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PHOTOOXIDATION BEHAVIOUR OF HMS-PP

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ABSTRACT

The radiation process has played an important role to produce polymers with controlled rheological properties. The main scope of the study is to evaluate the stability of High melt strength polypropylene (HMS-PP) prepared by gamma irradiation of PP (spheres) under acetylene atmosphere followed by a heating step to terminate reactions, in different doses of 12.5 kGy and 20 kGy. The samples submitted to the natural ageing for a period of one year were characterized by: thermogravimetry (TG), differential scanning calorimetry (DSC), infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The fundamental process that is believed to be the most significant in the mechanism of photooxidative degradation is the formation of hydroperoxides. The high energy UV light is capable of initiating bond scission within the polymer backbone, which leads to further chemical modification of the bonds via scissions and chain reactions through formation of radical species. The results showed that in pristine and HMS-PP samples exposed to UV radiation, oxidation reactions occur, resulting in chain scissions. The reactions occur preferentially in the amorphous phase owing to the higher permeability of oxygen.

1. INTRODUCTION

Large amounts of polypropylene have been produced globally and applied to a wide range of products owing to excellent properties, such as high stiffness and good thermal and chemical resistances. However, isotactic polypropylene (iPP), one of the linear polymers exhibits low melt strength and weak strain-hardening behavior. Thus, the resin has been difficult to process with certain processing methods dominated by elongational flow, generally it is unsuitable for blow molding, foaming, and thermoforming. A representative methodology to improve the elongational behavior is an addition of long-chain branching or grafting onto backbone species. It is possible to produce modified PP containing long side branches by the irradiation of an electron beam and the addition of peroxide, though PP usually has a tendency to decompose under the presence of radicals. Another option for improving the melt properties of a polymer is introducing a small quantity of high molecular weight components like a spike into a normal molecular weight distribution [1].

The oxidation of gamma-irradiated polymers continues for a long time after exposure. Various hypotheses have been proposed to explain the post-irradiation effects. These effects are frequently assigned to free-radicals that persist after irradiation in the crystalline area of irradiated films. These free-radicals are supposed to migrate to the crystalline/amorphous interface area where react with oxygen and initiate oxidation reactions. The photooxidation of polyolefins can be described as chain oxidation reaction, involving an hydrogen abstraction of the polymeric backbone, which leads to the formation of hydroperoxides [2].

Considering the influence of external parameters at any given temperature and moisture content, the rate of weathering increases with an increase in UV flux. Tensile stressing of stabilized types of iPP in thermooxidative and photooxidative environment has accelerated embrittlement of polymers. Singh and Sharma [3] investigated tensile stress applied to iPP, at constant load and observed the behavior of stabilized and unstabilized types of iPP in the course of thermooxidative ageing at 80-130ºC and photooxidative ageing at 45ºC and relative humidity of 65%. From kinetic evaluation of the temperature dependence of weight changes of unstabilized iPP during thermooxidative ageing, it has been found that the losses of unstressed and tension stressed specimens have obeyed the kinetic equations for a reaction of the first order [3].

Under the action of sun light, polymer materials undergo a series of oxidative reactions that lead to chemical degradation, with consequence of brittleness, loss of brightness, colour change, opacity and formation of surface cracks. Besides the reduction in molecular weight, a number of changes take place in the molecules during photodegradation with the formation of chemical groups like carbonyl, carboxylic acids, other than hydroperoxides [4,5].

The lower wavelength limit of sunlight at the earth's surface is about 300 nm. Many of the commercially important polymers, e.g. polyethylene or polypropylene, should not absorb any sunlight since the longest wavelength absorption band for the polyolefins is in the region below 200 nm, caused by a σ-σ* transition . Such hydroperoxide groups absorb in the UV region of sunlight and subsequent reactions lead to carbonyl groups formation. Catalysts used to produce the polymers, e.g. transition metals and Ziegler-Natta catalysts are present in resins and also contribute to degradation. The photodegradation of polypropylene occurs via chain scission reactions. The mechanism of chain scission operates according to a Norrish Type I reaction as well as β-scission of alkoxy leading to the formation of radicals which react with molecular oxygen for further oxidation products [6].

