



## UV stability of HMS-PP (high melt strength polypropylene) obtained by radiation process

W.L. Oliani\*, D.F. Parra, A.B. Lugão

Nuclear Energy Research Institute—IPEN—CNEN/SP, Av. Prof. Lineu Prestes, 2242, 05508-900 São Paulo, Brazil

### ARTICLE INFO

**Keywords:**  
Degradation  
Polypropylene  
UV ageing  
Crosslinking and scission

### ABSTRACT

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 pellet form. The accelerated weathering test of HMS-PP samples were performed under artificial ultra-violet light and in a condensation chamber Comexim (C-UV type) apparatus with UV exposure for 120 and 240 h. The results were compared to those from ageing caused by sunlight and dew under natural exposition. This work investigated changes in mechanical proprieties (elongation and rupture strength), Fourier transform infrared spectroscopy (FTIR), optical microscopy (MO), scanning electron microscopy (SEM) and rheological properties of HMS-PP after the UV ageing. We find that the HMS-PP has more degradation than regular PP and undergoes predominate chain scission in aggressive UV ageing conditions.

© 2009 Elsevier Ltd. All rights reserved.

### 1. Introduction

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

The effects of weathering on polymers are studied under artificial accelerated conditions. Many different methods exist to detect the ageing effects, from simple evaluation of color changes, to the determination of changes in the mechanical or chemical properties of the materials (Shyichuk et al., 2004).

The correlation between the obtained results under artificial and conditions of natural weathering conditions is not easy (Rivaton et al., 2005). Polyolefins rapidly lose most of their mechanical properties after severe exposure to heat and light (Attwood et al., 2006). Degradation is initiated by the near-ultra-violet (UV) component of sunlight and oxygen, especially important when the final product is exposed to weathering in outdoor applications. (Attwood et al., 2006).

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

The degradation from oxidative chain scission results in a decrease in the molecular weight of the polymer. Reduction of elongation at break is useful as an indicator for the evaluation of the degradation of the polymeric materials (Yoshii et al., 1995).

When UV irradiation is strong, the changes caused by photo-oxidation 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 far into the interior of the polymer. Reaction in the interior is very slow, except for the time immediately after the illumination when there is oxygen available that has diffused 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 chemicrystallization occurs primarily near the surface (Shyichuk et al., 2004; Rabello and White, 1996).

The UV stability 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

\* Corresponding author.

E-mail addresses: washoliani@usp.br, duclercp@iq.usp.br (W.L. Oliani).

casual oxidizing and acid atmospheric pollutants are principal atmospheric deteriorogens 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).

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).

The iPP and HMS-PP with tertiary hydrogen atoms are very vulnerable to oxidative degradation with the result that material becomes discolored 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 center 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 i.e. 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 acetylene atmosphere which promotes crosslinking. The HMS-PP has been gaining market in Europe in the production of foams and fibers. The investigation about the

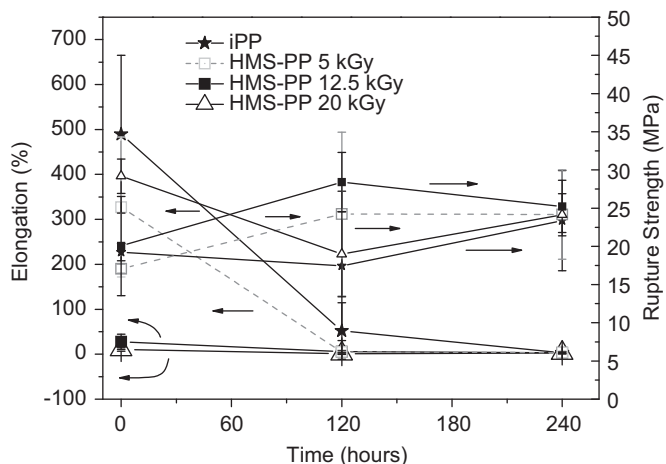


Fig. 1. Results of rupture strength and elongation of PP, HMS-PP 5; 12.5 and 20 kGy.

