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CHARACTERIZATION OF INJECTED LINEAR LOW DENSITY POLYETHYLENE (LLDPE) IRRADIATED BY GAMMA-RAY

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ABSTRACT

The aim of this paper is to investigate of gamma irradiation effects on linear low density polyethylene (LLDPE) injected. Polymers processed by gamma radiation have new physical–chemical and mechanical properties. The ionizing radiation promotes chain scission and creates free radicals which can recombine, providing their annihilation, for crosslinking or branching. The polymer was irradiated with a source of ^{60}Co at doses of 5, 10, 20, 50 or 100 kGy at about 5 kGy s^{-1} rate, at room temperature. The changes in molecular structure of LLDPE were evaluated using melt flow index, gel fraction, differential scanning calorimetry (DSC), fourier transform infrared spectroscopy (FT-IR) and thermogravimetry analysis (TG). The results showed that the properties depend on dose irradiation.

1. INTRODUCTION

The polyethylene is widely used as an injection moulding material. It has excellent flow characteristics, good heat stability being not sensitive to moisture. These properties permit the use of polyethylene in a wide variety of applications, including toys, bottles, containers, housewares and industrial parts [1].

Linear low density polyethylene (LLDPE) is produced by a low pressure process with the copolymerization ethylene and alpha olefin. LLDPE degrees of crystallinity and lowers the density.

The behavior and extension on various the application fields of this polymer with the expectation of new properties or the elimination of undesirable features are the alls of irradiation free of useful properties as initial polymer is possible to be infused by ionizing radiation [2].

The treatment of polymer with hide energy promotes the formation of very reactive intermediates namely free radicals, ions and excited molecules. The main processes in which they are involved are crosslinking and degradation. When one is there predominates it which obtained stable as less stable material [3].

The aim of this paper is the investigation on structural changes of injected LLDPE modified by ionizing radiation.

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2. EXPERIMENTAL

The commercial linear low density polyethylene with density 0,920 g/cm^3 was injected by the apparatus DEMAG ergo tech pro 35-115. The samples were placed in resistant bag in presence of air, for the irradiation procedure. These samples were irradiated with a ^{60}Co source CBE/EMBRARAD, at doses of 5, 10, 20, 50 or 100 kGy at about 5 kGyh^{-1} dose rates, at room temperature. After irradiation, samples were heated for 1 hour at 100 ºC to promote there combination and annihilation of residual radicals [4].

2.1. Melt flow rate (MFR) and Swelling

The analysis flow index measurement indicates the rate of extrusion of polymer material through a die of specific 48 mm length and 2 mm diameter under stated conditions of load and temperature. The material is allowed to flow through the die (2 mm), according to ASTM D1238-04c listed in Table 1 [5].

Table 1 – Standard test conditions.

Material	Condition	Temperature (ºC)	Total load including piston, (kg)
LLDPE	190/2,160	190	2,160

For the calculation of swelling the material tested by the apparatus CEAST, we used the following equation:

$$\text{Swelling (\%)} = [(D_p - 2)/2] * 100 \qquad (1)$$

where D_p is the diameter of the expanded polymer.

2.2. Gel Fraction

Specimens of the crosslinked polymer are weighed and evolved in a steel screen immersed in hot xylene for 24 h, removed, dried and reweighed. The percent extract are calculated from these weight measurements. According to ASTM D 2765-01 [6].

2.3. Differential scanning calorimetry (DSC)

The samples were heated from 25 to 180 °C at a heating rate of 10 °C min^{-1} under oxygen atmosphere; maintaining for 5 min at 180 °C, then cooled to 25 °C at a heating rate of 50 °C min^{-1}, according to ASTM D 3418-08 on the apparatus DSC822^e METTLER TOLEDO. The crystallinity was calculated according to equation 2:

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$$X_C(\%) = \frac{\Delta H_f \times 100}{\Delta H_0} \qquad (2)$$

ΔH_f = melting enthalpy of the sample, ΔH_0 = melting enthalpy of 100% crystalline PE which is assumed to be 279 J/g [7].

2.4. Fourier transform infrared spectroscopy (FT-IR)

The infrared spectra were obtained in reflectance mode in apparatus Thermo Nicolet Model 380 FT-IR with Smart Orbit accessory[8].

