

EFFECTS OF THERMAL AGEING ON HMS-PP CRYSTALLINITY

Washington L. Oliani, Duclerc F. Parra, Luis F. C. P. Lima and Ademar B. Lugão

Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP
Av. Prof. Lineu Prestes, 2242
05508-900 São Paulo, SP
washoliani@usp.br

ABSTRACT

The isotactic polypropylene is a linear polymer which exhibits 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 significant enhanced melt strength. This process, which is sometimes termed visbreaking, thus provides improvement of rheological properties. HMS-PP (High Melt Strength Polypropylene) was obtained by the irradiation in atmosphere of acetylene as crosslinker agent. It was employed doses of 12.5 and 20 kGy of gamma radiation. The objective of this study is to investigate the effects of thermal ageing on the crystallinity level and chemical structure of HMS-PP. The thermal stability of the HMS-PP was evaluated after thermal ageing of samples using a stove at temperature of 90 °C, in presence of air at different periods of time. The samples submitted to the thermal ageing were characterized by: thermogravimetry (TGA), differential scanning calorimetry (DSC), infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Since the long-term engineering properties of HMS-PP are intrinsically linked with the polymer microstructure, there is significant interest in understanding the effects of ageing, particularly due to prolonged exposure at service temperatures. In thermo-oxidative conditions, the formation of the oxidation products essentially involves a hydrogen abstraction by the peroxy radicals, leading to hydroperoxides as primary products and chemical degradation in the immediate crack tips. Oxidative degradation on the network of HMS-PP, created by radiation process of PP, was revealed by the analytical results showing the susceptibility of HMS-PP to thermal oxidative degradation. Yellowing of the samples surface and oxidative products of degradation among other evidences were observed.

1. INTRODUCTION

Radiation processing of polymeric materials is one of the main steps in certain modern technologies, and has extensive applications. Radiation-induced (crosslinking, grafting, etc.) modifications are commonly used to improve the creep behavior, thermal resistance, surface tension, adhesion properties, miscibility or compatibility with other polymers. Two main effects result when polyolefins (POs), such as isotactic polypropylene (iPP), are subjected to ionizing radiation: crosslinking and scission of macromolecules. The domination of these competitive processes is controlled by the structural peculiarities of the polymers and the experimental irradiation conditions such as atmosphere, radiation dose, dose rate, sample thickness, irradiation temperature and antioxidants and antirads agents [1].

The properties of iPP are intrinsically linked to the polymer microstructure and there is significant interest in understanding the effects of ageing on that, particularly due to prolonged exposure at service temperatures. A common approach for characterizing ageing response in a more practical time frame is to conduct accelerated ageing tests at temperatures above the expected service limits [2].

It is well known that the instability of polypropylene to thermal photo and radiation-oxidation is due to presence of tertiary hydrogen atoms in the polymer chain. Several studies have been

carried out on the thermal and photooxidative degradation of polypropylene in order to clarify the mechanisms of these reactions and to establish methods of stabilization for this resin [3].

The morphology of pristine iPP has a strong effect on the micro-mechanisms of deformation of irradiated samples at yield. The chain scission and cross-linking affect the response of the material, particularly at high temperatures. Two factors achieve resistance to deterioration of mechanical properties after irradiation: low crystal thickness and high tie chain density. Low crystal thickness favors crystal shear, giving a lower tendency for perpendicular cavitation, and thus less stress on the crystals. This means that brittle failure is less likely to occur. A high tie-chain density dilutes the effect of chain scission and cross-linking and there is therefore less effect on the fibril strength and propagation, thus creating a stable deformation zone and ductile behavior. Low crystal thickness and high tie-chain density are both achieved by low crystallization temperatures [4].

In thermal ageing of semicrystalline polymers, the mobility of molecular segments is increased by thermal activation even with no changes in the molecular size. The resultant annealing leads to secondary crystallization, which is facilitated by oxidative chain scission. It occurs at different rates depending on the depth below the surface and is influenced by oxygen diffusion and consumption in the polymer. Contraction of the surface layers is a consequence of chemicrystallization and results in surface cracks, one of the reasons for embrittlement of ductile semicrystalline polymers [5].

