

# **UV Stability of HMS-PP (High Melt Strength Polypropylene) obtained by radiation process**

**W. L. Oliani, D. F. Parra and A. B. Lugão**

Nuclear Energy Research Institute – IPEN-CNEN/SP, Chemical and Environmental Centre (CQMA), Av. Prof. Lineu Prestes, 2242, 05508-900, São Paulo, Brazil

**washoliani@usp.br - duclercp@iq.usp.br**

HMS-PP in grains was synthesized by the gamma irradiation of PP under a crosslinking atmosphere of acetylene, followed by thermal treatment for radical recombination and thermal treatment for annihilation of the remaining radicals.

The UV stability of the material was evaluated in reference to grains. Accelerated weathering test of HMS-PP samples were performed in artificial ultraviolet light and condensation chamber apparatus Comexim (C-UV type) in aging conditions of exposure for 120 hours and 240 hours. The results were compared to the deterioration caused by sunlight and dew under natural exposition.

This work investigated changes in mechanical proprieties (elongation and rupture strength) behavior, Infrared Spectroscopy (FTIR), Optical Microscopy (MO), Scanning Electronic Microscopy (SEM) and Rheological properties of HMS-PP.

The HMS-PP is more fragile than PP and undergoes predominately chain scission in aggressive environment degradation conditions.

**Key words:** degradation, polypropylene, crosslinking and scission.

## **1. Introduction**

Studies on isotactic polypropylene (iPP) degradation in natural environments are relatively few with respect to laboratory experiments carried out by irradiation of iPP and HMS-PP samples with ultra-violet light of constant intensity in a controlled atmosphere (Gallo et al., 2006).

Material degradation that occurs when a polymer is exposed outdoors can be monitored using a wide range of engineering or mechanical methods and chemical methods (Shyichuk et al., 2004).

One major problem associated with the applications of polymers is their instability to weathering. Various reaction are responsible for this including rearrangements of the chemical structure, formation of oxidation products, crosslinking and/or chain scission (Shyichuk et al., 2004; Rivaton et al., 2005; Rivaton et al., 2004).

The effects of weathering on polymers are studied under artificial accelerated conditions. Many different methods exist, from the simple evaluation of the color changes, to the determination of the technological properties of the materials. The correlation between the obtained results under artificial and the tests on conditions natural weathering conditions is not easy (Rivaton et al., 2005).

The main reasons for the reduction in the product lifetime are the scissions of molecules, specially the taut molecules, and the formation of surface cracks (Navarro et al., 2007).

When UV irradiation is strong, the changes caused by photo-oxidation that are described above occur preferentially near to the surface. This is because the oxidation process is so rapid that oxygen is consumed near the surface before it can diffuse very far into the interior of the polymer. Reaction in the interior is very slow, apart from the time immediately after the illumination is switched on, when there will be oxygen available that difused into the polymer during the preceding dark period. This phenomenon is known as oxygen diffusion limited reaction and gives rise to a distinctive “depth profile” of degradation beneath the exposed surface. In the case of a semi-crystalline polymer the chemi-crystallization occurs primarily near to the surface (Shyichuk et al., 2004; Rabello et al., 1996).

Degradation is initiated by the near-ultraviolet (UV) component of sunlight and oxygen and is especially important when the final product is exposed to weathering in outdoor applications. (Attwood et al., 2006).

Polyolefins rapidly lose most of their mechanical properties after severe processing or periods of thermal and light exposure (Attwood et al., 2006).

The degradation is due to chain scission by oxidation which results in a decrease in the molecular weight of the PP. Reduction of elongation at break is useful as one indicator for the evaluation of the degradation of the polymeric materials (Yoshii et al., 1995).

The data are essential for producers or suppliers of both polymers and various additives. Long-term application of any polymer is impossible without well selected stabilizers. Thermal, oxidative, photochemical or biochemical processes and their combinations are involved in long-term weathering (Pospisil et al., 2006).

Problems in investigation of outdoor photodegradation of various polymers are more complex due to concerted or cyclic attacks of regular as well as casual atmospheric environmental stresses and their combinations on polymers (Pospisil et al., 2006).

