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Total luminescence intensity (TLI) offers superior early oxidation detection in unstabilised polyethylene but is no better than FT-IR for stabilised polyolefins

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Abstract

In an earlier study, we have shown that chemiluminescence (CL) and the total luminescence intensity (TLI) method are highly sensitive to oxidation in degradable PE. In this study, stabilised PE and PP were characterised with CL in an inert (TLI) and in an oxygen atmosphere (CL-OIT) and the results were compared to those obtained by the commonly used techniques, FT-IR (carbonyl index (CI)) and thermal analysis (DSC-OIT). PE was aged at a low temperature (80 °C) and PP was aged at temperatures between 60 and 120 °C. Non-Arrhenius behaviour was observed in the oxidation of PP. This showed the importance of aging at a low temperature to obtain realistic results. TLI and CI of stabilised PP and most of the stabilised PE gave comparable results with the same sensitivity for oxidation detection. This was in contrast to our previous results for degradable PE. However, TLI of unstabilised PE showed earlier oxidation detection than CI, which agreed with our earlier results. TLI of PE had a higher sensitivity than CL-OIT, and both TLI and CI of PP were sufficiently sensitive to detect the effect of aging at different temperatures, whereas DSC-OIT was not.

Keywords: Chemiluminescence (CL); Infrared spectroscopy (FT-IR); Differential scanning calorimetry (DSC); Stabilisation; Polyolefins

1. Introduction

In most applications, e.g., in medical and food packaging, in pipes and in automobile components, knowledge about and an optimisation of the long-term properties and lifetimes of stabilised polyolefins are important. Sensitive and accurate characterisation techniques are required to achieve this, and rapid techniques to save time and expense are also essential. Chemiluminescence (CL) measured in an inert atmosphere has been shown to be a sensitive technique to detect both oxidation in polypropylene (PP) and early oxidation in degradable polyethylene (PE) [1]. Fourier transform infrared spectroscopy (FT-IR) is a reliable technique with simple sample handling and measurements are performed on the solid polymer with intact antioxidant action and morphology. Both CL and differential scanning calorimetry (DSC) are measured on the melted polymer, and this affects the distribution of

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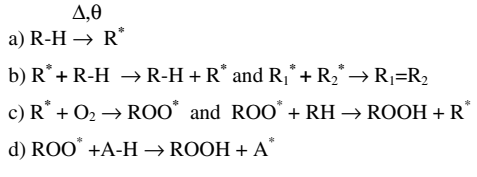
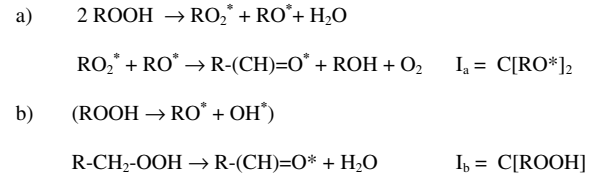
the antioxidant in the polymer. Thermal acceleration is commonly carried out to determine the long-term properties of a polymeric material within a reasonable time frame. For reliable results, the accelerated testing must be performed at the lowest possible temperature at which both time and performance are optimal, because the results of an accelerated test are not easily extrapolated to lower usage temperatures. It is of interest to use the CL technique to measure oxidation in polyolefins, since products initially formed in the oxidation process are monitored. Degradation in polyolefins is initiated during the processing step by the formation of unstable alkyl radicals (R^*) due to shear (θ) and high temperature (Δ) (Scheme 1a). In an unstabilised material, the alkyl radicals lead to the formation of double bonds and new radicals due to the low amount of oxygen (Scheme 1b). The oxidation starts in, e.g., a film-blowing process directly after the processing and continues due to auto-oxidation (Scheme 1c). In a stabilised material, consumption of the antioxidants occurs instead of degradation and oxidation. Phenolic antioxidants (AH) react primarily with alkoxy radicals (Scheme 1d) and their oxidation products, e.g., quinones react with alkyl radicals.

The CL technique is based on the measurement of light emitted from the surface of a material. The light-producing reaction requires an energy input of about 300 kJ/mol with a low quantum yield [2,3]. Spectral analysis of the emission agrees with emission from carbonyl chromophores [3]. The mechanism for the carbonyl formation is debated, but the direct decomposition of hydroperoxides (ROOH) [4] or the bimolecular termination of alkyl peroxy radical (ROO*) [5] (Scheme 2) are the most probable mechanisms in a solid material. A combination of several light emission processes may also occur [3]. An uncertainty in the mechanism causing CL can make the interpretation of CL data problematic, but the equality of the rates of initiation and termination for a linear steady-state chain reaction makes the luminescence intensity (I) of both mechanisms in



Scheme 1. (a) Initiation of degradation, (b) reactions with a lack of oxygen, (c) auto-oxidation, and (d) mechanism of a phenolic antioxidant.



Scheme 2. (a) Direct decomposition of hydroperoxides, (b) bimolecular termination of alkyl peroxy radical.

Scheme 2 equivalent for stationary experiments [6]. The kinetic relationship for CL generated under stationary conditions may therefore be written $I = C[\mathrm{ROOH}]$, where C is a constant.

