Thermochimica Acta, 215 (1993) 211–218
Elsevier Science Publishers B.V., Amsterdam

Avrami equation and nonisothermal crystallization of polyethylene investigated by DSC

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(Received 10 June 1992)

Abstract

The kinetics of the nonisothermal crystallization of polyethylene (alone and crosslinked with a peroxide or filled with silica) has been analyzed assuming a composed crystallization process (primary and secondary) and Avrami coefficients have been determined for each component of the process. It has been shown that the Avrami coefficient *n* of the secondary process increases from 1.8 to 3 with an increasing degree of polymer crosslinking, which indicates a continuous change in the mechanism of crystallization.

Filler (silica) affects this parameter, especially at a content up to 10 wt%, whereas at higher amounts (up to 35 wt%) the crystallization has apparently the same mechanism as in the pure polymer; in the former case the overall rate of the process, however, is lower.

INTRODUCTION

The kinetics of the crystallization of polymers investigated under isothermal conditions is usually interpreted in terms of the Avrami equation [1, 2], which describes the relation between the extent α of the crystal development and time t

$$\alpha = 1 - e^{-kt^n} \tag{1}$$

where k is the rate constant of crystallization and the value of n indicates a qualitative mechanism of nucleation and crystal growth. In all cases of practical importance, however, crystallization occurs under nonisothermal conditions and to obtain a proper dependence of α on temperature requires consideration also of the equation of heat conduction with appropriate boundary conditions.

At a linear rate of polymer cooling, a plot of $\ln[-\ln(1-\alpha)]$ vs. $\ln t$ yields a straight line, similar to that obtained under isothermal conditions [3],

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which justifies the extension of the formal use of the Avrami equation to nonisothermal conditions.

In the present paper an attempt has been made to find the parameters of the Avrami equation applied to nonisothermal conditions in the way usual to nonisothermal kinetics [4].

The experiments were performed for polyethylene (Marlex 5580) and for low density polyethylene crosslinked with different amount of peroxide (Luperox 130) or filled with silica (Ultrasil); these samples were those investigated under isothermal conditions in ref. 5.

In this paper it was assumed that crystallization curves represent a superposition of at least two independent processes and the parameters of the respective component process were found by the method of nonlinear regression analysis [6].

EXPERIMENTAL

Marlex 5580 polyethylene, of melt flow index 8.3, melting point 405 K and density 0.955 g cm^{-3}, was free of stabilizers.

Low density polyethylene Bralen RA 2-19, of melt flow index 2.0 and melting point 384 K, has been used as a matrix cross-linked with Luperox 130 and filled with silica, namely Ultrasil VN3 (surface area 139 $m^2\,g^{-1}$). The samples were prepared in the mixing chamber of a Brabender plastograph PLO 331 at 155°C for 5 min at 75 rev min^{-1}. The mixtures were compression moulded at 180°C for 20 min. The gel fraction was determined from the weight loss on extraction with boiling xylene for 14 h: 0.1 wt% Luperox, 0.37 wt% gel; 0.3 wt% Luperox, 27.6 wt% gel; 0.6 wt% Luperox, 45.2 wt% gel; 1.0 wt% Luperox, 53.0 wt% gel; 1.5 wt% Luperox, 63.0 wt% gel.

DSC measurements were carried out on a Perkin–Elmer DSC-2. A sample of about 5 mg was heated to 450 K at 10°C min^{-1}, kept at this temperature for 10 min and cooled down at the same rate. Crystallization exotherms were recorded as curves of $d(\Delta H)/dt$ vs. T, where ΔH is the heat of crystallization, t the time and T the temperature.

RESULTS AND DISCUSSION

Under nonisothermal conditions, the Avrami equation for the extent of crystallization α can be rewritten simply as

$$\frac{d\alpha}{dT}=\frac{n}{\beta}k^{1/n}\,|\ln(1-\alpha)|^{(n-1)/n}(1-\alpha) \qquad (2)$$

where k is the rate constant of the crystal growth, n is the Avrami parameter and β the rate of cooling. Some problems may arise with the temperature dependence of the constant k, which should increase with decreasing temperature. The simplest solution is to express k by a dependence analogous to the Arrhenius equation

$$k = A\mathrm{e}^{-E/R(T_0-T)} \tag{3}$$

where T_0 is a reference temperature of the polymer melt (in our case 450 K). Equation (2) assumes the determination of the rate $\mathrm{d}\alpha/\mathrm{d}t$ and of the extent of conversion α. The DSC output usually yields the rate of heat release vs. temperature T so it was more convenient to express α from eqn. (2) analytically as