Basic data on weather components reflected in polymer weathering are briefly mentioned. Solar radiation, oxygen and casual oxidizing and acid atmospheric pollutants are principal atmospheric deteriogens responsible together with environmental temperature and humidity for the reduced durability of outdoor exposed stabilized polymers.

Application of efficient and durable stabilizers has forced the development and application of accelerated tests simulating natural outdoor exposure as closely as possible (Pospisil et al., 2006).

The iPP and HMS-PP with tertiary hydrogen atoms, are very vulnerable to oxidative degradation with the result that material becomes discoloured and embrittled. The reaction sequence which is generally accepted to lead to the degradation of a polymer is the familiar peroxidation chain reaction, initiated by high temperatures and mechanical shear during processing or redox effects at photoactivated transition metal centres in catalyst residues and leading to formation of hydroperoxides (Knight et al., 1985).

Degradation of PP with peroxides is believed to occur by a series of free reactions involving steps as initiation, scission, transfer and termination (Lugão et al., 2007).

The reason behind the technical development of conventional and radiation stabilizers is related to the fact, that the UV degradation and thermo-oxidative degradation as well as radiation of polymers are all similar chain reactions (Czvikovszky, 2004).

PP has inherently low melt strength. Irradiation of PP under inert atmosphere causes a combination of chain scissioning and long-chain branching, and results in a material with significantly enhanced melt strength. This process, which is sometimes termed visbreaking, thus provides improvement of rheological properties. This allows different molding options for PP, and allows easier conversion of PP into fibers. This technology has been the subject of a number of patents, and has been incorporated into commercial processing of PP items (Cough, 2001; Lugão et al., 2000; Lugão, 2004).

The HMS-PP (High Melt Strength Polypropylene), the modified polypropylene by grafting under high energy ionizing radiation, is prepared in presence of atmosphere, which promotes crosslinking. The HMS-PP has been gaining market in Europe in the production of foams and fibers. The investigation about the thermal and photooxidation stability is important as to evaluate the lifetime of the material obtained through a radiation process, degradative in principle.

## **2. Experimental**

### **2.1 Materials and Methods**

The investigation was conducted with polypropylene in grains containing and modified polypropylenes (HMS-PP). The HMS-PP samples were obtained by irradiating with gamma rays in presence of acetylene at 5 kGy, 12.5 kGy and 20 kGy of total dose. After irradiation, the samples were heated for 60 min at 90°C to eliminate residual radicals. The ties samples were manufactured by mold pressure at temperature of 190 °C according to ASTM D 638-03, type IV. The ties were ageing tested in camera QUV (type C) and evaluated in 120 hours and 240 hours. The test conditions were 8 hours under UV radiation at 50 °C followed by 4 hours under 40 °C and condensed humidity. Source of UV, fluorescent lamps FS-40 with intensity of 12,4 w/m<sup>2</sup> in the range of 300 – 320 nm.

The samples were irradiated at Embrarad at a dose rate of 10 kGy. h<sup>-1</sup> and the dosimetry was performed with Harwell Red Perspex 4034.

#### **2.1 - Mechanical Tests**

The tests were performed with an EMIC DL 3000 electromechanical tensile machine with strain rate 2.10<sup>-2</sup> s<sup>-1</sup>. Longitudinal strain was measured by an extensometer and video-traction system. Tensile test was applied to evaluate the strength ( $\tau$ , MPa) and elongation at break ( $\epsilon$ , %) at 23°C, in EMIC equipment, according to ASTM D 638-03.

#### **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.

#### **2.3 - Optical Microscopy (MO)**

Light microscopy (MO) Olympus model PM E3, was used to observe the surface exposed to thermal ageing at a fixed magnification of 200 times.

#### **2.4 - Scanning Electronic Microscopy (SEM)**

Scanning electronic microscopy (SEM) was done using an EDAX PHILIPS XL 30. Magnification was used on the fracture region to observe the fracture surface

## 2.5 - Rheological Measurements

The characterization in shear flow was performed at 200°C using rotational Physica Rheometer (MCR 300) with parallel-plate geometry of 25 mm in diameter. The amplitude oscillatory was performed in the frequency range 0.1 – 100 Hz with a strain of 5% and a gap of 1.0 mm. Samples with 1.2 mm of thickness and 25 mm of diameter were produced by compression moulding at 190°C.

