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Influence of irradiance on the photooxidation of HALS stabilized low-density polyethylene

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Highlights

- The observed stabilizing efficiency of a given stabilizer (HALS) depends on the irradiance.
- The increase of photooxidation rate depends on the type of HALS stabilizer.
- Lifetime predictions based on exposures performed at different irradiances do not give the same lifetime for the same sample
- The predicted lifetime of HALS stabilized LDPE depends on the irradiance used.

Abstract

This paper concerns the experimental analysis of the effect of irradiance on the photooxidation of low-density polyethylene (LDPE) stabilized with different HALS. Infrared analysis in transmission mode was used to monitor the extent of oxidation provoked by the exposure of thin samples (100 microns thick) in a SEPAP MHE unit (Atlas/Ametek) at two different irradiances (90 W.m⁻² and 300 W.m⁻² between 300 and 420 nm). The temperature of the samples was maintained constant in order to focus on the impact of irradiance on the kinetics, without interfering with the temperature. The intended goal was to characterize the effect of the irradiance in accelerated testing and the consequences on the lifetime prediction. Previous results obtained in the case of unstabilized LDPE samples showed that no acceleration was obtained when increasing the irradiance from 90 W.m⁻² and 300 W.m⁻² while keeping the temperature constant. In the case of the stabilized samples, the results presented in the present article show that the rates of photo oxidation tended to increase when increasing the irradiance. However, the ratio of these rates never reaches the ratio of the irradiances, and these ratios depends on the stability of the samples.

Keywords: polyethylene, HALS, photooxidation, irradiance, acceleration, shift factors

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1. Introduction

Polymeric materials change their properties depending on the environmental parameters at the site of use. The most important parameters are the incident solar light and the temperature of the material. Accelerated testing is necessary for the development of new products within a commercially acceptable time with the aim of shortening the design-development-production cycle [1]. A conventional method of accelerated weathering is by irradiating materials at a radiant flux higher than the in-service flux and extrapolating the results back to in-service flux levels. Using highly severe tests, it would indeed be possible to estimate the time that will be required under the milder conditions in order to make a judgement concerning the most promising materials. Accelerating degradation has been indeed desired for years, and the influence of the light intensity and the temperature has been explored. Accelerated-ageing tests are carried out for two major purposes. The first is to establish the relative ranking of materials in a conveniently short time, and the second is to estimate or “predict” potential long-term serviceability of materials. Testing in accelerated conditions can indeed provide useful information in shorter time periods, but the stresses (light, heat, etc.) and their intensity have to be chosen accurately to avoid unrealistic degradation modes and failure mechanisms not observed in natural weathering [2,3]. Understanding the sources of errors is mandatory for developing relevant testing methods. Many articles have been published dealing with accelerated weathering and service life prediction in various industrial domains [4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19]. Most authors agree that sunlight, particularly the UV component is the primary factor in outdoor weathering, and as a consequence, artificial ageing is performed using UV sources with irradiances greater than the outdoor irradiance in order to achieve acceleration. It has been agreed for years that sources with wavelengths not present in the solar spectrum at the surface of the earth have to be excluded, and that irradiances that are too high (lasers for example) should not be used since they produce effects not encountered during natural weathering (*e.g.* biphotonic excitation, etc.) [20]. The effect of irradiance on the photodegradation of polymers has received much attention. Generally, the effect of irradiance on the rate of a photochemical process can be characterized by the Schwarzschild law [21]:

$$I^p \cdot t = \text{constant},$$

with I = irradiance, t = exposure time and p the Schwarzschild coefficient.

When $p = 1$, Schwarzschild's law becomes the reciprocity law:

$$I \cdot t = \text{constant.}$$

A material obeys reciprocity if the degradation is a function of the total radiant energy and not a function of the rate at which the energy is applied. The literature reports many studies of irradiation effects on the photodegradation of polymers [22,23,24,25,26,27]. Simplifying assumptions should not be made concerning the photodegradation process: polymer degradation is not linearly proportional to the energy dose and therefore is not linear in light intensity [28]. The p -coefficient ranges between 0.5 and 1 for many (unstabilized, stabilized or pigmented) polymeric systems, and moreover, the Schwarzschild coefficient p may vary from one given material to another.

In a previous article [29], we reported a study of the influence of light intensity on the rate of photooxidation of unstabilized polyethylene. Chemical modification provoked by UV light was characterized by infrared spectrometry measurements. The objective was to define the limits and accuracy of accelerated weathering of polyethylene and to discuss the relevance of "highly" accelerated UV weathering tools. We have shown in this article that no acceleration of the oxidation was obtained by increasing the irradiance above a certain level not considered high. It was also shown that reciprocity failure with a p from 0.5 to 0 occurred when increasing the irradiance while staying in a range of conventional irradiance values. This was explained by the fact that recombination and/or disproportionation are faster than propagation as a result of excessive free radical generation resulting from light absorption at high irradiance levels. This result is important from a practical point of view since it provides strong indications regarding the limits of accelerated ageing and lifetime prediction. This result was unexpected and raises the issue of lifetime prediction from accelerated ageing. It may be anticipated that, for a given polymer, the Schwarzschild coefficient p could vary with the stabilization brought by different stabilizers or different concentrations of a given stabilizer.

One could then question the influence of light intensity and how the rate of photooxidation varies in the case of stabilized samples when increasing the light intensity. The present study discusses the effect of varying UV intensity on the degradation rates of low-density polyethylene stabilized with various commercial hindered amine light stabilizers (HALS) used in LDPE films for agricultural applications [9]. The samples were exposed to accelerated ageing at two different irradiances (90 and 300 $\text{W}\cdot\text{m}^{-2}$ between 300 and 420 nm). Exposures

were performed at a constant temperature (60 °C) to avoid any undesirable acceleration due to the increase in temperature (we have shown that the activation energy of LDPE photooxidation is 74 kJ.mol⁻¹ [29]). The chemical modification provoked by UV light was characterized by infrared spectrometry measurements. The objective is to discuss the predictive aspect of accelerated weathering for stabilized samples.

