

THERMAL, TENSILE AND RHEOLOGICAL PROPERTIES OF LOW DENSITY POLYETHYLENE (LDPE) PROCESSED IRRADIATED BY GAMMA-RAY.

Hélio F. R. Ferreto, Ana C. F. de Oliveira, Duclerc F. Parra and Ademar B. Lugão

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
hferreto@ipen.br

ABSTRACT

The aim of this paper is to investigate structural changes of low density polyethylene (LDPE) modified by ionizing radiation (gamma rays). The gamma radiation process for modification of commercial polymers is a widely applied technique to promote new physical-chemical and mechanical properties. Gamma irradiation originates free radicals which can induce chain scission or recombination, providing its annihilation, branching or crosslinking. The samples were prepared in hydraulic press in temperature 180°C after was irradiated with gamma source of ^{60}Co at doses of 5, 10, 20, 50 or 100 kGy at a dose rate of 5 kGy/h in inert atmosphere. The changes in molecular structure of LDPE, after gamma irradiations were evaluated using thermogravimetric analysis (TGA) and tensile machine and oscillatory rheology. The results showed the variations of the properties depending on the dose at each atmosphere

1 INTRODUCTION

In the late twentieth century, research on radiation chemistry of polymers has increased considerably and even new applications were discovered for polymer modification and improvement of their properties through radiation [1]. Polyethylene (LDPE) is the polyolefin most commonly used as plastic. This is essentially due to its excellent chemical resistance, high impact strength and high gas permeability [2].

The use of gamma radiation for modification of commercial polymers for new physical, chemical and mechanical properties is a widely studied technique. This technique promotes the scission of the polymer chains with the generation of free radicals via gamma radiation; it can recombine leading to their annihilation, branching or crosslinking [3, 4, 5, 6].

The aim of this paper is to investigate structural changes of low density polyethylene (LDPE) processed modified by ionizing radiation (gamma rays).

2 Materials and Experimental

2.1 Materials

The polymer used in this study was high density polyethylene (LDPE) from Braskem (Brazil), a density of 0,923 g/cm³ and melt flow index of 0,33 g/10 min.

2.2 Modified HDPE preparation

Prepared samples in hydraulic press were put in a thermal-resistant bag with atmospheric air and after were irradiated with a ⁶⁰Co source CBE/Embrarad, at doses of 5, 10, 20, 50 or 100 kGy and about 5 kGy h⁻¹ dose rates, at room temperature. After irradiation, were heated for 60 min at 100 °C to promote the recombination and annihilation of residual radicals [3; 5].

2.3 Melt flow index

The analysis of the melt flow index of the samples was carried out with the MFI apparatus CEAST, according to ASTM D 1238-04c [7].

2.4 Gel Fraction

The analysis of the gel of the samples was carried according to ASTM D 2765-01 [8].

2.5 Differential scanning calorimetry (DSC)

Thermal properties of specimens were analyzed using a differential scanning calorimeter (DSC) 822a, Mettler Toledo. The thermal behavior of films sample obtained by heating from 25 to 200 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere, according to ASTM D3418-08 [9]. The crystallinity was calculated according to equation 1:

$$X_c(\%) = \frac{\Delta H_f \times 100}{\Delta H_0} \quad (1)$$

ΔH_f = melting enthalpy of the sample, ΔH_0 = melting enthalpy of 100% crystalline PE which is assumed to be 279 J/g [10, 11].

2.6 Thermogravimetry analysis (TGA)

In the Thermogravimetry analysis (TGA), the samples modified by gamma-irradiation were conducted with TG dynamics using a Mettler Toledo, model TGA/SDTGA 851e. The samples were heated at 10 °C/min starting from room temperature up to 600 °C, under oxygen flow, at a rate of 50 mL/min, according to ASTM D 6370-99 [12, 13].

2.7 Rheological measurements

Oscillatory measurements were performed in rotational Physical rheometer (MCR 300) in parallel plate mode. Oscillatory viscoelastic determinations were carried out over the range of frequencies 0.1-100 (1/s) in the linear viscoelastic region. The following viscoelastic

functions were measured: storage modulus $G'(\omega)$; loss modulus $G''(\omega)$; complex viscosity $\eta^*(\omega)$. The temperature of measurements was 180°C.

3 RESULTS AND DISCUSSION

When irradiated, there is a competition between degradation and crosslinking in the case of polyethylene. The prevalence of one or the other, under the same irradiation conditions (dose rate, temperature and oxygen pressure) is controlled by the structural properties of the polymer. One effect from irradiation is an increase in the concentration of polar carbonyl groups compared to the original apolar LDPE. The process of oxidative degradation increases the number of polar groups, while crosslinking leads to the formation of a network structure, which restricts the motion of macromolecules in the amorphous phase [15].