For the determination of the thermooxidative stability plastic materials, samples are usually subjected to accelerated ageing in an oven. To increase the effect of accelerated ageing even further in order to obtain faster estimates of a possible lifetime, measurement of the thermooxidative stability at temperatures above the melting point of the polymer has been suggested [6].

The concentration of peroxy radicals (and hydroperoxides) is, because of autoxidation, much greater than that of alkyl radicals ($\text{ROO}\bullet : \text{R}\bullet \gg 1$), which react immediately with oxygen dissolved in the polymer and form further peroxy radicals [7].

Gugumus [8, 9] investigated the ageing of polypropylene films temperatures between 60 and 150°C. Along with monitoring of the mechanical properties of polymers in the course of ageing, it is also possible to measure oxidation products resulting from thermooxidative degradation. Monitoring of the intensity of the C=O absorption in the IR-spectrum provides information regarding the progress of ageing [6].

The higher the stereoregularity of a polymer, with little or no chain branching, the more likely it is to exist in a crystalline state. The actual degree of crystallinity of polypropylene will depend on the process of manufacture of the polymer. Branching will increase the susceptibility of a polymer chain to thermal oxidation because of the reactivity of the tertiary carbon at the branch point [10].

TGA results under N_2 with heating rate of $10^\circ\text{C min}^{-1}$ show that polyethylene (PE) and iPP only start to decompose above 350°C, while in a comparable TGA experiment in oxygen much lower decomposition temperatures were found. From TGA results under inert atmosphere it is clear that at processing temperatures polypropylene and polyethylene hardly

degrade in the absence of oxygen. The same is the case for many other polymers, only at very high temperatures they tend to degrade in an inert atmosphere, but in all cases this degradation is accelerated by introducing oxygen [11].

In many types of degradation the interference of oxidative attack, which has an accelerating role, happens, i.e., autooxidation. However, in oxidative degradation, the most commonly known phenomena are photooxidation and thermal oxidation ($T < 300^{\circ}\text{C}$) and the effects are color changes, hardening, and surface cracking or flaking. Phenomena that are mainly differentiated by the initiation step, since other aspects are similar [12].

If an elevated temperature is applied to a polymer in the presence of an aggressive chemical agent (often oxygen) then this may give rise to chemical reactions that may occur only very slowly, or not at all, at ambient temperature. During both thermal oxidation and photo-oxidation, chain scission occurs with releasing of molecular chain segments from entanglements, facilitating conformational rearrangements. This allows the chain segments to take up lower energy states, characteristic of the equilibrium state for the material, so accelerating physical ageing. The material is changed irreversibly by the scission events; the physical ageing occurs alongside the changes and it is not always obvious which has the controlling influence over the material properties [13].

Fayolle et al [14], describe two distinct ageing in oven: 1) at 110°C under air atmospheric pressure, 2) 80°C under pure oxygen at 5 MPa pressure. Very different kinetic behaviors were observed since induction times differ at about one order of magnitude. In both cases, M_w decreases abruptly after the end of the induction period showing that oxidation induces predominant chain scission which in turn, induces chemicrystallization and embrittlement. It was employed doses of 12.5 and 20 kGy of gamma radiation.

In this study the effects of thermal ageing of high melt strength polypropylene (HMS-PP) [15] were evaluated.

2. EXPERIMENTAL

2.1. Materials and Methods

The investigation was conducted with the following polypropylenes:

- iPP (spheres), with Melt Flow Index (MFI) of 2.9 dg min^{-1} , not stabilized.
- HMS-PP obtained at the dose 12.5 kGy with MFI of 28.0 dg min^{-1} , not stabilized.
- HMS-PP obtained at the dose of 20 kGy with MFI of 39.0 dg min^{-1} , not stabilized.

