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ACCELERATED ENVIRONMENTAL DEGRADATION OF GAMMA IRRADIATED POLYPROPYLENE AND THERMAL ANALYSIS

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Abstract

Polypropylene (PP) is one of most important plastic commodities in the world. It can be used in many applications due to its relation of 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 and after irradiated using gamma radiation with different doses: 5 kGy, 12.5 kGy and 20 kGy. The irradiated samples were exposed to environmental aging during 90 days and characterized by Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TG) and Differential Scanning Calorimetry (DSC). The dumbbell samples PP 5 kGy, 12.5 kGy and 20 kGy, exposed to environmental aging, showed intense oxidation with presence of surface cracks compared with the PP non-irradiated.

Keywords: Polypropylene, Gamma Radiation, Environmental aging, Thermal Analysis

1. INTRODUCTION

Polypropylene is a thermoplastic obtained by polymerization addition 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 (Pasquini, 2005). Upon exposure to environmental condition, heat, pollution, humidity, oxygen, and UV rays, it is known that polymers suffer aging due to absorption of UV rays by impurities. The exposure to several environmental factors especially UV rays, heat and oxygen that may result in chemical reactions that generate carbonyl groups, hydroperoxides and peroxides, causing chain scission and the appearance of cracks in the material (Girois et al., 1996; Tidjani, 2000; Oliani et al., 2010). Free radicals formation is the key to begin the PP degradation process. Tertiary carbons present at macrochains are fundamental to undergo scission due to its lower binding energy. This macroradical can promote the molecular scission whenever the polymer is subjected to environmental stress or gamma radiation (Terano et al., 2005). Reactivity of chemical bonds will generate a macro radical P• that in presence of oxygen form a POO• peroxide. After gamma irradiation and environmental ageing, PP suffers predominantly chain scission and a reduction of molecular weight. In addition with the increase time of exposure occurs the displacement of melting temperatures to lower values. The chain scission at a high level causes fissures and cracks on polymer surface and the elasticity loss and consequently degradation of the polymer occurs (Al-Malaika, 2003; Komatsu et al., 2016).

2. OBJECTIVE

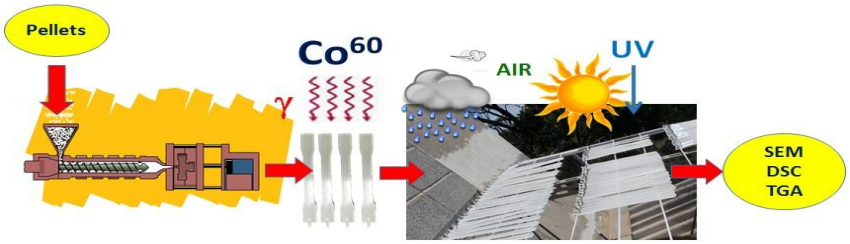
The aim of this study is the control of polypropylene degradation using gamma radiation at different doses (5 kGy, 12.5 kGy and 20 kGy) and to compare the effect of environmental aging of PP neat.

3. MATERIALS E METHODS

Materials and Experimental Procedure

The isotactic polypropylene (iPP) spheres 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}.

The PP dumbbell samples used in this study were manufactured by injection molding process, in Injection Molding Machine model ROMI PRIMATE 65-R. The PP were irradiated by gamma rays at doses of 5 kGy, 12.5 kGy and 20 kGy, in an irradiator with ^{60}Co source, in air atmospheric, at dose rate of 5 kGy h^{-1}. Scheme 1 shows the procedures.



Scheme1. Preparation and exposition of under environmental conditions in racks facing north at 45° inclination.

Methods

Scanning Electron Microscopy

Specimens were coated with gold sputtering coater prior to examination. The EDAX Philips XL 30 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. The program used was: 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 10 ºC min^{-1}. The samples were weighed and placed in aluminum crucibles with caps. The cristallinity was defined as follows:

$$Xc(\%) = \frac{\Delta Hf x 100}{\Delta Ho}$$

Where ΔHf is melting of the samples, ΔH_0 is melting enthalpy of the 100% crystalline PP which is assumed to be 209 kJ g^{-1} (MARK, 2007).

