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Isothermal crystallization of gamma irradiated LDPE in the presence of oxygen

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H I G H L I G H T S

- Isothermal crystallization of irradiated LDPE in different atmospheres was studied.
- At a given radiation dose, induction time is higher the lower is oxygen content present in the radiation process.
- The E_a for crystallization increases with the radiation dose and decreases with oxygen content.
- TTT diagrams reflected the effects of the doses and the oxygen content.

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This work is focused on the study of the effect of oxygen on the isothermal crystallization process of gamma irradiated low density polyethylene (LDPE). The induction time increased with the dose indicating a retarding effect. On other hand, at the same dose, this parameter decreased with the augment in the oxygen content. The classical Avrami equation was used to analyze the crystallization kinetic of these materials. n values suggested that both, the dose and the oxygen content, did not affect the mechanism of crystals growth. An Arrhenius type equation was used for the rate constant (k). Used models correctly reproduced the experimental data. TTT diagrams of studied materials were constructed and also reflected the effects of the doses and the oxygen content.

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1. Introduction

Polyethylene (PE) is one of the polyolefin most used in the world. The search and analysis of methods to produce new grade of polyethylene with specific properties is an area of increasing interest from an academic and industrial points of view. One way to find that new material is by the modification of existing commercially produced standard resins. The radiation with high-energy is one the most used methods to change the molecule structure of PE (Lyons and Weir, 1973; Clough and Shalaby, 1996; Barkhudaryan, 2000). This method is based on the production of macro-radicals that can participate in different chemical reactions. These reactions may involve chain scission and chain linking. In the case of PE the reactions that produce crosslinking, long chain branching and chain extension prevail (Barkhudaryan, 2000;

Randall et al., 1983; Gloor et al., 1994).

The effect of crosslinking on the thermal properties and crystallization behavior of polyethylene has also received some attention in the past (Kao and Phillips, 1986; Phillips and Kao, 1986; Hutzler et al., 2000; Jiao et al., 2005; Nilsson et al., 2010); nevertheless, the reports are still limited. Most of the studies analyzed the influence of the produced molecular network on diverse types of polyethylene. In general, it has been observed that increments in the amount of gel reduce the rate and the temperature of crystallization and also the degree of crystallinity of the final material (Alvarez and Perez, 2013). Other authors (Galovic et al., 2012; Milicevic et al., 2007; Stamboliev and Suljovrujic, 2010) have analyzed the effect of radiation on the dielectric relaxation behavior and on the uniaxial orientation of different types of polyethylenes but also the influence of the initial structural differences and gamma radiation on the evolution of the structure and thermal properties of different polyethylenes.

The final properties of polymeric materials are strongly

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dependent on the morphology generated during processing steps. So that, the knowledge of the parameters that influence the crystallization behavior is substantial, in order to optimize the processing steps and conditions and, the properties of the final product. The analysis of the crystallization process can be done under isothermal or non-isothermal conditions.

Non-isothermal crystallization behavior of gamma irradiated LDPE in presence of oxygen was previously studied (Alvarez and Perez, 2013). The experimental data have shown that the retarding effect increases with the increment of the dose and decrease with the oxygen content. In addition, it has been proved that the activation energy for crystallization process increased with the radiation dose and with the reduction of the oxygen content, indicating that the increment in molecular crosslinking restricts the crystallization process. The use of Avrami's model allows to determine the kinetic parameters as well as in order to compare the crystallization behavior with other polymer under isothermal crystallization conditions.

The aim of this work was to study the isothermal crystallization behavior of irradiated LDPE in presence of different oxygen concentrations. The effect of the dose and oxygen present during the radiation process will also be analyzed by application of theoretical models.

It is important to remark that, as in our previous work (Alvarez and Perez, 2013), there are some papers regarding the isothermal behavior of different types of chemically modified polyethylene (Hutzler et al., 2000; Janigova et al., 1992) or the influence of oxygen present in the radiation process (Ferreto et al., 2012; Hikmet and Keller, 1987; Suljovrujic, 2013) but there are no significant information regarding the effect of oxygen on the isothermal crystallization process of irradiated polyethylene.