The HMS-PP samples were obtained from iPP spheres by irradiating with gamma rays in the presence of acetylene at 12.5 kGy and 20 kGy of total dose [16,17]. After irradiation, the samples were heated for 60 min at 90°C to eliminate residual radicals. The HMS-PP samples were obtained by irradiation of ^{60}Co source, at a dose rate of 10 kGy h^{-1} monitored with Harwell Red Perspex 4034.

The dumbbell samples were manufactured by mold pressure at temperature of 190°C at dimensions type IV according to ASTM D 638-03 [18].

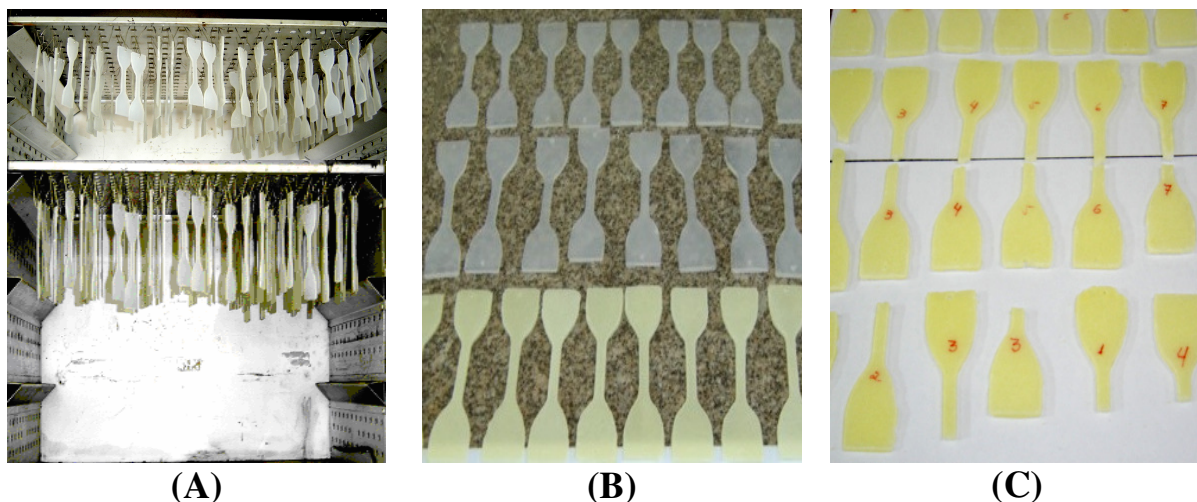


Figure 1. Experiment arrangement of the iPP and HMS-PP samples inside air circulation stove at the temperature of 90°C (A). Samples iPP before (up) and after (down) ageing in stove (B). Yellowing of HMS-PP 12.5 kGy and HMS-PP 20 kGy samples after ageing in stove (C).

iPP and HMS-PPs samples were set inside stove at temperature of 90 °C, in presence of air. Thermal stability was evaluated at different periods of time (6, 12 and 20 days), according to ASTM D 3045-2003 [19].

2.1.1. Thermogravimetry (TGA)

Thermogravimetry (TG) was recorded with a Mettler-Toledo TGA/SDTA 851 thermobalance in nitrogen atmosphere of 50 mL min⁻¹, in the range from 25 up to 600 °C at a heating rate of 10 °C min⁻¹. Samples at about 10 mg were placed in alumina pans, according to ASTM D 6370-2003 [20].

2.1.2. Differential Scanning Calorimetry (DSC)

The thermal behavior of pristine and irradiated polypropylenes was examined in a DSC Mettler Toledo apparatus. Samples (10-15 mg) were heated from -50 °C to 280 °C, at heating rate of 10 °C min⁻¹ under nitrogen atmosphere. The holding for 5 min at 280 °C, then cooled to -50 °C and reheating to 280 °C at 10 °C min⁻¹, according to ASTM D 3418-03 [21].

$$X_c(\%) = \frac{\Delta H_f \times 100}{\Delta H_0}$$

ΔH_f = melting enthalpy of the sample, ΔH_0 = melting enthalpy of the 100% crystalline PP which is assumed to be 209 kJ kg⁻¹.

