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Accelerated environmental degradation of gamma irradiated polypropylene and thermal analysis

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Abstract Polypropylene (PP) is one of the most important plastic commodities in the world. It can be used in many applications since it has outstanding properties at low cost. However, PP has very low environmental degradation rate; therefore, the discarded PP can accumulate in the environment. The aim of this study is the degradation control of PP using gamma radiation. Dumbbell samples were manufactured by injection molding followed by irradiation using gamma radiation at different doses: 5, 12.5 and 20 kGy. The irradiated samples were exposed to environmental aging during 90 days and characterized by scanning electron microscopy, thermogravimetric analysis, differential scanning calorimetry and X-ray diffraction. The irradiated dumbbell samples PP 5, 12.5 and 20 kGy, exposed to environmental aging, showed intense oxidation with the presence of surface cracks compared with the PP non-irradiated.

Keywords Polypropylene · Gamma radiation · Environmental aging · Thermal analysis

Introduction

Polypropylene is a thermoplastic obtained by addition polymerization reactions. PP has become one of the most important polymers used nowadays owing to its unique properties: good chemical resistance, non-toxicity, easy processability and a low cost, but in addition, PP has sensitivity to UV rays and other environmental factors [1]. During UV radiation, the polymer degrades into shorter chains which may continue to degrade by oxidation if exposed to environmental conditions such as heat, pollution, humidity and oxygen. It is known that polymers suffer aging due to UV absorption by impurities. The exposure to several environmental factors especially UV rays, heat and oxygen may result in chemical reactions that generate surface-oxidized functional groups: carbonyl groups, hydroperoxides and peroxides, causing chain scission and cracks in the material [2–4]. Free radicals formation is the key to begin the PP degradation process. Tertiary carbons present in macrochains are fundamental to undergo scission due to their lower binding energy. This macroradical can promote the molecular scission whenever the polymer is subjected to environmental stress or gamma radiation [5]. Reactivity of chemical bonds will generate a macroradical P· that in the presence of oxygen form a POO· peroxide. After gamma irradiation and environmental aging, PP suffers predominantly chain scission and a reduction of molecular weight. In addition, it is noteworthy that thermostability decreases. When time of exposure increases, the displacement of melting temperatures to lower values occurs. The chain scission at a high level causes fissures and cracks on polymer surface and elasticity loss; consequently, degradation of the polymer occurs [6–8]. The aim of this study is to promote the control of polypropylene degradation under environmental effects using gamma radiation at different doses (5, 12.5 and 20 kGy).

Materials and methods

Materials and experimental procedure

The isotactic polypropylene (iPP) spheres are supplied by Braskem, with melt flow index of 3.5 dg min^{-1}, density of

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0.905 g cm^{-3} and $Mw = 300{,}000$ g mol^{-1}. The PP dumbbell samples used in this study were manufactured by injection molding process. The PP was irradiated by gamma rays at different doses of 5, 12.5 and 20 kGy, in an irradiator with ^{60}Co source, in air atmosphere, at dose rate of 5 kGy h^{-1}. Figure 1 shows the total procedures.

Methods

Scanning electron microscopy

The SEM test specimens were coated with gold sputtering coater prior to examination. The EDAX Philips XL 30 (original manufacturing from Japan) SEM was used for collecting secondary electron images from the samples.

Differential scanning calorimetry

Assays were performed in DSC Mettler Toledo 822 equipment under nitrogen atmosphere (original manufacturing from Switzerland). The program used was: heating 50–280 °C for 10 °C min^{-1}, keeping at 280 °C for 5 min, cooling from 280 to −50 °C at a heating rate of −5 °C min^{-1} and reheating −50 to 280 °C at a rate 10 °C min^{-1}. The samples were weighed and placed in aluminum crucibles with caps. The crystallinity was calculated according to Eq. (1):

$$X_C(\%) = \frac{\Delta Hf \times 100}{\Delta H_0} \quad (1)$$

where ΔHf is melting enthalpy of the samples and ΔH_0 is melting enthalpy of the 100% crystalline PP which is assumed to be 209 kJ kg^{-1} [9].

X-ray diffraction

X-ray diffraction measurements were carried out in the reflection mode on a PANalytical, model X'Pert PRO with detector X'Celerator (original manufacturing from Portugal) operated at 40 kv voltage and a current of 45 mA with CuKα radiation (λ = 1,541841 Å). The samples were cut 2 × 2 cm^2 format.

