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Oxygen anomalous diffusion during photooxidation of polypropylene

José William de Lima Souza[1], Lucas Cordeiro de Oliveira[1], Taynah Pereira Galdino[1]*, Marcus Vinicius Lia Fook[1] and Rômulo Feitosa Navarro[1]*

[1]Laboratório de Avaliação e Desenvolvimento de Biomateriais do Nordeste, Unidade Acadêmica de Engenharia de Materiais – UAEMa, Universidade Federal de Campina Grande – UFCG, Campina Grande, PB, Brasil

**taynah.galdino@certbio.ufcg.edu.br; romulonavarro13@gmail.com*

Abstract

This research paper is about the calculation of the diffusion coefficient and the oxygen concentration profile along polypropylene samples exposed to photooxidation in a dry environment. In this degradation process, oxygen diffusion is anomalous, as it is affected by structural modifications that occur over the exposure time. Thus, the diffusion coefficient starts to depend on time and the common solutions for Fick's 2nd Law for diffusion become inoperative for importante time intervals. In this work, a modification is proposed in the calculation of the diffusivity and, consequently, of the solution for the oxygen concentration profile in diffusion.

Keywords: *anomalous diffusion, diffusion coefficient, oxygen diffusivity, photooxidation, time dependent.*

Data Availability: Research data is available upon request from the corresponding author.

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1. Introduction

In the process of photooxidation of polyolefins, the radiation source, atmospheric oxygen and temperature act together in the accelerated degradation of the exposed sample. The photodegradation of polypropylene in a dry environment involves the breakdown of the polymer chains due to exposure to ultraviolet (UV) radiation. PP absorbs UV radiation, which initiates the photodegradation process[1]. The absorbed UV energy causes the breaking of the polymer chains, leading to the formation of free radicals. These free radicals react with oxygen in the air, leading to the formation of oxidative products[2]. Over time, the oxidation process results in the formation of carbonyl groups (such as aldehydes and ketones) on the polymer chains[3]. The photodegradation process can also affect the crystalline structure of PP, leading to changes in its physical properties[1]. Some products are formed during photodegration of PP as those cited below:

- Carbonyl Compounds: the formation of carbonyl groups is a primary product of PP photodegradation[3];
- Volatile Organic Compounds (VOCs): small molecules such as alkenes and aldehydes can be released as volatile products[3];
- Microplastics: the breakdown of PP can result in the formation of microplastic particles, which are small plastic fragments[2];
- Gaseous Products: some degradation products can be in the form of gases, which can be released into the atmosphere[3].

Since the present work does not focus primarily on the photodegradation process of PP, but rather on the dependence of the oxygen diffusion coefficient on time and position, as well as its own concentration, the photodegradation process of PP will not be discussed in detail, for which we strongly recommend other papers in the literature[4].

Under constant temperature, irradiance and surface concentration, atmospheric oxygen, diffuses across the exposed surface in a process in which the concentration profile varies with time. In this case, diffusion obeys Fick's second law (Equation 1).

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \tag{1}$$

where C is the concentration, D is the diffusion coefficient, x the direction of diffusion and t is the time.

For the case where D is constant, Equation 1 becomes

$$\frac{dC}{dt}=D\left(\frac{d^2C}{dx^2}\right) \tag{2}$$

For semi-infinite solids immersed in a gaseous atmosphere with surface concentration, C, constant,

$$C(x,t)=C_S*\left[1-\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \tag{3}$$

$$C\left(x,t_{exp}\right)=C_s*\left[1-\mathrm{erf}\left(\frac{x}{2\sqrt{Dt_{exp}}}\right)\right] \tag{4}$$

with t_{exp} being the exposure time and measured after the formation of the first oxidation products, the so-called induction time, t_i. That is, Equation 4 is valid for $t_{exp} > t_i$.

Since oxygen diffusion during photooxidation may depend on structural changes during exposure time, the diffusion process may become anomalous due to a possible dependence of the diffusion coefficient on time. In this case, Equation 2 ceases to be valid as well as its particular solutions for all x and t. If $D = D(t)$, Costa et al.[5] and Navarro et al.[6] propose that

$$\frac{\partial C\left(x,t\right)}{\partial t}=D\left(t\right)\frac{\partial^2 C\left(x,t\right)}{\partial x^2} \tag{5}$$

Equation 5 can be solved by the method of fractional differential equations (FDE).