2.1.3. Infrared Spectroscopy (FTIR)

The analyses were performed using attenuation total reflectance accessory (ATR) by a Thermo-Nicolet spectrophotometer, model 670 FTIR. The samples were prepared in the pastilles device accessory using the proportion samples: KBr (1:100).

2.1.4. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was done using an EDAX PHILIPS XL 30. Magnification was used on the fracture region to observe the fracture surface and transversal cut of the samples. The nonconducting materials, like most of polymers, need to be coated using a metal including silver, gold or gold-palladium, or carbon to their outer surfaces conductive. In this work, very thick coating of gold is sputter-coated onto the samples.

The coated surface often exhibits a series of granular particles of metal, which at high magnification can be resolved and misinterpreted as a granular feature of the specimen [22,23].

3. RESULTS AND DISCUSSION

3.1. Thermogravimetry (TGA)

The TG results indicated decomposition of the samples.

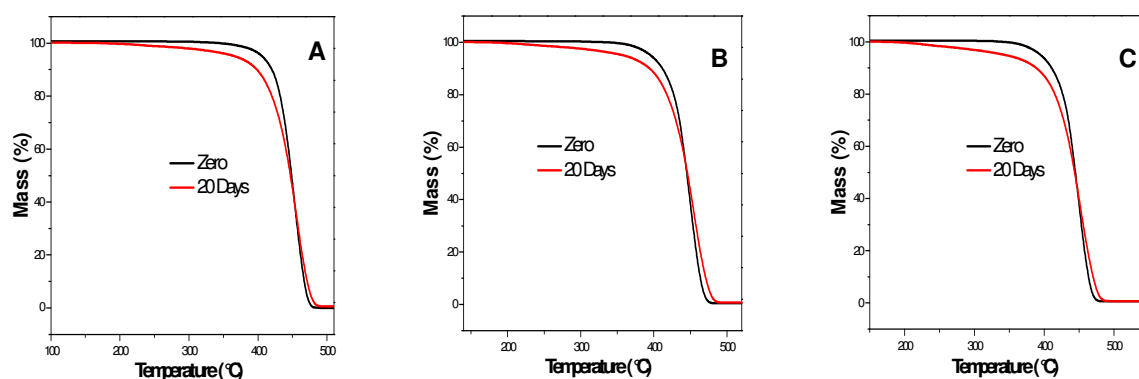


Figure 2. TG curves of samples: iPP (A), HMS-PP 12.5 kGy (B) and HMS-PP 20 kGy (C), under thermal ageing in stove for 20 days.

As observed in the curves, Fig. 2 A, significant variation of temperature in the onset point of decomposition ($439 \rightarrow 419$ °C) in samples. In the Fig. 2B, the onset temperature of decomposition of the sample pristine and aged samples for 20 days are ($430 \rightarrow 424$ °C). In

Fig. 2C, the temperature after 20 days is 418 °C while not aged is 432 °C. The higher difference between samples onset temperatures is evident in iPP, because the effect of scission chain is more accentuated in the non irradiated polyolefins. Volatile products displaced the Tonset to lower values. The decomposition profile (one step) does not change with the ageing time. Oxidized products of chain termination can cause the increasing of the end set temperature.

3.2. Differential Scanning Calorimetry (DSC)

Due to the non-equilibrium feature of the crystal structure of polymers, under favorable thermal conditions (such as during the heating for recording melting curves), perfection of the structure may proceed within the given crystalline modification. The shape of the calorimetric melting curve, the melting profile, provides valuable information about the complexity of the melting process as well as about the thermal history, structural characteristics and stability of the sample. Melting profiles of iPP may be very diverse. Often two or more peaks appear in the melting curve. Duplication or multiplication of melting peaks can be attributed to structural reasons and processes. For this reason, beside the main melting peak of folded-chain crystallites, a higher temperature peak or shoulder appears on the melting curve [24].

