STUDY OF HIGH MELT STRENGTH POLYPROPYLENE (HMS-PP) UNDER THERMAL AGEING

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Abstract

The irradiation of PP to obtain HMS-PP allows introducing energy into the material to generate favorable changes, when used in adequate doses. On the other hand, the stability to ageing of HMS-PP obtained by radiation process have not been evaluated until yet.

In this study HMS-PP was obtained by the irradiation in atmosphere of acetylene as crosslinker agent. It was employed doses of 12.5 kGy and 20 kGy of gamma radiation. Thermal treatment was used as a post irradiation in order to permit the annihilation of the remaining radicals. The thermal stability of the HMS-PP was evaluated in stove at temperature of 90 °C, in presence of air at different periods of time.

Physical and Mechanical properties were monitored during the ageing by the techniques of Tensile Mechanical Test, Thermogravimetry (TGA), Differential Calorimetry (DSC), Scanning Electronic Microscopy (SEM) and Optical Microscopy (MO).

Oxidative degradation on the network of HMS-PP, formed in the 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, loss of mechanical property of tension strength, oxidative products of degradation among other evidences were observed.

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, chemical degradation in the immediate crack tips.

Introduction

Polypropylene is a material that cannot be processed without adequate stabilization, and products made of this material have to be particularly well stabilized against thermo and photooxidative degradation [1,3].

Thermally initiated oxidation and degradation of unstabilized iPP can occur at temperatures as low as room temperature. The ease abstraction of hydrogen of tertiary carbon by oxidative species leads to tertiary oxidation products [2].

During thermooxidative degradation in a circulating air oven, the polymer undergoes thermooxidative degradation [1].

The oxygen attack is favored by temperature dispending of sample characteristics. Most polyolefins are quite stable at ambient temperature. The formation and decomposition of hydroperoxides constitute the key step of the degradation process [4].

The chemical changes accompanying thermal oxidation of PP consist mainly in the formation of aldehydes, ketones, carboxylic acids, esters. The physical changes resulting from the thermal oxidation of PP are essentially the consequence of main chain scissions. As a matter of fact it lead to a decreasing in polymer molecular weight and consequently, gradual reduction of the mechanical properties [3].

One of the structural peculiarities of PP is the presence of primary, secondary and tertiary hydrogen atoms. Although tertiary hydrogen atoms are most labile, oxidative attack of hydrogen atoms cannot be neglected in PP [3,4].

Degradation of PP with peroxides is believed to occur by a series of free radical reactions involving steps as initiation, scission, transfer, and termination [5].

Radiation processing was used early for polymer modification. The irradiation of polymeric materials with ionizing radiation (gamma rays, X-rays, accelerated electrons, ions beams) leads to the formation of very reactive intermediates, free radicals, ions and excited states [6].

Irradiation of iPP by gamma rays creates very energetic ions and excited states, which decay to reactive free radicals [5, 12].

High energy radiation induces structural modifications in the exposed polymers due to the consumption of transferred energy on material macromolecules. The thermally stimulated release of energy are trapped by moieties of molecules (branching chains, methylene groups, parts of other molecules) [7].

The degree of transformation depends on the structure of the polymer and the conditions of pre-treatment, during and after irradiation as well as dose rate [5, 12].

Depending on the process and atmosphere the product of irradiation is a high melt strength PP (HMS-PP).

The HMS-PP has gaining market in the Europe with production of foams and fibers [8].

The HMS-PP, modified polypropylene by grafting under high energy ionizing radiation, is prepared in the presence of acetylene atmosphere that promotes crosslinking [8,9].

The most important chemical changes that occur during the irradiation of polymers are those of crosslinking and degradation. From the point of view mechanical properties as polymer materials, crosslinking of polymers leads to increasing hardness, tensile strength and to decreasing elongation [10].

On the other hand, degradation of polymers due to main chain scission leads to the opposite effects on the mechanical properties [10].

Generally, radiation crosslinked plastics constitute a technical and economical compromise between engineering plastics that failed and high performance plastics, often overtailored and expensive [11].

Irradiation polymeric products are believed to be more fragile.