2.5. Thermogravimetry analysis (TG)

The samples were heated at a heating rate of 10 ºCmin^{-1} starting from 25 °C temperature up to 600 ºC, under oxygen flow at a rate of 50 mLmin^{-1} using a TA Mettler Toledo, model TGA/SDTGA 851e [9].

The TG measurements record only the loss of volatile decomposition fragments of polymers [10].

3. RESULTS AND DISCUSSION

The LLDPE prepared by Ziegler-Natta catalyst system have high heterogeneity in the intermolecular distribution along the polymer chains. The branches are located in the lower molecular weight chains. Linear molecules and low molecular weight, branched with a narrower molecular weight distribution (MWD) [11], show the elevated melt index.

In the case of irradiated polyethylene the competition between degradation and crosslinking takes place. It happens under the modifications in structural features can be occurred only in amorphous phase. The oxidative degradation increases the number of polar groups. The process crosslinking restricts the motion of macromolecules [12].

The decrease the flow index melting at increasing doses of radiation can be observed in fig. 1 (a). Because the irradiated samples were fragmented, the changing in the conformation of the chains occurred. Radiation scissors bonds of the main chain [13]. At doses exceeding 50 kGy, the free radical and another fragments are involved in crosslinking much easy if it compared to low doses.

For higher gel fraction values (fig. 1 (b)) due perhaps to the presence of a high insoluble fraction the polymer decreases in the melt flow index [14]. The MFI indicate the variation in crosslinking level of fused material. Thus, the absence of melt flow index values at doses

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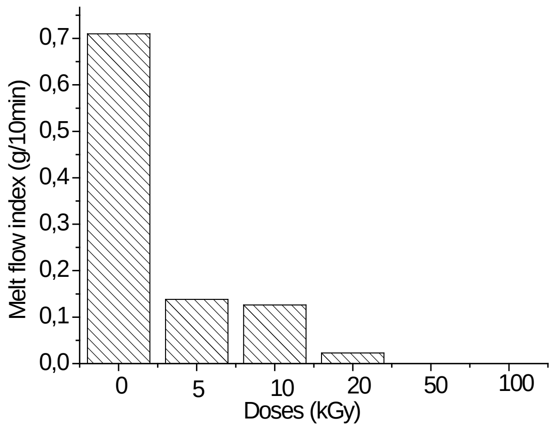
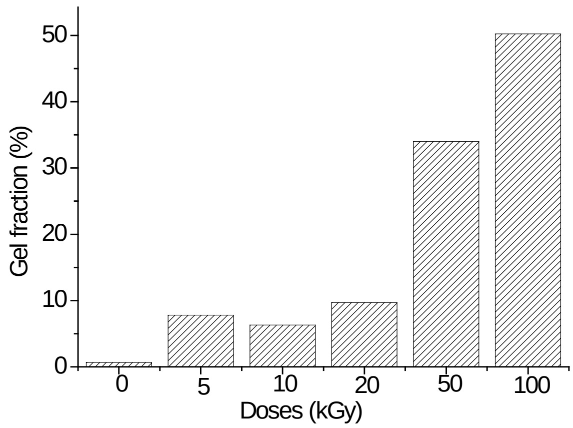
above 50 kGy, explains increase of crosslink with dose and the decrease of mobility. It seems indicates the limitation of MFI values to gamma radiation effect irradiation.



(a)



(b)

Figure 1: Melt flow index (a) and Gel fraction (b) of injected LLDPE on different doses.

The values of melting temperature (T_f) had a smooth variation (Table. 2).

Table 2- DSC results of irradiated and non-irradiated of polyethylene.

