

NATURAL AGING EFFECTS IN HMS-POLYPROPYLENE SYNTHESIZED BY GAMMA RADIATION IN ACETYLENE ATMOSPHERE

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Abstract

High melt strength polypropylene (HMSPP) is produced by γ -radiation process to improve the melt viscosity suitable for melt blow film process. The melt strength (MS) properties of a polymer increases with molecular weight and with long chain branching due to the increase chain entanglement levels in the polymer. The main scope of this study is to evaluate the stability of HMSPP prepared by gamma radiation with doses of 5, 12.5 and 20 kGy in comparison with virgin PP. The samples were subjected to the natural aging for a period of one year. These polymers were characterized by: Thermogravimetry analysis (TGA), Differential scanning calorimetry (DSC), Infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM). These results show predominantly chain scissions degradation mechanism, owing to the reactivity of the tertiary carbon of macro chains. The chemi-crystallization caused by degradation processes (thermal and photodegradation) was detected in HMSPP.

Introduction

Radiation processing of polymers received great interest because it can be a way to modify the molecular structure of polymers as an alternative to traditional chemical methods. Several basic studies of gamma-radiation induced modifications of polymers are reported. It is well known that the main effect of the interaction of ionizing radiation caused is chain scissioning and crosslinking of the polymer chain of PP, while crosslinking is predominant in the case of PE [1-4]. Physically, the success achieved by the irradiation of plastics is based on the fact that, currently, energy into the material generates favorable changes provided as used in the proper doses. On the other hand, it represents an economic advantage, because it reduces the uses of additives in the formula [2].

A number of factors affect the sensitivity of polymers during photooxidation: a) The nature, concentration, and absorptivity of impurity chromophores; b) The quantum yield of photolysis; c) The rate of subsequent photochemical and photophysical processes and d) The intensity of incident radiation and the extension of spectrum of light sources from that of natural sunlight at normal latitudes. The effects of temperature, humidity and other environmental factors can further complicate a proper evaluation of a photooxidation process [5,6].

In the natural aging process of photooxidative degradation is predominant. Decomposition of the material by the action of light, which is considered as one of the

primary sources of damage exerted upon polymeric substrates occurs at ambient conditions. The polypropylene is susceptible to degradation initiated by UV and visible light, normally the UV damaging at 370 nm wavelengths. The mechanisms of the degradation and oxidation reactions are determined by the extraneous groups and/or impurities in the polymer, which absorb light quanta and form excited states. The initially short-lived singlet state is transformed to long live triplet state. Excited triplet states may cleave the polymer chains and form radical pairs or pairs (Norrish Type I reaction) of saturated and unsaturated chain ends by hydrogen transfer (Norrish Type II reaction). Thus polymeric radicals formed may add molecular oxygen (in triplet ground state) to peroxy radicals, which absorb UV light or become excited by energy transfer, the weak O-O bonds break. The hydroperoxide binding energy is very low causing the disruption of this connection by forming thermolysis and pairs of alkoxy and hydroxyl radicals are formed which may react in various ways, e.g. by hydrogen abstraction, chain scission, rearrangement and accelerate photodegradation [7-9]. The polypropylene undergoes faster photooxidation compared with polyethylene because of the tertiary hydrogen atoms and the concerned mechanism of peroxide formation [8].

When iPP sample was exposed to UV radiation, oxidation reactions occur, resulting in chain scissions. The strained or entangled sections of the molecules can then be released, and further crystallization occurs by the rearrangement of these free molecule segments. The chemi-crystallization is connected with the reduction in molecular size and involves segments released by scission from entanglements or tethering to crystals. Evidence for this is given by the correlation between the increase in degree of crystallinity and the decrease in molecular weight. The melting peaks highly degraded specimens containing a higher amount of β -phase, double peaks were obtained in this research [10,11].

Our Institute developed the production of branched PP, based on the grafting of long chain branches on PP backbone using acetylene as a crosslink promoter under gamma radiation process. The aim of the present paper is to investigate the fundamental aspects of the environmental aging on the morphology of the radiation modified polypropylene (HMSPPs) and durability of these materials.

