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# INFLUENCE OF NUCLEATING AGENTS ON CRYSTALLIZATION OF POLYPROPYLENE *

## I. Talc as a nucleating agent

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The effect of talc as an artificial nucleating agent in different concentrations on the crystallization of polypropylene (PP) has been studied. It is considered that the induction time should be taken into account in the Avrami evaluation of isothermal crystallization. From a study of nucleated PP samples prepared in different ways, it has been proved that the nucleating effect of talc slightly decreases with increasing time spent by the sample in the state of the polymer melt. It has been shown that crystallization of non-nucleated polypropylene strongly depends on the material of the sample pan. It has been established that dilatometry cannot be used to study the isothermal crystallization of nucleated polypropylene, since microcracks appear in the sample, partly compensating the volume decrease due to the crystallization process.

Nucleating agents are widely used in the plastics industry to regulate the crystallite size of crystalline polymers. The study of the kinetics of crystallization of nucleated polymers is therefore of practical importance.

Isothermal crystallization of nucleated polypropylene has been studied by Binsbergen and de Lange [1], using polarization optical microscopy. In this series of publications a different method is (DSC) applied to study crystallization kinetics. In the present paper talc is used as a nucleating agent in different concentrations in polypropylene. The applicability of the Avrami equation is discussed and dilatometry is shown to be unusable for study of the isothermal crystallization of nucleated polypropylene.

## Experimental

Isotactic polypropylene (PP) Tipplen H331F (Tisza Chemical Works, Hungary) containing 0.05, 0.1, 0.5, 1.0, 2.5, 5.0, 7.5 or 10.0% of talc was used in this study (the melt index of the basic polymer at 503 K is 16 g/min). This type of PP corre-

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sponds to Pro-Fax 6331 F of Hercules. Talc with the commercial designation M-15 (average particle size 15 μm) was obtained from Yhtyneet Paperithaat Oy (Finland). Samples with different concentrations of talc were prepared in two ways:

(1) A 30% master batch of talc in PP was made in a Werner Pfleiderer 800 g internal mixer; this master batch was then diluted with PP in the internal mixer to the desired concentrations;

(2) The necessary amounts of PP and talc were mixed directly in the internal mixer. With the purpose of further homogenization, 1 mm thick plates were prepared in a Battenfeld BSKM 30/50 injection moulding machine.

The results described throughout this paper are those obtained on samples prepared by method 2. For several concentrations these results are compared with those for samples prepared by method 1.

DSC mesurements were performed with a Perkin—Elmer DSC-2 connected to an ICC computer (KFKI, Hungary). The sample weights were typically 5 mg. In isothermal crystallization experiments the samples were heated up to temperature $T_F$, kept at this temperature for 5 min, and then cooled down at 40 deg/min to the crystallization temperature. In non-isothermal crystallization measurements the samples were quickly (320 deg/min) cooled from $T_F$ to 440 K (in order to minimize the time spent by the sample in the melt state), and the desired cooling rate (C.r.) was then applied. $T_F$ was 493 K in most cases, though several experiments were performed in which $T_F$ was varied from 473 K to 523 K in order to study the influence of $T_F$ on the crystallization behaviour.

Isothermal crystallization experiments were also carried out by means of dilatometry. The capillary used was 1 mm in i.d., and the amount of PP was ~ 2 g. The samples were kept for 20 min in an oil bath, and the dilatometers were then quickly immersed in a silicone oil bath maintained at the desired temperature.

Crystallization was in some cases followed by polarization optical microscopy. The temperature of the hot-stage of a Reichert microscope (Austria) was regulated by a Chinoin temperature programmer (Hungary). Magnifications of 40x and 100x were used. The linear growth rate of H331F PP spherulites was also determined by optical microscopy in order to calculate the number of heterogeneous crystallization centres from the rate constants of crystallization. These growth rates will be described in a later paper [6].