## 3. Results and Discussion

### Mechanical Tests

From the view point of mechanical properties of polymer materials, crosslinking of PP promoted by irradiation modification leads to increasing of hardness and to decreasing of elongation (Yamaoka, 1991).

The influence of ageing process in the physical properties is shown in figure 1

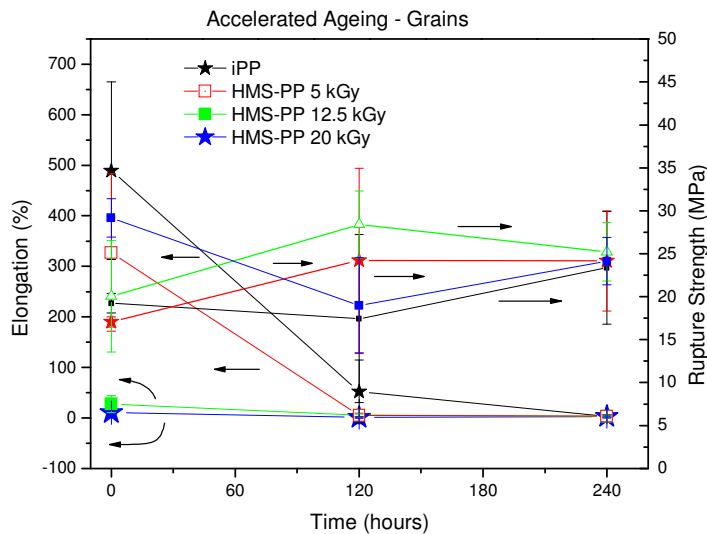


Figure 1 - Results of rupture strength and elongation of PP, HMS-PP 5 kGy; 12.5 kGy and 20 kGy.

The elongation (%) of the samples aged in camera after at 120 hours is very small, but the results of test rupture strength shown an increase in samples of the iPP, HMS 5 kGy and HMS 12.5 kGy, after 120 hours. The samples of the HMS 20 kGy with 120 hours of the exposure show a decrease in strength and at the end 240 hours the exposure increase the strength around 23 MPa.

Loss of physical properties in many polymers containing aliphatic backbone substituents results from the  $\beta$ -scission of alkoxy radicals. Alkoxy radicals are formed by hydroperoxide decomposition. They are also formed in the complex self-reaction of peroxy

radicals which may terminate the radicals. Elongation at break has been shown to be appreciably more sensitive to degradation than tensile strength (Carlsson and Chmela, 1990).

### Infrared Spectroscopy (FTIR)

Polypropylene photodegradation is initiated by UV radiation, which in the absorption of UV radiation by chromophores and in the activation of excited states in macromolecules. When the HMS-PP is exposed to UV 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 HMS-PP chain. Once free radicals have been produced, reaction with oxygen generate products of decomposition including aldehydes and ketones. The presence of these carbonyl groups in a degraded polymer can be used as a chemical index for degradation.

