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# STUDY OF THE WEATHERING OF HIGH MELT STRENGTH POLYPROPYLENE (HMS-PP)

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## ABSTRACT

One of the reasons for the good acceptance of the commercial PP is the fact that market requires products with features of “engineering plastics” with prices in the range of commodities. High melt strength polypropylene (HMSPP) grades are produced by radiation process and have improved rheology for melt blow processes. The melt strength (MS) properties of a polymer increase with molecular weight and with long chain branching due to the increase in the entanglement level. The main scope of this study was to evaluate the stability of HMS-PP prepared by gamma radiation with doses of 12.5, 20 kGy in comparison with virgin PP. Many variables influence the rate of degradation of polymers by photo-oxidation. The irradiance and permeability to oxygen are the most important factors but other factors such as temperature and moisture have also influenced the degradation rates. Polypropylenes are sensitive to oxidation due to the presence of the tertiary carbon atom. Therefore, effective stabilization against oxidation (thermo and photo oxidation) is required. The samples submitted to the natural aging for a period of six months were characterized by: tensile test, thermogravimetry analysis (TGA), optical microscopy, scanning electronic microscopy (SEM) and infrared spectroscopy (FTIR). SEM analysis showed particular aspects of cracks on the surface. The loss of tensile strength is associated to the presence of fractures. The results showed that pronounced oxidation followed by chain scission occur at the initial periods of weathering exposition of the HMS-PP.

## 1. INTRODUCTION

Polyolefin photodegradation is initiated by solar radiation, which results in the absorption of UV radiation by chromophores and in the activation of excited states in macromolecules. However, other climatic factors such as heat, moisture and airborne pollution influence the mechanisms of degradation and the subsequent results of ageing [1].

When a polymer is exposed to solar radiation the energy absorbed by the polymer results in formation of free radicals within the polymer by the dissociation of the C-H bonds in the polymer chains. Once free radicals have been produced, reaction with oxygen generates hydroperoxides (POOH) [1]. These hydroperoxides can dissociate further to produce a series of decomposition products including aldehydes and ketones. The presence of these carbonyl groups in a degraded polymer can be used as a chemical index for degradation [1].

The intensity of the UV radiation decreases with depth in the material, so that the reaction tends to be a surface process. Since oxygen is involved in the diffusion, and of course temperature that will also determine the kinetics of reaction and the transport of reactive species [1, 2].

Almost all materials are subject to the action of oxygen and by water under usual working conditions [2]. Environmental degradation is due to a combination of factors, such as: photo-oxidation, thermo-oxidation, humidity changes, erosion, chemical action due to pollutants and micro-and macro-organisms. Combination of these factors is usually cumulative [3] and can conduct to product failure in a short period of time.

The changes of iPP and HMS-PP and polyolefins in general can be monitored during ageing, e.g. by the observation of typical carbonyl groups of compounds in the region of 1640-1740 $cm^{-1}$in FTIR spectra [3].

Morphology and crystallinity changes, melting temperature ($T_m$), glass transition temperature ($T_g$) values are also helpful in properly describing the changes in the long-term properties. The investigation of surface morphology and fracture of the sample is usually performed by scanning electron microscopy (SEM) [3].

When radiation excites or ionizes the atoms or sub-units of polymeric materials the two principle effects are chain scission and crosslinking. Chain scission on its own, causing random rupture of the bonds that link the monomeric sub-units of the macromolecule, reduces chain length and leads to gas evolution and unsaturation [4].

In this work was evaluated the stability of HMS-PP spheres obtained by radiation process.

## 2. EXPERIMENTAL

### 2.1. Materials and samples

The investigation was conducted with the following polypropylenes:

- iPP (spheres), with melt flow index (MFI) of 1.5 g . 10 $min^{-1}$ , not stabilized.
- HMS-PP obtained at the dose 12.5 kGy with MFI = 2.2 g . 10 $min^{-1}$, not stabilized.
- HMS-PP obtained at the dose of 20 kGy with MFI = 3.3 g . 10 $min^{-1}$, not stabilized.

The HMS-PP samples were obtained by irradiating with gamma rays in the presence of acetylene at 12.5 and 20 kGy of total dose.

The samples were manufactured by mold pressure at temperature of 190 °C according to type IV of ASTM D 638-03, [5].

