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Photooxidative and thermal degradation of polyethylenes: interrelationship by chemiluminescence, thermal gravimetric analysis and FTIR data

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Abstract

The thermal and photooxidative behaviour of polyethylenes of different manufacturing histories (linear low, metallocene and high density) have been investigated by FTIR spectroscopy and the data related to the chemiluminescence (CL) and thermal analysis of the polymers. The CL intensity and activation energies for thermal decomposition were found to be dependent on the rates of oxidation of the polymers under light and heat. On thermal oxidation, the activation energies were found to decrease with time and followed the order HDPE > m-PE > LLDPE, which correlated with the results obtained by means of CL analysis, where a higher intensity of CL at low temperature was found for HDPE. On photooxidation, the order followed their instability, i.e. m-PE > HDPE > LLDPE. The rates of thermal oxidation in each case were found to be the same irrespective of the nature of the oxidation product, i.e. hydroperoxide, vinyl and carbonyl groups. The influence of branching in the polymer appears to be important, showing a decrease of thermal stability as branching in polyethylene increases.

Keywords: Polyethylene; Oxidation; Degradation; Chemiluminescence; Thermal analysis; Carbonyl index

1. Introduction

In the last 50 years, many investigations have been undertaken to elucidate the degradation mechanism of polyolefins. The degradation of polymeric materials is caused by exposure to various factors such as heat, UV light, irradiation ozone, mechanical stress and microbes. Degradation is promoted by oxygen, humidity and strain, and results in such flaws as brittleness, cracking, and fading. The mechanism of polymer degradation is extremely complicated, involving simultaneous formation and decomposition of hydroperoxides. Many workers have undertaken studies to follow the oxidative ageing of polymeric materials by means of several techniques. These tests need much time and are not sensitive enough in certain applications. On the other hand, due to the development of single-photon counting equipment, chemiluminescence (CL) analysis is sensitive to detect the very first stage of oxidation of polymers, and does not require long periods of time to obtain the information. Recently, CL has become a competitive analysis technique for polymers, due to its offered advantages with respect to many conventional techniques [1]. The 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 service life of the material under ambient conditions [2,3]. By means of the CL technique, it is possible to determine the degree of oxidation, and even to predict the long term stability of the polymer [4,5].

Generally, isothermal and constant heating rate thermogravimetric analysis (TGA) have been used to obtain kinetic information from the decomposition of polyolefins [6–8]. It provides information on frequency factor (A_0), activation energy (E_a), and overall reaction order (n). Several methods have been developed by different authors [9,10], and comparing the obtained results wide variations are observed depending on the mathematical analysis used. It seems that methods based on several curves (at different heating rates) present a lower risk of creating errors than methods based on a single curve.

In a previous paper [11], we studied the thermal and photooxidative stability of high, linear low and metallocene

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grade polyethylene, using FTIR and hydroperoxide concentration analysis. Thermal degradation of polyethylene was found to be influenced by the concentration and nature of different vinyl types. Hydroperoxide levels also appeared to be important and correlate with the carbonyl index oxidation rates. Whereas, the difference in the UV stability of various polyethylenes may be due to the presence of active chromophores, identified by fluorescence spectroscopy. These were found to be significant in the case of the metallocene polymer, which corresponded with its poor photostability.

The aim of this paper is to study the thermal and UV degradation of HDPE, LLDPE and metallocene grade materials, by means of the CL technique, and TGA in terms of determination of the frequency factor and the activation energy for the overall photooxidation process. For this purpose, our analysis is based on the kinetic analysis method developed by Park et al. [10], which allows calculation of A_0 and E_a, and to predict the degradation of polyolefins at any time. The polyethylenes have also been examined by FTIR and derivative UV spectroscopy, in order to follow the degradation of the samples, and the results compared with those obtained by CL and TGA.

2. Experimental

2.1. Materials

The metallocene, HDPE and LLDPE grade polyethylenes are from various manufacturers and are additive free grades supplied as powders. The powders were compression moulded into films of 280 μm thickness, using identical conditions (165 °C). The polymer densities, molecular weights and distributions and metal ion contents were determined by Repsol S.A., Madrid, and the data summarised in Table 1.

2.2. DSC analysis

Polymer films (5 mg) were characterised using a Perkin-Elmer DSC-7 instrument. Dynamic measurements were undertaken at a constant rate of heat of 10 °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 enthalpy of melting for polyethylene of 100% crystallinity $\Delta H_m = 293$ J/g [12]. The obtained values are compiled in Table 2.

Table 2
Melting point (T_m) and crystallinity of HDPE, LLDPE and m-PE films

Sample	T_m (°C)	Crystallinity (%)
HDPE	135	44
LLDPE	123	18
m-PE	122	14

2.3. Ageing

Polymer films were oven aged at 90 °C in a forced draught oven and irradiated using a Microscal Light exposure unit and Suntest/Atlas XLS 2200 W employing a solar standard filter which provides 550 W/m^2 in the wavelength region 300–800 nm (Irradiance acc. ISO 4892/DIN 53387). Oxidation rates were determined by means of an FTIR spectrometer using the standard carbonyl index method [13–15].

2.4. CL analysis

CL emission of film samples were obtained in a CL400 ChemiLUME analyser developed by Atlas Electric Devices. The film samples (10 mm diameter) were held in aluminium pan and heated with pre-test ramp (1 °C min^{-1}) in the temperature interval 25–250 °C, and at 170 °C for isothermal analysis, in flowing dry nitrogen (55 ml/min). CL signal from film samples were collected in a water-cooled photon counting photomultiplier, which was previously calibrated using a radioactive standard provided by Atlas.

2.5. Thermal analysis

The TGA was performed with a Perkin-Elmer TG model TGA 7. The HDPE, LLDPE and m-PE films were studied at various heating rates ranging from 10 to 50 °C min^{-1}. The initial mass of the samples was 4–6 mg. The experiments were carried out under nitrogen atmosphere with a flow rate of 20 ml/min and a purge time of 10 min.

