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Wavelength effect on polymer photooxidation
under LED weathering conditions

David Bourgogne, Sandrine Therias, Jean-Luc Gardette*

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Abstract

This paper is devoted to the investigation of the photooxidation of poly(N-vinylcarbazole (PVK) and polyethylene (LDPE) by exposure to $\lambda \geq 300$ nm polychromatic light (SEPAP 12.24) or UV light produced by a new setup equipped with LEDs emitting at 365 nm (LED 365), both at a temperature of 60 °C. Photooxidation was studied by infrared and UV-visible spectroscopies and emission spectroscopy in the case of PVK. The mechanisms by which the oxidation products were formed in both polymers were recalled. Depending on the conditions of ageing, i.e., polychromatic light or exposure to LED 365, the same oxidation products were obtained but with different rates and different relative amounts. This result reflected the influence of the wavelengths on the mechanisms. In the case of PVK, the formation of oxidation photoproducts and yellowing were not impacted, but the kinetics of the decrease in excimer fluorescence, which is linked to the crosslinking of the polymer, were dramatically modified. In the case of LDPE, wavelength effects on the photolysis of ketones by Norrish reactions were observed. As a consequence, irradiations with the LED 365 setup could not be claimed to be representative of polychromatic irradiations because the shortest wavelengths ($(300 \text{ nm} < \lambda < 350 \text{ nm})$) were missing and could not reproduce natural outdoor conditions of weathering.

Keywords: Photooxidation, UV LED 365, polychromatic irradiation, poly(N-vinylcarbazole, polyethylene

1. Introduction

Accelerated weathering testing of polymeric materials is expected to speed time to market and reduce the indirect costs associated with long-term outdoor exposures. Laboratory devices for artificial accelerated weathering of polymers have been the object of considerable interest in the last fifty years, and many commercial testing equipment have become available to study and predict the weathering performance of polymeric materials. Over the years, numerous technical improvements have been made in the design, construction and control of these devices.

However, testing conditions can seriously bias experimental results if performed in weathering conditions that are not relevant to weathering in “use” (generally outdoors) conditions. The UV weathering of polymeric materials depends on many factors, and it is currently admitted that several conditions must be respected to produce relevant results. Scientists working in the field of polymer photodegradation agree on some very basic rules. Among these rules, short wavelengths below 300 nm must be excluded since they produce nonrelevant phenomena¹, high intensities should be

avoided since they are likely to provoke heterogeneous oxidation due to diffusion limited oxidation² and a correct balance between photo- and thermo-ageing must be respected. Too high intensities (laser sources), which could provoke biphotonic excitation, should be also avoided.

One can currently observe a growing interest in the use of light emitting diode (LED) technology, and in particular, the lighting market for LEDs is rapidly expanding. White light output in LEDs can be generated using different methods, where the most widely used approach is based on the application of a blue light chip with yellow phosphor³. LED lighting systems consist of several components, which makes them relatively complex systems. The degradation of different optical materials in LED-based products, in particular that of the polymeric components of typical LED systems, has received attention and has been reviewed⁴. The mechanism of optical degradation for light emitting diode (LED) packages in light bars under high-temperature ageing conditions⁵ has also been investigated. Commercial testing equipment has recently become available to expose polymer samples to high-intensity blue light LEDs in the 400-500 nm domain and used to study the yellowing of polycarbonate⁶. A newly developed test setup to age optical plastics by visible radiation (450 nm) has been recently described and applied to the photodegradation of polycarbonate⁷. Ageing experiments were performed over a period of 5000 h to evaluate the stability of PLA under the influence of extreme levels of optical LED radiation ($\lambda_{\max} = 450 \text{ nm}$)⁸.

One issue that is not fully considered is the representativeness of the experiments performed with blue LEDs emitting in the visible range in comparison to conventional devices in the area of degradation and stabilization of polymers. The literature shows that, generally, the ageing experiments are conducted on polymers that do not absorb the incident light emitted by blue LEDs, and one can question the mechanisms involved. In the present article, we approach the issue of material degradation from the photochemistry viewpoint and focus on the impact of UV radiation, which is present in the solar spectrum. The present article describes the use of LEDs emitting at 365 nm to produce the photodegradation of polymers. The goal is to see whether such exposure conditions can reproduce the photodegradation provoked by exposure in a “conventional” device equipped with polychromatic light sources. To reach this goal, we selected two polymers whose photodegradation mechanisms are well characterized and which could discriminate the impact of different wavelengths in the emission spectra of the light sources. On the one hand, we focused on poly(N-vinylcarbazole (PVK), which contains intrinsic chromophores; on the other hand, we focused on polyethylene (LDPE), where photooxidation is initiated by chromophoric defects.

2. Experimental part

2.1. Materials

Free-standing thin (25 μm) films of PVK ($M_w = 1\,100\,000$, $T_g = 501 \text{ K}$ Aldrich, Germany) were

prepared by evaporating polymer solutions in 1-4 Dioxane solution on glass plates at room temperature. Then, the films were dried in vacuum at room temperature. The solvent evaporation was carefully controlled by IR analysis. The mean thickness of the samples was 25 microns.

The polyethylene (PE) in this work was a grade Repsol Alcludia PE033 (low density polyethylene grade) and irradiated in the form of free-standing films with a thickness of approximately 150 microns.

2.2. Irradiation

Irradiation was performed under artificial ageing conditions under either polychromatic light (λ above 300 nm) (SEPAP 12/24) or light emitted by LEDs centred at 365 nm (LED 365). The SEPAP test devices were developed based on numerous studies on the photoaging processes that affected polymer materials. The SEPAP 12/24 unit⁹ from Atlas is equipped with four medium pressure mercury lamps (Novalamp RVC 400 W) in a vertical position at each corner of the chamber. Wavelengths below 295 nm were filtered by the glass envelope of the sources. The temperature at the surface of the samples was fixed at 60 °C. The irradiance at 300-420 nm was measured as 90 W m⁻² (see spectrum in Fig. 1).

Irradiation under LED light was performed in a homemade LED 365 unit (see Scheme S1 of the supporting information). This chamber was equipped with four LEDs (365 nm LED Gen 2 Emitter from LED ENGIN) with an emission centred at 365 nm and a full width at half maximum (FWHM) of 10 nm (see spectrum in Fig. 1). The distance between the LEDs was 60 mm, and the distance from the LEDs to the polymer samples was 110 mm. The temperature inside the chamber was regulated using a silicone heater mat. The samples to be irradiated were placed on the mat, and the temperature during exposure was 60 °C. The irradiance in the LED 365 device was measured as 82 W m⁻². The irradiances in the SEPAP and in the LED 365 setup were measured using a radiometer ILT 800 CureRight (International Light Technologies) and a calibrated spectroradiometer QE6500 (Ocean Optics inc.)

