Gamma irradiated LDPE in presence of oxygen. Part I. Non-isothermal crystallization

V.A. Alvarez [a],[1], C.J. Perez [b],*

[a] Composite Materials Group (CoMP), Research Institute of Material Science and Technology (INTEMA), Engineering Faculty, National University of Mar del Plata (UNMdP), Solís 7575, B7608FDQ, Mar del Plata, Argentina
[b] Science and Technology Polymer Group, Research Institute of Material Science and Technology (INTEMA) – National University of Mar del Plata (UNMdP), Av. Juan B. Justo 4302, B7608FDQ, Mar del Plata, Argentina

ARTICLE INFO

ABSTRACT

Non isothermal crystallization of low density polyethylene (LDPE) samples irradiated under three different atmospheres was analyzed. The used doses were between 33 and 222 kGy and the atmospheres content 0, 21 and 100% of oxygen. At a given radiation dose, the amount of produced gel is higher when the oxygen content present in the radiation process is lower.

The temperature and the enthalpy of crystallization of the modified polymer decreased almost linearly with the radiation dose. Different classic models were used to predict the development of the relative degree of crystallinity (in the range 0.01–0.3 crystallinity fraction) as a function of temperature and several parameters were analyzed. The values of half-time of crystallization ($t_{1/2}$) and the parameter Z_c, from Avrami's method which characterize the kinetics of non-isothermal crystallization, showed that the crystallization rate, at the same cooling rate, decreased with increasing radiation dose and, at the same dose, with the decrease in the oxygen content. The activation energy for crystallization increased with the radiation dose and with the reduction of the oxygen content, indicating that the increment in molecular crosslinking restricts the crystallization process.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The properties of many semicrystalline polymers are routinely modified by molecular structural changes induced by free radicals that are generated by peroxides decomposition or other processes like high energy radiation or electron beams. In situ formed free radicals produce a variety of reactions on the main chain atoms that modifies the molecular macrostructure. Depending on the specific purpose of the molecular changes to be conducted; polyolefins can be modified in the solid or the melt states [1–3].

The generated free radicals, located at the high-mobility amorphous regions, will react relatively fast, mainly by reaction with other radicals, antioxidants, oxygen or other macromolecules. Some free radicals are located in the crystalline phase and will react at a much slower rate [4]. Reactions of free radicals with macromolecules main chain atoms may produce both, chain scissions or crosslinking, depending mainly on whether the reacted carbon is a secondary or a tertiary one. Secondary carbons produce much more crosslinking than tertiary ones [5].

The effect of crosslinking on the thermal properties and crystallization behavior of polyethylene has also received some attention in the past; nevertheless, the reports are still limited. Most of the studies have analyzed the influence of the produced molecular network on diverse types of polyethylene. In general, it was observed that increments in the amount of gel reduce the rate and the temperature of crystallization and also the degree of crystallinity [6–10].

The final properties of polymeric materials are 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 final product properties. The analysis of the crystallization process can be done under isothermal or non-isothermal conditions. The behavior of semicrystalline polymers during non-isothermal crystallization from the molten state is of increasing technological importance because real industrial processes such extrusion and film forming, usually proceeds under dynamic non-isothermal conditions. Generally, studies of crystallization are limited to idealized conditions, in which external conditions are constant. In such situations, the theoretical analysis is relatively easy and problems connected to cooling rates gradients within the specimen are avoided. In real situations, however, the external conditions change continuously; this fact makes the

---

* Corresponding author. Tel.: +54 2234816600x226.
E-mail address: cjperez@fi.mdp.edu.ar (C.J. Perez).
[1] Tel.: +54 223 4816600x323.

treatment of non-isothermal crystallization more complex. Though, the study of crystallization in a continuously changing environment is of greater interest, since industrial proceed generally under non-isothermal conditions. Moreover, from scientific point of view, the study of crystallization in dynamic conditions may expand the general understanding of crystallization behavior of polymers since many isothermal methods are often restricted to a narrow temperature range [11,12].

The aim of this work was to study the influence of obtaining the LDPE samples irradiating with different content of oxygen on the non-isothermal crystallization behavior. The other goal was to obtain a global kinetic model for the analysis and design of real processing operations. It should be also pointed out that there are a great number of papers regarding the dynamical behavior of different types of irradiated polyethylenes [8,13,14] or the influence of oxygen present in the radiation process [15–17] but practically there are no works regarding the effect of oxygen on the non-isothermal crystallization process of irradiated polyethylene.

2. Experimental

2.1. Material and sample preparation

Low density polyethylene (LDPE (203M)) supplied by Dow-PBB Polisur (Bahía Blanca, Argentina) was used throughout this study.

Samples of 0.2-0.3 mm of thickness were prepared by compression molding at 150 °C, without the antioxidant content provided by 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 and at room temperature. Subsequently, these samples were exposed to γ-rays generated by a ^{60}Co source, at room temperature. The dose rate, determined by dosimetry with a radiochromic thin-film dosimeter, was 8 kGy/h. Equal doses between 33 and 222 kGy were applied to the samples. The error in dose can be estimated in 5%.

2.2. Determination of gel content

The gel fraction was determined by extracting the soluble portion of different specimens of each modified polymer with xylene at 125 °C. The extraction was performed by placing a given amount of each sample (between 0.4 and 0.8 g) into a basket made of cellulose paper. The baskets were immersed in hot xylene for different periods of 4 h. After each period, the specimens were dried to constant weight. The extraction was considered complete when, after two consecutive periods of extraction, there was no detectable change of weight in the dried gel. The total time of extraction varied between 36 and 72 h depending on the sample. Fresh solvent was used in every extraction period. In order to prevent oxidation of the samples, nitrogen was bubbled continuously into the system and a small amount of Irganox 1010 was added as antioxidant.

The percentage of gel reported in this work is an average of those obtained from four specimens of each one of the modified polymers. The standard deviation of data was about 3-5%. Manipulation of the samples, necessary for carrying out the extraction of soluble and the small mass weighted, contributes to such dispersion in the values.

2.3. Non-isothermal crystallization process (differential scanning calorimetric tests)

Non-isothermal crystallization tests were carried out in a Perkin Elmer Pyris 2 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 ± 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 2 min to remove thermal history. Then, the non-isothermal crystallization studies were carried out by cooling the samples down to 20 °C at 5, 10, 20 and 30 °C/min.

Whole (not extracted) samples were used throughout for all DSC characterization.

3. Theoretical background

3.1. Modeling of non-isothermal crystallization process.

The relative degree of crystallinity as a function of temperature, $\alpha(T)$, can be calculated as:

$$\alpha(T) = \frac{\int_{T_o}^{T}((\partial Hc/\partial T)dT)}{\int_{T_o}^{T_\infty}((\partial Hc/\partial t)dT)} \tag{1}$$

where T_o and T_∞ represent the onset and final crystallization temperatures, respectively; and H_c is the crystallization enthalpy. Assuming that non-isothermal crystallization process may be composed by infinitesimally small isothermal crystallization steps, Ozawa [18] extended the Avrami equation to the non-isothermal case as follows:

$$1 - \alpha = \exp\left(\frac{-K(T)}{\varphi^m}\right) \tag{2}$$

where $K(T)$ is the function of cooling rate; φ is the cooling rate and m is the Ozawa exponent depending on the crystal growth. Eq. (2) can be transformed in:

$$\ln(-\ln(1-\alpha)) = \ln(K(T)) - m.\ln\phi \tag{3}$$

By plotting $\ln(-\ln(1-\alpha))$ vs $\ln\phi$, at a given temperature, a straight line should be obtained allowing to determine $K(T)$ and m.

