

EVALUATION OF ENVIRONMENTAL AGING OF POLYPROPYLENE IRRADIATED VERSUS PRISTINE

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Abstract

Polypropylene (PP) is the most common thermoplastic resin of the plastic market due to its very interesting physical, chemical and processing properties at very low market price, however after its use the resin does not degrade in the environment or it degrades at very low rate. This study has the objective of comparing the environmental exposure of PP irradiated with 20 kGy and pristine PP. Dumbbell samples were manufactured by injection molding and exposed to the environment during 90 days; another one set was subjected to gamma irradiation at 20 kGy total dose and exposed at the same conditions too. The samples were characterized by mechanical testing, visual inspection, infrared spectroscopy (IR), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). The irradiated samples, after environmental aging, showed oxidation and presence of cracks in samples of the PP 20 kGy.

Introduction

Polypropylene is a thermoplastic polyolefin obtained by polymerization of propylene monomer. PP is of great importance to the market due to its versatility, easy processing, and good mechanical properties, at very low market price and up to 20% lighter than other polymers [1]. The structural changes, typically chain scission and crosslinking, induced by ionizing radiation cause changes in the physical properties of irradiated polymers. Although the degradation reactions of the type crosslinking or chain scission occur simultaneously during irradiation of the polymer, one of these processes is generally dominant, depending on the chemical structure of the polymer, dose, dose rate, type of radiation and the conditions of the environment (pressure and temperature) in which the material is irradiated. The primary process due to irradiation of the polymer is the generation of excited species and free radicals resulting from the breakage of chemical bonds [2, 3]. Environmental aging is widely used in research and industrial assessment and strictly depends on geographical variables and atmospheric exposure conditions. Reasons for degradation may result from the combination of these variables such as heat, ultraviolet light, moisture, oxygen and pollutants. PP is a sensitive polymer due to the presence of tertiary carbon in their structure and suffers the effects of degradation and alteration of mechanical and aesthetic properties [4-7]. The energy to break the tertiary carbon may also be provided by gamma irradiation, which will modify the chemical structure of the polypropylene by increasing the content of carbonyl and hydroxyl groups suggesting the occurrence of oxidative degradation [8].

Disruptions in tertiary carbon may form macroradicals by P^\bullet . From that macroradicals, oxygen will interact with it and will form peroxide which is represented by POO^\bullet . Still

in the macromolecule there is the presence of macroradicals because there might be other points where that may have occurred formation of peroxides. At first, the oxygen interacts with the methyl radical, and in a second moment it can interact with hydrogen forming a hydroperoxide represented by POOH. The energy of the O-O bond hydroperoxide is very low and hydroperoxides may decompose at room temperature. Thermolysis at room temperature may break this bond quite easily. The termination or interruption of autocatalytic cycle may occur by recombination of two free radicals [9].

When the polymer is irradiated in an environment with oxygen like air, oxidation takes place promoting chain scission with formation of free radicals [10]. The irradiation dose will determine the initial content of free radicals formed, oxidation will follow and will be a function of time and temperature, influencing the occurrence of chain scission or crosslinking. The greater or lesser mobility of macro radicals formed will hinder or promote recombination. The association of radiation with warming will increase the mobility of free radicals and reduce the recombination [11]. The effects of ultraviolet radiation in the PP mechanical behavior have been reported by several authors. It is noted in general, a drastic reduction in the mechanical properties, attributed to the fact that oxidative reactions that lead to chain scission especially in the region of the molecules that participate in more than one crystalline lamellae which together with the formation of surface cracks causes great deterioration in strength [12]. Previous studies on the photodegradation of polyolefins showed that the tensile strength starts to fall drastically from 42 days of natural exposure [13]. In the case of PP 30 kGy and then exposed to the environment the study showed that the tensile strength decreases with time during the exposure period of 60 days, so the study showed that the PP exposed to environmental degradation is accelerated by irradiation [14]. The PP degradation and its variations showed that with the natural aging PP increases the crystalline fraction during the exhibition and the High Melt Strength Polypropylene (HMSPP) 20 kGy seems to be more stable to the chain scission reactions despite the irregularity of appearance during exhibition as it relates to UV radiation. Regarding the mechanical tests the samples HMSPP 20 kGy, initially showed maximum tensile values at breakage compared to the PP, but at the end of the natural aging it was found values lower than the PP, so there was loss of maximum stress at breakage in HMSPP samples that differed in PP at the beginning [15,16].