2.6. Spectroscopic analysis

FTIR spectra were obtained using a NICOLET 520 spectrometer. Derivative UV spectra were obtained on films using a Perkin-Elmer Lambda 16 spectrometer.

Table 1
Analytical characteristics of polyethylenes

Sample	Molecular weight data				Density	Metal ions (ppm)				
	Mn	Mw	Mz	Polidispersity		Al	Ti	Mg	Cr	Zr
HDPE	14700	267000	2112000	1,816	0.931	<2	9.3	0.1	3.2	–
LLDPE	31300	126400	559000	4,04	0.926	96	4.1	70	<2	–
m-PE	68400	134300	230900	1,96	0.921	41	–	–	–	0.58

Carbonyl index $= [\mathrm{Log}_{10}\, I_0/I_t]/100$ at absorption maximum in the carbonyl IR region.

3. Results and discussion

The thermal degradation for nonisothermal conditions was performed by TGA. The TG curves of HDPE, LLDPE, m-PE under a nitrogen atmosphere at various heating rates are shown in Fig. 1. It was observed that as the heating rate is increased, the curves are shifted to higher temperatures due to the heat transfer lag.

The activation energy, E_a, and the factor A_0 were determined using the following equation described by Park et al. [10]:

$$\ln\beta = \ln A_0 + \frac{3}{2}\ln T_{\max} - \ln\left(\frac{E_a}{RT_{\max}} + \frac{1}{2}\right)\frac{E_a}{RT_{\max}}$$

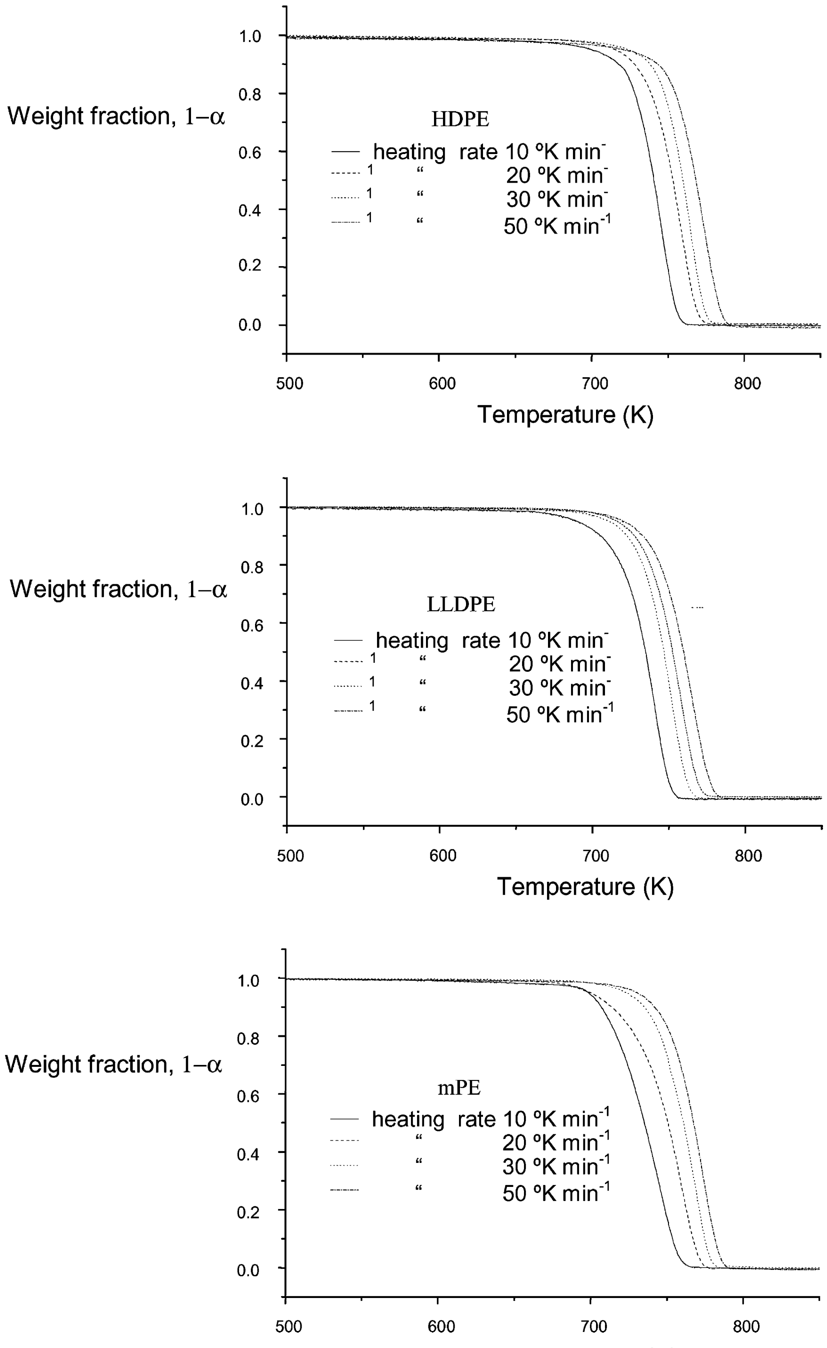


Fig. 1. TG curves for HDPE, LLDPE and metallocene polyethylenes m-PE, under nitrogen atmosphere at various heating rates.