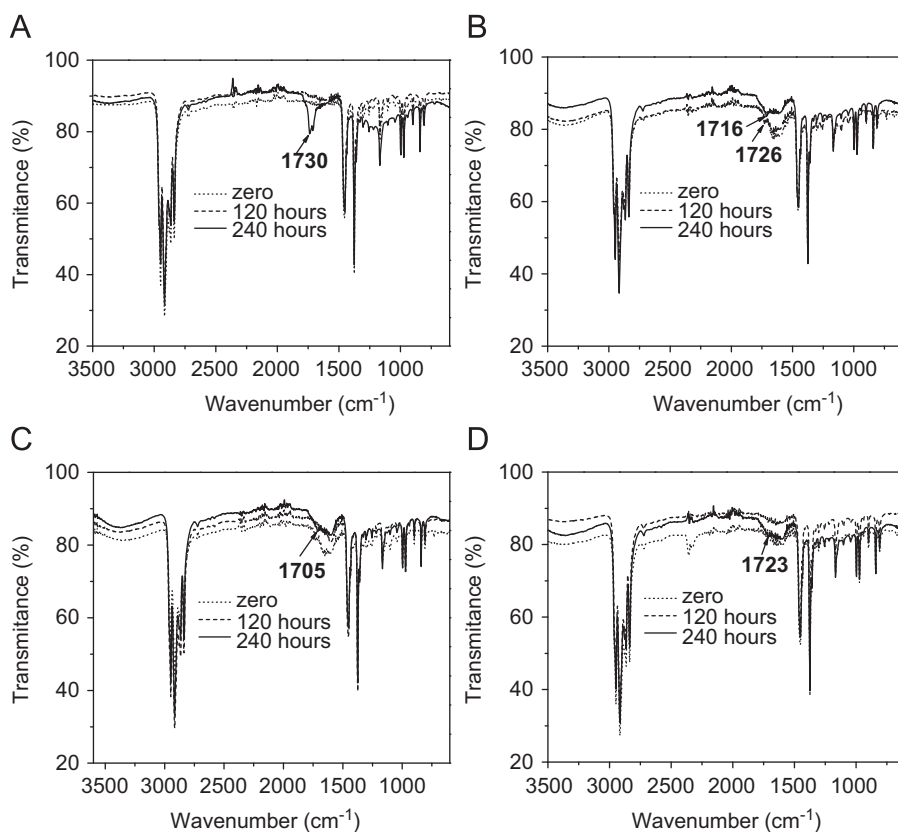


Fig. 2. Illustration of the ATR infrared spectrum of: (A) iPP, (B) HMS-PP 5 kGy, (C) HMS-PP 12.5 kGy and (D) HMS-PP 20 kGy under accelerated ageing.

thermal and photo-oxidation 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 using polypropylenes in pellets form. The HMS-PP samples were obtained by irradiating iPP samples with gamma rays in the presence of acetylene at 5, 12.5 and 20 kGy of total dose. The samples were irradiated in an Embrarad cell at a dose rate of 10 kGy/h and the dosimetry was performed with Harwell Red Perspex 4034.

After irradiation, the samples were heated for 60 min at 90 °C to eliminate residual radicals. The tensile specimens were manufactured by molding under pressure at a temperature of 190 °C according to ASTM D 638-03, type IV. The specimens were aged in a QUV (type C) chamber and evaluated after 120 and 240 h exposure. The test conditions were 8 h under UV radiation at 50 °C followed by 4 h under 40 °C and condensed humidity. The source of UV was fluorescent lamps FS-40 with an intensity of 12.4 W/m<sup>2</sup> in the wavelength range of 300–320 nm.

#### 2.1.1. Mechanical tests

The tests were performed with an EMIC DL 3000 electro-mechanical tensile machine with a strain rate of 0.02 s<sup>-1</sup>. Longitudinal strain was measured by an extensometer and video-traction system. Tensile test was carried out to evaluate the tensile strength ( $\tau$ , MPa) and elongation at break ( $\epsilon$ , %) at 23 °C using an EMIC equipment, according to ASTM D 638-03.

#### 2.1.2. Infrared spectroscopy (FTIR)

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

#### 2.1.3. Optical microscopy (MO)

Light microscopy was obtained using an Olympus model PM E3 instrument to observe the surface exposed to thermal ageing at a fixed magnification of 200 times.

#### 2.1.4. Scanning electron microscopy (SEM)

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

#### 2.1.5. 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 molding at 190 °C.

## 3. Results and discussion

From the view point of mechanical properties of polymer materials, crosslinking of PP promoted by irradiation modification

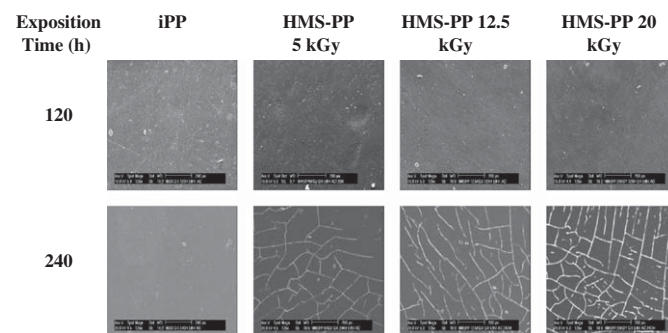


Fig. 4. Development of surface cracks, scanning electron micrographs, enlarged 125 times.

