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A chemiluminescence study of micron and nanoparticle titanium dioxide: effect on the thermal stability of metallocene polyethylene

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Abstract

The thermal activity of a series of nano and micron particle grade anatase and rutile titanium dioxide pigments, with various densities of surface treatments, particle size and surface area, have been determined in monomodal metallocene polyethylene. Their performance has been undertaken by chemiluminescence (CL), differential scanning calorimetry and hydroperoxide analysis. Chemiluminescence study under nitrogen on polyethylene containing nano and micron titania allows one to determine the thermal activity of pigment during processing. Such results show that for pigmented polymers, a marked suppression of emission is observed, which correlates well with the lower initial determined hydroperoxide content. This effect is enhanced with pigment content and coated grades. For untreated pigment, more oxidation is induced by the greater surface area of the pigment particle, which, in turn influences the dispersion and enhances the pigment–polymer contact. At temperatures below the polyethylene melting point, low chemiluminescence was observed due to the restricted mobility of hydroperoxides to give the disproportionation reaction responsible for the emission. Under oxygen, the high activity of Irganox 1010 as a long-term thermal stabiliser is observed, and the activity of titanium dioxide has been seen to be dependent on the particle size. In general, nanoparticles exhibit a greater thermal sensitising effect, which is reduced by the coating. Increasing the content of pigment, the oxidation induction times (OIT) are greatly reduced and are not detected by DSC. It is concluded that the CL method can be used to determine differences in the oxidation level of pigmented polyethylenes.

Keywords: Chemiluminescence; Titanium dioxide; Metallocene polyethylene

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1. Introduction

During the last decade, significant advances have been achieved in the synthesis of nanoparticles. The term nanoparticle is generally used to indicate particles with diameters smaller than 100 nm, and materials with at least one dimension in the nanometer scale are well known and used in industry for a long period. Around 1650, Jaquin isolated a silver shimmering material from fish scales, consisting of crystalline particles of thickness about 25–75 nm, and built up from guanine and hypoxanthine [1]. These particles are still used as pigments in high quality nail lacquers. Some of the advantages of nanoparticles are their low cost, easy dispersion, transparency, and compatibility with other additives. Nanocomposite technology offers advantages such as increased tensile strength, modulus and heat distortion, improved fire retardance and ultraviolet (UV) stability, reduced permeability to gases, etc. The small size is responsible for the different properties, making these materials attractive for many applications, solar cells and photodiodes [2], LEDs [3], lithography [4], magnetic storage [5], gas sensor [6], drug delivery system in medicine [7], catalysis [8], coating [9], etc.

Nanoparticles of TiO_2, SiO_2, Al_2O_3, ZrO_2, $BaTiO_2$, have been shown to have a significant effect on the properties of coating materials [10]. Recently, Illinois-based Nanophase Tech. Co. has developed three types of transparent functional coatings, using zinc and aluminium oxide, and titanium dioxide nanocrystalline particles: transparent coatings to protect against UV and infrared radiation; transparent wear-resistant coatings; and conductive antistatic coatings [11].

Organic and inorganic pigments are mixed into the plastics compound, to give colouring, so that the product does not require subsequent painting. Titanium dioxide is the most important white pigment used in the plastics industry. It has a higher refractive index than any other white pigment, good chemical stability, and improves the brightness of coloured pigments. TiO_2 nanoparticles deposited on

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platelet substrates are used to make pearlescent pigment [1]. By using multilayer techniques and depending on the layer thickness, pigments with very good interference colours or angle dependant colours can be prepared. The main criteria for pigment are opacity and tinting strength. They depend on light scattering power, which is governed by refractive index, particle size distribution, TiO_2 content and dispersion in the polymer. The control of those factors is critical in titanium dioxide properties. As the particle size increases, the ability of the particle to scatter light increases up to a maximum, it then starts to decrease. For conventional pigmentary titania light scattering is governed by the Mie theory, however, for titania nanoparticle Ralyleigh's scattering is applied. At an optimum particle size of 2–50 nm visible light will be transmitted, and the UV light below 400 nm will be scattered. Pigment particle size and surface area play an important role in dispersion. If the number of aggregates and agglomerates is few, good dispersion will be obtained and high opacity and tinting strength developed [12]. Consequently particle size selection has become one of the principal developments in pigment technology in recent years. Many studies have been undertaken to optimise the techniques used to manufacture pigments in as narrow a particle size distribution as possible.

In many cases pigments can influence the thermal and photochemical stability of a polymer material. Several authors have studied thermal and photoactivity of TiO_2 in a number of fields, including energy renewal and energy storage [13], photocatalyst for the destruction of organic compounds in polluted air and wastewaters [14], coating [15], etc. Here the effect of particle size, sample treatment and composition of titanium dioxide particles were found to control their activity. Titanium dioxide absorbs much of the ultraviolet radiation, protecting the polymers against UV light. However, the UV energy may be converted to heat, and creates radical sites on the surface of the pigment particle, which accelerates the breakdown of the polymer, having a marked influence on the thermal and photochemical stability of the polymer. Generally, the pigment is surface coated with alumina, silica or siloxanes to minimize photochemical activity at the polymer/pigment interface, and to improve the dispersibility of the pigment. However, high levels of surface treatment reduce the proportion of the titanium dioxide in the pigment, reducing opacity and tinting strength. Recent work has also indicated that physisorption and chemisorption processes in micron and ultrafine titania can significantly influence the activity of stabilisers in polymers [16,17].