Polymer exposed outdoors can degrade through the action of several agents, including solar ultraviolet (UV) radiation; moisture; pollutants (in gaseous form or, more potently, as acid-rain); oxygen and temperature changes [7,11,12,13,27,28]. In the majority the main cause of deterioration property is photooxidation, which is initiated by UV irradiation and, as a consequence, much laboratory photo-ageing testing is conducted to determine the weatherability of polymers and to test the effectiveness of stabilizers [7]. Similar to thermal degradation, a sequence of oxidative reactions follows in which both chain scission and crosslinking may occur. The reactions require oxygen, which diffuses through the surface. The reaction can be very rapid in intense sunlight, even at ambient temperature [7].

The principal stages at which degradation can occur are during the processing operation, storage (shelf-life) and service, particularly during exposure to the outdoor environment. However, it must be appreciated what happens to the polymer during the service life affects its performance during outdoor exposure [8].

High melt strength polypropylene (HMS-PP) has been recently developed and introduced in the market by the major international producers of polypropylene. Long chain branches characterize the improvement of the melt strength and extensibility of the polypropylene processed by gamma radiation [9].

According to Yakimets et al [10] the study of ageing is complicated by the heterogeneous distribution of the chain scissions. Ageing by photooxidation is a surface phenomenon and it is propagated locally. The scission of the macromolecules involves the formation of smaller molecules which allow easier crystallization. The heterogeneity of photooxidation and the spontaneous formation of cracks on the surface affect apparent mechanical behaviour of iPP samples. The aim of this work is to evaluate the HMS-PP stability under photooxidation conditions.

2. EXPERIMENTAL

2.1 Materials and Methods

The investigation was conducted with polypropylene in spheres and modified polypropylenes (HMS-PP). The HMS-PP samples were obtained by irradiation with gamma irradiation in presence of acetylene at 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 [14], type IV.

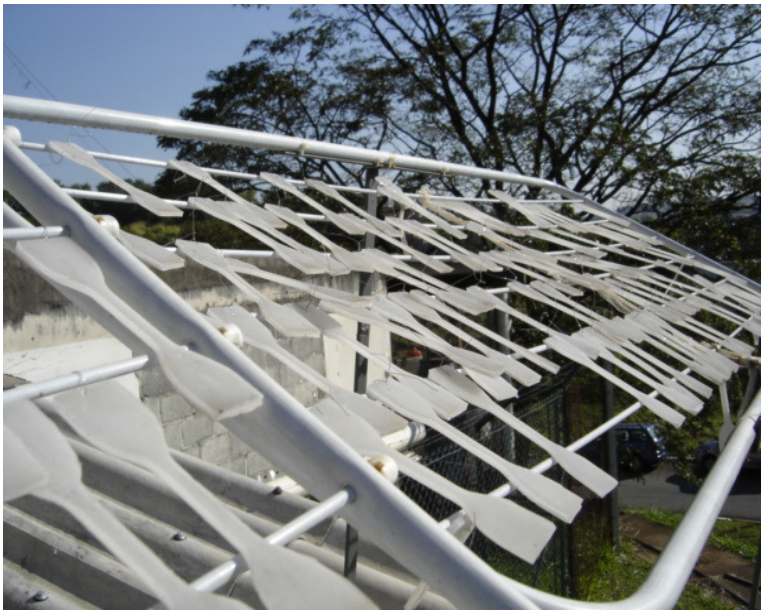


Figure 1 – Samples settled in a device for natural ageing assay in the IPEN.