This approach was applied to the early stages of crystallization, in order to avoid complications arise from the effects of secondary crystallization process. Thus, relative crystallinity data in the range from 10 to 40% were used.

It should be noted that n and Z_t ($K(T)$) in non-isothermal crystallization do not have the same physical significances as in the isothermal crystallization because, during non-isothermal crystallization, temperature is lowered constantly. Considering the non-isothermal character of the investigated process, Jeziorny [19] extended the isothermal Avrami's equation to the nonisothermal situation by proposing that the rate parameter, Z_t, should be corrected by cooling rate as follows:

$$\ln Zc = \frac{\ln Zt}{\phi} \tag{4}$$

where Z_c is the corrected kinetic rate constant.

A method developed by Mo [20] can be also employed to describe the non-isothermal crystallization process of
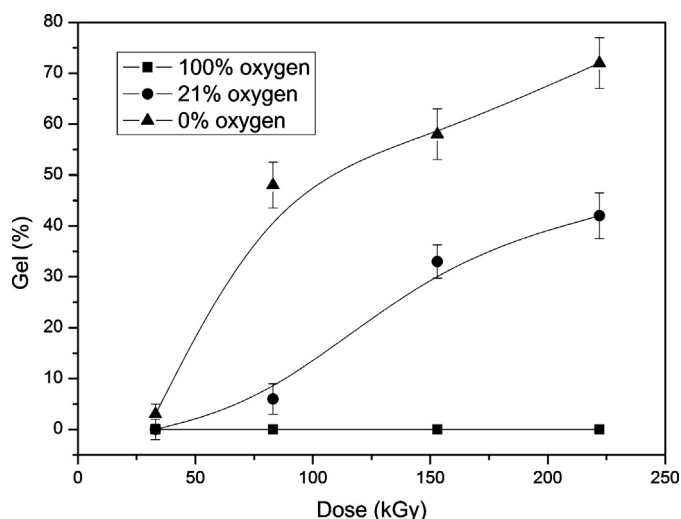
Fig. 1. Effect of oxygen concentration on the gel content of irradiated LDPE.

semicrystalline polymers. Both Eqs. (3) and (4) can be related as follows:

$$\ln Zt + n \ln t = \ln K(T) - m \ln \phi \qquad (5)$$

by rearrangement at a given crystallinity α, the equation is converted into:

$$\ln \phi = \ln F(T) - a \ln t \qquad (6)$$

where $F(T) = [K(T) \cdot Z_t^{-1}]^{1/m}$ refers to the cooling rate, which must be chosen within unit crystallization time when the measured system amounts to a certain degree of crystallinity and $a = n \cdot m^{-1}$ is the ratio between the Avrami's and the Ozawa's exponent.

As it was described above, the crystallization temperature depends on the cooling rate. For non-isothermal crystallization it is interesting to evaluate the effective energy barrier for the process that can be obtained by applying the differential iso-conversional method of Friedman, that uses the following equation [21]:

$$\ln \frac{d\alpha}{dt} = A - \frac{\Delta E_a}{RT} \qquad (7)$$

where $d\alpha/dt$ is the crystallization rate for a given relative crystallinity, A is an arbitrary factor and ΔE_a is the effective energy barrier of the process for a given relative conversion.

Thus the relative crystallinity as a function of time, $\alpha(t)$, was differentiated to obtain the crystallization rate as a function of time. Then, by plotting $\ln (d\alpha/dt)$, measured at various cooling rate, against the corresponding inverse temperature for a given relative crystallinity, ΔE_a can be estimated from the slope.

It should be pointed out that evaluation of the activation energy presumes that the Arrhenius equation holds only within a region of the temperatures related to a given value of relative crystallization degree. Each of these regions is much smaller than the complete non-isothermal crystallization temperature range

(usually smaller than 10 °C). So that, iso-conversional methods can be applied to non-isothermal crystallizations in order to evaluate the dependence of the effective activation energy on the relative crystallization degree and temperature [22].

4. Results and discussions

4.1. Effect of oxygen concentration on the gel content

The effect of oxygen concentration and radiation dose on the gel content of irradiated LDPE is shown in Fig. 1.

From the previous figure, it is clear that the gel content depends on both the irradiation dose and the oxygen concentration used during irradiation. In absence of oxygen, the gel content augments significantly with the radiation dose. On the other hand, the increasing oxygen concentrations accelerate the reaction with the free radicals formed by the irradiation process, reducing the chains crosslinking efficiency and, thus, favoring the chains scission processes [23–25]. In order to study the effect of oxygen in the non-isothermal crystallization tests, the higher dose was chosen because the differences are more significant than at lower doses.

4.2. Differential scanning calorimetric tests

The previous point is qualitatively reflected in the changes on the crystallization peak temperature (T_p), shown in Table 1a. The crystallinity degree (α) is displayed in Table 1b. Smaller changes were found for samples irradiated under atmosphere richer in oxygen, because there are two competitive process occurring at the same time: scission frees chains ends and crosslinking reduces chains mobility, needed for crystallization, by introduction of topological restraints [25,26]. Overall, the changes on the crystallization peak temperature with the radiation dose are not large, with a maximum of about 4% for the highest radiation dose under nitrogen atmosphere. This is in accordance with the results previously reported by other authors [15,27,28]. They have found no significant changes in the melting temperature and enthalpy of fusion after irradiation of polyethylene. On the other hand, the crystallinity of the polymer decreased mildly with the radiation dose (Table 1b). The gamma radiation produces modifications in polyethylene, preventing new crystal formation and, thus, reducing the crystallinity degree [1,25,29].

Fig. 2 shows the crystallization curves obtained at a cooling rate of 10 °C/min for samples irradiated at three different oxygen concentrations and with different doses (33, 83, 153 and 222 kGy). The incorporation of crosslinking in the molecular structure of LDPE influences in the crystallization process and causes that exothermic peak temperature moves slightly toward lower temperatures. The non irradiated LDPE has a single peak centered at 97.3 °C; only very small changes were observed in all irradiated samples with 100% 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

Table 1a

Crystallization peak temperatures (T_p) obtained at a cooling rate of 10 °C/min of samples prepared with different atmospheres (% oxygen) and irradiated with different doses.

	T_p (°C)				
	0% oxygen		21% oxygen		100% oxygen
Non-irradiated	97.3		97.3		97.3
33 kGy	–	95.9	–	97.3	97.7
83 kGy	–	95.5	–	96.3	96.9
153 kGy	97.3[a]	93.8	97.3	94.1	96.5
222 kGy	97.3	93.5	97.3	93.4	96.5

[a] Very soft shoulder.

Table 1b
Crystallinity (%) obtained at a cooling rate of 10 °C/min of samples prepared in different atmospheres (% oxygen) and irradiated with different doses.

