REVIVAL OF THE INDUCTION TIME CONCEPT IN THE THEORY OF POLYMER CRYSTALLIZATION*

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

To monitor early stages of spherulite growth, a microscopical method has been worked out based on the photometrical measurement of the intensity of depolarized light during isothermal crystallization. Application of the technique to polypropylene yields the evidence of existence of nucleation induction time which reflects the processes taking place prior to the onset of spherulite growth, viz. the formation of stable crystal nuclei. Using the method, it is possible to evaluate also systems with a dispersed phase, the interfacial relations being reflected in the induction time of the nucleation on the surface of the dispersed phase. Application to the model PP/carbon fibre system yields differing results for carbon fibres of various provenance and of various properties.

The concept of nucleation time, a time period necessary for a crystallization nucleus to start growing, dates back to the sixties[1]. Nucleation theories[2] presume that a primary nucleus is built up via thermal fluctuations and from this mechanisms it directly follows that some time is required until the nucleus becomes stable enough to commence crystal growth. It is therefore obvious that the existence of non-zero nucleation time is implicitly attributed to the nucleation mechanism. Kinetic theories of overall crystallization[2], however, are very reluctant to admit nucleation time different from zero. The reason can be seen in the fact that it is very difficult to postulate a parameter, the value of which could be measured only with a high degree of uncertainty.

To follow crystallization kinetics, a value characterizing the crystalline part of a system is measured, e.g. the intensity of depolarized light transmitted through the sample between crossed nicols of microscope. At the beginning of the experiment, when the whole sample is amorphous, that value is equal to zero. Increasing amount of

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the crystallized part results in an increase in the measured light intensity. Any measuring device requires a threshold signal and it is only natural that actual nucleation induction time may interfere with the time which is necessary for the crystal to achieve the size at which the measured signal attains the threshold value. We believe that this is the circumstance that caused the low credibility of real existence of the induction time.

The aim of this paper is to collect experimental evidence of nucleation time different from zero. For this purpose, a careful analysis is to be carried out of the relation between the measured signal and the sample thickness, crystallite size and the spreading of two-dimensional crystals (i.e. crystals the size of which is larger than the sample thickness) in the course of crystallization process. Polypropylene (PP) was selected to display the dependence of nucleation time on crystallization temperature. Moreover, the dependence of nucleation time on foreign crystallization substrate was demonstrated using carbon fibres dispersed in PP. Though the usage of high-grade carbon fibres within PP matrix is impracticable, carbon fibres with various surface treatments and of various properties have been selected as a model system. Theoretical considerations explaining the dependence of nucleation time on crystallization parameters are presented elsewhere[3,4].

EXPERIMENTAL

Samples were prepared by pressing polypropylene melt (PP Mosten 58.412 CHZ Litvínov, The Czech Republic) between two glass plates to prepare thin PP specimens suitable for visible-light microscopy. To prepare specimens with carbon fibres, the fibres were put between two thin plates of PP (30 μm) and after annealing ca 5 min at 200 °C in nitrogen, the plates were pressed. The samples thus prepared were up to 30 μm thick. Carbon fibres produced by SIGRI GmbH (SIGRIFIL HM, SIGRIFIL HF) and by Tenax (HM-S, HM-400, HM-S(U)) were used.

In order to exclude the influence of thermal history on crystallization, every sample was annealed at 200 °C in nitrogen for 5 min, prior to cooling (3 – 4 min) to the crystallization temperature which was in the region 130 – 138 °C.

The luminous flux was recorded during isothermal crystallization (Mettler FP 5 heating stage, Zeiss–Opton microscope Photomikroskop III). Immediately after the measurement of the initial stages of crystallization (about 10 min after reaching the crystallization temperature), crystalline structures were micrographed so that the pre-conditions of an independent crystal growth and of a sufficiently large crystallite size could be tested.

