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Thermal, tensile and rheological properties of linear low density polyethylene (LLDPE) irradiated by gamma-ray in different atmospheres

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ABSTRACT

The aim of this paper is to investigate structural changes of linear low density polyethylene (LLDPE) modified by ionizing radiation (gamma rays) in different atmospheres. 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. This polymer 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. The changes in molecular structure of LLDPE, after gamma irradiations were evaluated using thermogravimetric analyzer (TGA) and tensile machine and oscillatory rheology. The results showed the variations of the properties depending on the dose at each atmosphere.

1. Introduction

The increasing importance of linear low-density polyethylene (LLDPE) in the industry is due to its outstanding mechanical properties. These properties are a result of the short-chain branched molecular structure and its distribution. In contrast, the flow properties and the processing behavior are mainly influenced by the molecular mass distribution (Coutinho et al., 2003).

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 (Charlesby, 1960; Clegg and Collyer, 1991; Chapiro, 1962).

The aim of this paper is to investigate structural changes of linear low-density polyethylene (LLDPE) modified by ionizing radiation (gamma rays) in different atmospheres.

2. Experimental and materials

The polymer used in this study was linear low-density polyethylene (LLDPE) from Braskem (Brazil). This polymer has a density of 0.920 g/cm^3 and melt flow index of 0.80 g/10 min in the form of *pellets*.

2.1. Modified LLDPE preparation

The polyethylene was placed in a thermal-resistant bag with inert gas (N_2) or atmospheric air, for the irradiation procedure. These samples were irradiated with a ^{60}Co source Embrarad, at doses of 5, 10, 20, 50 or 100 kGy and about 5 kGy h^{-1} dose rates, at room temperature. After irradiation, the samples were heated for 60 min at 100 °C to promote the recombination and annihilation of residual radicals (Chapiro, 1962; Chen and Mesrobian, 1957).

2.2. Melt flow index

The analysis of the melt flow index of the samples was carried out with the MFI apparatus CEAST, according to ASTM D1238-04c.

2.3. Gel fraction

The gel content of the modified polyethylene was determined by extraction of soluble components in boiling xylene containing antioxidant Irganox 1010 for 12 h at 135 °C. After that, the residue was dried for 24 h at 150 °C or until it reached constant weight. These samples were used to determine the average gel content for each modified polyethylene (ASTM D 2765-01).

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Table 1
DSC results of irradiated and non-irradiated of LLDPE.

Doses (kGy)	T_f (°C) N_2	X_c (%)	T_f (°C) Air	X_c (%)
0	127.7	43.9	127.7	43.9
5	132.2	39.3	126.8	29.1
10	129.7	46.1	126.0	26.3
20	130.6	41.8	125.5	24.4
50	127.5	35.7	124.8	27.6

Table 2
Gel fraction and melt flow index results of irradiated and non-irradiated of LLDPE.

Doses (kGy)	Gel faction (%)		Melt flow index (gm./10 min)	
	N_2	Air	N_2	Air
0	4.6	4.6	0.80	0.80
5	2.8	2.7	0.32	0.59
10	2.1	3.8	0.19	0.34
20	4.4	2.6	0.12	0.23
50	3.1	9.9	0.15	0.07
100	2.6	39.9	0.50	–

2.4. Differential scanning calorimetry (DSC)

Thermal properties of specimens were analyzed using a differential scanning calorimeter (DSC) 822a, Mettler Toledo. The thermal behavior of films was obtained by heating from 25 to 200 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere; holding for 5 min at 200 °C, then cooled to 25 °C and reheating to 280 °C at 10 °C min^{-1}, according to ASTM D 3418-08. The crystallinity was calculated according to Eq. (1):

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

ΔH_f is the melting enthalpy of the sample, ΔH_0 is the melting enthalpy of 100% crystalline PE which is assumed to be 279 J/g (Atlas of polymer and plastics analysis, 1994, 1996).