Materials and Methods

The HMSPP samples were obtained from iPP pellets (MFI = 1.5 dg min⁻¹ from Braskem, Brazil). The iPP pellets were conditioned into nylon bags in which were fluxed with nitrogen in order to reduce as much as possible the internal oxygen concentration. The bags were submitted to the irradiation process in a ⁶⁰Co γ -source, at a dose rate of 5 kGy h⁻¹ monitored with Harwell Red Perspex 4034. Dose levels ranged from 5, 12.5 up to 20 kGy in presence of acetylene [12,13]. After irradiation, the samples were heat treated at 90 °C for 1 hour with the aim of promoting recombination and termination reactions and also eliminate residual radicals [14,15]. The dumbbell samples were prepared with mold pressure at temperature of 190°C in type IV according to ASTM D 638 (2014) [16]. For completion of the experimental aging tests of the iPP and HMSPP samples, was assembled in apparatus for environmental aging according to Figure 1.

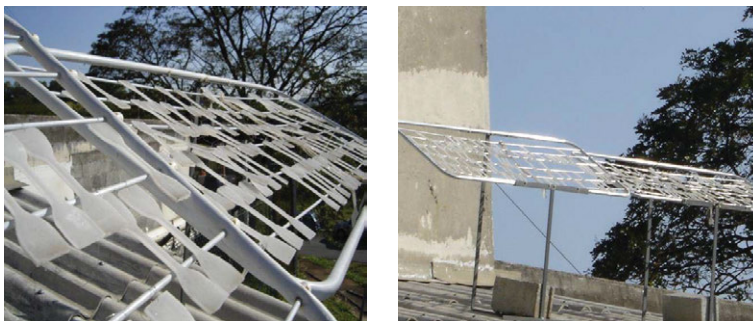


Figure 1. Device for environmental aging with polypropylene samples at IPEN

The disposal of the samples for natural exposition were placed 45° north, according to ASTM D 1435 (2013) [17]. Natural weathering was conducted for 12 months at the São Paulo exposure site of the Nuclear Energy Research Institute, IPEN, (São Paulo, Brasil), located at latitude 23°33' South, longitude 46°44' West and altitude 750 meters in São Paulo, IPEN-USP. After disposal of the samples for natural aging, three specimens of each sample were conditioned in air at 23.0 ± 1.0 °C, light absent and tested.

Thermogravimetry analysis

Thermogravimetry curves were obtained with an SDTA 851 thermobalance (Mettler-Toledo), using samples of about 10 mg in alumina pans, under nitrogen atmosphere of 50 mL min^{-1} , in range from 25 up to 600 °C, at a heating rate of 10 °C min^{-1} , according to ASTM D 6370-99 (2014) [18].

Differential scanning calorimetry

Thermal properties of specimens were analyzed using a differential scanning calorimeter (DSC) 822e, Mettler-Toledo. The thermal behavior of the samples (10-15 mg) were obtained by: (1) heating from 25 to 280 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere, (2) holding for 5 min at 280 °C, and (3) then cooling to 25 °C and reheating to 280 at 10 °C min^{-1} , according to ASTM D 3418 (2015) [19]. The crystallinity was calculated according to the equation (1):

$$X_c(\%) = \frac{\Delta H_f \times 100}{\Delta H_0} \quad (1)$$

Where ΔH_f is melting enthalpy of the sample, ΔH_0 is melting enthalpy of the 100% crystalline PP which is assumed to be 209 kJ kg^{-1} [20, 21].

Infrared spectroscopy

The FTIR was carried out with a Thermo Nicolet 6700 FTIR spectrometer with a Smart Orbit accessory, in the wavelength range 4000 to 400 cm^{-1} . In order to ensure satisfactory contact between the ATR diamond crystal and the sample, three or more FTIR spectra were recorded at various locations on the sample.

Scanning electron microscopy

Specimens were coated with gold in a sputter coater prior to examination to avoid charging. A Philips XL30 SEM was used for collect secondary electron images from the samples.

Results and discussion

Thermogravimetry

The TG results indicated decomposition of the samples, Figure 2 and 3.

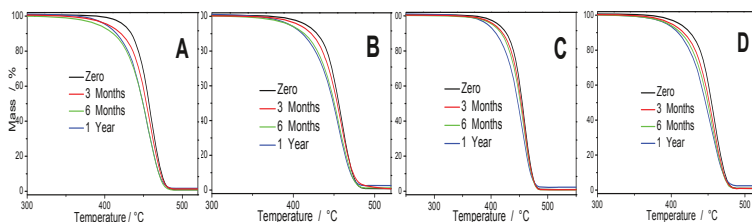


Figure 2. TGA decomposition curves of samples: iPP (A), HMSPP 5 kGy (B), HMSPP 12.5 kGy (C) and HMSPP 20 kGy (D), under environmental aging for 1 year

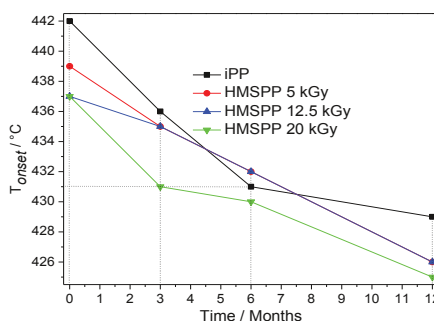


Figure 3. Values onset temperature of the decomposition step (T_{onset}) obtained from the TGA curves for iPP and HMSPPs.