To evaluate the increased part of crystallized phase, microphotometry was used to measure the time-dependent luminous flux of the polarized light passing through the crystallizing specimen[5]. Isothermal crystallization was measured at the early stage of the crystallite growth when the individual crystalline structures do not influence one another but when the linear growth rate can be already considered as constant. Another requirement is that the sizes of crystallites have to be comparable or higher than the sample thickness. Only under these conditions the dependence of the luminous flux on time is given by the time dependence of size of the crystalline structures projected into the image plain of the microscope[5].

RESULTS AND DISCUSSION

The relation between the luminous flux through the sample and time is given by the geometry of the growing crystals. Considering the thickness of a microscopic specimen, it is necessary to distinguish two growth phases. At the earliest stage of crystallization, the thickness of the growing crystal (spherulite) is smaller than sample thickness, the spherulite growth is three-dimensional and this fact is reflected in the corresponding increase in the luminous flux.

After the spherulite size has reached the specimen thickness, the following growth becomes two-dimensional. The crystal thickness is then equal to the specimen thickness and it is sufficient to take into account only an increase in its surface, when evaluating the increase in amount of the crystallized phase.

Under these circumstances, the situation is relatively simple in the case of single spherulites, as a quadratic dependence of the measured signal y on time t exists,

$$y = A\,(t - t_i)^2\,, \qquad (1)$$

where A is a constant depending on the square of the spherulite linear growth rate and t_i is nucleation induction time.

Experimental curve (Fig. 1) can be well described by Eq. (*1*) except for its very beginning, for the reasons described above. Thus, parameters A, and t_i of Eq. (*1*) can be obtained from experimental results by regression analysis. Polypropylene crystallization in the region 130 – 138 °C is characterized by nucleation times t_i from about 50 s at 130 °C to about 500 s at 138 °C (Fig. 2). When evaluating experimental curves, only those parts were taken into account where the conditions of both independent and two-dimensional crystal growth were met (Fig. 1). The results thus obtained in the measured crystallization temperature interval prove that induction time for spherulitic

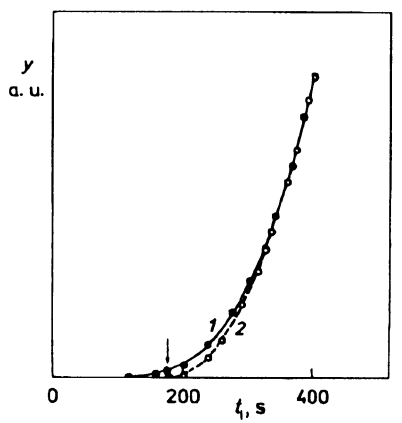

FIG. 1
Experimental (*1*) and theoretical (*2*) dependence of luminous flux y on time for polypropylene crystallized at 135 °C. (The arrow indicates induction time, t_i. The range used for regression analysis is 350 – 400 s.)

nucleation has a positive value, different from zero. The fact that induction time increases with crystallization temperature is in agreement with the concept according to which t_i reflects the time necessary for the formation of a stable crystal nucleus[5].

The evaluation of crystallization kinetics for a system in which the geometry of growing nuclei is substrate-dependent is more complicated. Planar circular spherulites can originate independently, in two different kinds of nucleation centres, viz., in the matrix and on the surface of the dispersed phase (carbon fibres). The recorded signal y can be then expressed as[3]

$$y = A\,[p(t - t_{if})^2 + p_m(t - t_{im})^2]\,, \qquad (2)$$

where A is the constant from Eq. (*1*), p and p_m are number fractions of the spherulites growing on carbon fibres and independently in the matrix, respectively, t is time, t_{if} and t_{im} are induction times for the spherulite growth on fibres and independently in the matrix, respectively. Values of t_{im} used for calculations were taken from Eq. (*1*) (cf. ref.[3]).

A similar relation can be written for the growth of a transcrystalline structure,

$$y = A'(t - t_{if})\,. \qquad (3)$$

Here A' is a constant depending on the linear growth rate of the transcrystalline structures, the contribution from freely-growing spherulites being neglected.

