



## THERMAL AGING AND ACCELERATED WEATHERING OF HMSPP: STRUCTURAL AND MORPHOLOGICAL STUDIES

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**Abstract** - This work focuses of the influence of weathering factors – UV radiation, humidity, and temperature on the structure and morphology polypropylene with high melt strength (HMSPP), also called polypropylene modified by irradiation. The HMSPP was prepared from iPP (isotactic polypropylene) in presence of acetylene at 110 kPa pressure and irradiated with  $\gamma$  of  $^{60}\text{Co}$  at doses of 5, 12.5 and 20 kGy. It has been observed that HMSPP deteriorates the weathering resistance, the thermal behavior and the long-term stability of HMSPP, beyond substantial color changes. The samples aged were characterized by infrared spectroscopy (FTIR), optical microscopy (OM) and differential scanning calorimetry (DSC). The optical microscopy images on the surface show that thermal aging and artificial weathering proceed by different mechanisms. The effects of elevated temperature aging were evaluated in HMSPPs exposed surface according to the order: HMSPP 20 > 12.5 > 5 kGy > iPP, showing intense crack formation in surface exposed due to thermooxidative degradation.

**Keywords:** *polypropylene; HMSPP; weathering; irradiation; acetylene*

### Introduction

Polypropylene (PP) has achieved a dominating position and hence, their consumption increases thereby littering, which lead to environmental pollution. Photodegradation seems to be a better choice because of naturally available sunlight as energy source for degradation [1].

Semi-crystalline isotactic polypropylene (iPP) has been extensively used in the daily life due to its high performance and wide applicability. As a consequence, various processing technologies such as injection, extrusion, spinning, compression, and blow have been employed for iPP based products [2].

Polypropylene irradiated with gamma-rays undergoes chain scission [3] and crosslink [4]. Alternatively it can be postulated that in the branching of polymer both crosslinking and main chain degradation occur simultaneously and the chain scission process requires a higher overall activation energy than crosslinking [4,5].

Besides heat and atmospheric oxygen, it is especially the UV portion of incident solar radiation that initiates chemical reactions, leading to irreversible changes in the polymer backbone. Despite that part of solar radiation is filtered by the atmosphere, its portion of 290–400 nm wavelength intervals, representing the UV-B and UV-A ranges, is critical for many hydrocarbon polymers. Activation spectra of polyethylene exhibiting maxima at 300–310 and 340 nm, polypropylene at 300, 330 and 370 nm fit into this interval very well [6]. The critical portion of UV radiation causes photo initiation of polymer due to the absorption of chromophores present in the matrix (hydroperoxides, catalyst residues, carbonyls, unsaturations) [7]. Excited chromophores then induce photooxidative decomposition of macromolecular chains, consequently leading to the basic changes in behaviour of the polymer and its properties. Due to the photo induced processes, the polymer usually first changes its appearance (surface gloss, colour) followed later by changes in mechanical properties (strength, strain, flexibility) [8].

Given the complexity of the phenomena involved, this purpose seeks to identify the main oxidation path. The hydroperoxides are at once the main propagation products and the species responsible for

the oxidation initiation by either thermolysis (in pure thermal oxidation) or photolysis (in photooxidation). The sequence of chemical reactions is schematized in Fig.1 in the general case of iPP photo thermal oxidation [9].

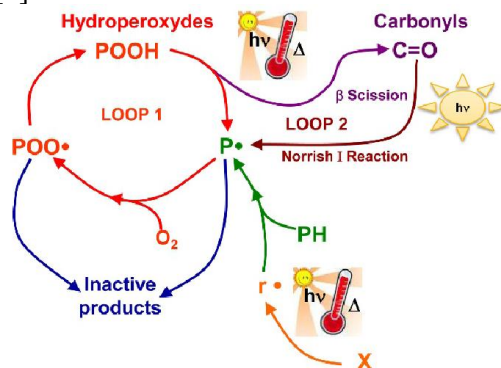


Figure 1: Photo thermal oxidation scheme [9]

This closed-loop character enables the accurate description of the auto accelerated behaviour of oxidation. Its monitoring is based on carbonyl species as secondary oxidation products [9]. The aim of this work is to study the effects of accelerated aging using oven and UV chamber, to polypropylene and polypropylene modified by irradiation.

## Experimental

### Materials and Methods

#### Materials

The HMS-PP samples were obtained from iPP pellets (MFI = 1.5 dg min<sup>-1</sup>) from Braskem - Brazil.

