express polymer letters

Research article

# Improving UV-C stability in polypropylene through synergistic phenolic or hydroxylamine-based additives with UV absorbers

Marcos Vinícius Basaglia<sup>1,2</sup>, Jessica Caroline Ferreira Gimenez<sup>3</sup>, Manoel Gustavo Petrucelli Homem<sup>3</sup>, Sandra Andrea Cruz<sup>3</sup>, Lucas Henrique Staffa<sup>1,2</sup>, Sílvia Helena Prado Bettini<sup>1,2\*</sup>

<sup>1</sup>Graduate Program in Materials Science and Engineering (PPGCEM), Federal University of São Carlos (UFSCar), São Carlos, SP, Brazil.

<sup>2</sup>Department of Materials Engineering (DEMa), Federal University of São Carlos (UFSCar), São Carlos, SP, Brazil.
 <sup>3</sup>Department of Chemistry (DQ), Federal University of São Carlos (UFSCar), São Carlos, SP, Brazil

Received 12 September 2024; accepted in revised form 29 October 2024

**Abstract.** UV-C radiation (200–280 nm) is recognized for its effectiveness in disinfection, but it also induces degradation in polymeric materials such as polypropylene (PP), reducing their service life. Stabilizing additives are a viable approach to mitigating or delaying the degradation process. However, the chemical groups within these additives may adversely affect stabilization under UV-C exposure due to their potential to absorb the radiation. This study investigates the degradation of PP under UV-C radiation and evaluates the performance of stabilization systems containing phenolic antioxidants (Irganox 1010), hydroxylamine (Irgastab FS 042), and UV absorbers (Tinuvin 1577). PP films were exposed to UV-C radiation for 24, 48, and 96 h, corresponding to doses of 1000, 2000, and 4000 J/cm<sup>2</sup>. Degradation was assessed using size exclusion chromatography (SEC), parallel plate rheometry, infrared spectroscopy (FTIR), static water contact angle, and mechanical testing. The independent use of antioxidants or UV absorbers resulted in reduced carbonyl group formation relative to neat PP, but these were insufficient to prevent PP brittleness after 96 h of exposure. In contrast, the combined use of hydroxylamine or phenolic additives with UV absorbers effectively preserved PP ductility, allowing deformations exceeding 300% without fractures, indicating a synergistic effect.

**Keywords:** degradation, mechanism, molar mass, aging, gel permeation chromatography, Fourier transform infrared spectroscopy, UV-C radiation, stabilization

# 1. Introduction

UV-C radiation, or ultraviolet germicide radiation (UVGI), is a part of the electromagnetic spectrum with wavelengths between 200 and 280 nm. Several studies in the literature [1–5] demonstrate its efficiency in inactivating fungi, viruses, and bacteria, rendering it a promising alternative for disinfecting objects and surfaces, especially in medical and hospital environments.

However, it is essential to recognize that UV-C radiation affects not only the microorganisms but also affects the materials. This range of the electromagnetic spectrum has energy close to the bonds present in polymeric materials. Consequently, it can induce photodegradation reactions, leading to changes in the properties and characteristics of the material and, consequently, diminishing its useful life [6, 7]. Polypropylene, a material widely used in medical and

<sup>\*</sup>Corresponding author, e-mail: <u>silvia.bettini@ufscar.br</u> © BME-PT

hospital environments [8], would be one of the materials subjected to disinfection processes and, consequently, to degradative processes caused by UV-C radiation.

The photodegradation process for polypropylene has been extensively studied, particularly concerning its exposure to solar radiation, UV-A, and UV-B. The main reactions involved in this process are predominantly  $\beta$ -scission, implying chain breakage and, consequently, reduction in the molar mass for PP [9, 10]. Additionally, reduction in elongation at break and tensile strength, formation of carbonyl groups, color changes, decrease in melting temperature, increase in the crystallinity, and formation of cracks on the surface are also observed [11–19]. The latter two phenomena are closely associated with the chemi-crystallization process.

Research on the impact of UV-C radiation in polymers is limited because the ozone layer effectively filters out UV-C radiation, preventing it from reaching the Earth's surface. However, it is gaining importance as it has proven to be effective in the medical field. The changes in properties reported in the literature [20–22] are similar to those observed in photodegradation caused by radiation in other ultraviolet regions but occur at greater intensity, even for shorter irradiation periods. Nevertheless, these studies do not provide an approach regarding the use of stabilizers against UV-C radiation.

Using additives is an alternative to minimize the degradative process in polymeric materials. The most commonly used additives for stabilization during the processing and service of polyolefins are phenolbased, such as pentaerythritol tetrakis[3-[3,5-di-tertbutyl-4-hydroxyphenyl]propionate (Irganox 1010). These additives are classified as primary antioxidants, acting as H-donors for peroxyl radicals. After donating hydrogen, the phenolic additives remain active through the internal delocalization of electrons, further stabilizing free radicals in the medium. However, despite the efficacy of these additives, quinones may be formed in their structure during the stabilization process. These groups result in polymer yellowing and can act as chromophores under UV-C radiation [23, 24].

As an alternative to phenolic additives, hydroxylamine-based antioxidants act as a stabilizer for polymers without forming chromophore groups. Their mechanism of action consists of donating labile hydrogen to peroxyl radicals, resulting in the formation of an aminoxyl radical in their structures. Through internal electron delocalization, they can remain active, capturing free radicals in the medium and donating more hydrogens to peroxyl radicals [6, 25].

Studies on bis(octadecyl)hydroxylamine, the main additive of this class, have primarily focused on processing [26–28]. However, the formation of aminoxyl radicals in their structure may suggest potential efficiency against photo-oxidation similar to Hindered Amine Light Stabilizers (HALS) [25].

Additionally, there are specific classes of additives designed for combating photodegradation, such as UV absorbers. These additives absorb incident radiation at specific wavelengths based on their molecular structures and compete with other chromophore groups in the polymer. After radiation absorption, the molecules return to their ground state by dissipating energy in heat without forming free radicals [7].

Hydroxyphenyl triazine-type is one of the additives present in the UV absorbers class, commonly for protecting polyesters against radiation in the UV-A range, and has proven to be effective in stabilizing [29–32]. However, these also show good absorption in the UV-C wavelength region and may present potential uses against UV-C radiation.

To address gaps in the literature regarding the effectiveness of additives in protecting polymers exposed to UV-C radiation, this study aimed to evaluate the performance of conventional phenolic (Irganox 1010) and hydroxylamine (Irgastab FS 042) antioxidants, as well as UV absorbers (Tinuvin 1577), in terms of stabilization capacity in polypropylene subjected to different doses of UV-C radiation. To our knowledge, this study marks the first instance in which a phenolic and hydroxylamine-based additive PP compound has demonstrated effective protection against UV-C radiation, relying on synergistic effects with UV absorber.