If $(t) = Kt^{-V}$, with $V \in \mathbb{R}$ and $K > 0$, the solution of (4) is:

$$C\left(x,t\right)=\frac{1}{2\sqrt{K\pi t}}\exp\left(-\frac{X^2}{4Kt}\right) \tag{6}$$

The fact that D decreases with time is due to some structural modification that hinders the diffusion process[5,7,8]. In this case, there is a simpler solution[9] in which

$$C\left(x,t\right)=C_s*\left[1-\mathrm{erf}\left(\frac{x}{2\sqrt{\frac{D_i}{1-n}t^{1-n}}}\right)\right] \tag{7}$$

Equation 7 is a variation of Equation 3 which takes into account the time-dependent D. D_i is the diffusivity at each time, t.

There are cases where D increases with time according to the relation $D = D_0 t^{\alpha}$, with D_0 being a reference diffusivity. According to Mangat and Molloy[7], Takewaka and Mastumoto[8] and Hirstov[9], in this case the FDE is also applied, as the case is similar to subdiffusion and super-diffusion in non-homogeneous porous media. However, the solution requires laborious numerical experiments since a simple analytical solution for Equation 5 is not possible.

During the photooxidation process of polypropylene, for instance, after a certain exposure time $t_{exp} \geq t_i$, the formation of carbonyl groups, CO, occurs from the reaction of diffused oxygen with free carbons. Other modifications also occur, as the crystallinity index, XC, increases. According to Rabello and White[4], the diffusion impedance factor, τ, increases with crystallinity, but at higher crystallinities it decreases, due to formation of defects in the crystallites with large thickness. The factor τ affects D according to[4]:

$$D=\frac{D}{\tau*\beta} \tag{8}$$

where D^* is the diffusion constant for a completely amorphous polymer, for completely amorphous PP, $D^*(300K) = 4.04$ x 10^{-10} m^2/s[4], and β is a chain immobilisation factor that increases with crystallinity. The estimate activation energy, Q, is taken as 32,000 J/mol and $D_0 = 8.3$ x 10^{-8} m^2/s[10], so, as $D(T) = D_0 e^{-Q/RT}$ that D(50°C) =5.5545 x 10^{-13} m^2/s.

Although only a fraction of the diffused oxygen reacts with carbon, with the remainder remaining distributed throughout the sample volume where diffusion occurred, the oxygen present in the CO molecule carried out the same diffusion process. In this work, the use of the carbonyl index, CI, which measures the intensity of the chemical degradation of the exposed sample, is used as prove of diffusion impedance modification with exposure time, as it changes during photooxidation.

2. Materials and Methods

The polymer used was an injection-moulded grade of isotatic polypropylene (Prolen KM 6100, manufactured by Polibrasil) with MFI 3.5 g/10 min. This is a general purpose grade used for injection moulding and does not contain additives to protect against ultravioleta radiation but we suppose it has termal stabilizers to avoid extensive degradation during processing. Test bars were produced with dimensions in accordance to ASTM D-638 standard using a MG 80/150 injection moulding machine operating at 180 °C (barrel temperature) and with na injection pressure of 32 MPa. The sample thickness was approximately 3 mm.

The exposures were carried out in a Comexim (C-UV type) weathering chamber using two fluorescent ultraviolet lamps. The chamber was programmed to operate at two cycles defined as follows: 4 h at 50°C with the UV lights on and absence of moisture. The ultraviolet source was lamps FS-40 UVB, produced by Phillips with intensity of 12.4 W/m2 in the same range of wavelength. The emission spectra for the lamps are given in[12].

The extent of chemical degradation was evaluated by the carbonyl index (CI), the most used parameter to estimate chemical degradation of polypropylene[6]. Samples were collected at a depth of 0.2 mm from the exposed surface using a custom-designed slicer developed by our team. The thickness of each slice was measured at 10 different positions along its length using a micrometer to ensure accuracy. The samples were then cold pressed and analysed in transmission mode using a NICOLET 360 FTIR Spectrophotometer, operating within therange of 400–4,000 cm^{-1} at resolution of 2 cm^{-1}. The spectra obtained are averages of 20 scans. The CI of the samples was determined from relative areas under the carbonyl peak (at ~1,600–1,800 cm^{-1}) and a reference peak (centred at 2,721 cm^{-1}). A typical FTIR-spectrum of an exposed polypropylene sample is given in Figure 1 showing the two peaks cited above.

