COMPARATIVE STUDY OF POLYPROPYLENE (HMS-PP) DEGRADATION UNDER DIFFERENT CONDITIONS

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Abstract:

The petrochemical industry has invested billions of dollars in research of additives to increase the useful life of its products. Today, however, these very industries that manufacture, process and transform polymers when faced with "ambient problems", must take into consideration the reduction of their products' life time. The polypropylene, when submitted to weathering exposition conditions, suffers structural changes resulting in the deterioration of mechanical properties and variations in the superficial appearance. The absorption of UV radiation influences the structure of the polymer through the impurities traces. The radical formation of reactive species starts the reactions of degradation. The exposition to the ambience includes real conditions of exposition of the product to weathering (sunlight radiation, humidity, temperature, oxygen, etc) that contributes to the polymer deterioration. Those phenomena affect the chemical and physical structure of the polymer as observed in our study. The resins used in this work are: iPP(spheres), with melt flow index of 1,5 g 10 min^{-1} 230℃ , HMS-PP with 3,3 g 10 min^{-1} to the dose of 20 kGy and 2,2 g 10 min^{-1} obtained at the dose of 12,5 kGy. The samples submitted to natural exposition for a period of six months were characterized by: tensile test, thermogravimetric analysis (TGA), scanning electronic microscopy (SEM), optical microscopy and infrared spectroscopy (FTIR). The results after one month of exposition showed a decrease of percentage of elongation at break and loss of maximum strength at break. The decrease is continuous until six months. The surface of the exposed samples presented fissures observed by optical microscopy, which is an indicative of the process of chain scissions. Particular aspects of the fracture surfaces were showed by the SEM analysis. In addition, the surface fracture pattern demonstrated important differences between iPP and HMS-PP associated to the morphology of the polymer processed by gamma radiation (HMS-PP in this case). FAPESP and CNPQ

Introduction

The use of polyolefins such as polypropylene (PP) in automotive, carcasses of household-electric, packings, toys, carpets, hospital material, boxes of batteries, thermoforming parts and lighter foams is increasing. They have advantages in recyclability, light weight, and cost compared to engineering resins [3]. However, polyolefins have significantly less resistance to scratch and damage.

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. 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.

The environmental conditions of exposition are important instruments to investigate the resistance to photodegradation, photooxidation and thermodegradation of the HMSPP. Nonetheless the diverse constituents of the environment as: ultraviolet radiation, visible light, temperature, weathering and humidity have been taken into account. Those parameters affect the chemical structure of polypropylene leading to material decomposition. Polypropylene (iPP) without stabilizers and pigments is very sensitive to this type of decomposition [4, 6], but little information is reported in the literature concerning the HMS-PP.

Evaluation of the HMSPP under continuous exposition, in natural conditions of environment, is an important prognostic of the material performance during the application.

Experimental

Material 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 of 20 kGy with MFI = 3,3 g 10 min^{-1} , stabilized.
- HMS-PP obtained at the dose 12,5 kGy with MFI = 2,2 g 10 min^{-1}, not stabilized.
- The samples were manufactured by mold pressure at temperature of 190 ℃ according to ASTM D 638-03, tie -type IV [1].

Fig. 1 - Samples settled in a device for assay of natural ageing, confectioned in laboratory.

The disposal of the samples for natural exposition were placed 45° north, according to ASTM D 1435-05 - Standart Practice for Outdoor Weathering of Plastics [2]. Geographic Position: Latitude (23° 33` South); Longitude (46° 44` West) and Altitude (750 meters).

Mechanical tests
Tensile test was applied to evaluate the strength (τ ,MPa) and elongation at break (ε, %) at room temperature, in EMIC DL 3000 equipment, according to ASTM D 638-03 [1]. The electromechanical tensile machine with longitudinal strain rate of 2.10^{-2} s^{-1} operates by extensometer and video-traction system.

Thermogravimetric Analysis (TGA)
Thermogravimetric Analysis (TGA) was recorded with a Mettler-Toledo TGA / SDTA 851 thermobalance, in nitrogen atmosphere of 50mL.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.

Infrared Spectroscopy (FTIR)
The analyses were performed at Thermo-Nicolet spectrophotometer, model – 0074-150/FTIR100, with attenuation total reflectance accessory (ATR).