## Results and discussion

Crystallization curves of PP samples containing different amounts of talc at a cooling rate of 40 deg/min are shown in Fig. 1. It is easy to see that the crystallization temperature increases with increasing talc content. From these curves and those recorded at other cooling rates (0.3125, 0.625, 1.25, 2.5, 5, 10 and 20 deg/min) the following characteristic temperatures were determined: initial temperature of crystallization ($T_{c,0}$), peak temperature of crystallization ($T_{c,p}$), and final tem-

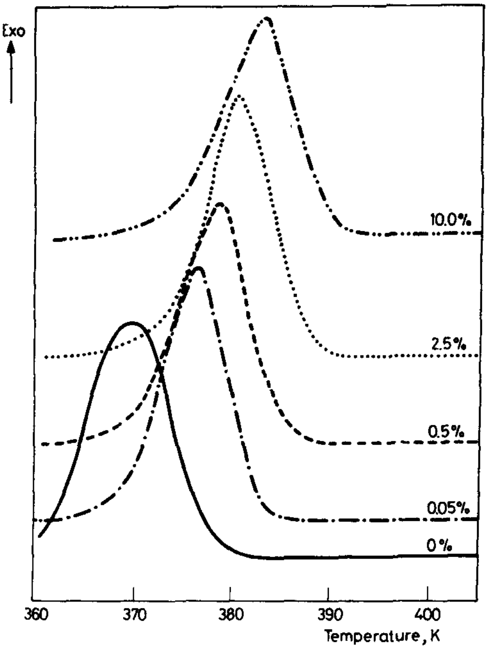

**Fig. 1** Crystallization curves of PP samples with different talc contents recorded at a cooling rate of 40 deg/min (the talc concentration is indicated beside the curves)

perature of crystallization ($T_{c,f}$). The initial temperature of crystallization as a function of cooling rate for several samples is shown in Fig. 2, while the dependence of the three characteristic temperatures of crystallization on the talc concentration at a cooling rate of 2.5 deg/min is demonstrated in Fig. 3. These figures demonstrate nuclesting effect of talc. At the same time it is clear from Fig. 3 that change in the crystallization temperature with increasing content of talc is rather strong up to 1%. Beyond this value increasing concentration of talc has little effect on the crystallization temperature (a similar dependence is observed at other cooling rates).

In order to study the crystallization kinetics of nucleated PP, isothermal crystallization experiments were carried out. In general, the isothermal crystallization of a polymer is interpreted in terms of the Avrami equation. This equation has been derived in several ways [2–4] and has the following form:

$$\alpha_t = \alpha_\infty[1 - \exp(-Kt^n)] \qquad (1)$$

where $\alpha_t$ is the crystallinity at the time $t$; $\alpha_\infty$ is the crystallinity at infinite time; $K$ is the rate constant of crystallization; and $n$ is an integer depending upon the type of nucleation and the geometry of the growing entities. In the case of spherulitic crystallization, $n$ would ideally be three or four, corresponding to heterogeneous or homogeneous nucleation, respectively. In the literature $n$ frequently has non-integral

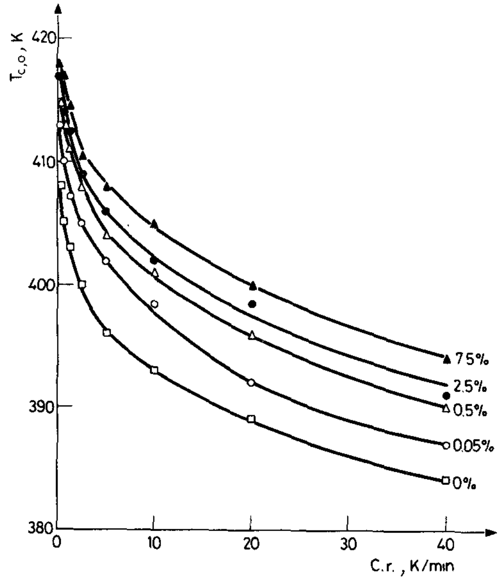

**Fig. 2** Starting temperatures of crystallization *vs.* cooling rate for different talc-containing samples (the talc concentration is indicated beside the curves)