# 2. Experimental

# 2.1. Materials

The polymer used was a polypropylene homopolymer free of any additives (DP 5000 SCPV, Braskem, Brazil). The stabilization system included four different types of additives: Irganox 1010 (BASF, Florham Park, USA), a phenolic primary antioxidant, Irgafos 168 (BASF, Basel, Switzerland), a secondary antioxidant phosphite-based, and Irgastab FS 301 FF (BASF, Basel, Switzerland), a blend of Irgafos 168 and Irgastab FS 042 (primary antioxidant and free radical scavenger), in a 1:1 ratio. Additionally, Tinuvin 1577 (BASF, Ludwigshafen, Germany), a hydroxyphenyl triazine-type UV absorber, was used due to its effective absorption in the UV-C wavelength range. The chemical structures, chemical nomenclature, and commercial names of these additives are presented in Table 1.

For the study, six formulations were prepared, the first formulation consisted of additive-free polypropylene. The subsequent two formulations consisted of primary and secondary antioxidants, maintaining a 1:2 weight ratio with the content of secondary antioxidants fixed at 1000 ppm. For these, the primary antioxidants were varied between phenolic and hydroxylamine. The remaining three formulations included the addition of 2000 ppm of Tinuvin 1577 to each of the previous formulations. The additive content for each formulation is detailed in Table 2.

The concentrations of primary antioxidants were calculated, conforming to the hydrogen-donating capacity by molecular weight. Irganox 1010 contains four reactive sites and has a molar mass of 1178 g/mol,

 Table 1. Chemical nomenclature, CAS number, trademark, abbreviations, and chemical structure of the additives used in this study.

Chemical nomenclature, CAS number and trademark	Abbreviation	Chemical structure		
Pentaerythritol tetrakis[3-[3,5-di-tert-butyl-4- hydroxyphenyl]propionate (6683-19-8) (Irganox <sup>®</sup> 1010)	A1			
Tris(2,4-di-tert-butylphenyl) phosphite (31570-04-4) (Irgafos® 168)	Р2	$\rightarrow \qquad \qquad$		
Bis(hydrogenated tallow alkyl)amines, oxidized (143925-92-2) (Irgastab® FS 042)	NI	OH N N		
Phenol, 2-(4,6-Diphenyl-1,3,5-triazin-2-yl)-5-hexyloxy (147315-50-2) (Tinuvin <sup>®</sup> 1577)	UV1	OC <sub>6</sub> H <sub>13</sub> OH N N		

Sample	Irganox 1010 (A1)	Irgastab FS 042 (N1)	Irgafos 168 (P2)	Tinuvin 1577 (UV1)
Neat PP	0	0	0	0
PP + A1/P2	500	0	1000	0
PP + N1/P2	0	500	1000	0
PP+UV1	0	0	0	2000
PP + A1/P2 + UV1	500	0	1000	2000
PP + N1/P2 + UV1	0	500	1000	2000

Table 2. Composition of prepared formulations [ppm].

resulting in a theoretical capacity of  $3.39 \cdot 10^{-3}$  H.mol/g of additive. In contrast, Irgastab FS 042 has a molar mass of 538 g/mol and possesses only one reactive hydrogen in its structure. However, this molecule remains active, achieving an experimental stabilization capacity of 1.8 radicals per molecule of additive, as reported in the literature [25]. This results in an effective capacity of  $3.35 \cdot 10^{-3}$  H.mol/g of additive. This unit represents the number of labile hydrogens available for radical stabilization per gram of additive.

# 2.2. Processing

The samples were processed in an internal mixer Haake Rheomix 600 (Thermo Fisher Scientific, USA), with counter-rotating roller-type rotors at 200 °C and 100 rpm under an air atmosphere. Additives were added to the system after 30 s of mixing, with the polymer in the molten state, and the total residence time in the mixer was 2 min. After preparation, the formulations were shaped in a hydraulic press (MPH-10, Til Marcon, Brazil) at a temperature of 190 °C and a pressure of 1 kgf (9.806650 N), resulting in films approximately 180 µm thick. Finally, the films were stamped into the shape of tensile test specimens according to ASTM D1708-18.

### 2.3. Exposure to UV-C radiation

The prepared specimens had both faces exposed to UV-C radiation (254 nm) in a chamber consisting of two low-pressure mercury lamps of 4 W each, type T5/G5. The chamber also included a ventilation system to remove ozone. The specimens were positioned 10 cm from the lamps, where the irradiance, measured with a ThorLabs PM 200 (ThorLabs, Newton, USA) device and an S140C sensor, was 60 W/m<sup>2</sup>. The specimens were exposed for 24, 48, and 96 h, corresponding to nominal doses of 1000, 2000, and 4000 J/cm<sup>2</sup>, respectively, based on the energy incident on the sample. Therefore, to calculate the absorbed dose, a unitary quantum yield was considered.

### 2.4. Characterization

### 2.4.1. Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) analyses were conducted on a Viscotek high-temperature size exclusion chromatograph, model GPC5351US - Viscotek Automated Conventional HT-GPC System (Malvern Panalytical Ltd, United Kingdom), with a refractive index detector (IR). The equipment operated with 3 columns (HT-806M, General mixed HT-GPC column 300×8 mm) (Shodex, Tokyo, Japan) suitable to detect molar masses between 1000 and 20000000 Da. Samples were solubilized in 1,2,4trichlorobenzene (TCB) HPLC grade (Sigma Aldrich, Saint Louis, USA) stabilized with 1% 2,6-di-tertbutyl-4-methylphenol (BHT) (Sigma Aldrich, Saint Louis, USA). The test temperature was maintained at 150 °C with a flow rate of 1 mL/min in the main and auxiliary pumps. The equipment calibration curve was obtained using 12 monodisperse polystyrene standards (UCS 2000, Malvern Panalytical Ltd, United Kingdom) with molar masses between 1050 and 3800000 Da.

### 2.4.2. Rheological analysis

Parallel plate rheometry was performed using a rotational rheometer, model AR-G2 (TA Instruments, New Castle, USA), under controlled stress. The measurements were conducted with a 25 mm diameter plate and a 0.5 mm gap. Steady-state tests were carried out at 180 °C in a nitrogen atmosphere with a flow rate of 10 L/min, at shear rates ranging from 0.01 to 10 s<sup>-1</sup>. The zero-shear viscosity values were calculated from a linear regression in the Newtonian plateau region.

# 2.4.3. Fourier transform tnfrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) tests were conducted on a Nicolet 6700 instrument (Thermo Fisher Scientific, Madison, USA) in transmission mode, with 64 scans at a resolution of 2 cm<sup>-1</sup>. The analysis was performed in triplicate. The carbonyl index (*CI*) was calculated according to the Equation (1), where  $A_{C=0}$  represents the area under the carbonyl peak (baseline between 1660 and 1800 cm<sup>-1</sup>) and  $A_{2722}$  represents the area under the reference peak (baseline between 2750 and 2696 cm<sup>-1</sup>):

$$CI = \frac{A_{\rm C}=0}{A_{\rm 2722}} \tag{1}$$

# 2.4.4. Contact angle

Contact angle measurements were performed using the sessile drop method, with deionized water, and a Ramé-hart 260-F4 Series-DROPimage Advanced v2.7 goniometer (Ramé-hart instrument, Succasunna, USA) for angle measurement. Three measurements were taken for each drop, and three drops were tested for each sample.