$$\alpha = 1 - \exp\left(-A/\beta^n\left\{\int_{T_i}^{T} \exp[-E/nR(T_0 - T)]\,\mathrm{d}t\right\}^n\right) \tag{4}$$

or

$$\ln(1-\alpha) = A/\beta^n\left\{\int_{T_i}^{T} \exp[-E/nR(T_0 - T)\,\mathrm{d}t\right\}^n \tag{5}$$

where T_i is the initial temperature of the crystallization process. Consequently, for a single crystallization peak we have

$$\begin{aligned} \mathrm{d}(\Delta H)/\mathrm{d}T &= n\,\Delta H_{\mathrm{cryst}}(A/\beta^n)\exp(-E/nRT) \\ &\quad\times\left\{\int_{T_i}^{T} \exp[-E/nR(T_0 - T)]\,\mathrm{d}T\right\}^{n-1} \\ &\quad\times\exp\left\{-A/\beta^n\left[\int_{T_i}^{T} (-E/nR(T_0 - T)\,\mathrm{d}T)\right]^n\right\} \end{aligned} \tag{6}$$

Nonlinear regression analysis of experimental curves $\mathrm{d}(\Delta H)/\mathrm{d}T$ vs. T based upon eqn. (6) makes possible the determination of the values of n, $\Delta H_{\mathrm{cryst}}$, E and A.

It should be emphasized that the results of the optimization technique used for the determination of the parameters depend significantly on the initial temperature T_i of the crystallization exotherms, which appears in eqn. (6). The Avrami parameter n_1 determined for the first component of the crystallization process [3] corresponds to the beginning of the exotherm (temperature T_i). Change ΔT_i of the temperature T_i to a higher or lower value or its erroneous determination has a strong effect on n, as follows: $\Delta T_i = 4$ K, $n_1 = 5.5$; $\Delta T_i = 3$ K, $n_1 = 4.9$; $\Delta T_i = 2$ K, $n_1 = 4.3$; $\Delta T_i = 0.1$ K, $n_1 = 3.1$; $\Delta T_i = -1$ K, $n_1 = 2.5$; $\Delta T_i = -2$ K, $n_1 = 2.1$. We are emphasizing this to indicate the possible sources of an erroneous interpretation of results when careful attention is not paid to the determination of the initial temperature.

If the nonisothermal crystallization process is composed of several components, the values of the above parameters can be determined independently for each separate crystallization process. This may be

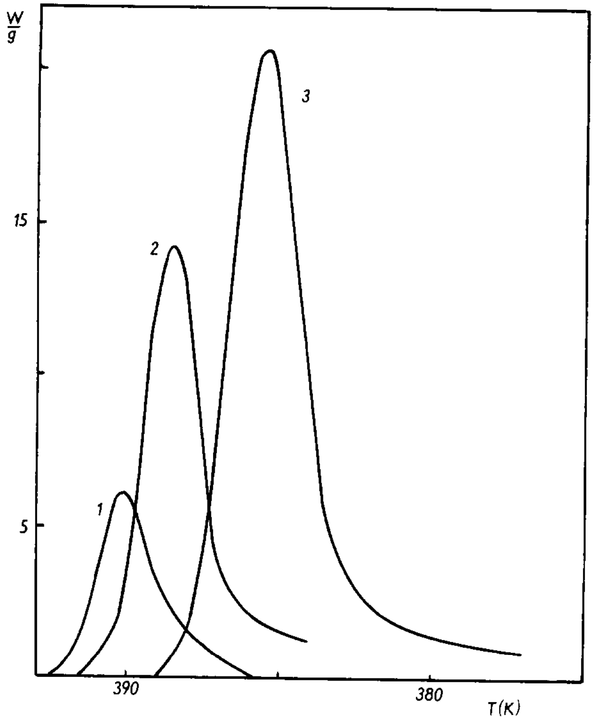

Fig. 1. Crystallization exotherms of polyethylene (Marlex 5580). Rate of cooling: curve 1, 5°C min^{-1}; curve 2, 10°C min^{-1}; curve 3, 20°C min^{-1}.

exemplified by the kinetics of the crystallization of polyethylene (Marlex 5580), for which the records of $d(\Delta H)/dt$ against T are shown in Fig. 1. The maximum rate of heat release is shifted towards lower temperatures with increasing rate of cooling while the value of the maximum rate of heat release increases. Analysis of the curves obtained according to eqn. (6) (assuming a two-component crystallization process) gives the data in Table 1. The rate constants of the primary crystallization show a certain kind of dependence on temperature (temperature coefficient

TABLE 1

The parameters of eqn. (6) determined for the crystallization of polyethylene (Marlex 5580) assuming it to be a two component process (eqn. (1))