Thermogravimetric Analysis

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

4. RESULTS E DISCUSSION

Scanning Electron Microscopy

Figure 1 shows SEM results for the PP and PP irradiated at 5 kGy, 12.5 kGy, 20 kGy in periods of 30, 60 and 90 days under environmental aging.

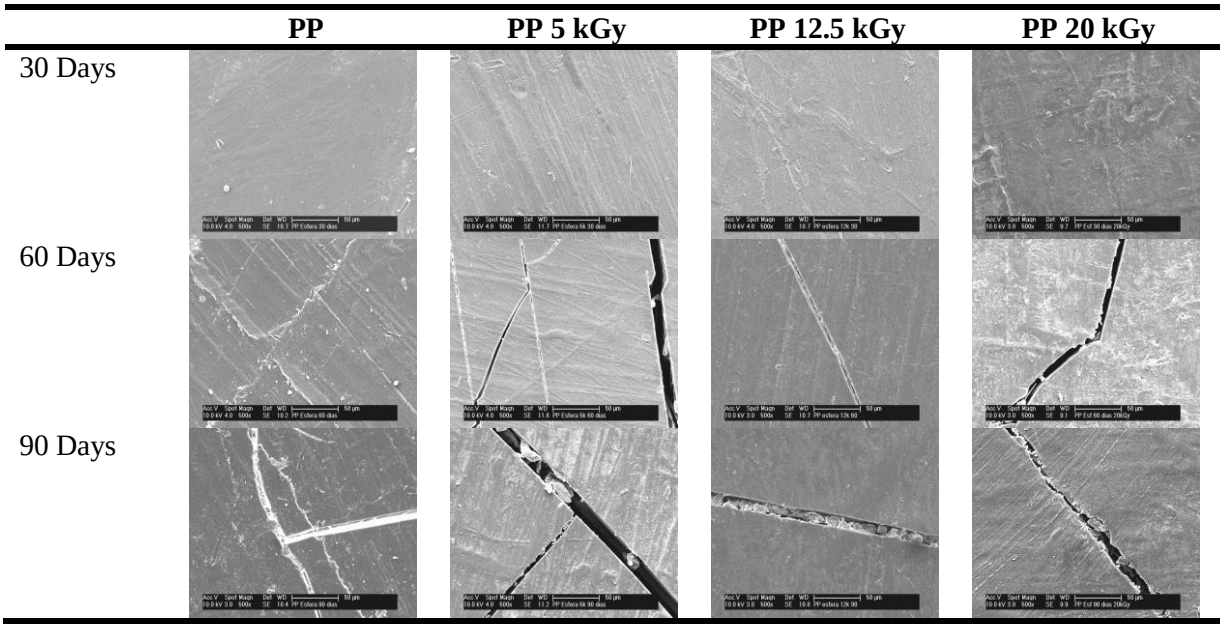


Figure 1. Photomicrographs obtained by SEM enlarged 500x times for: PP, PP 5 kGy, 12.5 kGy, PP 20 kGy.

The effect of gamma radiation plus UV rays and others environmental factors are evident in the results of SEM. The appearance of fissures and cracks on PP not irradiated, started 90 days after exposure. However for PP irradiated at all doses (5; 12.5 and 20 kGy), cracks and fissures appear at 60 days of exposure, demonstrating a faster degradation rate. The presence of fissures and cracks in the irradiated samples can be explained by the chain scission phenomenon, consequence of free radicals formation by gamma irradiation (Oliani et al., 2015).

Differential Scanning Calorimetry

DSC technique was applied to evaluate the second melting temperature (T_{m2}/ °C) and the degree of crystanillity (X*c* %). Figure 2 and Table 1 show the results.