2. Materials and experimental

2.1. Polyethylene grades

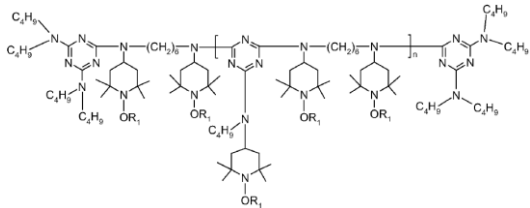
Two different low-density polyethylene (LDPE) grades were used in this study as raw materials and for formulated compounds: ALCUDIA® PE-033 commercially available at REPSOL and hereafter called PE033 (density 0.921; MFI 0.3 g/10 min), and Lupolen 2420 F from LyondellBasell Industries and later designed as PE2420F (density 0.923; MFI 0.75 g/10 min).

2.2. Stabilizers

The commercial names and amounts of stabilizers used in the preparation of the materials for photoageing studies are shown in Table 1.

Table 1: Commercial names and amounts of stabilizers used in the stabilized LDPE

Commercial name	Chemical structure	Supplier	Molar mass (g.mol ⁻¹)
Tinuvin® 622		BASF	3100 - 4000
Chimassorb® 944		BASF	2000 – 3100
Sabostab® UV 119		SABO	2286

<p>Tinuvin® NOR 371</p>		<p>BASF</p>	<p>2800 - 4000</p>
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2.3. Formulated samples

Two series of samples were successively studied. The first one was produced with PE033 as the carrier resin with 0.2% w/w of different HALS stabilizers (see Table 1). The compositions are given in Table 2. No processing antioxidant was added.

Table 2: Formulations based on PE033 with various HALS at the same concentration (0.2% w/w)

Sample	Polymer	HALS (% w/w)	Active groups (per 100 g of polymer)
T622	PE033 (99.8 % w/w)	Tinuvin® 622 (0.2)	7.0×10^{-4} mol
C944		Chimassorb® 944 (0.2)	7.3×10^{-4} mol
S119		Sabostab® UV 119 (0.2)	7.0×10^{-4} mol
T371		Tinuvin® 371 (0.2)	5.7×10^{-4} mol

The second series of samples was prepared using PE2420F as the carrier resin and Sabostab® UV 119 as the stabilizer with concentrations from 0.1 to 0.4% w/w (Table 3).

Table 3: Formulations based on PE2420F with Sabostab® UV 119 at various amounts

Sample	Polymer	HALS (% w/w)	Active groups (per 100 g of polymer)
S119-0.1	PE2420F (99.9 % w/w)	Sabostab® 119 (0.1)	3.5×10^{-4} mol
S119-0.2	PE2420F (99.8 % w/w)	Sabostab® 119 (0.2)	7.0×10^{-4} mol
S119-0.4	PE2420F (99.6 % w/w)	Sabostab® 119 (0.4)	14.0×10^{-4} mol

2.4. Preparation of polymer films

Raw and stabilized PE films with a thickness of 100 µm were obtained from blown extrusion at 200 °C on a single layer laboratory extruder at Barbier Group. The duration of the processing was 5 min.

2.5. Photothermal ageing

The samples were irradiated in a SEPAP MHE unit (Atlas/Ametek) at 60°C [29]. Three samples for each formulation were exposed and characterized to ensure the reproducibility of the spectrometry measurements. The SEPAP MHE was equipped with a medium-pressure mercury lamp located in the center of the apparatus, around which the samples were placed on a rotating carousel. Wavelengths below 300 nm were filtered out. The irradiance between 300 and 420 nm was fixed either at 90 W.m⁻² (M mode) or at 300 W.m⁻² (H mode). For comparison, the ISO/TR 17801:2014 (E) standard for peak AM 1 sunlight has an integrated irradiance of 99.5 W/m² over the range 300-420 nm [30]. Irradiance and black standard temperature (T_{BST}) were on-rack controlled on-rack by a wireless XENOSENSIV light and a BST monitor, respectively. The temperature of the air in the device (T_{ch}) was controlled by a sensor placed inside the chamber. As the polymer films used in this study were transparent, the temperature at the surface of the films was considered equal to the chamber temperature.

2.6. Characterization method

The thickness of the samples (100 μm) was low enough to allow for monitoring the chemical changes in transmission mode. The spectra were recorded with a Nicolet 6700 FTIR spectrometer working with OMNIC software. The spectra were obtained using 32 scans and a 2 cm⁻¹ resolution. Small differences in sample thickness were corrected by considering a reference band which is not affected by the ageing. In order to plot the oxidation kinetics, we measured the differences of absorbance with respect to t_0 ΔA at 1713 cm⁻¹ (C=O stretching in carboxylic acids).

3. Results and discussion

Infrared spectroscopy has proven to be a suitable and frequently used analytical technique for monitoring the oxidation process of polyethylene [31,32].

During the photooxidation, dramatic changes in the infrared spectra of the exposed samples are noted in the carbonyl, as illustrated in Figure 1, and hydroxyl absorption ranges.

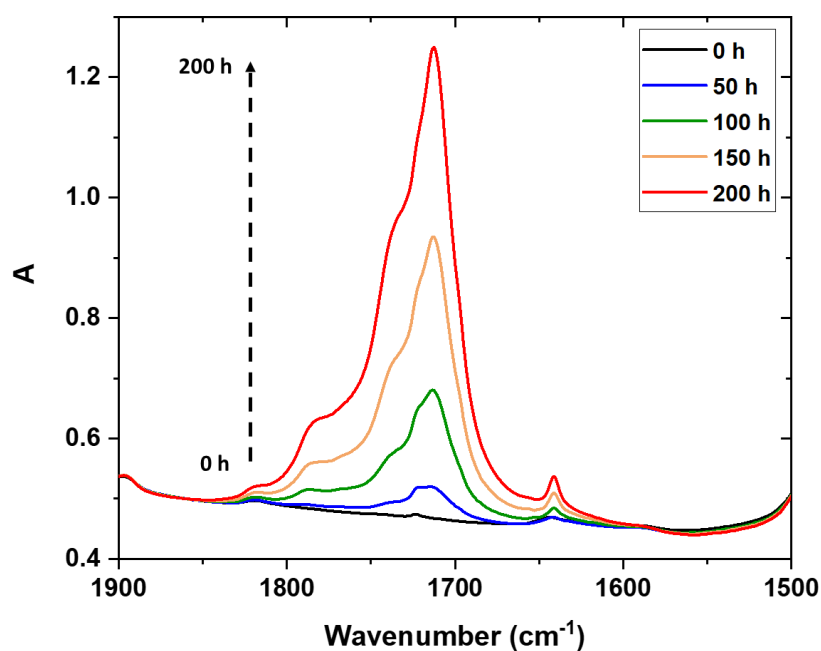


Figure 1: Infrared spectra of a LDPE PE033 film (100 microns) at different times of photooxidation with the MHE device (90 W.m^{-2} and 60°C)