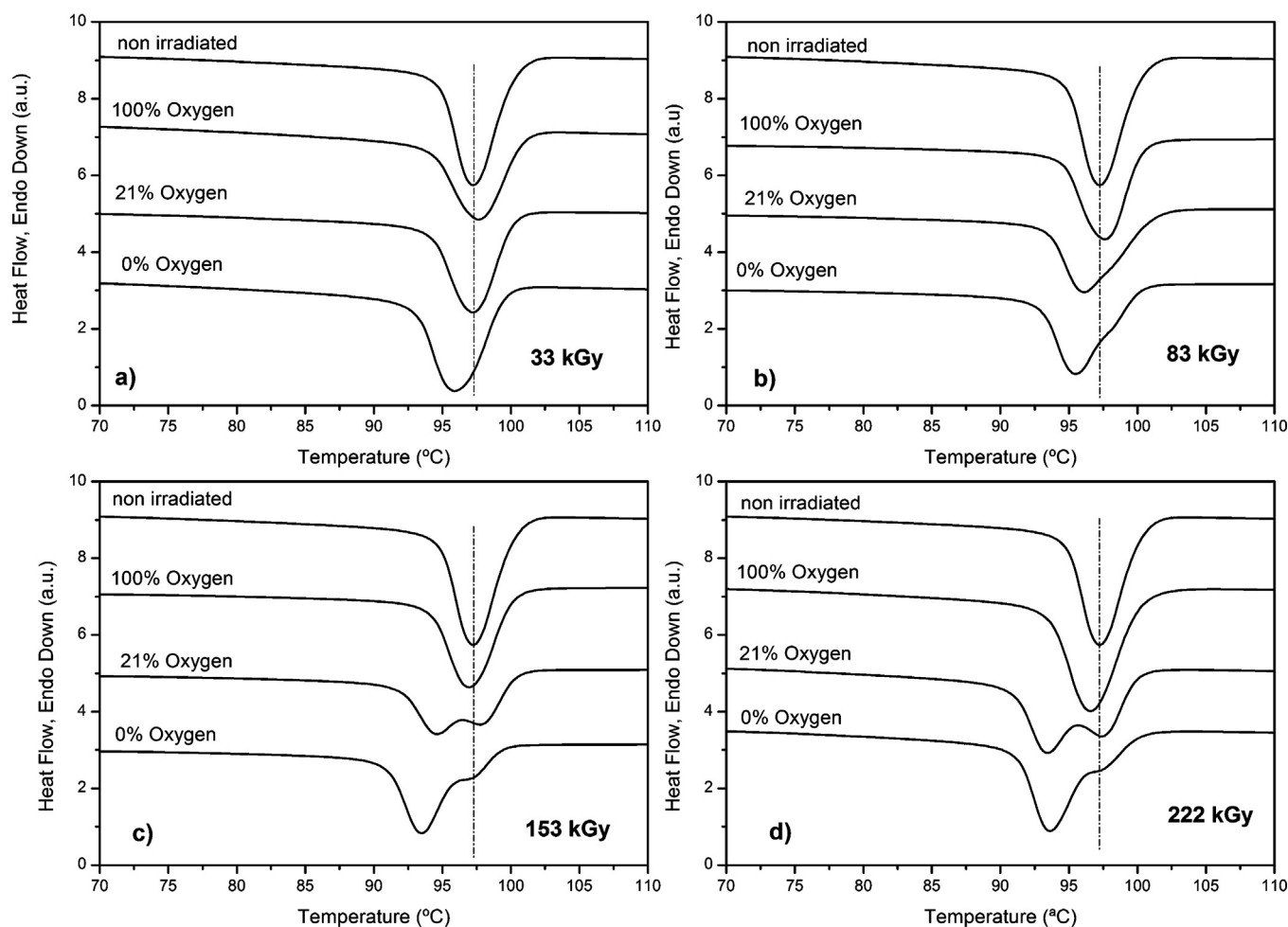|	Crystallinity (%)		
	0% oxygen	21% oxygen	100% oxygen
Non-irradiated	35.9	35.9	35.9
33 kGy	31.9	33.9	35.2
83 kGy	31.5	33.3	34.8
153 kGy	30.9	32.9	34.0
222 kGy	30.5	32.4	33.9

the samples. A similar behavior was previously reported by Hutzler et al. [8]. Some authors [15,25] have reported that the double peak is caused by reactions of peroxy radicals and is less pronounced for samples irradiated in oxygen than for samples irradiated in air. The sample irradiated at 83 kGy, in 21% oxygen, presents a wide peak which is coincident with low gel content [28].

Due to the crosslinking the macromolecular chains cannot crystallize; the crosslinks disrupt the molecular order and reduce crystallinity and melting point. On the other hand, the irradiation also produces chain scission and reduces the branching. The resulting shorter chains are able to pack together more easily, allowing the most of the branched segments to crystallize separately and at lower temperatures. The existence of two exotherms indicates the occurrence of a multiphase system and that the crystallization occurs in two stages: each part of the irradiated polymer crystallizes according to a characteristic distribution. The lower temperature peaks are attributed to solidification and crystallization of more branched polyethylene chains, whereas the higher temperature ones may be associated to the methyl regions and to the crystallization of irregular structures, such as carbonyl groups [24].
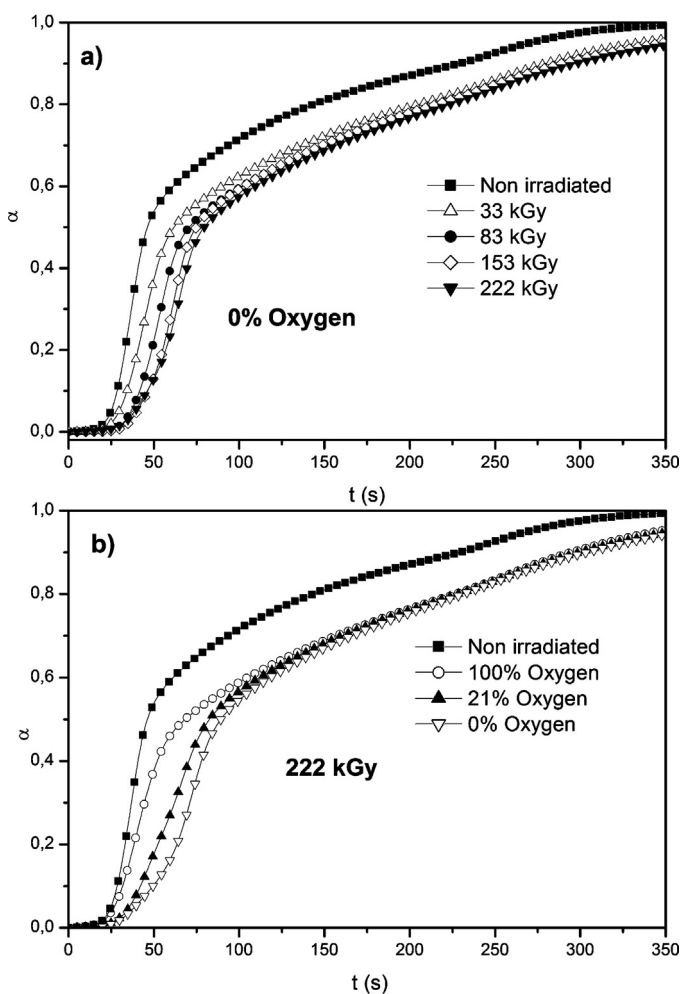
4.3. Non isothermal crystallization kinetics