Thermogravimetric analysis

Thermogravimetric curves were obtained with an SDTA 851 TGA thermobalance Mettler-Toledo (original manufacturing from Switzerland), using samples at about 10 mg in alumina pans, under nitrogen atmosphere of 50 mL min^{-1}, in the range from 25 up to 600 °C, at heating rate of 10 °C min^{-1}.

Results and discussion

Scanning electron microscopy

Figure 2 shows SEM results for the PP and PP irradiated at 5, 12.5, 20 kGy in periods of 30, 60 and 90 days under environmental aging.

The effect of gamma radiation plus UV rays and other environmental factors are evident in SEM images shown in Fig. 2. The appearance of cracks on non-irradiated PP started 90 days after exposure. However, cracks appear at 60 days of exposure for irradiated PP at all doses (5, 12.5 and 20 kGy) demonstrating a faster degradation rate. The presence of cracks in the irradiated samples suggests the contraction effect of the oxidized surface layers. The contraction may have created by the increased crystallinity that generates tensile stress and contributes to cracks formation. Another explanation is the formation of oxidized products from free radicals reactions during the chain scission caused by gamma irradiation and environmental aging [10].

Differential scanning calorimetry

The DSC technique was used to study the effect of gamma radiation and environmental aging on PP with and without gamma radiation. Figure 3 and Table 1 show the results.

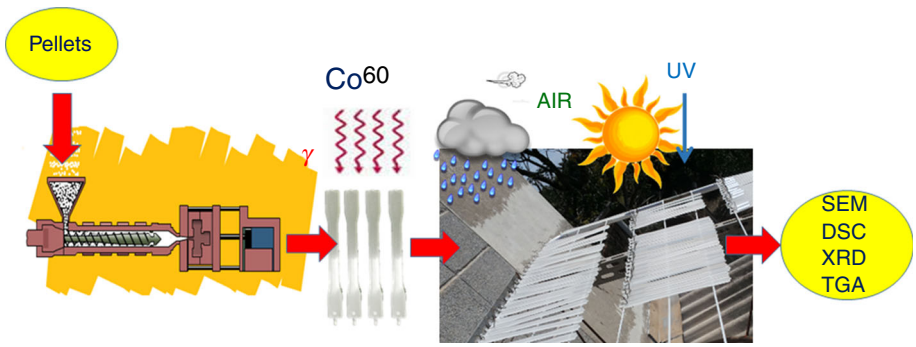

Fig. 1 Preparation and exposition of the dumbbell samples in racks

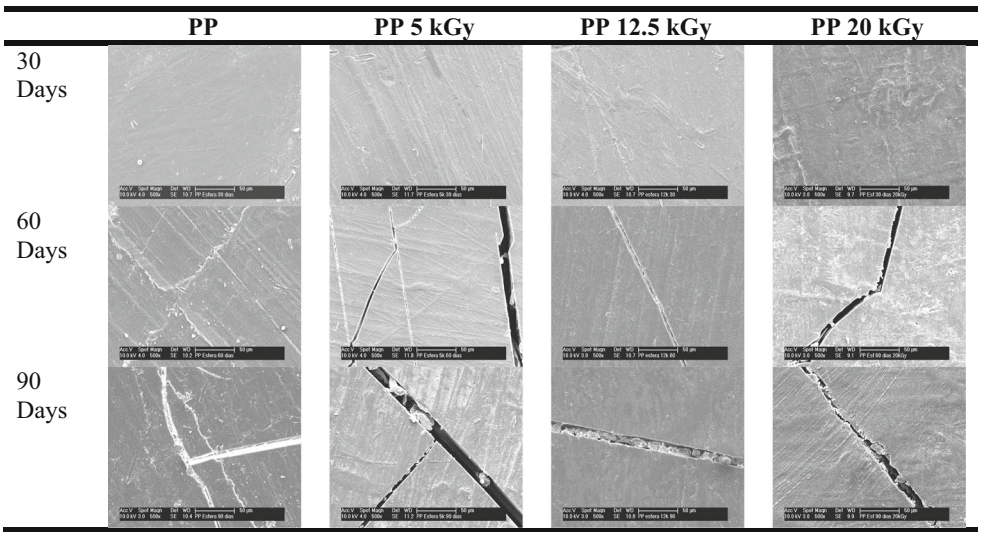

Fig. 2 Photomicrographs obtained by SEM magnification 500× for: PP, PP 5 kGy, PP 12.5 kGy, PP 20 kGy