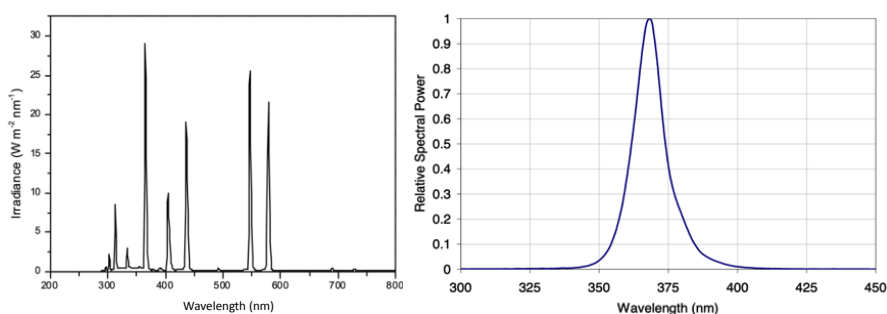


Fig. 1. Emission spectrum of the mercury lamps in the SEPAP (left) and LED 365 (right)

2.3. Analysis

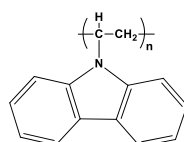
The chemical changes caused by oxidation reactions were followed by infrared spectrometry. The IR

spectra were recorded in transmission mode using a Thermo Scientific Nicolet 6700 FTIR spectrophotometer (nominal resolution of 4 cm^{-1} , 32 scans summation). Deconvolutions of the infrared spectra were performed using OMNIC software. The UV–visible spectra were recorded using a Shimadzu UV-2600 spectrophotometer with an integrating sphere. The fluorescence spectrum of PVK was measured under an excitation wavelength of 300 nm. It consisted of a band with a maximum at approximately 420 nm that was assigned to the low-energy excimer¹⁰. The fluorescence spectra were obtained using a Varian Cary Eclipse spectrofluorimeter. The spectra were not corrected for grating efficiency and photomultiplier response. The excitation and emission slits were 2.5 and 5 nm, respectively.

3. Results and discussion

3.1. Poly(N-vinylcarbazole) (PVK)

Poly(N-vinylcarbazole) (PVK) (Scheme 1) has been studied in recent years, and its photodegradation mechanism has been proposed^{11,12}.



Scheme 1. Structure of poly(N-vinylcarbazole) (PVK)

Infrared spectroscopy is a useful and frequently used analytical technique to monitor the oxidation process of polymers¹³. The modifications of the infrared spectra resulting from exposure in the SEPAP and LED 365 units were recorded and are represented in Figures 2 and 3, respectively.

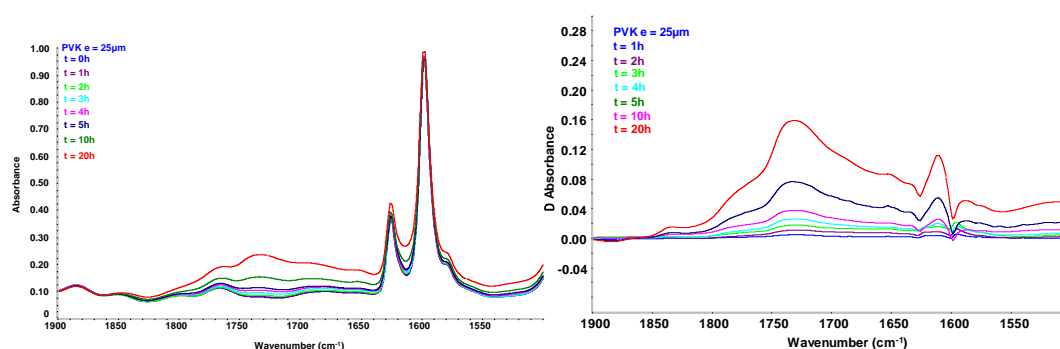


Fig. 2. Infrared spectra of a PVK film during photooxidation (SEPAP 12.24) in the range of carbonyl absorption: direct spectra (left), subtracted spectra (right) (thickness 25 microns)

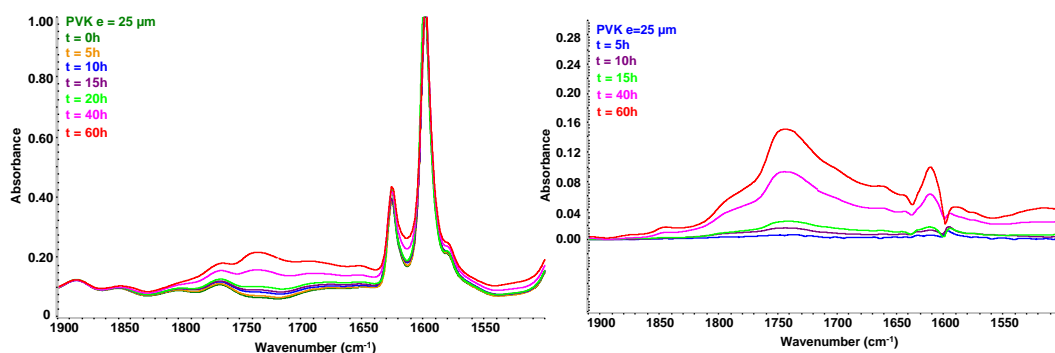


Fig. 3. Infrared spectra of a PVK film during photooxidation (LED 365) in the range of carbonyl absorption: direct spectra (left), subtracted spectra (right)

The shapes of the spectra are similar for both irradiation units, but the irradiation times required to reach a similar absorbance are different.

The products resulting from the photooxidation of PVK were identified¹¹ by physical treatments, involving photolysis and thermolysis, which showed evidence of the formation of quinonic structures, ketones, N-cetylcarbazole, hydroperoxides, and various chemical derivatizations based on SF₄ and NH₃ reactions to characterize the formation of acids, esters, and anhydrides. In the region of 1500-1900 cm⁻¹, the formation of a CO band with a maximum centred at 1720-1730 cm⁻¹ was attributed to anhydrides, acid groups and ketones, which were quantitatively identified as the main photoproducts. These products accumulate in the polymer during photooxidation. In the region between 2700–3700 cm⁻¹, which is not shown here, the formation of a broad band at 3100-3600 cm⁻¹ was observed and indicated the formation of OH, NH and COOH end groups. The formation of these photoproducts was accompanied by a decrease in the CH bands and a loss of C-N bonds. The increase in absorbance at 1730 cm⁻¹ can be used to follow the extent of photooxidation.