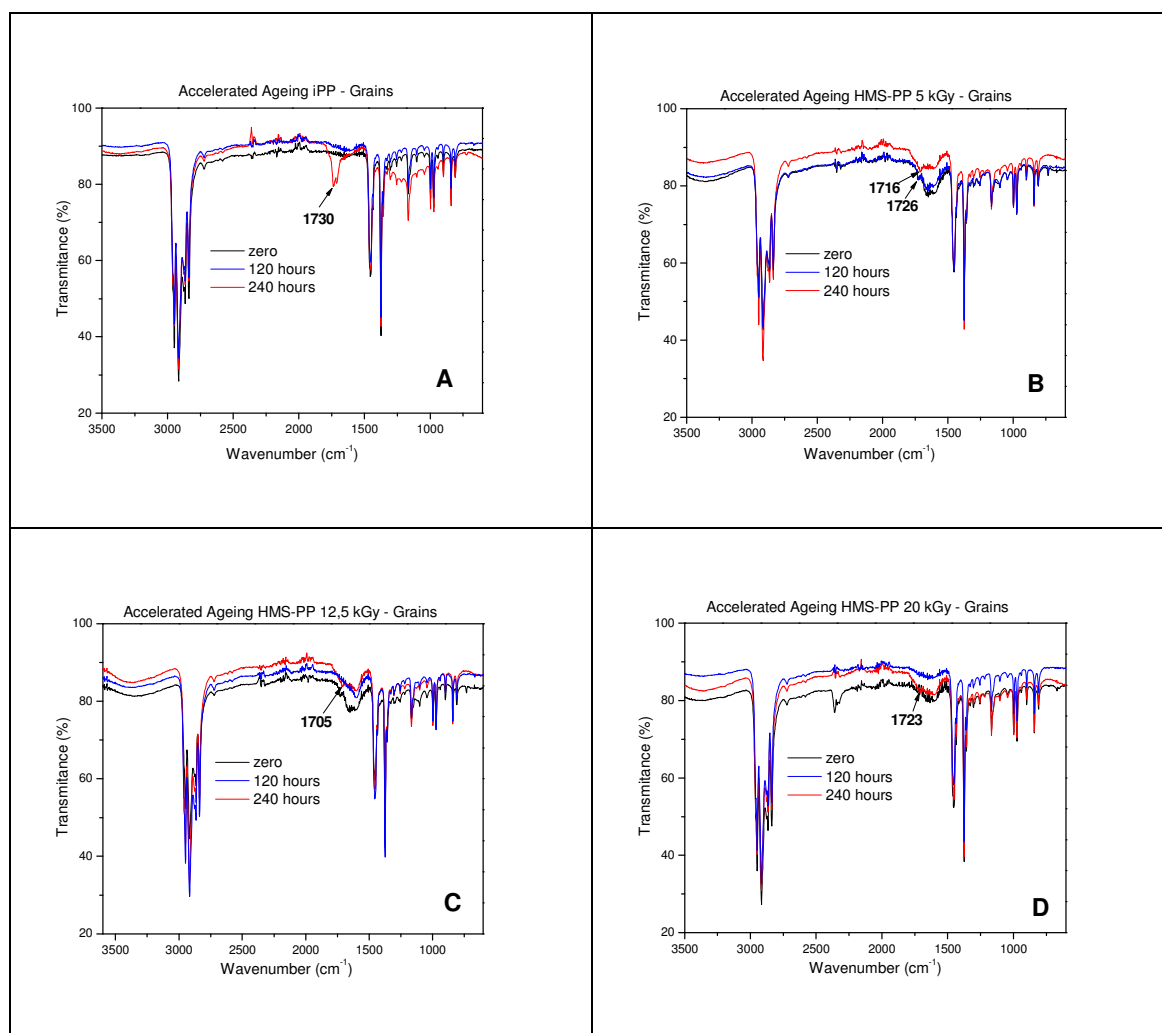


Figure 2 – Illustration of the ATR infrared spectrum of: (A) iPP, (B) HMS-PP 5 kGy, (C) HMS-PP 12.5 kGy, (D) HMS-PP 20 kGy under accelerated ageing.

The absorption peaks in the region of 1705-1730  $\text{cm}^{-1}$ , figure 2, 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 240 hours of the camera UV exposition.

### Optical Microscopy (MO)

The fracture surfaces of the grades are showed in samples HMS-PP 20 kGy with 120 hours of UV exposure returning more intense in samples with 240 hours of exposure, figure 3.