2. Experimental

2.1. Material

Low Density Polyethylene (LDPE (203 M)) supplied by Dow-PBB Polisor (Bahía Blanca, Argentina) was used throughout this study.

2.2. Sample preparation

Samples of 0.2–0.3 mm of thickness were prepared by compression molding at 150 °C, without the antioxidant content provided by the manufacturer.

To strip the antioxidant, about 100 g of polymer were dissolved in boiling xylene, and quickly precipitated in stirred cold methanol to obtain a fine powder. Most of the antioxidant and other additives are expected to remain in the thus formed xylene–methanol solution. The precipitated polymers were exhaustively dried at room temperature.

The films were inserted into tightly capped Pyrex flasks. The total film in each flask was set in order to get equivalent total mass. Flasks were placed in a gloves box and kept under constant atmosphere for 2 days. Before closing the flasks, the gloves box was kept filled with mixtures of nitrogen/oxygen to give oxygen concentrations of 0, 21 and 100% v/v at a total pressure of 1 atm at room temperature. Subsequently, these samples were exposed to γ -rays generated by a ^{60}Co source, at room temperature. The dose rate was 8 kGy/h determined by dosimetry with a radiochromic thin-film dosimeter. Equal doses between 33 and 222 kGy were applied to the samples. The error in dose can be estimated in 5%.

2.3. Isothermal crystallization process (differential scanning

calorimetric tests)

Isothermal crystallization tests were carried out in a TA M DSC Q200 DSC. Pure indium was used as a reference material to calibrate both the temperature scale and the melting enthalpy. All DSC runs were performed under nitrogen atmosphere. Samples of approximately 10.0 mg \pm 0.1 mg were placed in aluminum pans and loaded at room temperature to the DSC, heated up rapidly to 150 °C and maintained at this temperature for 10 min to remove thermal history. Then, the isothermal crystallization studies were carried out by cooling the samples down to 20 °C using constant cooling rate of 50 °C/min and maintained at the each crystallization temperature for 30 min to let complete crystallization. Then, the samples were heated from the crystallization temperature to 150 °C at 10 °C min⁻¹ in order to melt all crystals produced at the crystallization temperature and to find the melting temperature.

2.4. Theoretical background

The degree of crystallinity can be calculated from the following equation:

$$X_{cr}(\%) = (\Delta H_c / \Delta H_{100}) \times 100 \quad (1)$$

where ΔH_c is the experimental heat of fusion and ΔH_{100} is the heat of fusion of 100% crystalline LDPE and its value is 288 J g⁻¹ (Mandelkern, 1964).

The relative weight fraction of the crystallized part X is evaluated from the exothermic peak by using the following equation:

$$X = \Delta H_t / \Delta H_{total} \quad (2)$$

where ΔH_t and ΔH_{total} are obtained from integration of the crystallization exotherms and represents the portion of exothermic heat at time t , and total exothermic heat measured at the end of the transformation process respectively.

The crystallization curves were analyzed by following the theory of Avrami adapted to the crystallization kinetics of polymers (Mandelkern, 1964). The simplified form of the Avrami's equation is given by

$$X = 1 - \exp(-k \cdot t^n) \quad (3)$$

where n , the Avrami's exponent, is a coefficient that can be related to the geometry of the growing crystals and the nucleation conditions, and k is an overall crystallization rate constant. In order to analyze the crystallization kinetic data following the Avrami formalism; plots of $\log[-\ln(1-X)]$ as a function of $\log(t)$ were set up. The increase on the melting temperature (T_m) as a function of crystallization temperature (T_c) is probably related with the increase on the chains mobility (Iannace and Nicolais, 1997) or with the decrease in the lamellar thickness (Pérez et al., 2012). An approximation of the crystallization rate can be made by calculating the overall crystallization rate ($t_{1/2}^{-1}$), where $t_{1/2}$ (half crystallization time) is the time at which the relative degree of crystallinity (X) approach to 0.5. This parameter is proportional to both, the primary nucleation rate and the crystal/spherulite growth.