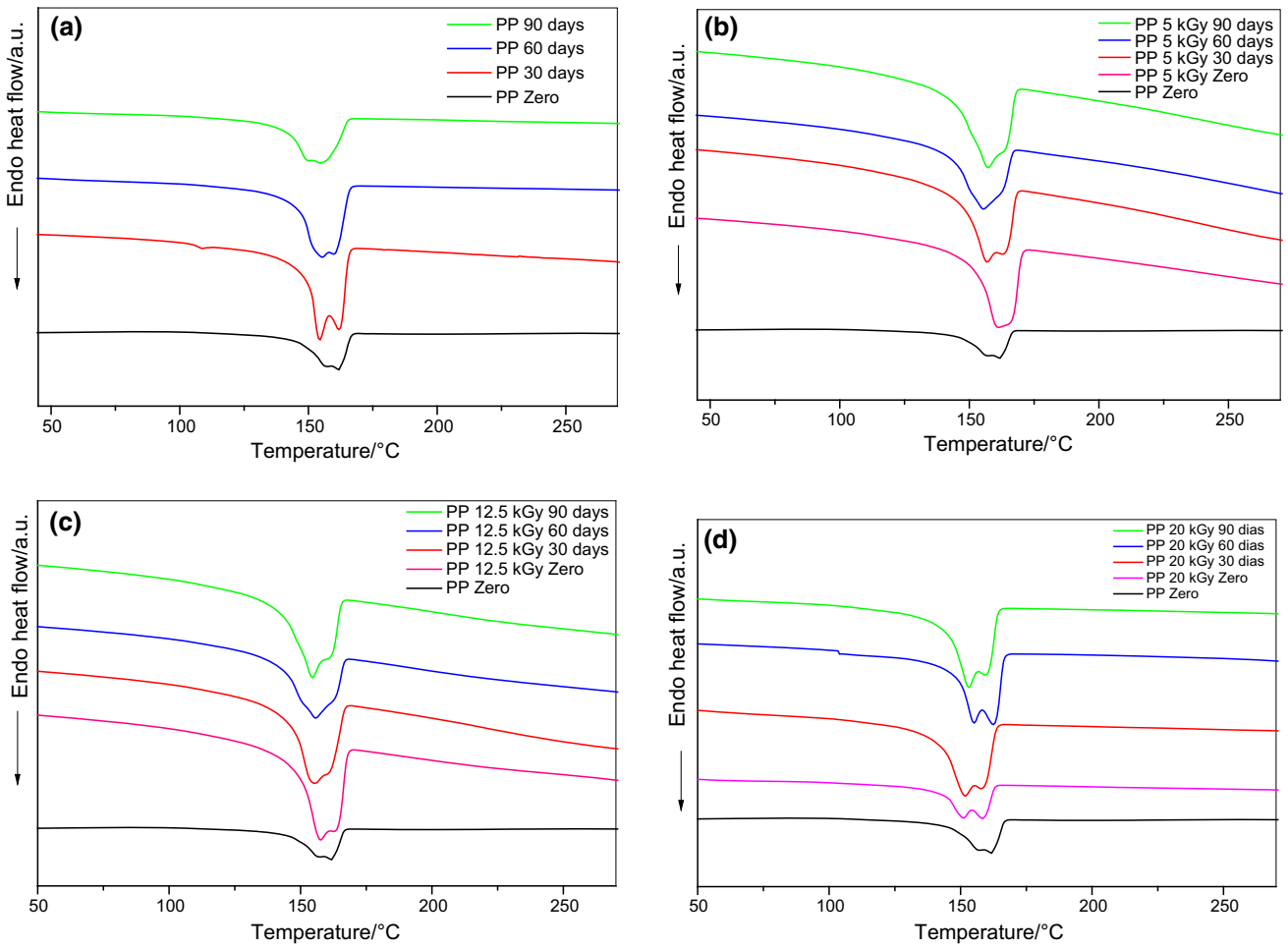

Fig. 3 DSC curves of samples PP (**a**), PP 5 kGy (**b**), PP 12.5 kGy (**c**) and PP 20 kGy (**d**), after environmental aging up to 90 days

