Effects of Environmental Aging in Polypropylene Obtained by Injection Molding

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Abstract: UV light, heat, and pollutants can interact with Polypropylene (PP) molecules, mainly with the tertiary carbon producing free radicals which can react with oxygen producing changes in its properties. PP has outstanding chemical and physical properties, and a good processability at very low market price. In addition PP is extensively used for manufacturing various kinds of products, however due to its large scale consumption a lot of waste is generated at the end of their life cycle to the environment with low rate degradation. This study has the objective of comparing the environmental exposure of PP (spheres) neat and PP (spheres) irradiated with 20 kGy. Dumbbell samples were manufactured by injection molding and exposed to the environment during 90 days. Another one set was exposed to gamma irradiation at 20 kGy total dose and exposed at the same conditions. The samples were characterized by Mechanical Testing, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Differential Scanning Calorimetry (DSC). The dumbbell samples PP 20 kGy, after environmental aging, showed oxidation with presence of surface cracks more intensely than the PP spheres neat.

Keywords: Polypropylene, Gamma Irradiation, Environmental Aging and Injection Molding

Introduction

Polypropylene (PP) is a polymer which offers a good balance of thermal, chemical and physical properties; plus low cost and processing facilities by injection molding, however it is necessary to deal with their low environmental factors resistance [1]. During exposure to weathering, such as UV, oxygen, pollution, humidity and heat, polypropylene undergoes changes in its main chain that lead to the start of the PP's oxidative degradation and later to the cracking and to lose mechanical properties. These occurrences are associated with the chain scission process [2-4]. The simulation of environmental conditions on the study of polymers degradation is a powerful tool to evaluate and predict the changes expected in real time life. The interaction of environmental factors with the PP influences the degradation and causes breaking in the bond of side groups, forming unsaturated molecules, peroxides, hydroxides and chain scission. Decrease in the elongation at break and tensile strength at break are caused by chain scission under UV exposure. [5-6]. The processing of polymers through ionizing radiation is frequently can be used to modify the molecular structure, mainly by crosslinking and chain scissions mechanism due to free radicals formation as a result of the interaction of gamma rays with polymers. The tertiary carbon present in PP molecules makes it susceptible to oxidation via macro radicals formation P • and consequent oxygen it reaction to a peroxide (represented by POO•) or hydroperoxides which in room temperature may form radicals such as hydroxyl and alkoxyl [7-9]. To explain the effects of gamma irradiation in the presence of oxygen as chain scission and loss of properties, some authors showed in their studies that after irradiation occurs the formation of radicals trapped in the amorphous phase they migrate to the interface between crystalline and amorphous region and react with oxygen and decompose. [10-11]. Previous studies have shown that in the case of PP irradiated at 30 kGy, and exposed to the environment, showed that the tensile strength decreases with time during the 60 days of exposure period, so that the study showed PP exposed to environmental degradation is accelerated by irradiation [12]. Another study conducted by Komatsu et.al showed that polypropylene with clay and irradiated at 12.5 kGy, when exposed to environmental aging for 12 months, showed large cracks and fissures [13]. Regarding the loss of mechanical properties in a study conducted by Oliani et. al samples of HMSPP (High Melt Strength PP) irradiated at 20 kGy were exposed to environmental aging for 120 days, initially presented maximum tensile values at break compared to PP, but after aging, it was found decreased values, and loss of maximum stress at rupture in HMSPP irradiated at 20 kGy [14]. In this work the process of injection molding was chosen because nowadays it is the most important method of polymers processing, and the most widely used in industry. Pieces manufactured by injection molding are present in several sectors like, automotive, medical equipment, and home appliances. The main advantages are minor index of defects induction and high processing velocity [15].

The aim of this work was to study the degradation of polypropylene spheres irradiated to 20 kGy using gamma radiation and compares the effect of environmental aging with PP spheres.

Materials and Methods

Materials

The isotactic polypropylene (iPP) spheres (neat) that were used are supplied by Braskem, suitable for injection with Melt Flow Index of 3.5 dg min^{-1}, density of 0.905 g cm^{-3}, Mw = 300,000 g mol^{-1}.

Methods

PP dumbbell samples (according to ASTM D-638-14 - type I) that were used in this study were manufactured by injection molding process. The PP was irradiated by gamma rays at dose of 20 kGy, in an irradiator with ^{60}Co source, at dose rate of 5 kGy h^{-1}.

Scanning Electron Microscopy

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

Differential Scanning Calorimetry

Assays were performed in equipment Mettler Toledo 822 DSC in a nitrogen atmosphere. The program was used: heating 50-280 ºC for 10 ºC min^{-1}, keeping at 280 ºC for 5 minutes, cooling from 280 to -50 ºC at a rate of -5 ºC min^{-1} and reheating -50 to 280 ºC at a rate of rewarming 10 ºC min^{-1} under N$_2$ (50 mL min^{-1}). The samples were weighed (around 10 mg) and placed in aluminum crucibles, according ASTM D 3418-14.