Several techniques are usually used to study the mechanism of polymer degradation. These tests often need much time and are not sensitive enough in certain applications. Recently, chemiluminescence (CL) has become a competitive analysis technique for polymers, due to its offered advantages with respect to many conventional techniques [18]. The chemiluminescence (CL) in polymers is due to the light emission that accompanies the thermal decomposition of the thermooxidative degradation products (hydroperoxides), which are formed during processing or in-service life of the material under ambient conditions [19,20]. This bimolecular reaction promotes ketone products to its lowest triplet state and the radiative deactivation gives chemiluminescence emission in the visible region. By means of the chemiluminescence technique, it is possible to study polymer degradation, oxidation mechanism and kinetics, and to evaluate the effectiveness of the antioxidant [21,22].

In previous work [9], a series of nano and micron particle grade anatase and rutile titanium dioxide pigments were prepared with various densities of surface treatments, particle size and surface area. And their thermal and photochemical activities were determined in monomodal metallocene polyethylene by FT-IR, hydroperoxide analysis, chalking, gloss change and weight loss following artificial weathering. The pigments were also examined by photodielectric microwave spectroscopy and luminescence.

The aim of this work is to study the chemiluminescence emission of metallocene polyethylene films including nano and micron particle grade anatase and rutile titanium dioxide pigments, and to determine the effect of particle size and surface treatments of titanium dioxide on the polymer thermal stability.

2. Experimental

2.1. Materials

The titania pigments used in this study were all experimental grades prepared in the laboratories of Millennium Inorganic Chemicals, Grimsby, UK and are summarised in Table 1. The phenolic antioxidant Irganox 1010 was obtained from Ciba Specialty Chemicals.

The employed polyethylene is an additive free grade supplied as a powder by a European manufacturer with a number average molar mass of 156.000. A metallocene catalyst was used in the production of this material. The polyethylene formulations were processed using a Brabender Plasticorder (Duisburg, Germany) fitted with W50E chamber and cam blades at 170 °C for 7 min. Polymer films of 120 μm thick were made by compression moulding, in a Collin-200 press under the same temperature (170 °C) and pressure cycle (1 min at 0 bar, and 1 min at 200 bar).

2.2. Thermal analysis

Polymer films (5 mg) were characterized by differential scanning calorimetry using a Shimatzu DSC-50 instrument. Dynamic measurements were undertaken at a constant rate of heat of $10\,^{\circ}\mathrm{C\,min^{-1}}$ under nitrogen atmosphere. The melting peak (T_m) and the melting enthalpy (ΔH_m) were obtained, and percentages of crystallinty were determined using the reference of $H_m = 293\,\mathrm{J\,g^{-1}}$ for crystalline polyethylene. All the polyethylene films prepared in this work exhibited the same crystalline level $X_c = 14\%$ and a melting point of 117 °C.

Table 1
Pigments used in this work

Sample	Titanium dioxide (%)	BET surface area (m^2/g)	Particle size	Sulphate SO_2 (%)	Alumina (%)	Other treatments
PC50 (nanoanatase)	>95	44.4	20–30 nm	<0.8		
PC105 (nanoanatase)	>95	77.9	15–25 nm	<0.8		
PC500 (nanoanatase)	>95	329.1	5–10 nm	<0.8		
S.D. (nanoanatase)	>95	52.1	70 nm	<0.8		Hydroxy apatite
A-T1 (anatase normal)	99	10.1	0.24 μm			
Nanorutile (untreated)	>95	140.9	25 nm			
Chlo (chloride rutile normal)	99	6.5	0.28 μm		1	
RCL 696 (rutile normal)	95	12.5	0.29 μm		3.4	

For oxidation induction time (OIT) a standard method (ASTM 3895-80, ISO 11357) was used to determine the thermal stability of the polymer materials and the performance of the titania pigments. The measurement was made using DSC in the isothermal mode, at a constant temperature of 200 °C. The sample was maintained under nitrogen (40 ml min^{-1}) until the test temperature was attained, then a flux of oxygen (40 ml min^{-1}) was supplied. The latter was taken as time zero. The OIT value is the time needed to reach the onset of oxidation, detected as the start of an exotherm, and can be correlated with the stability of the material.

2.3. Hydroperoxide analysis

Hydroperoxide concentration in the polymer films were determined by a combination of the methods of Mair and Graupner and Uri, previously described. Ten milligrams of film fragments were refluxed with 2.0 ml of a sodium iodide solution in isopropanol (200 g l^{-1}) after acidification with 7 ml of an acetic acid:isopropanol solution (1:10 (v/v)). After 30 min of reflux, the solution was cooled, diluted with 10 ml of distilled water and the iodide, generated as I_3^- by the reaction, $ROOH + 3I^- + 2H^+ \rightarrow I_3^- + H_2O + ROH$, was determined spectrophotometrically at a wavelength of 360 nm using an absorption coefficient of $2.5 \times 10^4\ l\ mol^{-1}\ cm^{-1}$.

2.4. Chemiluminescence

Chemiluminescence emission of film samples were obtained using an earlier described CL400 ChemiLUME apparatus developed by Atlas Electric Devices Co. [22]. The film samples (10 mm diameter) were held in aluminium dishes and heated up with pre-test ramp (1 °C min^{-1}) to the test temperature (110 and 170 °C), under constant flow (55 ml min^{-1}) of dry gas, nitrogen or oxygen.

