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Method of Determining the Kinetics of Spherulite Primary Nucleation from the Spherulite Shapes in Bulk Samples

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Summary

Using the mathematical approach it was shown that it is possible to find the time lag between nucleation acts of two adjacent spherulites from the curved border lines seen in the thin section of a bulk sample. The method of the determining time distribution of the primary nucleation is proposed to be done in the similar way as it was done in the two dimensional case (PAKUŁA et al. 1979).

Based on the above the measurements of the nuclei succesion were reconstructed in two different injection moulded poly methylene oxide samples. This shows a marked number of thermal nuclei.

Introduction

In our earlier work (PAKUŁA et al. 1979) we have presented the principles of the method of determination of the spherulite primary nucleation kinetics in two dimensional case. It is based on the calculation of the time lag between the nucleations of the two neighbouring spherulites. The value of the time lag is derived from the formula correlating the distances from the spherulite centers to the common border, the spherulite growth rate and the time lag. Repeating that procedure for a chain of pairs of neighbouring spherulites one obtains time distribution

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of primary nucleation. The calibration of the time axis is done by the direct measurement of the spherulite growth rate in condition at which the samples were prepared. The observation of the structure of the three dimensional sample is possible by means of thin sectioning. The plane of observation cuts at random the spatial structure of spherulites thus not all spherulite centers are in the section. In such a case the determination of the time distribution of the primary nucleation is more difficult and more information from the microscopic picture is needed.

Experimental

Spherulite shape and size were studied using poly methylene oxide Tarnoform product of Poland. Samples were prepared by injection moulding to a form at 125°C. The pressure in the cylinder of the injector was varied in order to introduce some changes in the kinetics of spherulites primary nucleation. The 1.5 μm sections of the central part of the samples were cut and examined by means of a polarizing microscope.

Results and discussion

Let us assume that the sectioning plane is tilted at the α angle with respect to the straight line passing through the centers of spherulites as it is shown in Fig.1. The projection of the distance between spherulite centers d as well as the projections of other distances are related to the true distance as follows:

$$d = d_1 \cos\alpha \qquad (1)$$

The border between spherulites can be:

1. the plane, if the time lag $\Delta t = 0$
2. one of the surfaces of a hiperboloid, if $\Delta t = 0$.

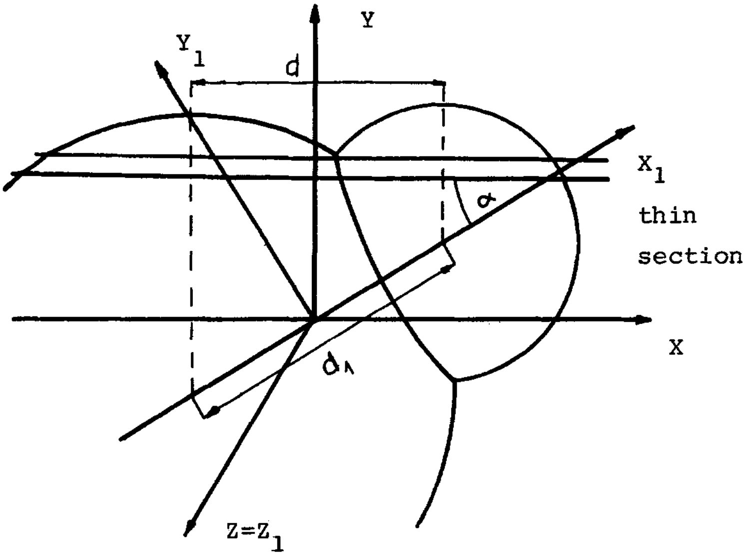


Fig.1. Schematic diagram of the respective positions of the thin section and the truncated spherulites.

In the first case in the sectioning plane one sees the border as a straight line while in the second the curve of the second order. Therefore, if one observes the straight border between spherulites there is no time lag between the primary nucleation acts. Each curvature of the border line indicates the time lag which should be determined.

