

# Crystallization of isotactic polypropylene containing carbon black as a filler

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## Abstract

Studies on the effect of carbon black on the properties and kinetics of crystallization of isotactic polypropylene are presented in this paper. Polypropylene samples containing 2–30% weight fraction of carbon black were prepared by mixing the initial sample containing 40% carbon black. The samples were produced using a screw injection moulding press. The analysis of melting, crystallization and kinetics of crystallization was carried out using the difference scanning calorimetry at seven stages whose aim was to melt and heat isothermally the filled samples of polypropylene. The analysis covered the dependence of melting and crystallization temperatures on the content of carbon black in the polypropylene. Two stages of crystallization were observed. They were described by means of the Avrami equation. It was found that both the nature of nucleation and growth mechanism of crystalline polypropylene changed depending on the crystallization temperature and black content. Half time of crystallization and induction period of crystallization enabled an in-depth analysis of the crystallization process which led to the conclusion that the rates of nucleation and crystallization increased significantly particularly in the case of samples with a small content of carbon black. © 2000 Published by Elsevier Science Ltd. All rights reserved.

*Keywords:* Polypropylene; Carbon black filler; Kinetics of crystallization

## 1. Introduction

One of the fillers applied in high-molecular materials is carbon used in the form of natural carbon black or graphite. It can be in the form of fibres or grains, with carbon black occurring only in the form of powder. The carbon black is an active strengthening material. Its strengthening action is the stronger the smaller are the dimensions and specific surface area and the higher is the surface energy of the particles. Black particles are composed of a large number of agglomerated crystalline elements called microcrystallites. In general, the system of microcrystallites in a carbon black particle is concentric and black particles are in the shape of spheres or agglomerated spheres which form less or more extended spatial chains [1]. The propensity to agglomeration of primary spherical particles of carbon black causes the formation of a spatial network in the polymer where black aggregates behave like fibrous fillers. This causes a decrease of resistance even for a small content of carbon black [2].

Polypropylenes filled a carbon black with content ranging from 10 to 20% are the materials, which conduct electrical current. Their mechanical properties as well as strength and

impact resistance are satisfactory for some applications, when black content does not exceed 20% [2]. Although additives immiscible with polymers such as carbon black are distributed in an amorphous fraction, their impact on the formation of a crystalline structure is enormous.

The investigations on the effect of carbon black filler on the properties and crystallization kinetics of isotactic polypropylene (IPP) were undertaken in the present work.

## 2. Experimental

### 2.1. Materials

IPP Malen P type J-400, of Polish make was used. The samples containing carbon black Sakap 6 (Carbochem, Gliwice) in the amount of 2, 5, 10, 20 and 30% wf were prepared by mixing adequate amount of pure polypropylene with a previously obtained sample containing a maximal amount of carbon black reaching 40%. Samples were made using a screw injection moulding press Formoplast 235 60 (Ponar, Żywiec S.A., Poland).

### 2.2. Methods

Melting and crystallization analysis and crystallization

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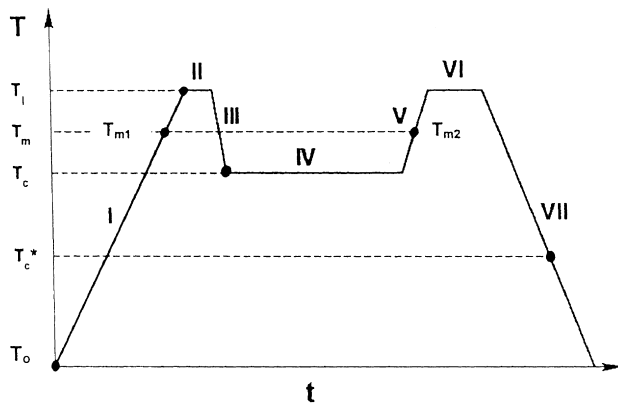


Fig. 1. Thermal program used for DSC measurements  $T_0 = 25^\circ\text{C}$ ;  $T_1 = 190^\circ\text{C}$ ;  $T_{m1}$ ,  $T_{m2}$ —melting temperatures;  $T_c$ ,  $T_c^*$ —isothermal and non-isothermal crystallization temperatures.