In parallel, we monitored the changes in the UV-visible absorption spectra of the irradiated samples. Figure 4 represents the UV-visible absorption spectra of a PVK film exposed under polychromatic (SEPA 12.24) or LED light (LED 365).

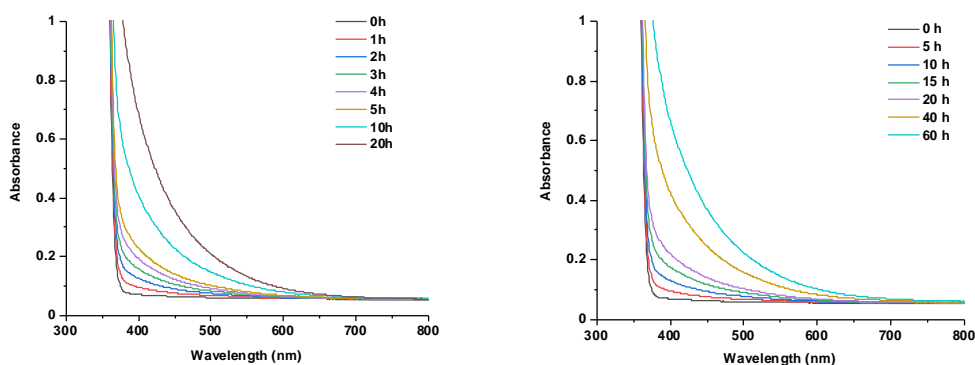
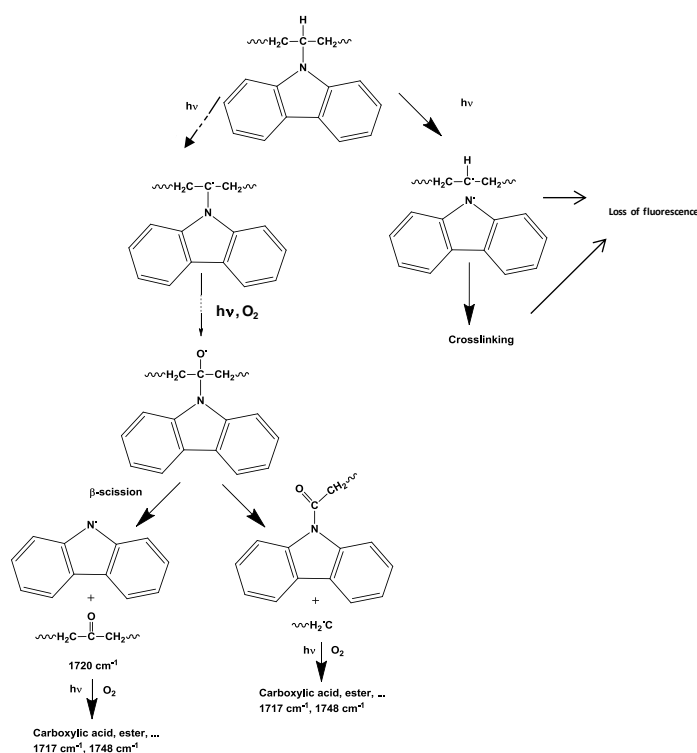


Fig. 4. UV-visible spectrum of a pristine PVK sample (thickness 25 microns) irradiated in the SEPAP unit (Left) and LED 365 device (right).

Figure 4 indicates that with increasing irradiation time, the development of an unstructured absorption above 370 nm is observed by UV-visible spectroscopy. This absorption reflects the formation of various conjugated structures and is responsible for the yellowing of the photooxidized film. The shapes of the UV absorption spectra are similar for both irradiation units. However, the rates at which the absorbance increases are different, and the yellowing is much more rapid when irradiations are performed in the SEPAP unit.

The main routes of photooxidation that account for the formation of oxidation products detected by infrared analysis and those responsible for the crosslinking of PVK are represented in scheme 2.



Scheme 2. Simplified photooxidation mechanism of poly(N-vinylcarbazole) (PVK)

The oxidative degradation of PVK involves many routes. The proposed photoageing mechanism¹¹ indicates that light absorption provokes the homolysis of C-N bonds on the macromolecular chains, which forms carbazolyl radicals and macroradicals on the polymeric chain. The macroradicals may recombine, which leads to cross-linking that may or may not include oxygen atoms. The carbazolyl radicals are likely to initiate chain oxidation by hydrogen abstraction on the macromolecular chains. The abstraction of a hydrogen atom preferentially occurs at the tertiary carbon of the structure and leads to polycarbazolyl radicals. The polycarbazolyl radicals can also react with oxygen to give hydroperoxides, which decompose to give alkoxy radicals. Then, several reactions likely occur; the main reaction is identified as the β-scission of the alkoxy radicals, which gives N-acetylcarbazole groups. This last reaction is accompanied by the formation of alkyl radicals that can be oxidized into

carboxylic acids or isomerize to more stable tertiary radicals. These last radicals continue the oxidation process and lead to chain-scissions.

The photophysics of PVK has been extensively studied, and most of the studies are devoted to excimer fluorescence. The published studies report the presence of two distinct excimer sites with typical photophysical properties, which is considered unique among vinyl aromatic polymers. A lower-energy excimer is formed when two carbazolyl groups have achieved an eclipsed fully overlapping “sandwich-like” conformation¹⁴. The emission spectrum of PVK under an excitation wavelength at 300 nm consists of a band with a maximum at approximately 420 nm assigned to the low-energy excimer¹⁵ (Fig. 5).

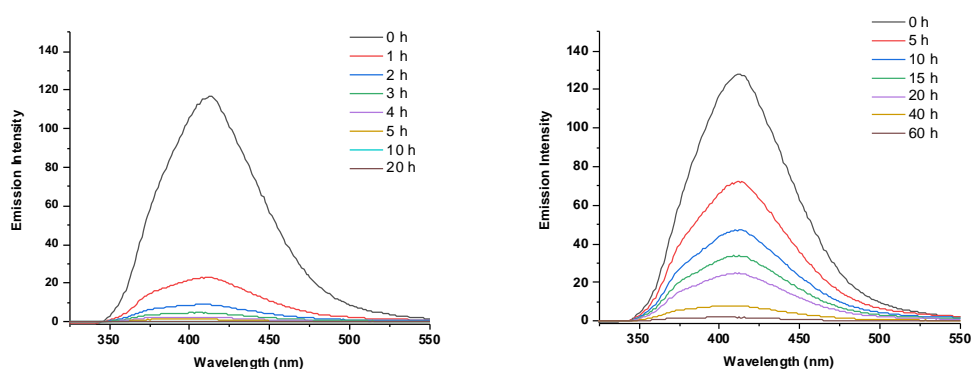


Fig. 5. Emission spectrum of PVK after exposure in the SEPAP device (left) or in the LED 365 unit (right)

A decrease in the emission intensity band is observed under irradiation in the SEPAP unit or LED 365 device. Obviously, the rate at which the intensity of the fluorescence decreases depends on the photooxidation conditions. After only 5 hours in the SEPAP, no more emission can be detected, whereas it necessitates 60 hours in the LED 365 device.