The equation of the hiperboloid of evolution being the border between two spherulites in the $OX_1Y_1Z_1$ coordinates has a form:

$$\frac{X_1^2}{a^2} - \frac{Y_1^2 + Z_1^2}{b^2} = 1 \qquad (2)$$

where $a = G\,|\Delta t|/2$

$b = \sqrt{d_1^2 - G^2\Delta t^2}/2$

G - the spherulite growth rate

Δt - the time lag

d_1 - the distances between the spherulites centers

In the coordinates tilted by the angle α around the z-axis above equation changes to:

$$Az^2 + Bx^2 + Cy^2 + Dxy - 1 = 0 \qquad (3)$$

where $A = -1/b^2$

$B = \cos^2\alpha\,/a^2 - \sin^2\alpha\,/b^2$

$C = \sin^2\alpha\,/a^2 - \cos^2\alpha\,/b^2$

$D = 2\cos\alpha\,\sin\alpha\left(1/a^2 + 1/b^2\right)$

For the sectioning plane y=const. and one gets the equation of a curve of the second order:

$$Az^2 + Bx^2 + D_1x + C_1 = 0 \qquad (4)$$

where $C_1 = Cy^2 - 1$

$D_1 = Dy$

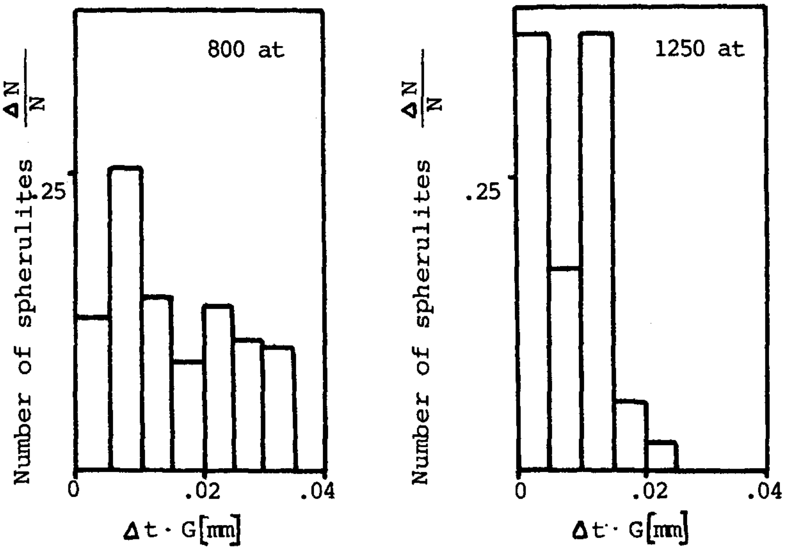
The time lag is easy to determine from the ratio B/A since after some transformations one obtains:

$$|\Delta t| = \frac{d}{G\sqrt{1-B/A}} \qquad (5)$$

It is necessary to know the coordinates of the three arbitrary points x_1, z_1, x_2, z_2 and x_3, z_3 on the border line on the section in order to find the ratio B/A:

$$B/A = -\frac{z_3^2 - z_1^2 + \left(z_2^2 - z_1^2\right)\dfrac{x_3 - x_1}{x_1 - x_2}}{x_3^2 - x_1^2 + \left(x_2^2 - x_1^2\right)\dfrac{x_3 - x_1}{x_1 - x_2}} \qquad (6)$$

The sign of the time lag can be determined regarding the curvature of the border line. The concave border line indicates that the spherulite arose earlier while the convex one that the spherulite was nucleated later than the neighbouring spherulite. If the border is a straight line it means that $\Delta t=0$. The above method allows to determine the time lag of nucleation acts for each pair of spherulites on the basis of the micrograph of the thin section of three dimensional sample and consequently to reconstruct the succesion of the nucleation process in the sample.



Figs.2. Time distribution of primary spherulitic nucleation in bulk samples of poly/methylene oxide/ obtained by injection moulding to a form having the temperature of 125°C from the cylinder at 195°C and pressure: 2a.800 at., 2b. 1250 at.

Using the above method the time distribution of the primary nucleation in two different poly/methylene oxide/ samples was obtained /Figs. 2a and 2b/ from the polarizing micrographs of the thin sections. Spherulites with centers not on the sectioning plane were easy distinguishable as well as their borders and positions of centers only if the thickness of the sections was less than 2 .

The graphs indicate the marked number of the thermal nucleations in both cases which was not believed very much previously for the poly/methylene oxide//see ISIKAWA, STEIN 1976, MISHURA et al. 1974, WUNDERLICH 1976/. There is the other effect which is worth mentioning, namely while increasing the pressure in the cylinder of the injector one observes an acceleration of the spherulite nucleation which could be due both to the increase in the growth rate and the increase in the primary nucleation rate or to one of these factors only. The results point out that the method of calculating the time distribution of the primary nucleation from spherulite shape is especially helpful in cases concerning the crystallization of polymers in a bulk when a direct observation of growing structures is difficult.

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