The comparison of crystallinity is usually performed in the second heating curves. In this controlled situation defected crystals have time to segregate.

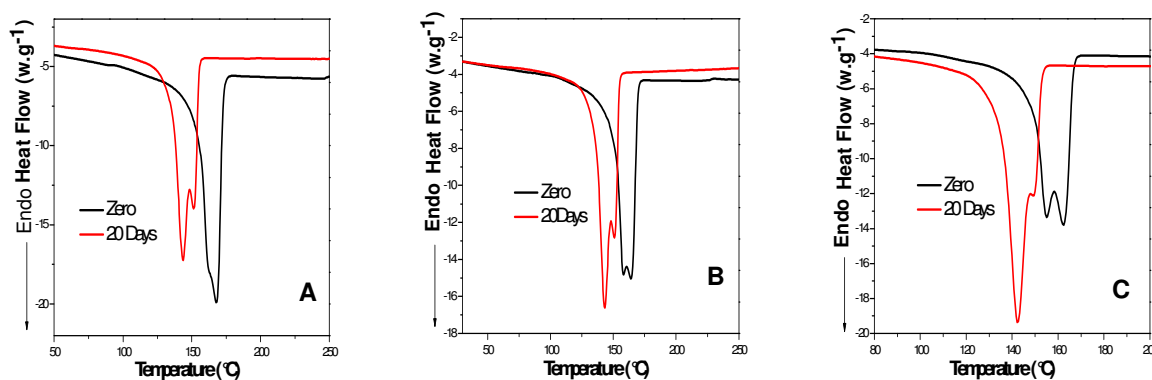


Figure 3. DSC second melting curves of samples: iPP (A), HMS-PP 12.5 kGy (B) and HMS-PP 20 kGy (C), second heating segment, after thermal ageing in stove for 20 days.

The melting temperature displacement (at about 15 °C), Fig.3, indicates morphology modifications of the samples crystalline phase. Decreasing in melting temperature demonstrate that chain scission is the main mechanism of degradation.

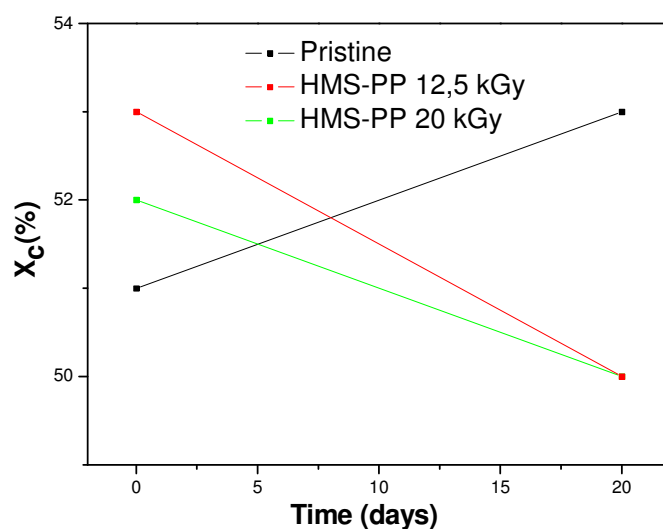


Figure 4. Crystallinity measurement of polypropylene after 20 days ageing time.

It was observed decrease of crystalline phase in HMS-PP 12.5 kGy and HMS-PP 20 kGy, Fig.4, owing to chain scission mechanisms on ageing. Contraction of the surface layers is a consequence of chemicrystallization and results in surface cracks.