In this work the thermal stability of HMS-PP is evaluated after thermal ageing.

Experimental

Materials and samples

The investigation was conducted with polypropylene (spheres not stabilized) and polypropylenes (HMS-PP), obtained by spheres irradiation.

The HMS-PP samples were obtained by irradiating with gamma rays of ^{60}Co source, at a dose rate of 10 kGy. h^{-1} monitored with Harwell Red Perspex 4034.

In presence of acetylene the process were carried out at 12.5 kGy and 20 kGy of total dose [9]. After irradiation, the samples were heated for 60 min at 90ºC to eliminate residual radicals.

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

Samples of PP and HMS-PP were disposed inside stove at temperature of 90 °C, in presence of air circulation. Thermal stability was evaluated at the different periods of time (6, 12 and 20 days), according to ASTM D 3045-92 (Reapproved 2003).

Figure 1 - The disposal to the samples of the PP and HMS-PP inside of stove with air circulation, at the temperature of 90 °C.

Mechanical Tests

The tests were performed with an EMIC DL 3000 electromechanical tensile machine. Longitudinal strain was measured by an extensometer and video-traction system. Tensile test was applied to evaluate the strength (τ, MPa) and elongation at break (ε, %) at 23°C, in EMIC equipment, according to ASTM D 638-03.

Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) 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 at 10 °C.min^{-1}. Samples at about 10 mg were placed at alumina pans, according to ASTM D 6370-99 (Reapproved 2003).

Differential Scanning Calorimetry (DSC)

The thermal behavior of pure and irradiated polypropylenes was examined in a DSC Mettler Toledo apparatus. Samples (10-15 mg) were tested at heating rate of 10 °C.min^{-1} from -50°C to 200°C under nitrogen atmosphere, 10 min at 200°C, followed by cooling at a rate -50° C.min^{-1} to -50°C and reheating to 200°C, according to ASTM D 3418-03.

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 fractures on transversal session and surface.

Optical Microscopy (MO)

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

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 to elongation [10]. In fact at time zero higher strength is noted in HMS-PP samples.

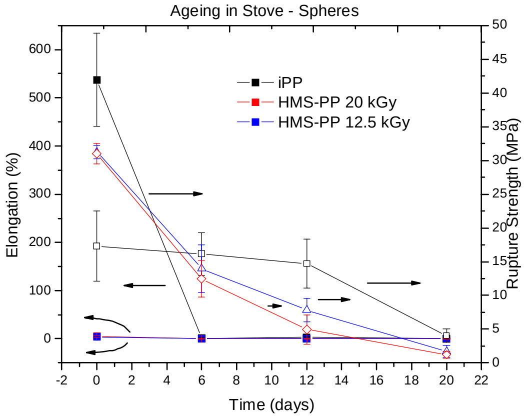


Figure 2 - The results of strength and elongation at break of PP, HMS-PP 12.5 and 20 kGy.

Under the thermal ageing, loss of strength and elongation at break was observed. The degradation caused was more pronounced in the HMS-PP while PP remains stable until six days and after this period it loss the mechanical resistance slowly.

Thermogravimetric Analysis (TGA)

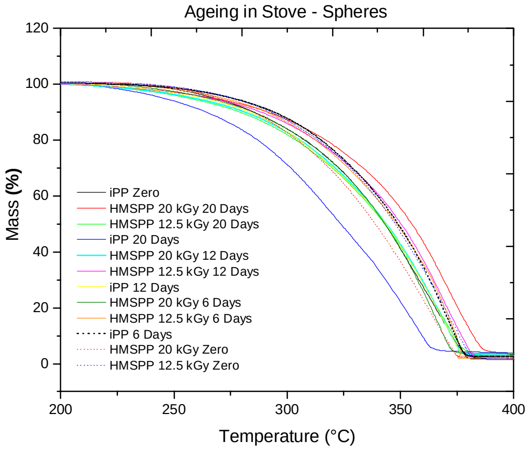


Figure 3 – TGA curves of mass (%) in function of temperature at heating rate of 10°C min^{-1}, to iPP, HMS-PP 12.5 and 20 kGy.