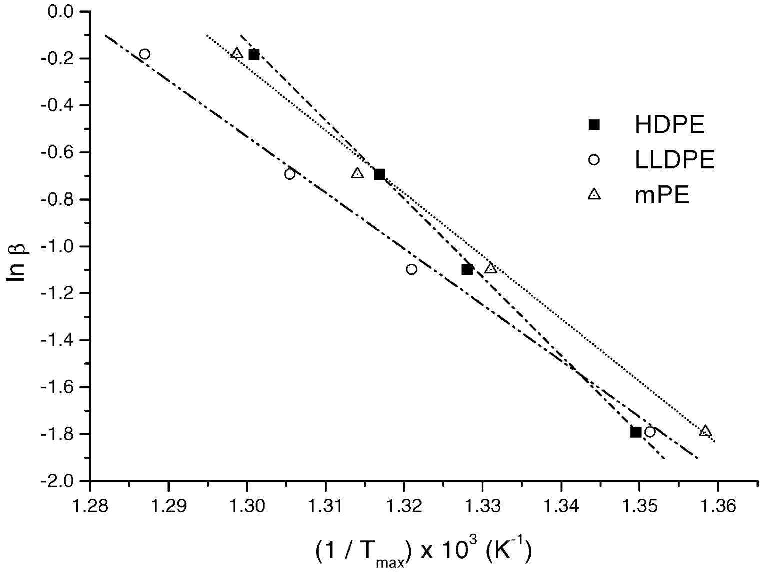


Fig. 2. Plot of $\ln \beta$ vs. $1/T_{\max}$ for the determination of E_a and factor A_0, of polyethylenes.

where β is the heating rate ($^{\circ}$C min^{-1}), $T_{\max}$ is the peak temperature (K), and A_0 and E_a are the pre-exponential factor (min^{-1}) and the activation energy (J mol^{-1}) at maximum rate, respectively, and R the gas constant (8314 J mol^{-1} K^{-1}). Fig. 2 shows the plot of $\ln \beta$ versus $1/T_{\max}$ for the different grades of polyethylene. From the slopes and intercepts of the curves, E_a and A_0 are calculated, respectively.

The activation energies and frequency factors for initial samples of HDPE, LLDPE and m-PE, are summarised in Table 3. The chain branching is expressed by the CH_3 content determined by FTIR as the ratio A/d, where A is the absorption at 1378 cm^{-1} corresponding to the deformation band of CH_3 groups $\delta(CH_3)$, and d the sample thickness. It was seen to increase in the following order: HDPE $<$ m-PE $<$ LLDPE. The results obtained indicate a clear relationship between activation energy and the chain branching of the polymers, E_a decreases as the chain branching increases.

Such behaviour can be explained by the mechanism of thermal degradation of polyethylene [16] shown in Scheme 1 , which assumes random scission of the carbon–carbon backbone to form secondary alkyl radicals in the earlier stages [1]. After initiation, random abstraction of hydrogen atoms by these alkyl radicals takes place [2]. This is followed by scission of the backbone at a carbon–carbon bond β to the new radical to give an allylic end group and a radical chain end as products [3]. Termination is considered to be mainly by radical–radical disproportionation at chain ends to give a saturated chain end and an unsaturated chain end [4].

On the branched polyethylenes the scissions at C–C and C–H bonds which involve a tertiary carbon atom may be easier than for linear polymers, which results in a lower apparent activation energy as branching increases. HDPE with lower chain branching gives rise to higher E_a values than the branched polymers LLDPE and m-PE.

An analysis of the three polymers before and after thermal ageing at 90 °C was undertaken using FTIR, the obtained data are compiled in Table 4. In general, the metallocene polymer exhibited the lowest initial concentration of oxidised products associated with a low oxidation level during the manufacturing process. Hydroperoxide concentration for m-PE was seen to gradually increase up to 144 h of ageing, whereas, for HDPE which gave the highest initial hydroperoxide values, and LLDPE, an autocatalytic oxidation process was observed. HDPE was the most unstable polymer, followed by LLDPE and m-PE.

A similar order for the stability of the polyethylenes was found through the measurement of carbonyl index growth (Fig. 3). The m-PE and LLDPE samples showed an initial

Table 3
Determination of E_a (KJ mol^{-1}), factor A_0, and chain branching (A/d, where A is the absorption $\delta(CH_3)$ at 1378 cm^{-1} and d the sample thickness in cm)

Sample	A/d	E_a	Factor A_0			
			β (10 °C min^{-1})	β (20 °C min^{-1})	β (30 °C min^{-1})	β (50 °C min^{-1})
HDPE	26.43	276.43	1.148×10^{16}	1.102×10^{16}	1.078×10^{16}	1.046×10^{16}
LLDPE	47.03	207.2	1.161×10^{11}	1.097×10^{11}	1.065×10^{11}	1.028×10^{11}
m-PE	34.76	238	1.42×10^{12}	1.35×10^{12}	1.3×10^{12}	1.26×10^{12}

$$P_nH \longrightarrow P_m^{\bullet} + P_{n-m}^{\bullet} \qquad [1]$$

$$P_m^{\bullet} + P_nH \longrightarrow P_mH + P_n^{\bullet} \qquad [2]$$

$$P_n^{\bullet} \longrightarrow P_{m-2}-CH{=}CH_2 + P_{n-m}^{\bullet} \qquad [3]$$

$$P_n{\bullet} + P_m{\bullet} \longrightarrow P_{n-2}-CH{=}CH_2 + P_{n-2}-CH_2-CH_3 \qquad [4]$$

Scheme 1. Mechanism of thermal degradation of polyethylene.

Table 4
IR absorbances of thermooxidative species formed (*A*/*d* values, where $d(=290 \times 10^{-4}\,\text{cm})$ is the samples thickness) in the thermal aged polyethylenes films, HDPE, LLDPE, m-PE at 90 °C

Time (h)	Hydroperoxides free associate		Hydroxyl, 3371 cm^{-1}	Esters, 1743 cm^{-1}	Aldehydes, 1733 cm^{-1}	Ketones, 1720 cm^{-1}	Acid groups, 1712 cm^{-1}
	3555 cm^{-1}	3410 cm^{-1}					
HDPE							
0	0.153	4.553	1.113	0.265	0.176	0.103	–
24	0.217	5.5	1.013	0.464	0.183	0.305	0.18
74	0.309	9.767	1.863	0.539	0.637	2.205	2.99
144	1.211	11.033	2.467	18.137	28.43	14.16	12.107
LLDPE							
0	0.097	4.213	0.871	0.495	0.030	0.064	–
24	0.122	4.580	0.882	0.516	0.056	0.071	0.037
74	0.176	6.066	0.891	0.524	0.094	0.176	0.044
144	0.333	10.766	1.002	0.983	0.289	0.633	0.091
m-PE							
0	0.068	4	0.888	0.216	0.103	0.017	0.007
24	0.074	4.752	0.933	0.245	0.117	0.027	0.013
74	0.087	5.233	1.118	0.274	0.151	0.089	0.019
144	0.116	5.5	1.245	0.562	0.326	0.928	0.081