Fig. 3 shows the relative degree of crystallinity as a function of time, at 10 °C/min, for all irradiated samples in atmosphere with 0% of oxygen (a) and samples irradiated at 200 kGy in different atmospheres (b). In concordance with other studies [30–32], it was shown that the crystallization process of the LDPE takes place over a broad range of temperature; this is characterized by a major high temperature exotherm followed by a small exotherm extending

Fig. 2. Non-isothermal crystallization curves obtained at a cooling rate of 10 °C/min of samples prepared with different oxygen concentrations (% v/v), irradiated with (a) 33 kGy, (b) 83 kGy, (c) 153 kGy and (d) 222 kGy.
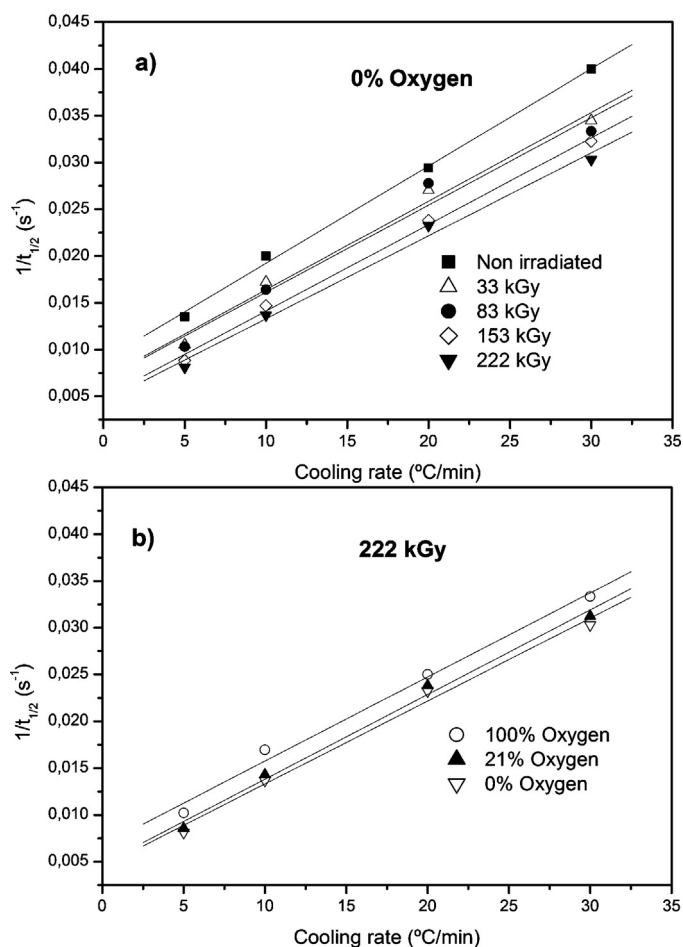
Fig. 3. Relative degree of crystallinity (α) as a function of time at 10 °C/min for (a) original and irradiated LDPE (nitrogen atmosphere) and (b) irradiated with 222 kGy in different atmospheres.

Fig. 4. Overall crystallization rate as a function of cooling rate for: (a) original and irradiated LDPE (nitrogen atmosphere) and (b) irradiated with 222 kGy in different atmospheres.

to lower temperatures. The existence of a primary crystallization followed by secondary one is a frequent feature observed during the non isothermal crystallization of neat and crosslinked LDPE. The previous described behavior is associated with the existence of two crystallization mechanisms occurring in separate temperature ranges [8,9,32]. The mechanism that occurs at high temperature is related to the formation of lamellar crystalline structures. On the other hand, the low temperature one is tentative ascribed to the formation of secondary crystal-fringed micellar type or to the growth of new lamellas crystal between the lamellae formed during the primary process [33,34]. It can be seen, in Fig. 3a, that the generation of crosslinking into the molecular structure of the polymers causes the higher temperature exotherm to move slightly toward lower temperatures while the small exotherm does not appreciably change, in terms of both, peak temperature position or intensity. These changes in the characteristics of the crystallization exotherms were similar for all studied samples and cooling rates. On the other hand, Fig. 3b shows that the presence of oxygen, during the radiation process, accelerates the crystallization process, which is related with the reduction on the crosslinking levels.

From the thermograms, at different cooling rates, some data that are useful to describe non-isothermal crystallization behavior can be extracted. Those are: the exothermic peak temperature (T_p), the crystallinity degree and the half-crystallization time ($t_{1/2}$), defined as the time at which the relative degree of crystallinity approaches to 0.5.

Tables 2a and 2b show the T_p obtained at different cooling rate of samples irradiated at 222 kGy in different atmospheres. In the case of the irradiated samples with 0 and 21% oxygen, two T_p are reported, as a consequence of the existence of two exotherms as previously mentioned.

It was observed that in all cases, T_p decreased (between 5 and 7 °C) with increased cooling rate; this is ascribed to the fact that nuclei became active at lower temperatures conducting to smaller spherulites during the heterogeneous nucleation process [35].

Fig. 4 shows the overall crystallization rate (measured as $1/t_{1/2}$) as a function of cooling rate for all irradiated samples in 0% oxygen (a) and samples irradiated at 222 kGy in three atmospheres (b). For a given sample, the rate of non-isothermal crystallization increased with the cooling rate. In addition, the rate of crystallization of pure LDPE is the highest and decrease as a function of radiation dose, which is in accordance with all previous findings.

4.4. Modeling of non-isothermal crystallization process

Fig. 5 shows the parameters obtained by using the Avrami's model as a function of the cooling rate. It can be observed that n has a decreasing tendency as a function of the radiation dose and with the decrease in the oxygen content. On the other hand, Z_c increased and then finds a pseudo-plateau (1.1-1.0 and lower to the value of the original LDPE) with the dose of radiation in a nitrogen environment. The last behavior is related with the decrease in the gel content and the degree of crystallinity with the radiation dose.

Table 2a
Crystallization peak temperatures (°C) obtained at different cooling rate in different atmospheres of samples irradiated at 222 kGy.

| Φ (°C/min)	T_p (°C)					
	Non irradiated	0% oxygen		21% oxygen		100% oxygen
5	99.5	99.1	95.5	99.1	95.5	98.6
10	97.3	97.3	93.5	97.3	93.4	96.5
20	95.3	95.2	91.3	95.5	90.7	93.9
30	92.8	93.9	88.9	94.2	88.7	91.3

Table 2b
Crystallinity (%) obtained at different cooling rate in different atmospheres of samples irradiated at 222 kGy.

Φ (°C/min)	Crystallinity (%)			
	Non irradiated	0% oxygen	21% oxygen	100% oxygen
5	35.7	32.5	33.0	34.4
10	35.9	30.5	32.4	33.9
20	35.6	31.0	32.5	33.4
30	35.4	30.8	32.1	32.7

In addition, for a fixed radiation dose (222 kGy), n increased as a function of oxygen content, because the material exhibited lower gel fraction and crosslinking degree. Z_c displayed a similar behavior than that observed in the previous case. Z_c increases with the increase of cooling rate; similar behavior was observed in previous works [9,13].

Fig. 6 shows the application of the method of Ozawa. The parameters obtained from Ozawa's model are included in Tables 3a and 3b.

