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NON-ISOTHERMAL CRYSTALLISATION KINETICS OF NUCLEATED POLY(ETHYLENE TEREPHTHALATE)

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Crystallisation of poly(ethylene terephthalate) in dependence on different crystallisation promotors has been studied by non-isothermal DTA runs with several heating and cooling rates. Using an evaluation method, proposed by Kissinger, activation parameters have been evaluated for crystallisation from the amorphous state and from the melt. Calculated rate constants and half time values of crystallisation, respectively, are in good agreement with crystallisation behaviour of different samples observed under technical conditions.

Due to high melting point, good dimension stability, thermal resistance, and electrical properties poly-(ethylene terephthalate) (PETP) finds increasing interest as material for injection molding. However the rate of crystallisation during the molding process must be enhanced to avoid post-crystallisation of molded articles.

Most of investigations on the crystallisation behaviour of pure and modified PETP have been performed by isothermal measurements [1–4]. But it is difficult to determine isothermal crystallisation rates, when the crystallisation proceeds very rapidly. Non-isothermal DTA is a suitable method to study the crystallisation behaviour of PETP and its changes by modification of the polyester.

Experimental

Method

DTA measurements were carried out with a Mettler-thermoanalyzer TA1, on-line coupled with a microcomputer MC 80.30, with Ni/Cr-Ni thermocouples. 20 mg of the sample were heated under nitrogen in an aluminium pan with 10 deg min^{-1} up to 280° and quenched by cold ethanol. These amorphous samples were heated up to 280° and cooled both with rates of 4, 10, 15, 25 deg min^{-1} respectively.

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Materials

Sample 1 – fibre grade PETP ($M = 24000$), sample 2 – a similar PETP nucleated by addition of 0.05 mol/kg sodium acetate in the polycondensation stage, sample 3 – a commercial engeneering PETP Rynite 530.

Results and discussion

In DTA runs of PETP samples a crystallisation peak is observed both under heating and cooling conditions representing the crystallisation from the amorphous state in heating and from the melt in cooling. The temperatures of these peaks are characteristic parameters for PETP, changing by modification of the polyester (Table 1). Fibre grade PETP exhibits a rather high temperature of crystallisation in heating (T_c) and a low temperature of crystallisation in cooling (T_{cc}). By addition of several modificators these temperatures could be altered.

Table 1 Crystallisation temperatures of PETP by DTA. Peak maximum in heating (T_c) and cooling (T_{cc}) experiments $q = 4$ deg min^{-1}

PETP	T_c °C	T_{cc} °C
1	146.2	200.7
2	127.5	216.6
3	101.8	216.5

An often used method for kinetic evaluation of DTA experiments under variation of heating rates basing on equation (1) was proposed by Kissinger [5].

$$\ln\frac{q}{T^2} = \ln\frac{A\cdot R}{E} - \ln g(\alpha) - \frac{E}{R\cdot T} \qquad (1)$$

where q: heating rate
T: temperature of peak maximum
$g(\alpha)$: conversion function
E: energy of activation
A: frequence factor
R: gas constant

The application of Eq. (1) presupposes a constant degree of conversion at the peak maximum. Kemeny and Šesták [6] recently postulated, that conversion at the peak maximum should be

$$\alpha_m = 1 - 1/e = 0.63 \tag{2}$$

In our investigation however we found deviations from this value and moreover it depends on the heating rate or cooling rate respectively (Table 2). Therefore we determined the activation energy also on the basis of the temperatures of several selected isofractional conversions from the slope of $\ln q/T^2$ against $1/T$ (Table 3). The frequency factor A were calculated using Eq. (1) with

$$g(\alpha) = [-\ln(1-\alpha)]^{1/n} \tag{3}$$

which corresponds to the Avrami rate equation. In our case the Avrami exponent n is not exactly known. Literature data vary from $n = 1$ to 3 [1–4]. As an average value we used $n = 2$.

The evaluated data of E and A obviously depend on the degree of conversion. As Table 2 shows in our investigation α at $T_{\max}$ is found to be < 0.5. Therefore E and A in Table 3 calculated at α greater than about 0.3 are expected to be influenced rather strongly by secondary effects and should not be taken into consideration.

Table 2 Crystallisation of PETP from the amorphous state. Degree of conversion α at peak maximum

q deg min^{-1}	Sample 1	2	3
4	0.54	0.53	0.44
10	0.49	0.31	0.39
15	0.46	0.33	0.29
25	0.39	0.29	0.34
− 4	0.36	0.30	0.2
−10	0.40	0.27	0.31

Table 3 Energy of activation (E in kJ/mol) and frequency factor (A in s^{-1}) of PETP crystallisation from the amorphous state (E_a, A_a) and from the melt (E_m, A_m) at several degrees of isofractional conversion calculated by Eq. (1)