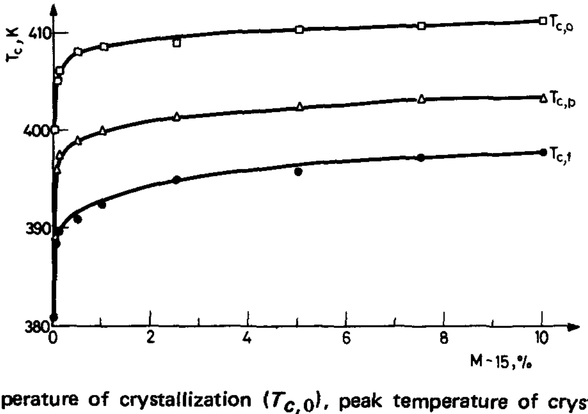

**Fig. 3** Starting temperature of crystallization ($T_{c,0}$), peak temperature of crystallization ($T_{c,p}$) and final temperature ($T_{c,f}$) of crystallization *vs.* concentration of talc in PP at cooling rate of 2.5 deg/min

values and is dependent upon the crystallization temperature and prehistory of the samples [7, 8]. This would raise theoretical problems, since *n* has a physical meaning for integral values only (although there have been some successfull attempts to interpret *n* for non-integral values (see e.g. [5]). However, it is clear that polymer samples containing nucleating agents should have *n* equal 3 for spherulitic crystallization (or 3/2 if the linear growth rate changes in time [5]). This is just the case with our samples. In spite of this, in our measurements *n* was found to be 3.4–3.6, indepen-

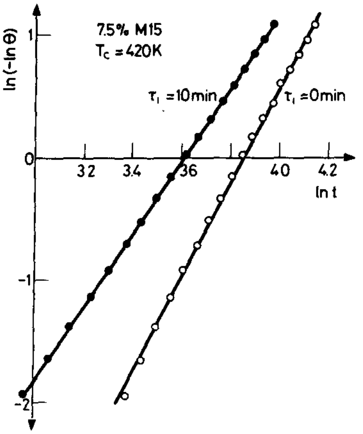

Fig. 4 Linearization of points according to Avrami, with and without the induction time ($\theta = 1 - \alpha_t/\alpha_\infty$)

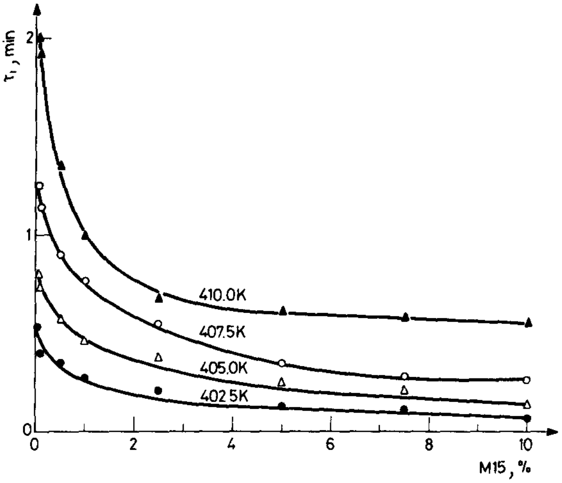

Fig. 5 Induction time as a function of talc content at different crystallization temperatures

dently of the concentration of the nucleating agent, and its value sometimes rose to 4.8 at the highest crystallization temperatures where the process can still be recorded by DSC. It is obvious that this value is unphysical. In calculations of $n$ and $K$ it has been supposed according to [6] that the induction time is zero. We have therefore introduced the induction time into the Avrami equation, which then assumes the following form:

$$\alpha_t = \alpha_\infty \{1 - \exp[-K(t - \tau_i)^n]\} \tag{2}$$

(where $\tau_i$ is the induction time). The value of the induction time was varied from an initial approximate value until the smallest deviation of the points in the diagrams of $\ln[-\ln(1 - \alpha_t/\alpha_\infty)] = f[\ln(t - \tau_i)]$ was obtained. Such a case is shown in Fig. 4. Although this is difficult to see from the figure, the standard deviation of the points decreases by almost an order of magnitude when the induction time is taken into account. As a result of this calculation, $n = 3.0 \pm 0.1$ was obtained for all the samples at every crystallization temperature. From these results it is concluded that the indunction time must be taken into account in the Avrami calculation. The variation of the induction time with the talc concentration for several crystallization temperatures is shown in Fig. 5. As may be expected, the induction time at a given crystallization temperature decreases with increasing talc content. It is not clear, however, why Binsbergen and de Lange [6] obtained just the opposite result in the interpretation of their measurements; they insist on the absence of any detectable induction time. There is no doubt that Binsbergen and de Lange used much more efficient nucleating agents in their study than we did. Moreover, the particle size of their nucleating agents was probably smaller than that of talc. This can clearly be seen if Figs 6 and 7