### 2.4.5. Mechanical tests

Tensile tests were performed using an Instron 5569 Universal Testing Machine (Instron, Norwood, USA) following the ASTM D1708:18 standard for microtensile specimens with a thickness of  $0.180\pm0.01$  mm. The tests were performed at a speed of 1 mm/min, using pneumatic side-action tensile grips, a 500 N load cell, and a grip separation distance of 14.5 mm. The environmental conditions followed the ASTM D618 standard, with a relative humidity of  $50\pm5\%$  at room temperature ( $23\pm2$  °C). Five specimens were tested for each formulation. The elongation at break was calculated using the crosshead displacement method, according to the Equation (2), where  $\varepsilon_b$  is defined as elongation at break,  $L_{\rm f}$  is the final length at the point of rupture and  $L_0$  is the initial distance between the grips:

$$\boldsymbol{\varepsilon}_{\mathrm{b}} = \frac{L_{\mathrm{f}} - L_{\mathrm{0}}}{L_{\mathrm{0}}} \cdot 100\% \tag{2}$$

### 2.4.6. Statistical tests

The statistical tests of ANOVA and Tukey for multiple comparisons of means were conducted using Minitab software, with a significance level of 5% ( $\alpha = 0.05$ ) for the results of carbonyl index, contact angle, and elongation at break. The analyzed results were designated by letters in each of the respective figures, with equal letters assigned to statistically similar values.

# 3. Results and discussion

Figure 1 presents the carbonyl index calculated for the test specimens as a function of UV-C radiation dose. Among the samples prepared without a UV absorber, an increase in the carbonyl index can be observed after exposure to a dose of UV-C radiation of 1000 J/cm<sup>2</sup>, which occurs more intensely for neat PP and, to a lesser extent, for the additive-containing samples. In other words, regardless of the class or set of additives used, all showed a lower carbonyl index compared to neat PP, indicating a positive effect of stabilizers. As the irradiation time increases, it is also noticeable that the evolution of the carbonyl index occurs nonlinearly, with the growth rate being higher at longer irradiation times. Both antioxidants used showed the same carbonyl group formation index.

It is important to emphasize that the FTIR analyses were conducted in transmission mode. Consequently, the entire sample thickness was considered in the calculations. Previous research demonstrated that photodegradation in polypropylene occurs heterogeneously, with the intensity of the degradative effects varying along the film's thickness due to the dependence on oxygen availability, with a higher concentration of carbonyl groups near the surface [33]. Nevertheless, a comparative analysis can still be conducted between the formulations, as they have the same thickness, allowing for a meaningful comparison of the different stabilizers despite the influence of oxygen concentration gradients.

The UV absorber alone in PP stabilization provides greater stability compared to those with antioxidants



Figure 1. Carbonyl index as a function of radiation dose for (Neat PP), (PP + A1/P2), (PP + N1/P2), (PP + UV1), (PP + A1/P2 + UV1) and (PP + N1/P2 + UV1). Significantly different values among groups are indicated by different letters ( $\alpha < 0.05$ ).

only. However, significant carbonyl group formation can still be observed after a dose of 1000 J/cm<sup>2</sup>, corresponding to 24 h of irradiation. In contrast, using a UV absorber in combination with other antioxidant additives effectively promoted stability in the polymer, as the variation in the carbonyl index did not show significant changes even after a dose of 4000 J/cm<sup>2</sup> (96 h). This behavior may indicate a synergistic stabilization effect.

A synergism between additives refers to an interaction combining two or more additives that leads to a performance enhancement that exceeds the sum of their individual effects. This occurs when the additives complement each other's functions, amplifying their protective or stabilizing capabilities [34]. In the context of photodegradation of polypropylene, synergistic effects have been widely reported in the literature, as various degradation pathways are addressed simultaneously, enhancing the overall stabilization of the material. For instance, the combination of low and high molecular weight HALS has been shown to enhance stability through synergistic effects [34], similar to the interactions observed through the combination of UV absorbers with HALS [35, 36] and the use of HALS alongside phosphites [37].

In the context of this study, the use of UV absorbers alone reduces the absorption of incident radiation by the chromophoric groups present in the material, thereby decreasing the generation of free radicals. However, it does not completely prevent their formation, leading to residual degradation. In contrast, antioxidants can stabilize some of the radicals formed, but their efficacy is limited by the sheer number of radicals in the system. Nevertheless, when UV absorbers and antioxidants are used together, fewer radicals are generated, allowing the antioxidants to neutralize the remaining radicals more effectively, which consequently slows down the material's degradation.

It is important to note that during the photodegradation process, different carbonyl group species are formed, which are contained in the spectral region between wavenumbers 1660 and 1800 cm<sup>-1</sup> and contribute to the calculation of the carbonyl index. This fact is evident in Figure 2, which shows the evolution of the FTIR spectrum for non-additivated PP as a function of radiation dose.

It is also possible to observe that with increasing the radiation dose, the maximum absorption peak shifts



Figure 2. Normalized FTIR spectra in the carbonyl absorption region for neat PP as a function of radiation dose.

from 1710 to 1714 cm<sup>-1</sup>. To better clarify this effect, the curves were deconvolved, as shown in Figure 3. The literature reports variations in wavenumber assignments depending on the formed groups [38–43]. In the model used in this study (Figure 3), the best mathematical fit was achieved using the Voigt model with seven peaks, attributed to possible products formed during the photo-oxidative degradation process. These groups include unsaturated ketones (1685 cm<sup>-1</sup>), conjugated ketones (1702 cm<sup>-1</sup>), carboxylic acids (1713 cm<sup>-1</sup>), ketones (1723 cm<sup>-1</sup>), esters and aldehydes (1736 cm<sup>-1</sup>), peresters and peracids (1757 cm<sup>-1</sup>), and lactones (1780 cm<sup>-1</sup>). Additionally, the evolution of the concentration of carbonyl compounds can be calculated according to the



**Figure 3.** Mathematical deconvolution of the FTIR spectrum in the carbonyl region for a sample of Neat PP after a radiation dose of 4000 J/cm<sup>2</sup> of UV-C radiation.



Figure 4. Concentration of carbonyl groups as function of UV-C radiation dose.

respective molar absorption coefficient for each product [42–44], as shown in Figure 4.

Ketones are the predominant carbonyl products, followed by carboxylic acids. These groups appear early in the degradation process and remain predominant at all analyzed exposure times. The use of antioxidants or UV absorbers alone is insufficient to inhibit the formation of these groups, as they are detectable in the first evaluation, with a dose corresponding to 1000 J/cm<sup>2</sup>. For the formulations (PP + A1/P2 + UV1) and (PP + N1/P2 + UV1), it was not possible to deconvolute the curves for the doses of 1000 and 2000 J/cm<sup>2</sup>, indicating very low concentrations of these groups at these radiation doses.