#### Methods

The iPP pellets were conditioned into nylon bags in which were fluxed with nitrogen in order to reduce as much as possible the internal oxygen concentration. The bags were submitted to the irradiation process in a <sup>60</sup>Co γ-source, at a dose rate of 5 kGy h<sup>-1</sup> monitored with Harwell Red Perspex 4034, with dose levels ranging from 5, 12.5 up to 20 kGy in presence of acetylene. After irradiation, the samples were heat treated at 90 °C for 1 hour with the aim of promoting recombination and termination reactions and also eliminate residual radicals [10].

The investigation was conducted with the following samples of polypropylene. (See Table 1).

Table 1 - MFI of samples of polypropylene pellets

Samples / pellets	Melt Flow Index / MFI = dg min <sup>-1</sup>
1 - iPP	1.5
2 - HMSPP 5 kGy	1.8
2 - HMSPP 12.5 kGy	2.2
3 - HMSPP 20 kGy	3.3

The dumbbell samples were prepared by thermopressing mold under pressure at a temperature of 190°C. After preparation of the samples, they were cooled to room temperature water tank (25 °C), favoring the amorphous phase.

#### Thermal aging

The dumbbell samples were fixed in the internal support of the oven, Fig. 2.



Figure 2 - Internal view of the oven with test samples.

Thermal aging of polypropylene was performed in laboratory oven at  $120\text{ }^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$  in air atmosphere.

#### *Accelerated aging in chamber (Artificial aging)*

Was used Comexim chamber (C-UV type), Fig. 3. The dumbbell samples were taken in stainless steel support with exposed face to the inside of the chamber, exposed to UV light action, heat and humidity. The test conditions were 8 hours under UV light at  $50\text{ }^{\circ}\text{C}$  and 4 hours in condensing humidity at  $40\text{ }^{\circ}\text{C}$ .

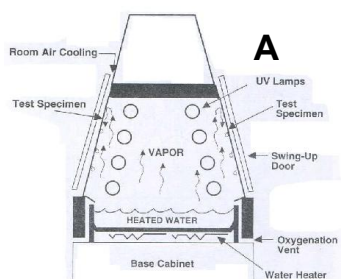


Figure 3 - Illustration (A) representing the accelerated weathering test (part with UV light and condensation) [11] and (B) Comexim external view of the chamber (C-type UV), where the accelerated aging tests were performed. *Courtesy of Prof. Rabello - UFCG/PB.*

Laboratory testing involves using environmental chambers and artificial light sources to approximately replicate outdoor conditions with a greatly reduced test time under highly controlled conditions [12]. Laboratory testing can quickly assess the relative stability of plastics, but are extremely useful to gain time before programming a natural aging [13].

#### *Infrared spectroscopy (FTIR)*

Specimens were examined using a Thermo Nicolet 6700 FTIR spectrometer with a Smart Orbit accessory, i.e. a horizontal attenuated total reflectance (ATR) accessory (single reflection) with a diamond crystal, in the wavelength range  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ . Each FTIR spectrum presented is based on a recording of 64 scans. In order to ensure satisfactory contact between the ATR diamond crystal and the sample, three or more FTIR spectra were recorded at various locations on the sample.

#### *Optical microscopy*

To view the details of the morphology of the polymer was used optical microscopes, equipment brand Olympus BX 51 and PM E3 model with polarized light.

#### *Differential scanning calorimetry (DSC)*

Thermal properties of specimens were analyzed using a differential scanning calorimeter DSC 822, Mettler Toledo. The thermal behavior of samples was obtained by (1) heating from 25 to 280 °C at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere; (2) holding for 5 min at 280 °C and (3) then cooling to 25 °C and reheating to 280 °C at 10 °C min<sup>-1</sup>. Melting enthalpy value for 100 % crystalline PP is 209 kJ kg<sup>-1</sup> [14, 15].

## Results and Discussion

### *Infrared spectroscopy*

The thermal aging of iPP and HMSPPs results in the formation of carbonyl groups in the region of 1640-1800 cm<sup>-1</sup> in the FTIR spectra. The exposed surface of PP specimens during thermal aging, are mainly focused on the insert shown in Fig.4.

