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GAMMA IRRADIATION EFFECTS IN LOW DENSITY POLYETHYLENE

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ABSTRACT

Low density polyethylene (LDPE) is obtained from ethylene gas polymerization, being one of the most commercialized polymers due to its versatility and low cost. It's a semi-crystalline polymer, usually inactive at room temperature, capable to attain temperatures within a 80 °C – 100 °C range, without changing its physical-chemical properties. LDPE has more resistance when compared to its equivalent High Density Polyethylene (HDPE). LDPE most common applications consist in manufacturing of laboratory materials, general containers, pipes, plastic bags, etc. Gamma radiation is used on polymers in order to modify mechanical and physical-chemical features according to utility purposes. This work aims to the study of gamma (γ) radiation interaction with low density polyethylene to evaluate changes in its physical-chemical properties. Polymer samples were exposed to 5, 10, 15, 20 and 30kGy doses, at room temperature. Samples characterization employed Thermal Analysis, Melt Flow Index, Infrared Spectroscopy and Swelling tests.

Key-Words: LDPE, gamma radiation, melt flow index, crystallinity.

1. INTRODUCTION

Polyethylene has as characteristic a structure partially crystalline and flexible and its mechanicals properties are directly influenced by the shape of its structure [1]. For the intended polymerization are used catalytic systems that according to reactions conditions generate different types of polyethylene and the most common are: Low Density Polyethylene (LDPE), High Density Polyethylene (HDPE) and Linear Low Density Polyethylene (LLDPE). Physical properties and processing characteristics of these resins are distinct due to different molecular structures, especially related to the degree and length of branches and polydispersion [2, 3].

LDPE is a semi-crystalline polymer (50-60%), with branched chains that influence in the viscosity of the polymer in solution and in the determination of crystallinity degree, which impart high resistance to impacts, high flexibility, tenacity, stability and processability. LDPE physical properties are shown in Table 1.

Table 1. LDPE physical properties [4]

Property	ASTM Method	LDPE
Density, g/cm^3	D792	0.912-0.925
Crystalline Melting Point	-	102-112
Refractive Index, n_D	D542	1.51-1.52
Tensile at Yield, MPa	D638	6.2-11.5
Elongation at Yield, %	D638	100-800
Tensile Strength, MPa	D638	6.9-16
Elongation, at maximum, %	D638	100-800
Modulus of Elasticity, MPa	D638	102-240
Hardness, Shore D	D676	40-50

LDPE has high resistance to water and to some aqueous solutions, even at high temperatures, but it is vulnerable to oxidizing agents besides aliphatic, aromatic and chlorate solvents, that cause swelling at room-temperature [4]. Due to its good characteristics, LDPE is especially used in films for packing [5].

The effects of gamma radiation on polymers depend on many factors, such as the chemical structure and the morphology and the environmental irradiation conditions [6, 7]. Ionizing radiation can profoundly alter the molecular structure and thereby the macroscopic properties of polymeric materials through mechanisms like chain scission, cross-linking and oxidation [8].

The effects of ionizing radiation on LDPE can be summarized as follows [9]: the evolution of hydrogen; the formation of carbon-carbon cross-links; an increase in unsaturation to an equilibrium level; a reduction in crystallinity; the formation of color bodies in the resin and surface oxidation during irradiation in air. The formation of carbon-carbon crosslinks is by far the most important effect and is the basis of the applications in wire and cable industry and for heat-shrinkable products. The factors affecting the changes of polyethylene by irradiation are the molecular weight distribution, branching, degree of unsaturation, and morphology [10, 11].

This work aims to the study of gamma (γ) radiation interaction with low density polyethylene to evaluate changes in its physical-chemical properties. Polymer samples were exposed to 5, 10, 15, 20 and 30kGy doses, at room temperature.

2. EXPERIMENTAL

2.1. Materials

In this study was used LDPE, EF-2126, from QUATTOR, in pellets.

2.2. Methods

Samples were irradiated in Embrarad/CBE, under gamma rays Cobalt 60 (^{60}Co) in air, at 5 kGy/h rate, within a 5, 10, 15, 20 and 30 kGy doses range.

For the characterization of triplicate samples, there were assessed following properties, before and after radiations.

2.2.1. Melt Flow Index

Melt Flow Index analyses were accomplished in a CEAST apparatus, *modular line*. Samples were analyzed at 190 °C temperature, 2.16 kg load, 240 seconds pre-heating time, according to ASTM D1238-04C.

2.2.2. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed in a Mettler-Toledo TGA / SDTA 851, equipped with thermobalance. Samples with approximately 10mg were analyzed in aluminum pans under nitrogen atmosphere, at 50 ml min^{-1} ratio, from 25 to 700 °C, 10 °C min^{-1} heating rate, according to ASTM E 1641-07.