kinetics of various polypropylene samples was carried out using Mettler differential scanning calorimeter (DSC) type FP85. The following conditions for determination of melting and crystallization behaviours together with calculation of characteristic parameters were applied (Fig. 1):

*Stage I:* heating of sample in the calorimeter with a rate of  $10^\circ/\text{min}$  from room temperature to temperature equal to  $190^\circ\text{C}$ , reading:  $T_{m1}$ —melting point (initial and after stage VII) and  $\Delta H_1$ —melting enthalpy;

*Stage II:* isothermal sample annealing at the temperature  $T_1 = 190^\circ\text{C}$  for 3 min was applied to remove crystalline nuclei (effected stage IV);

*Stage III:* fast cooling of the sample in the calorimeter to the crystallization temperature  $T_c$ ;

*Stage IV:* isothermal crystallization at constant temperature ranging from  $122$  to  $134^\circ\text{C}$  for the period equal to

about  $0.5$  h, reading: isothermal curves of polymer conversion to crystalline phase;

*Stage V:* heating of previously crystallized samples with a rate of  $10^\circ/\text{min}$  from crystallization temperature  $190^\circ\text{C}$ , reading: melting point  $T_{m2}$ , enthalpy (heat) of melting  $\Delta H_2$ ;

*Stage VI:* isothermal annealing at the temperature  $T_1 = 190^\circ\text{C}$  for 3 min (the same as in stage II);

*Stage VII:* cooling of sample with a rate of  $5^\circ/\text{min}$  from  $T_1$  to room temperature, reading non-isothermal crystallization curve, crystallization temperature— $T_c^*$ .

The studies were carried out for pure IPP and the IPP samples containing various amounts of carbon black as fillers.

### 3. Results and discussion

#### 3.1. Melting and crystallization temperatures

Fig. 2(a) and (b) illustrates DSC curves obtained by heating for pure IPP crystallized previously at the temperature range and IPP containing 2% of carbon black previously crystallized at the temperature range from  $126$  to  $134^\circ\text{C}$ . For IPP samples crystallized in the vicinity of  $130^\circ\text{C}$  a significant extension of melting towards lower temperatures and two melting peaks are observed. It means the presence of two different crystallographic forms of isotactic PP: an unstable pseudohexagonal  $\beta$  form of lower melting point and lower perfection, and a more stable monoclinic  $\alpha$  form of higher ordering and higher melting point [3–5]. Both  $\alpha$  and  $\beta$  phases share the same three-fold helical conformation and the transitions between the two phases can take place. In the case of IPP filled carbon black, the two observed melting peaks (in Fig. 2(b)) for crystallization