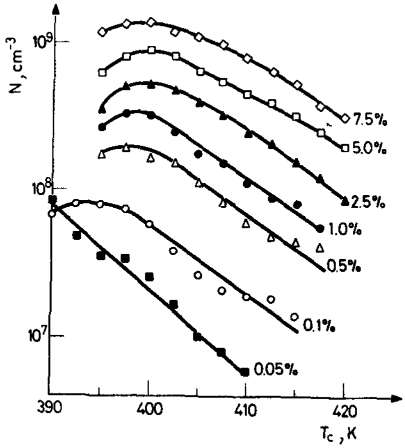

**Fig. 6** Number of crystallization centres *vs.* temperature, calculated with the induction time taken into account (the talc concentration is indicated beside the curves)

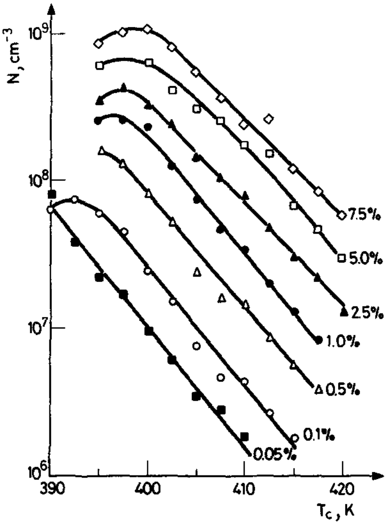

**Fig. 7** Number of crystallization centres *vs.* temperature, calculated with the induction time not taken into account (the talc concentration is indicated beside the curves)

are compared with Figs 5 and 6 reported in [6]. In Figs 6 and 7 the number of crystallization centres calculated via the formula

$$N=\frac{3K}{4\pi v^3} \tag{3}$$

(where $v$ is the linear growth rate of the spherulites) is shown as a function of the crystallization temperature (two figures are given, since calculation with the induction time causes changes in the value of $K$, as well). It is seen from these figures that the number of crystallization centres for the nucleating agents used in [6] is two orders of magnitude higher than for talc. Therefore, it cannot be excluded that the induction time is negligible under the conditions in [6].

Godovsky and Slonimsky [9] determined $n$ and $K$ from the maximum of the crystallization curve, using the formulae

$$n = 1/[1 + 2.3 \log (1 - \alpha_m)] \tag{4}$$

$$K = [(n - 1)/n] t_m^{-n} \tag{5}$$

where $\alpha_m$ is the crystallinity at the maximum of the curve and $t_m$ is the corresponding time. We have attempted to use this method to determine the value of $n$, since the problem of the induction time could be solved in this way. Unfortunately, this method is extremely sensitive to small changes in the peak position, and the accuracy of the maximum determination is rather poor between $n$ values of 3 and 4. This method is therefore not very reliable. Of course, $\alpha_m$ and the corresponding $t_m$ can be chosen so than $n = 3$ is obtained. In this case $K$ should be calculated from the formula:

$$K = [(n - 1)/n](t_m - \tau_i)^{-n} \tag{6}$$

and its value equals that determined from Eq. (2). With a slight change of $\alpha_m$ and $t_m$, $n = 3.5$ can be obtained, and the $K$ value calculated corresponds to that evaluated from Eq. (1). Thus, this method cannot easily be applied for the accurate determination of $n$.