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 regions.

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

Results and Discussion
The influence of the aging process in the physical properties is shown in figure 2. The HMSPP presents higher strength at break in the initial time (zero d) and after 30 days the value drops to the middle. On the other hand, the PP strength at break goes up in the first month and falls after this period. This fact indicates the existence of crosslink at earlier period in competition with degradation effects along the time. In addition, the natural ageing affects the HMSPP considerably more than the PP as observed in the latter periods.
The drop in the elongation at break (%) of the PP sample indicates the degradation process occurring by chain scissions mechanism. In the HMSPP the effect on elongation at break is less intense owing to the initial rigidity attributed to the synthesis process.

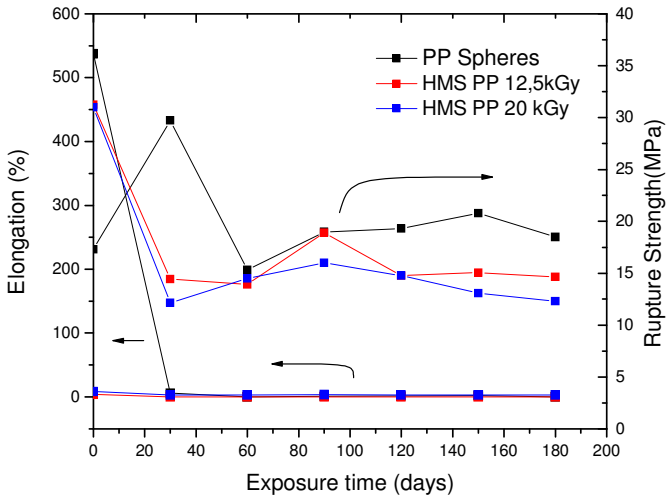


Fig. 2 – Results of elongation (%) and rupture strength (MPA) of the iPP and HMS-PPs, samples aged in natural exposition along six months.

The FTIR results, as illustrated in figure 3, indicate the formation of oxidized groups by the presence of peaks in the range 1700-1600 cm^{-1} . This spectrum profile is observed after 4 months of exposition to natural ageing.

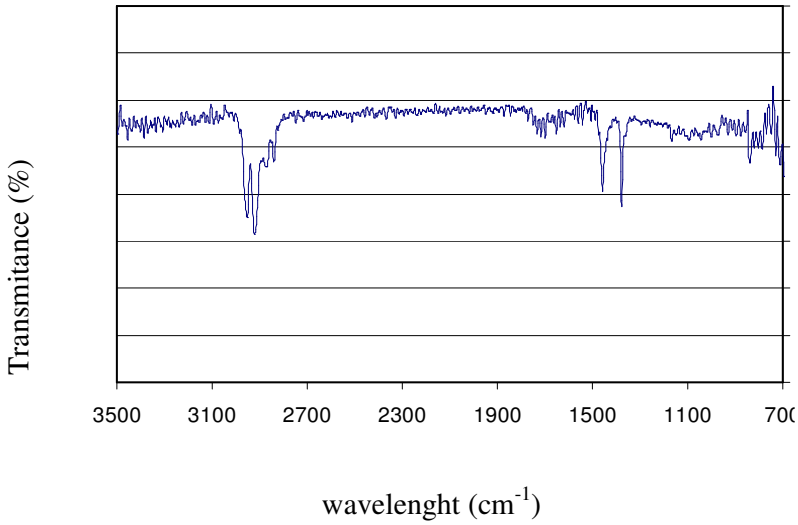


Fig. 3 – Illustration of the infrared spectrum by ATR technique of the HMS-PP 20 kGy after 4 months aging.

The TGA results of decomposition are shown in fig.4. As expected, the degradation degree of the samples was not sufficient to produce small fragments to be detectable by the TGA technique, and in consequence all degradation profiles are similar.