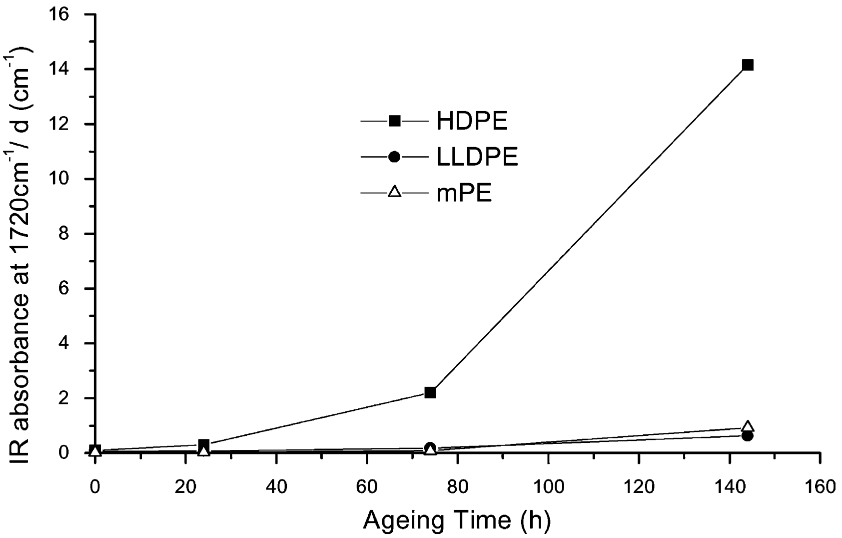


Fig. 3. Carbony index (1720 cm^{-1}) vs. oven ageing time at 90 °C for films of HDPE, LLDPE and m-PE polymers ($d(= 290 \times 10^{-4}\,\text{cm})$ is the film thickness).

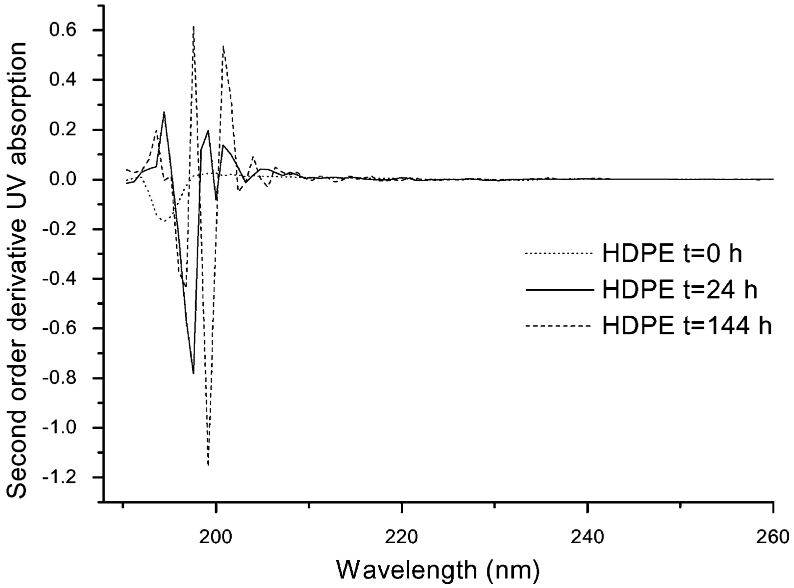


Fig. 4. Second-order derivative UV spectra of HDPE films at different thermal ageing times at 90 °C.

autoretarding effect, whereas, HDPE film exhibited a shorter induction period and the highest carbonyl levels up to 144 h heating.

As already described, different vinyl types are generated in the thermal degradation of polymers. The analysis of the initial concentration and evolution of those species in HDPE, LLDPE and m-PE after thermal ageing, was undertaken using second order derivative UV analysis (Figs. 4–6).

In general, HDPE exhibited the higher initial concentration of vinyl groups compared to LLDPE and m-PE. HDPE had a very strong band at 199 nm (not present in LLDPE and m-PE), assigned to less substituted vinyl [11]. m-PE showed a band at 205 nm corresponding to disubstituted vinyl, and was not present in HDPE and LLDPE. The three polymers have a band at 194 nm assigned to monosubstituted vinylidene groups, HDPE showed the highest absorbance of this band and a greater increase of those species with ageing time. From the results obtained, the order established for the oxidation susceptibility is as follow: HDPE > LLDPE > m-PE in accordance with carbonyl index results.

CL spectra of the initial polyethylenes films were measured at 170 °C (Fig. 7). The metallocene polymer exhibited the lowest CL intensity, at 170 °C, for initial sample which corresponds to the lowest concentration of oxidised

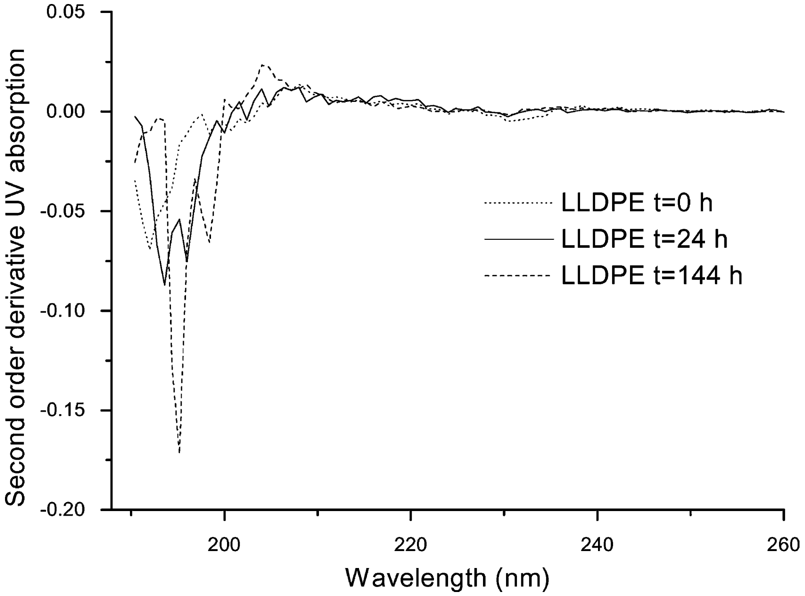


Fig. 5. Second-order derivative UV spectra of LLDPE films at different thermal ageing times at 90 °C.