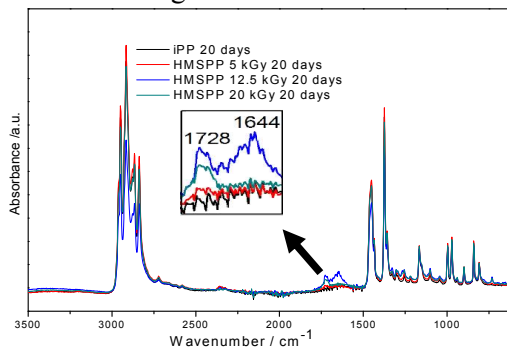


Figure 4 – Absorbance FTIR spectra of polypropylene: (A) iPP, (B) HMSPP 5 kGy, (C) HMSPP 12.5 kGy and (D) HMSPP 20 kGy, with 20 days of thermal aging.

The band attributed to stretching of the carbonylic group C=O, appears in the IR spectrum as an intense band, at around 1728 cm<sup>-1</sup> for HMSPP samples 12.5 and 20 kGy.

### *Optical microscopy*

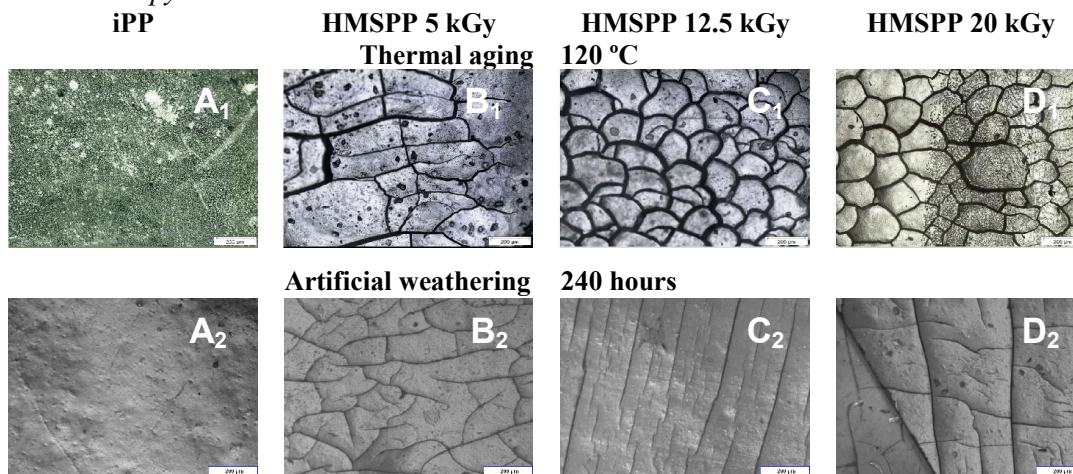


Figure 5 – Microphotographs on surface of iPP and HMSPPs.

Comparing with the previous work, where the temperature of test was of 90°C [16], it was observed at 120 °C, more pronounced effect of thermooxidative degradation on irradiated PP, Fig.5. Besides, the formation of cracks increases the porosity of material and thus opens the HMSPP structure to a more extensive diffusion of oxygen. It is observed in the artificial weathering (240 hours) that similar fact occurs for the irradiated samples, i.e. cracks on the surface of the polymers.

### Differential scanning calorimetry

Table 2 - Melting temperatures and crystallinity of polypropylene: iPP; HMSPPs 5 kGy, 12.5 kGy and 20 kGy, with 20 days of thermal aging.

Samples	$T_{m2}/^{\circ}\text{C}$	$T_{m2}/^{\circ}\text{C}$	$X_c/\%$	$X_c/\%$
	zero	20 days	zero	20 days
iPP	166	164	49	53
HMSPP 5kGy	163	162	46	53
HMSPP12.5kGy	161	141	51	48
HMSPP 20kGy	162	143	45	49

HMSPP 12.5 kGy presented melting temperature displacement of  $\Delta T_{m2} = 20^{\circ}\text{C}$  while  $\Delta T_{m2} = 19^{\circ}\text{C}$  for HMSPP 20 kGy. The results indicated morphology modifications of the samples crystalline phase. Melting temperature decreases as chain scission occurs the main mechanism of degradation. Contraction of the surface layers, resulting in surface cracks, is a consequence of chemicrystallization, similar results in [16]. The DSC of the artificial weathering test samples showed no significant changes.

### Conclusion

The effect of the acceleration of the thermooxidative degradation in the irradiated polypropylene was more evident in the order, HMSPP 20 > 12.5 > 5 kGy > iPP, showing intense crack formation in the exposed surfaces. Besides the formation of cracks increasing porosity of material and thus opens the HMSPP structure to a more extensive diffusion of oxygen. The same situation occurred for artificial weathering testing of irradiated samples, in which the cracks were less intense than thermal aged samples.

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