The disappearance of the excimer fluorescence at 420 nm of PVK resulted from a decrease in local mobility provoked by the crosslinking of the polymer film upon light irradiation in the presence of oxygen¹¹. The cross-linking of the polymer and decrease in the fluorescence simultaneously occur and at a low conversion degree of irradiated films.

These experiments indicate that the changes monitored by infrared, UV, and fluorescence spectroscopies are similar when irradiation is performed under both weathering conditions, e.g., SEPAP 12.24 and LED 365 units. However, our results demonstrate dramatic differences that concern the kinetic aspects. Figure 6 compares the increase in absorbance in the carbonyl region as a function of the dose for irradiation performed in the SEPAP (0-20 h) and LED 365 (0-60 h) units.

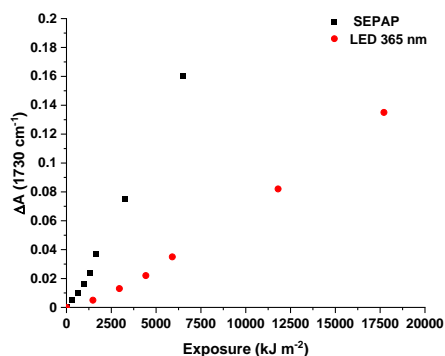


Fig. 6. Absorbance at 1730 cm^{-1} as a function of exposure in the SEPAP (irradiance 90 W m^{-2}) and in the LED 365 setup (irradiance 82 W m^{-2}).

The rate of photooxidation was higher in the case of SEPAP exposure. An absorbance of 0.1 is reached after 47 h (13875 kJ m^{-2}) of exposure in the LED 365 device, whereas only 14 h (4536 kJ m^{-2}) is required to reach the same absorbance in the SEPAP unit. Following a methodology reported in the literature by Gillen and Clough¹⁶, the rate enhancement can be determined by plotting the data on the same graph, which allows determining a shift factor, which is the relative rate. A shift factor of 3.5 was determined. The data obtained for LED irradiations were then superposed to SEPAP data using a shift factor of 3.5. This is illustrated in Fig. 7.

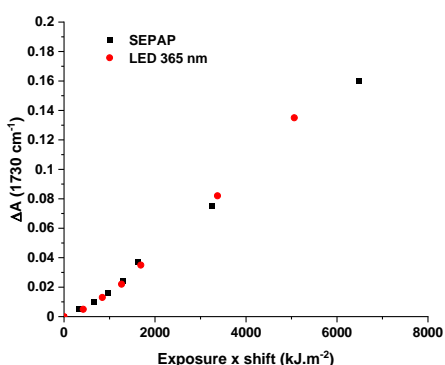


Fig. 7. Data for photooxidation (carbonyl formation) in the LED 365 setup superposed onto SEPAP data using a shift factor 3.5

Fig. 7 shows that the shaped of the curves are similar and that the data superpose well. The kinetic curves of yellowing provoked by exposure in both devices (Fig. 4) were also measured. This is shown in Figure 8, which represents the variations in absorbance at 400 nm .

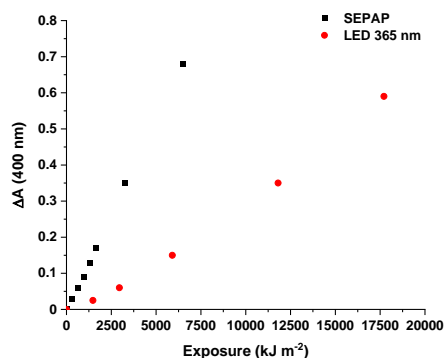


Fig. 8. Absorbance at 400 nm as a function of exposure in the SEPAP (irradiance 90 W m^{-2}) and in the LED 365 setup (irradiance 82 W m^{-2}).

Interestingly, the kinetic curves have a similar shape to those in Figure 6. The data shown in this figure were superposed using the shift factor 3.5 determined from the data given in Fig. 6. This is shown in Fig. 9.

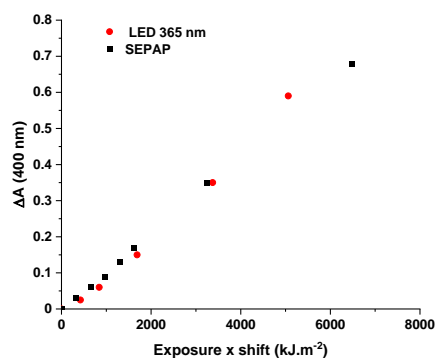


Fig. 9. Data for photooxidation (“yellowing”) in the LED 365 setup SEPAP superposed onto SEPAP data using a shift factor 3.5

As observed in Fig. 7, one notes a good superposition, which suggests that the mechanism proposed to explain the formation of the oxidation products and the yellowing is the same. This result was not unexpected since the proposed mechanisms to explain the photooxidation of PVK show that the formation of the photoproducts detected by infrared or by UV-visible analysis involve identical mechanisms¹¹, which can be verified by plotting the variations of absorbance at 400 nm vs. the increase of the absorbance at 1730 cm^{-1} in the SEPAP and LED 365 units, as presented in Figure 10.

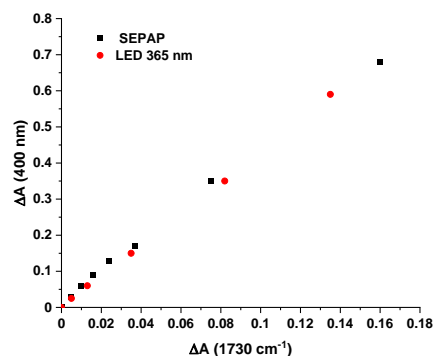


Fig. 10. Increase in absorbance at 400 nm vs. increase in absorbance at 1730 cm⁻¹ in the SEPAP and LED 365 units.

The results in Fig. 10 indicate that the correlation “yellowing” vs. “carbonyls” is identical in both irradiation units. This supports the conclusion obtained from the superposition method that the mechanism proposed to explain the formation of the oxidation products and the yellowing is the same.

From the fluorescence spectra in Figure 5, one can plot the kinetics of the fluorescence intensity (Fig. 11).