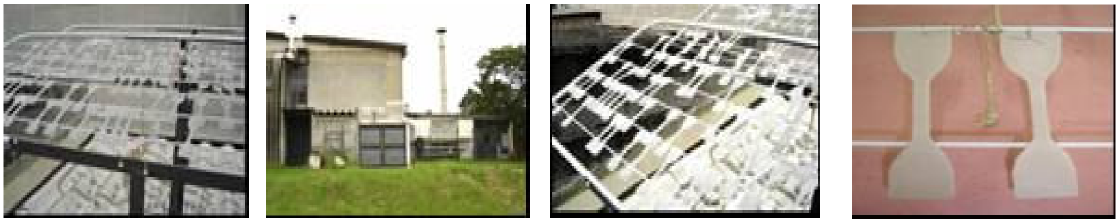


**Figure 1.** Samples settled in a device for natural ageing assay in the IPEN-CQMA department.

The disposal of the samples for natural exposition were placed 45° north, according to ASTM D 1435-05 - Standard Practice for Outdoor Weathering of Plastics [6]. Geographic Position: Latitude (23° 33` South); Longitude (46° 44` West) and Altitude (750 meters).

## 2.2. Characterization

### 2.2.1.Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) was recorded with a Mettler-Toledo TGA / SDTA 851 thermobalance, under oxygen atmosphere of 50 mL.min$^{-1}$, in the range of 25 up to 700 °C at a heating rate of 10 °C min$^{-1}$. Samples at about 10 mg were placed in alumine pans.

### 2.2.2. Infrared Spectroscopy (FTIR*)*

The analyses were performed using attenuation total reflectance accessory (ATR) by a Thermo-Nicolet spectrophotometer, model 0074-150, MID-FTIR 100.

### 2.2.3. Optical microscopy

Light microscopy (LM) OLYMPUS VANOX AHMT3 was used to observe the exposed surface of naturally aged samples at magnification of 125 times.

### 2.2.4. Scanning Electronic Microscopy (SEM)

Scanning electronic microscopy (SEM) was done using an EDAX PHILIPS XL 30. To observe the fracture surface, magnification at 1000 times was employed on the fracture region.

## 3. RESULTS AND DISCUSSION

### 3.1 Thermogravimetric Analysis (TGA)

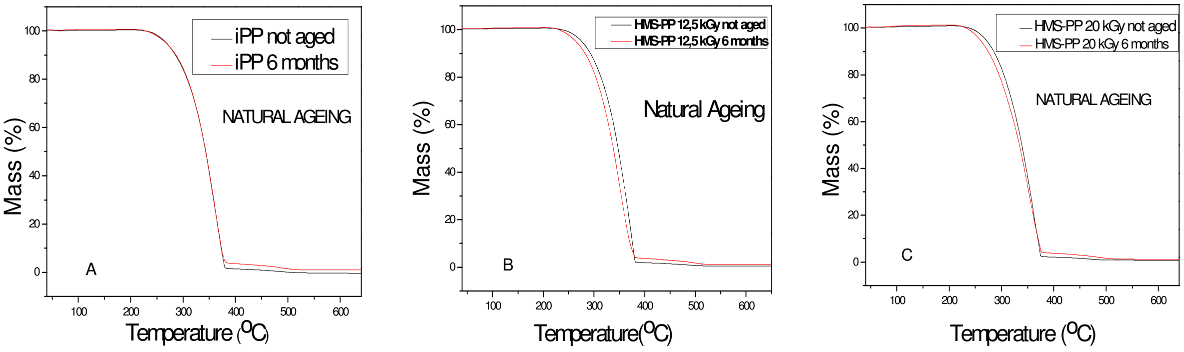


**Figure 2.** TGA curves of mass (%) in function of temperature at heating rate of 10°C min$^{-1}$, to iPP (A), HMS-PP 12.5 kGy (B) and HMS-PP 20 kGy (C) spheres.

As observed in the graph **A** , no significant variation of temperature in the onset point of decomposition 229 °C in both samples. In the Fig.2, **B**, the onset temperature of decomposition of the aged sample (6 months) is 235 °C while not aged is 241°C. In graph **C**, the temperature after 6 months is 233 °C while not aged is 239°C. Therefore, aged samples of HMS-PP are less thermally stable than not aged ones.