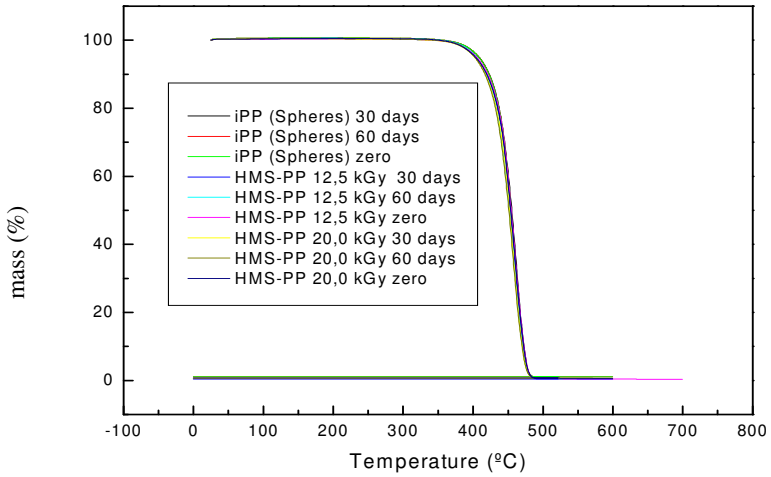
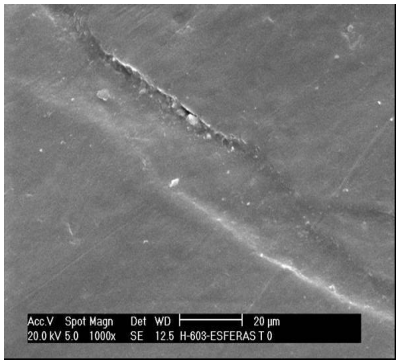


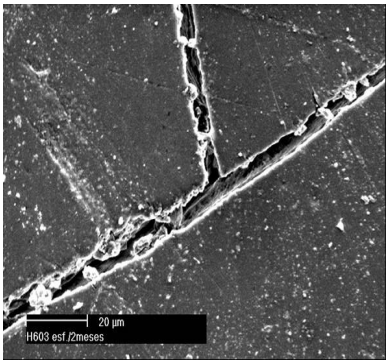
Fig. 4 - TGA Curves of mass (%) in function of temperature at heating rate of 10 $^{o}Cmin^{-1}$, to iPP and HMS-PPs.

It is known that thermo-oxidation is initiated by the reaction of free radicals with oxygen to form peroxide radicals. In spite of that, the concentration of free radicals can be significantly increased by interaction with light, ionizing radiation. The peroxide radicals undergo slower propagation reactions that break down the polypropylene chains. At the end of the process there is a rapid increase in degradation leading to a significant reduction in the mechanical properties of the polypropylene [9].

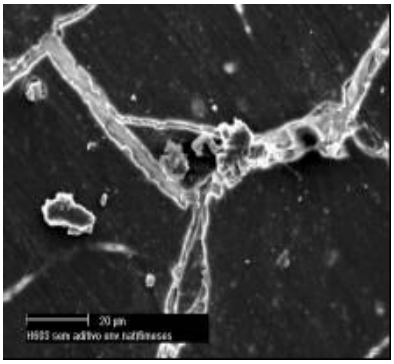
The SEM analysis (fig 5) shows interesting aspects of the fractured surface of the materials, as a result of the process of chain scissions. The cracks initiated in the second month of exposition and gradually increase with exposure time. The propagation of the fractures in the sample increases the surface exposed to the ageing agents. As a consequence, the photo-oxidation mechanism is developed in an affected surface layer. Similar results were reported describing the study of UV exposition of PP samples [5].



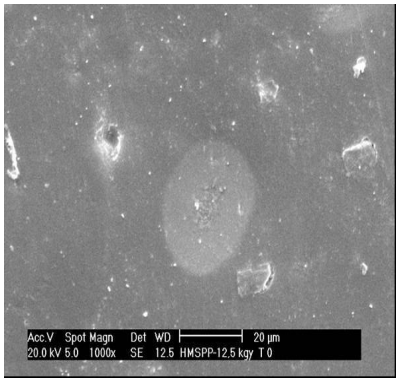
PP (spheres) not aged.



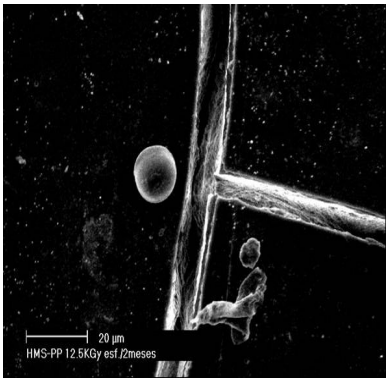
PP (spheres) 2 months natural ageing.