The formation of other carbonyl groups, such as esters, peresters, lactones, and unsaturated ketones, only appears at more advanced stages of degradation, indicating that during the photodegradation process, the formation of certain groups varies with time and the concentration of other carbonyl groups present. This fact has been reported by other authors in the literature [16, 21, 38, 41] and explains the shift of the peak maximum absorption from 1710 to 1714 cm<sup>-1</sup> observed earlier in Figure 3. Furthermore, using antioxidants combined with UV absorbers prevents the formation of these groups even after a dose of 4000 J/cm<sup>2</sup>. It is important to reiterate that the concentrations were measured across the entire sample. These concentrations may vary in intensity depending on the depth, meaning that the concentration of certain carbonyl groups may be more or less prominent at different depth levels.

Thus, it is possible to outline the possible reactions during the photodegradation process. In the initial stages, the main group responsible for initiating the photodegradation reactions is the hydroperoxides resulting from other oxidative processes [9]. As shown in Figure 5, after the absorption of radiation, there is a probability that hydroperoxides undergo homolytic cleavage of the O-O bond, resulting in the formation of alkoxyl macro radicals [45]. These macro radicals are susceptible to  $\beta$ -scission reactions, predominantly resulting in the cleavage of the polymer's main chain. In the presence of oxygen, propagation reactions of peroxyl and alkoxyl radicals may also occur, as shown in Figure 5. In this process, hydrogen will be extracted from the tertiary carbon (which has lower bond energy), leading to the sequential formation of hydroperoxides [6]. Another potential reaction pathway for macroradical alkoxyls involves abstracting hydrogen from adjacent polymeric chains, forming tertiary alcohols, as previously observed by other authors [46]. However, O-H bonds formed have an energy equivalent to 254 nm radiation (471 kJ/mol), making these bonds easily breakable. Thus, besides generating a new radical in the adjacent chain, the initial polymeric chain remains reactive, which is one of the reasons for the significant increase in free radicals in the system under UV-C radiation.

The ketone groups formed after  $\beta$ -scission reactions are also responsible for triggering the degradation process occurring by Norrish reactions, as illustrated in Figure 6. These reactions can be of type I, where  $\alpha$ -cleavage occurs through homolytic cleavage of the bond between the carbonyl group and the adjacent carbon ( $\alpha$ -carbon), or type II, where  $\beta$ -cleavage occurs through abstraction of the hydrogen from the third carbon in the main chain ( $\gamma$ -carbon). The



Figure 5. Initiation of photodegradation reactions, propagation reactions and formation of ketones from alkoxyl radicals.

products formed can vary depending on the group's position in the chain. If the ketone is in the middle of the polymer chain, type I Norrish reactions are more likely, while if the ketone is linked to a methyl group, the probability of type II Norrish reactions increases. Temperature also influences the kinetics of reactions. While type I reactions predominate at high temperatures, ambient temperature favors the occurrence of type II reactions [9, 10].

In the case of Norrish type I reactions, specifically  $\alpha$ -cleavage, the generated radicals can react with oxygen or other alkoxyl and peroxyl radicals, leading to the formation of carboxylic acids, esters, and peresters, as also shown in Figure 6. Carboxylic acids



Figure 6. a) Norrish type I and II reactions and formation of ketones, esters, peresters, carboxylic acids and b) lactones during photodegradation.



**Figure 7.** Water contact angle as a function of radiation dose for (Neat PP), (PP + A1/P2), (PP + N1/P2), (PP + UV1), (PP + A1/P2 + UV1) and (PP + N1/P2 + UV1). Significantly different values among groups are indicated by different letters ( $\alpha < 0.05$ ).

may also result from the reaction between peroxides and ketones. Additionally, the production of volatile compounds has been observed in other studies when the  $\alpha$ -cleavage reaction takes place in a ketone near the end of the polymer chain [47]. Finally, the formation of lactones, also observed with the deconvolution of the curves, occurs from carboxylic acids or sequential hydroperoxides.

After confirming the material functionalization in response to UV-C radiation, characterization was performed through measurements of static water contact angle using the sessile drop method. The results are presented in Figure 7.

The measured values of the contact angle show a good correlation with the calculated carbonyl index values, where an increase in the concentration of carbonyl groups results in a decrease in the water contact angle. As carbonyl groups have a more polar nature than the carbon bonds in the polymeric chains of PP, they promote an increase in surface hydrophilicity with prolonged exposure to UV-C radiation. Remarkably, similar to neat PP, which exhibits the highest concentration of carbonyl groups after the irradiation process, it also demonstrates lower contact angle values in measurements at all exposure times.

Additionally, it is observed that the presence of antioxidant additives or UV absorber alone results in a less pronounced decrease in the contact angle compared to neat PP. On the other hand, the combination of UV absorber with antioxidants, regardless of their class, maintains contact angles for doses up to  $2000 \text{ J/cm}^2$  of UV-C radiation, with statistical variation occurring only after exposure to a dose of  $4000 \text{ J/cm}^2$ .

Rheology and size exclusion chromatography tests were also conducted to analyze the effects of UV-C radiation on the reduction of PP molar mass, as well as the effects of the added additives.

The molar mass distribution curves are presented in Figure 8, and the values of the number-average molar mass  $(\overline{M_n})$ , weight-average molar mass  $(\overline{M_w})$ , polydispersity (PD), and zero shear viscosity  $(\eta_0)$  are shown in Table 3. Rheological test data were presented in relative terms (Figure 9), where the nonirradiated zero-shear viscosity for each composition was used as a reference. The  $\eta_0$  values obtained from the irradiated samples were divided by the  $\eta_0$  value of the corresponding non-irradiated sample. This approach was adopted because the incorporation of additives was performed in an internal mixer, and different stabilization systems resulted in varying molar mass and, consequently, different  $\eta_0$  values for the non-irradiated formulations. Thus, a relative comparison between the  $\eta_0$  values concerning their respective non-irradiated samples allows for a better interpretation of variations related to UV-C radiation-induced degradation.

To provide further clarity on the topic, it is important to first address the issue of degradation heterogeneity. It can be observed in Figure 8 that all presented curves exhibit a monomodal behavior, similar to that found in another study in the literature that analyzed the effects of degradation at different depth levels [48]. If any portion of the film were not subjected to degradative processes, one would expect to observe a bimodal distribution or polymer chains with unchanged molar mass. This suggests that, although the extent of degradation may have varied at different depths, it affected the entire thickness of the specimen, as evidenced by the observation of an unimodal distribution rather than a bimodal one.