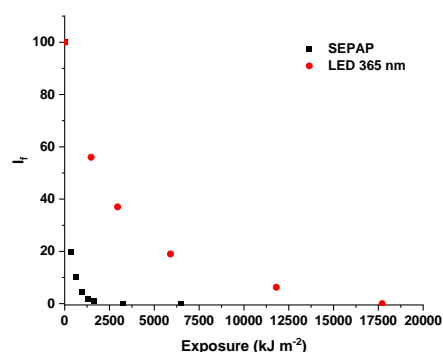


Fig. 11. Emission intensity at 420 nm as a function of exposure in the SEPAP (irradiance 90 W m⁻²) and in the LED 365 setup (irradiance 82 W m⁻²).

The formation of carbonyls and yellowing involve similar time scales (see Figures 6 and 8), which are much higher than the required time to decrease the fluorescence emission (Figure 11). Based on the results in Figures 6, 8 and 11, one can plot the emission intensity at 420 nm as a function of the absorbance at 1730 cm⁻¹ or 400 nm in the SEPAP and LED 365 units, as shown in Figure 12.

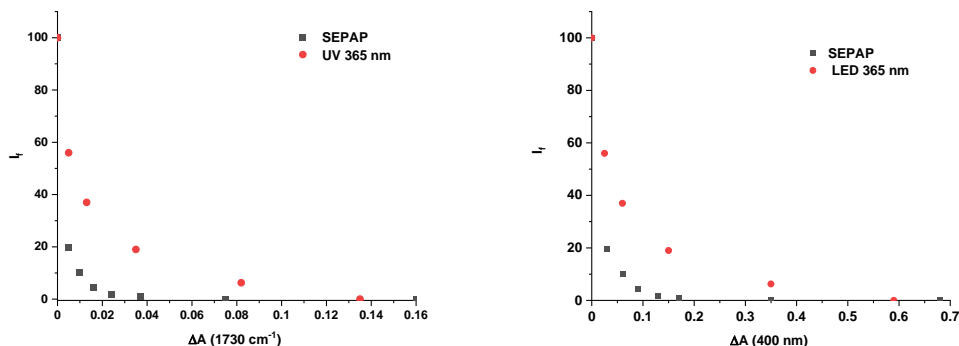


Fig. 12. Decrease of the emission intensity at 420 nm as a function of the increase in absorbance at 1730 cm^{-1} (left) and at 400 nm (right) in the SEPAP and LED 365 units

The superposition method was also applied to the disappearance of the excimer fluorescence, using the same shift factor of 3.5. This is shown in Fig. 13. Here, one observes no superposition, which indicates that the mechanism is changed.

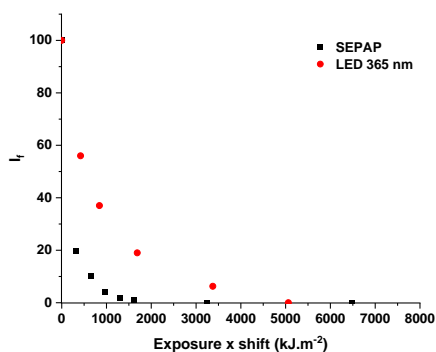


Fig. 13. Data for photooxidation (“Emission intensity at 420 nm”) in the LED 365 setup SEPAP superposed onto SEPAP data using a shift factor 3.5

The results represented in Figs. 12 and 13 unambiguously shows that the correlation between the disappearance of the excimer fluorescence of PVK at 420 nm and the oxidation of the polymer measured either by the carbonyl increase or by the yellowing depends on the wavelengths of irradiation. The disappearance of the fluorescence emission is closely related to the direct absorption of light by PVK, whereas the formation of oxidation products and subsequent yellowing result from direct photochemical reactions and induced photooxidation¹¹. Both routes can be discriminated by varying the irradiation conditions. The superposition of the emission spectra of the SEPAP and the LED 365 to the absorption spectrum of PVK (spectrum obtained from ref. 10c) clearly shows that in the case of the SEPAP, the narrow line at 365 is almost not absorbed by PVK, but the lines at 334, 313, and 305 nm are in the range of absorption of PVK and are fully absorbed. The exposure in the SEPAP provokes the formation of excited states by absorption of these photons at 334, 313 and 305 nm, which in turn leads to the fluorescence loss. In the case of the LED 365 setup, the emission band centered at 365 nm is relatively broad (see Fig.1) and part of this band (350-360 nm) is in the range

of PVK absorption. This is the absorption of these photons that is responsible for the fluorescence loss, which was experimentally observed (Fig. 5 – right).

On one side, more photons are absorbed in the case of exposures performed in the SEPAP, and on the other side, different excited states with higher energies can be populated. The result is a much faster loss of fluorescence (Fig. 5). However, it is difficult to discriminate both these contributions, more absorption vs. population of excited states of higher energy responsible for the loss of the fluorescence.

3.2. Polyethylene

Figure 14 illustrates the modification of PE spectra during exposure in the SEPAP 12.24 (the spectra are presented as subtracted spectra with the spectrum before irradiation as a reference).

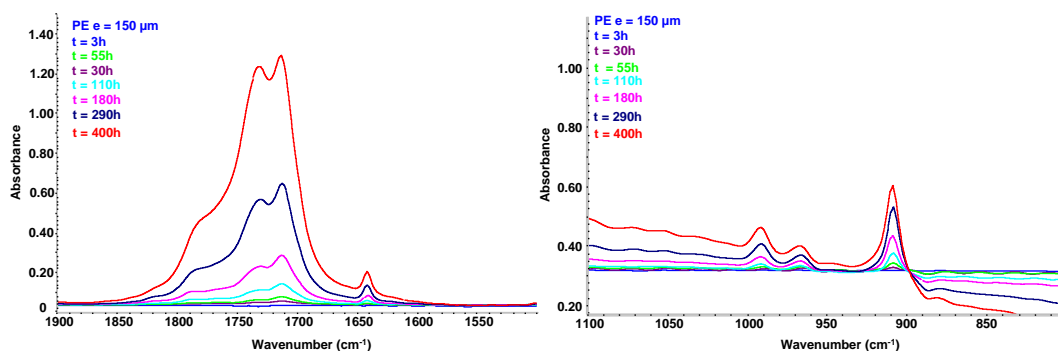


Fig. 14. Subtracted infrared spectra of a PE film during photooxidation (SEPAP 12.24) in the absorption range of carbonyl absorption (left) and in the absorption range of unsaturations (right) (thickness 150 microns).

In the range of carbonyl absorption, the modification of the spectrum indicates that ketones (1720 cm^{-1}) are formed in the initial steps, and carboxylic acids (1713 cm^{-1}), esters (1735 cm^{-1}) and lactones (1780 cm^{-1}) form in secondary processes. One can also notice the formation of double bonds (1640 cm^{-1}). The absorbance at 1713 cm^{-1} after 400 hours is approximately 1.3.