2.5. 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 400 °C, under oxygen flow, at a rate of 50 mL/min (Canevarolo, 2003).

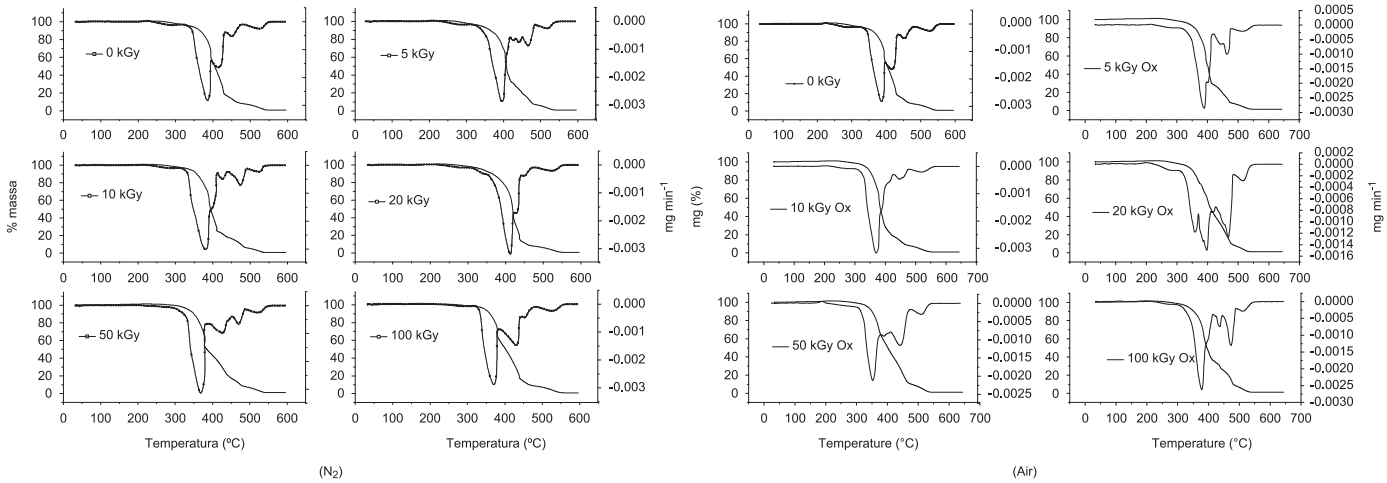

Fig. 1. TGA and DTGA as a function of temperature for LLDPE irradiated with different doses in atmospheres of N_2 and air.

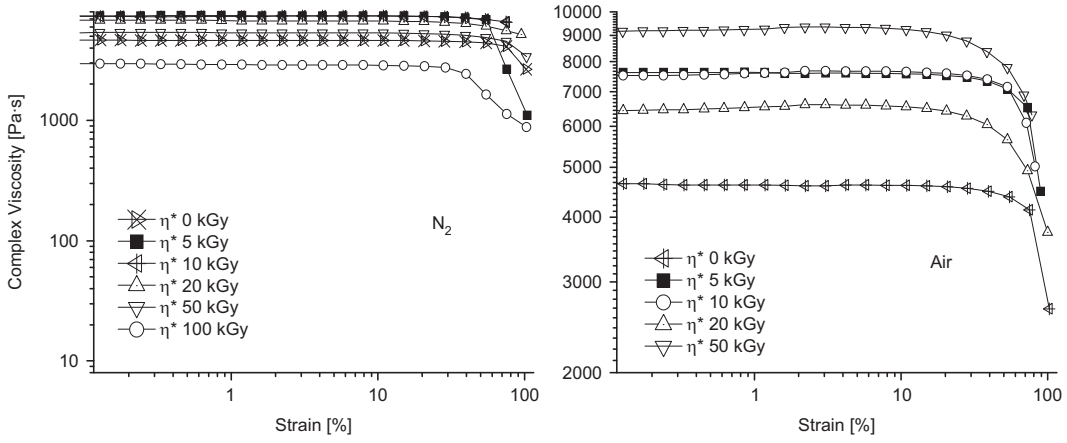

Fig. 2. Complex viscosity as a function of strain to LLDPE irradiated in presence N_2 and air.