Rate of cooling (°C min^{-1})	E_1 (J mol^{-1})	E_2 (J mol^{-1})	$A_1 \times 10^6$ (s^{-1})	$A_2 \times 10^6$ (s^{-1})	n_1	n_2	ΔH_1 (J g^{-1})	ΔH_2 (J g^{-1})
5	70	0	4.4	2.9	3.0	3.7	31	142
10	132	0	29.6	11.3	3.2	3.9	23	147
20	123	0	166.0	110.0	3.0	3.8	20	152

≈190 J mol^{-1}), whereas those of the secondary process do not. A much stronger dependence of these constants on the rate of cooling can be seen. Within the range of cooling rates 5–20°C min^{-1}, the rate constant of crystallization of the primary process increases approximately 40×, whereas that of the secondary process increases 30×. It is of interest to note that the Avrami exponent of the primary process (denoted by index 1) is about 3 whereas the exponent n of the secondary process lies somewhere between 3.5 and 4. The first process represents about 20% of the total heat (170 J g^{-1}). With increasing rate of heating, the ratio of this first process steadily decreases. This is in agreement with the observation of Monasse and Haudin [7] on polypropylene, who found that for nonisothermal crystallization at higher temperatures, n is close to 3; this can be associated with instantaneous nucleation and spherulitic growth, whereas at lower temperatures n approaches 4, associated with sporadic nucleation. From our analysis, one important point follows: the temperature dependence of the rate of crystallization, as can be seen from isothermal experiments [8], is only apparent and is obviously connected with the extent of the supercooling of the sample at a given isotherm.

The curves of the rate of heat release vs. temperature at the rate of cooling of 10°C min^{-1} (Fig. 2) for low density polyethylene crosslinked with Luperox 130 do not show any significant shift in the temperature of the maximum rate of crystallization. With increasing crosslinking, the exotherms merely become broader. Analysis of the curves obtained in terms of eqn. (6), however, provides some interesting data. The overall heat of crystallization is lower than in the case of polyethylene Marlex 5580, the primary process providing here 40–60% of the total heat. The rate of the

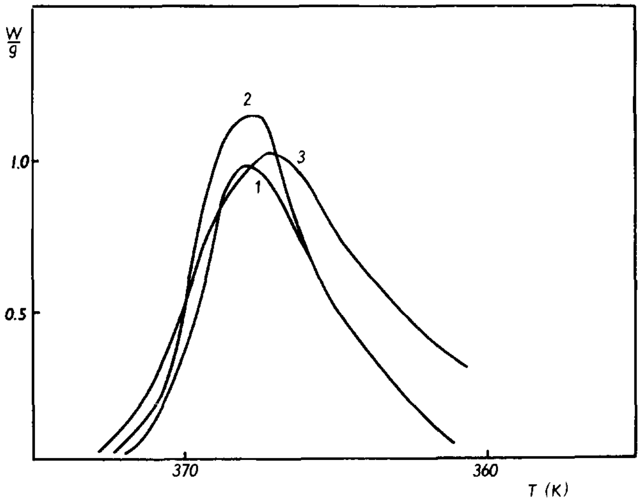

Fig. 2. DSC records of crystallization of low density polyethylene crosslinked with (curve 1) 0%, (curve 2) 0.1%, (curve 3) 1.5% of Luperox 130. The rate of cooling is 10°C min^{-1}.

TABLE 2

Parameters of crystallization obtained by using eqn. (6) for nonisothermal DSC crystallization exotherms of low density polyethylene (PE) crosslinked with various concentration of Luperox 130 (L) [a]

Sample	E_1 (J mol^{-1})	E_2 (J mol^{-1})	$A_1 \times 10^6$ (s^{-1})	$A_2 \times 10^6$ (s^{-1})	n_1	n_2	ΔH_1 (J g^{-1})	ΔH_2 (J g^{-1})	ΔH [b] (J g^{-1})
PE	12	≈0	23	260	3	1.8	23	29	52
PE + 0.1% L	142	≈0	35	101	3	1.9	29	36	65
PE + 0.3% L	144	≈0	25	122	3	1.8	28	36	64
PE + 0.6% L	132	≈0	12	52	3	2.5	34	33	67
PE + 1% L	238	≈0	12	1	3	2.9	32	22	54
PE + 1.5% L	70	≈0	12	1	3	3	28	21	49

[a] Rate of cooling 10°C min^{-1}. [b] Total heat of crystallization.

secondary process is higher than that of the primary process (also true for the original polymer). A flat maximum in the dependence of the overall heat of crystallization vs. the amount of crosslinking agent at 0.3–0.6% Luperox 130 can be observed (Table 2). The rate of the first process shows a maximum in the dependence on the initial amount of crosslinking agent. The rate of the second process steadily decreases with increasing amount of peroxide initially present (Fig. 3). A secondary process for this type of polyethylene has n_2 about 2 or lower, which corresponds to disc-like growth