The application of Ozawa's model presents contradictory results in the literature. Krumme et al. [36] have shown that the model is not valid for high density polyethylene blends with broad
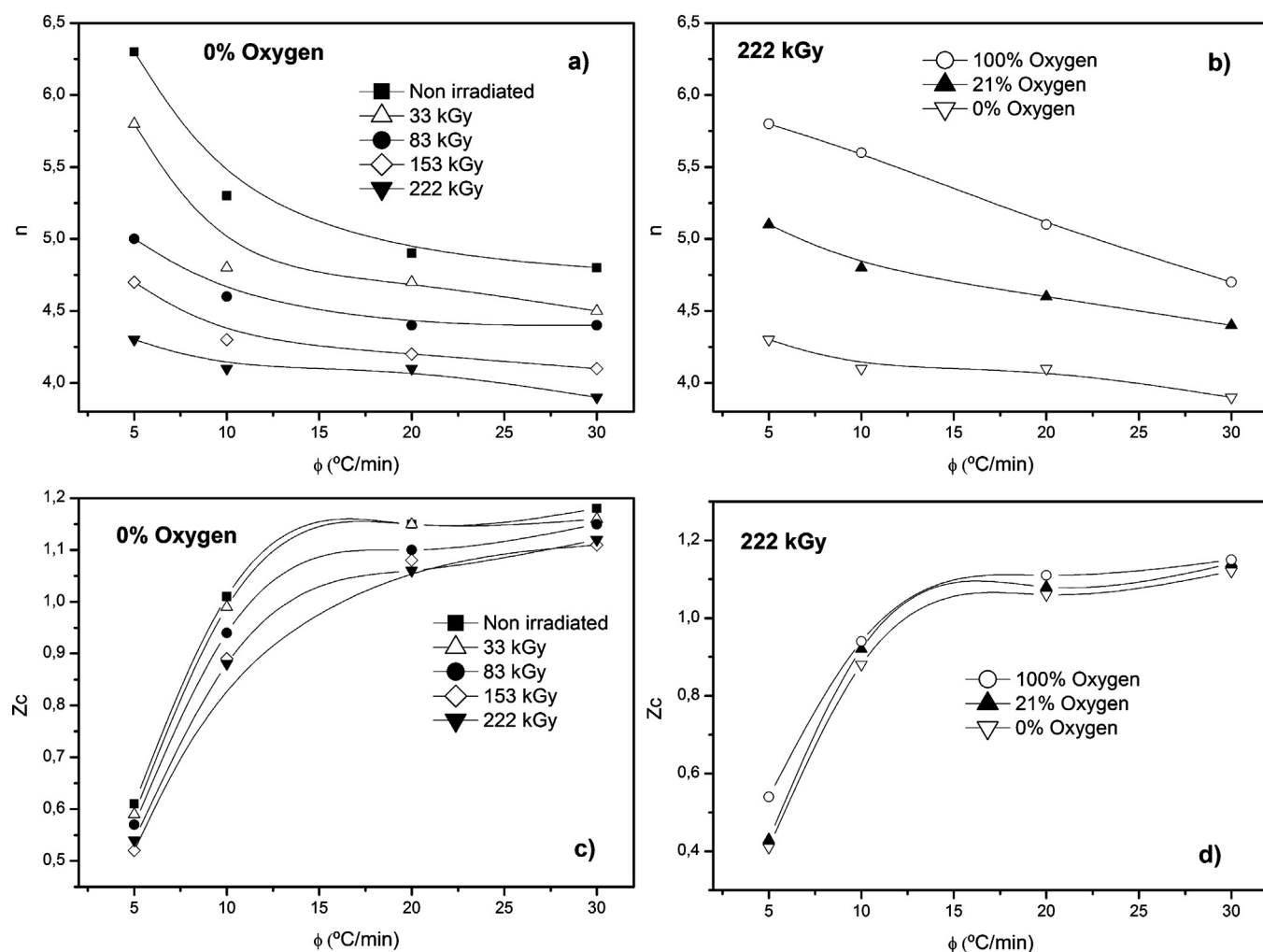
Fig. 5. Parameters of the Avrami's model as a function of the cooling rate for: (a) original and irradiated LDPE (nitrogen atmosphere) and (b) irradiated with 222 kGy in different atmospheres.
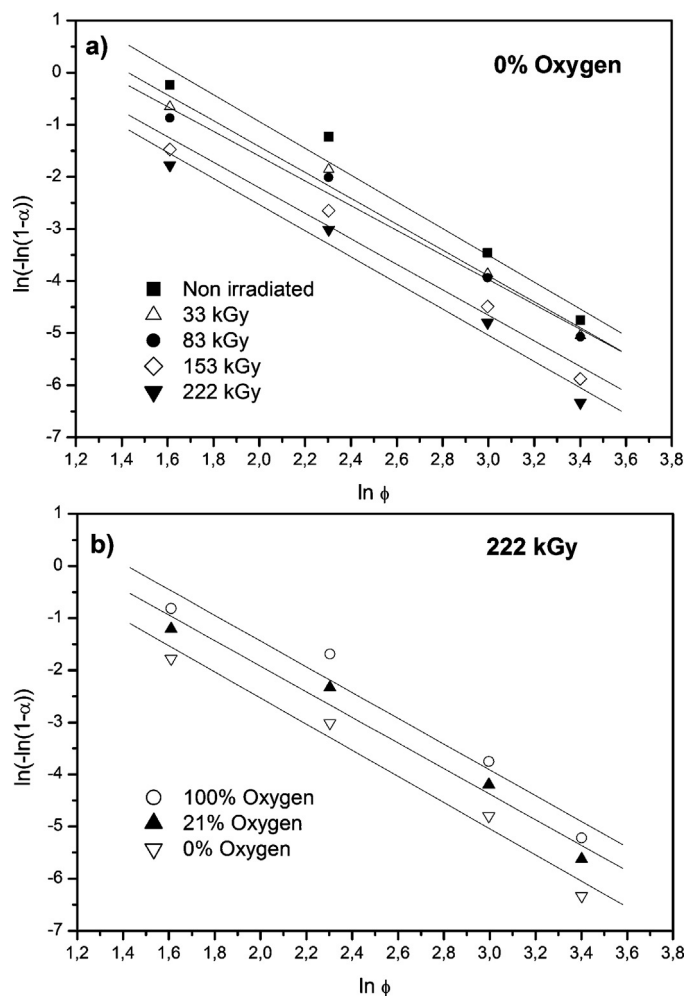
Fig. 6. Parameters of the Ozawa's model for (a) original and irradiated LDPE (nitrogen atmosphere) and (b) irradiated with 222 kGy in different atmospheres.

Table 3a
Non isothermal crystallization kinetic parameters based on the Ozawa's method of irradiated samples with different doses in nitrogen atmosphere.

Sample	Temperature (°C)	m	$K(T)$ (°C/min)
0 kGy	100	2.72	19.5
	99	2.62	39.6
	98	2.57	66.7
33 kGy	100	3.28	31.2
	99	2.98	33.1
	98	2.48	34.5
	96	2.06	67.3
83 kGy	100	2.88	10.8
	99	2.64	18.2
	98	2.37	23.1
	96	1.76	28.8
153 kGy	100	2.50	2.2
	99	2.41	5.3
	98	2.34	10.7
	96	1.64	15.2
	94	1.52	20.7
222 kGy	100		
	99	2.01	3.0
	98	1.82	3.5
	96	1.48	9.1
	94	1.33	10.3

Table 3b
Non isothermal crystallization kinetic parameters based on the Ozawa's method of irradiated samples in different atmospheres at 222 kGy.