The literature reports decrease in T_{m2} with increase in gamma radiation dose in PP at 21 kGy and dose rate at 4.8 kGy h^{-1}, and 25 kGy with dose rate at 6.05 Gy s^{-1}. The crystallinity results show a decrease with increasing gamma radiation dose. Therefore, the gamma irradiation of polypropylene led to noticeable changes in melting temperature and crystallinity of PP due to chain scission, oxygen effects and crosslinking activities that inhibit the

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 5 kGy	159.9	155.6	154.9	156.1	42.7	43.9	39.4	45.7
PP 12.5 kGy	157.1	154.8	154.4	154.1	43.3	44.2	43.9	41.7
PP 20 kGy	158.9	152.1	161.4	152.6	44.9	48.1	41.4	48.2

spherulitic growth and hence decrease the degree of crystallinity [11, 12].

It is known that PP is exposed to gamma irradiation and environmental aging promotes a molecular weight decrease caused by chain scission. When PP is exposed to environmental aging with the progressive oxidation, an increase in the number of chains scission events occurs, causing the T_{m2} displacement to lower temperatures accompanied by crystallinity increasing [13].

In addition, Table 1 shows that crystallinity increases and T_{m2} has a tendency to decrease with increase in radiation dose on zero time and at the end of 90 days of exposure.

DSC results also showed an increase in crystallinity that can be justified by chain scission mechanism, where molecules segments recrystallize by forming new crystals in the form of α- and β-phase (phenomenon chemicrystallization). These results are consistent with the XRD results presented in Table 2.

Double peaks were observed in the DSC curves and can be associated with the presence of separate groups of crystals, as a result of different thickness or lamellar crystals of different modification. In some cases, decomposition in oxidative products or free radicals reactions during heating can promote the decrease in crystallization rate of polypropylene. The melting of the two phases present takes place in two temperature peaks (double peaks) [14, 15].

Table 2 Peak position, half-width and area under curves of PP samples with and without irradiation

Samples	2θ/°	FWHM (2θ/°)	Area (CTS 2θ/°)
PP β	15.9	0.1840	3068 β
PP α	16.7	0.2676	7333 α
PP 90 days β	16.0	0.2175	2277 β
PP 90 days α	16.8	0.3346	9883 α
PP 5 kGy 90 days β	16.0	0.2509	1939 β
PP 5 kGy 90 days α	16.8	0.3346	6803 α
PP 12.5 kGy 90 days β	15.9	0.2007	1228 β
PP 12.5 kGy 90 days α	16.7	0.1673	3151 α
PP 20 kGy 90 days β	16.0	0.2342	1990 β
PP 20 kGy 90 days α	16.8	0.2844	5999 α

X-ray diffraction

The X-ray diffraction technique was used to study the effect of gamma radiation and environmental aging on PP with and without gamma radiation. Figure 4 and Table 2 show the results.

The XRD patterns of PP un-irradiated and irradiated are illustrated in Fig. 4. Peaks at $2\theta = 16.1°$ and 22° attributed to (300)β and (131) + (041)β, respectively, indicate the presence of β-crystals. Peaks at $2\theta = 14.1°$ and 18.5° attributed to (110)α and (130)α also indicate the presence of alpha crystals.

Table 2 represents the peak position (2θ), full width half maxima (intensities of the major peaks of β-phase, and α-phase) and area under curves of PP samples with and without irradiation after environmental degradation.

As shown in Table 2, the FWHM (full width half maximum) for PP β-phase is 0.1840, and it increased for 90 days (0.2175) and 5 kGy (0.250). This shows that the crystallinity is decreased because of the environmental effect in the presence or absence of irradiation. However, as expected the 12.5 kGy which has the maximum crosslinking has decreased the crystallinity much less than the other samples with the environmental conditions. The similar trend was also observed for PP α-phase. These results are also consistent with TGA results as shown in Table 4.