As observed in the curves, Figure 2 presents significant variation of onset decomposition temperature (T_{onset}) when decomposition starts, with decrease of stability under aging. According to Figure 3 the T_{onset} decomposition of the iPP sample displaced from 442 to 429 °C after environmental aging of 1 year. The HMSPP 5 kGy sample displaced from 439 to 426 °C, as well as, values the HMSPP 12.5 kGy displaced from 437 to 426 °C and HMSPP 20 kGy displaced from 437 to 425 °C after 1 year of the aging. T_{onset} decreases in all samples with increase of aging time. After 6 months iPP represents the higher decrease of T_{onset} reflecting the lower stability. In the final (1 year) the samples are in similar degradation state.

Differential scanning calorimetry

Figure 4 shows the DSC event of melting in the second heating run of the iPP, as well as the HMSPPs.

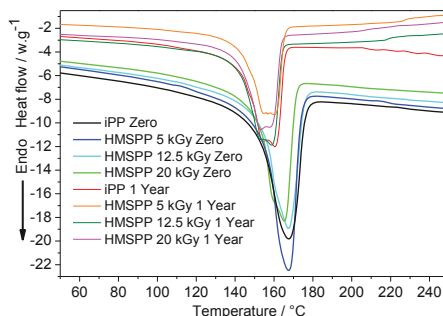


Figure 4. DSC 2nd heating curves of the iPP and HMSPP (5, 12.5 and 20 kGy)

The crystallinity is increased due to chain scission, with the consequence segregation of entangled molecule segments and crosslinks in the amorphous regions that were not able to crystallize during the original crystallization process. These free segments can reorganize themselves in a crystalline phase, with an appreciable mobility leading to an increase of crystallinity degree [22,23]. A progressive increase in crystallinity with UV exposure was observed in sample HMSPP 12.5 kGy. This behaviour can be attributed to the scission of the chain molecules in the amorphous phase that are released and hence may crystallize onto pre-existing crystals, a process called chemi-crystallization [24]. The crystallinity starts to increase when a sharp decrease in molecular weight occurs but the continuous increase is limited by chemical irregularities (like carbonyl and hydroperoxide groups) that appear after prolonged exposures and hence the molecules become too defective to continue chemi-crystallization [24].

The DSC concerning the T_{m2} and X_C results are presented in Table 1.

Table 1. DSC data of the iPP and HMSPPs during the second run of melting

Samples	Time	$T_{m2} / ^\circ\text{C}$		$X_C / \%$	
		Zero	1 Year	Zero	1 Year
iPP		167.0 ± 0.10	160.2 ± 0.12	49.2 ± 0.51	48.0 ± 0.53
HMSPP 5 kGy		168.1 ± 0.11	160.1 ± 0.11	47.1 ± 0.60	45.1 ± 0.54
HMSPP 12.5 kGy		167.0 ± 0.10	158.3 ± 0.13	44.3 ± 0.45	53.3 ± 0.55
HMSPP 20 kGy		165.1 ± 0.10	153.1 ± 0.11	51.4 ± 0.52	49.0 ± 0.49

T_{m2} : melt temperature; X_C : degree of crystallinity, as average of three specimens of each sample.

In the iPP sample was observed melting temperature displacement $\Delta T_{m2} = 7^\circ\text{C}$, HMSPP 5 kGy sample $\Delta T_{m2} = 8^\circ\text{C}$, HMSPP 12.5 kGy sample $\Delta T_{m2} = 9^\circ\text{C}$ and HMSPP 20 kGy $\Delta T_{m2} = 12^\circ\text{C}$, indicating morphology modifications of the samples crystalline phase. Melting temperature decrease demonstrates that chain scission is the main mechanism of the degradation. This can be attributed to modification in crystal structure of iPP which resulted in the mobility of the iPP molecules that increases with the radiation dose. More prolonged exposure of the PP plates decreased the crystallinity and the samples of 1 year (iPP, HMSPP 5 kGy and HMSPP 20 kGy) showed a minimum in degree of crystallinity. This may be attributed to the further increase of photooxidation products such as the carbonyls and hydroperoxides that act as chemical irregularities and limit the crystallinity [11, 25]. The decrease in crystallinity can be explained by the reduced size of the crystallites of the samples due to the degradation process occurring

during the long time exposure, which results in the increase of the amorphous region [26].