3.3. Infrared Spectroscopy (FTIR)

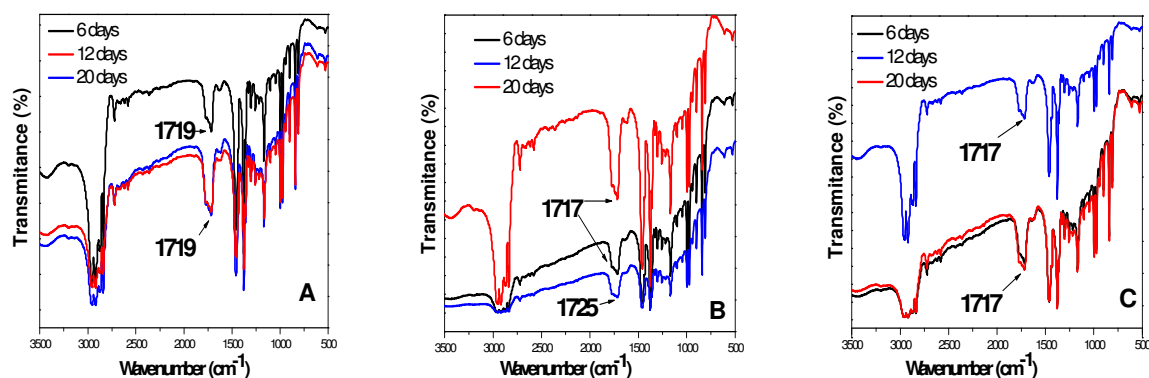


Figure 5. Illustration of the infrared spectrum by ATR technique of the: iPP (A), HMS-PP 12.5 kGy (B) and HMS-PP 20 kGy (C), under thermal ageing in stove for 20 days.

The iPP, HMS-PP 12.5 kGy and HMS-PP 20 kGy, aged in stove for 20 days show typical absorption bands of carbonyl stretching in the region 1717-1725 cm^{-1} , Fig.5, indicating a substantial content of oxidation products. During thermooxidative ageing in a circulation air oven, the polymer undergoes thermooxidative degradation. Carboxylic and carbonyl groups are present in the end products of this oxidation.

3.4. Scanning Electron Microscopy (SEM)

Magnification was used on the fracture region to observe the fracture surface.

