



Crystallization of irradiated polyethylene

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Abstract

This study compares the effects of radiation dose on the isothermal and non-isothermal crystallization of LLDPE, LDPE and HDPE by differential scanning calorimetry (DSC). It includes qualitative comparison of the non-isothermal data and quantitative calculations of Avrami parameters for crystallization rate and nucleation mode. The isothermal crystallization allowed the observation of the changes in the crystallization rate, related to the decrease in the crystallization temperature caused by the crosslinking of the polymer. It was also observed by the non-isothermal crystallization, the development of crystallites of very different sizes in the polymer. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene; Crystallization; Irradiation; Thermal analysis

1. Introduction

The crystallization behavior of polymers is influenced by two competitive factors: the cooling rate and the crystallization rate. The former is controlled by the heat transference from the sample by the medium; the other by the molecular orientation (Hammami and Spruiell, 1995). The differential scanning calorimetry (DSC) has been used more often in the study of crystallization during the cooling at a constant rate (Ozawa, 1971) than in the study of isothermal crystallization (Avrami, 1940). In this study, the two procedures were compared in order to determine the differences caused by gamma irradiation (Singh and Silverman, 1991) of three different polyethylene samples. The isothermal study includes the determi-

nation of the parameters K (constant related to the crystallization rate) and n (related to the nucleation mode and crystal growth) from Avrami's equation:

$$1 - X_t = \exp(-Kt^n)$$

where X_t is the fraction crystallized at time t , n is a parameter related to nucleation mode and crystallization growth and K is a constant that follows the Arrhenius relation; $K = A \exp(-E/RT)$.

2. Experimental

Three different polyethylene samples were used: LLDPE, LDPE and HDPE provided by Union Carbide, with densities of 0.921, 0.920 and 0.949 g/cm³ and melt flow index of 1.02, 1.10 and 1.22 dg/min, respectively. The samples were irradiated in a ⁶⁰Co source from EMBRARAD, with doses of 100, 200, 300 and 400 kGy. Dosimetry was performed using Harwell Red Perspex 4034. The crystallization of the

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Table 1
Gel fraction (%) of the irradiated samples

Relation dose (kGy)	LLDPE	LDPE	HDPE
100	40.4	64.3	65.7
200	48.9	67.5	71.7
300	57.0	72.5	76.7
400	61.4	73.5	78.5

samples irradiated and not irradiated was observed by a DSC-50 (Shimadzu). The non-isothermal crystallization was done with a 10°C/min cooling rate. For the isothermal crystallization, the samples were heated to 200°C and then cooled to 102 and 103°C for LDPE and 117.5 and 118.5°C for HDPE, depending on the radiation dose, under N₂ atmosphere. The kinetics parameters were calculated for the initial crystallization, until 5% of crystallization completion. For LLDPE it was not possible to find one temperature for the isothermal crystallization of at least two samples irradiated with different doses. The sol fraction was extracted with xylene at boiling temperature during 24 h. The crystallization of the gel fraction was studied under the same conditions.

3. Results and discussion

The crosslinking degree of a polymer is estimated by the mass percentage of its gel fraction. Table 1 shows the results of gel fraction of the irradiated samples. The values of gel fraction of the HDPE samples are slightly higher than the values for LDPE, due probably to the presence of double bonds at the end of the chains. The ratio of crosslinking to degradation reaction for LLDPE showed a marked decrease if compared with LDPE and HDPE. This is usually related to the tertiary double bonds and absence of unsaturation. The comparison of the data shown in Table 1

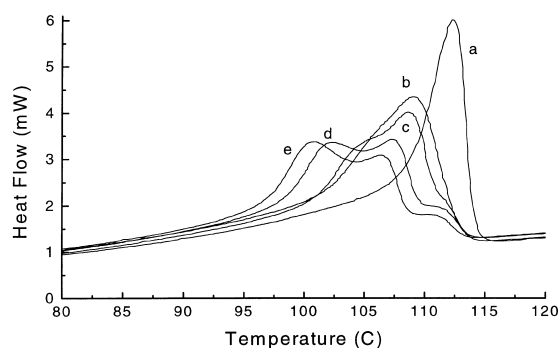


Fig. 1. Crystallization of LLDPE irradiated. (a) Not irradiated, (b) 100 kGy, (c) 200 kGy, (d) 300 kGy, (e) 400 kGy.