Comparing it to the curves of 6 days and 12 days is observed that decomposition (effect of chain scission) is more accentuated after 12 days.

The TGA profile presents less stability of PP 20 days comparing to the other profiles. The crosslinking partial of samples modified by radiation add to the material some resistance to decomposition.

It was observed that samples after 20 days ageing in stove they flow completely making impracticable the test.

Differential Scanning Calorimetry (DSC)

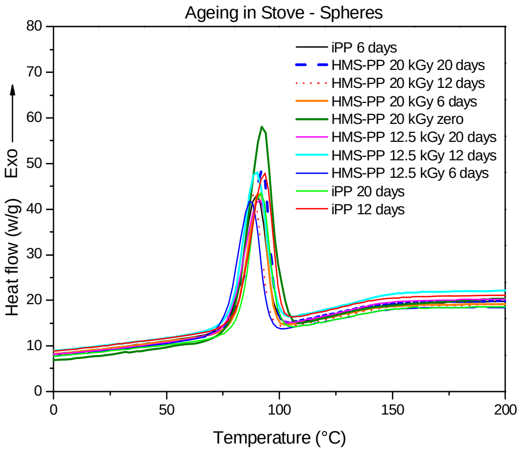


Figure 4 – DSC crystallization curves of PP and HMS-PP 12.5 and 20 kGy (cooling segment).

The crystallization peak of aged samples showed lower enthalpy owing to the difficult of crystallization after thermal degradation by scission. In some cases the crystallization are displaced to lower temperature reflecting the Mw decrease after scission mechanisms.

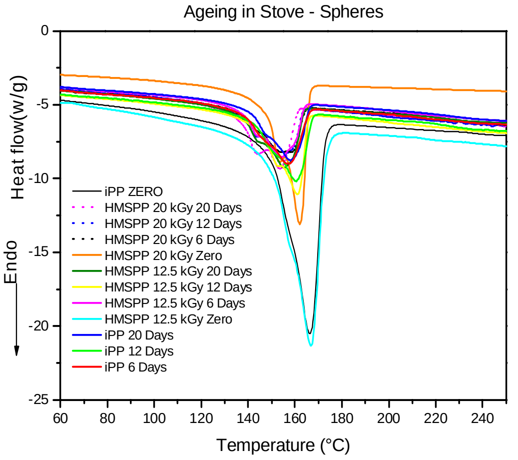
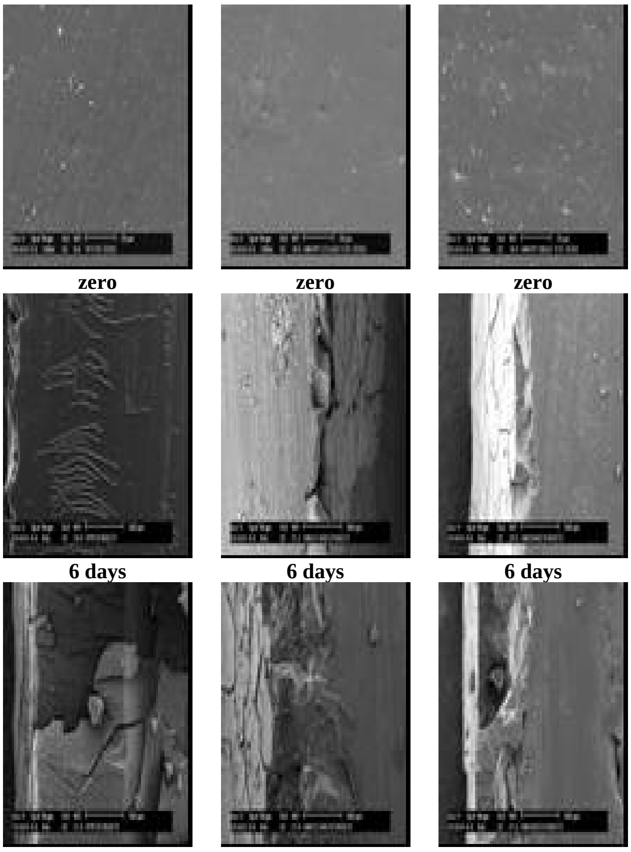


Figure 5 – DSC second melting curves of PP and HMS-PP 12.5 and 20 kGy (second heating segment)

It was observed decrease of crystalline phase also owing to chain scission mechanisms on ageing and corresponding with the effects observed in crystallization curves. The multiple fusion can be explained by the presence of the defective small molecules formed during the thermal degradation process. These small molecules contribute to the recrystallization process and imperfect and heterogeneous spherulites are formed also displacing the melting temperatures.