In real systems, evaluation may be complicated by the fact, that both transcrystalline structures and individual spherulites in the matrix and on the foreign surfaces can grow simultaneously. In that case, the equation describing the time dependence of the measured signal y would have a higher number of terms than in Eq. (*2*). The terms

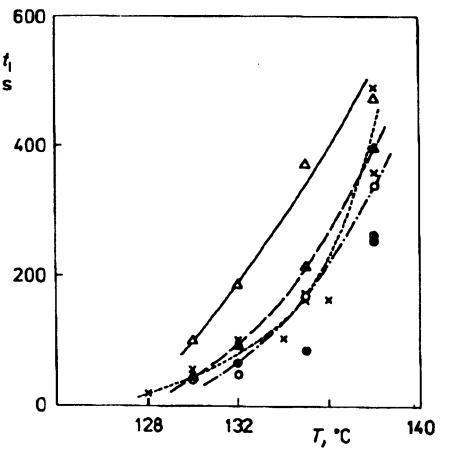

FIG. 2
Plot of induction time versus crystallization temperature for PP matrix with and without carbon fibres[3]: PP matrix (×), PP/SIGRIFIL HF (Δ), PP/SIGRIFIL HM (▲), PP/HM-S (○), PP/HM-400 (●) and PP/HM-S(U) (○)

taken into account are chosen according to actual situation which may be (in our measurement was) documented by corresponding micrographs. For the systems measured in this study, parameters A, A', and t_{if} were obtained from Eqs (*2*) and (*3*) by non-linear regression analysis using least squares.

Non-zero values of nucleation time were found also for crystallite nucleation on the surface of carbon fibres (Fig. 2). Differences in nucleation times are observed between the individual PP/carbon fibre systems. Though details of structure and surface properties of the fibre products used were not known, the obtained results clearly demonstrate their diverse character.

Evaluation of the nucleation on surfaces of the dispersed phase which do not initiate preferential crystallization is very difficult or impossible by any other method as the nucleation in the matrix overwhelms the retarded surface activity of the dispersed phase. The microphotometry method described in this paper makes it possible to measure systems with such dispersed material, the nucleation activity of which is low. The authors find the method advantageous as it makes possible evaluation of various surface treatments, not only those which cause an increase in surface nucleation activity, but also such treatments which decrease the activity and which are otherwise hardly measurable.

A proper selection of the microscope field of view can be helpful in restricting the measurement to either spherulites in neat matrix or to those in close vicinity of the surfaces of the dispersed phase. If the other spherulites (growing in the matrix, independently of the dispersed phase), which are in the minority, are not taken into account, the calculation is simplified to Eq. (*1*) or (*3*). We have tested the error caused by the simplification. In the cases of the dispersed phases which enhance nucleation on their surfaces, luminous flux is practically not influenced by the matrix as its crystallization starts later when crystallites nucleated on the dispersed phase are fairly developed. In the cases when the dispersed phase does not cause a preferential nucleation, the influence of the nucleation in the matrix could be found. Depending on actual amount of the minor spherulites in measured spot, difference of 2 – 10% could be found as calculated according to Eq. (*3*).

The restriction of the observation and microphotometry to the closest vicinity of the foreign phase need not be very strict. E.g., for a system in which merely spherulite structures arise, it is possible to make calculations of t_{if} using Eq. (*2*), where t_{im} is obtained from an independent measurement of induction time in a neat matrix according to Eq. (*1*). If the procedure takes into account the crystallites (spherulites) originating both on the foreign surfaces and in the matrix itself, more precise results can be obtained. The difference, at the very early stages of crystal growth, between the measured signal and the theoretical parabolic shape corresponding to the growth of two-dimensional crystals can be caused by the three-dimensional growth described above, and also by a certain distribution in nucleation times (cf. Fig. 1, the range up to

350 s). Only a very good coincidence of experimental and theoretical curves in further crystal growth (but before spherulites start to merge; in Fig. 1 the range 350 – 400 s) can set a basis for a reasonable regression analysis.