The degree of crystallinity and melting temperature of LDPE processed are indicated in Table 1. There was decreased crystallinity. This is a consequence of increased oxidative degradation and crosslinking. Crosslinking will restrict the movement of macromolecules in the amorphous phase.

Table 1: DSC results of irradiated and non-irradiated of LDPE processed.

Doses kGy	T_f °C	X_c %
0	112,5	33,4
5	110,7	18,2
10	113,5	14,5
20	110,7	14,6
50	111,2	14,9
100	109,7	17,8

LDPE processed has gel fractions lower than LDPE resin as are indicated in Fig. 1, because the samples are prepared at a temperature around 200°C and atmosphere air. Increasing the dose of irradiation in LDPE processed promotes a greater amount of crosslinking and less mobility and increases the gel fraction. The samples irradiated in the presence of air have higher values of gel fraction.

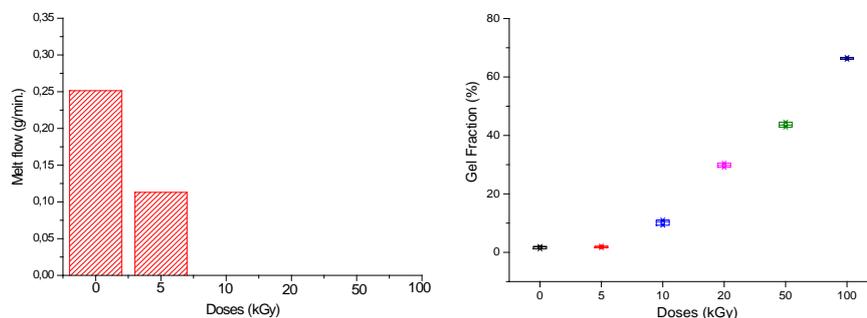


Figure 1 - Melt flow index and Gel fraction results of irradiated and non-irradiated of LDPE processed.

In Fig. 2, the non-irradiated sample of LDPE processed has one peak of the temperature (380~450 °C). The samples irradiated in the presence of air, have the lowest peak temperature (~400 °C) and high temperature (420°C). With increasing the dose, the peaks move to higher temperatures, showing less scission and more crosslink, which confirms the results of the gel fraction and melt index (Fig. 1).

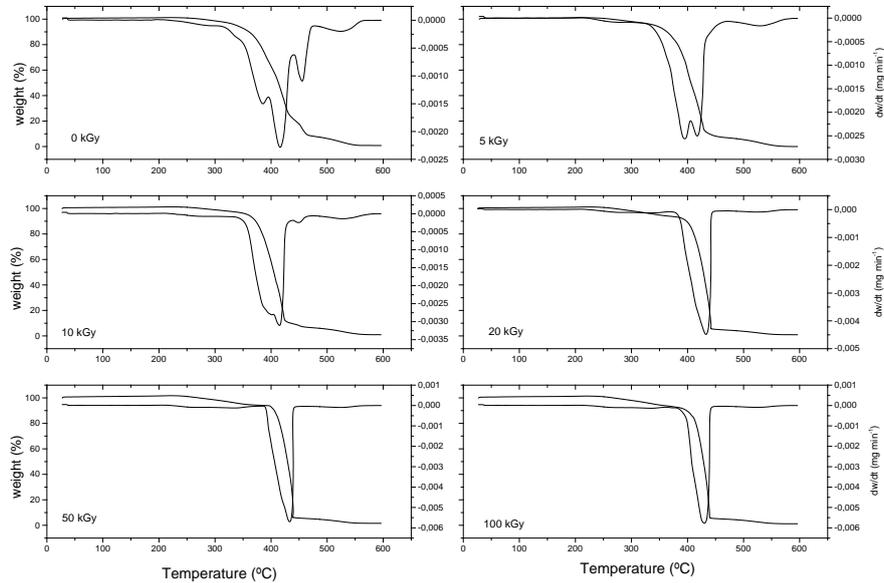


Figure 2 - TGA and DTGA as a function of temperature for LDPE processed irradiated with different doses in atmospheres of Air.

The rheological properties are dependent of reactions occurred during irradiation process: degradation by chain scission, branching and crosslinking. Different behaviors were observed by other authors [16] due to this.

The viscosity is influenced by the molecular structure of the polymer. Fig. 3 shows the highest viscosity when the samples are irradiated in air compared to the pure resin. The irradiation of these doses caused more scission, i.e., a decrease in molecular weight. This was confirmed by the results of the gel fraction and melt index (Fig. 1).

