

TALLER CIENTÍFICO: DURABILIDAD DE MATERIALES FRENTE AL CAMBIO CLIMÁTICO

Comparison between natural and artificial ageing of polypropylene: main impact factors

Presentación Oral

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1. INTRODUCCIÓN (MAYÚSCULA TIMES NEW ROMAN NEGRITA TAMAÑO 12 PTS).

Polyolefins and mainly polypropylene are the most common polymers encountered in industrial life and therefore have a high contribution at the end of the life time on environmental pollution. As a consequence, the understanding and the prediction the durability of these materials are important for sustainable development. Polypropylene (PP) is subjected to oxidative mechanisms under natural exposure conditions which induces a decrease of the mechanical properties leading to a premature rupture of the material. Oxidation of polypropylene have been investigated for decade [1-3] and one of the most common characterization techniques to follow the kinetic oxidation is infrared spectroscopy [4-6]. In this case, a particular attention is made to the evolution of the C=O carbonyl groups with the absorption band between 1700 cm⁻¹ and 1800 cm⁻¹. It is commonly accepted that oxidation is initiated by ultraviolet radiations, but despite the numerous papers published in literature trying to understand the mechanisms of oxidation of PP, the role of photo and thermo oxidations remains unclear [7,8].

In this work, oxidation kinetic of PP was studied using infrared spectroscopy. The PP samples were subjected to different artificial ageing conditions and the results were compare to those obtained under

natural ageing. To ensure that the oxidation mechanisms are identical regardless of the ageing protocols, the mains groups constituting the broad carbonyl bands were identified using a deconvolution technic. It is assumed that identical group distribution leads to the same oxidation mechanisms.

2. METODOLOGÍA

The polypropylene samples from ??? were without any additive in order to ensure a quick sample degradation. The samples were parallelepiped in shape with the following dimensions 10cmx5cmx0,2cm.

The samples were artificially aged under different conditions with temperatures ranging from 60°C to 80°C and UV irradiance ranging between 95 Wm⁻² to 320 Wm⁻² using a medium pressure mercury lamp. (see table 1).

Natural ageing was performed on 3 different sites located in Guadeloupe (a Caribbean Island) equipped with captors allowing the measurements of the main meteorological parameters such as temperature, global irradiation, humidity, amount of rain... Natural ageing results were similar, therefore only the one from Saint-Francois (SF) area will be presented.

The chemical degradation of the sample was studied by mean of infrared spectroscopy using a Perkin Elmer spectrum two spectrometer. The measurements were performed in the transmission

mode with a wave number ranging from 500 cm^{-1} to 4000 cm^{-1} . The intensity of the carbonyl band and its deconvolution into the main characteristic groups was performed using OriginPro 2020 from OriginLab analysis software. The oxidation kinetic is tracked measuring the carbonyl index, I_{ox} (group index I_g) defined as the area of the carbonyl band (groups) divided by the sample thickness.

Table 1: Conditions corresponding to the artificial ageing conditions

Protocol	Temperature ($^{\circ}\text{C}$)	Irradiance ($\text{W}\cdot\text{m}^{-2}$)
H60	60	95
H80	80	320
UAW	80	320

3. RESULTADOS

A typical histogram showing the kinetic oxidation obtained for H60 protocol for 200h and 300h of exposure is shown in figure 1a.

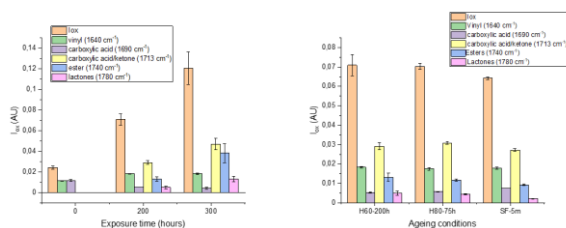


Figure 1: I_{ox} and group histogram for a) different exposure time under H60 protocol, b) different ageing conditions at the fixed I_{ox} value of about 0,07.

The carbonyl index as well as the group indexes (vinyl, acid carboxylic, ketones, esters, lactones) are presented. The relative distributions of the different groups evolved as a function of ageing time as already reported in literature [8,9]. In the early stage of ageing (I_{ox} close to 0,07 UA) the main oxidation products are carboxylic acid and ketones (1713 cm^{-1}) whereas the ester group increases for higher exposure time.

Figure 1b, reported the group distribution for different artificial (H60-200h, H80-75h) and natural (SF-5m) ageing condition for a similar oxidation index close to 0,07 UA. Regardless of the ageing condition, for the same level of oxidation, there is a strong similarity between the distribution of the different groups indicating that the oxidation mechanisms are similar for the various ageing conditions.

As indicated in figure 1b, an oxidation index of 0,07 is obtained after 200h for an exposure temperature

of 60 $^{\circ}\text{C}$ whereas only 75h of exposure is required at 80 $^{\circ}\text{C}$: increasing the temperature of 20 $^{\circ}\text{C}$ leads to a significant acceleration factor close to 2.6. Increasing the irradiance level to 320 $\text{W}\cdot\text{m}^{-2}$ with a temperature of 80 $^{\circ}\text{C}$ does not change the oxidation kinetic (not shown in the figure). This result clearly indicates that for polypropylene, the temperature is the main parameter controlling the oxidation mechanisms.

According to figure 1b, 5 months natural exposure time is required to reach an I_{ox} of 0,07 compare to 200h or 75h for artificial conditions at temperature of 60 $^{\circ}\text{C}$ or 80 $^{\circ}\text{C}$ respectively. As a consequence, H80 protocol leads to a high value of the accelerating factor close to 50 (26 for H60 protocol).

4. CONCLUSIONES

In this work, different artificial ageing protocols have been tested to predict the durability of polypropylene samples. It was shown that the artificial protocols used were compatible with the natural one since the distribution of the by-products of oxidation is the same in both cases. Thermo oxidation process appears to be the mean parameter in the degradation mechanisms of polypropylene. One of the artificial protocols used leads to accelerated factor close to 50 which is high compare to the classical protocol.

5. REFERENCIAS

- [1] I. Audoin, S. Girois, L. Achimsky and J. Verdu, *Polymer degradation and Stability*, **60**, 137 (1998)
- [2] L.M. Rincon-Rubio, B. Fayolle, L. Audouin and J. Verdu, *Polymers degradation and Stability*, **74**, 177 (2001)
- [3] A. François-Heude, E. Richaud, E. Desnoux and X. Colin, *Polymer Degradation and stability*, **100**, 10 (2014)
- [4] Y. Zhou, B. Li and P. Zhang, *Applied Spectroscopy*, **66**, 566 (2012)
- [5] C. Billotte, L. Romana, A. Flory, S. Kaliaguine and E. Ruiz, *Polymers Composite*, 28585 (2024)
- [6] T. Pertin, G. Minatchy, M. Adoue, A. Flory and L. Romana, *Polymer testing*, **81**, 106194 (2020)
- [7] T. Pertin, G. Minatchy, M. Adoue, A. Flory and L. Romana, *Polymer testing*, **81**, 106194 (2020)
- [8] T. Pertin, G. Minatchy, M. Adoue, A. Flory and L. Romana, *Polymer testing*, **81**, 106194 (2020)