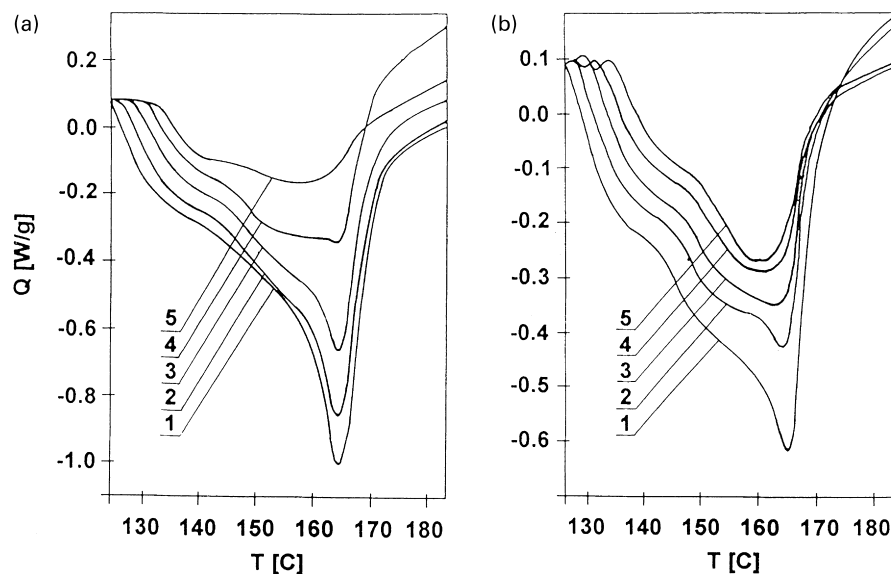


Fig. 2. DSC curves (1–5) of (a) pure IPP previously crystallized at temperatures: (1)  $124^\circ\text{C}$ , (2)  $126^\circ\text{C}$ , (3)  $128^\circ\text{C}$ , (4)  $130^\circ\text{C}$ , (5)  $132^\circ\text{C}$ ; and (b) IPP with carbon black content  $C = 2\%$  previously crystallized at temperatures (1)  $126^\circ\text{C}$ , (2)  $128^\circ\text{C}$ , (3)  $130^\circ\text{C}$ , (4)  $132^\circ\text{C}$ , (5)  $134^\circ\text{C}$ .

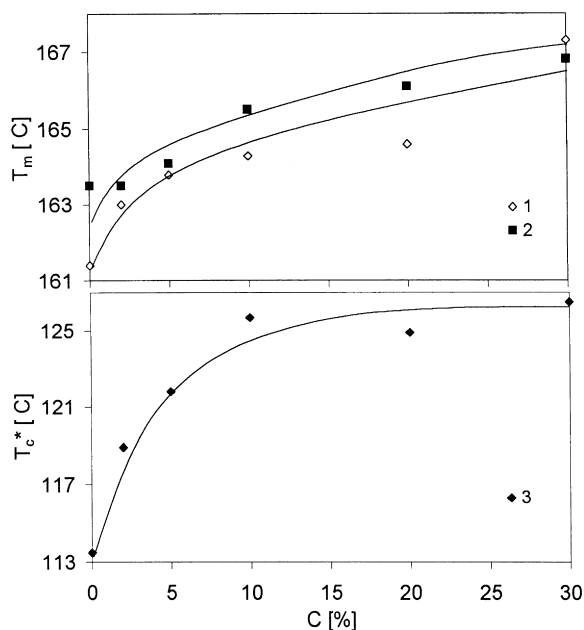


Fig. 3. Melting temperatures  $T_{m1}$  (curve 1),  $T_{m2}$  (curve 2) and non-isothermal crystallization temperature  $T_c^*$  (curve 3) drawn versus carbon black content  $C$ .

temperatures lower than  $130^\circ\text{C}$  are found. The hexagonal form  $\beta$  grows faster than the  $\alpha$  form in the range of crystallization temperatures under study. Thus the general rate of isothermal crystallization of the filled IPP is higher as compared to pure polypropylene (carbon black appears as the nucleus of IPP crystallization in the  $\beta$  form). The melting peak of the  $\alpha$  form is also shifted towards higher values with increasing content of carbon black in IPP.

Fig. 3 (curves 1 and 2) shows dependence of both  $T_{m1}$  and  $T_{m2}$  of IPP (samples were crystallized at  $128^\circ\text{C}$ ) on carbon black content. We have purposed that the effect of  $T_m$  increase may result from some hindrance in the melting process of IPP caused by the presence of carbon black. The carbon black particles rejected previously to the amorphous phase during crystallization of polypropylene delays the starting mobility of polymer segments in the regions of lamellae surfaces during the polymer melting process. Thus,

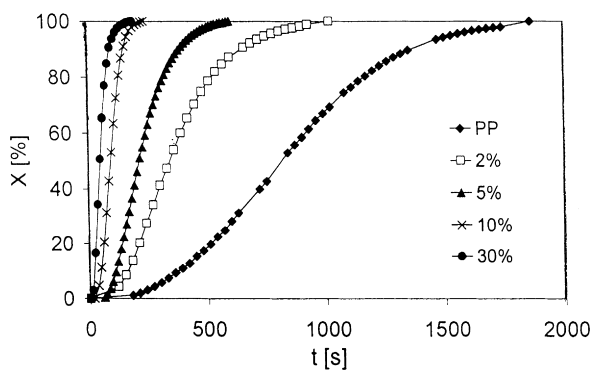


Fig. 4. Integral crystallization curves (conversion versus time) obtained at  $T_c = 130^\circ\text{C}$  for various carbon black content  $C$  (in %).