Infrared spectroscopy

In order to study the chemical and morphological modifications induced during the outdoor exposure on the PP plates, absorption infrared analysis on samples exposed for zero, 2 months, 6 months and 1 year have been carried out. The photo-oxidation of PP plates was investigated by ATR experiments in order to detect oxidant species at the beginning of the exposure, Figure 5.

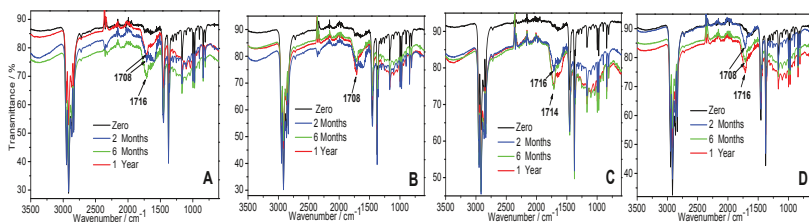


Figure 5. Illustration of the ATR infrared spectrum of the: iPP (A), HMSPP 5 kGy (B), HMSPP 12.5 kGy (C) and HMSPP 20 kGy (D), under environmental aging for 1 year

The iPP and HMSPP (5, 12.5 and 20 kGy) samples natural aged for 1 year show typical absorption bands of carbonyl stretching in the region $1708\text{--}1716\text{ cm}^{-1}$, Figure 5, with a substantial content of oxidation products. During thermal and photodegradation processes, carboxylic and carbonyl groups are present as end products of the oxidation.

Scanning electron microscopy

The surface and section morphology of PP plates exposed for 1 year were observed by means of scanning electron microscopy, Figure 6.

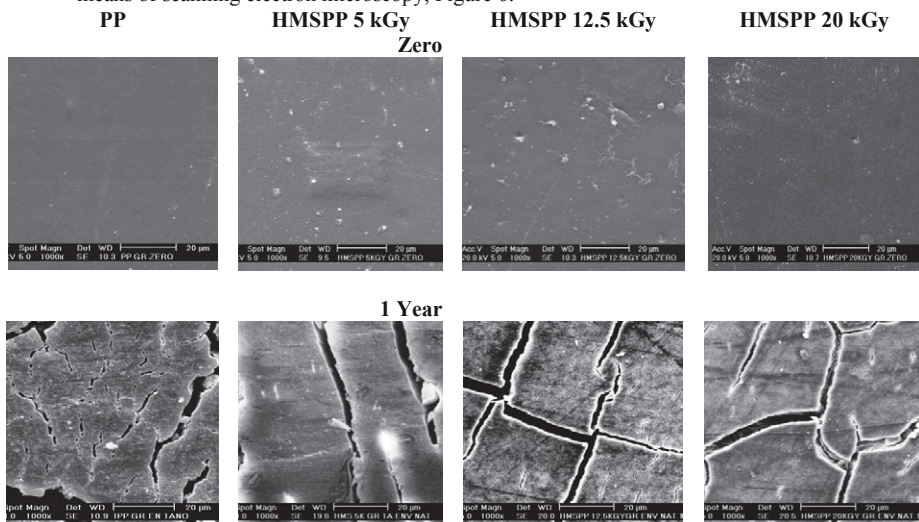


Figure 6. SEM images of the surface with development of samples cracks, 20 μm , aged by 1 year

In the similar work [27], the SEM of iPP plates were investigated with 5 months, 6 months and 16 months of exposure at Messina (Italy) after natural aging. The material close to the surface directly exposed to the sunlight shows several micro-fractures. SEM images of 1 year exposed samples, at magnification 20 μm of the surface, Figure 6, show a dense net of micro-fractures on the flat surface. At high time (1 year) of exposure, also the inner material is involved and the surface morphology is heavily affected.

Conclusions

The effects of thermal and photodegradation on iPP and HMSPPs were of the intense cracks formation on the surfaces. The thermo and photo oxidation acceleration at period of 6 months were more evident in samples of the iPP, according the results of decomposition temperature variation. However the thermal stability decreased with increase of exposition time. In addition, it was found a progressive increase of crystallinity degree in sample HMSPP 12.5 kGy of 1 year of environmental aging test attributed to the scission of tie chain molecules that may crystallize onto pre-existing crystals as effect of chemi-crystallization process.

Acknowledgements

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