3. Results and discussions

Fig. 1 show the crystallization curves at 30 °C/min. It is possible to observe, in the Fig. 1a, that the crystallization temperature decreases as a function of the radiation dose. This behavior was probably related with the decrease on the chain mobility as consequence of crosslinking reactions. In order to analyze the effect of oxygen, the samples with higher radiation dose (222 kGy) was

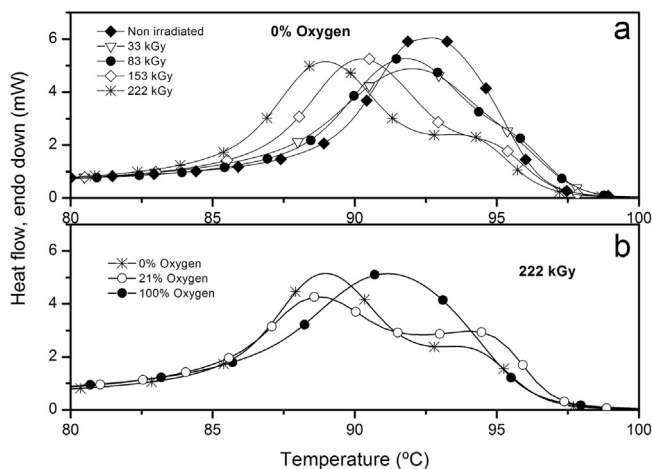


Fig. 1. Crystallization curves obtained at a cooling rate of 30 °C/min of (a) original and irradiated LDPE (nitrogen atmosphere) and (b) irradiated with 222 kGy in different atmospheres.

selected. Fig. 1b, presents the crystallization curves of LDPE irradiated at 222 kGy in different atmospheres (several oxygen contents). The crystallization temperature is lower in the case of the sample irradiated in the presence of 0% and 21% of oxygen with respect to the samples irradiated in 100% of oxygen. In the case of samples irradiated with 153 and 222 kGy (with 0 and 21% oxygen); double peak can be observed. The appearance of a new peak at lower temperature can be related with the crosslinking reactions and coincides with the appearance of gel in the samples. A similar behavior was previously reported by Hutzler et al. (2000). Some authors (Pérez et al., 2012; Zoepfel et al., 1984b) have reported that the double peak is caused by reactions of peroxy radicals and that is less pronounced for samples irradiated in air than for samples irradiated in nitrogen, which is also in agreement with our results.

From ΔH_m of the irradiated samples, and by using Eq. (1), it is possible to determine the degree of crystallinity. The obtained values are summarized on Tables 1a and 1b.

From the previous table, it is possible to see that the crystallinity of the polymer decreases mildly with the radiation dose. The gamma radiation produces modifications in polyethylene, preventing new crystal formation and, thus, reducing the crystallinity degree (Zoepfel et al., 1984a; Alamo and Mandelkern, 1991). These results are in agreement with previous works (Alvarez and Perez, 2013; Pérez et al., 2010; Vilaplana et al., 2004) in which it has been suggested that the decrease on the crystalline content and the melting point could be attributable to the increase of the imperfections in the polymeric chains originated by the radiation. These defects of the polymeric chains could inhibit the crystallization process, leading to smaller and less-perfect crystallites (Alvarez and Perez, 2013; Pérez et al., 2010; Vilaplana et al., 2004).

3.1. Nucleation process

The induction time (t_{ind}), which is defined as the time needed

Table 1a
Crystallinity, activation energy and pre-exponential factor of induction time for original and irradiated LDPE (nitrogen atmosphere).

Sample	X (%)	K_{ti} (s)	E_{ti} (J/mol)
Non-irradiated	35.9	4.66	181.8
33 kGy	31.9	0.40	300.8
83 kGy	31.5	0.12	605.8
153 kGy	30.9	0.0939	1534.5
222 kGy	30.5	0.00166	1653.7

Table 1b
Crystallinity, Activation energy and pre-exponential factor of induction time for irradiated samples with 222 kGy in different atmospheres

Sample	X (%)	K_{ti} (s)	E_{ti} (J/mol)
222 kGy 0% Oxygen	30.5	0.00166	1653.7
222 kGy 21% Oxygen	32.4	0.00213	951.5
222 kGy 100% Oxygen	33.9	0.010	876.7

for the formation of the equilibrium nucleus with critical dimensions at a given T (Janevsky and Bogoeva-Gaceva, 1998), was determined for all the samples. This parameter may be considered as the most suitable macroscopic parameter representative of nucleation process in calorimetric experiments (Torre et al., 1995) and it can be related with temperature. Some of the studied relationships are the following:

$$t_{ind} = K_{tind} \cdot \exp\left(\frac{E_{tind}}{R \cdot \Delta T}\right) \quad (4)$$

where K_{tind} is the preexponential factor, E_{tind} is the activation energy, R is universal gas constant and ΔT is undercooling degree and is defined as $T_m^0 - T_c$, where T_m^0 is 141 °C (Wunderlich and Czornyj, 1977).