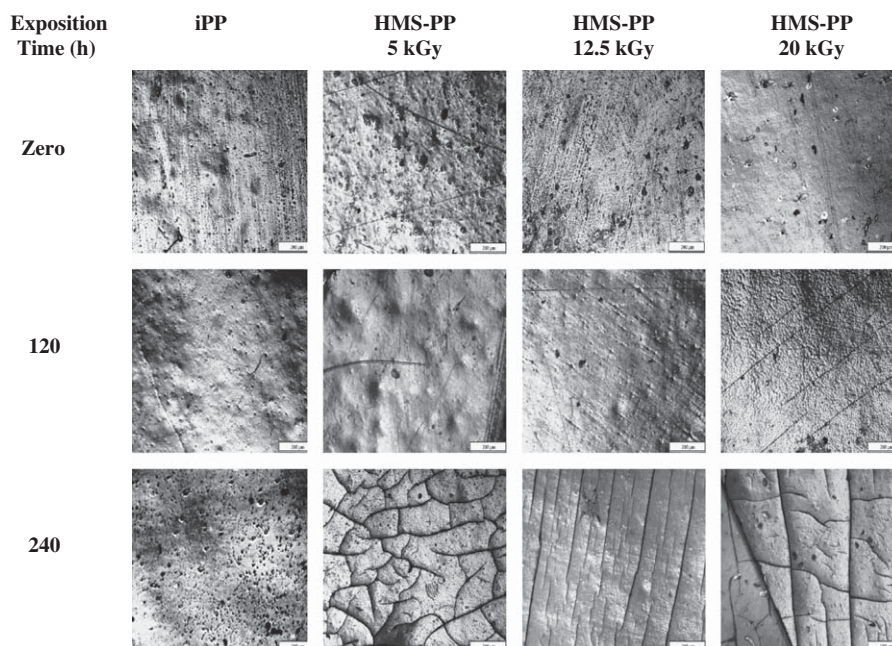


Fig. 3. Photomicrographs obtained by MO, enlarged 200 times, for iPP and HMS-PPs in grains, aged for 240 h in QUV chamber.

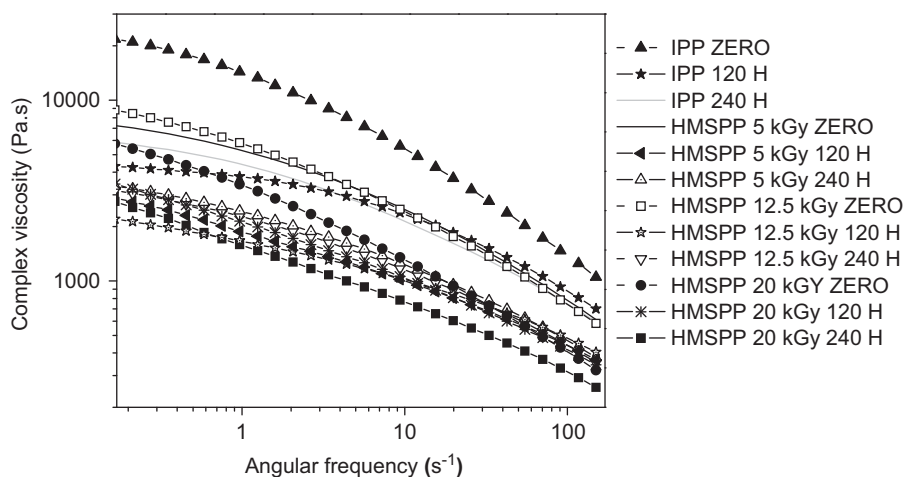


Fig. 5. Complex viscosity vs. angular frequency of the PP and HMS-PPs.

leads to increasing of hardness and to decreasing of elongation (Yamaoka, 1991).

The influence of ageing process conducted in a QUV (type C) chamber on the physical properties is shown in Fig. 1.

The elongation (%) of the samples aged for 120 h is very small, but the results of test rupture strength showed an increase in samples of the iPP, HMS 5 kGy and HMS 12.5 kGy, after 120 h. The samples of the HMS 20 kGy with 120 h of the exposure show a decrease in strength and at the end of 240 h the exposure increases 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).