Chemiluminescence signal from film samples were collected in a water-cooled photon counting photomultiplier, which was previously calibrated using a radioactive standard provided by Atlas. The data collected were processed using the specific software supplied with the instrument.

For titania powders, 20 mg of each product was placed in the aluminium pan covering its surface as a powder layer.

3. Results and discussion

3.1. Chemiluminescence of titanium dioxide pigments

Firstly, the chemiluminescence of micron and nanoparticles titanium dioxide was examined in order to determine their possible emission which can affect the polyethylene chemiluminescence measurement. It has been observed that some pigments in a polymer matrix may show chemiluminescence. This fact could be due to the oxidation species produced during their manufacturing process. In some cases, it could be attributed to spontaneous ignition during treatment at high temperatures, which generates an extensive amount of light [23]. Unlike conventional techniques, chemiluminescence can detect this phenomenon which could have an effect on polymer properties.

The chemiluminescence emission observed under nitrogen at 170 °C with the different titanium dioxide samples employed in this work (1 mg) are shown in Fig. 1. All the samples exhibited very low intensity of chemiluminescence emission under this condition. The most interesting feature here is the high emission intensity from the PC105 particles.

In the presence of oxygen, the chemiluminescence emission was enhanced for all the titania pigments as compared to those obtained under a nitrogen atmosphere. The titanium dioxide is a well known catalyst for polymer oxidation [24]. Recently, the study of chemiluminescence generated on the surface of nanosized titanium dioxide has been used to develop a gas sensor method [25]. Fig. 2 shows the chemiluminescence emission for TiO_2 pigments under oxygen at 170 °C.

In general, the emission increases with particle size. Anatase and rutile micron size particles exhibit the highest values of chemiluminescence, and the emission is enhanced when the particles are coated. Although the pigments and nanoparticles exhibit chemiluminescence in bulk, the emission may be considered negligible in polyethylene samples, since the TiO_2 content is relatively low, i.e. <2%. It can only be assumed that traces of peroxides or hydroperoxides on the surface of the titania are responsible for the observed weak emissions. These could be present as weakly bound molecular oxygen complexes with acidic species.

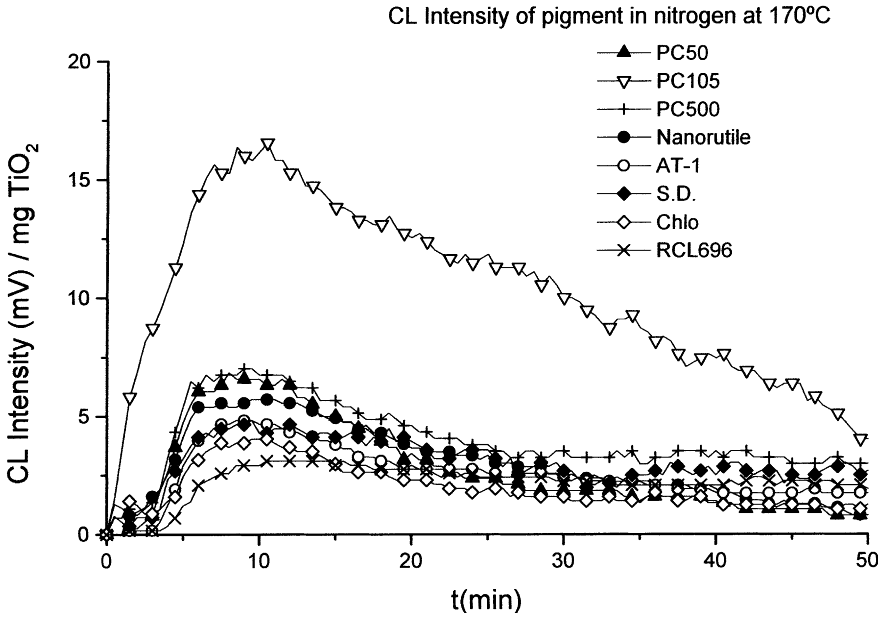

Fig. 1. Chemiluminescence curves for the micron and nanotitanium dioxide, in powder bulk obtained at 170 °C under nitrogen.

3.2. Chemiluminescence of metallocene polyethylene under nitrogen

In nitrogen, the species responsible for the chemiluminescence correspond to the initial concentration of peroxy radicals and it is proportional to the hydroperoxide content which is generated during the processing of the material [26]. The chemiluminescence analysis under nitrogen allows one to determine the effect of titanium dioxide pigments and nanoparticles on the thermal stability of the polymer during melt processing, and to obtain information about the efficiency of stabilizers. Hindered phenols such as Irganox 1010, in an oxygen deficient environment (such as in melt processing), can act as an antioxidant by chain-breaking donor and acceptor mechanisms, contributing to reduce the rate formation of hydroperoxides and subsequently the value of the chemiluminescence intensity (I_{CL}).