It would be of interest to compare the results obtained on the talc-containing PP samples with the kinetic data on pure PP samples. The latter are given in Table 1. It is probable that the nucleation can be considered as heterogeneous beyond 392.5 K, but no induction time was found for these samples, in contrast with the nucleated PP. It is difficult to explain this contradiction, though it is important whether or not isothermal crystallization curves of non-nucleated PP can be recorded by DSC in the temperature range where the induction time for the nucleated samples is very close to zero, since the crystallization process may start before $T_c$ is reached. Further, it

**Table 1** The Avrami exponent and the rate constant for H331F polypropylene

| $T_c$, K | $n$ | $K$ | $N$, cm$^{-3}$ |
|---|---|---|---|
| 387.5 | 3.9 | 1.71 | – |
| 390 | 3.6 | 0.14 | – |
| 392.5 | 3.2 | $4.4 \times 10^{-2}$ | $5.4 \times 10^5$ |
| 395 | 3.1 | $8.36 \times 10^{-3}$ | $2.9 \times 10^5$ |
| 397.5 | 3.1 | $1.59 \times 10^{-3}$ | $1.6 \times 10^5$ |
| 400 | 3.1 | $3.08 \times 10^{-4}$ | $1.0 \times 10^5$ |
| 402.5 | 3.1 | $4.70 \times 10^{-5}$ | $5.3 \times 10^4$ |
| 405 | 3.2 | $6.52 \times 10^{-6}$ | $2.8 \times 10^4$ |

**Table 2** Non-isothermal crystallization data on PP in sample pans made from different materials

| *C.r.*, deg/min | $T_{c,0}$ K | $T_{c,p}$ K | $T_{c,f}$ K |
|---|---|---|---|
| | Al pan | | |
| 5 | 396 | 387 | 378 |
| 10 | 393 | 383 | 372.5 |
| 20 | 389 | 377 | 363.5 |
| 40 | 380 | 369 | 354 |
| | Au pan | | |
| 5 | 398 | 385 | 376 |
| 10 | 394 | 381 | 371 |
| 20 | 390 | 376 | 363 |
| 40 | 381 | 368 | 354 |
| | Pt pan | | |
| 5 | 401 | 384 | 375 |
| 10 | 395.5 | 380 | 369 |
| 20 | 391.5 | 374 | 361 |
| 40 | 383.5 | 364.5 | 350 |

is possible that the PP modification changes at ~410 K ($\alpha_{\text{mixed}} \rightarrow \alpha_{\text{II}}$) and ~413 K ($\beta \rightarrow \alpha$) [10] may play a role in this difference. Another interesting phenomenon has been observed, and its consequences should be kept in mind when the isothermal crystallization of PP is studied by means of DSC: the material of the sample pan can have a strong influence on the crystallization of polymers. This can be seen well from Table 2, which gives data on the non-isothermal crystallization of PP in Al, Au and Pt sample pans. Crystallization of the samples in Au and Pt pans starts at higher temperatures and finishes at a lower (!) temperature. This difference is apparent in the shape of the recorded crystallization curves to such an extent that the crystallization in Pt pans obviously consists of two blurred peaks (Fig. 8). This means that part of the sample in contact with the pan material crystallizes separately from the inside part (Pt therefore behaves as a nucleating agent). It should be mentioned that the crystallization curves recorded in Pt sample pans do not change after repeated crystallization of a given sample, so that the doubling of the crystallization curves cannot be attributed to degradation or the presence of row nuclei left behind in the melt [7]. Nevertheless, this phenomenon did not appear in the nucleated samples.

As already mentioned, the crystallization characteristics of talc-containing PP samples prepared in different ways have been compared (Table 3). The table reveals that the crystallization is always slower and the induction time is always longer for the samples prepared by method 1 (dilution of the 30% master batch). It can be supposed

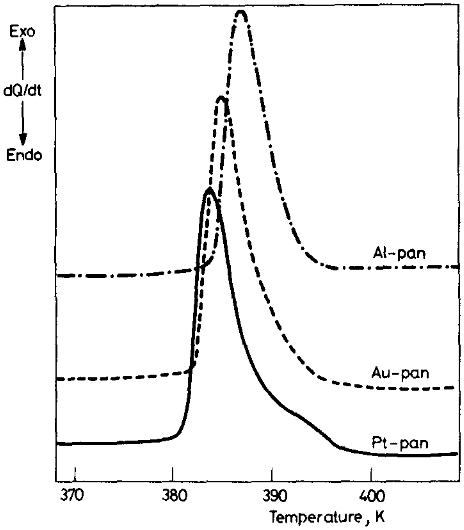

**Fig. 8** Crystallization curves of non-nucleated PP, recorded in sample pans made from different materials at cooling rate of 5 deg/min