Study on the effects of accelerated thermal aging on polypropylene modified by irradiation process showed that aging on PP and HMSPP causes the intense cracks formation. Chain scission and oxygen diffusion were more evident in the PP as concluded by Oliani et al. [17]. Surface cracks propagation showed increases with the aging time. The results indicated that PP suffered greater thermooxidative degradation and chain scission than HMSPP 12 kGy and HMSPP 20 kGy. During the process of irradiation, the ionizing radiation permits the formation of reactive sites which may modify chains of the polypropylene [18].

The main objective of this paper was to study the degradation of polypropylene irradiated at 20 kGy using gamma radiation and compares the effect of environmental aging with pristine PP.

Materials and Methods

Materials

The isotactic polypropylene (iPP) pellets 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, $M_w = 300,000$ g mol⁻¹, and pristine (without factory additives) polypropylene.

Methods

The PP dumbbell samples that were used in this study were manufactured by injection molding process. The Injection Molding Machine model used for manufacturing samples ROMI PRIMATE 65-R. The PP were irradiated by gamma rays at dose of 20 kGy, in an irradiator with ⁶⁰Co 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.

Fourier Transform 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.

Differential Scanning Calorimetry

Assays were performed in equipment Mettler Toledo 822 DSC in a nitrogen atmosphere. The program was used: heating 50-280 °C for 10 °C min⁻¹, keeping at 280 °C for 5 minutes, cooling from 280 to -50 °C at a rate of -5 °C min⁻¹ and reheating -50 to 280 °C at a rate of rewarming 10 °C min⁻¹. The samples were weighed and placed in crucibles with aluminum caps ASTM D 3418-08 [19].

Tensile strength at breakage

Tensile strength at breakage analyses were accomplished according to ASTM D-638-14 [20], by using type I specimen, in an essay universal Instron machine-model 5567-of 300 kN maximum capacity and 500 mm min⁻¹ grips speed, under a strain rate of 0.17 s⁻¹ at room temperature.

Results

The samples were exposed in an environmental aging device in which a North position 45°, according to ASTM D 1435-05. Geographical position: Latitude (23° 33° South) Longitude (46° 44° West) and Altitude (750 meters) [21]. Figure 1 shows how this was done.



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

Scanning Electron Microscopy

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

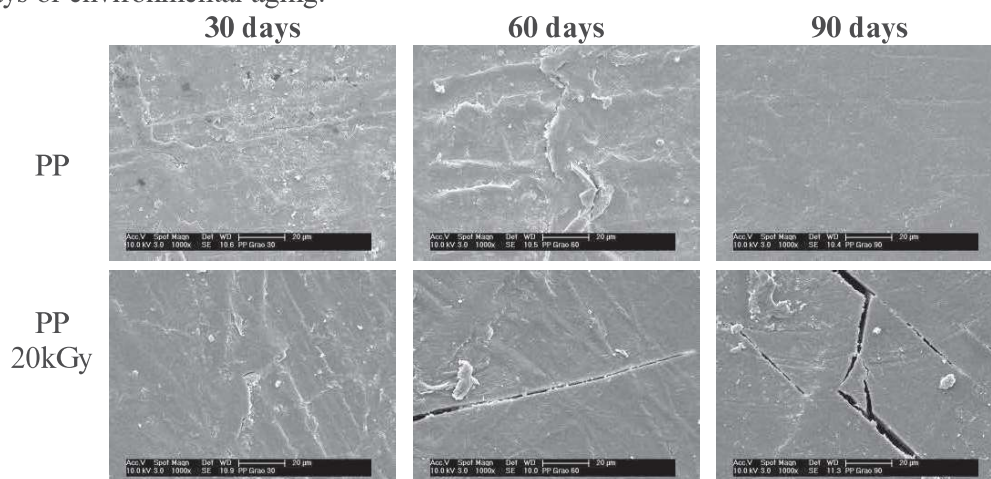


Figure 2. Photomicrographs obtained by SEM enlarge 1000 times for PP and PP20 kGy.