if the IPP sample has a more rigid amorphous phase containing more carbon black it melts at a higher temperature. Because the melting point temperature of polymers increases with rising lamella thickness  $l$  and depends on the specific fold surface free energy  $\sigma_e$  according to the formula [6]:

$$T_m = T_m^0(1 - 2\sigma_e/\Delta h_f l) \quad (1)$$

A modification of  $\sigma_e$  (decreasing) due to the presence of carbon black (assuming constant  $l$ ) can explain the observed change in  $T_m$ . The presence of carbon black in IPP affects the crystallization process of the polymer in the non-isothermal condition. Fig. 3 (curve 3) shows the dependence of non-isothermal crystallization temperature  $T_c^*$  on the content of carbon black  $C$ . IPP samples containing a higher amount of carbon crystallize earlier (at a higher temperature) during cooling of the molten sample. This confirms the effect of heterogeneous nucleation of polymer on carbon black particles, which are nucleating agents for the growing  $\beta$  form of IPP. The crystallinity degree of polypropylene calculated based on DSC [7] data changes slightly and it grows with increase of carbon black content ranging from 37 to 48%.

### 3.2. Isothermal crystallization

To describe isothermal crystallization of IPP samples the Avrami equation (2) was used:

$$1 - X = \exp(-Kt^n) \quad (2)$$

where:  $1 - X$  is the content of non-crystallized material,  $X$  the content of crystallized material (conversion degree to crystalline phase) and  $K$ ,  $n$ , the Avrami parameters depending on the geometry of the growing crystals and on the nucleation process. They are also a convenient means to represent empirical data of crystallization.

The Avrami equation in the simple form represents unimpeded crystal growth and required sigmoidal shape. However, the sample does not reach complete crystallization as required for the model. To continue an analysis one assumes that complete crystallization is reached. After integration of differential DSC curves the dependence of  $X$  and  $1 - X$  on the crystallization time was determined. The values of  $X$  and  $1 - X$  were calculated assuming that at the onset of the crystallization process  $X = 0$ , while at the end  $X = 100\%$ . The calculations were made for various samples and different temperatures.

Fig. 4 shows as an example, integral curves found in the isothermal crystallization process at  $T_c = 130^\circ\text{C}$  obtained for pure IPP and IPP filled with various content of carbon black. A strong effect of the enhancement of polypropylene crystallization is observed in relation to the nucleating action of carbon black particles. Similar relations were observed during crystallization at other temperatures.

Figs. 5 and 6 show Avrami lines obtained from the

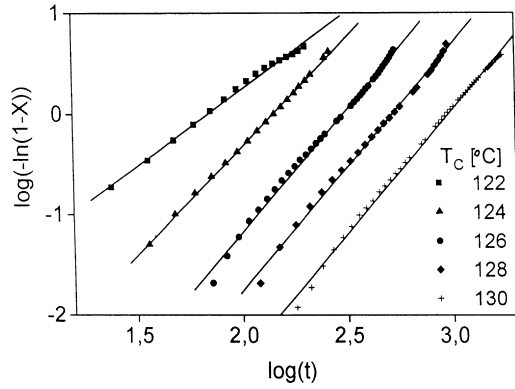


Fig. 5. Avrami plots for pure IPP.

following double logarithmic equation:

$$\log[-\ln(1 - X)] = \log K + n \log t \quad (3)$$

In the case of pure polypropylene (Fig. 5) these relationships are rectilinear in the entire range of crystallization time. Slight deviations from the rectilinear relation are observed at the beginning and at the end of the process. Polypropylene conversion at 122–130°C does not necessarily lead to the crystalline  $\beta$  form which is observed at higher crystallization temperatures [8].

Two stages of crystallization of polypropylene filled with carbon black (Fig. 6) are observed. In the early stage of crystallization, which is related to the heterogeneous process of polypropylene nucleation on carbon black particles, there is only little restriction of crystallization due to impingement. The next stage of slower crystallization occurs due to increasing impingement. The diffusion of crystallizing macromolecules is restricted in the crystallization front by increasing the concentration of rejected carbon black particles.