Differences in the nucleation induction times are clearly reflected in morphology. A variety of supermolecular structures were obtained (Fig. 3) ranging from transcrystalline structures (samples Tenax HM-S, HM-400, HM-S(U)) to individual spherulites, when the numbers of the spherulites in the matrix and of those nucleated on fibres are commensurable (SIGRIFIL HF) or the spherulites nucleated on carbon fibres are much

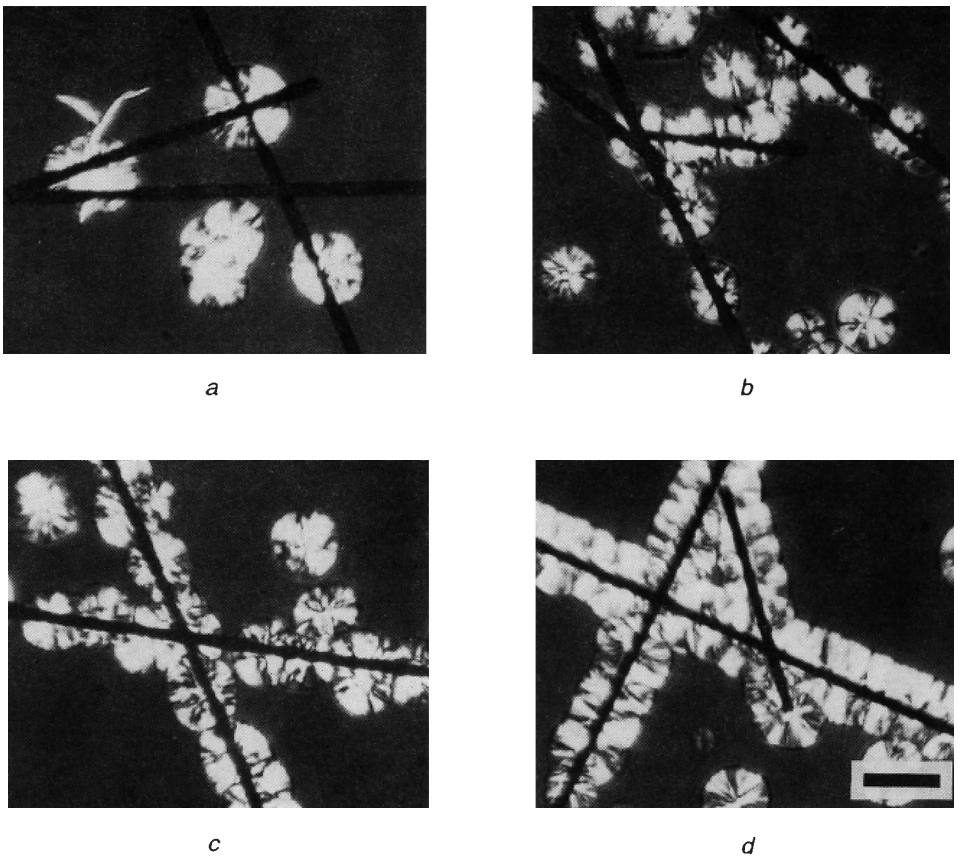

FIG. 3
Isothermally growing crystalline structures in PP filled with carbon fibres[3]: *a* SIGRIFIL HF, *b* SIGRIFIL HM, *c* Tenax HM-S(U), *d* Tenax HM-400. (Scale bar 50 μm.)

more frequent and a transcrystalline-like structure occurs (SIGRIFIL HM). The most intense nucleation and the shortest induction times occur for fibres HM-400 and HM-S(U) (cf. Figs 2 and 3), whereas an almost negligible nucleation in the samples with SIGRIFIL HF is accompanied by the highest induction times. Induction times of the sample with HM-S fibres are commensurable with those of the neat PP matrix.

Theoretical analysis, which postulates the condition of stable crystal nuclei prior to the actual onset of the spherulite growth, yields semiquantitative relations connecting thermodynamic parameters of the growing crystals with the induction time[1,5]. Comparison of the theoretical calculations of induction time with the measured values can serve as a means for testing assumptions made in crystal nucleations theories.

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