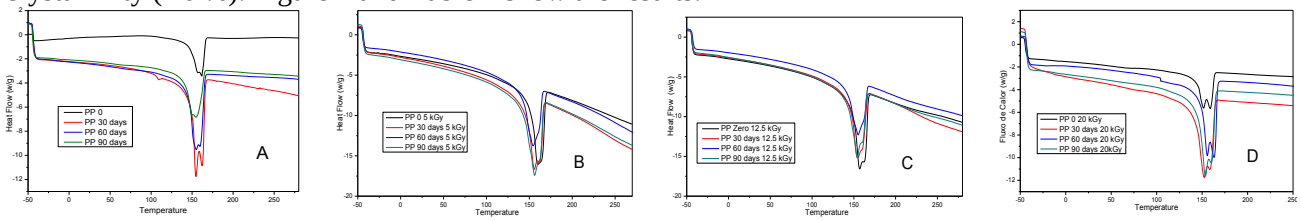


Figure 2. DSC curves of samples PP (A), PP 5 kGy (B), PP 12.5 kGy (C) and PP 20 kGy (D), after environmental aging up to 90 days.

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

	T_{m2} / °C (±0.1%)				X_C / % (±0.5%)			
Samples	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

The results of DSC show that the increase of dose irradiation at PP on zero time decreases T_{m2} .To lower temperature and are accompanied by cristallinity increase. It is known that when PP is exposed to gamma irradiation and environmental aging, occurs a decrease of molecular weight caused by chain scission (Perera et al., 2004). The chain scission is the cause of the displacement of T_{m2} and increased crystanillity increase due to the formation of new crystals with imperfections (phenomenon chemicrystallization). PP 12 kGy after 90 days showed an decrease of crystallinity, which can be justified by chain scission reactions accompanied by crosslink, and consequently an increase of amorphous region. The increase of amorphous region allows a higher diffusion of oxygen (Rabello and White, 1997; Parparita et al., 2015, Abiona and Osinkolu, 2010).

Thermogravimetric Analysis

The TG results indicated the decomposition of the samples, Table 2.

Table II. 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	322.3	364.0

Studies show that increasing irradiation dose reduces the thermal stability of the polymers. At zero time was observed decrease of (T*onset*) with increase of radiation dose. In some cases (T*onset*) increased, in PP 5 kGy under aging suggesting a low level of crosslink stabilized the samples, and for PP 20 kGy the increase of (T*onset*) suggest that free radicals formed crosslink under ageing in competition with scission mechanism. After 90 days, all samples show decrease of (T*onset*) specially that prepared at higher doses radiation (PP 12.5 kGy and PP 20 kGy). It is therefore clear that when PP is exposed to gamma irradiation plus environmental aging, the irradiated PP decomposes at temperatures lower than the non-irradiated PP (Muthukumar et al., 2010).

5. CONCLUSION

The irradiated PP suffered more intense degradation than PP non-irradiated. The results show that the occurrence of chain scission resulted in: cracks and fissures in samples irradiated at all doses from 60 days of environmental exposure, while the non-irradiated PP after 60 days still showed no sign of degradation in the SEM analysis. DSC results show that at zero time occurs a decrease of T_{m2} with increase of irradiation doses and after 90 days under environmental aging also occurs a decrease of T_{m2}. In addition was observed an increase crystallinity, for more higher irradiation doses, it is possible to note that after 90 days under environmental aging occurs an increase of crystallinity for all samples except for PP 12 kGy that show an decrease of cristallinity that can be justified by an increase of amorphous region. TGA results show at zero time occurs a decrease of initial decomposition temperature (T*onset*) with increase of irradiation doses consequence of gamma irradiation. After 90 days of environmental aging all samples show decrease of (T*onset*) specially samples irradiated with a higher doses. All these factor are consequences of chain scission. Therefore the gamma irradiation proved to be a great method to accelerate the degradation when PP is exposed to environmental aging.

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