Fig. 7 shows the dependence of time ( $\log t$ ) in the spot of straight lines refraction (time after which the rate of crystallization changes) on crystallization temperature  $T_c$  for different weight content of carbon black 2, 5 and 10%. From the analysis of this figure, it is seen that the results of the higher crystallization temperatures and the observed

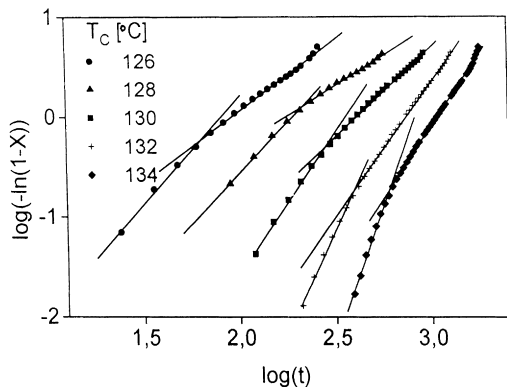


Fig. 6. Avrami plots for IPP filled with carbon black ( $C = 2\%$ ).

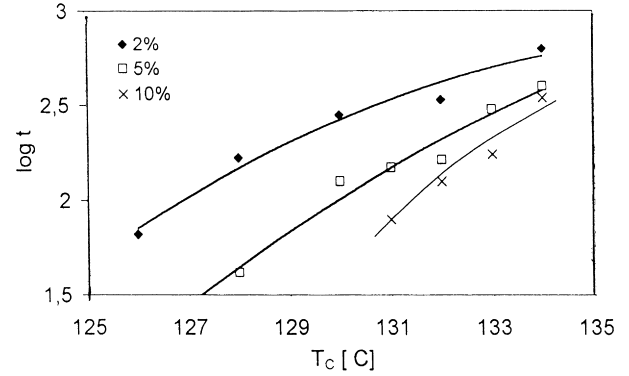


Fig. 7. Dependence of  $\log t$  ( $t$ —time after which crystallization rate changes) on crystallization temperature and carbon black content in the sample.

change of crystallization rate starts later. In addition, for a higher carbon black content the change of crystallization rate takes place earlier, which is in agreement with the above-proposed explanation of the process. Fig. 8 shows the dependence of  $\log K$  (a parameter in the Avrami equation) on crystallization temperature  $T_c$  for selected composites (for stage I of the crystallization). It is obvious that  $\log K$  decreases with an increase of crystallization temperature  $T_c$ , and with an increase of the amount of carbon black in the composite. The other Avrami parameter, i.e. exponent  $n$  shows a tendency to grow with an increase of the crystallization temperature. For pure polypropylene the mean value of parameter  $n$  is equal 2.16.

In the case of filled IPP the parameter  $n_1$  in the early stage of the crystallization assumes the mean value  $\approx 2.0$  and  $n_2$  in the second stage of the crystallization after impingement of the crystals increasing the mean value to 3.0 is observed. Thus both the nucleation character and the mechanism of crystalline phase growth of polypropylene change depending on the crystallization temperature and carbon black content in the sample. The  $t$  exponent ( $n$  parameter) is expected to be equal to three for heterogeneously nucleated spherulites [7].

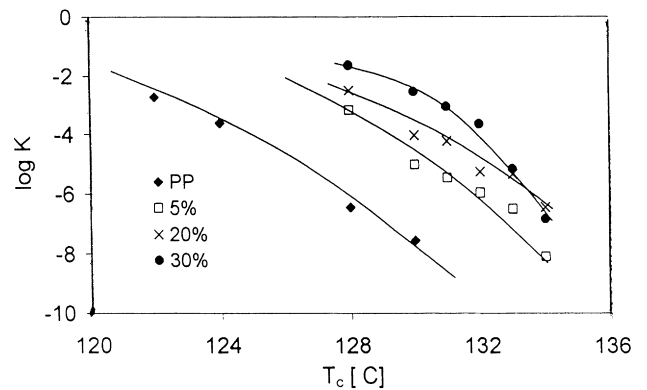


Fig. 8.  $\log K$  ( $K$ —Avrami parameter) versus crystallization temperature  $T_c$  for pure IPP and filled with various content of carbon black.