Polypropylene photodegradation is initiated by UV radiation, with absorption by chromophores and 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, reactions 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.

The absorption peaks in the region of 1705–1730  $\text{cm}^{-1}$ , Fig. 2, were attributed to the C=O stretching of oxidized chain terminals and oxidation products. The bands relative to carbonyl and carboxylic groups of polypropylene are evident after 240 h of the QUV (type C) chamber exposition.

The fracture surfaces of the grades are observed in sample of HMS-PP 20 kGy with 120 h of UV exposure returning more intense with 240 h of exposure as shown in Fig. 3.

It 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 h was drastically aged in QUV (type C) chamber.

When the cracking occurs, oxygen gains access to the inner parts of the molding and the degradation depth profile will be significantly modified in 240 h of the exposure, Fig. 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 > 12.5 > 5 kGy, showed the highest frequency of cracking.

It is important to point out that polypropylene contains impurities which make it specially sensitive to the presence of ultra-violet rays. Particularly when PP is made without stabilizers and pigments is very sensitive to this type of degradation (Yakimets, et al., 2004). In the present work HMS-PP was processed after reactor and showed to be more sensitive to the ageing effects also if containing stabilizers.

Fig. 5, showed which in the presence of antioxidants the effect of ageing in QUV (type C) chamber is to modify the complex viscosity of samples in minor intensity. The action of the thermal antioxidants for processing and storage changes with less intensity of the viscosity complex of the different samples. The effect of time exposure on the decrease of viscosity was evident in samples after 240 h ageing mainly in samples of HMS-PP 20 kGy. However, all the samples irradiated to 20 kGy did not show any trend to reach the Newtonian plateau. They were clearly scissioned by radiation and oxidation but somehow crosslinked, as they show a trend of reaching high viscosity values at very low frequency. This is an evidence of branched and/or crosslinked polymers.

#### 4. Conclusions

The frequency of cracks increases with increasing the irradiation dose in the synthesis of HMS-PP 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 HMS-PP.

#### Acknowledgements

The authors acknowledge CNPq (The National Council for Scientific and Technological Development), process 382891/2007-4 (NV) for grants; Centre of Science and Technology of Materials—CCTM/IPEN, for microscopy analysis (SEM), Centre of Fuel Nuclear—CCN/IPEN, for microscopy analysis (MO) and Dr. Marcelo Silveira Rabello—Federal University of Campina Grande, PB Brazil, for the accelerated weathering test.

## References

- 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.
- Czvikovszky, T., 2004. Advances in radiation chemistry of polymers. IAEA—International Atomic Agency. *Degradation Effects in Polymers*. 91, 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.
- Carlsson, D.J., Chmela, S., 1990. Mechanisms of polymer degradation and stabilisation. In: Scott, Gerald (Ed.), *Chapter 4—Polymers and High-Energy Irradiation: Degradation and Stabilization*, pp. 109–113.
- Gallo, R., Brambilla, L., Castiglioni, C., Severini, F., 2006. Characterization of naturally weathered polypropylene plates. *Journal of Macromolecular Science* 43, 535–554.
- 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.
- 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.
- Navarro, R.F., Almeida, J.R., Rabello, M.S., 2007. Elastic properties of degraded polypropylene. *Journal of Material Science* 42, 2167–2174.
- Pospisil, J., Pilar, J., Billingham, N.C., Marek, A., Horak, Z., Nespurek, S., 2006. Factors affecting accelerated testing of polymer photostability. *Polymer Degradation and Stability* 91, 417–422.
- Rivaton, A., Gardette, J. L., Mailhot, B., Therlas, S. M., 2005. *Basic Aspects of Polymer Degradation*. 225, pp. 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.
- 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.
- Shyichuk, A.V., Turton, T.J., White, J.R., 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.
- Yoshii, F., Meligi, G., Sasaki, T., Makuuchi, K., Rabie, A.M., Nishimoto, S., 1995. Effect of irradiation on the degradability of polypropylene in the natural environment. *Polymer Degradation and Stability* 49, 315–321.
- Yamaoka, H., 1991. *Radiation chemistry of polymers. Regional Training Course on Radiation Chemistry*. .
- Yakimets, I., Lai, D., Guigon, M., 2004. Effect of photo-oxidation cracks on behaviour of thick polypropylene samples. *Polymer Degradation and Stability* 86, 59–67.