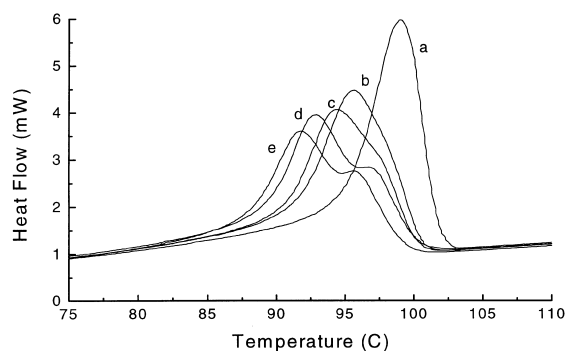


Fig. 2. Crystallization of LDPE irradiated. (a) Not irradiated, (b) 100 kGy, (c) 200 kGy, (d) 300 kGy, (e) 400 kGy.

showed that, for an incremental dose from 300 to 400 kGy in the irradiation of LDPE, there was a small difference in the percentage of gel. On the other hand, Fig. 4 shows that there is a big difference in the crystallization temperature of the gel fraction of LDPE irradiated with those doses. It may be concluded that the crosslinking density of the polymer irradiated with 400 kGy is much greater.

Figs. 1–3 show, respectively, the crystallization curves of LLDPE, LDPE and HDPE related to the radiation dose. It is possible to observe the reduction of the crystallization temperature of the polymer as the radiation dose arises. For the LLDPE and LDPE samples we also observe the development of new peaks in the crystallization curves and the peak broadening for HDPE, although not so pronounced as for LDPE and LLDPE. Both effects, the decrease in crystallization temperature and the peak broadening concurrently or not with the appearance of new peaks, appear as a result of the development of a network followed by the increase in the crosslinking density of PE molecules. These effects increase with dose as shown in Figs. 1–3. From these data, it is possible to conclude that the various crystallization peaks in LDPE and

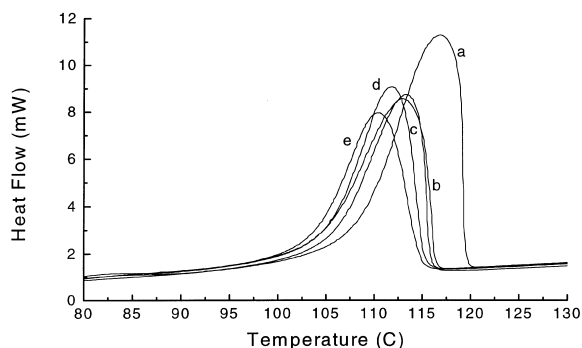


Fig. 3. Crystallization of HDPE irradiated. (a) Not irradiated, (b) 100 kGy, (c) 200 kGy, (d) 300 kGy, (e) 400 kGy.

LLDPE appear due to the existence of groups with different molecular weights and due to the increase in the crosslinking density which may work as a physical barrier for the crystal growth. The higher crosslinking density yields peaks with lower crystallization temperatures.

The behavior of HDPE showing only a comparatively small broadening can be attributed to a different crosslinking mechanism. It is possible to imagine that the initial network is formed homogeneously based on terminal unsaturation, evenly distributed in the polymer bulk. On the other hand, for LDPE and LLDPE, microgel formation, i.e. formation of network by diffusion mechanism of local microgels, increases slowly, yielding a heterogeneous distribution.

The comparison of the crystallization curves of the irradiated polymer before and after the extraction of the sol fraction observed in Fig. 4 showed:

- there is a trend of one of the crystallization peaks to disappear after the extraction of the sol fraction;
- the crystallization temperature of the pure gel is lowered;
- the crystallization temperature of the pure gel is almost coincident with the peak of lower crystallization temperature of the non-extracted sample;
- the sol fraction crystallizes before.

