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Isothermal crystallization of gamma irradiated LDPE in the presence of oxygen

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HIGHLIGHTS

- 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 Ea 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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ABSTRACT

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.

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 Polisur (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 ± 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

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

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