

APPLICATION OF DSC TO STUDY CRYSTALLIZATION KINETICS OF POLYPROPYLENE CONTAINING FILLERS

M. Mucha and Z. Królikowski*

Faculty of Process and Environmental Engineering, Technical University of Łódź,
Wólczajska 213, 93-005 Łódź, Poland

Abstract

The present work is concerned with the comparison of nucleating efficiency of various organic and inorganic fillers of isotactic polypropylene: talc, chalk, wood flour, nano clay particles, carbon black, chitosan in the form of powder of the same content equal to 5 mass%. The kinetics of isothermal crystallization of isotactic polypropylene in the composite systems was evaluated by using DSC. Avrami equation was applied to the results. Calculated K and n parameters depend on filler applied. The $\sigma\sigma_c$ surface free energies were also found. The best nucleating agent found here was talc and carbon black. The organic filler as a chitosan powder forms amorphous inclusions in the composites on which IPP molecules cannot be adsorbed. Their presence disturbs a macromolecular diffusion and delays crystallization process of IPP.

Keywords: chalk, crystallization, fillers: chitosan, polypropylene, talc, wood flour

Introduction

Crystallization occurs when a polymer is cooled below its melting temperature and the phase transformation takes place. The process is described by a nucleation and growth mechanism [1–3].

A useful parameter in properties – structure correlation is the nucleation density, i.e. the total number of nuclei developed per unit of volume. Nucleating agents cause shortening of the induction time of crystallization providing foreign surfaces of nuclei that reduce the free energy required for formation of a new polymer nuclei. Thus the critical size of the nuclei is decreased and the nucleation takes place earlier, nuclei are formed more rapidly. Well nucleating efficiency of fillers or special nucleating agents is also an important problem in polymer industry. Application of nucleating species causes the shortening of injection molding cycle time, thus reducing production costs and generation of smaller spherulites improves the optical and mechanical properties of the polymers. It is a common industrial practice to mix a polymer with another material or polymer to improve the properties.

* Author for correspondence: E-mail: muchama@wipos.p.lodz.pl

The polymers are also filled with various materials because of material savings (fillers such as chalk or talc are cheap), strengthening (glass and carbon fibers, natural fibers), biodegradability (biodegradable fillers). An important problem is to determine their efficiency in polymer nucleation in such complex systems. The microstructure of polymer composites depends on applied fillers [4–15, 30–32]. For example, short silicone carbide whiskers affect the crystallization rate of isotactic polypropylene (IPP) [9]. The most ideal nucleating agent found was sodium benzoate (increasing crystallization temperature was $\Delta T_c=26^\circ\text{C}$).

Both nucleation (also heterogeneous nucleation by addition of foreign seed material) and crystallization processes of IPP have been intensively investigated for more than twenty years [16–28]. Our previous studies [10, 29] were concerned with crystallization kinetics of IPP filled with various content of carbon black and other fillers. Carbon black Sakap 6 applied as a filler for the isotactic polypropylene reveals typical properties of a nucleating agent [10]. Here the nucleating efficiency of various organic and inorganic fillers of IPP of the same content is evaluated by using DSC.

Experimental

Materials

Sample 1: pure isotactic polypropylene (IPP). Samples 2–7: IPP with various fillers of the same content equal to 5 mass%, were prepared by blending fillers with IPP powder and melting in a hydraulic press to form thin films (Table 1).

Table 1 Sample characterization

No.	Sample	Sample characterization
1	IPP	Malen P type J-400
2	Talc	type J-800 (Polish Company ORLEN)
3	Chalk	type J-400 (Polish Company ORLEN)
4	Carbon black	Sakap 6 (Carbochem, Gliwice)
5	Nano clay	Cloisite 24A, AR 128.013 – (Southern Clay Products, Texas, USA) Nano – a montmorillonite organically modified with dimethyl 2-ethylhexyl ammonium cation contains 26 mass% of organic materials
6	Wood flour	Pinhopo, Ponta Gross – Parana
7	Chitosan powder	Sea Fishery Institute, Gdynia, deacetylation degree=85%

Methods

Analysis of melting and crystallization kinetics of various polypropylene samples was carried out using Mettler differential scanning calorimeter type FP85. The fol-

lowing conditions for determination of melting and crystallization behaviors together with calculation of characteristic parameters were applied:

1 – Heating of sample in the calorimeter at a rate of $10^{\circ}\text{C min}^{-1}$ from room temperature to the temperature equal to 195°C ; 2 – Isothermal sample annealing at the temperature $T_1=195^{\circ}\text{C}$ for 2 min to remove crystalline nuclei; 3 – Fast cooling of the sample in the calorimeter to the crystallization temperature T_c ; 4 – Isothermal crystallization at constant temperature ranging from 126 to 134°C for the period equal to about 0.5 h; 5 – Heating of previously crystallized samples at a rate of $10^{\circ}\text{C min}^{-1}$ from crystallization temperature to 195°C . Melting point T_m , enthalpy (heat) of melting ΔH were measured.

