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

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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.

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

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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