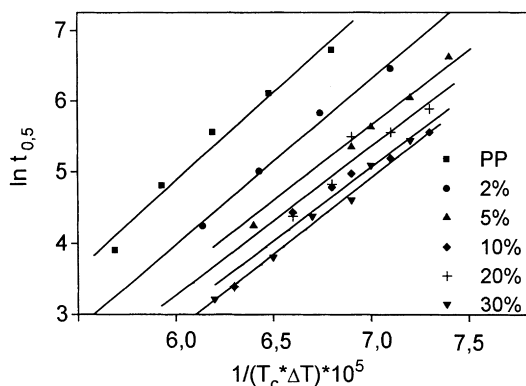


Fig. 9.  $\ln t_{0.5}$  ( $t_{0.5}$ —half crystallization time) versus  $1/T_c \Delta T$  ( $\Delta T$ —supercooling) for pure IPP and filled with various content of carbon black.

### 3.3. Half time of crystallization and induction period of crystallization

The kinetic data of polymer crystallization has been analyzed in terms of the biexponential equation for the growth rate:

$$\nu = \nu_0 \exp[-(\Delta G^* + \Delta G_\eta)/kT_c] \quad (4)$$

where  $\nu$  is the growth rate,  $\nu_0$  the preexponential factor,  $\Delta G^*$  the free enthalpy of nucleation of a nucleus of critical size,  $\Delta G_\eta$  the free enthalpy of activation of molecular diffusion across the phase boundary and  $k$  the Boltzmann constant.

The free enthalpy of the heterogeneous nucleus formation can be given [9]:

$$\Delta G^* = 16\Delta\sigma\sigma_e T_m^2 / (\Delta h_f \rho_c \Delta T)^2 \quad (5)$$

Thus  $\Delta G^*$  remains proportional to  $1/(\Delta T)^2$  which is the inverse square of the supercooling  $\Delta T = T_m - T_c$ .  $T_m^0$  is the equilibrium melting temperature,  $b_0$  the single layer thickness taken here as  $4.65 \times 10^{-10}$  m,  $\Delta h_f = \Delta h_f \rho_c = 1.98 \times 10^8$  J/m<sup>3</sup> the enthalpy of melting,  $\sigma$ ,  $\sigma_e$  the specific side surface (lateral) and fold surface (end) free energies

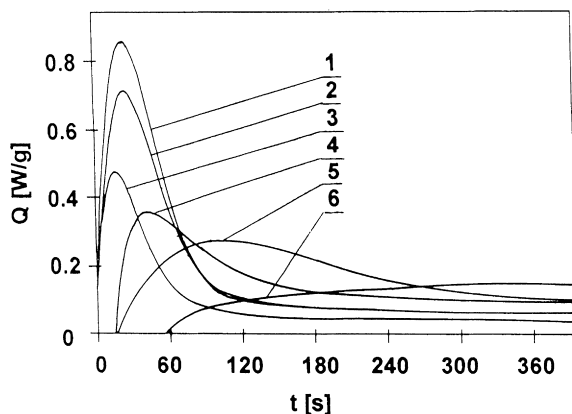


Fig. 10. DSC crystallization curves obtained at 128°C for pure IPP (curve 6) and the samples containing various amount of carbon black from  $C = 2\%$  (curve 5) to  $C = 30\%$  (curve 1).

which measure the work required to create a new surface and  $\Delta\sigma$  the specific interfacial free energy difference parameter accounting for one surface contacting the melt and one surface contacting the heterogeneous nucleus. For sufficiently large  $\Delta T$  and  $\Delta\sigma$  goes to zero (the substrate resembles in its action the polymer crystal itself), Eq. (5) refers to secondary nucleation. Thus for secondary and heterogeneous nucleation the value of  $\Delta G^*$  can be presented as follows:

$$\Delta G^* = 4\sigma\sigma_e b_0 T_m / \Delta h_f \rho_c \Delta T \quad (6)$$

where  $\Delta G^*$  remains inversely proportional to supercooling  $\Delta T$ . A foreign surface reduces frequently the nucleus size needed for crystal growth, since the creation of the interface between the polymer crystal and the substrate, may be less hindered than the creation of the corresponding free polymer crystal surface. A heterogeneous nucleation path makes use of foreign preexisting surfaces to reduce the free energy opposing primary nucleation, the lower overall free energy  $\sigma\sigma_e$  decreasing  $\Delta G^*$ , the faster nucleation rate.