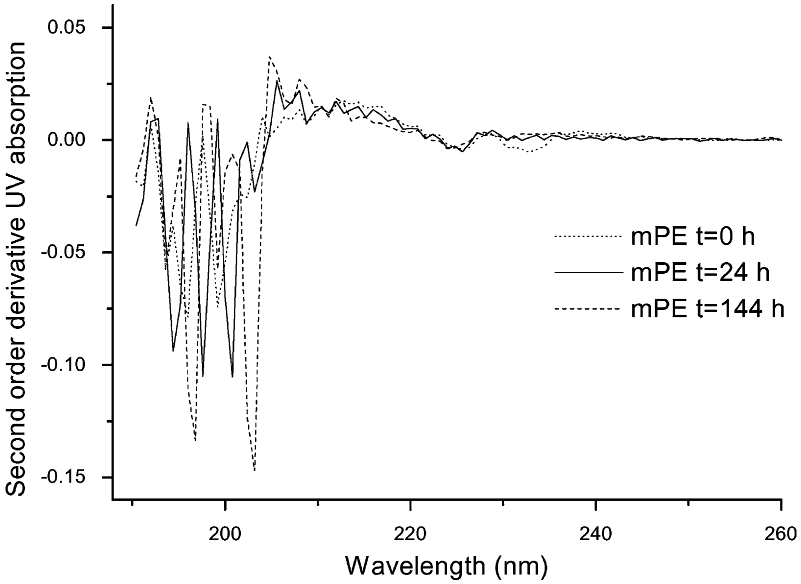


Fig. 6. Second-order derivative UV spectra of m-PE films at different thermal ageing times at 90 °C.

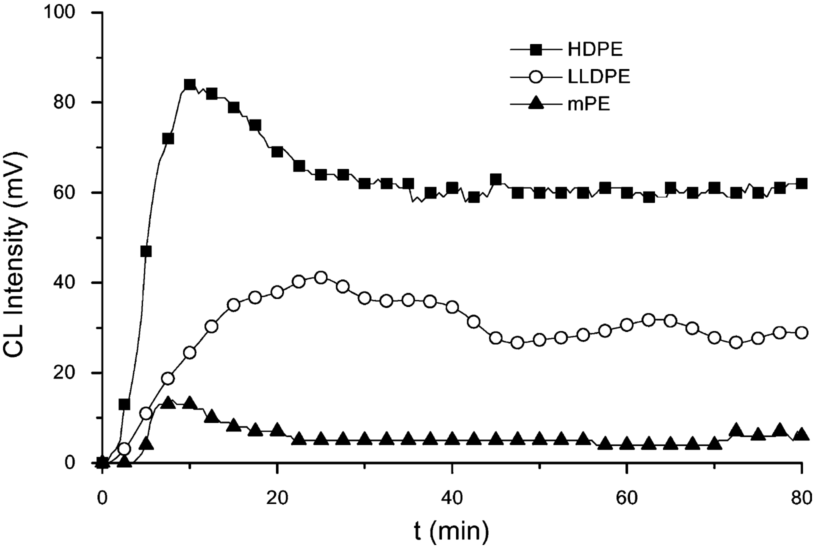
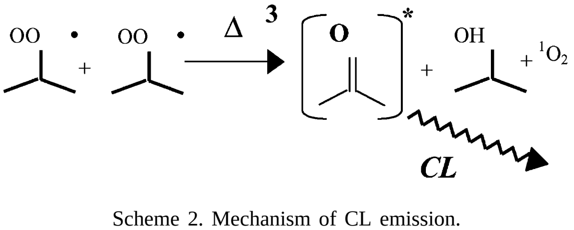


Fig. 7. CL spectra under nitrogen of HDPE, LLDPE and m-PE polymers at 170 °C.

products as determined by FTIR (Table 4). The most likely photon emitting reaction is the exothermic termination of two alkylperoxy radicals [17] (Scheme 2); this reaction produces alcohol, singlet oxygen and excited carbonyl species.



Scheme 2. Mechanism of CL emission.

This thermogenerated carbonyl triplet state deactivates by phosphorescence emission (CL) to its ground state. The generation of peroxy radicals depends on the peroxide concentration, and the CL can be related to the hydroperoxide content of the polyolefin [18].