2.2.3. Gel-fraction Essay

In this test it was used around 0.3 g of sample, wrapped in a 500 mesh steel screen and the entire assembly (120 µm) was further immersed in xylene (approximately 250 ml) in a 500ml bottle. The test was accomplished in triplicate and samples were subjected to a reflux system, by solvent ebullition at 135 °C, via a heating mantle, and a ball condenser is used in its condensation, adapted to the bottle mouth. This system was subjected to a 24 hour reflux, in accordance with ASTM D 2765-01. During the extraction, gel-fraction did not dissolve in the solvent and remained inside the steel screen, while the non-crosslinked fraction was dissolved, migrating to the solvent. Samples drying process was accomplished in an oven at 60 °C for 15 hours. Wrappings were weighed and gel-fraction was calculated, by applying the equation:

$$Gel\ \ Fraction\ (\%) = \left(\frac{Mf}{Mi}\right) 100$$

Where M_f is the final mass and M_i is the initial mass for each sample.

2.2.4. Infrared (IR)

The infrared spectroscopy by ATR-IR was carried out on FTIR of Thermo Nicolet spectrometer to record the spectra of non irradiated and irradiated samples. The pellets were put between the machine base and the probe of ATR.

2.2.5. Swelling

Swelling test is intended for the assessment of material capacity in absorbing solvents. This essay was performed using xylene. Irradiated and non-irradiated samples were dipped in xylene and weighing was accomplished each 15 minutes at first hour, each 30 minutes at the second hour and each 1 hour, for an 8 hour period after starting the test. Samples were centrifuged for one minute before the final weighing, for eliminating in a standardized way solvent excess.

3. RESULTS AND DISCUSSION

The infrared spectra are shown in Fig. 1 and in spite of the irradiation process made under oxygen atmosphere does not cause any change in the structural polyethylene. The prominent bands of LDPE at 1464, 1377 and 719-720 cm^{-1} arising from the CH_2 group in the PE chain [12], appear almost without modification, the same happens with bands of the methylene groups stretches at 2920 and 2850 cm^{-1}. The peaks refer to the carbonyl (1700 cm^{-1}) and hydroxyl (3500 cm^{-1}) group do not appear, probably because the doses used in this study didn't cause high degradation in the polymer chain.

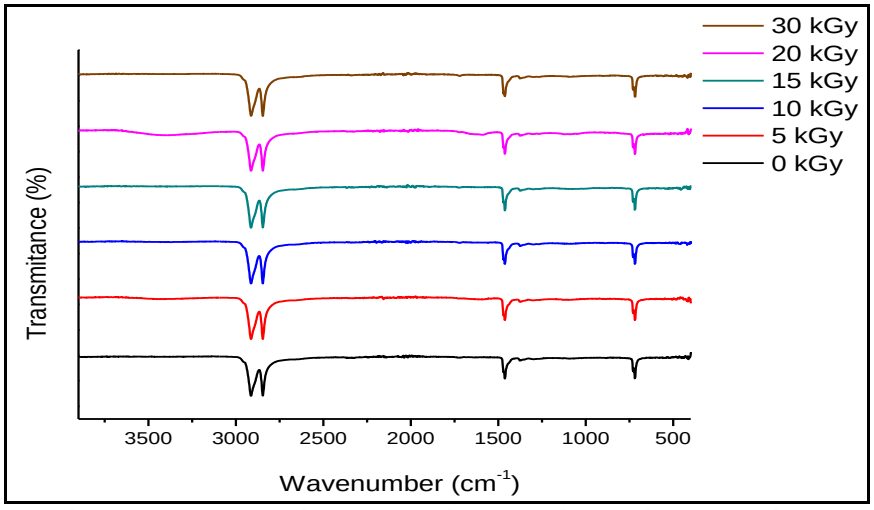

Figure 1. Infrared spectra (ATR-IR) for the samples.

Thermogravimetric curves are in Fig. 2 and reveal the same profile for all samples. The initial degradation temperature did not affect the polymer, the temperature, from 465 °Cfor non-irradiated, 473 °C for 5kGy, 470 °C for 10kGy, 469 °C for 15 kGy, 471 °C for 20kGy and 469 °Cfor 30kGy. These thermograms indicate that the radiation does not influence LDPE degradation process.