The samples were irradiated at CBE at a dose rate of 10 kGy h^{-1} and the dosimetry was performed with Harwell Red Perspex 4034. The disposal of the samples for natural exposition were placed 45° north, according to ASTM D 1435-05 [15] – Standard Practice for Outdoor Weathering of Plastics. Geographic Position: Latitude (23° 33' South); Longitude (46° 44' West) and Altitude (750 meters) in São Paulo, IPEN-USP, Fig.1.

2.1.1. Thermogravimetry (TG)

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 2-3 mg were placed at alumina pans, according to ASTM D 6370-2009 [16].

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, holding for 5 min. Then, cooled to -50 °C at -10 °C min^{-1} and reheating to 280 °C at 10 °C min^{-1}, according to ASTM D 3418-03 [17].

2.1.3. Infrared Spectroscopy (FTIR)

The analyses were performed using attenuation total reflectance accessory (ATR) Smart orbit in the Thermo-Nicolet spectrophotometer, model 380 FT-IR.

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. 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. Gold is the metal most frequently deposited on organic nonconducting surfaces, as is the case with most of the commercial polymers [18] and also in our samples.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetry (TG)

The decomposition profiles were evaluated in the TG curves, Fig. 2 A, B and C.

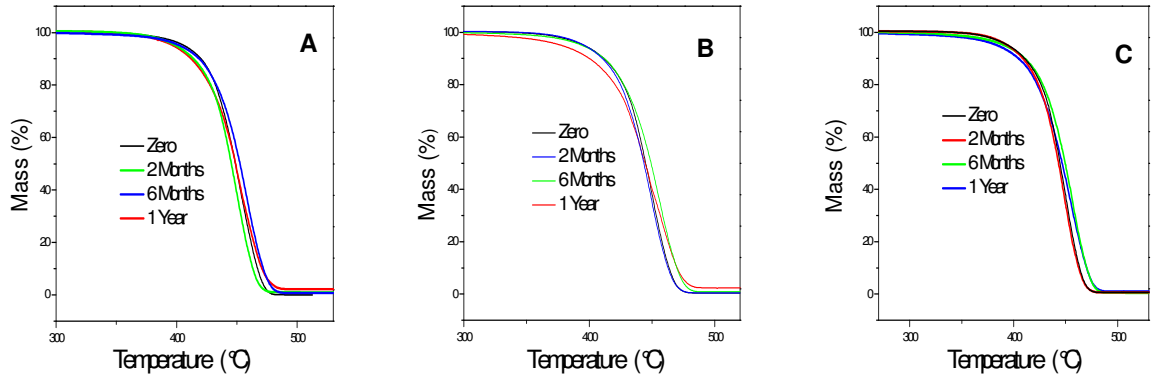


Figure 2 – TG curves of samples: pristine iPP (A), HMS-PP 12.5 kGy (B) and HMS-PP 20 kGy (C), under natural ageing for one year.

Table 1 - Values of initial decomposition temperature (Tonset) in samples from spheres, naturally aged.

Time / Samples	T_{onset} (°C)			
	zero	2 months	6 months	1 year
iPP	439	428	427	419
HMS 12.5 kGy	430	425	428	424
HMS 20 kGy	432	423	430	424

In all cases the thermal decomposition occurs in one step. In pristine sample aged for 2 months, Fig. 2 A and table 1, is observed a significant variation of onset decomposition temperature (439 → 428 °C). The lowest thermal stability is verified for pristine iPP at the end of ageing test (1 year). In this case the ageing resistance due to the crosslink effect was not observed.

3.2 Differential Scanning Calorimetry (DSC)

DSC curves showed differences in the melting point of the aged samples, Fig. 3. Melting temperature displacement to lower values were observed in all the cases.