For the three polyethylenes, the intensity of CL of the fresh and aged samples were measured from 25 to 250 °C (Fig. 8). The intensity of CL of the aged samples is very much higher than that of the initial polymers, due to the decomposition of the hydroperoxides generated during the thermal degradation. LLDPE and m-PE show a gradual increase of the intensity of CL with ageing time, whereas, for HDPE an autocatalytic oxidation process was observed;

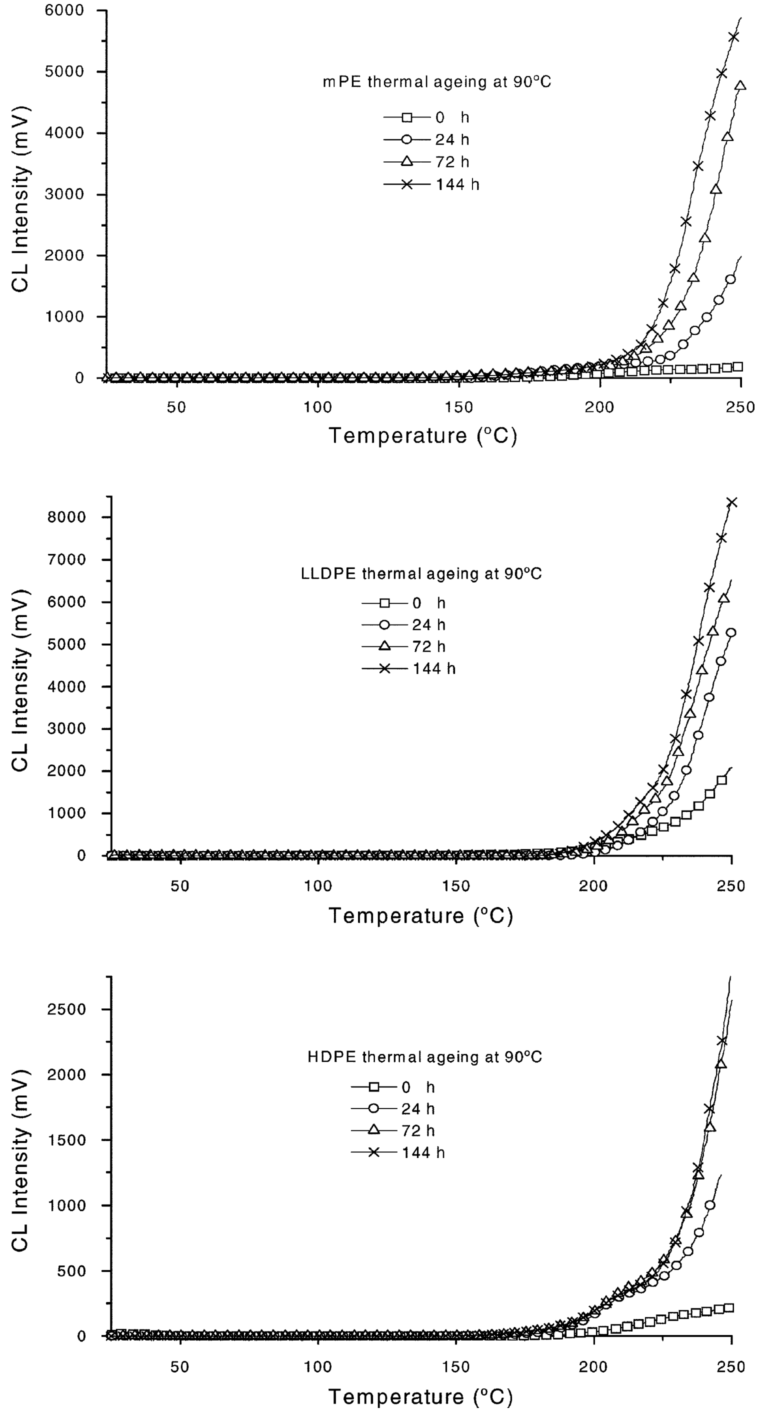


Fig. 8. CL spectra under nitrogen of HDPE, LLDPE and m-PE polymers at different oven ageing time at 90 °C.

and the emission was detected at lower temperature than LLDPE and m-PE, which showed an inhibition period. This result would indicate that HDPE is more susceptible to oxidation, followed by LLDPE and m-PE, in agreement with the above commented results.

Activation energies for the thermal degradation of polyethylenes were determined at different oven ageing times (Fig. 9). HDPE gave rise to a significant decrease in the activation energies with ageing; whereas, LLDPE and m-PE showed an decrease in those values. The thermal stability could be expressed by means of $\Delta E_a/\Delta t$. As the sample is degradating, the scission of bonds may be easier and this is in agreement with the decrease in the activation energy with ageing time. The thermal stabilities $\Delta E_a/\Delta t$ were determined for HDPE, LLDPE and m-PE, and values of 0.92, 0.179 and 0.218 were found, respectively. HDPE,

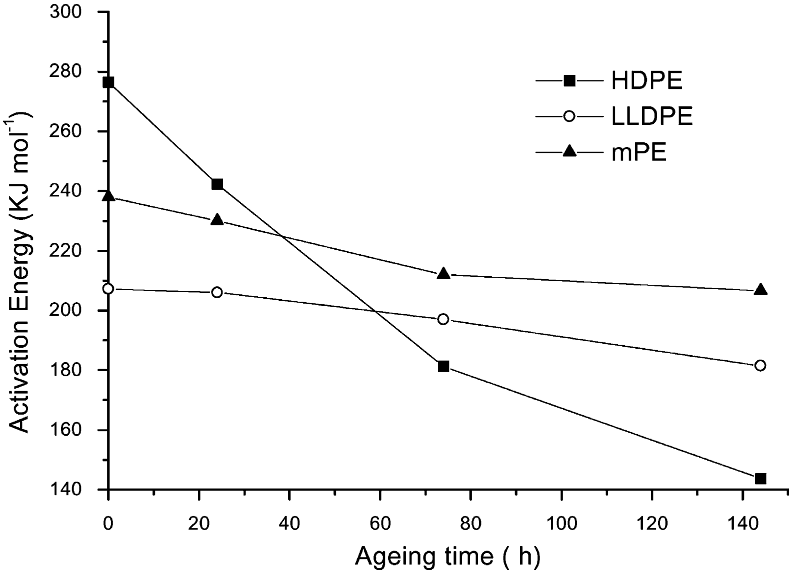


Fig. 9. Activation energies E_a vs. oven ageing time at 90 °C for films of HDPE, LLDPE and m-PE polymers.

which exhibited the highest initial oxidised species, seems to be the most unstable, showing the highest value; whereas, LLDPE and m-PE with lower initial hydroperoxide and vinyl concentration, showed a similar thermal stability with a longer induction period, as was seen by the evolution of carbonyl index in Table 5.