**Table 3** Comparison of nucleated PP samples (0.5% talc) prepared by direct mixing of PP and talc and dilution of a 30% master batch

| | Direct mixing | | | Dilution | | |
|---|---|---|---|---|---|---|
| $T_c$, K | $\tau_i$, min | $n$ | $K$ | $\tau_i$, min | $n$ | $K$ |
| 395 | 0 | 3.0 | 4.89 | 0.1 | 3.0 | 3.12 |
| 400 | 0.2 | 3.0 | 0.487 | 0.24 | 3.0 | 0.213 |
| 405 | 0.69 | 3.0 | $2.56 \times 10^{-2}$ | 0.78 | 3.0 | $1.07 \times 10^{-2}$ |
| 410 | 1.35 | 3.0 | $7.23 \times 10^{-4}$ | 1.85 | 3.0 | $3.06 \times 10^{-4}$ |
| 415 | 4.2 | 3.0 | $3.25 \times 10^{-5}$ | 6.2 | 3.0 | $1.57 \times 10^{-5}$ |

that slow agglomeration of the talc particles occurs in the polymer melt, and therefore the active surface of the talc is decreased.

The influence of the final temperature of heating before crystallization ($T_F$) on the kinetics of crystallization has also been studied. It has been established that $T_F$ does not influence the crystallization parameters between 473 and 523 K.

The temperature-dependence of the rate constants of crystallization has been characterized by the equation given by Godovsky and Slonimsky [9]:

$$\frac{1}{n}\log K + \frac{\Delta F_{\mathrm{WLF}}}{2.3\,RT_c} = A_n - \frac{K_g T_m^0}{2.3\,T_c \Delta T} \tag{7}$$

where $T_m^0$ is the equilibrium melting point; $\Delta T = T_m^0 - T_c$ is the supercooling; $A_n$ is a constant characterizing the number of heterogeneous nuclei; and $\Delta F_{\mathrm{WLF}}$ is the activation energy of transport processes, which is determined according to Hoffman and Weeks [11] as

$$\Delta F_{\mathrm{WLF}} = \frac{C_1 T_c}{C_2 + (T_c - T_g)} \tag{8}$$

where $C_1 = 17.22$ kJ/mol and $C_2 = 51.6$ K.

The value of $K_g$ in Eq. (7) is given by

$$K_g = \frac{4 b_0 \sigma \sigma_e}{k \Delta H_f} \tag{9}$$

where $\sigma$ and $\sigma_e$ are the surface free energies parallel and perpendicular to the molecular chain direction, respectively; $\Delta H_f$ is the heat of fusion per unit volume; $b_0$ is the thickness of secondary nuclei; and $k$ is the Boltzmann constant.

The following parameters were used in the calculations: $T_m^0 = 481$ K [12], $T_g = 265$ K [13], $\sigma = 8.79 \cdot 10^{-3}$ J/m$^2$ [9]; $\Delta H_f = 134.0$ J/cm$^3$ [14], and $b_0 = 0.656$ nm [15].

For PP containing no talc, the value of $\sigma_e = 0.157$ J/m$^2$ has been obtained; this value is much higher than that reported in [9]. However, there is nothing wrong with the values of $K$ used for the calculations. This can be seen from Table 4, where we compare different $\sigma_e$ values calculated from different works. It is obvious that Godovsky and Slonimsky [9] used an unjustifiably low $T_m^0$, and their value for $\sigma_e$ is greatly increased with $T_m^0 = 481$ K, as can be seen from Table 4. Furthermore, it is noteworthy that $\sigma_e$ for nucleated samples is considerably smaller: its value decreases with increasing content of the nucleating agent, as shown in Fig. 9. This is also consistent with the literature data (Table 4). Thus, it seems that the structure of the surface layer is changed under the influence of the nucleating agent. It is possible