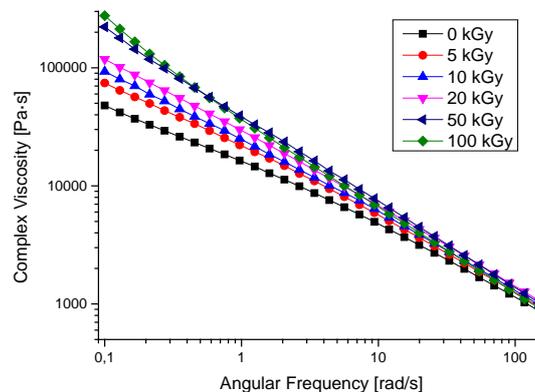


Figure 3 – Complex viscosity as a function of frequency angular to LDPE processed in presence Air.

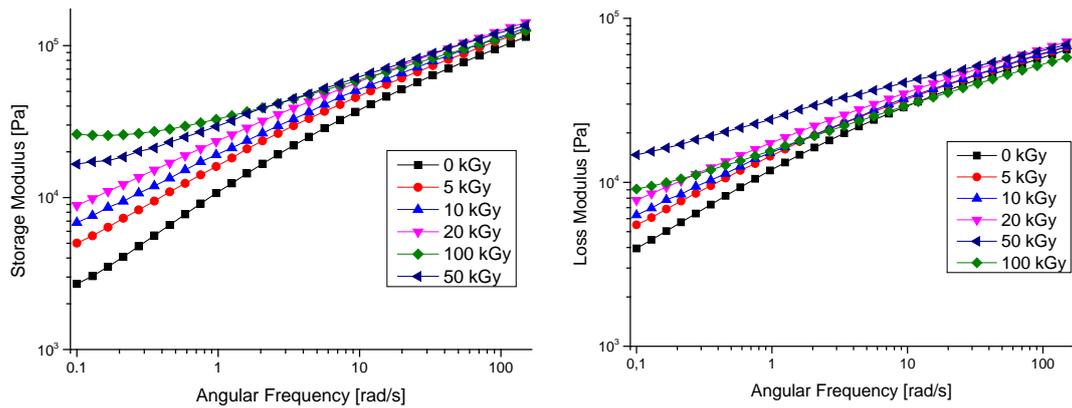


Figure 4 –Storage (G'') and Loss (G') moduli as a function of frequency angular to LDPE processed irradiated in presence Air.

The storage and loss modulus are even sensitive to long chain branches. In the terminal zone, where only the longest relaxation times contribute to the viscoelastic behavior, G'' of linear polymers follow the well-known frequency dependence, i.e., $G'' \propto \omega^2$. The dynamic modulus (G') is not affected at higher frequencies, where they approach a rubber plateau. G' of all samples plotted as a function of frequency is shown in Fig. 4. A similar behavior of complex viscosity was verified for dynamic modulus – in Fig. 3. All irradiated modified samples show higher values of this property than their respective pure resin at low frequency [17].

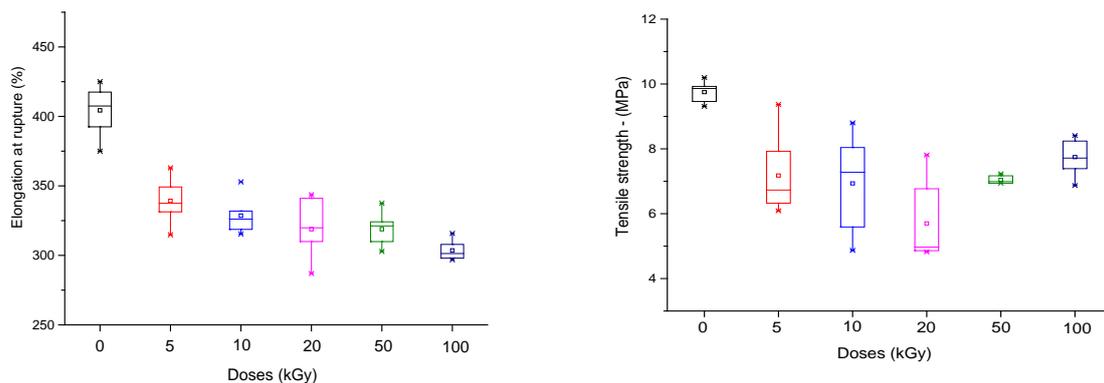


Figure 5 - Tensile strength and elongation at rupture to LDPE processed irradiated in presence Air

The tensile strength and elongation at rupture are shown in Fig. 5. All samples showed decrease of tensile strength and elongation at rupture in relation to pure LDPE. Therefore, the main differences in mechanical properties must be attributed to crosslinking, branching and chain scission instead of crystallinity, which presented small changes [14, 18].

4 CONCLUSION

Crosslinking and scission processes take place simultaneously in processes of LDPE radiation. The main conclusions are: the effect of gamma radiation is clearly seen in the specimens irradiated with different doses; the higher the irradiation dose, the higher is the degradation; the fracture behavior is influenced by gamma irradiation; the gamma irradiation in air significantly modifies the properties.

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