From $\ln t_{ind}$ as a function of ΔT^{-1} plots for all samples the pre-exponential factor, K_{tind} , and the activation energy, E_{tind} were obtained, using a typical linear regression. The results of this approach are shown on Tables 1a and b. The linear dependence between $\ln t_{ind}$ and ΔT^{-1} is an indication that there were not morphological changes during crystallization; for the selected crystallization temperatures. Activation energy increased with the increase in the radiation dose and decrease with oxygen content. In a similar way, the pre-exponential factor decreased with the increase in the radiation dose and increase with oxygen content present during the radiation process.

It is widely known that crosslinking produce increase of molecular weight (Pérez et al., 2002; Pérez et al., 2012) producing a shifting of crystallization range to higher temperatures (Pérez et al., 2002).

Fig. 2 show the comparison by samples irradiated in nitrogen atmosphere (a) and irradiated with 222 kGy in different atmospheres (b). Despite of the radiation dose and the oxygen content, induction time increased when crystallization temperature increased; due to the decrease on the undercooling degree which is driving force for the crystallization process.

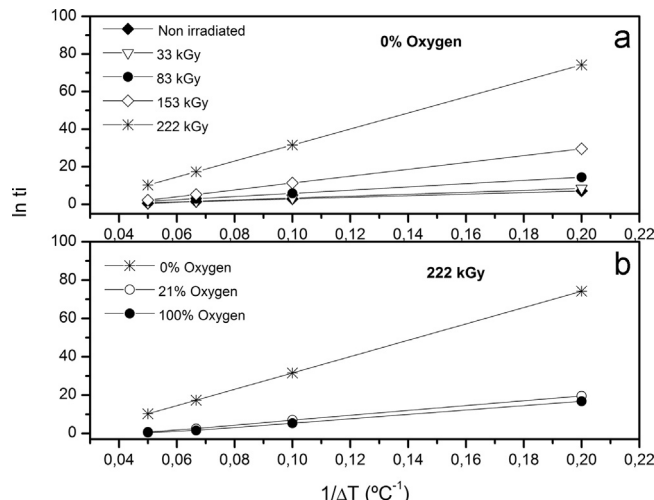


Fig. 2. $\ln t_i$ vs $1/\Delta T$ for (a) original and irradiated LDPE (nitrogen atmosphere) and (b) irradiated with 222 kGy in different atmospheres.