These changes in the carbonyl absorption range indicate the formation of ketones (1718 cm^{-1}), carboxylic acids (1713 cm^{-1}), esters (1735 cm^{-1}) and lactones (1780 cm^{-1}) [31]. One can also notice the formation of isolated double bonds (1640 cm^{-1}). In the range of hydroxyl frequencies, a broad band with a maximum at 3420 cm^{-1} and a sharp absorption band at 3550 cm^{-1} appeared in the spectrum. These bands were attributed to the formation of monomeric hydroperoxides (3550 cm^{-1}) and hydrogen-bonded alcohols and hydroperoxides (3420 cm^{-1}). The intensities of both bands remained very low, confirming that the stationary concentrations of hydroperoxides were rather small under the conditions of photooxidation [33]. The mechanism of photooxidation accounting for the main routes of degradation of PE is fairly well understood [31]. Plotting the absorbance at 1713 cm^{-1} with the exposure time allows for comparing the rate of oxidation of the different formulations.

3.1 Influence of the irradiance (90 W.m^{-2} and 300 W.m^{-2}) at a constant temperature on the photooxidation of non-stabilized LDPE PE033 and PE2420F

The influence of the irradiance on the oxidation of samples was first evaluated for non-stabilized films of PE 033 and PE 2420F with a thickness of 100 microns exposed at 90 and 300 W.m^{-2} in the chamber of the MHE device at a sample temperature of 60°C . The

difference of absorbance with respect to t_0 $\Delta A(1713 \text{ cm}^{-1})$ was measured and plotted as a function of the exposure time (Figure 2).

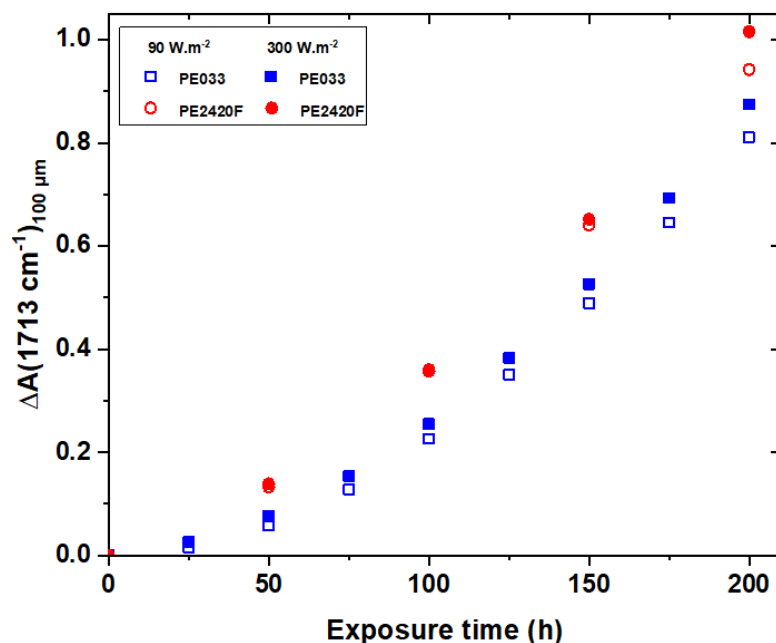


Figure 2: Carbonyl absorbance $\Delta A(1713 \text{ cm}^{-1})$ vs. ageing time at 90 and 300 W.m^{-2} for non-stabilized samples PE033 and PE2420F ($T = 60 \text{ }^\circ\text{C}$ and film thickness = 100 microns)

As expected from our previous results reported in reference 29, the kinetic curves obtained from exposing the unstabilized samples to these two different irradiances (90 W.m^{-2} and 300 W.m^{-2}) at the same temperature were the same, confirming that no acceleration of photooxidation was observed, although the irradiance increased by a factor of 3.33. This result is obtained for both polymers PE033 and PE2420F, which degrade at very similar rates.

3.2 Influence of the irradiance on formulations based on PE033 with various HALS at the same concentration and determination of shift factors

The formulations studied here were elaborated on the basis of PE033 and 0.2% w/w of different HALS (Tables 1 and 2). Figure 3 shows the corresponding $\Delta A(1713 \text{ cm}^{-1})$ values as a function of the exposure time.

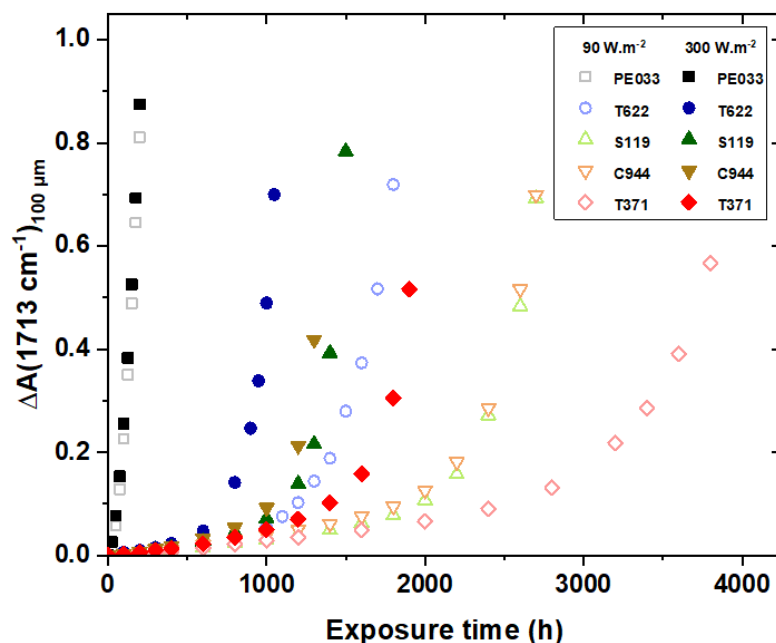


Figure 3. Carbonyl absorbance $\Delta A(1713 \text{ cm}^{-1})$ vs. ageing time at 90 and 300 W.m^{-2} for PE033 samples stabilized with different HALS ($T = 60 \text{ }^\circ\text{C}$ and film thickness = 100 microns)

We can observe a stabilizing effect of the HALS that were used, which depends on their nature. It is not the objective of this article to comment on the influence of the stabilizers and on the stabilities, which are brought by the various HALS at a concentration of 0.2% w/w. One will summarize that the observed order of stability was Tinuvin® NOR 371 (T371) > Sabostab® 119 (S119) > Chimassorb® 944 (C944) > Tinuvin® 622 (T622). Figure 3 shows that the order of stability is the same when irradiations are performed either at 90 or 300 W.m^{-2} . More importantly, the relative rates of oxidation (90 W.m^{-2} vs. 300 W.m^{-2}) are not similar for the various stabilizers that were used. Table 4 gives the time to reach an absorbance difference ΔA of 0.4 at 1713 cm^{-1} , which allows comparing the photostability of the different formulations.