**Table 4** Surface free energies perpendicular to the molecular chain direction for PP and nucleated PP, calculated with parameters given in the text

| Source of K | $\sigma_e$, J/m$^2$ |
|---|---|
| I. PP | |
| Godovsky calorimetry [9] | 0.127 |
| Godovsky dilatometry [9] | 0.156 |
| von Falkai [16, 17] | 0.157 |
| II. Nucleated PP | |
| Godovsky [9] | 0.065 |
| Binsbergen [1] 0.03% Na (ptBB) | 0.147 |
| 0.1% Na (ptBB) | 0.139 |
| 0.3% Na (ptBB) | 0.125 |

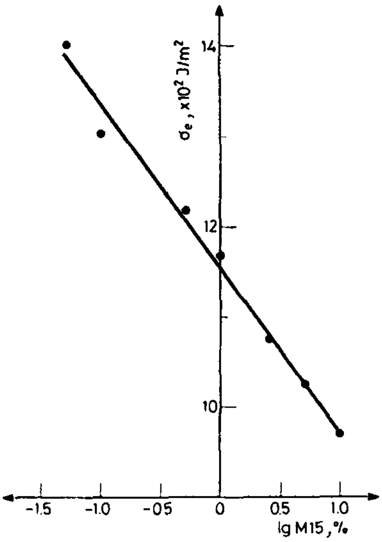

Fig. 9 Surface free energy perpendicular to the molecular chain direction vs. logarithm of talc content (calculated from Eq. (7))

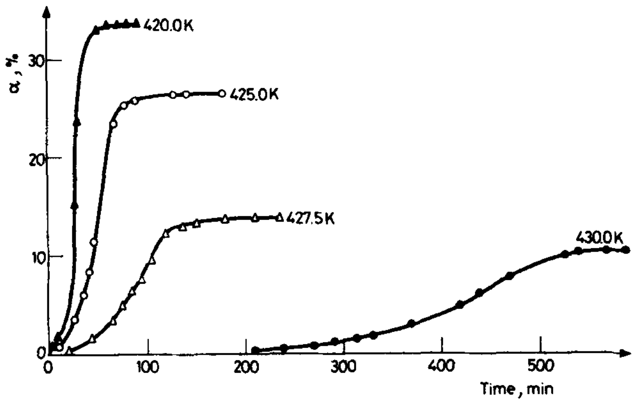

Fig. 10 Crystallinity of PP containing 10% of talc, calculated from dilatometric data vs. time at different crystallization temperatures

that this phenomenon can also be attributed to the mentioned PP modification changes. Nevertheless, the extremely high value of $\sigma_e$ obtained for non-nucleated PP casts doubt on the validity of Eq. (7).

We have also tried to follow the crystallization of nucleated PP by means of dilatometry, but without any success. The degree of crystallinity vs. time for samples containing 10% of talc is shown in Fig. 10. It is surprising that the degree of crystallinity decreases to very low values (~ 10%) according to the dilatometric data. This