In the absorption range of unsaturations, one notices an increase in intensity of the bands at 909 cm^{-1} and 991 cm^{-1} , which indicates the formation of vinyl unsaturations, and at 965 cm^{-1} , which is characteristic of t-vinylene groups. No modification is observed in the intensity of the vinylidene group at 888 cm^{-1} .

In the range of hydroxyl frequencies (not shown here), a broadband band with a maximum at 3420 cm^{-1} and a sharp absorption band at 3550 cm^{-1} appear in the spectrum. These bands are known to come from the formation of monomeric hydroperoxides (3550 cm^{-1}) and hydrogen-bonded alcohols and hydroperoxides (3420 cm^{-1}). The intensities of both bands remain very low, where a stationary concentration of hydroperoxides reaches a plateau at approximately $5 \cdot 10^{-2}\text{ mol/L}$ ¹⁷.

Figure 15 illustrates the modification of PE spectra during exposure in the LED 365 device.

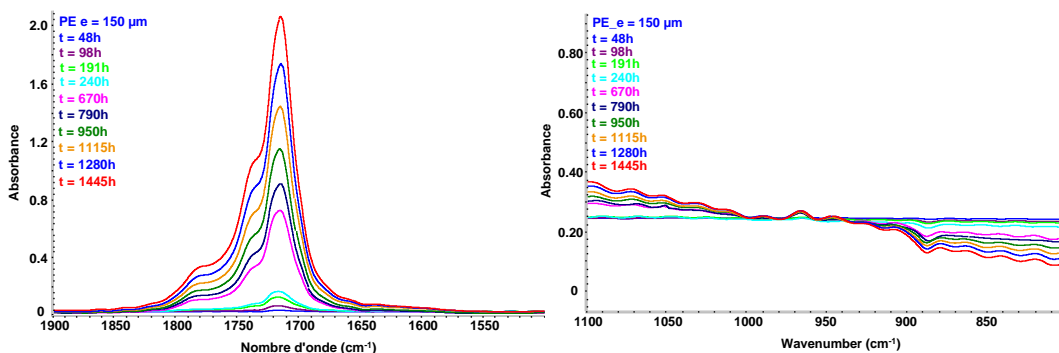


Fig. 15. Infrared subtracted spectra of a PE film during photooxidation (LED 365): in the range of carbonyl absorption (left); in the range of the absorption of unsaturated groups (right).

In the range of 1500-1900 cm^{-1} , absorption bands form at similar frequencies to those reported for photooxidation in the SEPAP device (1720 cm^{-1} , 1713 cm^{-1} , 1735 cm^{-1} , 1780 cm^{-1}), which indicates that the same products are formed. However, the shape of the complex carbonyl band strongly differs, which reflects dissimilar relative concentrations of the photoproducts. The main absorption maximum is observed at 1720 cm^{-1} , which is characteristic of ketones, whereas it appears at 1713 cm^{-1} in the case of photooxidation in the SEPAP unit. Then, ketones are the main products formed by exposure in the Led 365 device. No absorption band at 1640 cm^{-1} can be observed, which would have reflected the formation of double bonds. This is confirmed by the spectra in the range of 1000-800 cm^{-1} , which do not indicate the formation of absorption bands that could be attributed to unsaturation. The absorbance at 1720 cm^{-1} after 1280 hours is approximately 1.8. In the range of hydroxyl frequencies (not shown here), the modifications of the spectra provoked by irradiation in the SEPAP unit or in the LED 365 setup were similar, showing a very weak increase of the absorbance with a broad band at 3420 cm^{-1} .

We have checked that the oxidation of PE exposed in the LED 365 device did not come from a thermal effect, by exposing a PE film to 60 °C without light (dark control). No modification of the infrared spectrum could be detected after more than 1500 hours.

Based on the pioneering work by Carlsson and Wiles¹⁸, one can deconvolute the complex spectrum in the carbonyl domain to highlight the main bands that contribute to the broad absorption of carbonyls. Curve fitting analysis of the IR carbonyl band can be achieved by direct mathematical treatment of the spectra, considering the absorption maxima identified by chemical and physical treatments of the oxidized samples¹⁹. The carbonyl envelop into the component peaks was resolved following a procedure previously reported²⁰. The selected absorption maxima to perform deconvolution are shown in Table 1.

Table 1. Infrared characteristics of some of the oxidation products in PE

Product	Conjugated ketone	Carboxylic acid	Ketone	Ester	Peracid	Lactone
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Absorption maximum (cm ⁻¹)	1695	1713	1720	1735	1765	1785
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The deconvoluted spectra in the carbonyl domain after 400 h of exposure in the SEPAP unit and 1115 h of exposure in the LED 365 unit are presented in Figure 16.

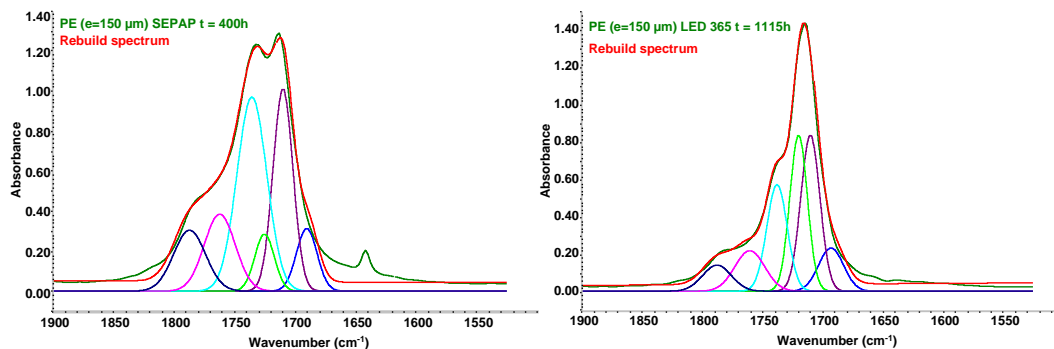


Fig. 16. Deconvoluted IR spectrum of a PE film after exposure in the SEPAP device (left) or in the LED 365 unit (right)

Nice fits were obtained between the recorded “experimental” spectra and the spectra rebuilt after deconvolution. The deconvolution of the infrared spectra confirms the above interpretations: dissimilarity between relative concentrations of the photoproducts. The concentration of saturated ketones is proportionally higher in the case of irradiation in the LED 365 setup than in the case of irradiation in the SEPAP unit. Ketones are indeed photochemically unstable and should degrade when exposed to light. Ketones do not absorb light in the LED 365 unit and subsequently accumulate, which is not the case for irradiation in the SEPAP device. To verify this issue, a PE was first irradiated in the LED 365 device for 2270 h and subsequently irradiated in the SEPAP unit for relatively short durations (1-20 h). The modification of the spectra is presented in Figure 17.