Table 4. Time to reach an absorbance difference ΔA of 0.4 as a function of the stabilizer and the irradiance (data obtained from Figure 3)

Sample	Time 300 (in hours) to reach $\Delta A (1713 \text{ cm}^{-1}) = 0.4$ at 90 W.m^{-2}	Time 90 (in hours) to reach $\Delta A (1713 \text{ cm}^{-1}) = 0.4$ at 300 W.m^{-2}
PE033	130	130
T622	1620	970

S119	2540	1400
C944	2520	1290
T371	3610	1850

Comparing the oxidation rates represented in Figure 3 allows a shift factor to be calculated. The shift factor is simply obtained by multiplying the time scale by some fixed number. This is represented in Figure 4, which shows the carbonyl absorbance data obtained for irradiation at 300 W.m^{-2} as a function of the exposure time multiplied by the shift factor. These data are compared to the carbonyl absorbance data obtained for irradiation at 90 W.m^{-2} as a function of the exposure time. This factor was determined experimentally by considering the mean ratio of the exposure times to reach the same degradation along the whole kinetic curves and are reported in Table 5.

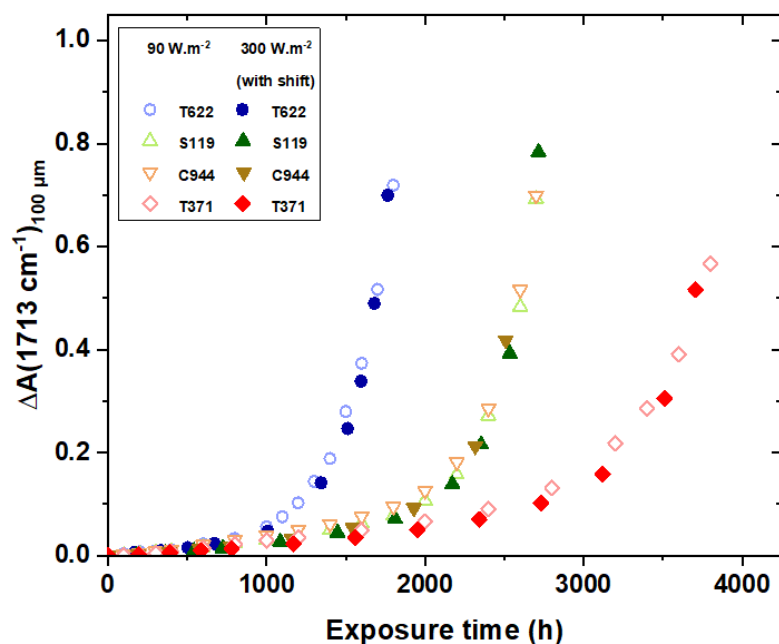


Figure 4. Carbonyl absorbance $\Delta A(1713 \text{ cm}^{-1})_{100 \mu\text{m}}$ vs. ageing time at 90 and 300 W.m^{-2} for PE033 samples stabilized with different HALS, with time scale multiplied by the shift factors reported in Table 5 in the case of the curves at 300 W.m^{-2}

For each formulation, we obtain a perfect superposition of the kinetic curves using the shift factors given in Table 5. In addition, these shift factors can be used to estimate the

Schwarzschild coefficient p associated to each sample from the equation $I^p \cdot t = \text{constant}$ (as recalled in the introduction). The p coefficients were calculated as:

$$p = \log(\text{shift factor}) / \log(\text{irradiance ratio})$$

Table 5. Shift factors and Schwarzschild coefficient p determined by superposition of the kinetic curves at 90 and 300 W.m⁻² presented in Figure 3

Sample	Shift Factor	Schwarzschild coefficient p
PE033	1.0	0
T622	1.7	0.44
S119	1.8	0.49
C944	1.9	0.53
T371	2.0	0.58

The results presented in this table clearly indicate that the shift factor is closely related to the stability of the sample, and the shift factor increases with the stabilizing effect brought by the stabilizer. The shift factor is 1 in the case of the unstabilized polymer, and consequently, the Schwarzschild coefficient p is 0, which means that increasing the irradiance above 90 W m⁻² does not provoke any acceleration of photooxidation. Then, when the stability of the polymer brought by the used HALS increases, the shift factor increases progressively to reach a value of 2, and the Schwarzschild coefficient p reaches a maximum value of 0.58. This value is comparable to that reported by Vink [27] which was 0.54 for HDPE with 0.1 % of Tinuvin 770.

3.3 Influence of the irradiance on formulations based on PE2420F with the same HALS at different concentrations and determination of shift factors

The previous results clearly show that the shift factor and the associated Schwarzschild coefficient p are dependent on the stabilizing effect of the considered HALS. It could be expected that the stabilizing effect brought by an increase of the HALS concentration for a same LDPE would also affect these parameters, and the objective of this part was to determine the influence of the irradiance on the photooxidation of formulations using the same stabilizer, but at different amounts. In this experiment, PE2420F with Sabostab® 119 at different amounts (from 0.1 to 0,4% w/w) was used. The obtained results are reported in Figure 5, which shows the oxidation kinetics at two levels of irradiance considered for the samples reported in Table 3.