The fractional crystallinity, XC, was calculated from X-ray diffractograms obtained from a D-5000 SIE- MENS diffractometer, in the range of 2h = 5–35°, operating at 40 kW and using the K$_\alpha$Cu radiation. Crystallinity was determined by averaging the values obtained from integrating the diffractogram curves of each of the five samples at each exposure time, following the method described by[6].

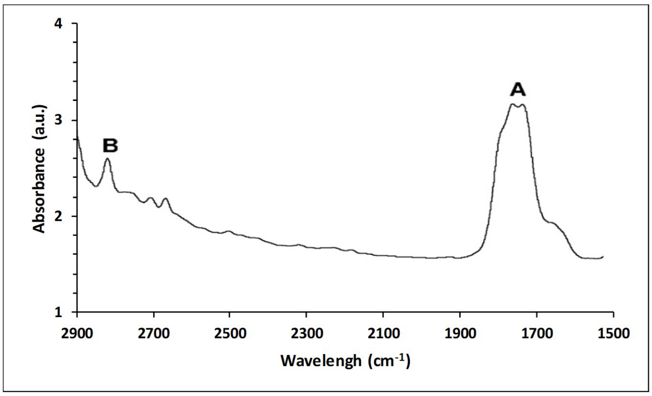

Figure 1. Part of a FTIR spectrum of a PP sample exposed to UVB for 1,584 h at 50 °C. A and B are, respectively, the carbonyl and the reference peaks[6].

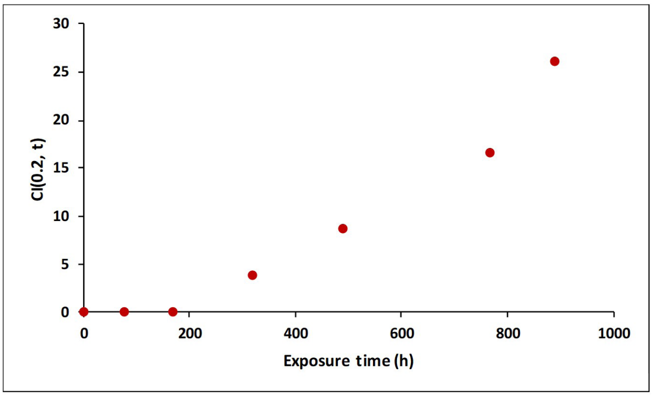

Figure 2. Oxygen concentration profile, based on carbonyl index, (CI), at 0.2mm depth of the exposed PP sample.

3. Results and Discussions

For $x \rightarrow 0$ and $t \rightarrow \infty$, the local concentration is practically constant and approaches CS. In this case, one can use Equation 3 to estimate the local oxygen concentration.

Figure 2 shows the values of $(0.2, t)$ over the exposure time, taking D=5.5545x10^{-13}m^2/s. Although the values are around an average value of 10.476, the shape of the curve indicates growth according to a power law. This indicates that there is an increase in the facility for the diffusion process, that is, a decrease in the impedance factor for diffusion, τ, which is expected given the increase in crystallinity in the same time interval, as shown in Figure 3.

In Figure 4, the data for $C(0.2, t)$ are plotted. The $C(0.2, t)$ behaviour indicates an increase in the reacted oxygen content with the exposure time. Even though if the carbonyl index is contested as an indication of the degree of degradation of polypropylene exposed to photooxidation[6], it indicates the amount of diffused oxygen that reacted with the carbon, and its variation with time also indicates how the diffusion impedance factor, τ, varied with exposure time.