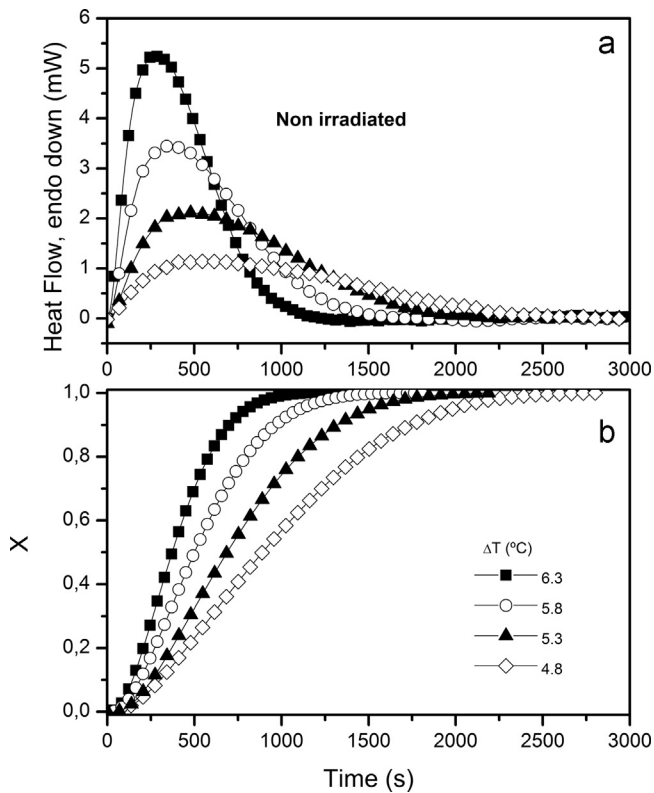


Fig. 3. (a) Exotherms crystallization (DSC) for non irradiated LDPE at the indicated temperature. (b) Relative crystallinity as a function of time for non irradiated LDPE.

In the Fig. 2a, the induction time increase with the radiation dose, this implies that, due to crosslinking reactions, more time is necessary for LDPE spherulites to nucleate so, act as retarding agent (the increase in the crosslinking density which may work as a physical barrier for the crystal growth (Hutzler et al., 2000)). In the case of Fig. 2b, the induction time decreased with the oxygen content and this also is related with a lower crosslinking density as major is the oxygen content.

3.2. Growth

The DSC exothermic peak is related with both, the nucleation and growth processes. Fig. 3a shows crystallization peaks by non irradiated LDPE. Time was scaled by the induction time of each temperature.

As it was expected, the crystallization rate decreased as the crystallization temperature increased, nevertheless of analyzed material. That is due to the lower undercooling degree. Curves were transformed in degree of crystallinity as a function of time as is shown on Fig. 3b for non irradiated LDPE. A shift of the curves toward lower times and an increment of the slope of their linear portion can be seen as the undercooling degree becomes higher, and this implies that a higher undercooling degree leads to a higher crystallization rate. A similar trend was observed in the case of irradiated samples.

The reciprocal of the half crystallization rate was used to estimate the overall crystallization rate (OCR). As defined previously, the overall crystallization rate is $t_{1/2}^{-1}$, where $t_{1/2}$ (half crystallization time) is the time at which the relative degree of crystallinity (X) approach to 0.5. This parameter can be modeled as:

$$\sqrt[n]{\frac{k}{\ln 2}} = \frac{1}{t_{1/2}} = OCR \quad (5)$$

Table 2a

Activation energy and pre-exponential factor of half crystallization time for original LDPE and irradiated samples (nitrogen atmosphere)

Sample	K_0 (s)	$-E_a$ (J/mol)
Non-irradiated	0.084	215
33 kGy	0.12	366
83 kGy	0.33	475
153 kGy	60.9	1299
222 kGy	1983	4569

Table 2b

Activation energy and pre-exponential factor of half crystallization time for irradiated samples with 222 kGy in different atmospheres.

Sample	K_0 (s)	$-E_a$ (J/mol)
222 kGy -0% O ₂	1983	4569
222 kGy -21% O ₂	10.5	800
222 kGy -100% O ₂	2.64	612

$$k = k_0 \cdot \exp\left(-\frac{E_a}{R \cdot (\Delta T)}\right) \quad (6)$$

where k_0 is the preexponential factor, E_a is the activation energy, R is universal gas constant and ΔT is undercooling degree.

Tables 2a and b shows the results of the modeling of k whereas Fig. 4 show the tendency of overall crystallization rate as a function of radiation doses and oxygen. The pre-exponential factor (k_0) and activation energies (E_a) were obtained from a typical linear regression. The values are included in Tables 2a and b. The increase in the radiation dose produced an increase in k_0 and E_a indicating a retarding effect during the crystallization process. The opposite effect was observed as a function of the oxygen content, in the irradiated samples at 222 kGy. The same tendency was observed in