The photostability of the three polyethylenes was studied using FTIR spectroscopy, before and after irradiating the samples, the obtained results are compiled in Table 5. Hydroperoxide analysis showed a higher light stability for LLDPE compared to HDPE and m-PE. Metallocene polymer was found to be the most unstable of the three polyethylenes, through carbonyl index analysis (Fig. 10). In previous work [11], the lower photostability of m-PE was related to the presence of high levels of photoactive fluorescent species which would contribute to the photodegradation of the polymer.

The study of the degree of oxidation for UV degraded samples was undertaken by means of CL analysis (Fig. 11). In general, the aged samples showed an increasing intensity of CL emission with irradiation time. Higher light stability was found for LLDPE, which did not exhibit any CL emission at lower temperatures; whereas, for m-PE and HDPE CL was also observed below the melting point, with a shorter inhibition period for m-PE. This is in agreement with the measurement of carbonyl group values obtained by FTIR,

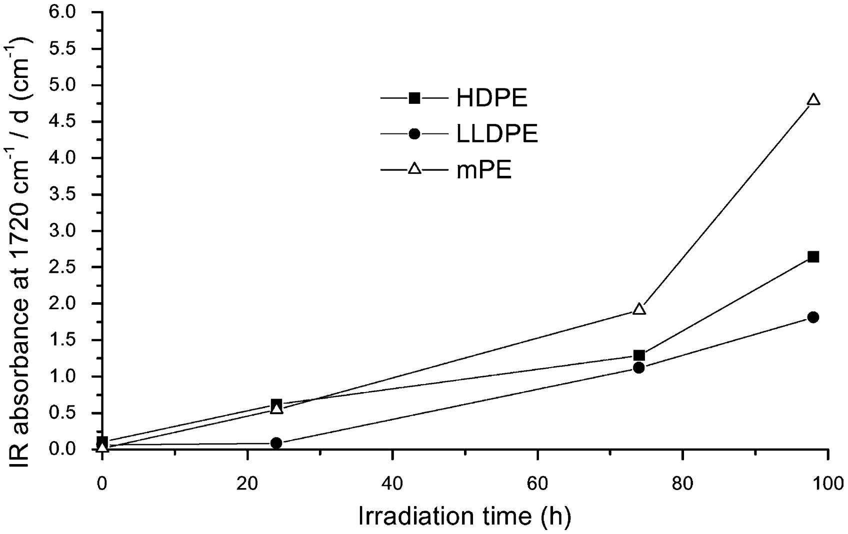


Fig. 10. Carbony index (1720 cm^{-1}) vs. irradiation time in a Microscal Suntest Atlas 2200 W with solar filter 300–800 nm, 550 W/m^2, for films of HDPE, LLDPE and m-PE polymers.

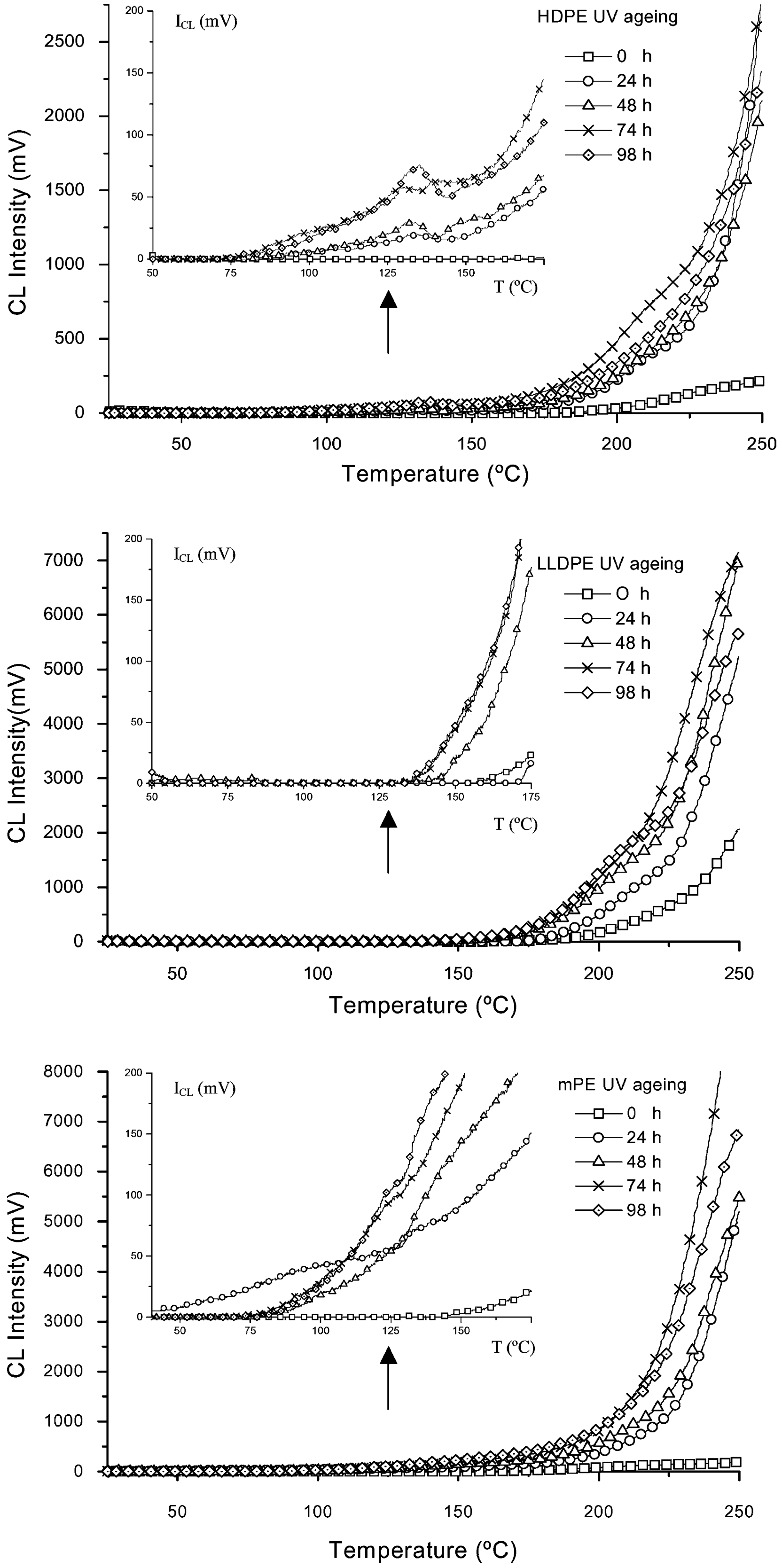


Fig. 11. CL spectra under nitrogen of HDPE, LLDPE and m-PE polymers at different irradiation time in a Microscal Suntest Atlas 2200 W with solar filter 300–800 nm, 550 W/m^2.