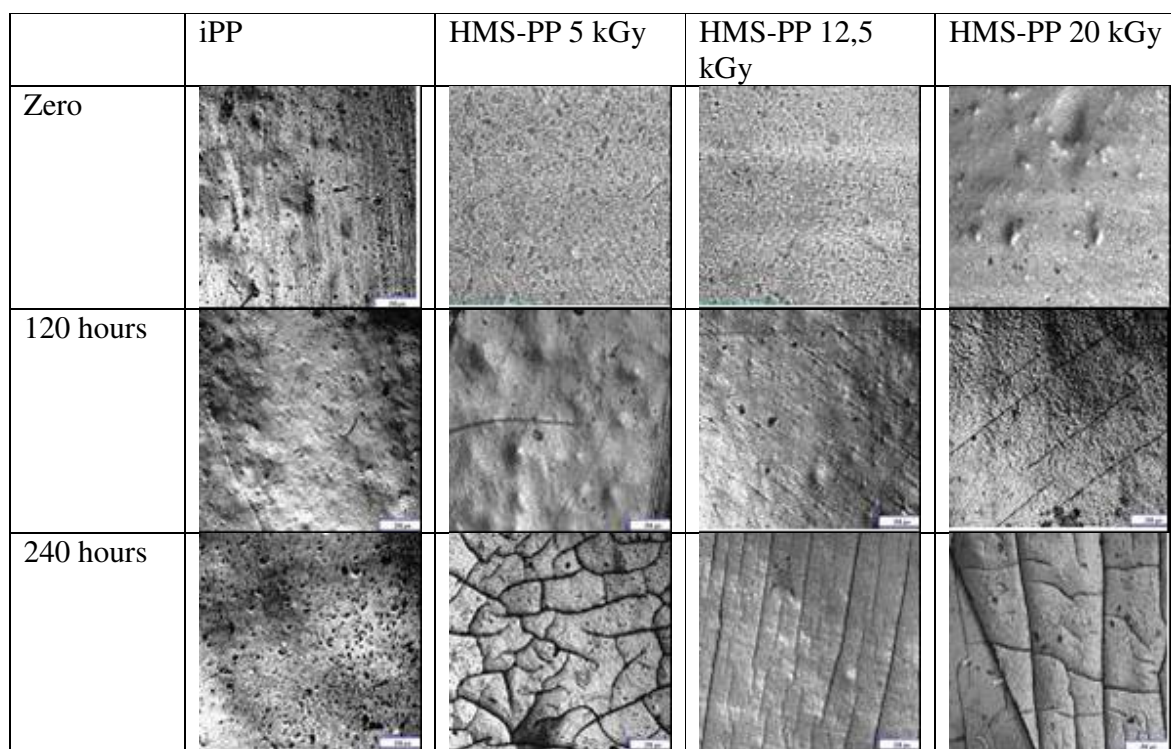


Figure 3 – Photomicrographs obtained by MO for iPP and HMS-PPs in grains, aged for 240 hours in camera UV.

### Scanning Electronic Microscopy (SEM)

Is evident that scission occurred more extensively at the layers near the surface and the images of a steep profile of degradation confirmed that 240 hours was drastically aged in UV camera.