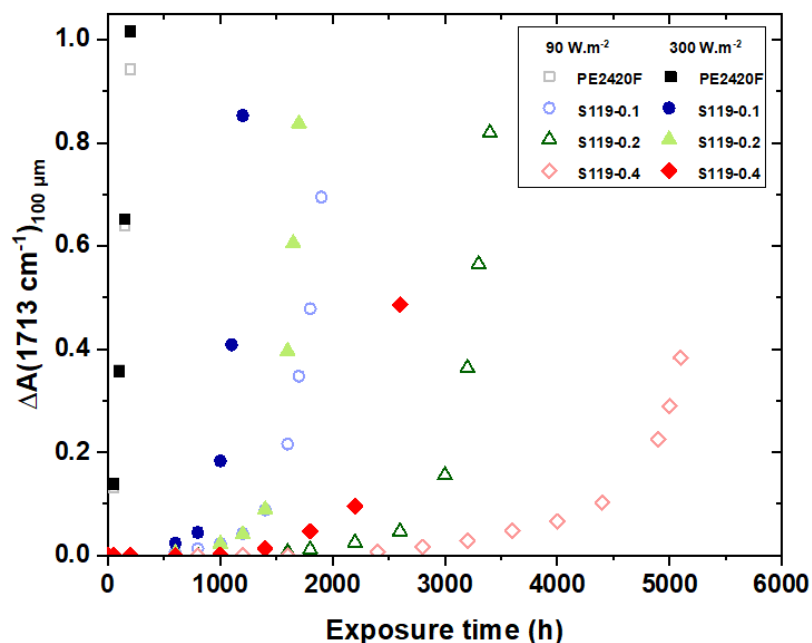


Figure 5. Carbonyl absorbance $\Delta A(1713 \text{ cm}^{-1})$ vs. ageing time at 90 and 300 W.m^{-2} for PE2420F samples stabilized with different amounts of Sabostab® 119 ($T = 60 \text{ }^\circ\text{C}$ and film thickness = 100 microns)

The results reported in this figure indicate that the photostability increases with the amount of stabilizer, which was expected. Table 6 gives the time to reach ΔA of 0.4 at 1713 cm^{-1} , which allows comparing the photostability of the various formulations.

Table 6. Time to reach an absorbance difference ΔA of 0.4 as a function of the stabilizer and the irradiance (from data presented in Figure 6)

Sample	Time (in hours) to reach $\Delta A (1713 \text{ cm}^{-1}) = 0.4$ at 90 W.m^{-2}	Time (in hours) to reach $\Delta A (1713 \text{ cm}^{-1}) = 0.4$ at 300 W.m^{-2}
PE2420F	110	110
S119-0.1	1750	1100
S119-0.2	3220	1600
S119-0.4	5110	2560

The results given in Figure 5 and Table 6 show that, similar to what was observed above (Section 3.2), the relative stabilizing effect is not the same when irradiations are performed at 90 or 300 W.m⁻².

The shift factor was determined following the procedure reported above. The values that allow the best superposition of the kinetic curves are given in Table 7, and the kinetic curves obtained when multiplying the exposure time by the shift factor are displayed in Figure 6.

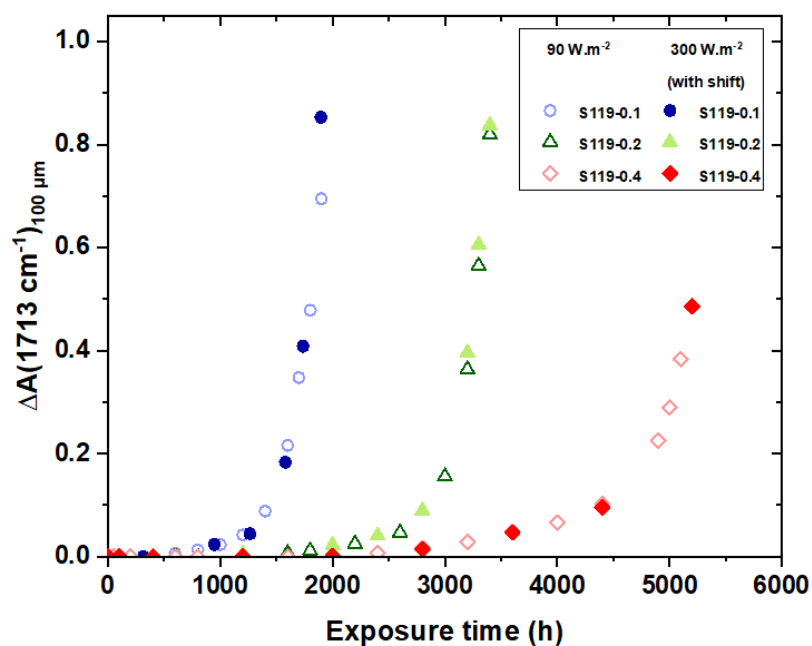


Figure 6. Carbonyl absorbance $\Delta A(1713 \text{ cm}^{-1})_{100 \mu\text{m}}$ vs. exposure time at 90 and 300 W.m⁻² for PE2420F samples stabilized with different amounts of Sabostab® 119, with time scale multiplied by the shift factors reported in Table 7 in the case of the curves at 300 W.m⁻²

Table 7. Shift factors and Schwarzschild coefficient p determined by superposition of the kinetic curves presented in Figure 6.

Sample	Shift Factor	Schwarzschild coefficient p
PE2420F	1	0
S119-0.1	1.6	0.39
S119-0.2	2.0	0.58
S119-0.4	2.0	0.58

Here, again, one can see that the kinetic curves obtained when multiplying the exposure time by the shift factor superpose rather well. Moreover, the shift factors are not constant and increase with the stability of the exposed samples. The values range from 1.6 for an amount of stabilizer of 0.1 % up to 2.0 in the case where the stabilizer amount was 0.4 %. The Schwarzschild coefficient p increases again up to 0.58.

Figure 7 summarizes the results obtained for the two series of samples. These data, which were given in Tables 4 to 7, compare the shift factors and the Schwarzschild coefficient p for the various formulations considered in the current article.

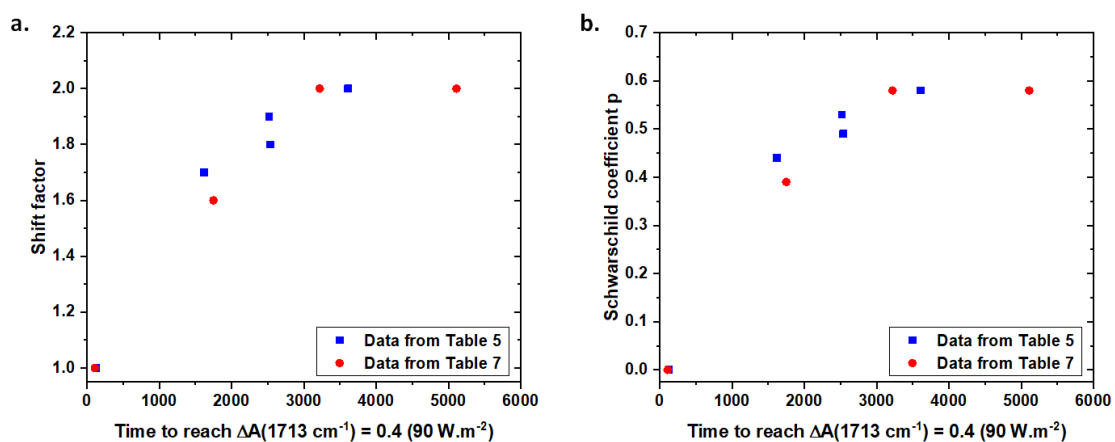


Figure 7. Shift factor (300 W m^{-2} vs. 90 W m^{-2}) (7a) and Schwarzschild coefficient p (7b) as a function of the exposure time at 90 W m^{-2} to reach $\Delta A(1713 \text{ cm}^{-1}) = 0.4$ (film thickness = 100 microns)