Sample (°C/min)	Temperature (°C)	m	$K(T)$
222 kGy-0% oxygen	100	–	–
	99	2.01	3.0
	98	1.82	3.5
	96	1.48	9.1
	94	1.33	10.3
222 kGy-21% oxygen	100	–	–
	99	2.27	17.6
	98	2.15	19.9
	96	1.97	31.2
	94	1.19	19.0
222 kGy-100% oxygen	100	2.52	9.5
	99	2.53	19.9
	98	2.47	33.1
	96	2.94	53.4

molecular weight distribution, but is successful in the prediction of crystallinity development of short chain branched PE with narrow molecular weight distribution. On the other hand, Eder et al. [37] have reported that cooling crystallization of HDPE does not follow the Ozawa's equation, probably because of factors neglected in the theory of Ozawa, such as secondary crystallization, dependence of lamellar thickness on crystallization temperature and variation of Avrami's exponent with crystallization temperature. In general terms, polyethylene and its blends and composites exhibit complicated crystallization behavior due to an additional slow process, referred to as secondary crystallization, which is considered to involve the improvement of the crystalline order. The secondary crystallization effect for polyethylene may be due to the unfulfilled Ozawa equation [12].

However, we failed to get a linear plot when Ozawa's equation was applied. Possible reason is that no secondary crystallization is assumed in Ozawa's theory. Nevertheless, the overlapped crystallization temperature range at various cooling rates corresponds to the early crystallization stage at large cooling rate, but it corresponds to the late crystallization stage at small cooling rate. As it is well known, secondary crystallization frequently occurs in the late crystallization stage [38].

In order to obtain reliable and comparable results, from least-square lines drawn through plots of at least three points, the temperature ranges vary from sample to sample, lying in the range of 94-100 °C for all samples, considering the range 1-30% of relative crystallinity. It was obviously in Fig. 6 that the lines of the Ozawa plots for a certain sample were linear and parallel.

For each sample, the Ozawa's exponent, m, increased as a function of temperature and the rate constant $k(T)$ decreased with increasing temperature, indicating that at higher temperature the material crystallizes slower [9,39]. On the other hand, for a given temperature, $k(T)$ decreased with the radiation dose suggesting a decrease in the crystallization rate. This result was in agreement with the previous results of the overall crystallization rate. In addition, at a constant dose (222 kGy) and a fixed temperature, $k(T)$ increases with the oxygen content.

Moreover, values between 0.98 and 1 were found for the correlation coefficient (R^2); this is an indication that the Ozawa's method satisfactory describes the non-isothermal crystallization kinetics of LDPE, regardless of whether or not is crosslinked [39].

Fig. 7 shows the parameters obtained from Mo's model. These parameters (α and $F(t)$) were obtained by using the Eq. (5); by plotting $\ln \theta$ versus $\ln t$, the parameter $F(t)$ is obtained from slope and
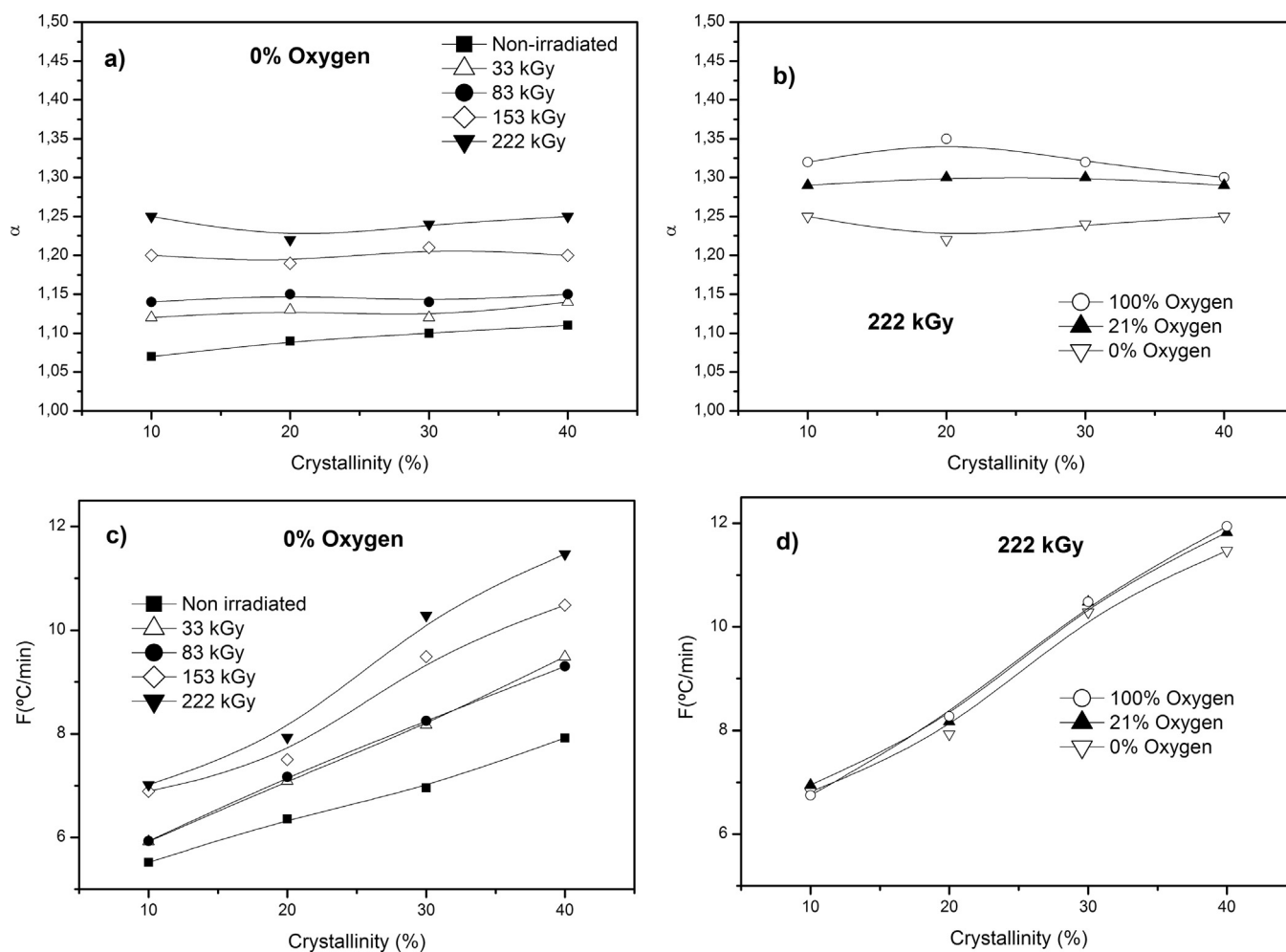
Fig. 7. Parameters of the Mo's model for (a) original and irradiated LDPE (nitrogen atmosphere) and (b) irradiated with 222 kGy in different atmospheres.