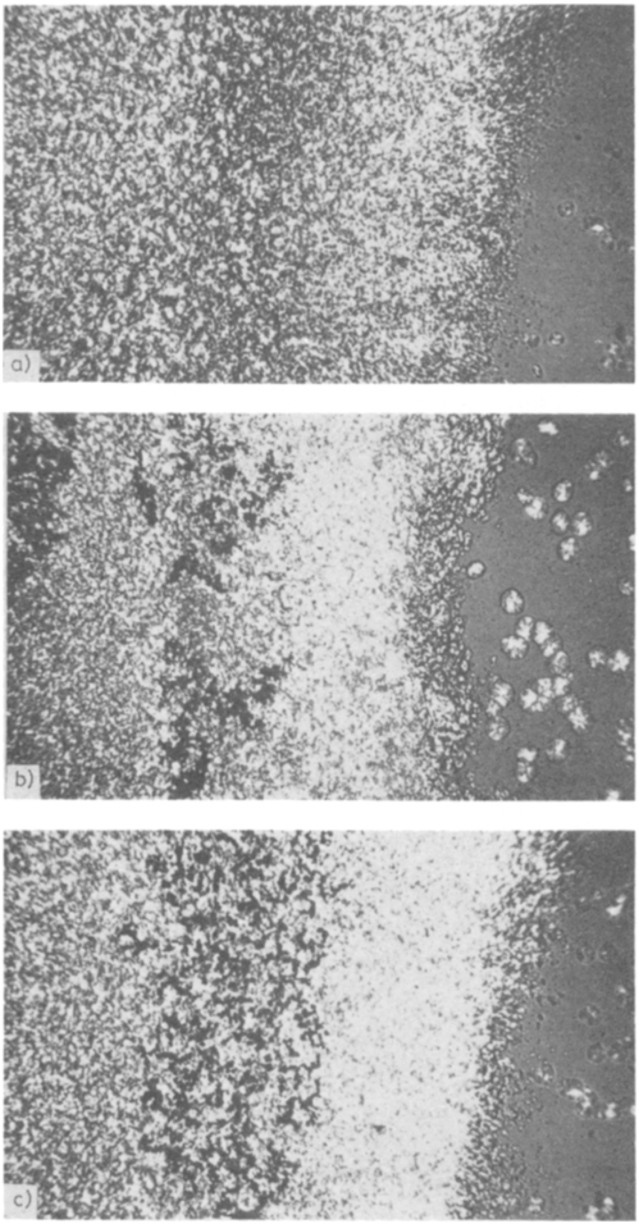

**Fig. 11** Micrographs taken during crystallization of PP (PP containing talc on the left-hand side, and no talc on the right-hand side). The number and volume of microcracks increase as the crystallization proceeds. Magnification 100x

apparent degree of crystallinity decreases with increasing talc concentration at a given crystallization temperature, and with increasing crystallization temperature at a given talc content. At the same time, the DSC melting curves of these samples point to at least 50% crystallinity when 10% was obtained dilatometrically (the melting peaks corresponding to the fraction of the sample crystallized at 430 K and that crystallized during cooling to room temperature are fairly weel separated). It follows that some process partly compensating the volume decrease is going on during the crystallization. The answer to this problem was sought by polarization optical microscopy. A series of photographs is shown in Fig. 11 during the course of crystallization of samples containing talc (on the left-hand side) and containing no nucleating agent (on the right-hand side). The original photos were taken on colour slides using a first-order red filter. Black–and–white copies of these slides are shown in the figure. It can be seen that microcracks (black areas) appear on the side containing the nucleating agent, and their number and volume increase in time. It is probable that these microcracks are responsible for the volume increase. It should be mentioned that this phenomenon is characteristic not only of talc, but of other nucleating agents as well. For some nucleating agents this effect is so pronounced that the volume increase due to the microcracks is greater than the volume decrease due to the crystallization process. Thus, dilatometry should be applied with great care in the study of the isothermal crystallization of nucleated PP.

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**Zusammenfassung** — Die Wirkung von in unterschiedlichen Konzentrationen als künstliches Keimbildungsmittel angewandtem Talk auf die Kristallisation von Polypropylen wurde untersucht. Bei der Auswertung der isothermen Kristallisation nach Avrami ist die Induktionszeit in Betracht zu ziehen. Bei der Untersuchung von auf verschiedene Weise hergestellten Polypropylenproben wurde festgestellt, dass die keimbildende Wirkung von Talk desto geringer ist, je länger sich die polymere Probe im geschmolzenen Zustand befand. Es wird gezeigt, dass die Kristallisation von keimbildenden Mitteln nicht ausgesetztem Polypropylen stark vom Material des Probengefässes abhängt. Es wurde festgestellt, dass die Dilatometrie nicht zur Untersuchung der isothermen Kristallisation von mit keimbildenden Mitteln versetztem Polypropylen geeignet ist, da in der Probe Mikrokrackprodukte auftreten, die die durch den Kristallisationsprozess verursachte Abnahme des Volumens teilweise kompensieren.

**Резюме** — Изучалось влияние талька как искуственного зародышеобразователя на процесс кристаллизации полипропилена. Было показано, что при обработке результатов изотермической кристаллизации по уравнению Аврами необходимо учитывать индукционный период. Установлено, что действие зародышеобразователя снижается при увеличении времени нахождения образца в расплавленном состоянии. Показано сильное влияние качества материала тигеля на кристаллизацию чистого полипропилена. Дилатометрия оказалась не пригодной для изучения изотермической кристаллизации полипропилена, содержащего талька, поскольку появляющиеся в образце микротрещины частично компенсируют уменьшение объема, обусловленного процессом кристаллизации.