For all formulations, a reduction in molar mass and viscosity at zero-shear rate is noticeable with increasing the dose of UV-C radiation. This is due to the photodegradation reactions of polypropylene, primarily involving chain scission, resulting in a decrease in molar mass and, consequently, a decrease in material flow resistance. As shown in Table 3, this reduction in molar mass is accompanied by a narrowing of the molar mass distribution of PP, decreasing its polydispersity.



**Figure 8.** Molar mass distribution curves in the function of radiation dose for a) Neat PP, b) PP + A1/P2, c) PP + N1/P2 and d) PP + N1/P2 + UV1.

It is also observed, as expected, that the formulation completely free of stabilizers was the most affected in the early exposure times, showing a reduction in the values of  $\overline{M_w}$  from 316 000 to 233 000 Da, which resulted in a relative  $\eta_0$  close to 20% after a radiation dose of 1000 J/cm<sup>2</sup>.

Incorporating primary and secondary antioxidants without UV absorbers proved effective, particularly for doses up to 1000 J/cm<sup>2</sup>, demonstrating a  $\eta_0$  retention close to 50%. However, for radiation doses greater than 2000 J/cm<sup>2</sup>, the relative  $\eta_0$  values approached those of the non-stabilized PP.

As mentioned earlier, UV-C radiation has enough energy to break bonds that would remain stable with exposure to other wavelength ranges within the ultraviolet region, leading to a significant concentration of free radicals in the system. Consequently, the effectiveness of stabilizers may not be as pronounced after a radiation dose of 4000 J/cm<sup>2</sup>.

When a UV absorber was added to the stabilization system containing antioxidants, it was observed that, even after exposure to 2000 J/cm<sup>2</sup>, the values of  $\overline{M_w}$ and viscosity remained practically unchanged compared to those same non-irradiated formulations, showing a reduction of 9% for the PP + A1/P2 +UV1 and less than 2% for the PP + N1/P2 + UV1. This outcome is attributed to the synergistic effect of the additives described previously, in which the UV absorber competes with chromophore groups for radiation absorption, thereby balancing the rate of free radical generation in the system with their capture by antioxidant additives. This effect was particularly noticeable within doses of 2000 J/cm<sup>2</sup>, while after a radiation dose of 4000 J/cm<sup>2</sup>, changes in molar mass due to the degradation process were observed. Furthermore, the formulations containing UV absorbers and antioxidants (regardless of class) demonstrated superior maintenance of molar mass

Sample	UV-C radiation dose [J/cm <sup>2</sup> ]	Mn     [Da]	M      [Da]	PD	η₀ [Pa·s]
Pristine PP	-	213 000	695 000	3.26	6400
Neat PP	0	120 000	316000	2.63	1300
	1000	102 000	233 000	2.28	280
	2000	87 000	185 000	2.12	200
	4000	57 000	99 000	1.73	90
	0	168 000	423 000	2.52	5200
	1000	127 000	336 000	2.64	2300
PP + AI/P2	2000	121 000	273 000	2.25	1400
	4000	65 000	130 000	2.00	340
PP + N1/P2	0	158 000	403 000	2.55	4500
	1000	150000	347 000	2.31	2200
	2000	101000	215 000	2.12	700
	4000	66000	136 000	2.06	170
PP + UV1	0	128000	320 000	2.50	1450
	1000	109 000	249 000	2.28	500
	2000	85 000	183 000	2.15	330
	4000	78 000	142 000	1.82	100
PP+A1/P2+UV1	0	169 000	428 000	2.52	5000
	1000	160 000	400 000	2.50	4000
	2000	157 000	390 000	2.48	3500
	4000	145 000	335 000	2.30	2200
	0	160 000	405 000	2.53	4700
DD + N1/D2 + 117/1	1000	160 000	410 000	2.56	3900
PP + NI/P2 + UVI	2000	156 000	400 000	2.56	3400
	4000	145,000	330,000	2 27	2000

**Table 3.** Number average molar mass ( $\overline{M_n}$ ), weight average molar mass ( $\overline{M_w}$ ), polydispersity (PD) and zero shear rate viscosity ( $\eta_0$ ) for (Neat PP), (PP + A1/P2), (PP + N1/P2), (PP + UV1), (PP + A1/P2 + UV1) and (PP + N1/P2 + UV1).



Figure 9. Relative shear zero viscosity for (Neat PP), (PP + A1/P2), (PP + N1/P2), (PP + UV1), (PP + A1/P2 + UV1) and (PP + N1/P2 + UV1).

and viscosity over exposure time compared to other formulations studied.

Through these tests, a certain differentiation in the performance of phenol-based and hydroxylaminebased stabilizers became apparent. Despite exhibiting lower values of  $\overline{M_w}$  and  $\eta_0$  for non-irradiated samples, after 24 h of irradiation (1000 J/cm<sup>2</sup>), the values of molar mass and viscosity at zero shear rate were higher for samples containing Irgastab FS 301 FF, indicating a greater effectiveness of hydroxylamine-based additives compared to phenolic ones for shorter irradiation times. The same trend was observed for formulations containing hydroxylamine in conjunction with a UV absorber, and in this case, the relationship persisted for up to 48 h (2000 J/cm<sup>2</sup>).

However, for prolonged exposure times (radiation doses equivalent to 4000 J/cm<sup>2</sup>), it was observed that the presence of phenolic stabilizers in the system resulted in higher stabilization efficacy, with the formulation (PP + A1/P2 + UV1) showing the highest retention in  $\eta_0$  values. In other words, the stabilization

strategy, in the absence of UV absorbers, depends on predicting the exposure time of the polymeric material to UV-C radiation.

As planned in the experimental procedure, the hydrogen donation capacity of both additives was found to be comparable. Additionally, we aimed to remain within the solubility limits for both additives in polypropylene, as the concentrations used were low and close to the recommended lower threshold, suggesting that the entire amount of each additive would be available for reaction.

This finding implies that one of the factors influencing the observed differences in stabilization efficacy may be related to the kinetics of the reactions involved. This relationship can be attributed to the mobility of the additives. The phenolic additive, Irganox 1010, presents significant steric hindrance, restricting its movement within the polymer matrix. In contrast, Irgastab FS 042 is less impeded in its movement, allowing for greater mobility among the polymer chains. This increased mobility may enhance hydroxylamine's availability to donate hydrogen in regions where radicals are formed, thereby contributing to its effectiveness.

Additionally, there are reports in the literature that measure the consumption and degradation of Irgafos 168 when used to stabilize polyolefins against irradiation [49, 50]. Figure 10 shows a region of the FTIR spectrum for PP between wavenumbers 1065 and 1125 cm<sup>-1</sup>. The absorption peak between 1066 and 1090 corresponds to the P–O–C<sub>6</sub>H<sub>5</sub> bond present



Figure 10. Evolution of the FTIR spectrum in the Irgafos 168 consumption observation region.

in Irgafos 168. Because it is a narrow absorption peak and does not overlap with other peaks in the PP spectrum, it can be used to quantify the content of this antioxidant even at low concentrations [51].