CL has been compared to other techniques to determine its accuracy and sensitivity and to gain information on the mechanism. During the early stages of oxidation, the concentration of titratable peroxides in unstabilised PP has been shown to be proportional to the total luminescence intensity (TLI) emitted when an oxidised polymer is heated in an inert atmosphere [7]. Blakey et al. have monitored the simultaneous response in CL emission and in FT-IR emission spectra of unstabilised and soxhlet-extracted PP with a combined CL instrument and FT-IR spectrophotometer [8]. They found that the CL vs. time curve in an oxygen atmosphere was proportional to the carbonyl growth vs. time curve. However, in non-soxhlet-extracted, unstabilised PP, the concentration of hydroperoxides increased rapidly to a maximum and then decreased while the carbonyl curve increased [9]. This gives a relationship where the concentration of carbonyls at a given point in time is proportional to the integral of the hydroperoxide concentration [8]. CL in an air atmosphere and thermogravimetry have been shown to be more effective techniques for detecting oxidation in degradable PE than FT-IR, DSC and size exclusion chromatography [10]. TLI has also been shown to be more sensitive and to give an earlier detection of oxidation than FT-IR on pre-oxidised degradable PE [1]. Chromatographic analysis has been shown to be a useful complement to TLI [11]. The oxidation of stabilised polyolefins has been studied by CL in both oxygen and nitrogen atmospheres. Catalina et al. [12] investigated the process stability of phenolic antioxidants in PE with CL in an inert atmosphere and made iodometric measurements, which measure the concentration of titratable peroxides in a material. In the isothermal measurements, the peak intensity and the area under the peak were proportional to the reaction rate of peroxides [12,13].

In earlier studies we have shown that the relatively new technique of chemiluminescence (CL) is highly sensitivity to oxidation in degradable PE. The aim of this study has been to characterise stabilised polyolefins (PE and PP) with CL in both an inert (TLI) and an oxygen atmosphere (CL-OIT) and to compare the results with those from the more commonly used techniques, FT-IR (carbonyl index) and thermal analysis (DSC-OIT). PP has been aged at temperatures between 60 and 120 °C to observe the effect of temperature on the oxidation and on the sensitivity of the techniques. PE has been aged at a low temperature (80 °C) to obtain reliable and realistic results. Our first hypothesis is that antioxidant action in the stabilised materials will reduce both the TLI and carbonyl index so that they will be equally sensitive to oxidation in the materials, and our second hypothesis is that OIT-values determined with CL and DSC will be similar and that these methods will be less sensitive than TLI and FT-IR.

2. Experimental

2.1. Materials

Unstabilised linear low-density polyethylene (PE) (crystallinity = 43%, melting point = 123 °C) was supplied by Borealis (Stenungsund, Sweden) and unstabilised polypropylene (PP) was supplied by Borealis (Switzerland). 3,4-Dihydro-2,5,7, 8-tetramethyl-2-(4,8,12-trimethyltridecyl)-2H-1-benzopyran-6-ol (α-tocopherol) and octadecyl 3,5-di(tert)-butyl-4-hydroxyhydrocinnamate (Irganox 1076) were obtained from Ciba Specialty Chemicals (Basel, Switzerland). Oat starch (OS) was obtained from the Avena group (Finland). The chemical constitution of the OS was 29% amylose, 71% amylopectin, 10% moisture, 0.2% ash, 0.6% protein and 0.7% total lipids. Poly(ethylene-co-acrylic acid) (EAA), with 15 wt% acrylic acid, and calcium stearate (Ca St) were obtained from Sigma–Aldrich (Sweden). PE 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. PP films with a thickness of 45 ± 5 μm were film-blown on a two-layer axon line with an extruder screw diameter of 18 mm. The content of additives in the films is presented in Table 1. Samples 5×10 cm in size were cut from the films. The PE samples were placed in a circulating air oven from Heraues (Hanau, Germany) under a tensile load of 10 g and at a temperature of 80 °C. The films were characterised only up to 35 days of aging because the low thickness of the films and the applied weight were expected to give faster aging than in commonly studied thicker films. The PP samples were place in a circulating air oven (Venticell 111, Germany) at 60, 80, 100 or 120 °C.

2.2. Analytical techniques

2.2.1. Chemiluminescence (CL)

CL of the materials was studied using a Lumipol-2 CL instrument (Polymer Institute SAS, Slovakia). Standards that luminesce when they are heated were used to calibrate the temperature. The analysis of CL data is often complex because light emitters may be quenched and photons may be absorbed in the sample [14]. Care was therefore taken to ensure that the PE and the PP samples in this study had the same geometries and histories [7]. The specimens were prepared by punching circular discs with a diameter of 6 mm from the films and they were placed in aluminium pans with a diameter of 10 mm.

Table 1
Composition of the PE and PP films, values in wt%

Material	Antioxidant		Additive		
	α-Tocopherol	Irganox 1076	Oat starch	EAA	Ca St
PE-ref	–	–	–	–	–
PE-toc	0.1	–	–	–	–
PE-Irg1076	–	0.1	–	–	–
PE-EAA/toc	0.1	–	–	1	–
PE-EAA/Irg1076	–	0.1	–	1	–
PE-OS/toc	0.1	–	1	–	–
PE-OS/Irg1076	–	0.1	1	–	–
PP-toc	0.1	–	–	–	0.1
PP-Irg1076	–	0.1	–	–	0.1

All CL values are the means of duplicate measurements.