### 3.2 Infrared Spectroscopy (FTIR)

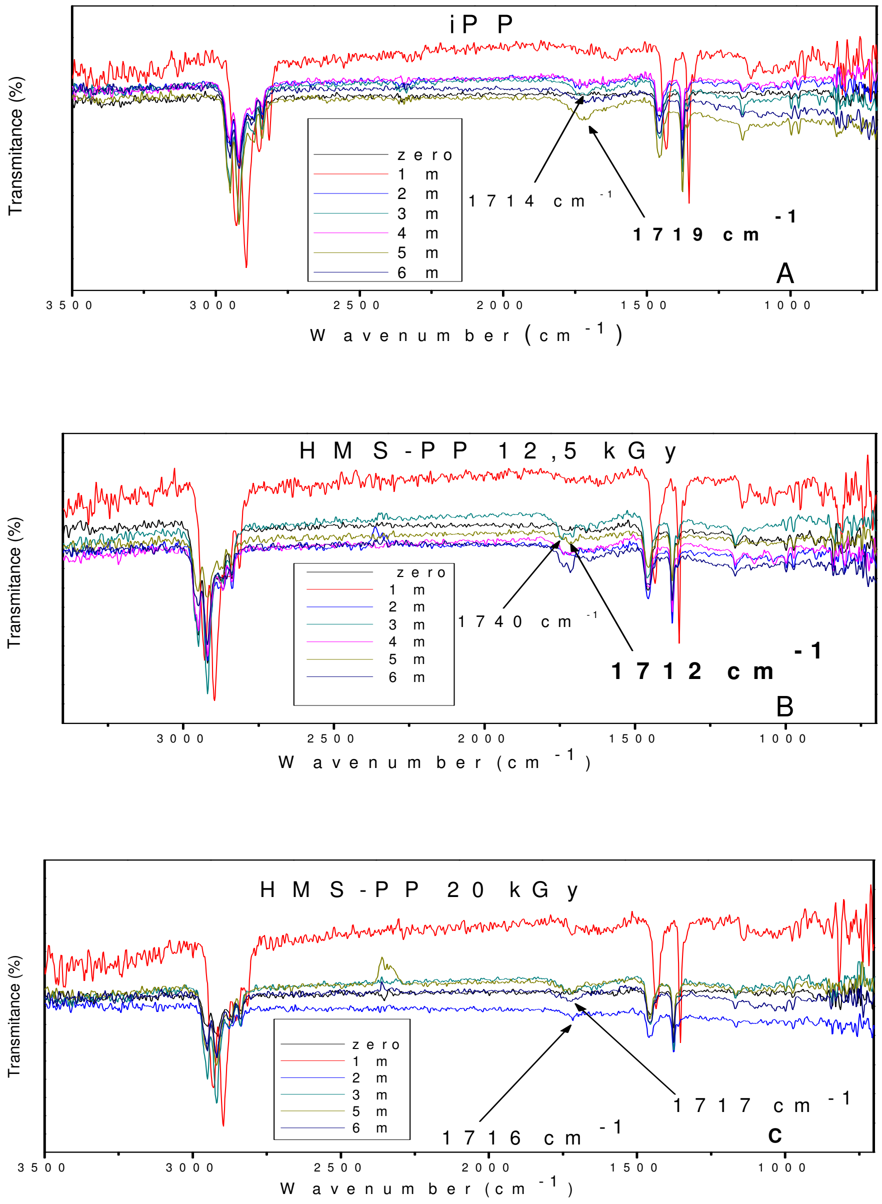
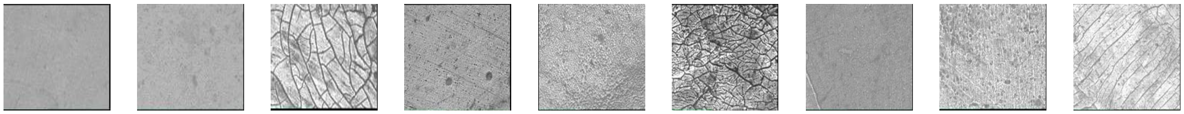


**Figure 3.** Illustration of the infrared spectrum by ATR technique of the: iPP (A), HMS-PP 12.5 kGy (B) and HMS-PP 20 kGy (C), spheres, under natural ageing.

In the Fig. 3 are shown the absorption peaks in the region of 1712 - 1740 $cm^{-1}$, that were attributed to the C=O stretching of oxidized chain terminals and oxidation products. The bands relative to carbonyl and carboxylic groups of polypropylene is evident after 3 month although the aspect only qualitative of the analyses. Both samples iPP and HMS-PPs showed absorptions related to oxidized groups.

### 3.3 Optical microscopy

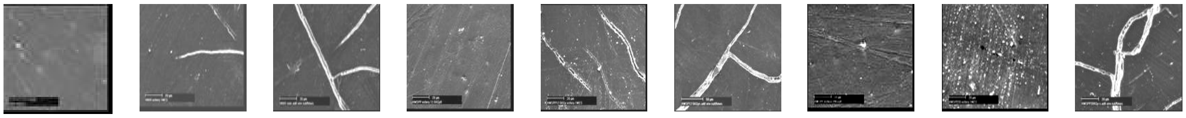


iPP not aged | iPP 1 month | iPP 5 month | HMS-PP 12,5 kGy not aged | HMS-PP 12,5 kGy 1 month | HMS-PP 12,5 kGy 5 month | HMS-PP 20 kGy not aged | HMS-PP 20 kGy 1 month | HMS-PP 20 kGy 5 month

**Figure 4.** Photomicrographs obtained by LM, 125 times magnifications, to iPP and HMS-PP spheres, aged naturally in São Paulo – IPEN.

The OM results, Fig.4, show a drastic fractured surfaces after 5 months aged. According to the SEM results those fractures have started in the early periods of 1 month, Fig.5.