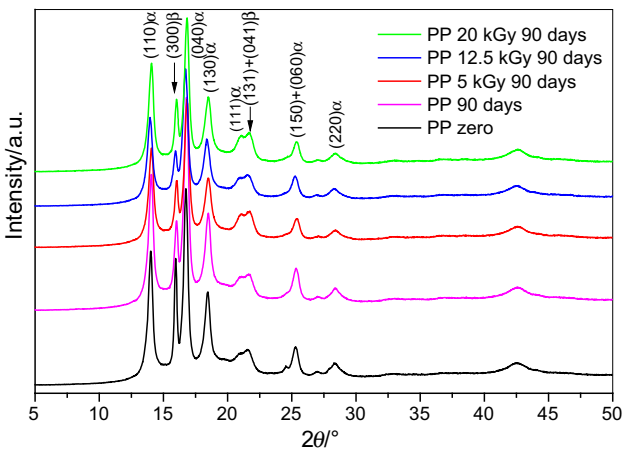

Fig. 4 X-ray diffractograms of neat PP and irradiated PP

The literature describes the increase in amorphous region allows a higher diffusion of oxygen [16, 17]. The increase in crystallinity is due to chain scission followed by chemicrystallization forming new lamellae, and the decrease in crystallinity was accompanied by formation of defects. Ultimately, neither radiation nor aging showed, through formation of defect crystals, the preference of either crystalline phase of α or β [13].

Thermogravimetric analysis

The TGA results indicated the thermal decomposition of the samples, as shown in Fig. 5 and Tables 3 and 4.

In Fig. 5, at zero time T_{onset} decreases with increase in radiation dose revealing the different morphology obtained by radiation process. It promotes mechanisms of chain scission and crosslinking in the PP macromolecule. This corroborates with DSC results of Table 1.

Differently, studies reported by researchers [18] showed results of environmental aging and UV exposure in PP. They showed T_{onset} displacement on PP after 60 days of UV exposure. Another study demonstrated that irradiation lowered the thermal stability of PP with intense displacement of T_{onset} starting from 25 kGy [19]. The literature reports a marked mass loss observed in thermal

Table 3 Values of initial degradation temperature of the samples exposed to environmental aging

T_{onset}/°C	Zero	30 days	60 days	90 days
PP	397.9	393.3	396.3	376.0
PP 5 kGy	395.7	401.0	384.4	394.4
PP 12.5 kGy	391.3	385.0	398.4	344.9
PP 20 kGy	375.8	387.8	380.0	364.0

Table 4 Comparison of the maxima decomposition temperature

T_{max}/°C	PP	PP 12.5 kGy	PP 20 kGy
Zero	461	471	449
30 days	460	468	454
60 days	458	467	456
90 days	458	433	456