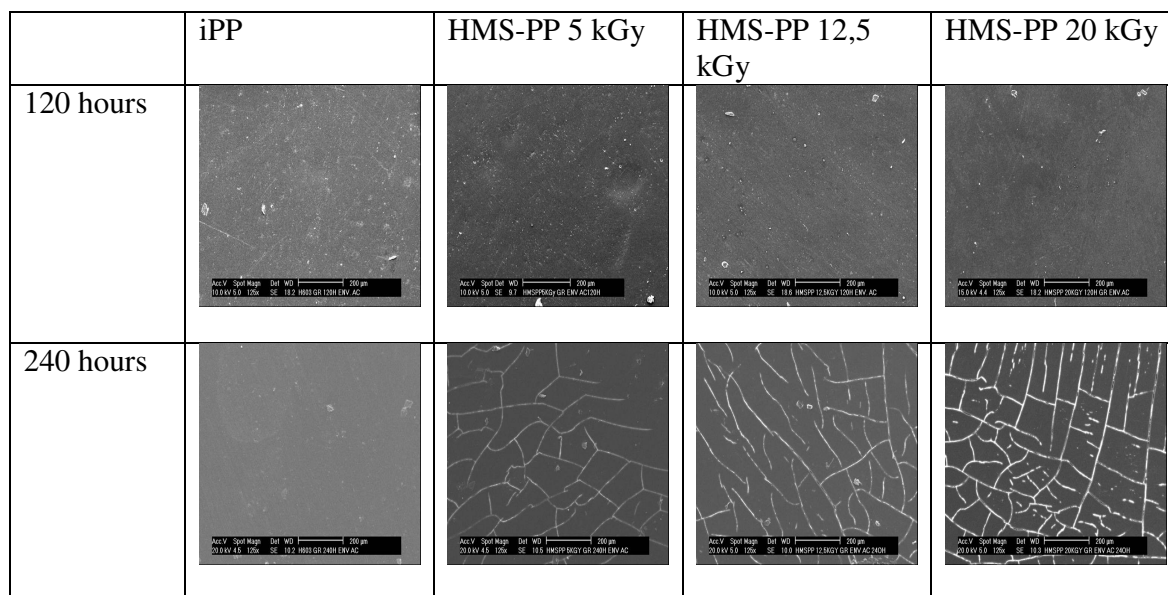


Figure 4 – Development of surface cracks, scanning electron micrographs, enlarged 125 times.

When the cracking occurs, oxygen gains access to the inner parts of the moulding and the degradation depth profile will be significantly modified in 240 hours of the exposure, figure 4.

The HMS-PPs presented more sensitivity to accelerated ageing (UV) compared to the PP. Chiefly, the surface exposed in the order: HMS-PP 20 kGy>12.5kGy>5 kGy , showed the highest frequency of cracking.

Is important pointed out that polypropylene contains impurities which make it specially sensitive to the presence of ultraviolet rays. On the other hand HMSPP was processed after reactor and showed be more sensitive to the ageing effects also if containing stabilizers, particularly when PP is made without stabilizers and pigments is very sensitive to this type of degradation (Yakimets, et al., 2004).

### Rheological Measurements

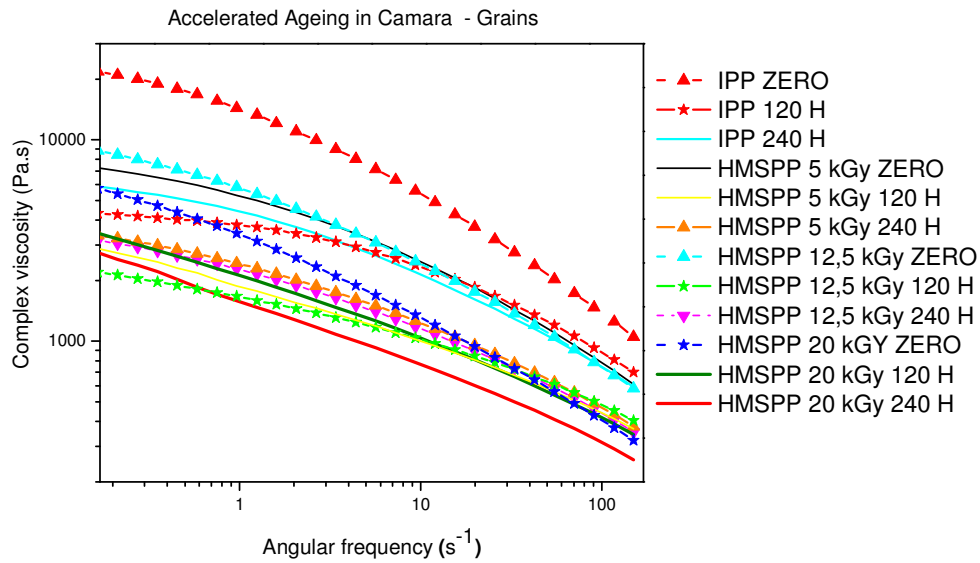


Figure 5 – Complex viscosity versus angular frequency of the PP and HMS-PPs.

The figure 5, showed which in presence of antioxidants the effect of ageing in camara UV modify with smaller intensity the complex viscosity of samples. The action of the thermal antioxidants for processing and storage changes with less intensity the viscosity complex of the different samples. It was evident the effect of time exposure on the decrease of viscosity in samples after 240 hours ageing accelerated, mainly in samples of HMS-PP 20 kGy. The photomicrographs of the figure 4, confirmed the scission chain occurrence.