Results and discussion

Melting and crystallization temperatures

Figure 1 shows DSC curves obtained by heating of pure IPP and IPP containing various fillers previously crystallized at the temperature equal to 128°C .

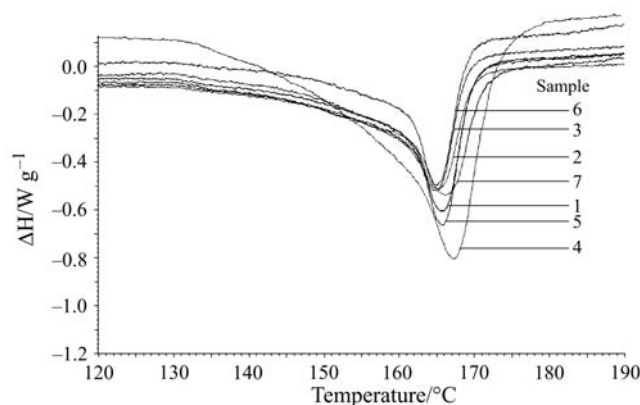


Fig. 1 DSC curves of IPP crystallized at 128°C (1) and IPP with various fillers (samples no. 2–7). Containing the same amount of filler equal to 5% (heating rate equal to $10^{\circ}\text{ min}^{-1}$)

The melting curves appear similar with melting peak in the vicinity of 164 – 167°C . Crystallinity degree values were in the narrow range from 35 to 45%.

Isothermal crystallization

Figure 2 presents the examples of isothermal crystallization curves of IPP in nano (5) filled samples at various crystallization temperatures. The induction times t_0 (the starting time of crystallization) are clearly seen and measured.

Figure 3 shows DSC curves of isothermal crystallization of IPP at 128°C drawn for various samples 1–7 to compare the effect of fillers.

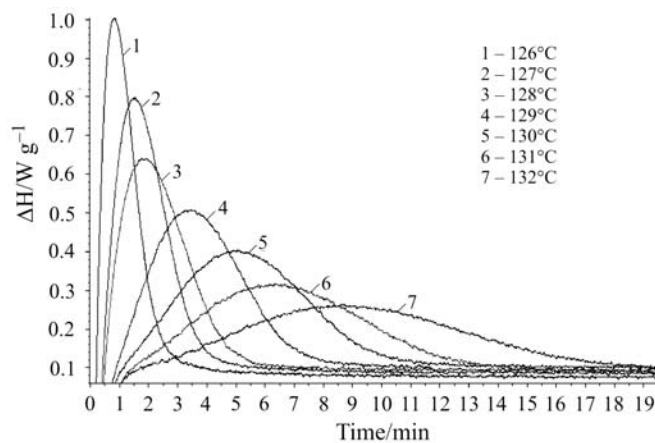


Fig. 2 DSC curves of isothermal crystallization of nano filled IPP samples at $T_c=126\text{--}132^\circ\text{C}$

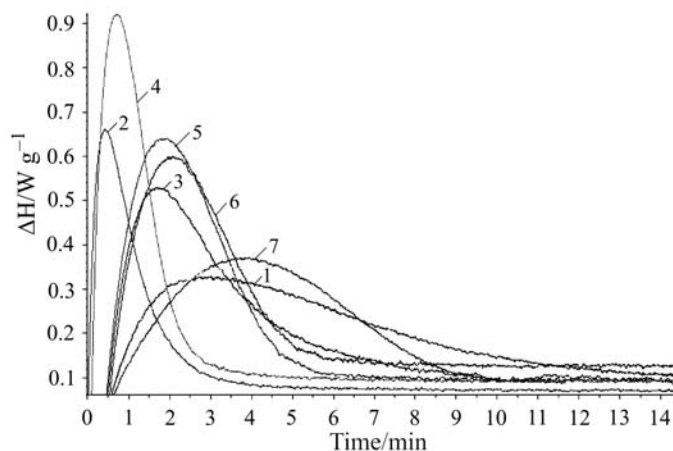


Fig. 3 DSC curves of IPP isothermal crystallization at 128°C in various samples no. 1–7

The example of integral curves presenting isothermal crystallization at two various temperatures for comparison of IPP, both pure and in composites with carbon black and chitosan (samples 1, 4 and 7) is shown in Fig. 4.