According to[13], crystallinity could have little effect on diffusion, since this mass transport predominantly occurs in the amorphous phase of the material. This may be true if comparing two unexposed samples with different degrees of crystallinity. However, during the photooxidation process of polypropylene, there is an increase in crystallinity (see Figure 3), which implies that fewer amorphous regions are available for oxygen diffusion. Thus, the accumulation predicted by Fick's 2nd Law becomes greater between layers along the thickness of the exposed polypropylene and, therefore, will hinder the diffusion process. So it is possible to correlate $C(x, t)$ with the τ factor as $CI{\sim}\tau{-}1$, since the impedance decreases with increasing crystallinity for $XC > 50\%$[6]. On the other hand, $\beta{\sim}X$. Thus, it is proposed that, for $XC > 50\%$, as XC increases with exposure time, the product $\tau * \beta$ will also increase with exposure time, since D decreases with exposure time (see Figure 5) due to structural modification at PP exposed samples. So the Equation 8 may be modified to take the following form:

$$D(x,t) = \frac{D^*}{X_C} \tag{9}$$

and $D(x, t)$ will decrease with the exposure time. In Figure 5, is shown the sharp drop in diffusivity with exposure time.

Introducing Equation 9 in Equation 4 we get:

$$C(x,t) = C_S * \left[1 - erf\left(\frac{x}{2\sqrt{\frac{D^*}{\overset{\text{ÿ}}{X}_c}t}}\right)\right] \tag{10}$$

In Figure 6, the values for the concentration profile at 0.2 mm depth obtained by Equation 4 and by Equation

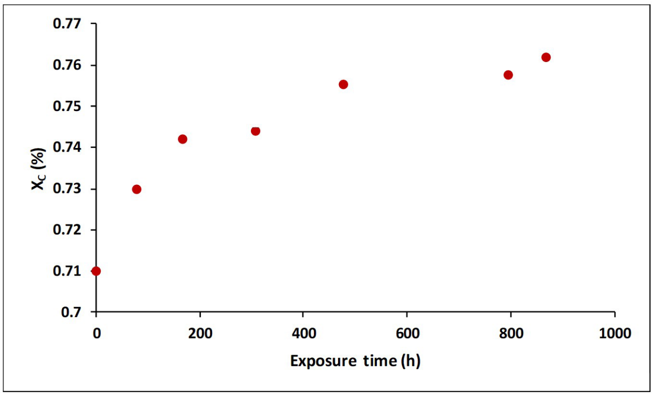

Figure 3. Crystallinity degree of the collected samples (0.2 mm thick) from the exposed PP samples with exposure time.

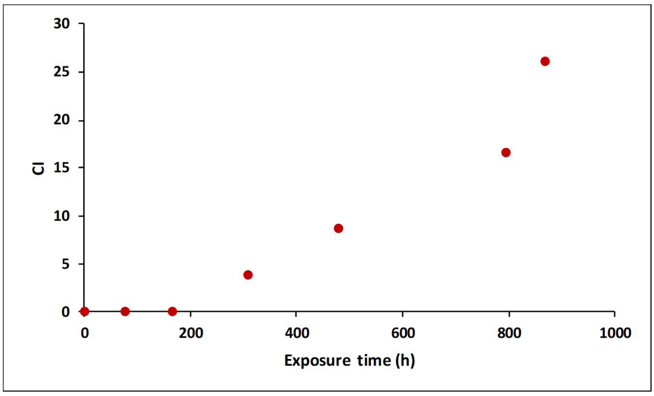

Figure 4. Carbonyl Index (CI) of the collected samples (0.2 mm thick) from the exposed PP samples.

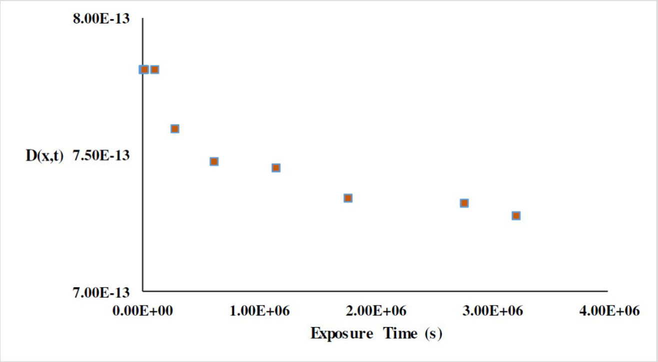

Figure 5. Decreasing of diffusivity of the collected samples (0.2 mm thick) from the PP exposed samples with exposure time.