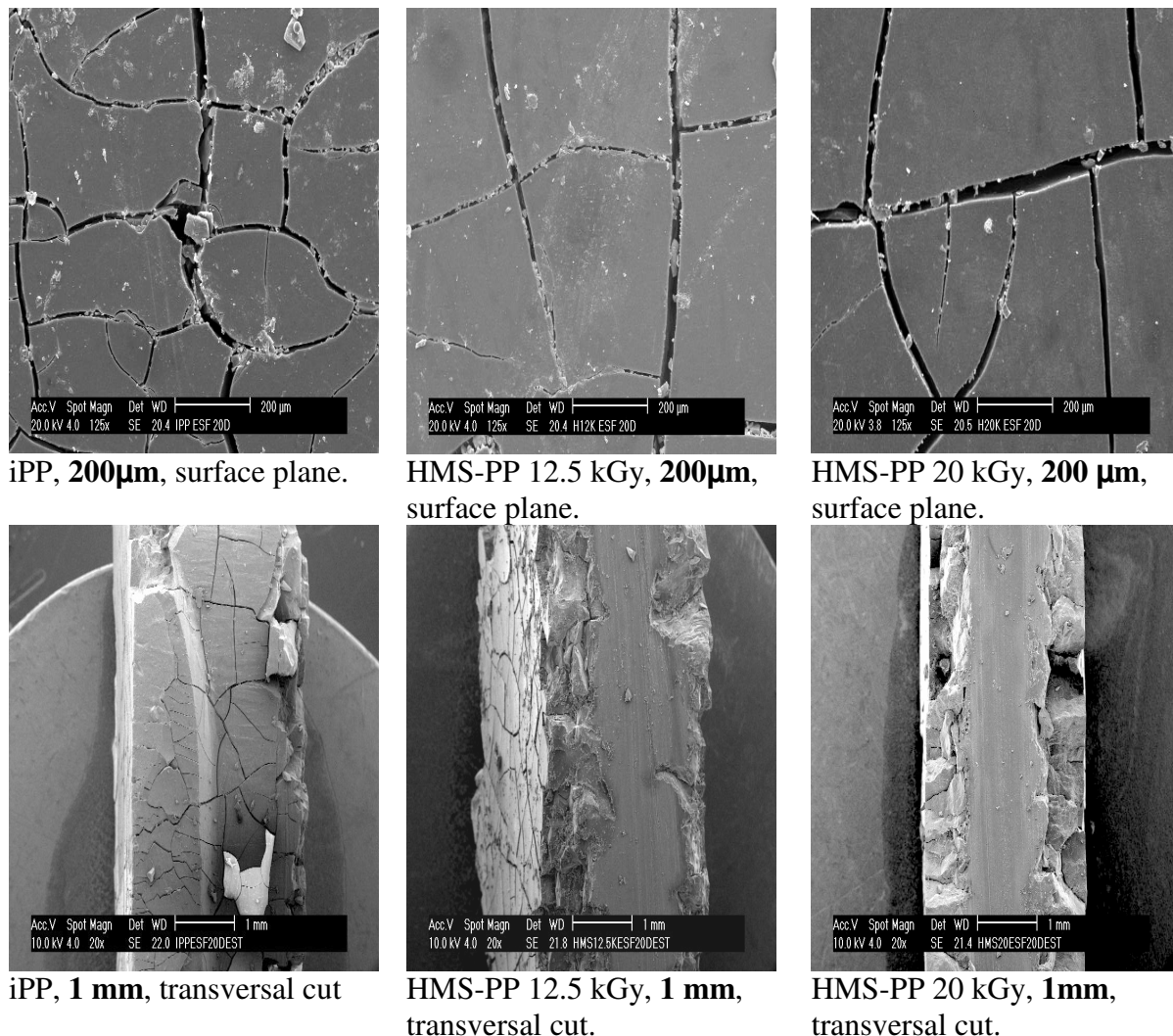


Figure 6. Development of cracks in surface plane, 200 μm scale, and surface plus transversal cross section (at 30° - 45° of the samples corner), 1 mm scale, times 20 days.

These exposed surfaces show cracks propagation that increases with the ageing time in stove and penetrate the layer near surface. The diffusion of oxygen is considered as significant in accelerated test, especially in rapidly oxidizing polymers. Essentially all polyolefins, and particularly polyethylene and polypropylene, oxidize exclusively in the amorphous phase because the crystalline phase is impermeable to oxygen [3, 5].

The SEM analysis, Fig. 6, shows interesting aspects of the fractured surface of the materials, as a result of the process of chain scission. The cracks are more pronounced in iPP than HMS-PP 12.5 kGy and HMS-PP 20 kGy. A possible explanation to this fact is the crosslinking formation in irradiated samples with formation of protection barrier to oxygen diffusion. Intense changes in material properties were showed after thermal ageing as well as

colour yellowness, crack formation, weight loss, surface roughness and changes in morphology.

4. CONCLUSIONS

The effects of thermal ageing on iPP and HMS-PPs were mainly the intense crack formation. Chain scission and oxygen diffusion were more evident in the iPP. Surface cracks showed propagation that increases with the ageing time. The HMS-PP 12.5 kGy and HMS-PP 20 kGy samples have more resistance than iPP to crack propagation.

ACKNOWLEDGMENTS

The authors acknowledge CNPq (The National Council for Scientific and Technological Development), process 382891/2007-4 (NV) for grants, FAPESP, CAPES ; Sandra M. Cunha for FTIR analysis and the Centre of Materials Science and Technology – CCTM/IPEN, for microscopy analysis (SEM).