Doses	T_f	ΔH_f	ΔH_c	X_c
(kGy)	(ºC)	(J/g)	(mJ)	(%)
0	124,25	67,04	589,82	24,03
5	124,41	82,30	616,28	29,50
10	125,00	90,84	718,34	32,56
20	126,16	78,76	741,93	28,23
50	124,45	80,43	800,60	28,83
100	122,99	78,31	537,03	28,07

It can be observed In fig. 2 (a) that upon exposure to high energy radiation, linear polyethylene exhibits an increase in the crystallinity degree. Regarding, the radiation effects changes occurred in the amorphous regions are due for scission preferential, and advanced

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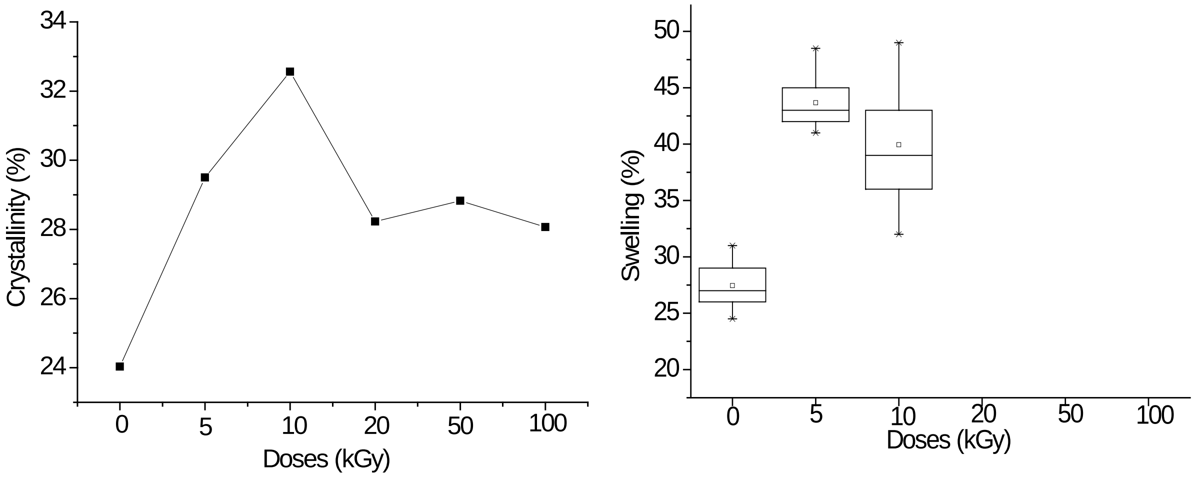
recrystallization [15]. It was observed that the increase of irradiation dose in polyethylene promotes a greater amount of crosslinking.

The elastic deformation of the material at the inlet of the die causes the extrudate to swell at the die outlet. This swelling behavior is affected by molecular structure. The side-chain branches in LLDPE are short chains. It doses not cause any molecular entanglement [16]. In fig. 2 (b) we can observe that the increase in swelling was due to chain scission. It may be explained by changed their morphology and increased friction between the chain and cylinder wall.



(a) **(b)**

Figure 2: Crystallinity (a) and Swelling (b) of injected of LLDPE on different doses.

In fig. 3 observed characteristic bands of LLDPE around 2941, 2855, 1471 cm^{-1} to -CH_2 and wavelength 714 cm^{-1} to (CH_2) n> 4 [8]. It did not have a large variation with the irradiated.

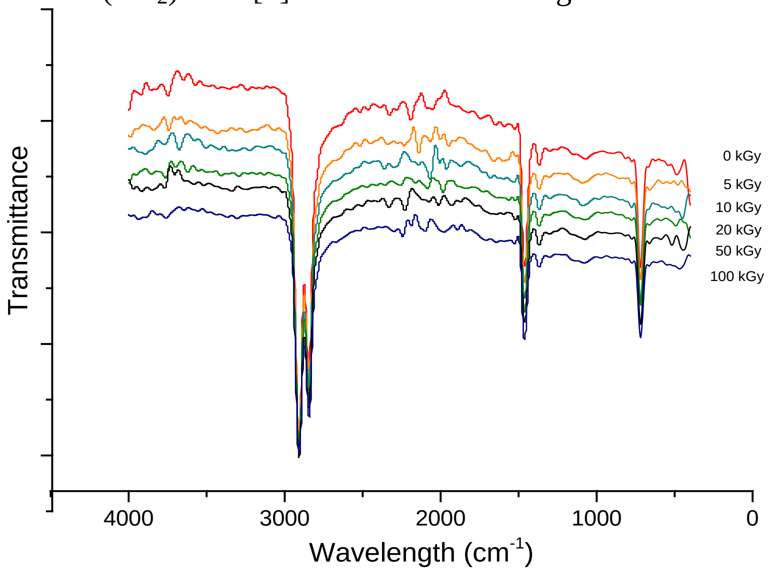


Figure 3: Spectra of FT-IR of injected of LLDPE on different doses.