The intensity of chemiluminescence can be determined as the peak-top intensity $I_{CL\text{-}max}$ or area of the peak, $A_{CL\text{-}max}$. The chemiluminescence analysis under nitrogen

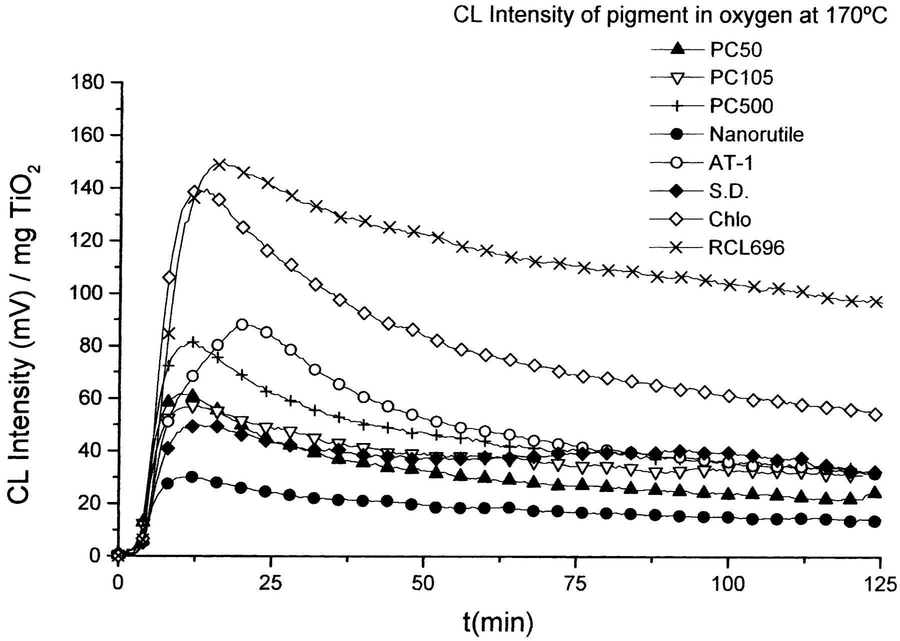

Fig. 2. Chemiluminescence curves for the micron and nanotitanium dioxide, in powder bulk obtained at 170 °C under oxygen.

Table 2
Chemiluminescence under nitrogen at 170 °C of metallocene polyethylene films containing the nano and micro grade titania pigments at 0.5% (w/w) concentrations with 0.05% (w/w) Irganox 1010 antioxidant together with control unpigmented samples

Pigment (0.5% (w/w))	Pigment type	$I_{\text{CL-max}}$ (mV)	$A_{\text{CL-peak}} \times 10^{-2}$ (mV)	$[\text{ROOH}]_0$ (mg/g)
None (PE control-unstabilised)		200	46.8	172
None (stabilised Irganox 1010)		154	41.3	61
PC50	Nanoanatase (20 nm)	54	12.1	35
PC105	Nanoanatase (15 nm)	135	38.4	67
PC500	Nanoanatase (5 nm)	105	24.4	125
S.D.	Nanoanatase coated (70 nm)	47	10.3	19
AT-1	Micronanatase (0.24 μm)	65	21.1	26
Nanorutile	Nanorutile (25 nm)	407	154.1	112
Chlo	Micronrutile 1% alumina (0.28 μm)	115	37.8	43
RCL 696	Micronrutile 3.4% alumina (0.28 μm)	66	16.3	32

were undertaken for metallocene polyethylene films including 0.5% pigment, and compared to unpigmented polyethylene, stabilised with Irganox 1010 and no stabilised (PE control). The results obtained are compiled in Table 2, and the chemiluminescence curves are showed in Fig. 3.

The first feature from this data is the observation that the values of $I_{\text{CL-max}}$ for metallocene polyethylene with and without antioxidant indicate a minor effect on thermal stabilisation. It would indicate the low antioxidant efficiency under processing of Irganox 1010, since no chemiluminescence due to the additive was detected under nitrogen [22]. Here the stabilised polymer exhibits a lower intensity than that for the unstabilised material. Marked suppression of chemiluminescence emission is observed however, for the anatase pigment in conjunction with Irganox 1010, which correlates well with the lower initial hydroperoxide content determined in the material. This effect is enhanced for coated grades, where the S.D. nanoanatase grade exhibited the lowest value of hydroperoxide indicating the protective influence of the hydroxy apatite coating. For uncoated pigments, the chemiluminescence varies with particle size, PC50 $<$ PC500 $<$ PC105. Apparently, a greater surface area pigment allows higher contact with the polymer, and induces more oxidation during processing as measured by the hydroperoxide analysis. However, the chemiluminescence data exhibits an anomaly between the PC105 and PC500 grades. Here dispersion and light transmission of the nanoparticles may be a contributing factor. A similar trend is observed for the rutile grade. Nanorutile untreated showed the highest emission, and the thermal sensitisation is decreasing with the alumina content, RCL <696 Chlo. Here the dispersion of the rutile may be more effective and comparable.

The influence of pigment concentration on the thermal degradation during processing has also been studied by chemiluminescence analysis for metallocene polyethylene films including 2% pigment, at 110 and 170 °C. Data are