2.6. Rheological measurements

Samples with 1.4 mm thickness and 25 mm disks were produced by compression molding at 170 °C and fast cooled with a water bath. The characterization in shear flow was conducted at 180 °C using rotational Physical rheometer (MCR 300) with parallel-plate geometry of 25 mm in diameter and 1.0 mm gap. The test was performed in the frequency range 0.1–100 (1/s) with a strain of 5%.

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 LLDPE. 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 (Suljovrujié et al., 2003).

The degree of crystallinity and melting temperature of LLDPE are indicated in Table 1. In both atmospheres, N_2 and air, there was decreased crystallinity. However, in the presence of air the crystallinity was lower than with N_2. This is a consequence of increased oxidative degradation and crosslinking. Crosslinking will restrict the movement of macromolecules in the amorphous phase.

The gel fractions are indicated in Table 2. Increasing the dose of irradiation in LLDPE 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.

In Fig. 1, the non-irradiated sample of LLDPE has four peaks, three superimposed. The samples irradiated in the presence of N_2, have the lowest peak temperature (~360 °C) and high temperature (~420 °C) moving in the opposite direction, leading to a more centralized temperature. Increasing the dose, the peaks move to lower temperatures, showing more scission, which confirms the results of the gel fraction and melt index (Table 2).

In Fig. 1, the samples irradiated in the presence of air, show the peaks of lower temperature (~360 °C) moving toward the high temperature peak (~420 °C). These samples have more branching and crosslinking, which confirms the results of the gel fraction and melt index (Table 2).

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 (Vega et al., 2002) due to this.

The viscosity is influenced by the molecular structure of the polymer. Fig. 2 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. In the N_2 atmosphere, an increase of viscosity occurs, but at a lower increase than in air. At 100 kGy, there is more scission. This was confirmed by the results of the gel fraction and melt index (Table 2).

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,

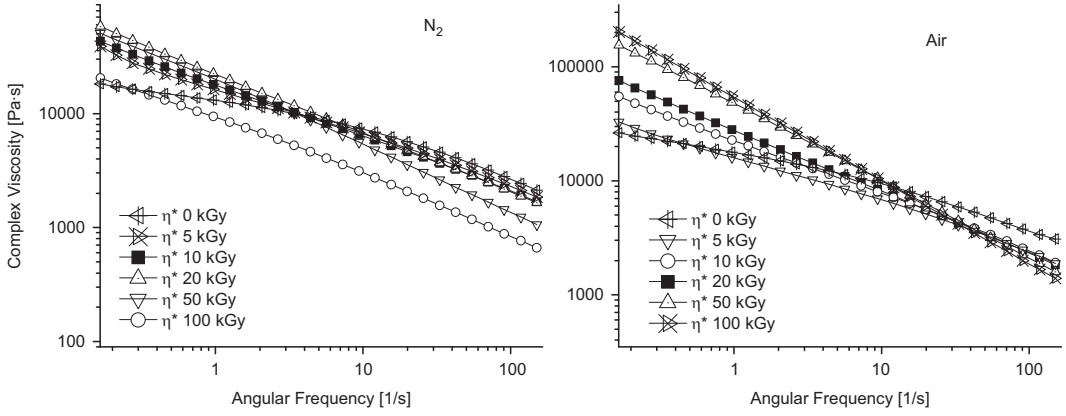

Fig. 3. Complex viscosity as a function of frequency angular to LLDPE irradiated in presence N_2 and air.