Mechanical Tests

Tensile strength at break analyses were accomplished according to ASTM D-638-14, by using type I specimen, in Universal Instron machine-model 5567.

Fourier Transform Infrared Spectroscopy

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

Environmental Aging

The samples were exposed in environmental aging device, according to ASTM D 1435-05. Geographical position: Latitude (23º 33º South) Longitude (46º 44º West) and Altitude (750 meters), and North position 45º position. Figure 1 shows the essay structure.

FIGURE 1. Device with dumbbell samples exposed outside for environmental ageing at the polymer processing laboratory IPEN.

Results

Scanning Electron Microscopy

Figure 2 shows the SEM results for the PP and irradiated PP to 20 kGy after environmental aging for 30, 60 and 90 days.
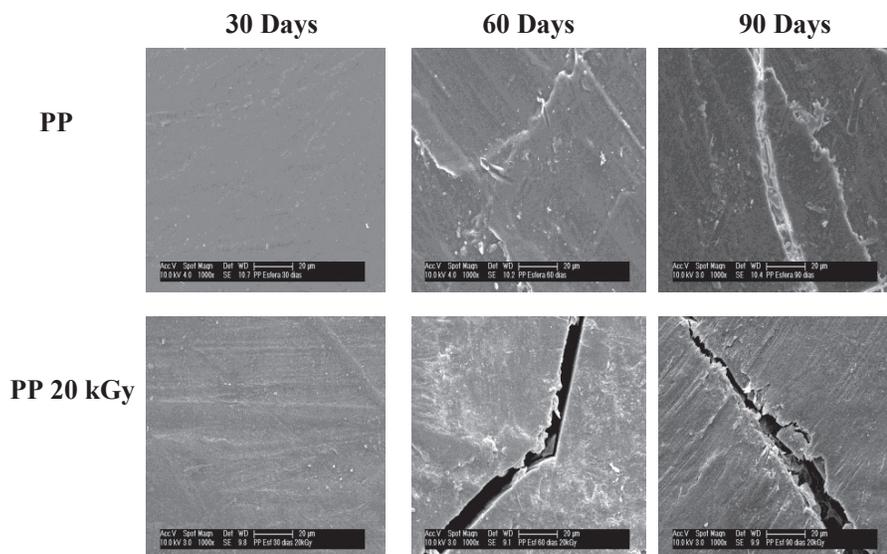

FIGURE 2. Photomicrographs obtained by SEM enlarge 1000x times for PP and PP 20 kGy.

All samples were exposed to same environment conditions such as UV rays, heat, humidity, pollutants and oxygen. When PP is exposed to those factors, changes in its structure occurs, attributed to the phenomenon of chain scission. Visible cracks and fissures can be observed in Figure 2, starting at 60 days of aging for irradiated PP and increases with the aging time, while non-irradiated PP shows visible fissures only at 90 days of exposure to environmental aging. The cracks observed on Figure 2 can be explained by the contraction of oxidized layers on the surface of the samples. The contraction may have been created by the increased crystallinity of the surface layers, consequence of free radicals formation under gamma irradiation and environmental aging with UV rays and atmospheric oxygen. [16-18].

Differential Scanning Calorimetry

The temperatures of second melting (Tm_2) and the degree of crystallinity (X_c) are presented Figure 3 and Table 1.
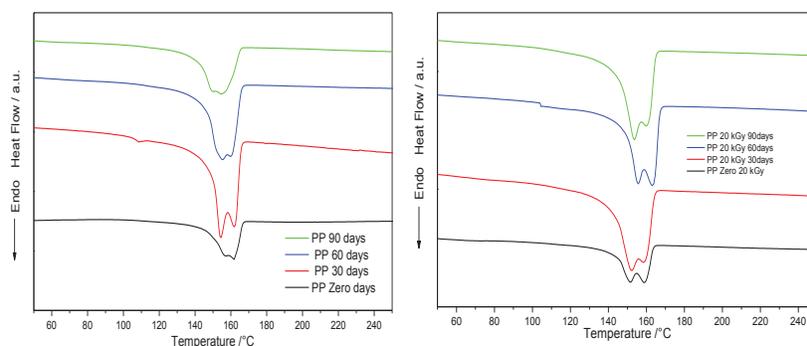

FIGURE 3. DSC curves of samples PP (A) and PP 20 kGy (B) under environmental aging.

TABLE (1) - Melting temperature of samples and the degree of crystallinity.

Samples	T_{m2} / °C (±0.1%)				X_C / % (±0.5%)			
	zero	30 days	60 days	90 days	zero	30 days	60 days	90 days
PP	161.6	154.5	161.4	154.5	41.5	47.7	47.5	44.5
PP 20 kGy	158.9	152.1	161.4	152.6	44.9	48.1	41.4	48.2

The DSC results show that at zero time the melting temperature of the PP 20 kGy is lower than the non-irradiated PP. The displacement the T*m2* at lower temperatures also occurs at the end 90 days for PP and PP 20 kGy of environmental aging. Previous studies showed that this behavior is consequence of oxidative degradation of PP, when is exposed to gamma irradiation, in air atmosphere, and environmental parameters such as UV rays, temperature, pollutants and oxygen which promotes chain scission reactions. Table 1 shows increasing of crystallinity after exposure it can be justified by small crystals formation (phenomenon chemicrystallization), generated by chain scission [19-20].