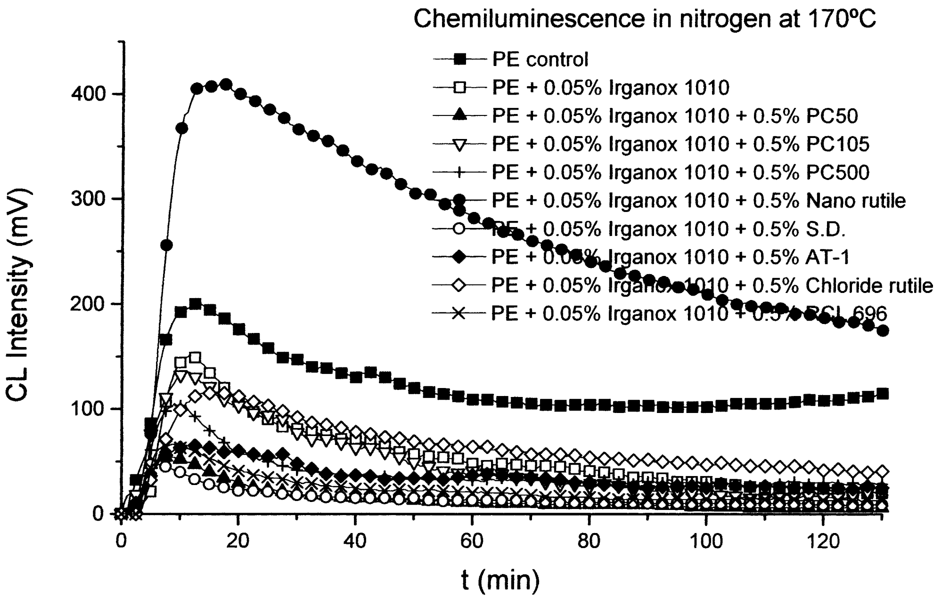

Fig. 3. Chemiluminescence emission profiles vs. time of metallocene polyethylene films free, stabilised with Irganox 1010 (0.05% (w/w)), and pigmented with micron and nanotitanium dioxide (0.5%), determined at 170 °C under nitrogen.

Table 3
Chemiluminescence under nitrogen at 110 and 170 °C of metallocene polyethylene films containing the nano and micron grade titania pigments at 2% (w/w) concentrations with 0.05% (w/w) Irganox 1010 antioxidant together with control unpigmented samples

Pigment (2% (w/w))	Pigment type	At 110 °C		At 170 °C		$[ROOH]_0$ (mg/g)
		$I_{CL\text{-}max}$ (mV)	$A_{CL\text{-}peak} \times 10^{-2}$ (mV)	$I_{CL\text{-}max}$ (mV)	$A_{CL\text{-}peak} \times 10^{-2}$ (mV)	
None (PE control-unstabilised)		46	12	200	46.8	172
None (Stabilised with Irganox 1010)		14	3.4	154	41.3	61
PC50	Nanoanatase (20 nm)	7	0.8	53	16.1	43
PC105	Nanoanatase (15 nm)	3	0.1	67	19.8	52
PC500	Nanoanatase (5 nm)	10	0.9	36	8.6	69
S.D.	Nanoanatase coated (70 nm)	7	0.5	88	16.9	27
AT-1	Micronanatase (0.24 μm)	3	0.1	136	20.1	24
Nanorutile	Nanorutile (25 nm)	65	7.5	212	64.4	72
Chlo	Micronrutile (0.28 μm) 1% alum	15	2.2	104	31.9	39
RCL 696	Micronrutile (0.29 μm) 3.4% alum	14	1.7	148	29.9	30

compiled in Table 3 and the CL-curves at 170 °C are shown in Fig. 4.

The stabilisation effect observed in the presence of titania is enhanced with the content of pigment, and lower values of $I_{CL\text{-}max}$ and $A_{CL\text{-}peak}$ are obtained for metallocene polyethylene with 2% pigment in comparison with 0.5% content data showed in Table 2. Anatase nanoparticles exhibited lower values than micron pigments, and the coating of the particle surface reduces the thermal degradation of polymer films, as commented before.

The chemiluminescence emission of the polyethylene films heated at 110 °C was undertaken. In general, the lowest emission was observed due to the more restricted mobility of hydroperoxide below the melting point. In this case, the bimolecular termination reaction of two peroxy radicals is the only possible mechanisms responsible for chemiluminescence emission in the visible region, through the deactivation of the generated excited carbonyl state.

3.3. Chemiluminescence of metallocene polyethylene under oxygen

With the polymer samples studied here, a much higher intensity of chemiluminescence was observed under oxygen compared to that obtained under a nitrogen atmosphere. Under these conditions, the samples are highly oxidised in a diffusion-controlled reaction giving rise to the emission. Macroradicals react with the oxygen to give peroxy radicals