Sample	1		2		3	
α	E_a	A_a	E_a	A_a	E_a	A_a
at T_{max}	67.2		120.4		110.2	
0.1	77.6	$8 \cdot 10^6$	125.0	$7 \cdot 10^{13}$	121.2	$3 \cdot 10^{14}$
0.3	66.9	$5 \cdot 10^5$	111.5	$1 \cdot 10^{12}$	109.7	$6 \cdot 10^{13}$
0.5	61.0	$1 \cdot 10^5$	95.1	$1 \cdot 10^{10}$	95.0	$9 \cdot 10^{10}$
0.7	52.8	$1 \cdot 10^4$	78.7	$7 \cdot 10^7$	79.0	$5 \cdot 10^8$
	E_m	A_m	E_m	A_m	E_m	A_m
0.3	−111	$2 \cdot 10^{-15}$	−209	$2 \cdot 10^{-25}$	−206	$4 \cdot 10^{-25}$

For calculation of rate constants of crystallisation by the Arrhenius equation at several selected temperatures therefore we choosed data obtained at $\alpha = 0.3$, i.e. near or below the peak maximum. In order to get a descriptive presentation of the different crystallisation behaviour of the PETP samples we calculated the half times values by the rearranged Avrami equation (5).

$$t_{0.5} = \frac{[-\ln(0.5)]^{1/2}}{k} = \frac{0.8326}{k} \tag{5}$$

The plots in Fig. 1 represent in the left hand side the crystallisation of amorphous PETP by heating and in the right hand side the crystallisation of the PETP melt by cooling. The figure rather well demonstrates the differences in crystallisation of the PETP samples. The long crystallisation times of fibre grade PETP (sample 1) are distinctive shortened by nucleating agents used in sample 2. Additional acceleration of crystallisation from the amorphous state is to be observed when a supplementary plasticising agent is present as in sample 3. Such additive however has no accelerating effect on the crystallisation of the melt, as to be expected.

A similar figure we got by evaluation the kinetic parameters by an integral method on the basis of single DTA runs. The overall shape is the same, however the curves are shifted to lower temperatures by about twenty Kelvin, and they are characterised by a rather high temperature dependence, especially in the range of melt crystallisation, which seems not to be true.

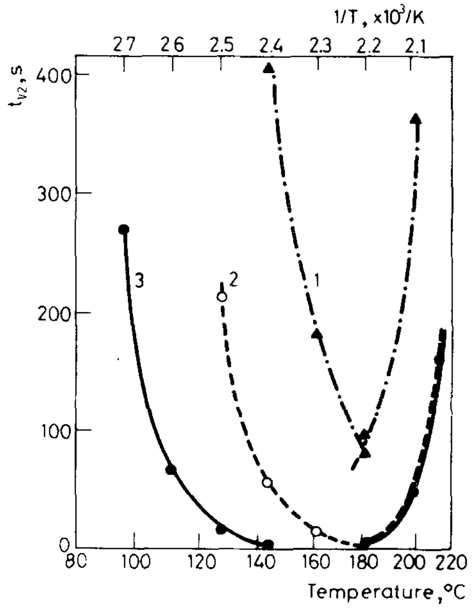

Fig. 1 Half time of crystallisation of PETP from the amorphous state and from the melt calculated from activation parameters in Table 3
1: sample 1 — · —, 2: sample 2 – – –, 3: sample 3 —

Conclusions

The crystallisation of PETP is a complex process, including at least the nucleation step, the growth of the crystals, and a secondary nucleation by the growing crystals. Of course, the non-isothermal DTA investigations discussed give only "formal" kinetic data of the overlapping processes. They are however useful to compare the crystallisation behaviour of different PETP samples and the factors influencing on it. Moreover, comparison of these data with cyclus times necessary in injection molding of PETP demonstrates the calculated half times necessary in injection molding of PETP demonstrates the calculated half times of crystallisation to be in a rather good accordance with the crystallisation behaviour in the technical process. Thus the thermoanalytical data can be utilised to optimise the composition of injection molding PETP.

References

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Zusammenfassung — Die Kristallisation von Polyethylenterephthalat in Abhängigkeit von verschiedenen Kristallisationspromotoren wurde durch nicht-isotherme DTA bei verschiedenen Aufheiz- und Abkühlgeschwindigkeiten gemessen. Unter Verwendung einer auf Kissinger zurückgehenden Auswertemethode wurden Aktivierungsparameter für die Kristallisation aus dem amorphen Zustand bzw. aus der Schmelze ermittelt. Die berechneten Geschwindigkeitskonstanten und Halbwertszeiten der Kristallisation zeigen gute Übereinstimmung mit dem Kristallisationsverhalten verschiedener Proben unter technischen Bedingungen.

РЕЗЮМЕ — Методом неизотермического ДТА при нескольких скоростях нагрева и охлаждения была изучена кристаллизация полиэтилентерефталата в зависимости от природы активаторов кристаллизации. Используя предложенный Киссинджером метод оценок, проведено определение активационных параметров кристаллизации из аморфной фазы и из расплава. Вычисленные константы скорости и полупериод кристаллизации хорошо согласуются с характером кристаллизации различных образцов в технологических условиях.