#### 4. Conclusions

The frequency of cracks increases with increasing the irradiation dose in the synthesis of HMSPP visbreaking products.

The HMS-PPs presented more sensitivity to accelerated ageing (UV) compared to the PP. It reveals that previous degradation has influence in the post-use of HMSPP.

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## References

- Gallo, R., Brambilla, L., Castiglioni, C. and Severini, F., 2006. Characterization of Naturally Weathered Polypropylene Plates. *Journal of Macromolecular Science*. 43, 535-554.
- Shyichuk, A. V., Turton, T. J., White, J. R. and Syrotynska, I. D., 2004. Different degradability of two similar polypropylenes as revealed by macromolecule scission and crosslinking rates. *Polymer Degradation and Stability*. 86, 377-383.
- Rivaton, A., Gardette, J. L., Mailhot, B., Therlas, S. M., 2005. Basic Aspects of Polymer Degradation. 225, 129-146.
- Rivaton, A., Lalande, D., Gardette, J.L., 2004. Influence of the structure on the  $\gamma$  - irradiation of polypropylene and on the post-irradiation effects. *NIM B – Nuclear Instruments and Methods in Physics Research B*. 222, 187-200.
- Navarro, R. F., Almeida, J. R., Rabello, M. S., 2007. Elastic Properties of Degraded Polypropylene. *J. Mater. Sci*. 42, 2167-2174.
- Rabello, M.S., White, J.R., 1996. The role of physical structure and morphology in the photodegradation behaviour of polypropylene. *Polymer Degradation and Stability*. 56, 55-73.
- Attwood, J., Philip, M., Hulme, A., Williams, G., Shipton, P., 2006. The effects of ageing by ultraviolet degradation of recycled polyolefin blends. *Polymer Degradation and Stability*. 91, 3407-3415.
- Yoshii, F., Meligi, G., Sasaki, T., Makuuchi, K., Rabie, A. M. and Nishimoto, S., 1995. Effect of irradiation on the degradability of polypropylene in the natural environment. *Polymer Degradation and Stability*. 49, 315-321.
- Pospisil, J., Pilar, J., Billingham, N. C., Marek, A., Horak, Z. and Nespurek, S., 2006. Factors affecting accelerated testing of polymer photostability. *Polymer Degradation and Stability*. 91, 417-422.
- Knight, J.B., Calvert, P.D., Billingham, N.C., 1985. Localization of Oxidation in Polypropylene. *Polymer*. 26, 1713-1718.
- Lugão, A.B. et al., 2007. Production of High Melt Strength Polypropylene by Gamma Irradiation. *Radiation Physics and Chemistry*. 76, 1691-1695.
- Czvikovszky, T., 2004. Advances in Radiation Chemistry of Polymers. IAEA – International Atomic Agency. Degradation Effects in Polymers. 91 -102.

Cough, R. L., 2001. High-energy radiation and polymers: A review of commercial processes and emerging applications. NIM B – Nuclear Instruments and Methods in Physics Research B. 185, 8-33.

Lugão, A.B., Hutzler, B., Ojeda, T., Tokumoto, S., Siemesns, R., Makuuchi, K., Villavicencio, A.L., 2000. Reaction mechanism and rheological properties of polypropylene irradiated under various atmospheres. Radiation Physics and Chemistry. 57, 389-392.

Lugão, A.B. U.S Patent 0171712, 2004. Process for preparing high melt strength polypropylene and crosslinked prepared therewith.

Yamaoka, H., 1991. Radiation Chemistry of Polymers. Regional Training Course on Radiation Chemistry.

Carlsson, D.J. and Chmela, S., 1990. Mechanisms of Polymer Degradation and Stabilisation. Chapter 4 - Polymers and High-Energy Irradiation: Degradation and Stabilization. Edited by Gerald Scott. 109-113.

Yakimets, I., Lai, D. and Guigon, M., 2004. Effect of photo-oxidation cracks on behaviour of thick polypropylene samples. Polymer Degradation and Stability. 86, 59 – 67.