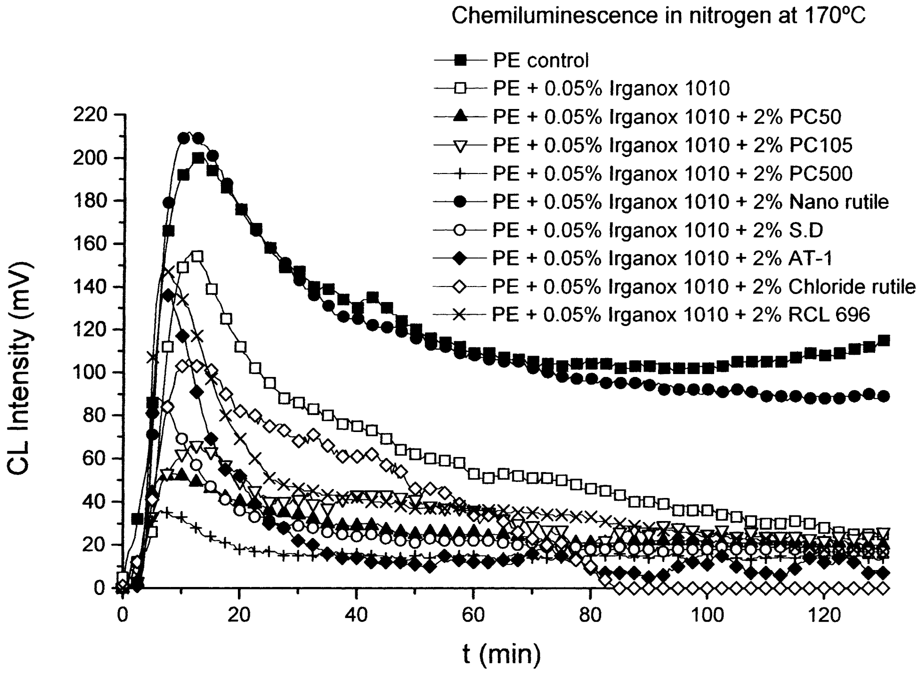

Fig. 4. Chemiluminescence emission profiles vs. time of metallocene polyethylene films free, stabilised with Irganox 1010 (0.05% (w/w)), and pigmented with micron and nanotitanium dioxide (2%), determined at 170 °C under nitrogen.

Table 4
Chemiluminescence under oxygen in melt condition at 170 °C of metallocene polyethylene films containing the nano and micro grade titania pigments at 0.5% (w/w) concentrations with 0.05% (w/w) Irganox 1010 antioxidant together with control unpigmented samples

Pigment (0.5% (w/w))	Pigment type	$I_{\text{CL-max1}}$ (mV)	I_s (mV)	t_{max2} (h)	$I_{\text{CL-max2}} \times 10^{-4}$ (mV)	OIT-$_{\text{CL}}$ (h)	OIT-$_{\text{DSC}}$ (min)
None (PE control-unstabilised)		–	–	4.7	3.9	0.7	0
None (Irganox 1010)		289	118	12.5	4.9	8.1	7.2
PC50	Nanoanatase (20 nm)	246	99	10	5.7	5.6	11.3
PC105	Nanoanatase (15 nm)	302	205	7.5	4.0	2.3	0
PC500	Nanoanatase (5 nm)	–	–	4.8	2.9	0.6	0
S.D.	Nanoanatase coated (70 nm)	354	113	–	>9	6.8	2.2
AT-1	Micronanatase (0.24 μm)	341	131	13.5	8.5	9.7	9.1
Nanorutile	Nanorutile (25 nm)	–	–	6.4	5.8	1.8	0
Chlo	Micronrutile (0.28 μm) 1% alumina	449	150	–	>9	8.2	3.6
RCL 696	Micronrutile (0.29 μm) 3.4% alumina	299	60	14.3	5.8	10.4	6.2

and its concentration will be large and the bimolecular termination reaction of two peroxy radicals to give ketone products will be enhanced. The obtained results for polyethylene samples with 0.5% pigment are summarised in Table 4, and the chemiluminescence graphs are plotted in Figs. 5 and 6, respectively.

Under oxygen conditions, two emission peaks are detected for stabilised polymer films. A weak emission due to the thermal history of the film is observed at the onset of heating and this is shown in Fig. 5. Furthermore, a second intense peak is observed when the oxidation induction period is attained, Fig. 6. In the induction period of oxidation, the rate of formation of peroxy radicals is nearly similar to their rate of termination by recombination, and the CL signal is low. At the end of this period, the radical concentration increases due to autoacceleration of the oxidation, and the chemiluminescence emission is enhanced.

The first feature is the effect of Irganox 1010 as a long-term thermal stabiliser in polyethylene film, as may be evidenced by the oxidation induction time (OIT). In the presence of this hindered phenol antioxidant, peroxy radicals are trapped by the antioxidant during the induction period, the CL-emission is low (I_s) until the antioxidant is consumed and the oxidation starts (OIT-$_{\text{CL}}$) which is reflected by an increase in the chemiluminescence intensity. The efficiency of the antioxidant is modified in the presence of pigments. The activity of the titanium dioxide has been seen to be dependent on the particle size [9]. Nanoparticles of rutile pigment exhibit a thermal sensitising effect and lower t_{max2}, $I_{\text{CL-max2}}$, and OIT are observed. This effect is