Table 5
IR absorbances of oxidative species formed (*A*/*d* values, where $d(=290 \times 10^{-4}$ cm) is the samples thickness) in the UV aged polyethylenes films, HDPE, LLDPE, m-PE (550 W/m^2, 300–800 nm)

Time (h)	Hydroperoxides free associate		Hydroxyl, 3371 cm^{-1}	Esters, 1743 cm^{-1}	Aldehydes, 1733 cm^{-1}	Ketones, 1720 cm^{-1}	Acid groups, 1712 cm^{-1}
	3555 cm^{-1}	3410 cm^{-1}					
HDPE							
0	0.153	4	1.113	0.265	0.176	0.103	–
24	0.217	4.713	1.178	0.372	0.392	0.618	1
74	0.219	4.986	1.309	0.432	0.608	1.294	2.304
98	0.37	6.007	1.363	1.063	1.912	2.646	3.273
LLDPE							
0	0.097	4.553	0.871	0.495	0.103	0.064	–
24	0.101	4.789	0.966	0.597	0.132	0.083	0.427
74	0.125	5.068	1.112	0.725	0.196	1.118	1.294
98	0.151	5.153	1.463	1.568	0.294	1.814	2.666
m-PE							
0	0.068	4.213	0.888	0.216	0.030	0.017	0.007
24	0.082	4.553	0.869	0.385	0.105	0.546	0.348
74	0.240	5.62	1.168	0.539	1.029	1.912	3.92
98	0.307	5.753	1.219	1.422	1.936	4.786	6.569

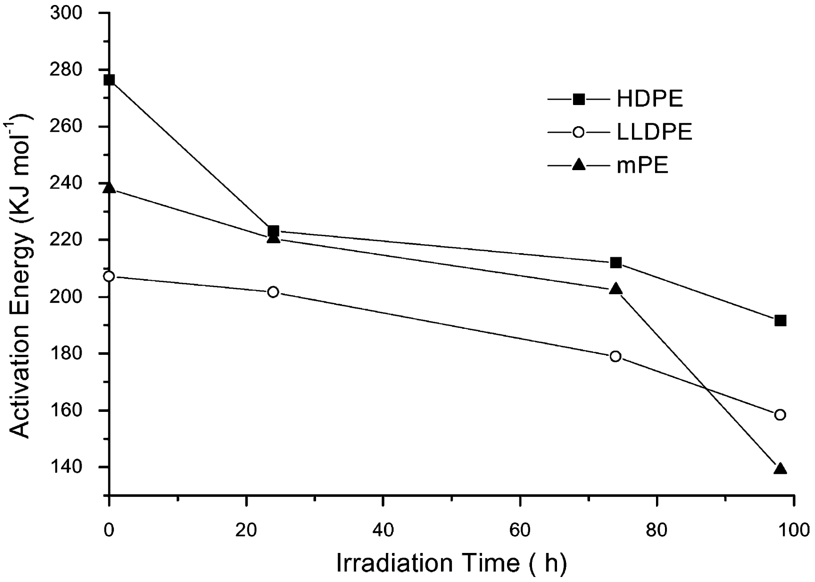


Fig. 12. Activation energies E_a vs. irradiation time in a Microscale Suntest Atlas 2200 W with solar filter 300–800 nm, 550 W/m^2 for films of HDPE, LLDPE and m-PE polymers.

where m-PE showed the highest absorbances up to 98 h irradiation.

The activation energies were calculated at different irradiation times using TGA (Fig. 12). The UV stability expressed as $\Delta E_a/\Delta t$ was determined and compared for polyethylenes. Values of 0.86, 0.499 and 1.01 were found for HDPE, LLDPE and m-PE, respectively. For all samples, E_a decreases with the irradiation time, metallocene polymer is the most unstable followed by HDPE and LLDPE. This result would confirm again the data obtained by CL analysis, where higher stability for LLDPE under UV irradiation was found.

4. Conclusions

The thermal and photooxidative stabilities of different polyethylenes have been analysed by CL and TGA; and their activation energies of thermal and photoageing determined. TGA is shown to be a viable technique to obtain quantitative information on the decomposition rates of polyolefins. The presence and degree of chain branching was found to be implicated in controlling the rates of thermal oxidation of the polymers. The results are in good agreement with the CL measurement. This study shows that CL provides useful data for the characterisation of the stability of several polyethylenes having various structures; in order to a certain correlations between structure–property relationships.

Decrease in activation energies in thermal degradation were found to follow the order HDPE > m-PE > LLDPE, while in photooxidation they followed the order m-PE > HDPE > LLDPE. These changes in activation energies for thermal decomposition were found to correlate with the respective rates of oxidation of the different polyethylenes as measured by the carbonyl index method employing FTIR spectroscopy under thermal and light induced oxidation. These results are also in agreement with the CL data where thermally degraded HDPE exhibited CL emission at lower temperatures than LLDPE and m-PE, and an autocatalytic oxidation process was observed with ageing time. However, a higher light stability was determined for LLDPE, which exhibited no emission at lower temperatures when compared to HDPE and m-PE, which also showed CL emission below their melting points.

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