m from intercept. As it was previously indicated, values between 10 and 40% of relative crystallinity were considered.
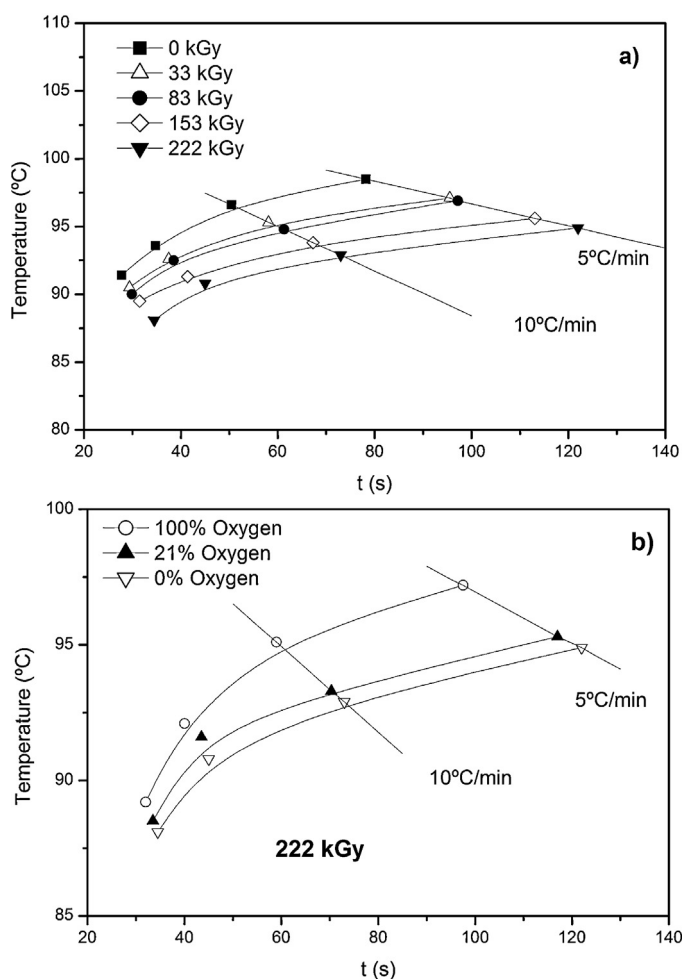
The values of $F(T)$ systematically increased as a function of the relative degree of crystallinity. On the other hand, at a given degree of crystallinity, $F(T)$ slightly increased with the radiation dose, indicating the higher difficulty of polymer for crystallization [9]. In addition, by considering the same radiation dose (222 kGy) and at a given degree of crystallinity, the values of $F(T)$ remained practically constant with the increase in the oxygen content. It is important to note that the model does not allow showing the differences observed by other studied methods [25].

As it was described above, the crystallization temperature depends on the cooling rate. Thus, for extending the analysis of the non-isothermal crystallization process, the effective energy barrier for crystallization was evaluated. It was found that the values of ΔE_a were dependent on the conversion degree [21,22]. The results are presented in Table 4, and were evaluated in the range of crystallinity between 10 and 30% [32]. Similar behavior was obtained for all studied samples. The experimental values of the activation energy take greater negative values at low extents of crystallization that correspond to the temperatures closer to the melting point, which adequately reflects the changes in the crystallization kinetics that occur with changing the temperature of the process [22]. It can be seen in the table that at same crystallinity degree, the activation energy increased with the radiation

Table 4
Activation energies of studied materials as a function of the relative degree of crystallinity.

Sample	α	$-E_a$ (kJ/mol)
Non-irradiated	0.1	237 ± 10
	0.2	188 ± 5
	0.3	184 ± 7
33 kGy-0% oxygen	0.1	289 ± 12
	0.2	261 ± 8
	0.3	235 ± 9
83 kGy-0% oxygen	0.1	292 ± 2
	0.2	275 ± 3
	0.3	249 ± 2
153 kGy-0% oxygen	0.1	305 ± 15
	0.2	281 ± 10
	0.3	255 ± 4
222 kGy-0% oxygen	0.1	330 ± 14
	0.2	267 ± 13
	0.3	261 ± 2
222 kGy-21% oxygen	0.1	279 ± 10
	0.2	257 ± 2
	0.3	246 ± 8
222 kGy-100% oxygen	0.1	262 ± 22
	0.2	236 ± 12
	0.3	193 ± 9

Fig. 8. CCT plots for (a) original and irradiated LDPE (nitrogen atmosphere) and (b) irradiated with 222 kGy in different atmospheres.

5. Conclusions

The crystallization behavior of polyethylene crosslinked by radiation in different atmospheres, under non-isothermal conditions, was studied by differential scanning calorimetry.

The crystallization rate, the crystallization temperature and the crystallinity degree decreased with the radiation dose in nitrogen atmosphere, and with decreasing oxygen content at same dose. On the other hand, 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.

The full model was also used in order to build the CCT diagrams. These diagrams allow the determination of the evolution of crystallinity degree for different processing conditions, which will be very useful for the design and optimization of processing steps and clearly showed the retarding effect with the irradiation dose increase and with oxygen content decrease.

Acknowledgements

References

[1] I. Chodak, Properties of crosslinked polyolefin-based materials, Prog. Polym. Sci. 20 (1995) 1165–1199.
[2] B.A. Krentsel, Y.V. Kissin, V.I. Kleiner, L.L. Stotskaya, Polymers and Copolymers of Higher alpha-Olefins. Chemistry, Technology, Applications, Hanser Publishers, Munich, 1997, pp. 299.
[3] N. Andreucetti, C.J. Pérez, M. Failla, E. Vallés, Modification of model ethylene-butene copolymers using gamma radiation and an organic peroxide, Macromol. Symp. 245–246 (2006) 93–105.
[4] M. Ghaffari, V. Ahmadian, Investigation of antioxidant and electron beam radiation effects on the thermal oxidation stability of low-density polyethylene, Radiat. Phys. Chem. 76 (2007) 1666–1670.
[5] C.J. Pérez, E.M. Vallés, M.D. Failla, Modification of model ethylene–butene copolymers using organic peroxide, Polymer 46 (2005) 725–732.
[6] Y.H. Kao, P.J. Phillips, Crystallinity in chemically crosslinked low density polyethylenes: 1. Structural and fusion studies, Polymer 27 (1986) 1669–1678.
[7] P.J. Phillips, Y.H. Kao, Crystallinity in chemically crosslinked low density polyethylenes: 2. Crystallization kinetics, Polymer 27 (1986) 1679–1686.
[8] B.W. Hutzler, L.D.B. Machado, A.L.C.H. Villavicencio, A.B. Lugao, Crystallization of irradiated polyethylene, Radiat. Phys. Chem. 57 (2000) 431–434.
[9] C. Jiao, Z. Wang, X. Liang, Y. Hu, Non-isothermal crystallization kinetics of silane crosslinked polyethylene, Polym. Test. 24 (2005) 71–80.
[10] S. Nilsson, T. Hjertberg, A. Smedberg, Structural effects on thermal properties and morphology in XLPE, Eur. Polym. J. 46 (2010) 1759–1769.
[11] J.T. Xu, Y.Q. Zhao, Q. Wang, Z.Q. Fan, Isothermal crystallization of intercalated and exfoliated polyethylene/montmorillonite nanocomposites prepared by in situ polymerization, Polymer 46 (2005) 11978–11985.
[12] P. Zou, S. Tang, Z. Fu, H. Xiong, Isothermal and non-isothermal crystallization kinetics of modified rape straw flour/high-density polyethylene composites, Int. J. Therm. Sci. 48 (2009) 837–846.
[13] L. Tang, M. Yan, C. Liu, P. Wang, B. Qu, Effect of UV-photocrosslinking on the nonisothermal crystallization kinetics of polyethylene, J. Appl. Polym. Sci. 108 (2008) 174–180.
[14] M.A. Islam, I.A. Hussein, M. Atiqullah, Effects of branching characteristics and copolymer composition distribution on non-isothermal crystallization kinetics of metallocene LLDPEs, Eur. Polym. J. 43 (2007) 599–610.
[15] F.J. Zoepfl, V. Markovic, J. Silverman, Differential scanning calorimetry studies of irradiated polyethylene: II. The effect of oxygen, J. Polym. Sci. 22 (1984) 2033–2045.
[16] M. Deng, S.W. Shalaby, Effects of gamma irradiation, gas environments, and postirradiation aging on ultrahigh molecular weight polyethylene, J. Appl. Polym. Sci. 58 (1995) 2111–2119.
[17] M.D. Failla, A. Brandolin, C. Sarmoria, E.M. Vallés, The effect of oxygen on the irradiation process of ethylene–butene copolymer, Polym. Degrad. Stabil. 97 (2012) 1485–1494.
[18] T. Ozawa, Kinetics of non-isothermal crystallization, Polymer 12 (1971) 150–158.