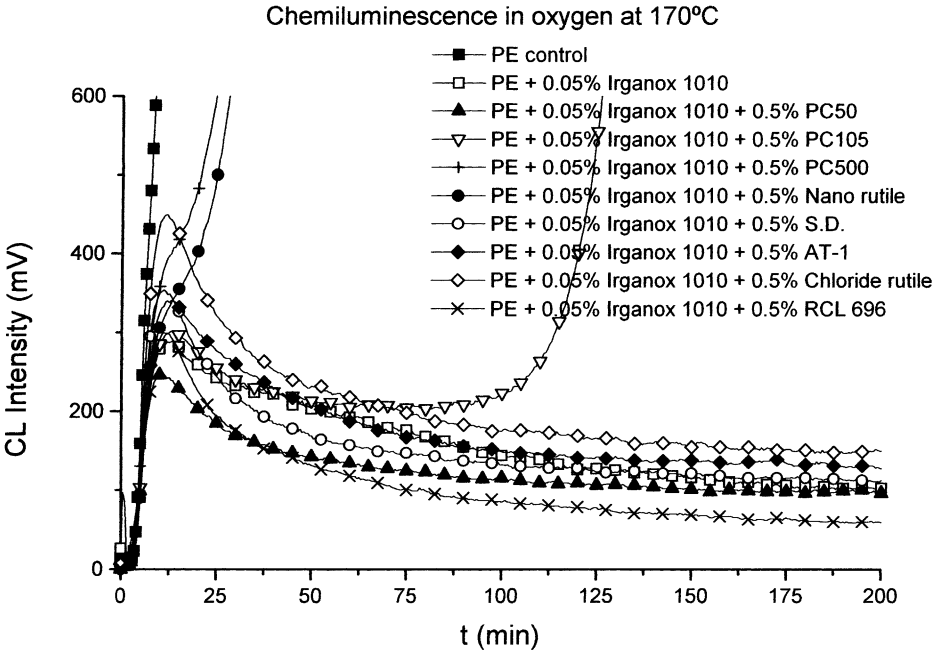

Fig. 5. First chemiluminescence peak curves vs. time of metallocene polyethylene films free, stabilised with Irganox 1010 (0.05% (w/w)), and pigmented with micron and nanotitanium dioxide (0.5%), determined at 170 °C under oxygen.

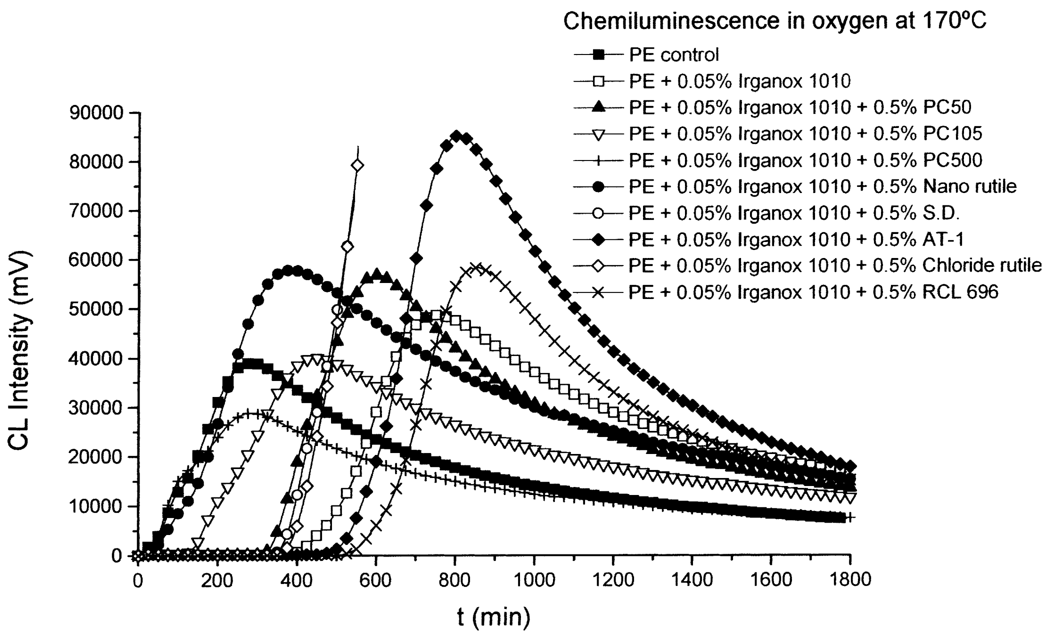

Fig. 6. Second chemiluminescence peak curves vs. time of metallocene polyethylene films free, stabilised with Irganox 1010 (0.05% (w/w)), and pigmented with micron and nanotitanium dioxide (0.5%), determined at 170 °C under oxygen.

suppressed for micron pigmented samples. Chlo and RCL 696 exhibit longer induction periods than that for the unpigmented polymer, and the protective effect is enhanced with coating, as was observed under nitrogen. A similar trend is observed for anatase grade titania. For nanoparticles, the OIT is reduced with respect to the micron particles. In previous work [9], it has been seen via TEM, that nanoparticles form agglomerates. Oxidation of the polymer matrix occurred around the particle site, and the particles appear to be embedded in holes in the film surface. For the untreated nanoparticles the OIT decreased in the order PC50 > PC105 > PC500, which follows the decrease in particle size. The greater surface area of particle allows greater contact with the polymer, and induces more oxidation. In general, a similar order in the oxidation of polymer films is found with all the chemiluminescence parameters. A good correlation was found between the thermal activity of pigments determined by means of chemiluminescence OIT-$_{\mathrm{CL}}$ and the OIT-$_{\mathrm{DSC}}$ obtained by calorimetry.

The stability of polyethylene containing 2% pigment was studied, and the results are compiled in Table 5, and the chemiluminescence curves shown in Fig. 7.

Higher oxidation in all polyethylene samples is observed when the content of pigment is increased. OITs are greatly reduced, and for nanoparticles the first emission peak is not well defined appearing as a shoulder on the intense second peak, Fig. 7. At 2% of pigment content, no significant differences are observed with several particle sizes. The coating seems to play the main role to reduce the thermal activity of the pigments, and OITs similar to the unpigmented (stabilised) samples, are found for Chlo and RCL 696 titania.