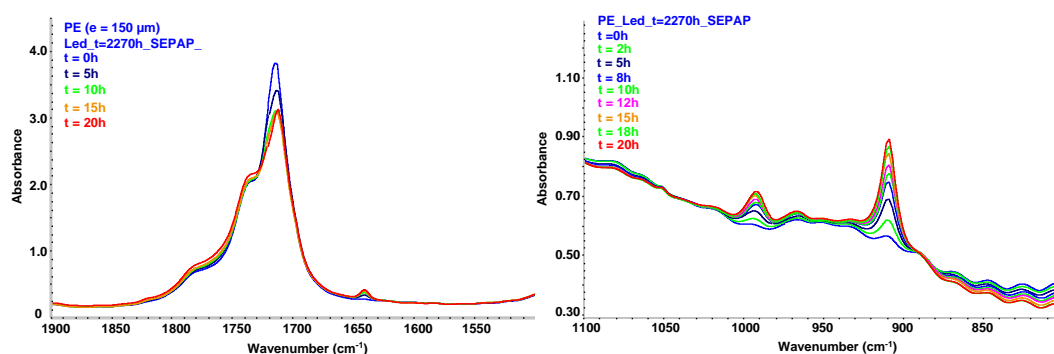
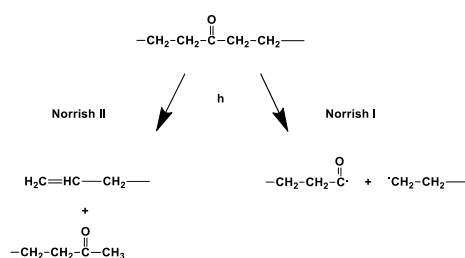


Fig. 17. Infrared spectra in the absorption range of carbonyl (left) and unsaturation (right) absorption of a PE film irradiated for 2270 h in the LED 365 device and then irradiated in the SEPAP unit.

The spectra in Figure 17 indicate that the absorbance at 1720 cm⁻¹ (ketones) decreases upon exposure in the SEPAP unit, whereas the absorbances at 1785 and 1735 cm⁻¹ increase. The absorption bands at 1640 cm⁻¹ and 909 cm⁻¹ (unsaturations) appear. These results clearly demonstrate the reactivity of ketones.

As recalled above, photooxidation of polyethylene produced by exposure to both SEPAP and LED 365 produces almost identical oxidation products, but their relative concentrations are different. The Norrish reactions that occur in photooxidation are responsible for these differences. The same carbonyl products are formed in both cases but not in the same quantities: ketones and conjugated ketones accumulate during exposure in the LED 365 device because they do not absorb the 365-nm light, whereas they disappear to yield new unsaturations upon exposure in the SEPAP unit due to the absorption of light in the range of 300-330 nm. Vinyl and vinylene unsaturations can appear through Norrish reactions²¹.



Scheme 3. Photolysis of ketones involving Norrish type-I and type-II reactions

The reactivity of ketones may be further confirmed when recording the UV–visible spectra of the PE films exposed in both irradiation units. No modification of the UV–visible absorption characteristics was observed during exposure in the SEPAP unit, but some notable changes appeared in the spectra as a result of exposure in the LED 365 device (Figure 18).

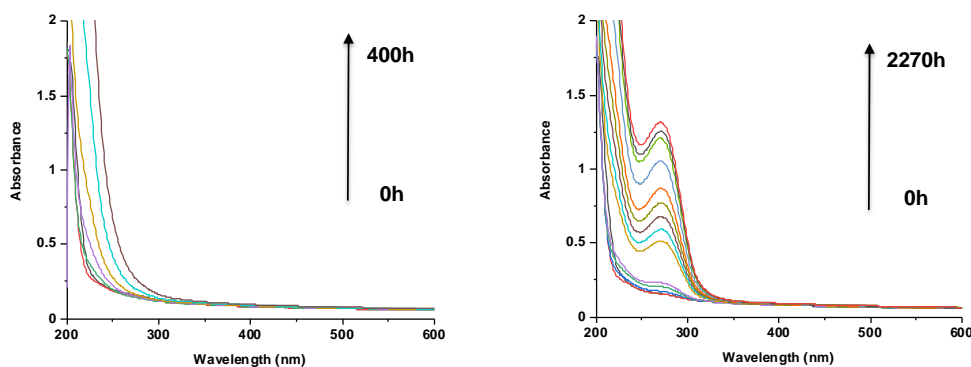


Fig. 18. UV–visible spectra of a PE A film during photooxidation in the SEPAP unit (left) and in the LED 365 unit (right)

One can observe an absorption maximum at 275 nm that develops during exposure in the LED 365 device (the maximum at 215 nm is not considered, since the response of the detector cannot be considered relevant below 250 nm). The maximum at 275 nm indicates the formation of ketones. As recalled above, ketones are not stable under UV-light irradiation, and we have shown that a short irradiation time in the SEPAP unit (1-20 h) made ketones disappear from a film that was first photooxidized in the LED 365 unit for 2270 h. Recording the UV absorption spectra confirms the

results in Figure 17. Figure 19 indicates that the absorption band of ketones at 275 nm disappears in only a few hours of exposure and is converted into an absorption below 230 nm with an isosbestic point at 247 nm.

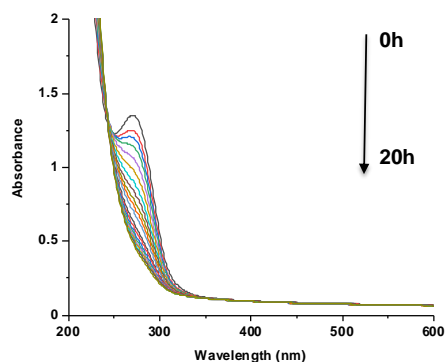
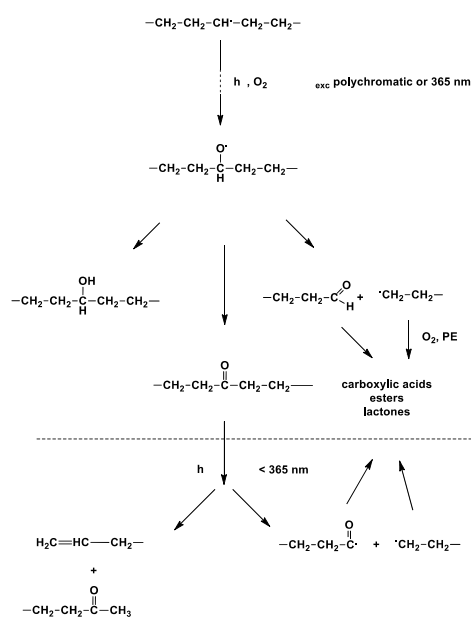


Fig. 19. UV-visible spectra during exposure in the SEPAP setup of a PE film pre-irradiated for 1270 h in the LED 365 device.