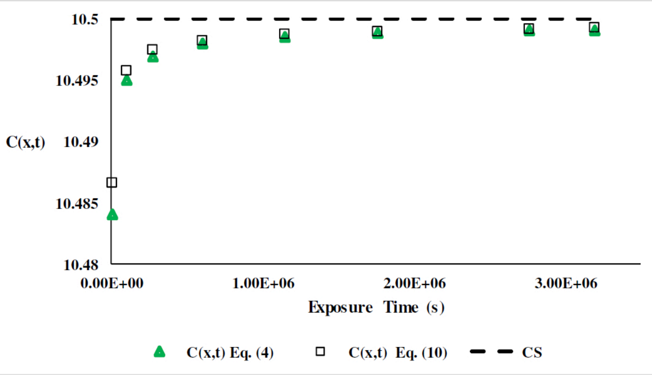

Figure 6. $C(x, t)$ calculed by Equations 4 and 12 versus theoretical value CS for PP exposed samples.

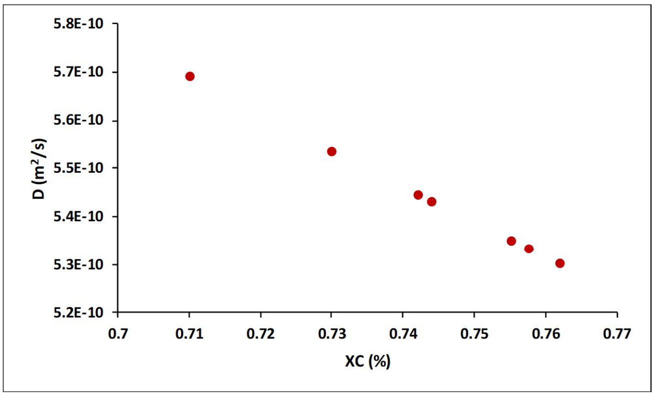

Figure 7. Variation of the diffusion coefficient (calculed by Equation 8) with the crystallinity index measured at 0.2mm from the exposed surface of polypropylene samples.

10 are presented versus CS value. For very thin layers, is expected that $\forall t > ti$, $(x, t) \rightarrow CS$. Although the values obtained by Equation 4 are very close to CS, even after 37h there was still no convergence to this value. On the other hand, Equation 10 produces data that very quickly converge to CS, showing the importance of crystallinity on the diffusion coefficient as can be seen in Figure 7. The data shown in Figure 7 is in agreement with Mucha[12], since the oxidation rate is inversely proportional to the degree of crystallinity, as oxygen attacks only the amorphous fractions of semicrystalline polymers.

4. Conclusions

The variation in carbonyl index and crystallinity of polypropylene samples exposed to accelerated degradation by photooxidation in a dry environment at 50°C prove that the process of oxygen diffusion during photooxidation is na anomalous process. This process imposes a timeand position-dependent diffusion coefficient, (x, t). This prevents the use of simple solutions to Fick's 2nd Law for diffusion, requiring the use of fractional differential equations to obtain analytical solutions for (x, t), when diffusivity decreases with time. However, these solutions imply a large number of variables to be statistically obtained. In the present work, an equation for the calculation of diffusivity as a function of the degree of crystallinity was proposed and its substitution in the solution for Fick's 2nd Law for diffusion in a semi-infinite solid. The results obtained showed excellent equivalence with the theoretically predicted values for the oxygen concentration profile during photooxidation of layers of exposed polypropylene samples with thickness of $2x10^{-4}$ m. Discussions on the influence of surface microcracks on oxygen permeation and diffusion during photooxidation should be made in future papers.