Table 5
Chemiluminescence under oxygen at 170 °C of metallocene polyethylene films containing the nano and micro grade titania pigments at 2.0% (w/w) concentrations with 0.05% (w/w) Irganox 1010 antioxidant together with control unpigmented samples

Pigment (2% (w/w))	Pigment type	$I_{\mathrm{CL\text{-}max1}}$ (mV)	I_{s} (mV)	t_{max2} (h)	$I_{\mathrm{CL\text{-}max2}}$ (mV) $\times 10^{-4}$	OIT-$_{\mathrm{CL}}$ (h)
None (PE control-unstabilised)		–	–	4.7	3.9	0.7
None (stabilised with Irganox 1010)		289	118	12.5	4.9	8.1
PC50	Nanoanatase (20 nm)	–	–	4.3	5.1	0.6
PC105	Nanoanatase (15 nm)	229	227	4.7	2.3	0.9
PC500	Nanoanatase (5 nm)	–	–	3.6	2.2	0.5
S.D.	Nanoanatase coated (70 nm)	459	459	–	>9	1.9
AT-1	Micronanatase (0.24 μm)	212	134	10.5	6.2	5.9
Nanorutile	Nanorutile (25 nm)	–	–	6.8	5.8	1.9
Chlo	Micronrutile (0.28 μm) 1% alum	342	125	–	>9	7.1
RCL 696	Micronrutile (0.29 μm) 3.4% alum	696	298	–	>9	10.4

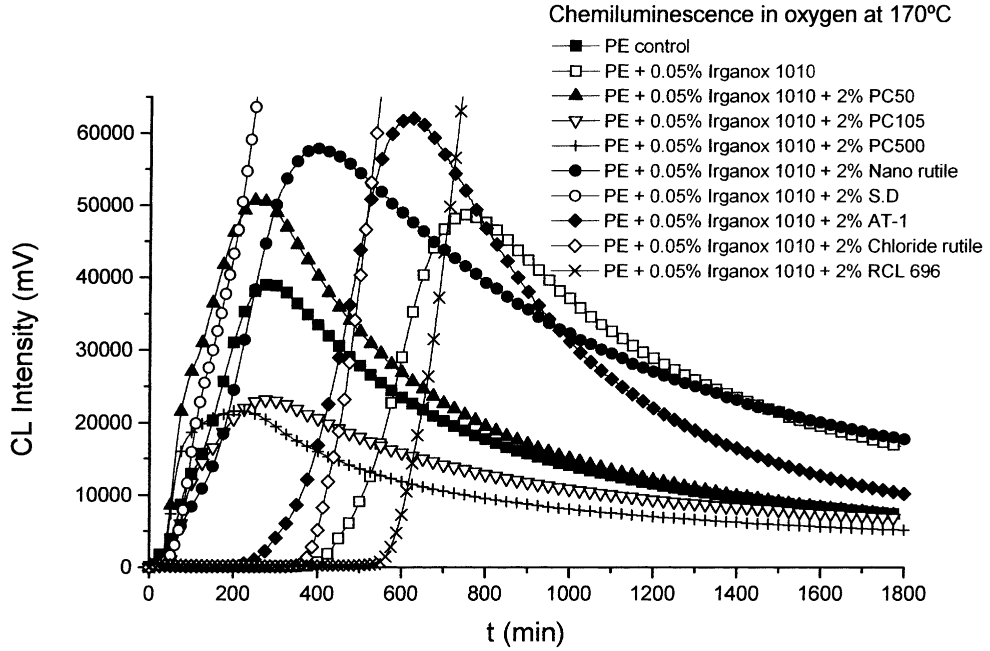

Fig. 7. Second chemiluminescence peak curves vs. time of metallocene polyethylene films free, stabilised with Irganox 1010 (0.05% (w/w)), and pigmented with micron and nanotitanium dioxide (2%), determined at 170 °C under oxygen.

Due to the higher oxidation rates of the pigmented polyethylene samples, OITs are greatly reduced and are not detected by DSC. In contrast CL provides useful data for the characterisation of the stability of the polyethylene [18]. CL exhibits higher sensitivity and it allows one to make measurements at lower temperature, closer to the real degradation conditions in the solid state. Whereas DSC is insensitive to detect the OIT below the melting point, and the curve obtained is the sum of many different exothermic oxidation reactions which, is difficult for the determination of the OIT.

4. Conclusions

The thermal activity of a series of nano and micron particle grade anatase and rutile titanium dioxide pigments, with various densities of surface treatments, particle size and surface area, have been related to the chemiluminescence properties of the materials in monomodal metallocene polyethylene. Analysis of the data indicates that for pigmented polymers, a marked suppression of emission is observed, which correlates well with the lower initial determined hydroperoxide content. This effect is generally enhanced with pigment content and coated grades. For untreated pigment, more oxidation is induced by the greater surface area of the pigment particle, which, in turn influences the dispersion and enhances the pigment–polymer contact. At temperatures below the polyethylene melting point, low chemiluminescence intensities were observed due to the restricted mobility of hydroperoxides to give the disproportionation reaction responsible for the emission. Under oxygen, the higher activity of Irganox 1010 as a long-term thermal stabiliser is observed, and the activity of titanium dioxide is seen to be mostly dependent on the particle size. In general, nanoparticles exhibit a greater thermal sensitising effect, which is, in turn reduced by the coating. Increasing the content of pigment, the oxidation induction times (OIT) are greatly reduced and are not detected by DSC. It is concluded that the CL method can be used to determine differences in the oxidation level of pigmented polyethylenes.

Finally, the titania pigments and nanoparticles themselves also give rise to CL which, although low, at this moment in time is being investigated further in relation to the surface activity of these commercially important materials.

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