Scanning Electronic Microscopy (SEM)

Is evident that scission occurred more extensively at layers near the surface and the images of a steep profile of degradation to confirmed this evidence (6 and 20 days of 12,5 and 20 kGy surfaces images).



zero **zero** **zero**

6 days **6 days** **6 days**

20 days
PP

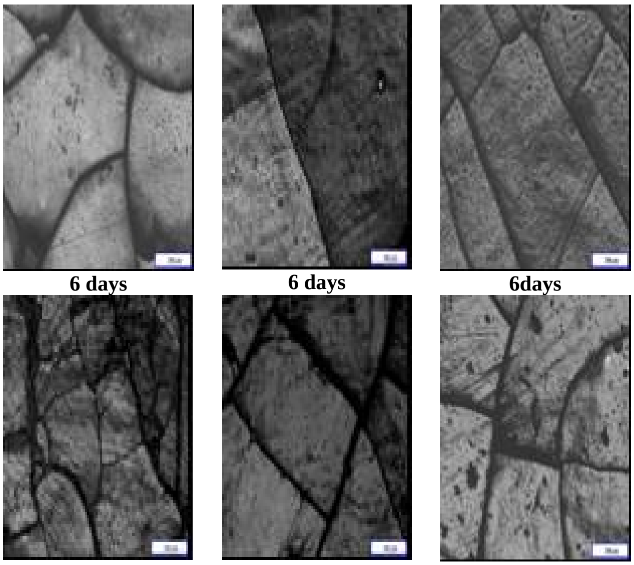
20 days
HMS-PP 12.5 kGy

20 days
HMS-PP 20 kGy

Figure 6 – Development of cracks in surface (time zero) and surface plus transversal cross section (at 30^o – 45^o of the samples corner; time 6 and 20), SEM images, magnified 50 times.

These exposed surfaces show cracks propagation that increases with the ageing time in stove and penetrate the layers near surface. The SEM analysis (fig 6) shows interesting aspects of the fractured surface of the materials, as a result of the process of chain scissions. The cracks initiated in the period of six days of exposition are gradually increased until twenty days. Intense yellowing of the surfaces was observed in 20 days of exposition different from the inner (white) for all of samples PP and HMS-PP.

Optical Microscopy (MO)



6 days **6 days** **6days**

20 days
PP

20 days
HMS-PP 12.5 kGy

20 days
HMS-PP 20 kGy

Figure 7 – Photomicrographs obtained by MO, magnified 200 times s, to iPP and HMS-PP spheres, aged in stove.

The Optical Microscopy (MO) at magnification of 200 times shows the frequency of cracks on surface; (fig.7). HMS-PP 20 kGy presented the highest frequency of fractures, followed by HMS-PP 12,5 kGy. PP samples show the lowest cracks frequency. Those results indicated that the HMS-PPs are less stable to thermal 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.

Conclusions

The oxidation stability of PP and HMS-PP decreases when the material is exposed to thermal ageing.

PP and HMS-PP samples exposed to heat are subject to many types of physical and chemical changes and in consequence reduction in mechanical properties was more intense in HMS-PP.

The physical aspect of degradation is pronounced in the layers near the surface where the cracks are intensely observed and yellowing in the further periods of time.

Acknowledgements

The authors acknowledge FAPESP (The State of São Paulo Research Foundation), CNPq (The National Council for Scientific and Technological Development), process n° 380795/2007-8 (NV), 382891/2007-4 (NV) for grants; Centre of science and Technology of Materials - CCTM/IPEN, for microscopy analysis (SEM) and Centre of Fuel Nuclear - CCN/IPEN, for microscopy analysis (MO).

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