2.2.1.1. Inert measurements. Measurements on both the PE and PP samples were carried out in an inert atmosphere of pure nitrogen with a gas flow rate of 70 ml/min. Isothermal measurements were made on the PE samples, after they had been preheated to the test temperature (180 °C) at which the temperature was kept constant. The PP samples were tested dynamically with a ramp of 2.5 °C/min from 60 to 180 °C. The total luminescence intensity (TLI) was calculated from the area under the curve of the isothermal measurements of PE [12,13] and of the ramp measurements of PP [7]. The *TLI induction time* was determined for the PP samples as the time before a distinct increase of the TLI was observed.

2.2.1.2. Oxidative measurements. CL measurements were made on the PE samples in an oxidative atmosphere under isothermal conditions at 180 °C with a gas flow rate of 70 ml/min, and the oxygen induction time (CL-OIT) was determined as the point of intersection between the base line and the tangent to the curve. The samples were preheated to the test temperature under a nitrogen atmosphere.

2.2.2. Fourier transform infrared spectroscopy (FT-IR)

Changes in the carbonyl region during oxidation were monitored by a Perkin Elmer 2000 FT-IR Spectrometer. The spectra were taken as an average of 20 scans at a resolution of 4 cm^{-1}. The carbonyl index (CI) was calculated as the ratio of the peak height at 1712–1717 cm^{-1} (chain-end and backbone ketones), to that at 1463 cm^{-1} (–CH_2-scissoring peak) for PE and with that at 1452 cm^{-1} for PP. The reference peak was close to the carbonyl peak. This is important when ATR measurements are made due to differences in the information depth otherwise. The instrument was equipped with a Golden Gate Attenuated Total Reflection (ATR) unit (Specac Inc., Smyrna, GA, USA) with a diamond crystal. Triplicate measurements were made on each sample. The *CI induction time* was determined for the PP samples as the time before a distinct increase in the CI was observed.

2.2.3. Differential scanning calorimetry (DSC)

A Mettler Toledo 820 DSC equipped with a TSO801RO sample robot was used to measure the oxygen induction times (DSC-OIT) of the materials. High purity indium ($T_m = 156.6$ °C) was used for temperature and enthalpy calibration before the analyses. 5 ± 1 mg samples were enclosed in 100 μl Al crucibles with one hole in the cover. The measurements were made in an oxygen atmosphere with a flow rate of 80 ml/min at 180 °C. During the first 2 min, the samples were kept under nitrogen (80 ml/min) and this time was taken as zero time. The values were obtained as the point of intersection of the base line and the tangent to the curve at 1 mW deviation from the base line. Triplicate measurements were made for each sample.

3. Results and discussion

The sensitivity and repeatability in the detection of oxidation by chemiluminescence (CL) in an inert and in an oxygen atmosphere were compared to those of the commonly used techniques, FT-IR and thermal analysis, in monitoring unstabilised and stabilised polyethylene (PE), aged at 80 °C, and stabilised polypropylene (PP) aged at temperatures between 60 and 120 °C.

3.1. Non-Arrhenius behaviour of stabilised PP

Stabilised PP was subjected to accelerated aging at 60, 80, 100, and 120 °C. Fig. 1 shows the Arrhenius plot of the induction time versus the inverse of the aging temperature. The plot shows a curvature at low temperature. This is well known [15,16]. This

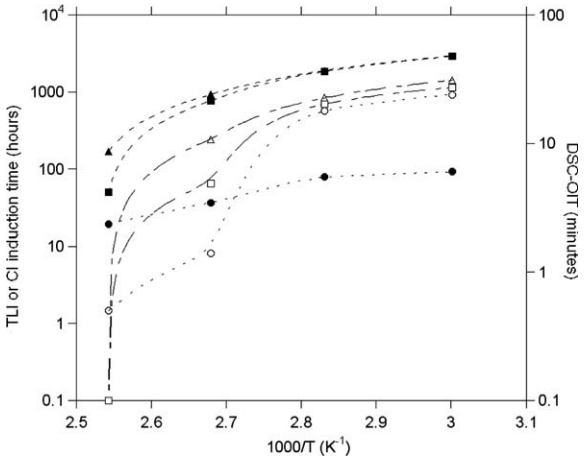


Fig. 1. The Arrhenius plot (60–120 °C) of PP containing 0.1% α-tocopherol (PP-toc) (un-filled spots), and PP containing 0.1% Irganox 1076 (PP-Irg1076) (filled spots). DSC-OIT (○, ●) after 7 days of aging, carbonyl index induction times (△, ▲), and TLI induction time (□, ■).

curvature means that a linear extrapolation of the induction time from a higher to a lower temperature will be misleading, and that the extrapolated induction time will be shorter than the real induction time. The nonlinearity in the Arrhenius plot of PP has been explained as being due to a catalyst effect of residues from the processing step [17] and also by temperature-dependent mechanisms and processes [18]. It is said that Ti-catalysed hydroperoxide decomposition occurs at a low but not at a high temperature, and that this leads to a temperature-dependence of the peroxide concentration in the material [17]. This leads to an additional oxidation mechanism at low temperature, causing the observed nonlinearity. A cross-over temperature [19] of about 80 °C where a change in mechanism occurs [18] has been seen in PP. This is due to a difference in activation energy between the reactions occurring at high and low temperature. The polymer morphology, the solubility and migration of additives and the mechanism of antioxidant loss depend on the temperature [20]. The antioxidants are retained in the amorphous phase in semi-crystalline polymers and the free volume fraction changes with increasing temperature. The morphology and diffusional characteristics change with the temperature, affecting the oxygen permeability of the material.