Setting  $\ln \nu = -\ln t_{0.5}$  ( $t_{0.5}$ —half time of crystallization) and assuming  $\Delta G_\eta = \text{constant}$  one obtains:

$$\ln t_{0.5} = \text{constant} + \Delta G^* / kT_c \quad (7)$$

However,  $\Delta G_\eta$  should be dependent on an impurity content at constant temperature.

From the slopes of the kinetic lines  $\{\ln t_{0.5} = f[1/(T_c \Delta T)]\}$  presented in Fig. 9 the  $\sigma\sigma_e$  values are calculated. A clear tendency to decrease of  $\sigma\sigma_e$  is observed as compared to pure polypropylene from  $8.3 \times 10^{-4}$  J<sup>2</sup>/m<sup>4</sup> for pure IPP to about  $7.0 \times 10^{-4}$  J<sup>2</sup>/m<sup>4</sup> for filled IPP (besides points scatter in Fig. 9). Assuming an approximately constant  $\sigma$  value, the observed decrease of  $\sigma_e$  can have a significant effect on the increase of melting point of the polypropylene filled with carbon black. In addition, values of  $\ln \nu_0$  decrease with an increase of the filler content (Fig. 9). From these values the factor related to  $\Delta G_\eta$ —free enthalpy of molecular diffusion across the phase boundary depending on the amount of carbon black in the sample, can be subtracted.

Fig. 10 presents an example of the differential curves (taken from DSC) of isothermal crystallization of pure polypropylene and its composites at constant temperature  $T_c = 128^\circ\text{C}$ . There is strong correlation between  $t_0$  (induction time)—the starting time of crystallization and coefficients  $K$  and  $n$  of the Avrami equation. It is suggested that the induction time must be more than 0.3 times the crystallization half-time before it can be safely detected through the fitting of the Avrami equation to experimental data. In the case of filled IPP the  $t_0$  value is sometimes shorter. The induction period  $t_0$  of the crystallization process is defined as proportional to the time needed for critical nucleus formation and depends both on the carbon black content and crystallization temperature. The  $t_0$  results are shown in Fig. 11(a) and (b). The presence of carbon black crystal reduces both the work required to create a new surface (decreasing  $\sigma_e$ ) and the nucleus size for crystal growth (decreasing  $t_0$ ).

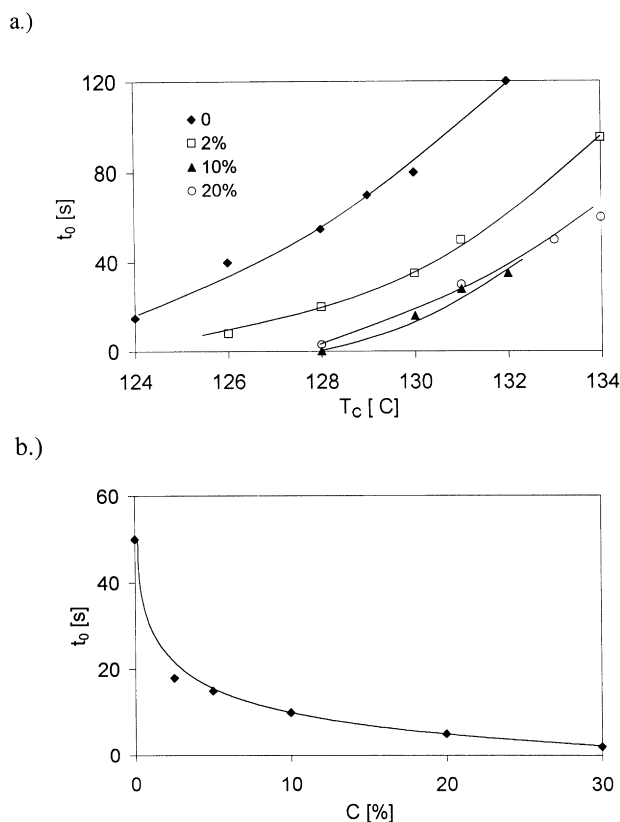


Fig. 11. Induction period of crystallization  $t_0$ : (a) versus  $T_c$  obtained for pure IPP and some filled samples; (b) versus carbon content  $C$  in IPP obtained at  $T_c = 128^\circ\text{C}$ .