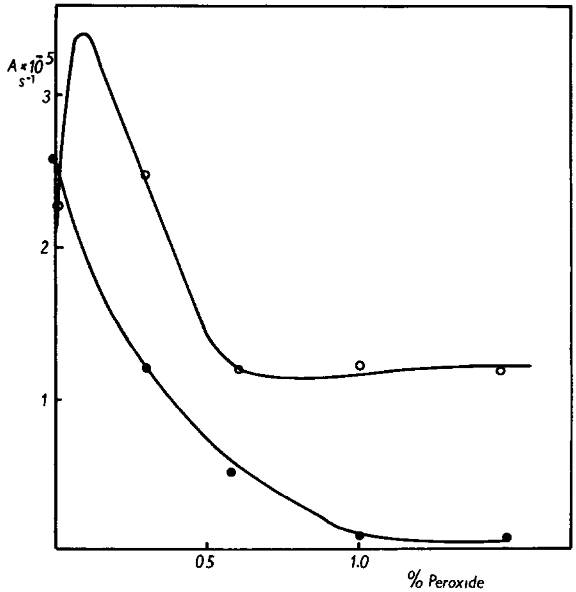

Fig. 3. The dependence of crystallization rates A_1 and A_2 on the initial amount of peroxide in low density polyethylene. The rate of cooling is 10°C min^{-1}.

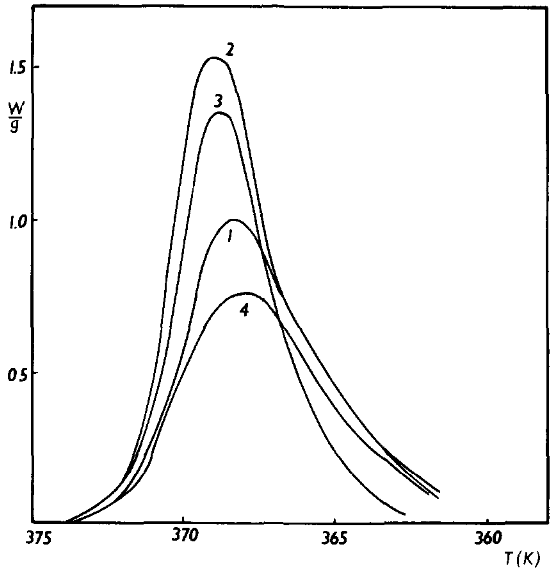

Fig. 4. DSC records of crystallization of LDPE with Ultrasil: curve 1, 0%; curve 2, 5%; curve 3, 10%; curve 4, 35%. The rate of cooling is 10°C $\min^{-1}$.

from instantaneous nuclei. With increasing extent of crosslinking, however, n_2 approaches 3, which may indicate disc-like growth from sporadic nuclei. Two-dimensional growth appears to be faster than three-dimensional growth under conditions of instantaneous nucleation.

The sample of PE containing filler (Ultrasil) gives a rather large scatter of results (Table 3). A minimum amount of Ultrasil (5%) brings about an increased rate of heat release. With further increase of the amount of Ultrasil in a polymer, the rate of heat release starts to decrease (Fig. 4). The system exhibits a much stronger temperature dependence of the primary process. The secondary process of (Avrami coefficient 2) appears to be more like a road-like growth with sporadic nucleation than a disk-like nucleation.

TABLE 3

Parameters of crystallization obtained by the use of eqn. (6) on nonisothermal DSC crystallization exotherms of low denisty polyethylene (PE) filled with Ultrasil (U)[a]

Sample	E_1 (J mol^{-1})	E_2 (J mol^{-1})	$A_1 \times 10^6$ (s^{-1})	$A_2 \times 10^6$ (s^{-1})	n_1	n_2	ΔH_1 (J g^{-1})	ΔH_2 (J g^{-1})	ΔH[b] (J g^{-1})
PE	12	≈0	23	260	3	1.8	23	29	52
PE + 5% U	948	≈0	246	19	3.2	2.4	32	15	47
PE + 10% U	621	≈0	14	7	3.3	2.7	28	17	45
PE + 20% U	245	≈0	51	105	2.9	1.8	26	33	59
PE + 35% U	560	≈0	76	38	2.9	2.0	23	30	53

[a] Rate of cooling 10°C $\min^{-1}$. [b] Total heat of crystallization.

ACKNOWLEDGEMENTS

The authors thank Dr. I. Chodák of the Polymer Institute of Slovak Academy of Sciences for supplying the crosslinked and filled samples of low density polyethylene.

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