Our results indicate that oxidation resulting from exposure to UV light at irradiances equal to 90 or 300 W.m^{-2} between 300 and 420 nm and performed at a temperature of 60°C , which is considered medium to highly accelerated ageing conditions, did not follow the reciprocity law. The Schwarzschild coefficient p was always below 1 and the maximum value that was reached was 0.58 .

Moreover, it was reconfirmed that the coefficient was equal to 0 for the unstabilized LDPE samples above 90 W.m^{-2} , which indicated that increasing the irradiance above this value did not provoke any increase in the oxidation rate. As reported in our previous article, a plausible hypothesis to explain that in the case of unstabilized LDPE samples, no acceleration was observed above a certain level of UV light intensity, was that the free radical generation is so high that recombination and/or disproportionation are faster than propagation for these unstabilized samples. This result was *a priori* unexpected because an irradiance of 90 W.m^{-2} in the range of 300 and 420 nm is generally considered not too high. Hindered Amine

Light Stabilizers inhibit the oxidative degradation of polymers and then decrease the rate of free radical concentration, which has for consequence to change the ratio of recombination and/or disproportionation vs. propagation. Then the shift factor increases when changing the irradiance from 90 W.m^{-2} or 300 W.m^{-2} , but it never reaches the ratio of the irradiances, which is 3.3, and the Schwarzschild coefficient p remains below 0.58.

It is often stated by various standards in use to expose the sample at a given dose when testing the photostability of polymers. Figures 8 and 9 shows the kinetic curves already presented above as Figures 3 and 5, but with the carbonyl absorbance reported as a function of the dose (in MJ.m^{-2}).

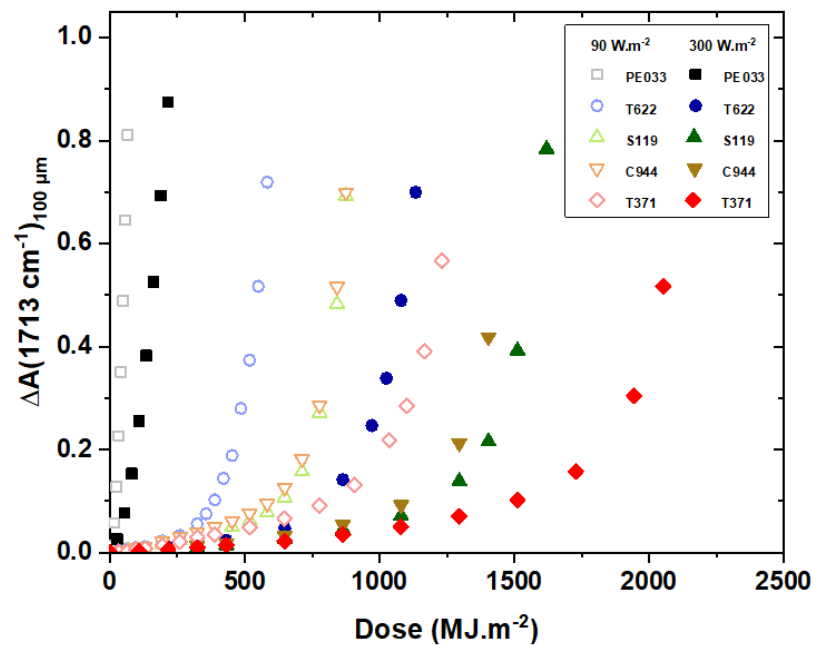


Figure 8. Carbonyl absorbance $\Delta A(1713 \text{ cm}^{-1})$ vs. dose (in MJ.m^{-2}) at 90 and 300 W.m^{-2} for formulations presented in Table 2 and Figure 3 ($T = 60 \text{ }^\circ\text{C}$ and film thickness = 100 microns)

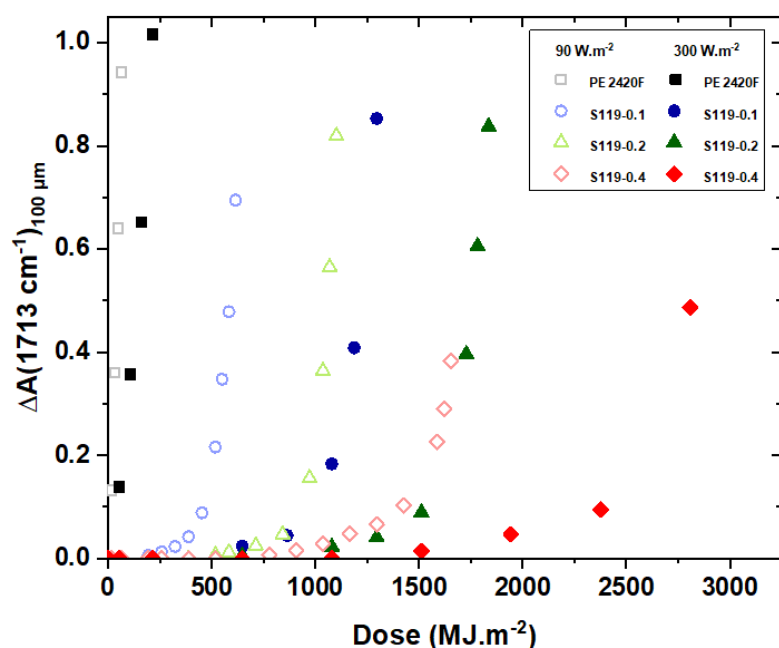


Figure 9. Carbonyl absorbance $\Delta A(1713 \text{ cm}^{-1})_{100 \mu\text{m}}$ vs. dose (in MJ.m^{-2}) at 90 and 300 W.m^{-2} for formulations presented in Table 3 and Figure 5 ($T = 60 \text{ }^\circ\text{C}$ and film thickness = 100 microns)

Using the results presented in Figures 8 and 9 to compare the fate of stabilized samples would lead to false conclusions. In the case of the first series, Figure 8 shows that the formulations exposed at an irradiance of 300 W.m^{-2} require greater doses to reach the same carbonyl absorbance than the formulations exposed at an irradiance of 90 W.m^{-2} . In contrast, Figure 3 clearly shows that the formulations exposed at an irradiance of 90 W.m^{-2} requires longer exposure times to reach the same carbonyl absorbance than the formulations exposed at an irradiance of 300 W.m^{-2} . This illustrates that the reciprocity law is not fulfilled, with a Schwarzschild coefficient p that is well below one. We have similar conclusions in the case of the second series, as shown in Figures 5 and 9.

