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CRYSTALLIZATION KINETICS OF POLY(ETHYLENE ADIPATE) INVESTIGATED BY DIFFERENTIAL SCANNING CALORIMETRY

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Crystallization of poly(ethylene adipate) from the amorphous state under non-isothermal conditions with several heating rates has been investigated. The activation energy values, evaluated for different degrees of conversion, using the Ozawa plot, show a slightly decreasing tendency for the higher degrees of conversion.

Poly(ethylene adipate) is widely used in the polyurethane chemistry. As a polyester of a relatively low molecular weight, poly(ethylene adipate), (PEA), easily crystallizes from the amorphous state and from the melt. The influence of crystallization conditions on the obtained morphological forms had been studied by Schuster [1] and thorougly by Teitelbaum [2], by DTA and microscopical investigations. The first of the two exothermic peaks, observed during heating of quenched samples, was attributed to the primary crystallization, whereas the second to a polymorphic transition.

The object of the present work is to investigate the activation energy level during the primary crystallization of PEA.

Experimental

The materials investigated was poly(ethylene adipate), Poles 60/20, from Zaklady Chemiczne "Zachem" (Poland). Throughout this work, a Perkin-Elmer DSC 7 thermal analyser was used. All samples were run in aluminium standard sealed cups and a nitrogen atmosphere. The sample was first heated to 100° and kept at this temperature for 5 minutes to avoid any previous morphological history. Then the sample was rapidly cooled to - 70°, with the cooling rate of 200 deg/min. The heating runs were performed from

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-70° to 80° with the scanning rates of 2, 5, 8, 10, 15 and 20 deg/min. The peaks were measured by planimetry and then the degrees of conversion were calculated.

Results and discussion

A typical DSC curve of a PEA sample is shown in Fig. 1. On heating from the amorphous state above T_g, PEA begins to crystallize. The first appearing morphological form cannot be obtained on cooling from melt. Such a transition is usually described as cold, or primary crystallization. The second exothermic peak, which precedes the melting peak, corresponds to a polymorphic transition and has not been further investigated in this work.

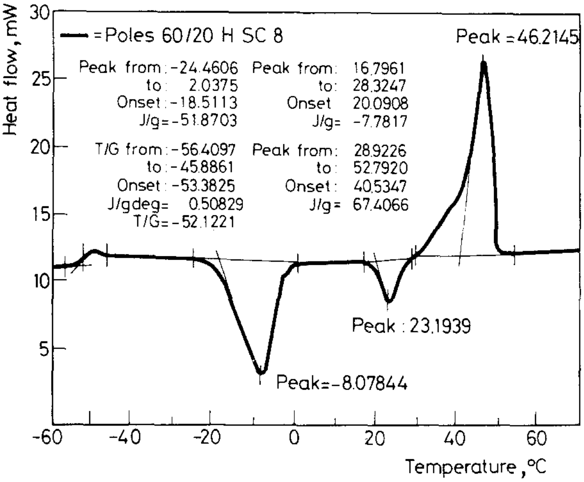

Fig. 1 Typical DSC curve of non-isothermal crystalization and melting of PEA at heating rate 8 deg/min

The degrees of conversion at the peak maxima were not constant, but varied with the heating rate (Table 1). Therefore evaluation methods based on shifts of the peak maxima in a correlation to heating rates could not be used. To overcome this difficulty, the plots by Ozawa [3] were obtained. In this method, the logarithm of the heating rate is plotted against the reciprocal absolute temperature, at which a constant degree of conversion is reached (Fig. 2), accordingly to Eq.1.

$$\log\beta = 0.5467\, \Delta E / RT - 2.315 + \log A\Delta E / R - \log G(\alpha) \qquad (1)$$

where β, ΔE, R, α, T_α, A are the heating rate, the activation energy, the gas constant, the degree of conversion, the absolute temperature at the degree of conversion equal to α, the frequency factor, respectively. $G(\alpha)$ is a function of the frequency factor and the generalized time for the reaction (ref. [3]).

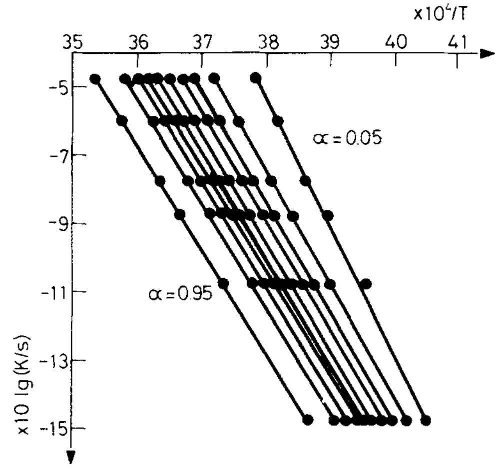

Fig. 2 Ozawa plots according to Eq. (1). Lines from the left to the right were obtained for conversion degree of 0.95, 0.85, 0.75, 0.65, 0.55, 0.45, 0.35, 0.25, 0.15 and 0.05

Table 1 The primary crystallization of PEA. Degrees of conversion at peak maxima

Heating rate, deg/min	Peak maximum, °C	Degree of conversion
2	−20.05	0.625
5	−9.49	0.617
8	−8.07	0.603
10	−5.71	0.587
15	0.10	0.582
20	1.87	0.562

From the slopes of the obtained straight lines activation energy values for chosen degrees of conversion have been calculated by the least squares method (Table 2).

Table 2 Activation energy values at different degrees of primary crystallization of PEA

α	0.05	0.15	0.25	0.35	0.45	0.55	0.65	0.75	0.85	0.95
ΔE, kJ/mol	62.1	58.1	57.7	57.2	58.5	55.8	54.9	54.7	54.2	54.0

The effective activation energy covers both the nucleation and growth processes. The earlier stages of crystallization are more influenced by the nucleation then by growth. In the investigated cases of the primary crystallization of PEA the effective activation energy values decreases more significantly at the beginning of the crystallization. The reasonable conclusion is, that the activation energy of nucleation is in case of PEA higher then that of growth.

References

1 P. Schuster, Thermochim. Acta, 3 (1972) 485.
2 B. Yu. Teitelbaum, J. Thermal Anal., 8 (1975) 511.
3 T. Ozawa, J. Thermal Anal. 2, (1970) 301.

Zusammenfassung — Es wurde die Kristallisation von Polyethylenadipat aus dem amorphen Zustand unter nichtisothermen Bedingungen und mit verschiedenen Aufheizgeschwindigkeiten untersucht. Die unter Anwendung der Darstellung von Ozawa für verschiedene Konversionsraten erhaltenen Werte für die Aktivierungsenergie zeigen für höhere Konversionsraten eine leicht sinkende Tendenz.