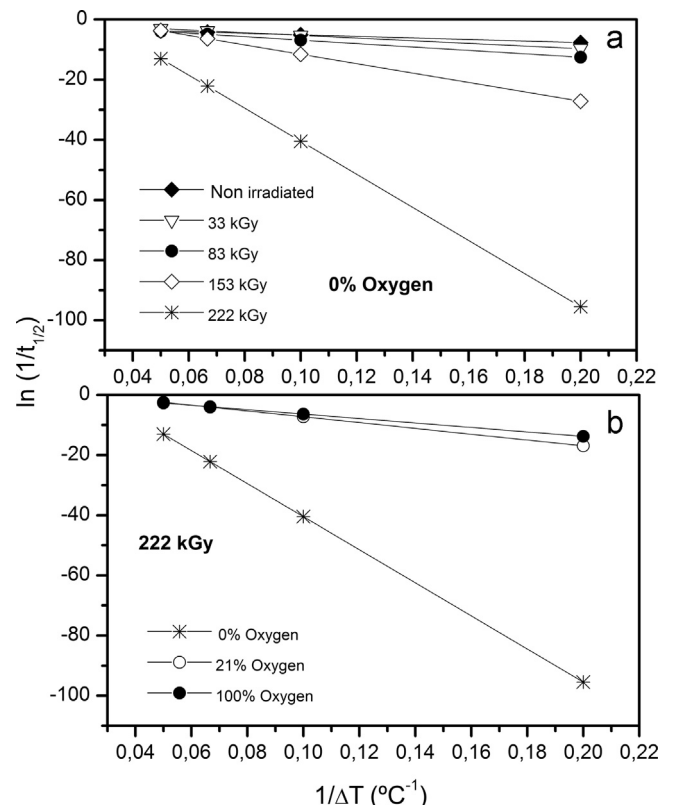


Fig. 4. $\ln(1/t_{1/2})$ vs $1/\Delta T$ for (a) original and irradiated LDPE (nitrogen atmosphere) and (b) irradiated with 222 kGy in different atmospheres.

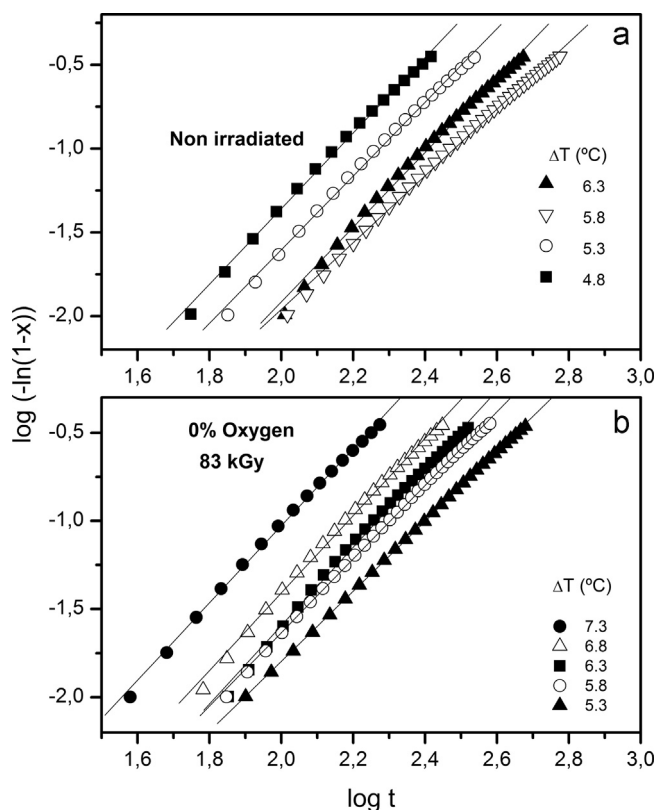


Fig. 5. $\log(-\ln(1-x))$ as a function of $\log t$ for: (a) original LDPE and (b) irradiated LDPE with 83 kGy.

the case of dynamic crystallization of the same system (Alvarez and Perez, 2013) in accordance with other studies (Tang et al., 2008) and experimental results.

3.3. Modeling of isothermal crystallization process

The crystallization kinetics of polymeric matrices under isothermal conditions can be modeled by using the Avrami's equation, as was previously mentioned in Eq. (3). Plots of $\log(-\ln(1-X))$ as a function of $\log(t)$ were set up. As an example, in Fig. 5, the results for non irradiated and LDPE irradiated with 83 kGy (in nitrogen atmosphere) are presented over the relative crystallinity range from about 0.01 y 0.3.