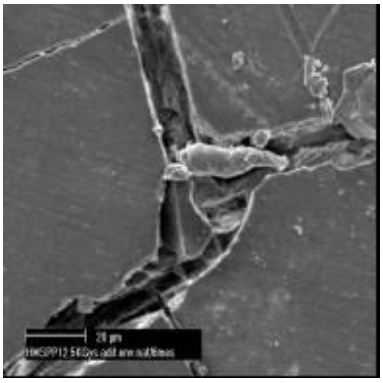
PP (spheres) 6 months natural ageing.



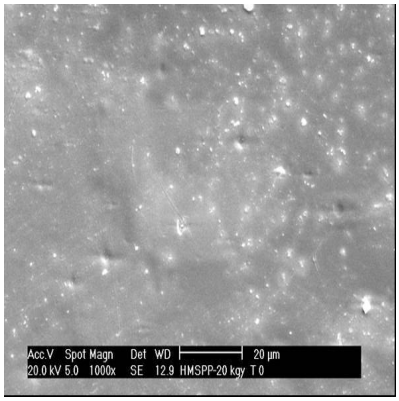
HMS-PP 12,5 kGy not aged.



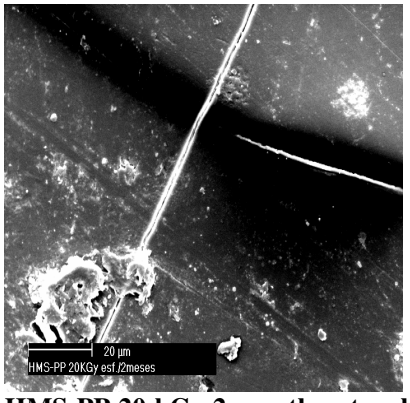
HMS-PP 12,5 kGy 2-month natural ageing.



HMS-PP 12,5 kGy 6-month natural ageing.



HMS-PP 20 kGy not aged.

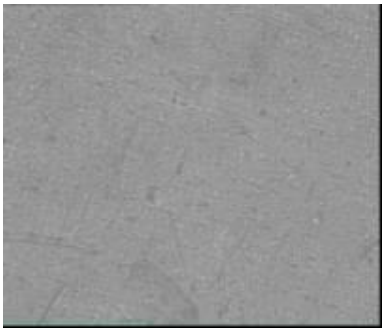


HMS-PP 20 kGy 2-month natural ageing.

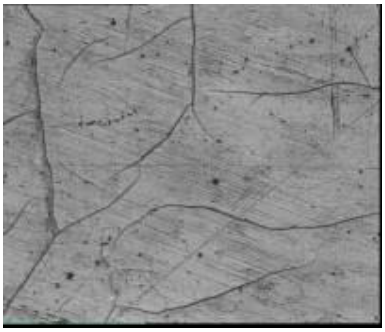
HMS-PP 20 kGy 6-month natural ageing.

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

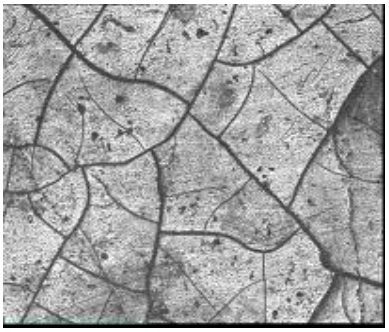
The light microscopy (LM) at magnification of 125 times has shown the frequency of cracks;(fig 6). HMS-PP 20 kGy presented the highest frequency of fractures, and after it the HMSPP 12,5 kGy. In the end, the lowest frequency was observed in the PP sample. Important effects were also observed by LM technique and are reported in literature[8].
Those results indicated that the HMS-PPs are less stable to natural ageing when compared to the PP material. As the radiation process is, in principle, a degradative process, the material became more sensitive to the ageing causes.