3.2. CL techniques: Comparison of oxidation detection in PE by TLI and OIT

Figs. 2 and 3 and Table 2 show the results of chemiluminescence (CL) measurements on stabilised PE performed in an inert atmosphere and in an oxygen atmosphere. As mentioned in the introduction the CL intensity is related to the concentration of hydroperoxides in the material. In an inert atmosphere, no further oxidation of the polymer is possible but they still emit light. The CL intensity increases up to a maximum when the polymer is heated and then decreases. The inert atmosphere measurements were made at 180 °C. It has earlier

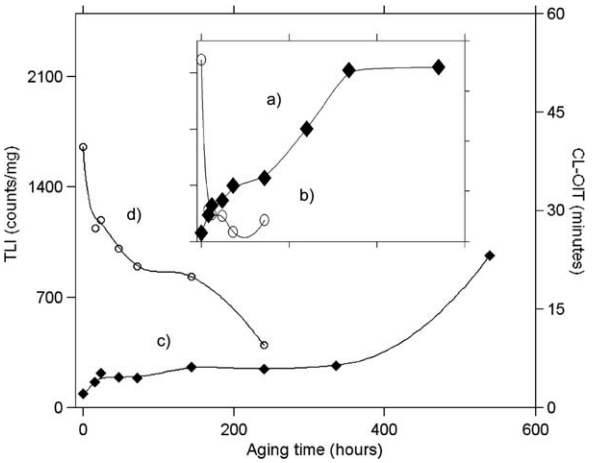


Fig. 2. TLI (–◆–) and CL-OIT (–○–) versus the aging time, in air at 80 °C: (a) TLI of PE containing 0.1% α-tocopherol (PE-toc), (b) OIT of PE-toc, (c) TLI of PE containing 0.1% Irganox1076 (PE-Irg1076), and (d) OIT of PE-Irg1076. The scales on the inserted graphs are the same as in the figures.

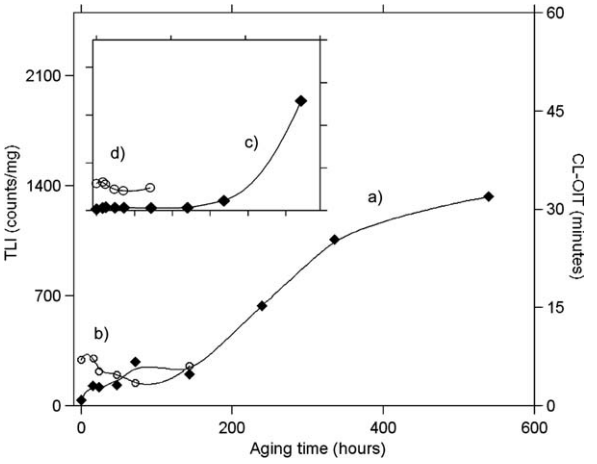


Fig. 3. TLI (–◆–) and CL-OIT (–○–) versus the aging time, in air at 80 °C: (a) TLI of PE containing 0.1% α-tocopherol and 1% EAA (PE-EAA/toc), (b) OIT of PE-EAA/toc, (c) TLI of PE containing 0.1% Irganox 1076 and 1% EAA (PE-EAA/Irg1076), and (d) OIT of PE-EAA/Irg1076. The scales on the inserted graphs are the same as in the figures.

Table 2
TLI and CL-OIT of PE containing oat starch and α-tocopherol (PE-OS/toc) or Irganox1076 (PE-OS/Irg1076), during aging in air at 80 °C

Material	Method	Aging time (h)					
		0	16	24	48	72	144
PE-OS/toc	TLI × 10^3 (counts/mg)	12.5	286.6	477.5	453.2	619.0	648.2
	OIT (min)	41.0	5.5	5.3	4.5	3.8	3.8
PE-OS/Irgl076	TLI × 10^3 (counts/ing)	92.9	151.2	118.1	188.5	189.5	132.3
	OIT (min)	31.5	28.3	23.0	22.5	28.8	16.5