The initial observation is that incorporating the Irgafos 168 results in a peak at 1082 cm<sup>-1</sup> for all formulations containing the phosphite-based stabilizer. Notably, this peak is absent for neat PP, indicating that the additive has been integrated into the polymer. Furthermore, it is important to highlight a gradual decay in the intensity of this peak, which occurs with the increase in UV-C radiation dose. Therefore, after 10 h of irradiation (equivalent to a dose of 420 J/cm<sup>2</sup>), this peak is no longer detectable, signifying that it has been entirely consumed during the process. The same behavior could be observed for the peak at 1191 cm<sup>-1</sup>, another peak that could also be used to monitor the consumption of Irgafos 168 [52]. As suggested in the literature, hydroxylamine-based additives may also act as decomposers of hydroperoxides [6]. This implies that, in the initial stages, this additive could play a crucial role in the decomposition of hydroperoxides, thereby enhancing its stabilization efficiency. Furthermore, the consumption of Irgafos 168 over the exposure duration may be correlated with the observation that samples without UV absorbers demonstrate superior stabilization capacity compared to neat polypropylene only up to 1000 J/cm<sup>2</sup> of UV-C radiation. Beyond this dose, it appears that the availability of the additives diminishes, leading to properties that closely resemble those of neat PP.

The data obtained from rheological tests and sizeexclusion chromatography (SEC) can also be correlated using a well-established relationship between the zero-shear viscosity ( $\eta_0$ ) and the weight-average molar mass  $\overline{M}_w$  of a polymer. For linear homopolymers above a certain critical molar mass, this relationship follows the equation  $\eta_0 = k \cdot \overline{M}_w^{3.4}$  where k is a constant specific to the polymer and the experimental conditions.

In Figure 11, the zero-shear viscosity values are plotted as a function of the weight-average molar mass. The green line represents a fixed slope of 3.4 based on the mentioned equation. For this curve, the  $R^2$  value was 0.89. Samples less susceptible to degradation exhibit a good correlation with the theoretical fit, remaining closer to this ideal behavior. In contrast, samples subjected to higher doses of radiation without adequate stabilization systems show significant



Figure 11. Relationship between zero-shear viscosity  $(\eta_0)$  as a function of the weight-average molar mass  $(\overline{M_w})$ .

deviations from this expected performance. This deviation can be attributed to two primary factors. The first involves the sample conditions during rheological testing, where the extremely low viscosity may have allowed the sample to escape the rheometer plates, especially at higher shear rates, thus compromising the accuracy of the data. Additionally, the heterogeneity of the samples in terms of thickness and composition may have negatively impacted the consistency of the results, leading to greater dispersion in the viscosity values. This dispersion may have been exacerbated by differential degradation across the sample thickness, affecting its rheological response. The degradative effects of UV-C radiation on mechanical properties were also analyzed. Table 4 contains the values of elongation at break.

For radiation doses up to 1000 J/cm<sup>2</sup>, all samples exceeded 300% elongation during the test without fracturing. However, for doses of 2000 J/cm<sup>2</sup>, this property begins to be affected depending on the stabilization system used. For non-additive PP, for example,

**Table 4.** Elongation at break of samples as function of radiation dose to UV-C radiation. Significantly different values among groups are indicated by different letters ( A, B, C, D) ( $\alpha < 0.05$ ).

Sample	Elongation at break [%]				
	0 h	24 h	48 h	96 h	
Neat PP	>300 <sup>A</sup>	>300 <sup>A</sup>	65±29 <sup>B</sup>	8.0±5.0 <sup>D</sup>	
PP + A1/P2	>300 <sup>A</sup>	>300 <sup>A</sup>	80±13 <sup>B</sup>	13.5±4.7 <sup>D</sup>	
PP + N1/P2	>300 <sup>A</sup>	>300 <sup>A</sup>	87±20 <sup>B</sup>	11.2±3.5 <sup>D</sup>	
PP+UV1	>300 <sup>A</sup>	>300 <sup>A</sup>	200±42 <sup>C</sup>	15.1±4.1 <sup>D</sup>	
PP + A1/P2 + UV1	>300 <sup>A</sup>	>300 <sup>A</sup>	>300 <sup>A</sup>	>300 <sup>A</sup>	
PP + N1/P2 + UV1	>300 <sup>A</sup>	>300 <sup>A</sup>	>300 <sup>A</sup>	>300 <sup>A</sup>	

the elongation at break values was close to 65%. Furthermore, the samples stabilized with conventional systems, those containing only primary and secondary antioxidants, and the ones with only UV absorbers also had this property affected after being exposed to radiation doses of 2000 J/cm<sup>2</sup>, showing a reduction in the values of elongation at break.

After exposure to 4000 J/cm<sup>2</sup> of UV-C radiation, the test specimens of these formulations exhibit brittle behavior. This behavior can be primarily associated with the decrease in the molar mass of polymer chains resulting from chain breaks during the degradation process, as evidenced by SEC tests and the reduction in viscosity at zero shear rates.

Samples containing a combination of primary antioxidants and UV absorbers exhibited ductile behavior during the test for all exposure times evaluated, withstanding deformations exceeding 300% without fracturing. This once again confirms the synergistic effect between the additives.

# 4. Conclusions

Degradation levels for polypropylene films subjected to UV-C radiation were evaluated using two different stabilization systems (phenol-based and hydroxylamine-based) in the presence and absence of UV absorbers.

After exposure to UV-C radiation, polypropylene's molar mass was reduced, and carbonyl groups of different species formed, resulting in a decrease in material viscosity in the molten state, a reduction in static water contact angle, and a decrease in elongation at break for the tested specimens. This specific property was more critically affected after 96 h of exposure (4000 J/cm<sup>2</sup>), during which the fracture mechanism changed from ductile to brittle without an adequate stabilization system.

It is also concluded that the level of influence of these properties depends on the proposed stabilization system. Using phenolic antioxidants or hydroxylaminebased stabilizers in conjunction with UV absorbers resulted in the maintenance of rheological properties for up to 48 h of exposure (2000 J/cm<sup>2</sup>). It was able to promote maintenance of elongation at break even after 96 h of irradiation (4000 J/cm<sup>2</sup>), preserving the ductile behavior of the material, suggesting a synergistic effect in the joint use of these additives, reinforcing the importance of choosing an appropriate stabilization system because of the prediction of the dose used in various disinfection cycles. Finally, replacing phenolic antioxidants with hydroxylamine-based stabilizers showed significant differences in the retention of rheological properties and molar masses. Hydroxylamine-based stabilizers were more effective in shorter exposure periods, while phenolic antioxidants were more efficient in longer exposures. However, concerning the formation of carbonyl groups, mechanical properties, and contact angle, there was no significant distinction between the use of these additives.

### Acknowledgements

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001. The present work was carried out with the support of the Conselho Nacional de Desenvolvimento Científico e Tecnológico – Brasil (CNPq) (Process 161111/ 2021-1). Additionally, the present work received funding from the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) (Process 2020/07633-2).