### 3.4 Scanning Electronic Microscopy (SEM)



iPP not aged | iPP 1 month | iPP 5 month | HMS-PP 12,5 kGy not aged | HMS-PP 12,5 kGy 1 month | HMS-PP 12,5 kGy 5 month | HMS-PP 20 kGy not aged | HMS-PP 20 kGy 1 month | HMS-PP 20 kGy 5 month

**Figure 5.** Scanning electron micrographs (SEM) of the surface cracks development, magnification of 1000 times, samples of iPP and HMS-PP spheres, after natural ageing in São Paulo – IPEN.

The PP is a sensitive polymer to the weathering in reason of the tertiary carbon present in the monomer unit [8,9,10]. Our results of PP degradation can be explained by the mechanism represented by the Norrish type I and II reactions, Fig. 6 [7], with formation of C=O groups in various oxidized products considering that HMSPP obtained by radiation process of synthesis suffered previous radiation effects [11].

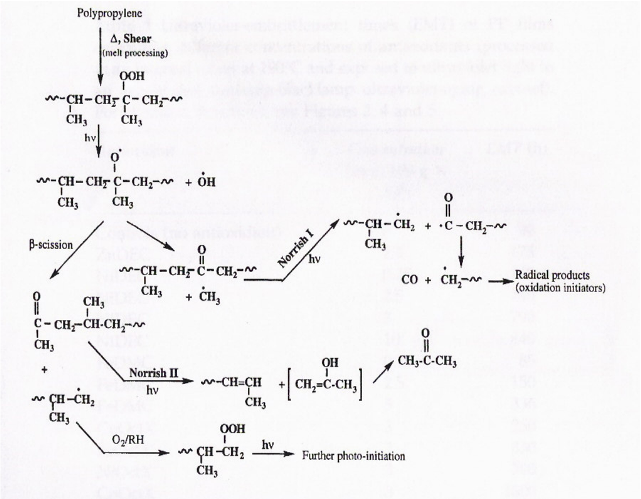


**Figure 6.** Photoinitiation by the hydroperoxides and the derived carbonyl compounds [7].

## 4. CONCLUSIONS

Isotactic PP suffers the ageing damage under natural conditions and, as verified, HMS-PP obtained at 12.5 and 20 kGy suffers more drastically ageing process under the same conditions. The frequency of cracks increases with increasing of irradiation dose in the synthesis. Oxidized products leading to the formation of C=O groups are detectable by spectroscopic analysis and yields a relative less stable material.

Lifetime of polymers exposed to natural environment can not be predicted accurately because of complexity of the natural weathering phenomenon and multitude of weather parameters interacting simultaneously [12]. On the other hand products more degradable present expectation of lower lifetime.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Maxwell, A.S., et al., NPL REPORT DEPC MPR 016 - National Physical Laboratory, Review of accelerated ageing methods and lifetime prediction techniques for polymeric materials, 2005.
2. Rodriguez, F., et al., Principles of Polymer Systems, Taylor&Francis, Fifth Edition, 2003.
3. Karlsson S. and Albertsson A. C., Techniques and mechanisms of polymer degradation. Degradable Polymers, Edited by Gerald Scott &Dam Gilead, 1995.
4. Halls, N. A., Gamma-irradiation Processing. Irradiation Effects on Polymers, Edited by D. W Clegg & A.A. Collyer, 1991.
5. ASTM D 638-03 – Standard Test Method for Tensile Properties of Plastics
6. ASTM D 1435-05 – Standard Practice for Outdoor Weathering of Plastics.
7. Karger J. & Kocsis, Polypropylene Polymer Science and Technology. Photostabilizers, S. Al-Malaika, pgs.(582 and 583). Edited by J. Karger-Kocsis, Klewer Academic Publishers, 1999.
8. Oliani, W. L., Otaguro H., Lima, L.F.C.P., Lugão, A. B., Parra, D. F., PPS-23 – Comparative Study of Polypropylene (HMS-PP) Degradation Under Different Conditions, 2007.
9. Lugão, A. B., Tese de Doutorado: Estudos da Síntese por Irradiação, da Estrutura e do Mecanismo de Formação de Polipropileno com Alta Resistência do Fundido, 2004, IPEN.
10. Paoli, M. A ., Degradação e Estabilização de Polímeros, 2007, www.chemkeys.com, acessado em 04 de junho de 2007.
11. Sousa, A.R., Medeiros, K.L.E., Melo, T.J.A., Rabello, M.S., Pol. Degrad. Stab. 91, 2006, 1504-1512.
12. Hussain, I. and Hamid, H., Plastics and the Environment, Chapter 5 – Plastics in Agriculture, Edited by Anthony L. Andrady, Wiley – Interscience, A John Wiley&Sons Publication, 2003.