been shown that at a given temperature the emission of CL from the polymer samples, i.e., the area under the curve, denoted the total luminescence intensity (TLI) is proportional to the hydroperoxide concentration before measurement [12,13]. In an oxygen atmosphere, the CL measurements on stabilised samples show an induction period before a rapid increase in oxidation, during which the antioxidants are consumed. This oxidation induction time (CL-OIT) was monitored. The mechanism for CL emission in polyethylene is believed to involve the steps in Scheme 2. It requires at least one of the combining radicals to be primary or secondary. Fig. 2 shows the TLI and CL-OIT graphs for the material containing α-tocopherol (PE-toc) and for the material containing Irganox 1076 (PE-Irg1076) during the aging. The samples were pre-oxidised by oven-aging. A low aging temperature (80 °C) was used to enable more true long-term properties of the materials to be determined. As discussed in Section 3.1, a cross-over temperature of about 80 °C has been observed for PP. Non-Arrhenius behaviour of the induction time has also been observed for PE [21,22]. An aging temperature that is below the melting temperature is important; a temperature of 80 ± 20 °C will give more realistic results in an acceptable period of time. The two methods (TLI and OIT) agreed for both PE-toc and PE-Irg1076. The TLI increased at almost the same time as the OIT decreased. For PE-Irg1076, very good agreement is visible; depletion of almost all antioxidant from the material occurs at the same time as the TLI and the concentration of hydroperoxides in the material increase. Table 2 presents TLI and CL-OIT data for the materials containing α-tocopherol and starch (PE-OS/toc) and Irganox 1076 and starch (PE-OS/Irg1076). Behaviour similar to that of PE-toc and PE-Irg1076 is visible, showing that the addition of starch had only a small effect on the long-term properties of the materials. TLI and CL-OIT of the materials containing poly(ethylene–co-acrylic acid) (EAA), (PE-EAA/toc and PE-EAA/Irg1076) during aging are shown in Fig. 3. No agreement between the two techniques is evident. The OIT values were low, indicating a low antioxidant concentration in the materials. The TLI curve showed an induction time, which was over 150 h for PE-EAA/toc and 300 h for PE-EAA-Irg1076, meaning that the hydroperoxide concentration in the materials was low until the rapid increase occurred. This indicates, in contrast to the OIT, that the material was efficiently stabilised. A plausible explanation of the low TLI is that the material somehow hindered the hydroperoxide build-up; EAA has earlier been shown to act as a migration-controller for surfactants [23]. Another explanation is that the TLI results are more reliable since they are performed in a nitrogen atmosphere and only show the inherent oxidation. The TLI curve also agreed with the carbonyl index measurements presented in the next section. We have earlier shown that OIT measurements are suitable to for screening a materials thermo-oxidative stability after processing [24,25].

3.3. Sensitivity of TLI and carbonyl index for oxidation detection in stabilised PP and in unstabilised and stabilised PE

The TLI and carbonyl index data for all the studied PE materials are shown in Fig. 4. For legibility, no error bars are presented in the figures. The standard deviation of the carbonyl index measurements was low (7%), but that of the TLI measurements was larger (13%). FT-IR ATR measurements were performed and not transmission measurements. It is of interest to compare ATR to TLI because ATR gives an earlier indication of oxidation since the surface is analysed and not both the surface and the bulk of the sample. Unstabilised polyethylene (PE-ref), PE-toc, and PE-OS/toc exhibited a higher build-up in TLI than in carbonyl index during the aging. The other materials: PE-Irg1076, PE-OS/Irg1076, PE-EAA/Irg1076 and PE-EAA/toc showed similar results with the two techniques. The agreement between the CL and FT-IR techniques in monitoring the long-term properties of polyolefins is also evident in Fig. 1, where the induction times determined from both TLI and FT-IR measurements of stabilised PP are shown. Table 3 presents the data on which the induction times are based. The agreement between the techniques is explained by the phenolic antioxidant mechanism in the material. Hindered phenols act primarily as hydrogen donors (Scheme 2d). The transformation of peroxy radicals into hydroperoxides prevents a rapid increase in the total amount of free radicals. The reaction of the antioxidants with peroxy radicals decreases both the CL signal and the carbonyl build-up in the materials until the induction time is reached. During the induction period, only a slow oxygen uptake takes place, the stabiliser is consumed and a small increase in hydroperoxides can be seen in the TLI values. After the induction period, degradation of the material occurs with carbonyl build-up and a rapid

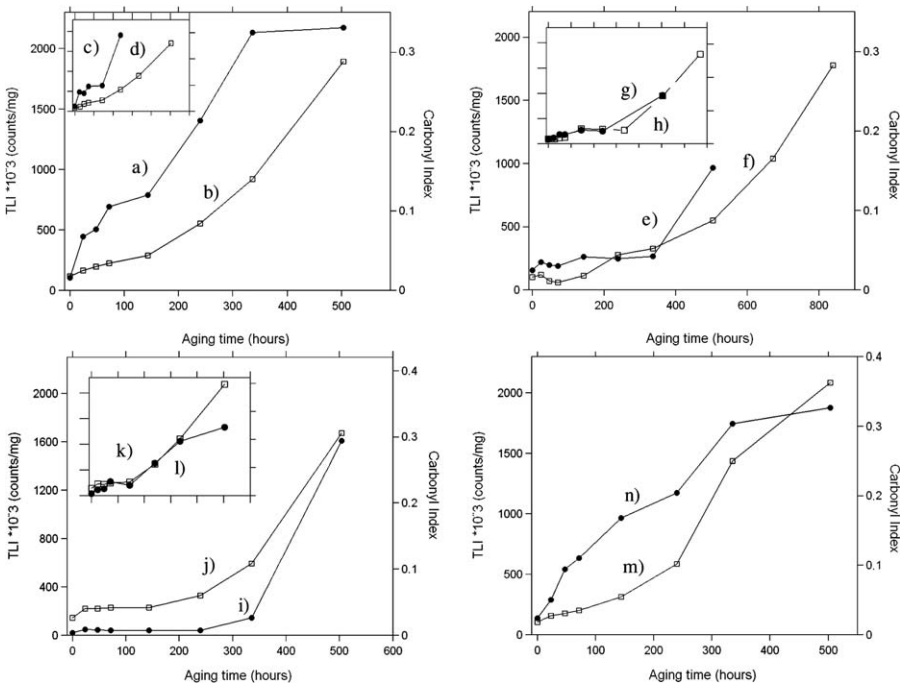
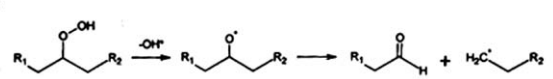