#### References

- [1] Green A., Popović V., Warriner K., Koutchma T.: The efficacy of UVC LEDs and low pressure mercury lamps for the reduction of *Escherichia coli* O157:H7 and *Listeria monocytogenes* on produce. Innovative Food Science and Emerging Technologies, 64, 102410 (2020). https://doi.org/10.1016/j.ifset.2020.102410
- [2] Coohill T. P., Sagripanti J-L.: Overview of the inactivation by 254 nm ultraviolet radiation of bacteria with particular relevance to biodefense. Photochemistry and Photobiology, 5, 1084–1090 (2008). https://doi.org/10.1111/j.1751-1097.2008.00387.x
- [3] Rose L. J., O'Connell H.: UV light inactivation of bacterial biothreat agents. Applied and Environmental Microbiology, 75, 2987–2990 (2009). https://doi.org/10.1128/AEM.02180-08
- [4] Rogers W. J.: Sterilisation techniques for polymers. in 'Sterilisation of biomaterials and medical devices' (eds.: Lerouge S., Simmons A.) Elsevier, Amsterdam, 151–211 (2012).
  - https://doi.org/10.1533/9780857096265.151
- [5] Schmid J., Hoenes K., Rath M., Vatter P., Hessling M.: UV-C inactivation of *Legionella rubrilucens*. GMS Hygiene and Infection Control, **12**, ISSN 2196-5226 (2017). https://doi.org/10.3205/dgkh000291
- [6] Zweifel H., Maier R. D., Schiller M.: Plastics additives handbook. Hanser, Munich (2009).
- [7] Hawkins W. L.: Polymer degradation and stabilization. Springer-Verlag, New York (1984).
- [8] Kowalski W.: Ultraviolet germicidal irradiation handbook: UVGI for air and surface disinfection. Springer, Berlin (2010).

- [9] Rabek J. F.: Polymer photodegradation. Mechanisms and experimental methods. Springer, Berlin (1995). https://doi.org/10.1007/978-94-011-1274-1
- [10] Geuskens G., Kabamba M. S.: Photo-oxidation of polymers Part V: A new chain scission mechanism in polyolefins. Polymer Degradation and Stability, 4, 69–76 (1982). https://doi.org/10.1016/0141-3910(82)90007-6
- [11] Rabello M. S., White J. R.: Crystallization and melting behaviour of photodegraded polypropylene – I. Chemicrystallization. Science, 38, 6379–6387 (1997). <u>https://doi.org/10.1016/S0032-3861(97)00213-9</u>
- [12] Lv Y., Huang Y., Yang J., Kong M., Yang H., Zhao J., Li G.: Outdoor and accelerated laboratory weathering of polypropylene: A comparison and correlation study. Polymer Degradation and Stability, **112**, 145–159 (2015). https://doi.org/10.1016/j.polymdegradstab.2014.12.023
- [13] Butylina S., Hyvärinen M., Kärki T.: A study of surface changes of wood-polypropylene composites as the result of exterior weathering. Polymer Degradation and Stability, 97, 337–345 (2012). https://doi.org/10.1016/j.polymdegradstab.2011.12.014
- [14] Mena R. L., Cacuro T. A., de Freitas A. S. M., Rangel E. C., Waldman W. R.: Polymer photodegradation followed by infrared: A tutorial. Revista Virtual de Quimica, **12**, 959–968 (2020).
  - https://doi.org/10.21577/1984-6835.20200077
- [15] Rosa D. S., Angelini J. M. G., Agnelli J. A. M., Mei L. H. I.: The use of optical microscopy to follow the degradation of isotactic polypropylene (iPP) subjected to natural and accelerated ageing. Polymer Testing, 24, 1022– 1026 (2005).

https://doi.org/10.1016/j.polymertesting.2005.07.009

- [16] la Mantia F. P.: Influence of processing conditions on the photo-oxidation of polypropylene films. Polymer Degradation and Stability, 15, 283–290 (1986). <u>https://doi.org/10.1016/0141-3910(86)90075-3</u>
- [17] Butler C. H., Whitmore P. M.: Measurement of peroxides in the volatile degradation products of polypropylene photooxidation. Polymer Degradation and Stability, 98, 471–473 (2013).

https://doi.org/10.1016/j.polymdegradstab.2012.10.004

- [18] Guadagno L., Naddeo C., Vittoria V.: Structural and morphological changes during UV irradiation of the crystalline helical form of syndiotactic polypropylene. Macromolecules, **37**, 9826–9834 (2004). https://doi.org/10.1021/ma040129j
- [19] White J. R., Turnbull A.: Weathering of polymers: Mechanisms of degradation and stabilization, testing strategies and modelling. Journal of Materials Science, 29, 584–613 (1994).

https://doi.org/10.1007/BF00445969

[20] Alariqi S. A. S., Mutair A. A., Singh R. P.: Effect of different sterilization methods on biodegradation of biomedical polypropylene. Journal of Environmental & Analytical Toxicology, 6, 1000373 (2016). https://doi.org/10.4172/2161-0525.1000373

- [21] Aslanzadeh S., Kish M. H.: Photo-oxidation of polypropylene fibers exposed to short wavelength UV radiations. Fibers and Polymers, **11**, 710–718 (2010). https://doi.org/10.1007/s12221-010-0710-8
- [22] Kauffman R. E., Wolf J. D.: Study of the degradation of typical HVAC materials, filters and components irradiated by UVC energy-Part II: Polymers. ASHRAE Transactions, **118**, 648–659 (2012).
- [23] Tocháček J.: Effect of secondary structure on physical behaviour and performance of hindered phenolic antioxidants in polypropylene. Polymer Degradation and Stability, 86, 385–389 (2004). https://doi.org/10.1016/j.polymdegradstab.2004.05.010
- [24] Allen N. S., Edge M.: Perspectives on additives for polymers. 1. Aspects of stabilization. Journal of Vinyl and Additive Technology, 27, 5–27 (2021). https://doi.org/10.1002/vnl.21807
- [25] Ohkatsu Y., Baba R., Watanabe K.: Radical scaveging mechanism of distearyl hydroxylamine antioxidant. Journal of the Japan Petroleum Institute, 54, 15–21 (2011). <u>https://doi.org/10.1627/jpi.54.15</u>
- [26] King R. E., Stadler U.: Impact of stabilization additives on the controlled degradation of poly(propylene). Angewandte Makromolekulare Chemie, 261–262, 189–204 (1998).

https://doi.org/10.1002/(sici)1522-9505(19981201)261-262:1 <189::aid-apmc189>3.0.co;2-x

- [27] King R. E.: Discoloration resistant polyolefin films. Journal of Plastic Film & Sheeting, 18, 179–211 (2002). https://doi.org/10.1177/8756087902018003004
- [28] Voigt W., Todesco R.: New approaches to the melt stabilization of polyolefins. Polymer Degradation and Stability, 77, 397–402 (2002). https://doi.org/10.1016/S0141-3910(02)00089-7
- [29] Tang R., Liggat J. J., Siew W. H.: Filler and additive effects on partial discharge degradation of PET films used in PV devices. Polymer Degradation and Stability, 150, 148–157 (2018).