4. Conclusion

The prediction of durability requires accelerated photoageing which is by nature based on irradiations performed at irradiances higher than the irradiances encountered in natural conditions. It has been admitted for years that too high levels of irradiance must be avoided since they can produce undesired effects, but in this study the irradiances are limited to an conventional range. Obviously, this article clearly indicates that increasing the irradiance,

even staying at conventional levels (i.e., those levels that are used in most conventional ageing devices) cannot provide solid data concerning the durability of the exposed materials, and even more critically, could give false predictions of the protective effect of stabilizers.

The most important conclusion of this study concerns the testing of the degradation of stabilized LDPE samples and the prediction of their durability. The experimental results reported in this article have indeed notable consequences:

- The observed stabilizing efficiency of a given stabilizer (HALS) depends on the irradiance: Depending on the irradiance, characterized here by a ratio of the irradiances equal to 3.3, different relative oxidation rates are found for stabilized LDPE.
- Lifetime predictions based on exposures performed at different irradiances will not give the same lifetime for the same sample, *i.e.* lifetime prediction is dependent on the irradiance used.
- Acceleration of the ageing is not equal to the ratio of the irradiances, that is to say $I_{300 \text{ W.m}^{-2}}/I_{90 \text{ W.m}^{-2}} = 3.3$, is never the acceleration factor observed for stabilized LDPE.

It is apparent that the rate of photooxidative degradation in stabilized or unstabilized LDPE is a function of the light intensity and that the nature of this dependence is controlled by the amount and type of stabilizer in the polymer. This means that, even if light intensities in accelerated testing are identical, a valid comparison of the results of photooxidation cannot be made.

Acknowledgments

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Figure Captions

Figure 1: Infrared spectra of a LDPE PE033 film (100 microns) at different times of photo oxidation with the MHE device (90 W.m^{-2} and 60°C)

Figure 2: Carbonyl absorbance $\Delta A(1713 \text{ cm}^{-1})$ vs. ageing time at 90 and 300 W.m^{-2} for non-stabilized samples PE033 and PE2420F ($T = 60^\circ\text{C}$ and film thickness = 100 microns)

Figure 3. Carbonyl absorbance $\Delta A(1713 \text{ cm}^{-1})$ vs. ageing time at 90 and 300 W.m^{-2} for PE033 samples stabilized with different HALS ($T = 60^\circ\text{C}$ and film thickness = 100 microns)

Figure 4. Carbonyl absorbance $\Delta A(1713 \text{ cm}^{-1})$ vs. ageing time at 90 and 300 W.m^{-2} for PE033 samples stabilized with different HALS, with time scale multiplied by the shift factors reported in Table 5 in the case of the curves at 300 W.m^{-2}

Figure 5. Carbonyl absorbance $\Delta A(1713 \text{ cm}^{-1})$ vs. ageing time at 90 and 300 W.m^{-2} for PE2420F samples stabilized with different amounts of Sabostab® 119 ($T = 60 \text{ }^\circ\text{C}$ and film thickness = 100 microns)

Figure 6. Time to reach an absorbance of 0.4 as a function of the stabilizer and the irradiance (from data presented in figure 6)

Figure 7. Shift factor (300 W m^{-2} vs. 90 W m^{-2}) (7a) and Schwarzschild coefficient p (7b) as a function of the exposure time at 90 W m^{-2} to reach $\Delta A(1713 \text{ cm}^{-1}) = 0.4$ (film thickness = 100 microns)

Figure 8. Carbonyl absorbance $\Delta A(1713 \text{ cm}^{-1})$ vs. dose (in MJ m^{-2}) at 90 and 300 W.m^{-2} for formulations presented in Table 2 and Figure 3 ($T = 60 \text{ }^\circ\text{C}$ and film thickness = 100 microns)

Figure 9. Carbonyl absorbance $\Delta A(1713 \text{ cm}^{-1})$ vs. dose (in MJ m^{-2}) at 90 and 300 W.m^{-2} for formulations presented in Table 3 and Figure 5 ($T = 60 \text{ }^\circ\text{C}$ and film thickness = 100 microns)

Table 1 Commercial names and amounts of stabilizers used in the stabilized LDPE

Table 2. Formulations based on PE033 with various HALS at the same concentration (0.2 % w/w)

Table 3. Formulations based on PE2420F with Sabostab® UV 119 at various amounts

Table 4. Time to reach an absorbance difference ΔA of 0.4 as a function of the stabilizer and the irradiance (data obtained from Figure 3)

Table 5. Shift factors and Schwarzschild coefficient p determined by superposition of the kinetic curves at 90 and 300 W.m^{-2} presented in Figure 3.

Table 6. Time to reach an absorbance difference ΔA of 0.5 as a function of the stabilizer and the irradiance (from data presented in figure 6)

Table 7. Shift factors and Schwarzschild coefficient p determined by superposition of the kinetic curves presented in Figure 6.

¹ Pospisil J., Pilar J., Billingham N.C., Marek A., Horak Z., Nespurek S. Factors affecting accelerated testing of polymer photostability. Polym Degrad Stab 2006; 91: 417-422.

² Avenel C., Raccurt O., Gardette J.L., Therias S. Review of accelerated ageing test modelling and its application to solar mirrors. Sol Energy Mater Sol Cells 2018;186: 29-41.