It may be concluded that smaller crystals due to their lower molecular weight compose the sol fraction. The sol portion may also have a small nucleation effect, as it crystallizes before. This effect seems to be not important for the crystallization of the gel portions of the polymer bulk, as the crystallization peaks are almost coincident. This finding is against our previous hypotheses of the importance of orientation in the crystallization kinetics.

Table 2 shows that the parameter n , which is related to the nucleation mode and crystallization growth, does not vary much in function of the radiation dose as was expected. This can be explained by the fact that

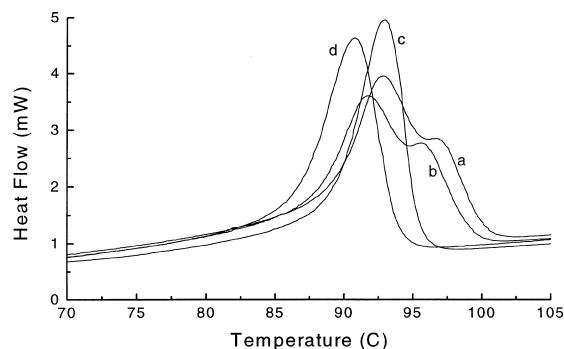


Fig. 4. Crystallization of LDPE irradiated. (a) 300 kGy, (b) 300 kGy after the extraction of sol fraction, (c) 400 kGy, (d) 400 kGy after the extraction of sol fraction.

the isothermal crystallization was performed in a temperature where it was always observed the crystallization of the same fraction, the one that crystallizes before. The larger differences were observed when the curves were performed with different temperatures, which is well known. However, it is still possible to associate the larger change in n value for HDPE with the large change in the crystallization enthalpy as observed in the crystallization curves.

The parameter K and the parameters of reciprocal time to 1% or 50% of crystallization still in Table 2 showed a trend to decrease in function to radiation dose. It was observed that the crystallization is much slower as the radiation dose increases. This is in agreement with the decrease in the crystallization temperature observed in the crystallization curves. However, this trend is less intense for higher doses. It can be concluded that the crosslinking density, when already very high, plays a less important role for the crystallization kinetic, if compared to the network formation itself.

Table 2

Results of the Avrami equation related to the radiation dose and the temperature

Sample parameter	LDPE						HDPE				
	$T = 103^{\circ}\text{C}$		$T = 102^{\circ}\text{C}$				$T = 118.5^{\circ}\text{C}$			$T = 117.5^{\circ}\text{C}$	
Dose (kGy)	0	100	100	200	300	400	100	200	300	300	400
N	2.48	1.98	2.48	2.28	2.16	2.12	2.46	2.19	1.78	2.32	2.03
K	0.066	0.047	0.120	0.074	0.055	0.062	0.066	0.019	0.007	0.056	0.033
$1/t$ (1%) ^a	0.840	0.440	0.560	0.480	0.325	0.350	1.096	0.635	0.370	0.610	0.460
$1/t$ (50%) ^b	0.263	0.136	0.300	0.234	0.164	0.163	0.265	0.101	0.027	0.105	0.110

^a Time to 1% of crystallization.

^b Time to 50% of crystallization.

4. Conclusions

The isothermal crystallization allowed the observation of the changes in the crystallization rate, related to the decrease in the crystallization temperature caused by the crosslinking of the polymer. It also allowed the observation of the variation in the nucleation mode. The non-isothermal crystallization allowed observation again of the decrease in the crystallization temperature caused by the crosslinking of the polymer and also the development of crystallites of very different sizes in the polymer. It also allowed the observation of the easiness of the crystallization promoted by the presence of the sol fraction. The isothermal and non-isothermal crystallization give complementary results to the study of the modifications promoted in the crystallization of the irradiated polymers.

Acknowledgements

We wish to thank R. Siemens (IBM, Almaden) for technical support and discussion and Union Carbide for samples donation.

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