Fig. 4. Plots of TLI (●) and carbonyl index (CI) (□) up to 504 h or 840 h of aging in air at 80 °C: (a) TLI of PE-toc, (b) CI of PE-toc, (c) TLI of PE-OS/toc, (d) CI of PE-OS/toc, (e) TLI of PE-Irg1076, (f) CI of PE-Irg1076, (g) TLI of PE-OS/Irg1076, (h) CI of PE-OS/Irg1076, (i) TLI of PE-EAA/Irg1076, (j) CI of PE-EAA/Irg1076, (k) TLI of PE-EAA/toc, (l) CI of PE-EAA/toc, (m) TLI of PE-ref, and (n) CI of PE-ref. The scales on the inserted graphs are the same as in the figures.

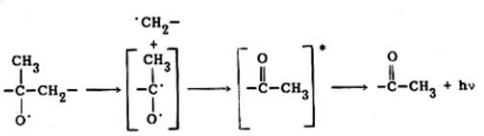
increase in hydroperoxide concentration. This is visible in Fig. 4e–l and in Table 3. With FT-IR, the carbonyl absorption at 1712 cm^{-1} in the IR spectra was measured, and related to a reference peak. The formation of carbonyls on the polymer main chain is believed to occur through the decomposition of hydroperoxides (Scheme 3a). β-Scission can also lead to carbonyl formation by decomposition of a hydroperoxide and the formation of aldehydes [26]

a) ROOH → [$ROO^{*} + OH^{*}$] → -(C=O)- + H_2O

b)



c)



Scheme 3. (a) Formation of carbonyls on the polymer main chain through the decomposition of hydroperoxides, (b) formation of carbonyls through β-scission, and (c) mechanism for CL emission in PP by β-scission of alkoxy radicals.

(Scheme 3b). The CL mechanism in an oxygen atmosphere is debated. The existence of an excited ketone is known, but its origin has not been determined. Both unimolecular hydroperoxide decomposition and bimolecular hydroperoxide decomposition are possible routes for the creation of the ketone. Since the main site of oxidation of PP is the tertiary C–H bond, no CL is expected from this polymer. Actually, PP does luminesce and it is more emissive than PE. For PP the route in Scheme 3c is proposed [27].

In the case of PE-ref, PE-toc and PE-OS/toc oxidation was detected earlier with TLI than with the carbonyl index. It has earlier been shown that the concentration of carbonyls in unstabilised PP at a given point in time is proportional to the integral of the hydroperoxide concentration [8]. The difference seen in Fig. 4a–d between the CL and FT-IR measurements for PE-toc and PE-OS/toc may have been due to the oxidation of α-tocopherol [28,29], which would have contributed to an early increase in TLI. It has been revealed that antioxidants can add to the CL intensity and they are therefore often removed from the polymer by soxhlet-extraction before CL analysis. Our results show that α-tocopherol gave

Table 3
TLI and carbonyl index of PP containing α-tocopherol (PP-toc) and containing Irganox 1076 (PP-Irg1076) aged at different temperatures

Aging temperature (°C)	Aging time (h)	TLI × 10^3 (counts)		Carbonyl index	
		PP-toc	PP-Irg1076	PP-toc	PP-Irg1076
60	0	143.7	122.8	0	0
	144		163.5		
	264	425.7	201.7	0	0
	912	1555.77	247.0		
	1416	15067.2	234.1	0	0
	1944	35232.8	263.2	0.172	0.029
	2640		1985.5		
	2952		7003.0		0.015
	3120		29235.4		0.136
80	0	143.7	122.8	0	0
	96	193.0	208.8		
	264	338.7	89.9	0	0
	504	696.5	166.4		
	840	1105.5	511.2	0	
	1176	4421.3	219.6	0.047	0
	1512		432.0		0.012
	1872		86.0		0.009
	2208		40880.7		
100	0	143.7	122.8	0	0
	24	124.2	91.2		
	72	185.9	100.7		
	168	361.0	213.4	0	
	240	413.3	201.4		
	336	754.0	196.8	0.023	
	408	810.2	163.0		
	504		347.0	0.034	
	600		473.5		0
	912		342.5		
	1440		3389.2		0.041
120	0	143.7	122.8	0	0
	24	250.4	238.3	0.013	
	48	290.7	291.5		
	96	478.0	423.7	0.012	0
	168	598.0	693.6		0
	264		1402.9		
	336		2781.0		0.061