Mechanical Tests

The mechanical testing is a good method to evaluate the changes in properties and analyze structural modifications from degradation such crosslinking and chain scission. Each result of Tensile Strength at break was an average of eight measurements. Figure 4 show the results of tensile strength at break versus tensile strain at break.
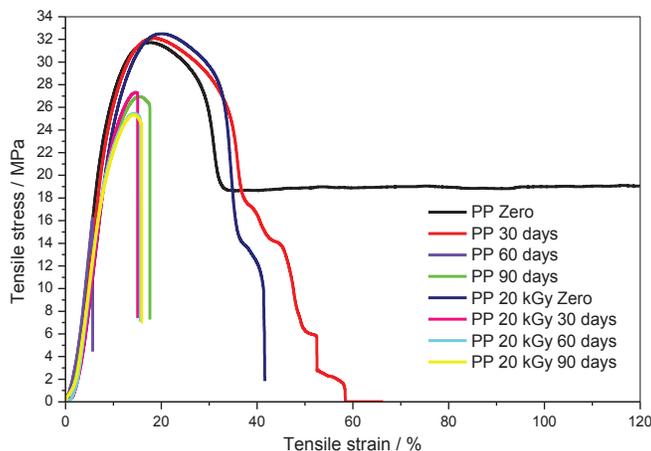

FIGURE 4. Results of tensile strength of samples PP and PP 20 kGy after environmental aging.

It was observed that from 60 days PP, has a low tensile strength at break indicating an influence of weathering at the samples. On the other hand, after 30 days of exposure, occurs a decrease of tensile strength at break in PP 20 kGy. In Figure 4, is shown that after gamma irradiation and environmental aging, the early loss of mechanical properties for PP 20 kGy was higher than PP non-irradiated. Mechanical damage can be justified by chain scission and crosslinking formation caused by combination of gamma irradiation and UV rays [21].

Fourier Transform Infrared Spectroscopy

FTIR spectra of the samples in the environmental aging, Figure 5. FTIR-ATR was used here into identify any functional group that indicating one sign of chain degradation.
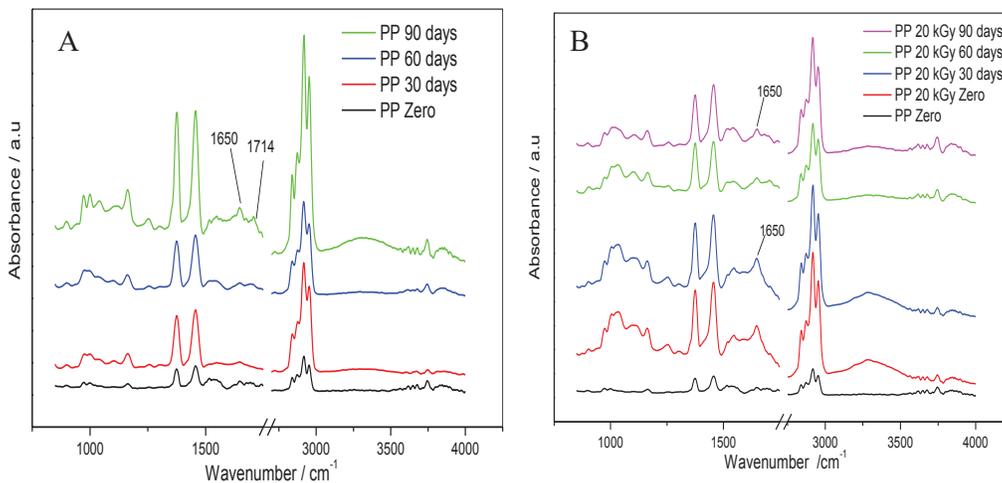

FIGURE 5. Infrared spectra PP (A) and PP 20 kGy (B).

During environmental aging and gamma radiation, PP undergoes oxidative degradation. Carbonyl groups could be found as result of oxidation. Figure 5A shows that PP with 90 days under environmental aging, presented peaks around 1714 cm-1 which correspond to carbonyl groups (C=O) and 1650 cm^{-1} which corresponds to unsatured groups (C=C). In Figure 5B was possible to note that the bands of unsatured groups started after 60 days of environmental aging. In Figure 5B at 90 days of exposure, it was observed that the intensity of unsatured groups at the same time that the carbonyl groups decreases begin to be evidenced report previously [22].

Conclusion

The PP irradiated at 20 kGy suffered more intense degradation than PP non-irradiated. The mechanism degradation was justified by the displacement of second melting temperature, fissures and cracks on surface, loss mechanical properties and the presence of unsatured and carbonyl groups. All these results showed that gamma irradiation can accelerate the degradation allowing a faster elimination of PP wastes from the environment.

ACKNOWLEDGMENTS

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