https://doi.org/10.1016/j.polymdegradstab.2018.02.003

- [30] Diepens M., Gijsman P.: Photodegradation of bisphenol A polycarbonate with different types of stabilizers. Polymer Degradation and Stability, 95, 811–817 (2010). <u>https://doi.org/10.1016/j.polymdegradstab.2010.02.005</u>
- [31] Fechine G. J. M., Rabello M. S., Souto-Maior R. M.: The effect of ultraviolet stabilizers on the photodegradation of poly(ethylene terephthalate). Polymer Degradation and Stability, 75, 153-159 (2002). https://doi.org/10.1016/S0141-3910(01)00214-2
- [32] Fechine G. J. M., Christensen P. A., Egerton T. A., White J. R.: Evaluation of poly(ethylene terephthalate) photostabilisation using FTIR spectrometry of evolved carbon dioxide. Polymer Degradation and Stability, 94, 234–239 (2009).

https://doi.org/10.1016/j.polymdegradstab.2008.10.025

- [33] Girois S., Delprat P., Audouin L., Verdu J.: Oxidation thickness profiles during photooxidation of non-photostabilized polypropylene. Polymer Degradation and Stability, 56, 169–177 (1997). https://doi.org/10.1016/S0141-3910(96)00175-9
- [34] Gugumus F.: Possibilities and limits of synergism with light stabilizers in polyolefins 1. HALS in polyolefins. Polymer Degradation and Stability, 75, 295–308 (2002). <u>https://doi.org/10.1016/S0141-3910(01)00233-6</u>
- [35] Kurumada T., Ohsawa H., Yamazaki T.: Synergism of hindered amine light stabilizers and UV-absorbers. Polymer Degradation and Stability, 19, 263–272 (1987). <u>https://doi.org/10.1016/0141-3910(87)90059-0</u>
- [36] Shenoy M. A., Marathe Y. D.: Studies on synergistic effect of UV absorbers and hindered amine light stabilisers. Pigment and Resin Technology, 36, 83–89 (2007). https://doi.org/10.1108/03699420710733510
- [37] Alariqi S. A. S., Pratheep Kumar A., Rao B. S. M., Tevtia A. K., Singh R. P.: Stabilization of γ-sterilized biomedical polyolefins by synergistic mixtures of oligomeric stabilizers. Polymer Degradation and Stability, 91, 2451–2464 (2006).

https://doi.org/10.1016/j.polymdegradstab.2006.03.010

[38] Antunes M. C., Agnelli J. A. M., Babetto A. S., Bonse B. C., Bettini S. H. P.: Abiotic thermo-oxidative degradation of high density polyethylene: Effect of manganese stearate concentration. Polymer Degradation and Stability, **143**, 95–103 (2017).

https://doi.org/10.1016/j.polymdegradstab.2017.06.012

- [39] Philippart J-L., Sinturel C., Arnaud R., Gardette J-L.: Influence of the exposure parameters on the mechanism of photooxidation of polypropylene. Polymer Degradation and Stability, 64, 213–225 (1999). https://doi.org/10.1016/S0141-3910(98)00191-8
- [40] Fodor Z. S., Iring M., Tüdős F., Kelen T.: Determination of carbonyl-containing functional groups in oxidized polyethylene. Journal of Polymer Science, 22, 2539– 2550 (1984).

https://doi.org/10.1002/pol.1984.170221021

 [41] Grause G., Chien M-F., Inoue C.: Changes during the weathering of polyolefins. Polymer Degradation and Stability, 181, 109364 (2020).

https://doi.org/10.1016/j.polymdegradstab.2020.109364

- [42] Carlsson D. J., Wiles D. M.: The photodegradation of polypropylene films. III. Photolysis of polypropylene hydroperoxides. Macromolecules, 2, 597–606 (1969). <u>https://doi.org/10.1021/ma60012a007</u>
- [43] Carlsson D. J., Wiles D. M.: The photodegradation of polypropylene films. II. Photolysis of ketonic oxidation products. Macromolecules, 2, 587–597 (1969). https://doi.org/10.1021/ma60012a006
- [44] 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. Polymer Degradation and Stability, 98, 2383–2390 (2013). https://doi.org/10.1016/j.polymdegradstab.2013.07.017

- [45] Commereuc S., Vaillant C. D., Philippart J. L., Lacoste J., Lemaire J., Carlsson D. J.: Photo and thermal decomposition of iPP hydroperoxides. Polymer Degradation and Stability, 57, 175–182 (1997). https://doi.org/10.1016/S0141-3910(96)00183-8
- [46] Vaillant D., Lacoste J., Dauphin G.: The oxidation mechanism of polypropylene: Contribution of <sup>13</sup>C-NMR spectroscopy. Polymer Degradation and Stability, 45, 355–360 (1994). https://doi.org/10.1016/0141-3910(94)90205-4
- [47] Fernando S. S., Christensen P. A., Egerton T. A., White J. R.: Carbon dioxide evolution and carbonyl group development during photodegradation of polyethylene and polypropylene. Polymer Degradation and Stability, 92, 2163–2172 (2007).

https://doi.org/10.1016/j.polymdegradstab.2007.01.032

[48] Girois S., Audouin L., Verdu J., Delprat P., Marot G.: Molecular weight changes during the photooxidation of isotactic polypropylene. Polymer Degradation and Stability, 51, 125–132 (1996). https://doi.org/10.1016/0141-3910(95)00166-2

- [49] Yang Y., Hu C., Zhong H., Chen X., Chen R., Yam K. L.: Effects of ultraviolet (UV) on degradation of Irgafos 168 and migration of its degradation products from polypropylene films. Journal of Agricultural and Food Chemistry, 64, 7866–7873 (2016). https://doi.org/10.1021/acs.jafc.6b03018
- [50] Blázquez-Blázquez E., Cerrada M. L., Benavente R., Pérez E.: Identification of additives in polypropylene and their degradation under solar exposure studied by gas chromatography-mass spectrometry. ACS Omega, 5, 9055–9063 (2020). https://doi.org/10.1021/acsomega.9b03058
- [51] Ruvolo-Filho A., Pelozzi T. L. A.: Correlation between onset oxidation temperature (OOT) and Fourier transform infrared spectroscopy (FTIR) for monitoring the restabilization of recycled low-density polyethylene (LDPE). Polimeros, 23, 614–618 (2013). https://doi.org/10.4322/polimeros.2013.095
- [52] Djouani F., Richaud E., Fayolle B., Verdu J.: Modelling of thermal oxidation of phosphite stabilized polyethylene. Polymer Degradation and Stability, 96, 1349–1360 (2011).

https://doi.org/10.1016/j.polymdegradstab.2011.03.014