5. Author's Contribution

- **Conceptualization** – Rômulo Feitosa Navarro.
- **Data curation** – Rômulo Feitosa Navarro; José William de Lima Souza Oliveira; Lucas Cordeiro de Oliveira; Taynah Pereira Galdino; Marcus Vinicius Lia Fook.
- **Formal analysis** – Rômulo Feitosa Navarro; José William de Lima Souza Oliveira; Lucas Cordeiro de Oliveira; Taynah Pereira Galdino; Marcus Vinicius Lia Fook.
- **Funding acquisition** – NA.
- **Investigation** – Rômulo Feitosa Navarro; José William de Lima Souza Oliveira; Lucas Cordeiro de Oliveira; Taynah Pereira Galdino; Marcus Vinicius Lia Fook.
- **Methodology** – Rômulo Feitosa Navarro.
- **Project administration** – Rômulo Feitosa Navarro; Marcus Vinicius Lia Fook.
- **Resources** – Rômulo Feitosa Navarro; José William de Lima Souza Oliveira; Lucas Cordeiro de Oliveira; Taynah Pereira Galdino; Marcus Vinicius Lia Fook.
- **Software** – José William de Lima Souza Oliveira; Lucas Cordeiro de Oliveira; Taynah Pereira Galdino.
- **Supervision** – Rômulo Feitosa Navarro; Marcus Vinicius Lia Fook.
- **Validation** – Rômulo Feitosa Navarro; Marcus Vinicius Lia Fook.
- **Visualization** – Rômulo Feitosa Navarro; José William de Lima Souza Oliveira; Lucas Cordeiro de Oliveira; Taynah Pereira Galdino; Marcus Vinicius Lia Fook.
- **Writing - original draft** – Rômulo Feitosa Navarro; José William de Lima Souza Oliveira; Lucas Cordeiro de Oliveira; Taynah Pereira Galdino.
- **Writing – review & editing**– Rômulo Feitosa Navarro; José William de Lima Souza Oliveira; Lucas Cordeiro de Oliveira; Taynah Pereira Galdino.

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7. References

1. Rajakumar, K., Sarasvathy, V., Chelvan, A. T., Chitra, R., & Vijayakumar, C. T. (2009). Natural weathering studies of

polypropylene. *Journal of Polymers and the Environment*, *17*(3), 191-202. http://doi.org/10.1007/s10924-009-0138-7.

2. Ibrahim, A. M. (2024). *Plastics: photodegradations and mechanisms*. In V. Sivasankar & T. G. Sunitha (Eds.), Microplastics and pollutants (pp. 25-49). Cham: Springer. http://doi.org/10.1007/978-3-031-54565-8_2.
3. Liu, X., & Yang, R. (2020). Conversion among photo-oxidative products of polypropylene in solid, liquid and gaseous states. *BMC Chemistry*, *14*(1), 44. http://doi.org/10.1186/s13065-020-00698-y. PMid:32696017.
4. Rabello, M. S., & White, J. R. (1997). The role of physical structure and morphology in the photodegradation behaviour of polypropylene. *Polymer Degradation & Stability*, *56*(1), 55-73. http://doi.org/10.1016/S0141-3910(96)00202-9.
5. Costa, F. S., Oliveira, E. C., & Plata, A. R. G. (2021). Fractional diffusion with time-dependent diffusion coefficient. *Reports on Mathematical Physics*, *87*(1), 59-79. http://doi.org/10.1016/S0034-4877(21)00011-2.
6. Navarro, R. F., d'Almeida, J. R. M., & Rabello, M. S. (2007). Elastic properties of degraded polypropylene. *Journal of Materials Science*, *42*(6), 2167-2174. http://doi.org/10.1007/s10853-006-1387-7.
7. Mangat, P. S., & Molloy, B. T. (1994). Prediction of long term chloride concentration in concrete. *Materials and Structures*, *27*(6), 338-346. http://doi.org/10.1007/BF02473426.
8. Takewaka, K., & Mastumoto, S. (1988). Quality and cover thickness of concrete based on the estimation of chloride penetration in marine environments. *ACI Symposium Publication*, *109*, 381-400. http://doi.org/10.14359/2124.
9. Hristov, J. (2017). Subdiffusion model with time-dependent diffusion coefficient: integral-balance solution and analysis. *Thermal Science*, *21*(1), 69-80. http://doi.org/10.2298/TSCI160427247H.
10. Müller-Plathe, F. (1992). Molecular dynamics simulation of gas transport in amorphous polypropylene. *The Journal of Chemical Physics*, *96*(4), 3200-3205. http://doi.org/10.1063/1.461963.
12. Mucha, M. (1986). Oxygen uptake by isotactic polypropylene of different morphological structure. *Colloid & Polymer Science*, *264*(2), 113-116. http://doi.org/10.1007/BF01414835.
13. Rouillon, C., Bussiere, P.-O., Desnoux, E., Collin, S., Vial, C., Therias, S., & Gardette, J.-L. (2016). Is carbonyl index a quantitative probe to monitor polypropylene photodegradation? *Polymer Degradation & Stability*, *128*, 200-208. http://doi.org/10.1016/j.polymdegradstab.2015.12.011.

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