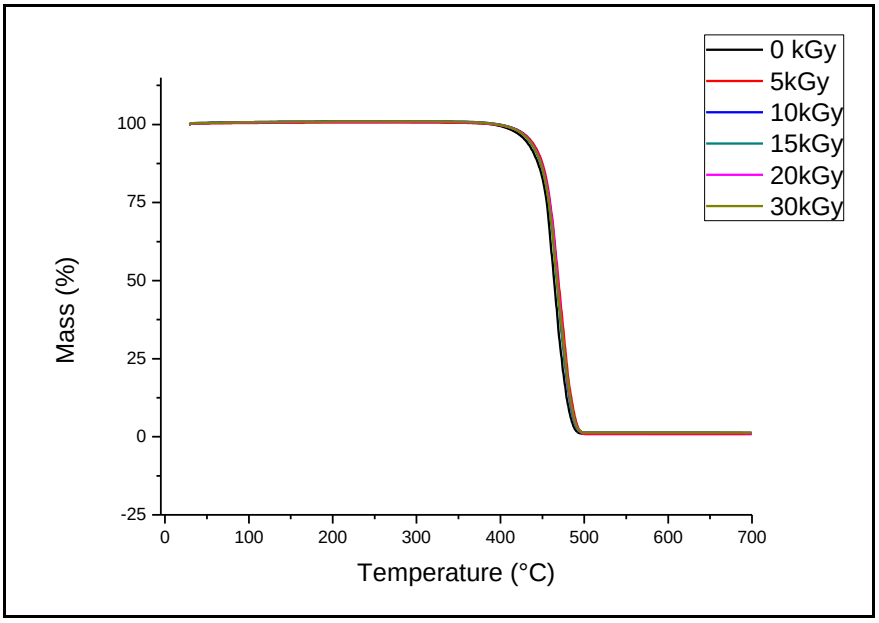

Figure 2. Thermogravimetric curves for pellets irradiated and non-irradiated.

The impossibility for obtaining a melt flow index in the plastometer above 5kGy is associated to a high viscosity presented by irradiated materials, pointing for the efficacy of inserted branches, even at low doses (lower than 30kGy). Table 2 presents results obtained for melt flow index, for irradiated and non-irradiated samples.

Table 2. Melt Flow Index for 0, 5, 10, 15, 20 and 30kGy samples.

Absorbed dose	*Melt Index ($g.10^{-1}min^{-1}$)*
0 kGy	2. 62
5 kGy	1. 51
10 kGy	None flow in plastometer
15 kGy	None flow in plastometer
20 kGy	None flow in plastometer
30 kGy	None flow in plastometer

In Table 3 are presented results for gel-fraction for irradiated and non-irradiated samples. Low results for gel-fraction were previously expected for modified LDPE samples, because even at low radiation doses (≤ 30kGy) there was the build-up of branches and consequently the occurrence of the crosslinking. High viscosity shown by melt flow index corroborates this assertive.

Table 3. Gel-fraction for 0, 5, 10, 15, 20 and 30kGy samples.

Absorbed dose (kGy)	*Gel-fraction(%)*
0	0.73
5	0.60
10	0.62
15	1.53
20	1.77
30	5.45

Figure 3 indicates swelling for 0, 5, 10, 15, 20 and 30kGy film samples, although theoretically the higher irradiation dose, the lesser swelling capacity, this characteristic was not clearly proved. Behavior shown for 20 and 30kGy samples was not expected, because these both more irradiated samples should have presented a lower swelling capacity.

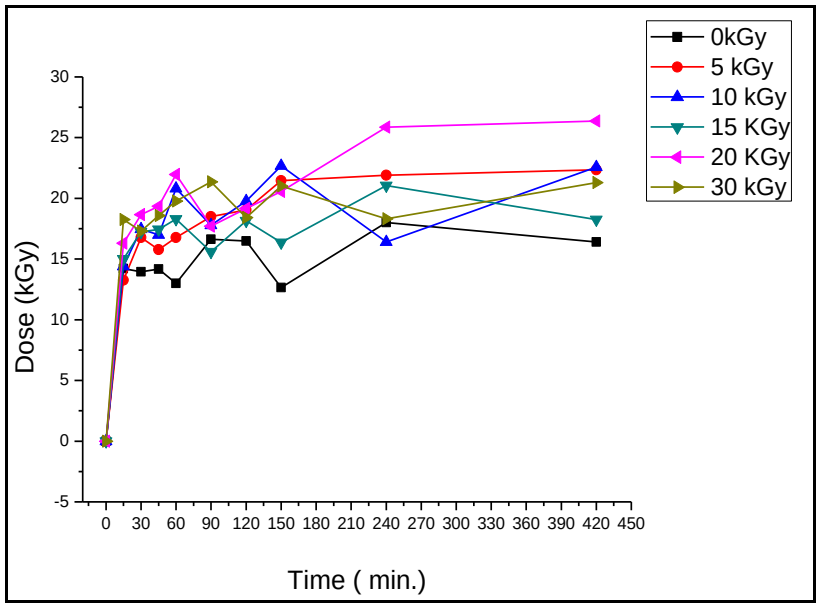

Figure 3. Swelling for 0, 5, 10, 15, 20 and 30kGy samples.

3. CONCLUSIONS

Thermogravimetric analysis, melt flow index, gel-fraction and swelling techniques showed to be effective in LDPE characterization after its gamma radiation at 5, 10, 15, 20 and 30kGy, at a 5kGy/h ratio, being possible to detect differences in function of irradiation doses and crosslinking, branching or scission effects.

Thermal degradation temperature with volatile products loss is indicated by mass loss in TGA curve; this slight slope indicates that in spite of crosslinking, chain scission and oxidation, practically there is no LDPE thermal stability variation on irradiation.

By ATR-IR was not possible to verify the presence of carbonyl and hydroxyperoxide groups. By swelling test it is possible to confirm the degradation process due to swelling non proportional to absorbed dose. Lack of flow for irradiated samples above 5kGy and low results obtained for gel-fraction proves that presented high crosslinking index, even at low doses.

4. ACKNOWLEDGMENTS

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