Our results confirm that ketones are a key intermediate photoproduct in the photooxidation of polyethylene. Irradiation at “long” wavelengths that are not absorbed by ketones allows these photoproducts to accumulate in the polymer, which changes the photooxidation mechanism reported for irradiation under polychromatic light. Photooxidation at “long” wavelengths is more similar to thermooxidation than photooxidation.



Scheme 4. Simplified scheme of polyethylene photooxidation under polychromatic light or under “long” wavelength irradiation

Conclusion

The results in this article unambiguously show that irradiations in a wavelength domain that covers only a narrow part of the solar light and omits the shortest wavelengths ($300 \text{ nm} < \lambda < 350 \text{ nm}$)

produce irrelevant data to natural weathering. The two selected polymers photodegraded with wavelength-dependent mechanisms.

In the case of poly(N-vinylcarbazole (PVK) exposed to polychromatic irradiation (SEPA), direct excitation of PVK units provokes scissions of the C-N bonds, a decrease in local mobility due to cross-linking, and the fluorescence attributed to the excimer rapidly decreased. In parallel, photooxidation occurs and provokes a yellowing of the material. Photooxidation involves the abstraction of a hydrogen atom that preferentially occurs at the tertiary carbon of the structure and leads to the formation of macro radicals that are likely to initiate the oxidation of the polymer, which propagates following a classical chain oxidation mechanism. The chain oxidation mechanism can also be initiated by light absorption due to chromophoric defects, but this does not provoke direct scissions of the C-N bonds. In the case of irradiation with LEDs with a peak wavelength of 365 nm and an FWHM of approximately 10 nm, only a minor part of the incident light is directly absorbed by PVK, which means that a minor importance is given to the direct scissions of the C-N bonds, and then the excimer fluorescence slowly decreases. The chain oxidation mechanism can be initiated by light absorption due to chromophoric defects, provoking the formation of oxidation products and yellowing. The formation of oxidation products and the yellowing follow the same routes, but the decrease of the fluorescence follows a different mechanism, which involves direct light absorption by PVK. Irradiations performed in the LED 365 setup cannot be claimed to be representative of conditions relevant to natural weathering.

Similar conclusions can be given in the case of polyethylene, even if the reasons are different. In the case of PE irradiated under polychromatic light, the reported photooxidation mechanism in the literature involves the photoreactivity of ketones as intermediates. In the case of irradiation with LEDs with a peak wavelength of 365 nm, the photooxidation mechanism is different, since the ketones do not absorb and are subsequently relatively stable. Then, the photooxidation mechanism is more similar to a thermooxidation mechanism.

To make this type of irradiation acceptable to weather polymers in relevant conditions to natural weathering, it is necessary to add a source of light with shorter wavelengths, e.g., supplementary LEDs with a peak wavelength of 305 nm, to our setup. The results will be the object of a forthcoming paper that also considers the case of polycarbonate and polyethylene terephthalate as examples to prove the relevance of this new setup.

Figures captions

Scheme 1. Structure of poly(N-vinylcarbazole) (PVK)

Scheme 2. Simplified photooxidation mechanism of poly(N-vinylcarbazole) (PVK)

Scheme 3. Photolysis of ketones involving Norrish type-I and type-II reactions

Scheme 4. Simplified scheme of polyethylene photooxidation under polychromatic light or under “long” wavelength irradiation

Table 1. Infrared characteristics of some of the oxidation products in PE

Fig. 1. Emission spectrum of the mercury lamps in the SEPAP (left) and LED 365 (right)

Fig. 2. Infrared spectra of a PVK film during photooxidation (SEPAP 12.24) in the range of carbonyl absorption: direct spectra (left), subtracted spectra (right) (thickness 25 microns)

Fig. 3. Infrared spectra of a PVK film during photooxidation (LED 365) in the range of carbonyl absorption: direct spectra (left), subtracted spectra (right)

Fig. 4. UV-visible spectrum of a pristine PVK sample (thickness 25 microns) irradiated in the SEPAP unit (Left) and LED 365 device (right).

Fig. 5. Emission spectrum of PVK after exposure in the SEPAP device (left) or in the LED 365 unit (right)

Fig. 6. Absorbance at 1730 cm^{-1} as a function of exposure in the SEPAP (irradiance 90 W m^{-2}) and in the LED 365 setup (irradiance 82 W m^{-2}).

Fig. 7. Data for photooxidation (carbonyl formation) in the LED 365 setup superposed onto SEPAP data using a shift factor 3.5

Fig. 8. Absorbance at 400 nm as a function of exposure in the SEPAP (irradiance 90 W m^{-2}) and in the LED 365 setup (irradiance 82 W m^{-2}).

Fig. 9. Data for photooxidation (“yellowing”) in the LED 365 setup SEPAP superposed onto SEPAP data using a shift factor 3.5

Fig. 10. Increase in absorbance at 400 nm vs. increase in absorbance at 1730 cm^{-1} in the SEPAP and LED 365 units.

Fig. 11. Emission intensity at 420 nm as a function of exposure in the SEPAP (irradiance 90 W m^{-2}) and in the LED 365 setup (irradiance 82 W m^{-2}).

Fig. 12. Decrease of the emission intensity at 420 nm as a function of the increase in absorbance at 1730 cm^{-1} (left) and at 400 nm (right) in the SEPAP and LED 365 units

Fig. 13. Data for photooxidation (“Emission intensity at 420 nm”) in the LED 365 setup SEPAP superposed onto SEPAP data using a shift factor 3.5

Fig. 14. Subtracted infrared spectra of a PE film during photooxidation (SEPAP 12.24) in the absorption range of carbonyl absorption (left) and in the absorption range of unsaturations (right) (thickness 150 microns).

Fig. 15. Infrared subtracted spectra of a PE film during photooxidation (LED 365): in the range of carbonyl absorption (left); in the range of the absorption of unsaturated groups (right).

Fig. 16. Deconvoluted IR spectrum of a PE film after exposure in the SEPAP device (left) or in the LED 365 unit (right)

Fig. 17. Infrared spectra in the absorption range of carbonyl (left) and unsaturation (right) absorption of a PE film irradiated for 2270 h in the LED 365 device and then irradiated in the SEPAP unit.

Fig. 18. UV-visible spectra of a PE A film during photooxidation in the SEPAP unit (left) and in the LED 365 unit (right)

Fig. 19. UV–visible spectra during exposure in the SEPAP setup of a PE film pre-irradiated for 1270 h in the LED 365 device.

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