film for which the bulk and the surface are uniformly degraded[30] because the oxidation is chemically controlled and not diffusion-controlled.[29] Our results nevertheless show heterogeneous degradation in the samples, but it was presumably more homogeneous than for thicker compression-molded samples. The antioxidants were efficient during the aging, especially in the bulk of the polymer. Our explanation for this higher surface oxidation is that it is due to the higher surface-limited oxidation in the processing step and due to evaporation and loss of the antioxidant from the surface. The oxidation started therefore on the surface and continued into the bulk. It has been shown that there is an equal distribution of antioxidants in a whole sample after longer aging times,[31] and this indicates that the surface and bulk are evenly degraded. After aging, PE had higher carbonyl absorbance in the bulk than on the surface. One explanation for this is that the carbonyl-containing oxidation products evaporated and were lost from the surface. Our group earlier showed that the gradual increase in carbonyl groups during the oxidation of the polymer chain is followed by a decrease in carbonyl groups when short-chain carboxylic acids are released to the surroundings.[32]

α-Tocopherol exhibited good long-term stabilizing efficiency in the compression-molded material (Fig. 10), especially at the beginning of the aging, although the residual antioxidant content was lower than that of Irganox 1076 (Fig. 6). The residual content of Irganox 1076 was almost constant during the aging, whereas the amount of α-tocopherol decreased. After 1600 h of aging, OIT for PE-toc had decreased to the same level as OIT for PE-Irg1076. This was due to the faster decrease in the residual content of α-tocopherol. There

was no visible carbonyl absorbance in the FTIR ATR spectra of PE_CM after aging. This was due to lower oxidation during the processing, to a thicker material, and to the differences in the aging conditions. The film-blown materials were hanged with a small weight, and a fan affected their aging, whereas the compression-molded materials were aged in sealed glass vials. The stress to which the film-blown materials were exposed during the thermal aging was designed to imitate real conditions in which a modest stress can accelerate chain scission and cause structural weakening with disentanglement, chain slip, and void opening.[33] The tougher aging conditions for the film-blown materials gave earlier and higher oxidation than for the compression-molded materials, according to the FTIR measurements.

CONCLUSIONS

The efficiency of α-tocopherol as a process and long-term antioxidant was studied in comparison with Irganox 1076. The following conclusions can be drawn:

- α-Tocopherol was an efficient antioxidant in the film-blown LLDPE material, especially in the processing. During the long-term stabilization, the efficiency was more reduced than that of the commercial phenolic antioxidant.
- There was less α-tocopherol than commercial phenolic antioxidant in both the film-blown and compression-molded materials after processing, but the process-stabilizing efficiency was nevertheless higher for the material containing α-tocopherol.
- In the compression-molded samples, the long-term stabilizing efficiency of α-tocopherol was equal to that of Irganox 1076 because of the gentler processing conditions, the thicker film, and the lower loss.

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