It was found that, in this range of relative crystallinity, that Avrami's equation can describe the crystallization process with a good linear correlation of the experimental data. The solid lines in the plots represent the best fit of the experimental data. Similar behavior was obtained for all samples.

The parameters of Avrami model (Avrami exponent, n , and rate constant, k) were calculated. In the case of the matrix, n was 2.5 ± 0.1 ; on the other hand, in all irradiated samples, the obtained values of n varied between 2 and 2.2. These values indicate a two-dimensional crystal growth (Wunderlich, 1976) and are in concordance with that published by other authors (Hutzler et al., 2000; Wunderlich, 1976). Phillips and Lambert (1990) have reported a wide range of n (between 1.3 and 2.4) for the gel fractions of crosslinked polyethylene; they have suggested that this changes were related with changes in the morphology of the gel fractions changes from heterogeneously nucleated disks to fibrils or rods. The variation of Avrami coefficients, as the crosslink density increases, is associated with the fact that the gel fractions contain large amounts of rod-like units; probably caused by an intrinsic change in the growth mechanism. In the present work; the samples were tested without separating the sol and gel fractions, but

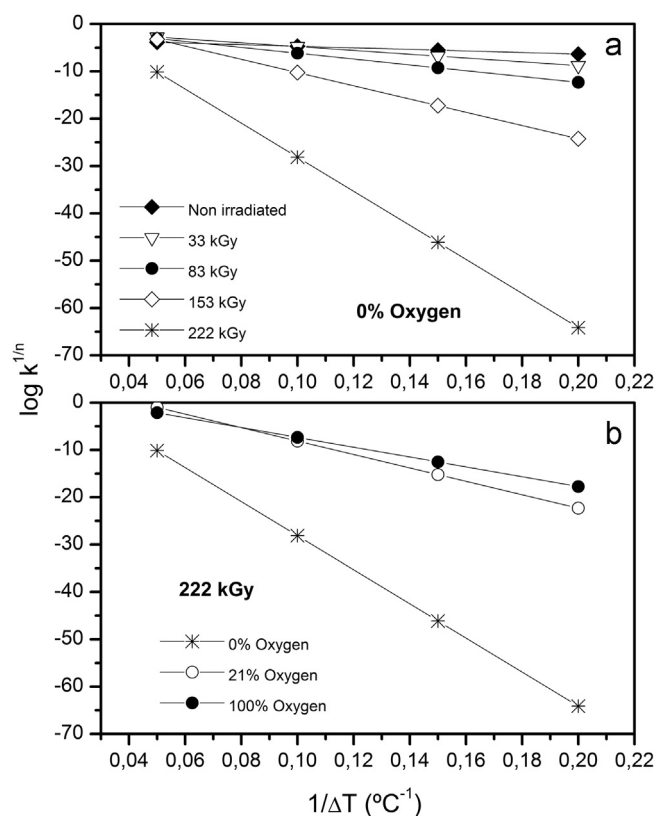


Fig. 6. $\log k^{1/n}$ vs $1/\Delta T$ for (a) original and irradiated LDPE (nitrogen atmosphere) and (b) irradiated with 222 kGy in different atmospheres.

the presence of both, crosslinking and gel fractions, (as the radiation doses became higher) is useful to justify the low values of n obtained compared to pure polyethylene.

By other hand, the displayed results suggest that the characteristics of the crystallization process is not affected by the modification suffered by the molecular structure of LDPE as n takes similar values for all radiation doses and in the different atmospheres at any used temperature of crystallization.

By using the Arrhenius equation the rate constant, k , can be modeled with a linear regression (using the Eq. (6)). In all cases, the rate constant, k , decreased with the increase of the crystallization temperature. From this regression it is possible to obtain the activation energies for studied materials. Fig. 6 shows the comparison by samples irradiated in nitrogen atmosphere (a) and irradiated with 222 kGy in different atmospheres (b). All the plots in the figure are reasonably linear. The results of this regression are reported in Tables 3a and b. The activation energy increases with the dose in nitrogen atmosphere and decreases with the oxygen content. This is in agreement with the crystallization process restrictions imposed by the molecular crosslinking (Pérez et al., 2012). At a constant ΔT , k decreased when the dose is increased. This indicates the slower bulk crystallization in

Table 3a
Results of linear regression for the Arrhenius equation for original and irradiated LDPE (nitrogen atmosphere).