dose; this is in agreement with the crystallization process restrictions imposed by the molecular crosslinking that increases with the radiation dose. Similar behaviors were reported by other authors [13]. Another interesting result is that at a given radiation dose (222 kGy), the activation energy decreased with the oxygen content used during irradiation; this is in accordance with the fact that as the content gel decreased the crystallization process was accelerated.

Fig. 8 shows the CCT, continuous cooling transformations plots (constant cooling rate) where the crystallinity is related with time and temperature at a constant cooling rate. This approach allows the knowledge of the entire crystallization process [40,41]. The curves representing the relative degree of crystallinity at 0.3 are plotted as a function of time. Each point on these curves has been obtained by the integration of the full model (nucleation and growth) at given cooling rate. So, when the degree of crystallization curve is intercepted by a constant cooling rate one, the obtained point represents the time necessary to reach a specific relative degree of crystallization under specific thermal conditions. From Fig. 8a it can be observed that the time necessary to reach the relative crystallinity degree of 30% increased with the radiation dose, indicating a retarding effect with the dose increase. On the other hand, the diagrams of samples irradiated in different atmospheres at 222 kGy (Fig. 8b) disclose that the retarding effect increased when the oxygen content decreased.

[19] A. Jeziorny, Parameters characterizing the kinetics of the non-isothermal crystallization of poly(ethylene terephthalate) determined by d.s.c, Polymer 19 (1978) 1142–1144.

[20] T.X. Liu, Z.S. Mo, S.E. Wang, H.F. Zhang, Nonisothermal melt and cold crystallization kinetics of poly(aryl ether ketone), Polym. Eng. Sci. 37 (1997) 568–576.

[21] S. Vyazovkin, N. Sbirrazzuoli, Isoconversional analysis of calorimetric data on nonisothermal crystallization of a polymer melt, J. Phys. Chem. B 107 (2003) 882–888.

[22] S. Vyazovkin, N. Sbirrazzuoli, Estimating the activation energy for non-isothermal crystallization of polymer melts, J. Therm. Anal. Calorim. 72 (2003) 681–686.

[23] L. Audouin-Jirackova, G. Papet, J. Verdu, Effect of radiochemical ageing on the tensile properties of high density polyethylene, Eur. Polym. J. 25 (1989) 181–186.

[24] L. Audouin-Jirackova, G. Papet, J. Verdu, Diffusion controlled radiochemical oxidation of low density polyethylene-II kinetic modeling, Int. J. Radiat. Appl. Instrum. C: Radiat. Phys. Chem. 33 (1989) 329–335.

[25] C.J. Pérez, M.D. Failla, J.M. Carella, Advantageous use of SSA technique to study of effects of thickness, antioxidant and oxygen in gamma irradiated low density polyethylene, Thermochim. Acta 538 (2012) 67–74.

[26] R.G. Alamo, L. Mandelkern, Crystallization kinetics of random ethylene copolymers, Macromolecules 24 (1991) 6480–6493.

[27] H.A. Khonakdar, S.H. Jafari, U. Wagenknecht, D. Jehnichen, Effect of electron-irradiation on cross-link density and crystalline structure of low- and high-density polyethylene, Radiat. Phys. Chem. 75 (2006) 78–86.

[28] C.J. Pérez, E.M. Vallés, M.D. Failla, The effect of post-irradiation annealing on the crosslinking induced by gamma-irradiation of high density polyethylene, Radiat. Phys. Chem. 79 (2010) 717–724.

[29] J.C.M. Suarez, E.E.C. Monteiro, E.B. Mano, Study of the effect of gamma irradiation on polyolefins-low density polyethylene, Polym. Degrad. Stabil. 75 (2002) 143–151.

[30] S. Vanden Eyndea, V. Mathot, M.H.J. Kochb, H. Reynaers, Thermal behaviour and morphology of homogeneous ethylene–propylene and ethylene

-1-butene copolymers with high co-monomer contents, Polymer 41 (2000) 3437–3453.

[31] M.A. Islam, I.A. Hussein, M. Atiqullah, Effects of branching characterisrtics and copolymer composition distribution on no-isothermal crystallization kinetics of metallocen LLDPES, Eur. Polym. J. 43 (2007) 599–610.

[32] C.J. Pérez, V.A. Alvarez, E.M. Vallés, M.D. Failla, Crystallization behavior of random ethylene-butene copolymers modified with organic peroxide, Thermochim. Acta 528 (2012) 15–22.

[33] B. Crist, P.R. Howard, Crystallization, Melting of model ethylene-butene copolymers, Macromolecules 32 (1999) 3057–3067.

[34] A. Alizadeh, L. Richardson, J. Xu, S. McCartney, H. Marand, Y.W. Cheung, S. Chum, Influence of structural and topological constraints on the crystallization and melting behavior of polymers. 1. Ethylene/1-octene copolymers, Macromolecules 32 (1999) 6221–6235.

[35] M.L. Di Lorenzo, C. Silvestre, Non-isothermal crystallization of polymers, Prog. Polym. Sci. 24 (1999) 917–950.

[36] A. Krumme, A. Lehtinen, A. Viikna, Crystallisation behaviour of high density polyethylene blends with bimodal molar mass distribution: 2. non-isothermal crystallisation, Eur. Polym. J. 40 (2004) 371–378.

[37] M. Eder, A. Wlochowicz, Kinetics of non-isothermal crystallization of polyethylene and polypropylene, Polymer 24 (1983) 1593–1595.

[38] T. Xu, Q. Wang, Z.Q. Fan, Non-isothermal crystallization kinetics of exfoliated and intercalated polyethylene/montmorillonite nanocomposites prepared by in situ polymerization, Eur. Polym. J. 41 (2005) 3011–3017.

[39] H. Wu, M. Liang, C. Lu, Non-isothermal crystallization kinetics of peroxide-crosslinked polyethylene: effect of solid state mechanochemical milling, Thermochim. Acta 545 (2012) 148–156.

[40] S. Chew, J.R. Griffiths, Z.H. Stachurski, The crystallization kinetics of polyethylene under isothermal and non-isothermal conditions, Polymer 30 (1989) 874–881.

[41] C.J. Perez, V.A. Alvarez, Effect of different inorganic filler over isothermal and non-isothermal crystallization of polypropylene homopolymer, J. Therm. Anal. Calorim. 107 (2012) 633–643.