When exposed to a source of chemical degradation, the morphology of semi-crystalline polymers can be modified, and in some cases disruption of the crystalline order occurs as detected by reduction in the fractional crystallinity. In other cases, however, the crystallinity has been reported to increase during exposure. It is generally accepted that the latter occurs because chemical degradation causes molecular chain scission, with the consequent release of entangled and tie molecules in the amorphous region that were unable to crystallize during the original solidification process. Chemi-crystallization caused by a variety of degradation processes has been detected in many polymers and there are some examples that involve the photodegradation of polypropylene [19]. In other work Rabello and White [20] evidenced

double melting peaks in the DSC thermograms due to reorganization during heating. In some cases the segregation of highly defective molecules was the major reason for peak doubling.

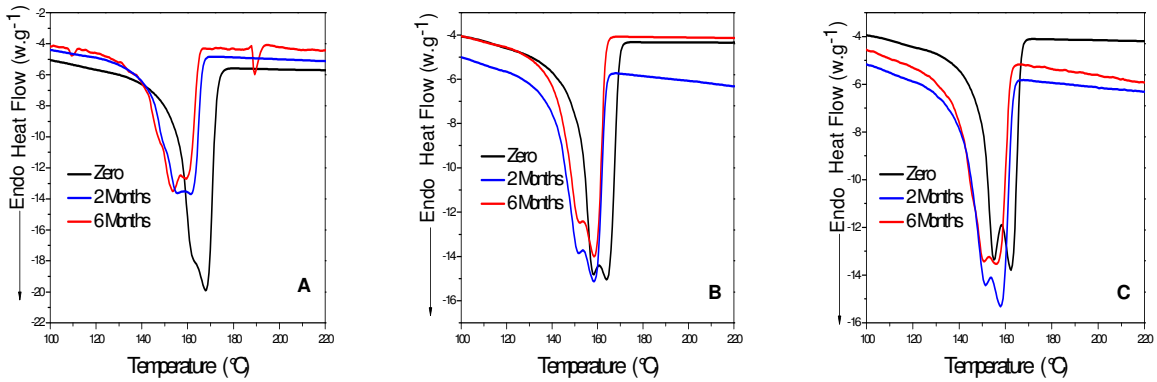


Figure 3 – DSC second melting curves of samples: pristine iPP (A), HMS-PP 12.5 kGy (B) and HMS-PP 20 kGy, second heating segment, under natural ageing for six months.

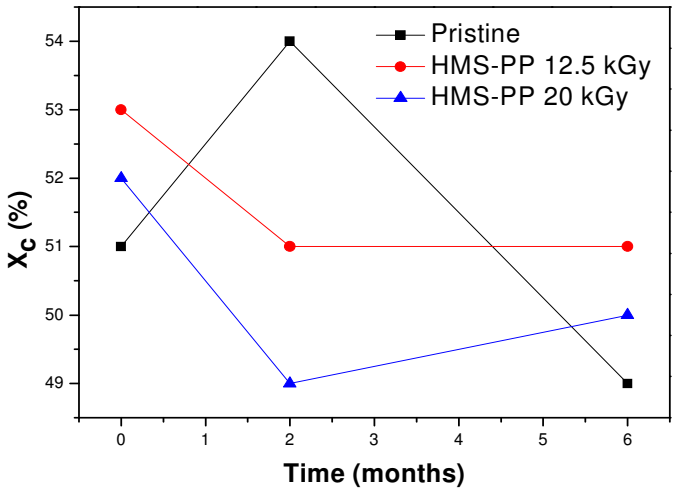


Figure 4 - Crystallinity measurements of polypropylene after different photo ageing times.

In terms of crystallinity, Fig. 4, the more affected was the pristine sample with decrease to the lowest value after 6 months.

3.3 Infrared Spectroscopy (FTIR)

The chemical structure of molecules in a degraded polymer sample may be substantially different from that present initially because chemical degradation causes several changes in molecules, including chain scission, crosslinking and the introduction of other chemical groups like carbonyls, hydroperoxides, esters, etc [20].

The, Fig. 5, shows the infrared spectrum by ATR technique of the samples submitted to natural ageing.