#### 4. Conclusions

In the process of isothermal and non-isothermal crystallization which takes place during cooling of a molten polymer sample, a disperse nucleating additive (carbon black included) becomes a nucleation centre leading to crystal growth. The main effect of such nucleation is a modification of polymer morphology which can result even in a total collapse of the polymer spherulitic structure [10]. Another effect being a nucleation factor is an increase of the polymer crystallization temperature (e.g. by reducing  $\sigma_c$ ). Because of the higher crystallization temperature, the crystals also have a somewhat higher melting temperature than the unseeded (unseeded) polymer. It is found elsewhere [11] that by reducing the surface free energy of the nucleating agent (silica by coating surface), the crystallization temperature of polydimethylsiloxane increased.

The next result of the nucleation is the change of crystallographic form of the polymer as in the case of IPP, where the nucleating additive enables a transformation of  $\alpha$  structure into  $\beta$  structure. A maximum efficiency of this process is most often obtained for a very small concentration of the nucleating agent [8,12–14]. Heterogeneous nucleation by addition of foreign seed material to the bulk polymer melt was extensively studied for polypropylene [15,16] (no carbon black). The most ideal nucleating agent found was

sodium benzoate (increasing crystallization temperature was  $\Delta T_c = 26^\circ\text{C}$  but in the present work  $\Delta T_c = 12^\circ\text{C}$ ). The best known nucleating agents IPP are the derivatives of sorbitol (for  $\alpha$  form) and of anthracene (for  $\beta$  form) [17]. Carbon black Sakap 6 applied as a filler for the IPP reveals typical properties of a nucleating agent.

Application DSC to study the isothermal and non-isothermal crystallization of polypropylene enabled us, not only to confirm the nucleating effect of carbon black particles, but also to calculate some parameters, such as  $\sigma\sigma_c$  which change can help to explain the crystallization process, and the observed increase of the melting and crystallization temperatures of IPP samples filled with carbon black. It also seems that carbon black as a filler leads to the nucleation of the  $\beta$  crystal form, which is not observed in pure IPP at the temperature under study. Maximum efficiency in a change of the nucleation and crystallization rates for samples with a low content of carbon black is found.

In general, it was shown that carbon black filler caused dramatic changes of the rate of polypropylene crystallization. The resulting thermal properties of filled IPP such as melting temperature and its supramolecular crystalline structure cause basic changes of mechanical and electrical properties due to which it found application.

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#### References

- [1] Sichel EK, editor. Carbon black polymer composites. New York: Marcel Dekker, 1989.
- [2] Koszkuł J. *Energochemia, Ekologia, Karbo* 1997;42:84.
- [3] Mucha M. *J Polym Sci, Polym Symp* 1981;69:79.
- [4] Varga J. *J Thermal Anal* 1989;35:1891.
- [5] Fillon B, Thierry A, Wittmann JC, Lotz BJ. *J Polym Sci, Part B: Polym Phys* 1993;31:1383, 1407.
- [6] Chivers RA, Barham PJ Ed., Martinez-Salazar, Keller JA. *J Polym Sci B* 1982;20:1717.
- [7] Wunderlich B. *Macromolecular physics*, 1–3. New York: Academic Press, 1980.
- [8] Lotz B. *Polymer* 1998;39:4561.
- [9] Binsbergen FL, De Lange BGM. *Polymer* 1970;11:309.
- [10] Starzyński T, Lambla M, Georgi F, Thomas H. *Int Polym Process* 1997;12:64.
- [11] Yim A, St. Pierre LE. *J Polym Sci B* 1970;8:241.
- [12] Varga J. *J Mater Sci* 1992;27:2557.
- [13] Bartczak Z, Gałęski A, Martuscelli E. *Polym Eng Sci* 1984;24:1155.
- [14] Quijada-Garrido, Barrales-Rienda JM, Perena JM, Frutas G. *Polymer* 1997;38:5125.
- [15] Beck HN. *J Appl Polym Sci* 1967;11:673.
- [16] Binsbergen FL. *Polymer* 1970;11:253.
- [17] Zhang X, Shi G. *Thermochim Acta* 1994;235:49.