Sample	K_0 (s)	$-E_a$ (J/mol)
Non-irradiated	$9.8e-4$	138
33 kGy	$1.8e-1$	334
83 kGy	$1.2e0$	512
153 kGy	$5.5e3$	1162
222 kGy	$7.2e7$	2991

Table 3b

Results of linear regression for Arrhenius equation for irradiated samples with 222 kGy in different atmospheres.

Sample	K_0 (s)	$-E_a$ (J/mol)
222 kGy –0% O ₂	7.2e7	2991
222 kGy –21% O ₂	1.2e6	1180
222 kGy –100% O ₂	1.1e3	864

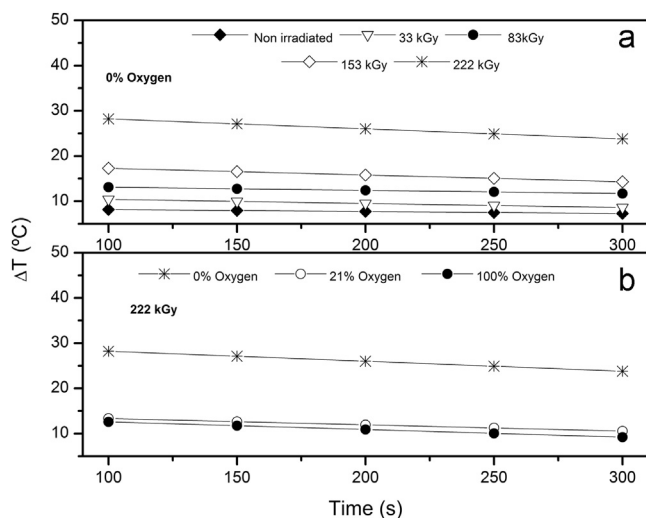


Fig. 7. Diagrams TTT for (a) original and irradiated LDPE (nitrogen atmosphere) and (b) irradiated with 222 kGy in different atmospheres.

comparison with the non irradiated sample. On the other hand, the presence of oxygen accelerates the bulk crystallization, which is related with a minor crosslinking grade.

3.4. TTT curves

It is possible to obtain global kinetic model that allow predicting the crystallinity development under any cooling conditions, such as real industrial processing conditions. That is a very important tool to design the processing steps of semicrystalline polymers. That full model is also useful for the construction of phase diagrams. These diagrams allow estimating the nucleation and growth of crystals for specific cooling conditions. Two types of diagrams are commonly used: (1) TTT: Time–Temperature–Transformations plots (isothermal processes) and (2) CCT: Continuous Cooling Transformations plots (at constant cooling rate) in which the crystallinity is related with time and temperature. This approach permits the knowledge of the entire crystallization process (Long et al., 1995; Hubert et al., 2001).

TTT plots, for pre-fixed times, of studied materials are shown in Fig. 7. These figures show the comparison by samples irradiated in nitrogen atmosphere (a) and irradiated with 222 kGy in different atmospheres (b). The curves of undercooling degree for the relative degree of crystallinity of 0.3, are plotted as a function of time, for pre-fixed times. Fig. 7a shows that higher the dose, greater is the undercooling degree necessary to crystallize the material, supporting the retarding effect. In the same manner, Fig. 7b shows that the undercooling degree decrease with the oxygen increase.

4. Conclusions

The isothermal crystallization of crosslinked LDPE by radiation at several doses and in different atmospheres (oxygen content)

was studied. The augment of dose retard the crystallization process. On the other hand, the increase in the oxygen content accelerated the crystallization process, due to a reduced molecular restriction. Avrami's model was able to predict the development of the crystallinity as a function of time for all studied materials and selected crystallization temperatures. Avrami's exponent (n) values suggested that all materials experienced a pseudo-two dimensional crystal growth with a linear growth rate.

The activation energy increased with the radiation dose and decreased with the oxygen content; these results are related to the increase in the degree of crosslinking, which restricts the crystallization process. It was demonstrated that TTT diagrams were able to predict the crystallization behavior of studied materials as well as the effect of radiation dose and the presence of oxygen during irradiation.

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