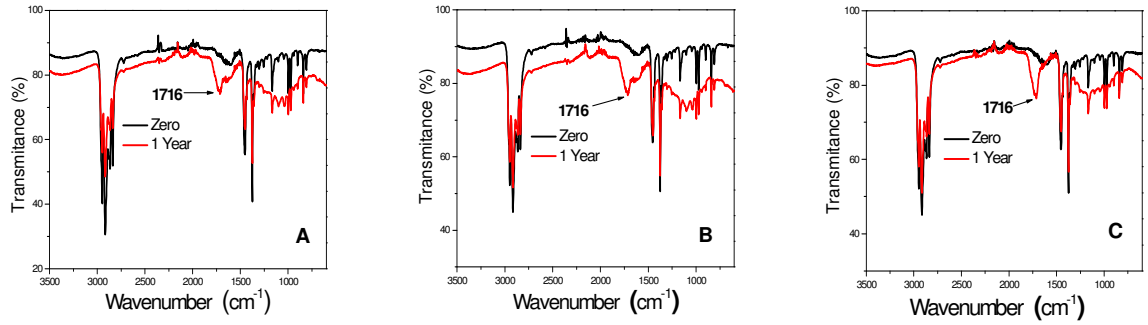


Figure 5 – Illustration of the infrared spectrum by ATR technique of the: pristine iPP (A), HMS-PP 12.5 kGy (B) and HMS-PP 20 kGy (C), under natural ageing for one year.

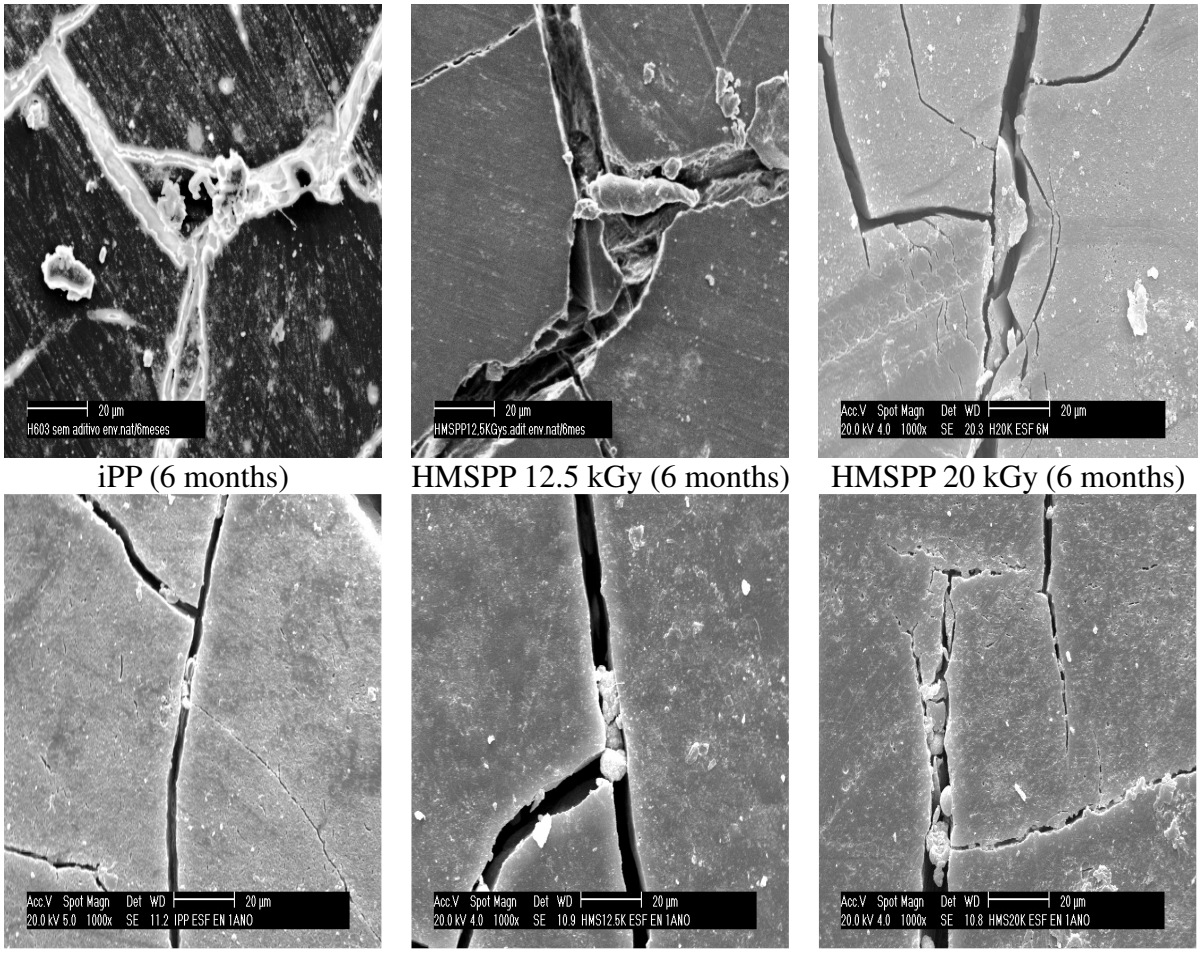
The shoulder at around 1740 cm^{-1} that appears in the thermo or photooxidation of iPP was assigned to an acidic group that would be hydrogen-bonded to a vicinal hydroperoxide [21]. Philippart et al [22] investigated spectral changes in iPP under natural outdoor exposure. They attributed the broad carbonyl band of carboxylic acids to a main absorption maximum at 1712 cm^{-1} and two shoulders at 1735 and 1775 cm^{-1}. In the carbonyl domain, the absorption maxima at 1712, 1735 and 1775 cm^{-1} were still observed.