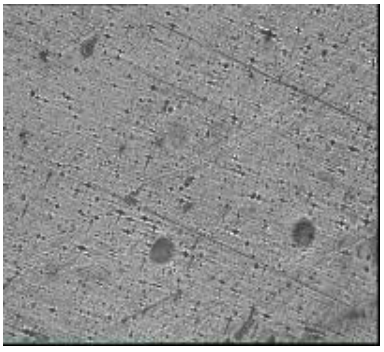
PP (spheres) not aged.



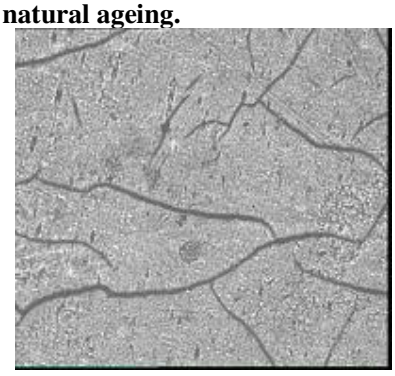
PP (spheres) with 2–month natural ageing.



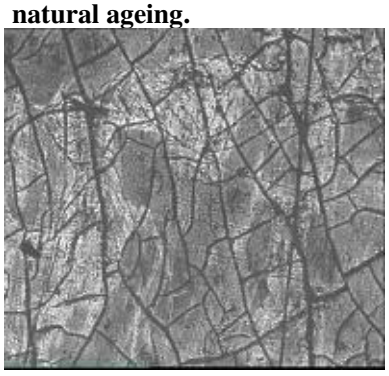
PP (spheres) with 6-month natural ageing.



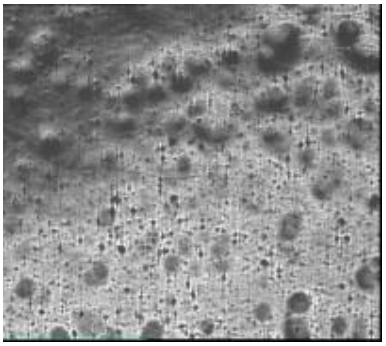
HMS-PP 12,5 kGy not aged.



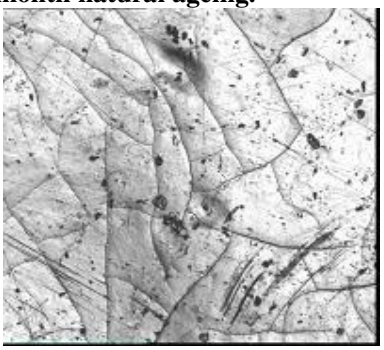
HMS-PP 12,5 kGy with 2-month natural ageing.



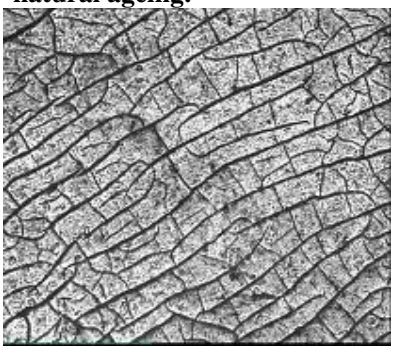
HMS-PP 12,5 kGy with 6-month natural ageing.



HMS-PP 20 kGy not aged.



HMS-PP 20 kGy with 2–month natural ageing.



HMS-PP 20 kGy with 6-month natural ageing.

Fig. 6 – Photomicrographs obtained by LM, 125 times magnification, to iPP and HMS-PP aged naturally in São Paulo – IPEN-CQMA.

Conclusion

A comparison of the LM, SEM, associated to a mechanical test was quite satisfactory to monitor the degradation of HMS-PP. The mechanical properties results showed the competition of degradation and crosslinking effects.

The HMS-PPs presented more sensitivity to natural ageing compared to the PP. Chiefly, the surface exposed of HMS-PP 20kGy showed the highest frequency of cracking.

According to literature, the important factor of polypropylene degradation is the weathering photo-oxidation. It refers to the chemical and physical changes that occur when radiation is absorbed by a polypropylene. Solar radiation starts the photo-degradation process, which results in the absorption of UV radiation by impure chromophores and in the activation of excited states in macromolecules. The intensity of the UV radiation decreases dramatically in the material, so that the reaction tends to be nearly a surface process [9].

Acknowledgements

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