no contribution to the CL intensity in the inert atmosphere measurements because the TLI build-up of PE-ref was very similar to that of PE-toc and PE-OS/toc. Our explanation is that PE-toc and PE-OS/toc were poorly stabilised during the aging, with a high peroxide concentration in the materials and consequently high TLI-values. No antioxidant action could be seen during the aging. Fig. 5 shows the CL intensity, measured under isothermal conditions in an inert atmosphere, of PE-ref, PE-toc and of PE-Irg1076 at two aging times and for the unaged samples. Fig. 6 shows the FT-IR spectra for the same samples. A considerable increase in TLI was seen already after 16 h in the case of PE-ref and PE-toc, whereas the FT-IR spectra show no increase in the carbonyl region after this period of aging. After 144 h, PE-Irg1076 showed a small increase in TLI but no carbonyl absorbance. The detection of CL before the detection of carbonyls in the materials is expected, since hydroperoxides can be formed already during the processing (Scheme 1c). They also show a gradual decrease in stability, decomposing to carbonyl groups (Scheme 3a and b) [30]. This is in accordance with our earlier study where TLI, determined from ramp experiments, was shown to be more sensitive and to give an earlier detection of oxidation than FT-IR on degradable PE [1]. The FT-IR measurements were less sensitive to this

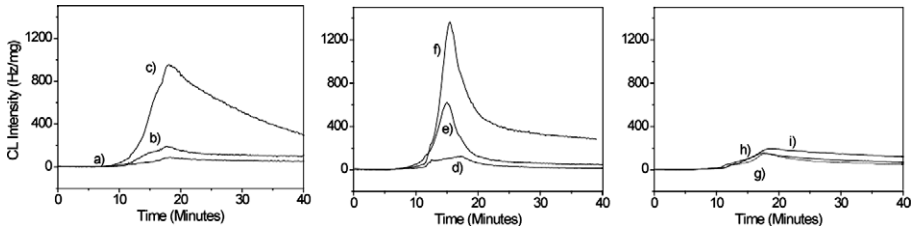


Fig. 5. TLI versus the aging time, in air at 80 °C, of PE: (a) unstabilised (PE-ref) unaged, (b) PE-ref aged 16 h, (c) PE-ref aged 144 h, (d) containing 0.1% α-tocopherol (PE-toc) unaged, (e) PE-toc aged 16 h, (f) PE-toc aged 144 h, (g) containing 0.1% Irganox 1076 (PE-Irg1076) unaged, (h) PE-Irg1076 aged 16 h and, (i) PE-Irg1076 aged 144 h.

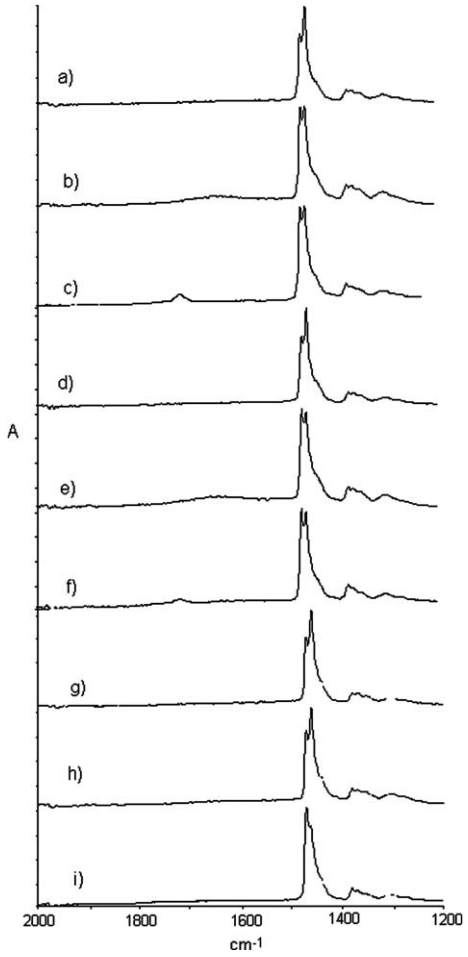


Fig. 6. FT-IR ATR spectra of PE: (a) unstabilised (PE-ref) unaged, (b) PE-ref aged 16 h, (c) PE-ref aged 144 h, (d) containing 0.1% α-tocopherol (PE-toc) unaged, (e) PE-toc aged 16 h, (f) PE-toc aged 144 h, (g) containing 0.1% Irganox 1076 (PE-Irg1076) unaged, (h) PE-Irg1076 aged 16 h and, (i) PE-Irg1076 aged 144 h, in air at 80 °C.

early oxidation. The TLI method was therefore considered to be a suitable technique for determining the stability of the materials at an early stage of aging.