REFERENCES

1. E. Suljovrujic, "The influence of molecular orientation on the crosslinking/oxidative behaviour of iPP exposed to gamma radiation", *European Polymer Journal*, **45**, pp. 2068-2078 (2009).
2. A. Law, L. Simon and P. L. Sullivan, "Effects of thermal aging on isotactic polypropylene crystallinity", *Polymer Engineering and Science*, **48**, pp. 627-633 (2008).
3. T. Kagiya, S. Nishimoto, Y. Watanabe and M. Kato, "Importance of the amorphous fraction of polypropylene in the resistance to radiation-induced oxidative degradation", *Polymer Degradation and Stability*, **12**, pp. 261-275 (1985).
4. X. C. Zhang, M. F. Butler and R. E. Cameron, "The relationships between morphology, irradiation and the ductile-brittle transition of isotactic polypropylene", *Polymer International*, **48**, pp. 1173-1178 (1999).
5. J. Pospisil, Z. Horak, J. Pilar, N. C. Billingham, H. Zweifel and S. Nespurek, "Influence of testing conditions on the performance and durability of polymer stabilizers in thermal oxidation", *Polymer Degradation and Stability*, **82**, pp. 145-162 (2003).
6. H. Zweifel, *Stabilization of Polymeric Materials*, Springer-Verlag, Berlin (1998).
7. H. Zweifel, *Polymer Durability. Degradation, Stabilization, and Lifetime Prediction*. Edited by : R.L.Clough, N.C.Billingham, and K. T.Gillen, (1996).
8. F. Gugumus, *Conference Proceedings*, Rapra Technology Ltd., (1995)
9. F. Gugumus, "Effect of temperature on the lifetime of stabilized and unstabilized PP films", *Polymer Degradation and Stability*, **63**, pp. 41-52 (1999).
10. M. Philip and J. Attwood, *Evaluation of Weathering in mixed Polyethylene and Polypropylene Products*. Published by: The Waste & Resources Action Programme (2004).
11. P. Gijsman, "Review on the thermo-oxidative degradation of polymers during processing and in service", *e-Polymers*, **065**, pp. 1-34 (2008).
12. C.Vasile, *Handbook of Polyolefins: Synthesis and Properties*, Edited by Cornelia Vasile and Raymond B. Seymour (1993).

13. J. R. White, "Polymer ageing: physics, chemistry or engineering? Time to reflect", *Comptes Rendus Chimie*, **Vol. 9**, pp. 1396-1408 (2006).
14. B. Fayolle, E. Richaud, J. Verdu and F. Farcas, "Review: degradation-induced embrittlement in semi-crystalline polymers having their amorphous phase in rubbery state", *J. Mater. Sci.*, **Vol. 43**, pp. 1026-1032 (2008).
15. D.F. Parra, A. Yoshiga, H. Otaguro, L.F.C.P. Lima and A.B. Lugão, "Controlled degradation and crosslinking of polypropylene induced by gamma radiation and acetylene", *Polym. Bull.*, **Vol. 63**, pp. 397-409 (2009).
16. A. B. Lugão, *Tese de Doutorado*, Instituto de Pesquisas Energéticas e Nucleares – (IPEN/CNEN/USP) (2004).
17. A. B. Lugão, *U. S. Patent 0171712*, (2004); Process for preparing high melt strength polypropylene and crosslinked prepared therewith.
18. ASTM D 638-03 – *Standard Test Method for Tensile Properties of Plastics*.
19. ASTM D 3045-92 (Reapproved 2003) - *Standard Practice for Heat Aging of Plastics without Load*.
20. ASTM D 6370-99 (2009) – *Standard Test Method for Rubber – Compositional Analysis by Thermogravimetry (TGA)*.
21. ASTM D 3418-03 – *Standard Test Method for Transition Temperatures of Polymers by Differential Scanning Calorimetry (DSC)*.
22. J. Goldstein, D. Newbury, D. Joy, C. Lyman, P. Echlin, R. Lifshin, L. Sawyer and J. Michael, Scanning Electron Microscopy and X-Ray Microanalysis. In: Goldstein, J., Newbury, D., Chapter 12, *Specimen Preparation of Polymer Materials*, 3^a ed., Springer Science, pp. 565-589 (2003).
23. L. C. Samyer and D.T. Grubb, *Polymer Microscopy*, Chapman & Hall (1996).
24. J. Karger-Kocsis, *Polypropylene: Structure, blends and composites*, In: J. Varga, Chapter 3, Crystallization, melting and supermolecular structure of isotactic polypropylene, Chapman & Hall, London, pp. 56-113 (1995).