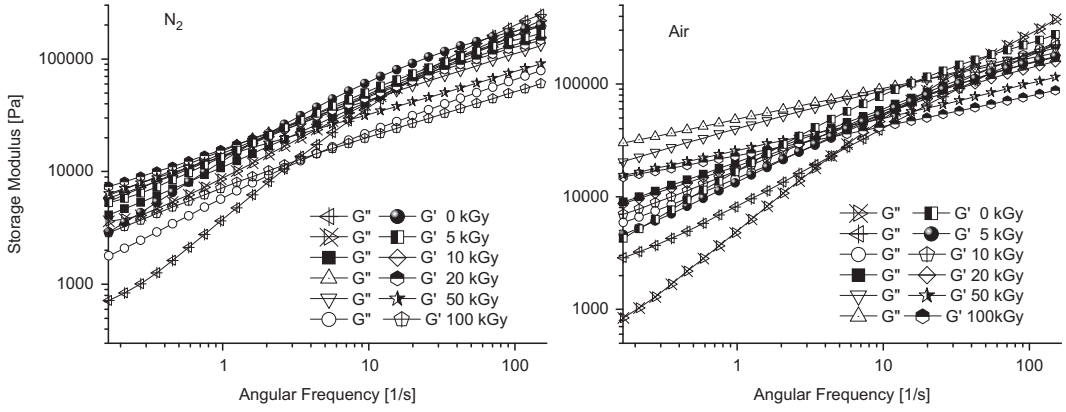

Fig. 4. Storage (G'') and loss (G') moduli as a function of frequency angular to LLDPE irradiated in presence N_2 and air.

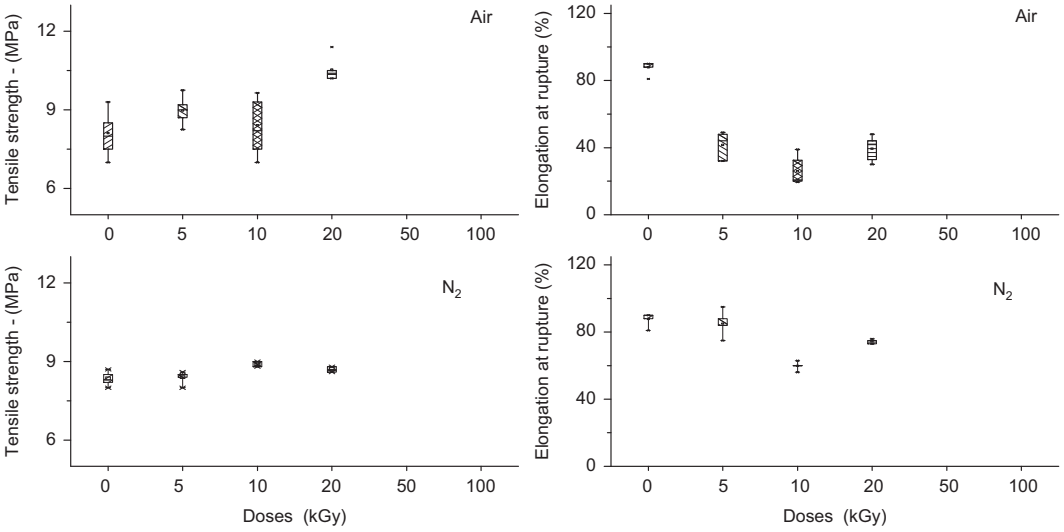

Fig. 5. Tensile strength and elongation at rupture to LLDPE irradiated in presence N_2 (a) and air (b).

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 (Naddeo et al., 2001; Claus and Helmut, 2003).

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 LLDPE. Therefore, the main differences in mechanical properties must be attributed to crosslinking, branching and chain scission instead of crystallinity, which presented small changes (Tian et al., 2006).

4. Conclusions

Crosslinking and scission processes take place simultaneously in processes of LLDPE 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 compared to N_2.

Acknowledgments

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