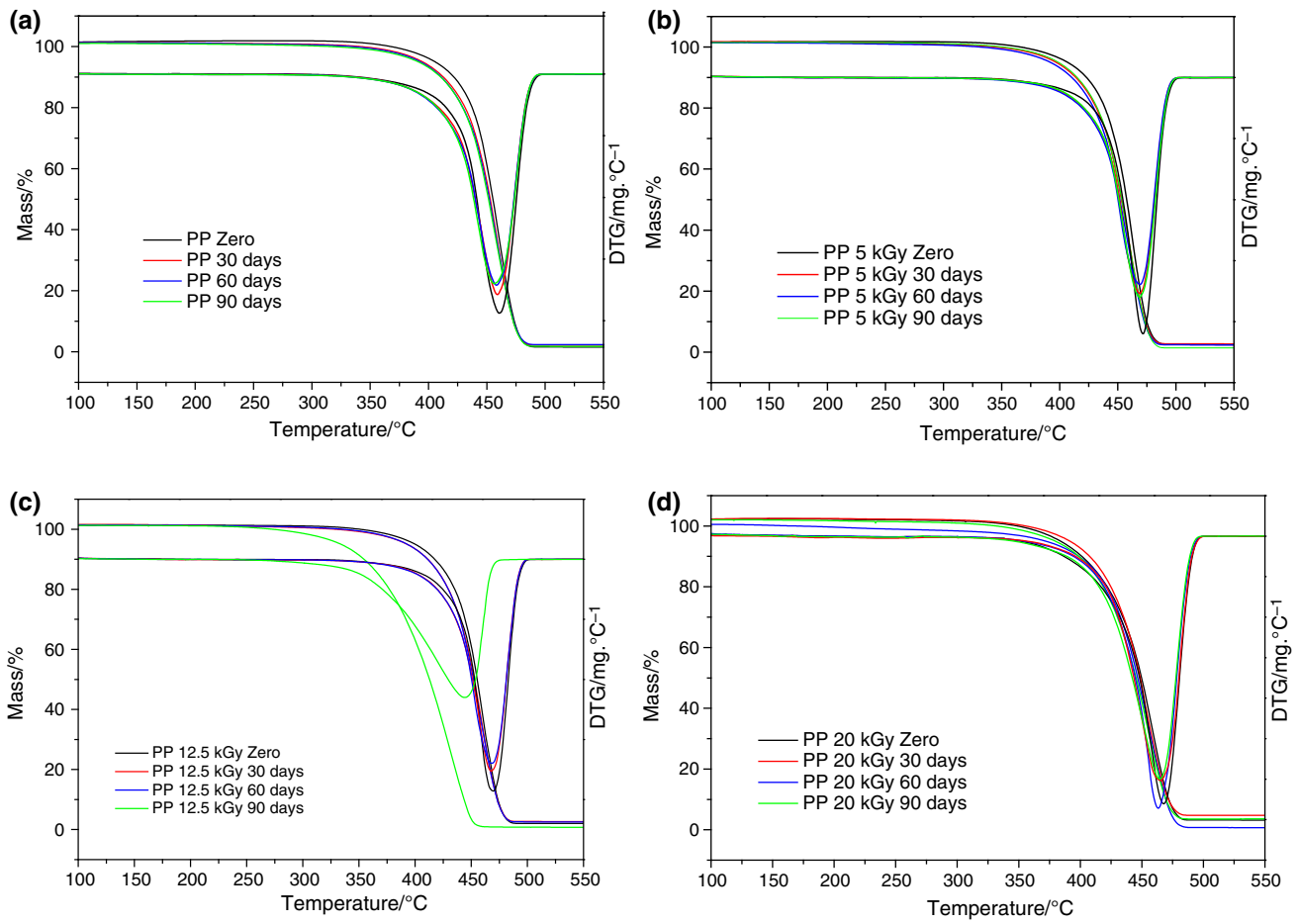

Fig. 5 TGA/DTGA curves of samples PP (**a**), PP 5 kGy (**b**), PP 12.5 kGy (**c**) and PP 20 kGy (**d**), after environmental aging up to 90 days

decomposition, under environmental aging [20, 21]. The actual results of intermediary's periods confirm the crosslinking mechanism in competition with chain scission which allows the increase in T_{onset}.

Table 4 clearly shows that the degradation temperature maximum (T_{max}) increased for PP at 12.5 kGy (471 °C) as compared to the neat PP (461 °C) and 20 kGy (469 °C). As expected, this trend is continued for 30–90 days environmental exposure and also these results are consistent with the XRD results. From these results, it can be concluded that the crosslinking is maximum at 12.5 kGy irradiation and at 20 kGy the polymer scissoring starts to increase. From the table, it is also clear that after scissoring of polymer, the environmental effect is minimum to negligible. These results also have consistence with the XRD results as explained in the previous section.

Conclusions

PP irradiated and exposed to environmental aging may cause molecular structural changes. The crystallinity changes mainly depend on chain scission, crosslinking and radiation dose. The increase in crystallinity is due to chain scission followed by chemicrystallization forming new lamellae, and the decrease in crystallinity was accompanied by the absence of spherulites formation. Gamma radiation and environmental aging did not enhance the formation of either type of crystals significantly. The irradiation strongly degraded with chain scission of the polypropylene samples and intensified the brittleness at 20 kGy. The results show that the occurrence of chain scission resulted in cracks and fissures in samples irradiated at all doses after 60 days of environmental exposure, while the non-irradiated PP after 60 days still showed no sign of degradation in the SEM analysis. Moreover, decrease in thermal stability of PP, especially for higher dose of radiation such as 20 kGy confirms the mechanisms of chain scission. These results are in consistence with DSC and X-ray results. The irradiated at 12.5 kGy PP suffered more intense degradation than PP non-irradiated under environmental conditions for 90 days. After scissoring of polymer, the environmental effect is minimum to negligible.

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