The effect of UV radiation (chain scission), in the irradiated PP 20 kGy, was more intense and the pictures showed cracks formation. Surface cracks increased with the aging time. The figures showed the appearance of cracks and fissures in the samples of 60 and 90 days environmental aging. The SEM analysis, Figure 2 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 the irradiated PP 20 kGy, than PP. A possible explanation for this fact is the gamma irradiation accelerated the degradation due to the appearance of free radicals. However in the PP with stabilizers at the end of the end 90 days was not noted cracks or fissures [22].

Fourier Transform Infrared Spectroscopy

FTIR spectra of the samples exposed in the environmental aging, Figure 3.

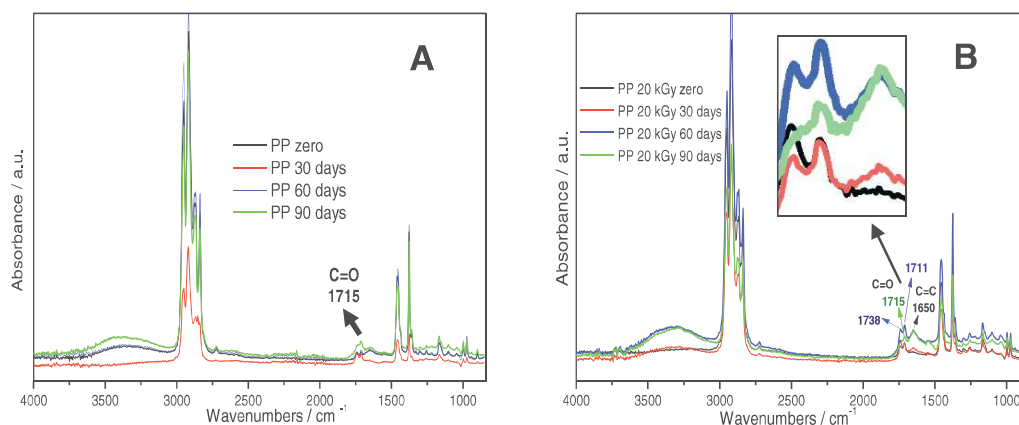


Figure 3. Infrared spectra: (A) PP and (B) PP 20 kGy.

When PP is exposed to UV radiation in air, the energy absorbed by the polymer results in free radicals formation followed by oxidation. Radical reactions with the oxygen generated oxidative and decomposition products specially carbonyl groups ($\text{C}=\text{O}$). In Figure 3, it was observed an absorption peaks attributed to stretching of carbonyl group at 1715 cm^{-1} and deformation of $\text{C}=\text{C}$ from unsaturated groups at 1650 cm^{-1} . In Figure 3, these groups are of relative low intensity. In Figure 3B the absorption bands at around 1715 cm^{-1} , indicating the presence of carbonyl unsaturated groups of higher intensity. It was observed relative higher intensity in those irradiated PP samples that characterized the oxidative degradation of the material. Peaks attributed to $\text{C}=\text{C}$ absorption at 1650 cm^{-1} of the double bonds are common of early periods of the degradation as indicated in the literature [23-25].

Differential Scanning Calorimetry

DSC technique was applied to evaluate the temperatures of second melting (T_{m2}) and the degree of crystallinity (X_c). Table I and Figure 4 show the values.

Table I. Melting temperature of samples and the degree of cristanillity.

Time	$T_{m2} / ^\circ\text{C} (\pm 0.1\%)$				$X_c / \% (\pm 0.5\%)$			
	zero	30 days	60 days	90 days	zero	30 days	60 days	90 days
iPP	162.2	161.9	161.7	161.7	50.2	49.8	49.6	45.1
PP 20kGy	160.3	159.5	151.3	159.1	48.5	44.4	47.7	52.7