3.4. Characterisation of oxidation of stabilised PE and PP by OIT

3.4.1. Comparison of OIT of PE measured by CL and DSC

The relation between the OIT determined by CL and by differential scanning calorimetry (DSC) of PE-toc and PE-Irg1076 during aging is shown in Fig. 7. The correlation between the techniques was good for PE-toc but less good for PE-Irg1076. The standard deviation of the DSC-OIT measurements was 10% and that of the CL-OIT measurements was 20%. OIT-values determined by DSC and by CL on PP have earlier been shown to be in good agreement [31]. The OIT-values were determined on pre-oxidised samples. The DSC-OIT then measures the remaining phenolic antioxidant efficiency in the materials [32]. That is, the time at which all the antioxidants are consumed and a significant oxidative

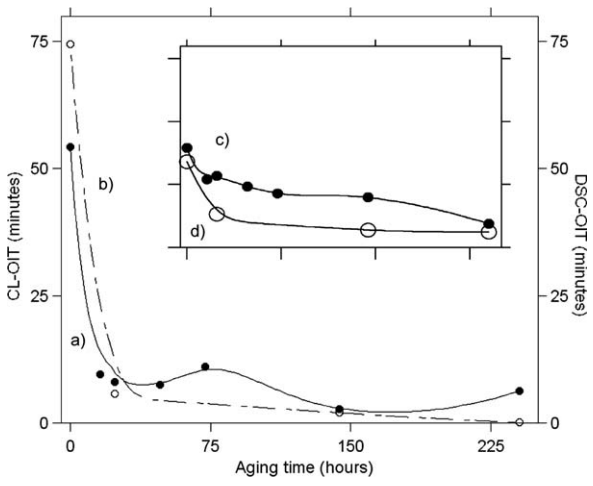


Fig. 7. CL-OIT (●) and DSC-OIT (○) versus the aging time, in air at 80 °C: (a) PE containing 0.1% α-tocopherol (PE-toc), (b) PE-toc, (c) PE containing 0.1% Irganox 1076 (PE-Irg1076), and (d) PE-Irg1076. The scales on the inserted graphs are the same as in the figures.

exothermic response is obtained. CL-OIT also measures the time to consumption of all antioxidant in the sample, but the CL intensity is related to the hydroperoxide concentration in the material and measures the chain termination. The chain propagation measured by DSC is linearly related to the square root of the CL intensity [33]. The techniques were no expected to give different results for PP-Irg1076 and the difference observed may have many plausible explanations; the higher standard deviation of the CL-OIT measurements could contribute to the disparity. Another explanation is that the detection of the luminescence from a sample is more sensitive and may be better related to what really occurs in the sample than the detection of all the exothermic responses by DSC. All the exothermic reactions may not be directly linked to the stability of the material.

3.4.2. DSC-OIT of PP aged at different temperatures

The DSC-OIT values of PP containing α-tocopherol (PP-toc) and PP containing Irganox1076 (PP-Irg1076) after 7 days (168 h) of aging at temperatures between 60 and 120 °C are shown in Fig. 1, together with TLI and carbonyl index induction times. The DSC-OIT values did not agree with the TLI and carbonyl index induction times. PP-Irg1076 shows an almost constant OIT independent of the temperature. This indicates that the sensitivity in the OIT measurement was too low to detect the differences given by aging at different temperatures. At low OIT, the sensitivity of DSC is especially low because of the small amount of antioxidant in the material [34]. Remarkably is the high OIT of PP-toc after processing. This has been observed before in PE and it is very probably due to its transformation products, quinones that are efficient radical scavengers at high temperature in the processing step [24].

4. Conclusion

The sensitivities towards oxidation detection of chemiluminescence (CL) in an inert (TLI) and in an oxygen atmosphere (CL-OIT) were compared to those of the commonly used techniques: FT-IR (carbonyl index (CI)) and thermal analysis (DSC-OIT) of stabilised polyolefins. Polyethylene (PE) was aged at 80 °C and polypropylene (PP) was aged at temperatures between 60 and 120 °C. Non-Arrhenius behaviour was observed for the oxidation of PP. This emphasised the importance of low temperature aging of PE for reliable and realistic results. The TLI and carbonyl index (CI) were comparable with equal sensitivities in oxidation detection in the case of the stabilised PP materials and most of the presumably well-stabilised PE materials. This was consistent with our first hypothesis. The very good agreement between the techniques was most probably due to the antioxidant function in the materials, which decreased both the hydroperoxide and carbonyl build-up. The equality of the techniques was in contrast to our earlier results for degradable PE. However, for unstabilised PE and for two other probably poorly stabilised materials, TLI showed an earlier oxidation detection and a higher sensitivity than the CI measurements. The earlier detection with TLI is expected for poorly stabilised materials with a weak antioxidant function, since the hydroperoxides are initial oxidation products and carbonyls secondary products. CL was compared in an inert and in an oxidative atmosphere and the CL-OIT of two of the PE materials disagreed with both TLI and CI. This showed that TLI had a higher sensitivity and greater accuracy than CL-OIT in the detection of oxidation. One explanation of this is that the conditions during the OIT were more severe than those throughout the TLI analysis. Both TLI and CI were sufficiently sensitive to detect the influence of the aging temperature on the time to oxidation of stabilised PP, but DSC-OIT was not. This confirmed our second hypothesis. CL-OIT and DSC-OIT of stabilised PE disagree for one of the materials and this was not in accordance with our hypothesis. The CI and the DSC-OIT had a smaller uncertainty than both the TLI and the CL-OIT analyses for all the materials; with CI showing the best repeatability and DSC-OIT a good repeatability.

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