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The crosslinking turns the consistency of thermoplastic polymer to desirable properties at high temperature [17]. Compared to non-irradiated sample, indicate the Fig. 4, with doses of 5 or 10 kGy move the main peak (at about 380 °C) to lowest temperature 340 °C, promoting more scission leading to decrease average molecular weight of the sample. With increasing the dose, the peaks move to higher temperatures, demonstrating the less scission and more crosslink of the polymer (Fig. 1b).

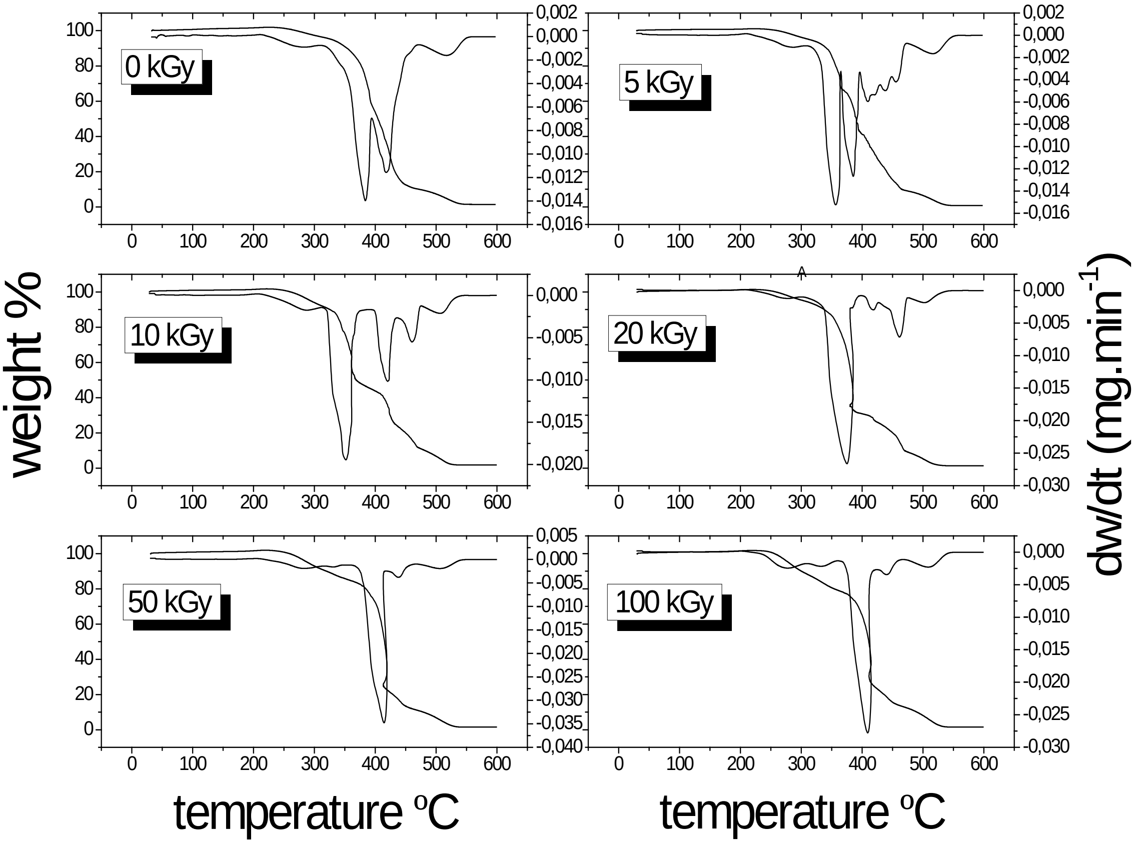

Figure 4: TG and DTG of injected of LLDPE on different doses.

4. CONCLUSIONS

The injected linear low density polyethylene subscribed to irradiation with different doses, was characterized by variation in for melt flow index, gel fraction, swell, DSC, FT-IR and TG-DTG. The induced effects by gamma radiation on injected LLDPE are scission and crosslinking. These analyses make evident the effect of the radiation in the LLDPE.

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