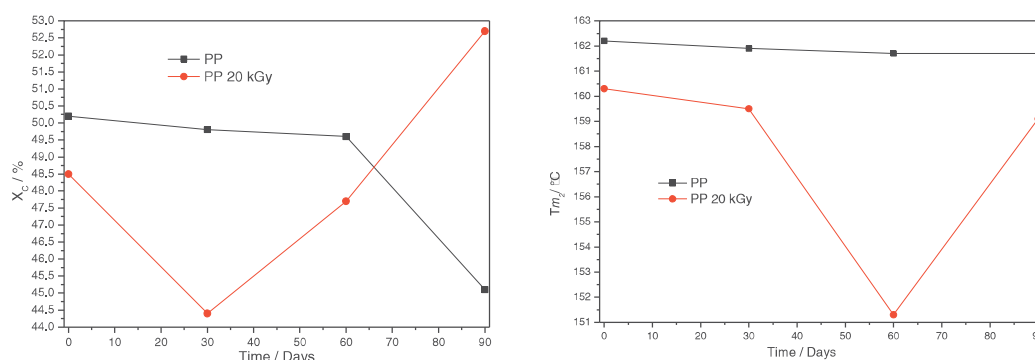


Figure 4. Polypropylene crystallinity (A), and Melting temperature (B) of samples PP and PP 20 kGy.

The DSC results showed small changes in crystallinity and melting temperature, while the polymer morphology had not undergone significant changes. It is known that when the PP exposed to UV radiation, there is a decrease of its molecular weight, due to presence of carbonyl groups (identified in Figure 3), indicating a probable increase in the number of chain scission events, especially in the cases of short-term exposure, wherein the chain scission effect dominates on morphological irregularities, thus justifying the increase of crystallinity and the melting temperature decreasing [26].

More prolonged exposure, 90 days of the PP plates, decreased the crystallinity. This can be attributed to defects in macro chains derived from photooxidation such as the carbonyls, and hydroperoxides compounds, Figure 3A. Chemical reactions that occur during the PP photodegradation can lead to chain scissions and carbonyl group formation, observed in sample of the PP 20 kGy in 90 days. The oxidation reactions occur predominantly in the amorphous phase where oxygen can be accessed easily. During the photodegradation process new imperfect crystals are formed due to the chemicrystallization in the crystal phase. The increased crystallinity in the sample PP 20 kGy at 90 days, could be attributed to the recombinations of the radicals in the more ordered forms, and to chemicrystallization.

Tensile Strength

The mechanical testing is an important method to evaluate the changes in properties and correlate them with structural modifications from degradation such as crosslinking and chain scission. Each result of Tensile strength at break was an average of eight measurements. Figure 5A shows the results of tensile strength at break results from zero to 90 days and figure 5B shows tensile strength at break versus strain at break.

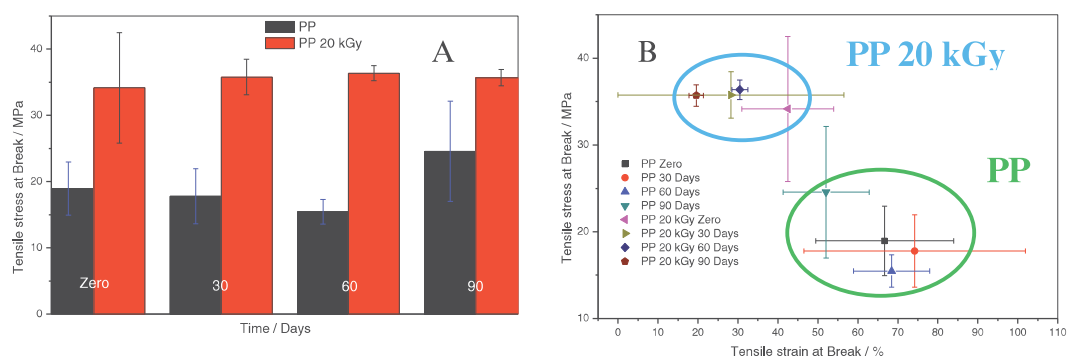


Figure 5. Results of tensile strength at break (A), and tensile strength at break versus strain at break (B) of samples PP and PP 20 kGy.

Polyolefins rapidly lost most of their mechanical properties after severe exposure to heat and light. The irradiated samples showed higher tensile stress at break as presented in Figure 5B. This result can be explained by the crosslinking formation caused by irradiation but also by induced crystallization by chain scission.

Conclusion

The appearance of cracks and fissures as well as the presence of carbonyl groups were explained as results of oxidative reactions after environmental aging. Mechanism of chain scission are competitive and identified as displacement on melting temperature and chemicrystallization. Moreover, SEM results showed clearly that PP 20 kGy suffered more intense degradation than PP.

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