The photooxidation of iPP and HMS-PPs samples were investigated by ATR experiments in order to detect oxidation signals at the beginning of the exposure. The presence of carbonyl groups detected as absorption peaks in the range of 1690-1760 cm^{-1}, is evidence of oxidative degradation degree [23].

In Fig. 5 A, B and C, are shown peaks in the region 1684 - 1810 cm^{-1}, that are attributed to the C=O stretching of oxidized chain terminals and oxidation products. The occurrence of bands relative to carbonyl and carboxylic groups of polypropylene was observed after 3 months aged and reported previously [24]. Both samples iPP and HMS-PPs showed absorptions related to oxidized groups at those wavelenghts.

3.4 Scanning Electron Microscopy (SEM)

The intensity of the UV radiation decreases with depth in the material, so that the reaction tends to be a surface process. Since oxygen is involved in the diffusion, irradiation with temperature will determine the reaction kinetics and the transport of reactive species [25,26] into the sample.



iPP (6 months) HMSPP 12.5 kGy (6 months) HMSPP 20 kGy (6 months)

iPP (1 Year) HMSPP 12.5 kGy (1 Year) HMSPP 20 kGy (1 Year)

Figure 6 – Photomicrographs obtained by SEM for iPP and HMSPPs, in 20 µm scale, natural ageing for 6 months and 1 year.

The SEM results, Fig. 6, showed drastically fractured surfaces in consequence of ultraviolet (UV) radiation; moisture; pollutants and temperature changes, conditions reported by Oliani [12] in environmental weathering study. The same surface pattern of degradation is observed for iPP and HMSPPs, after 6 months. This fact suggests that after 6 months the degradation is oxygen operative in the inner of the samples.

4 CONCLUSIONS

The results showed that when pristine and HMS-PP samples are exposed to UV radiation, oxidation reactions occur, resulting in chain scissions. The reactions occur preferentially in the amorphous phase owing to the higher permeability of oxygen and in consequence different crystals are formed, with defects or not, displacing the melting temperature. The crystallinity of pristine samples are more affected, decreasing with weathering ageing and this surfaces showed identical cracking pattern.

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