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- ³ Avenel C., Raccurt O., Gardette J.L., Therias S. Accelerated aging test modeling applied to solar mirrors. *npj Mater Degrad* 2019; 3: Article number: 27.
- ⁴ Torikai A., Mitsuoka T., Fueki K. Wavelength sensitivity of the photoinduced reaction in polycarbonate. *J Polym Sci A* 1993; 31:2785–2788.
- ⁵ Andradý A.L. Wavelength sensitivity in polymer photodegradation. *Adv Polym Sci* 1997; 128:47–94.
- ⁶ Gardette J.L., Lemaire Wavelength effects on the photo-chemistry of poly(vinyl chloride). *Polym Degrad Stab* 1986; 16: 147-158.
- ⁷ Gaumet S., Gardette J.L., Lemaire J. Photo-chemistry of copolymers of vinylidene chloride and vinyl chloride: Part I-Wavelength effects on discoloration. *Polym Degrad Stab* 1987; 18: 135-143.
- ⁸ Lemaire J., Gardette J.L., Lacoste J., Delprat P., Vaillant D. Mechanisms of photooxidation of polyolefins: prediction of lifetime in weathering conditions. *Adv Chem Sci* 1996; 249: 577-598.
- ⁹ Scoponi M., Cimmino S., Kaci M. Photo-stabilization mechanism under natural weathering and accelerated photo-oxidative condition of LDPE films for agricultural applications. *Polymer* 2000 ;41 :7969-7980.
- ¹⁰ Bauer D.R. Global Exposure models for automotive coating photo-oxidation. *Polym Degrad Stab* 2000; 39: 307-316.
- ¹¹ Bauer D.R. Interpreting weathering acceleration factors for automotive coatings using exposure models. *Polym Degrad Stab* 2000; 39: 297-306.
- ¹² Pickett J.E., Gibson D.A., Gardener M.M. Effects of irradiation conditions on the weathering of engineering thermoplastics. *Polym Degrad Stab* 2008; 93: 1597-1606.
- ¹³ Brunner S., Richner P., Müller U., Guseva O. Accelerated weathering device for service life prediction for organic coatings. *Polym Test* 2005; 24: 25-31.
- ¹⁴ Pickett J.E., Sargent J.R. Sample temperatures during outdoor and laboratory weathering exposures. *Polym Degrad Stab* 2009; 94: 189-195.
- ¹⁵ Larché J-F., Bussière P.O., Gardette J.L. Characterization of accelerated ageing devices for prediction of the service life of acrylic-melamine/urethane thermosets. *Polym Degrad Stab* 2011; 96: 1530–1536.
- ¹⁶ Haillant O. Accelerated weathering testing principles to estimate the service life of organic PV modules. *Sol Energy Mater Sol Cells* 2011; 95:1284-1292.
- ¹⁷ Shi Y., Qin J., Tao Y., Jie G., Wang J. Natural weathering severity of typical coastal environment on polystyrene: Experiment and modeling. *Polym Test* 2021; 76: 138-145.
- ¹⁸ Frigione M., Rodrigo-Prieto A. Can Accelerated Aging Procedures Predict the Long-Term Behavior of Polymers Exposed to Different Environments? *Polymers* 2021; 13:2688.
- ¹⁹ Qin J., Jiang J., Tao Y., Zao S., Zeng W., Shi Y., Lu T., Guo L., Wang S., Zhang X., Jie G., Wang J., Xiao M. Sunlight tracking and concentrating accelerated weathering test applied in weatherability evaluation and service life prediction of polymeric materials: a review. *Polym Test* 2021; 93:106940.
- ²⁰ Gardette J.L. in *Handbook of Polymer Degradation*. S. Halim Hamid Ed. (Marcel Dekker, Inc.). 2000; 699-726.
- ²¹ Schwarzschild K., On the law of reciprocity for bromide of silver gelatin. *Astrophys. J.* 1900; 11: 89.
- ²² Martin J.W., Chin J.W., Nguyen T., Reciprocity law experiments in polymeric photodegradation: a critical review, *Prog Org Coat* 2003; 7: 292–311.

-
- ²³ Diepens M., Gijsman P. Influence of light intensity on the photodegradation of bisphenol-A polycarbonate. *Polym Degrad Stab* 2009; 94: 34–38.
- ²⁴ Santos R.M., Bothelho G.L., Cramez C., Machado A.V. Outdoor and accelerated weathering of acrylonitrile-butadiene-styrene: A correlation study. *Polym Degrad Stab* 2013; 98: 2111-2115.
- ²⁵ Pickett J.E., Kuvshinnikova O., Sung L.-P., Ermi B.D. Accelerated weathering parameters for some aromatic engineering thermoplastics. *Polym Degrad Stab* 2019; 166: 115-144.
- ²⁶ Fairbrother A., Hsueh H.C., Kim J.H., Jacobs D., Perry L., Goodwin D., White C., Watson S., Sung L.P, Temperature and light intensity effects on photodegradation of high-density polyethylene. *Polym Degrad Stab* 2019; 165: 153–160.
- ²⁷ Vink P., Wisse J.D.M. The photo-oxidation of polyolefins containing a hindered piperidine compound, *Polym Degrad Stab* 1982; 4: 51-57.
- ²⁸ Allan D.S., Maecker N.L., Priddy D.B., Schrock N. Modeling Photodegradation in Transparent Polymers. *Macromolecules* 1994; 27: 7621-7629.
- ²⁹ Therias S., Rapp G., Masson C., Gardette J.L. Limits of UV-light acceleration on the photooxidation of low-density polyethylene. *Polym Degrad Stab* 2021; 183: 109443.
- ³⁰ Plastics — Standard table for reference global solar spectral irradiance at sea level — Horizontal, relative air mass 1. <https://standards.iteh.ai/catalog/standards/sist/7cf16f4b-144c-4a6e-b2d93ae35486d65f/iso-tr-17801-2014>.
- ³¹ Gardette M., Perthue A., Gardette J.L., Janecska T., Földes E., Pukánszky B., Therias S. Photo- and thermal-oxidation of polyethylene: Comparison of mechanisms and influence of unsaturation content, *Polym Degrad Stab* 2013; 98: 2383-2390.
- ³² Davidson R.G. *Polymer Degradation Studies by FTIR. Progress in Pacific Polymer Science 2* Y. Imanishi Ed. (Springer-Verlag Berlin Heideberg) 1992; 101-111.
- ³³ Gin hac J.M., Gardette J.L., Arnaud R., Lemaire J. Influence of hydroperoxides on the photothermal oxidation of polyethylene. *Makromol Chem* 1981; 182: 1017-1025.