Figure 5 shows the integral curves presenting isothermal crystallization process at $T_c=128^\circ\text{C}$ obtained for pure IPP and IPP filled with various materials. A strong effect of the enhancement of polypropylene crystallization is observed in relation to the nucleating action of added particles especially of talc and carbon black. The organic filler, such as chitosan powder, delays in visible way the crystallization process of IPP. Similar relations were observed during crystallization at other temperatures.

To describe isothermal crystallization of IPP samples the Avrami equation (1) was used:

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

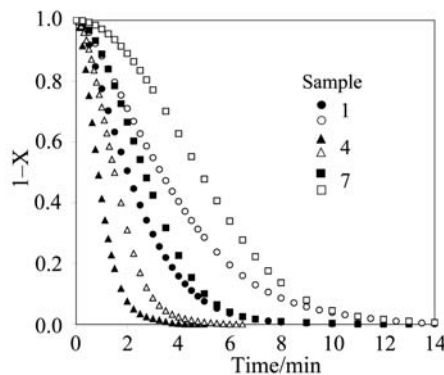


Fig. 4 Integral curves of IPP isothermal crystallization pure and in blend with carbon black and chitosan (samples no. 1, 4, 7) found for various crystallization temperatures 128 and 130°C

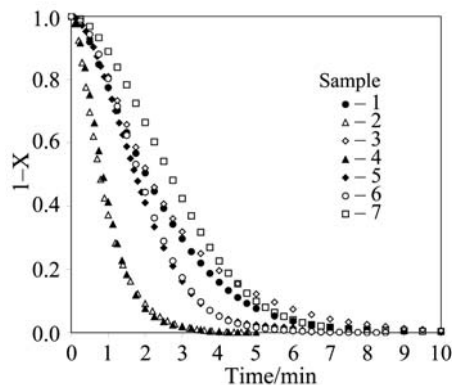


Fig. 5 Integral curves of IPP crystallization (samples no. 1–7). Crystallization temperature $T_c=128^\circ\text{C}$

where $1-X$ is the content of non-crystallized material, and K , n the Avrami parameters depending on the geometry of the growing crystals and on the nucleation process.

The Avrami equation in the simple form represents unimpeded spherical crystal growth and required sigmoidal shape. However, the sample does not reach complete crystallization as required for the model. To continue the analysis one assumes that complete crystallization is reached. Equation (1) is thus used to fit experimental data and to compare crystallization behavior of pure and filled IPP.

Figure 6 shows examples of Avrami lines obtained from the following double logarithmic equation:

$$\lg[-\ln(1-X)] = \lg K + n \lg t \tag{2}$$

Figure 7 shows the dependence of $\lg K$ on the crystallization temperature T_c obtained for the composites (samples 1–7). K value decreases with increasing crystallization temperature T_c , and depends on a filler. The value of second Avrami param-

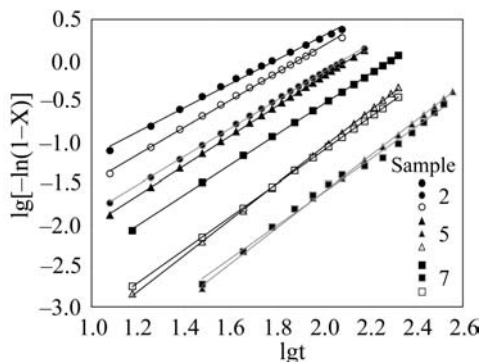


Fig. 6 Avrami plots for samples 2, 5 and 7. Crystallization temperatures were equal to 128, 130 and 132°C, respectively

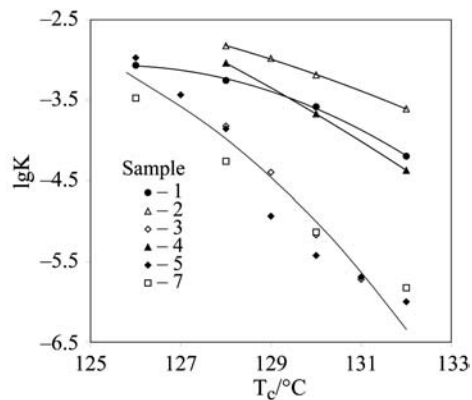


Fig. 7 $\lg K$ (K – Avrami parameter) vs. crystallization temperature T_c for samples no. 1–7

ter, n has a tendency to grow with increasing crystallization temperature and is equal to 1.5–1.6 for pure IPP and 1.7–2.1 for the composites. The values do not reflect the character of a structural crystal growth.

Induction period of crystallization and half time of crystallization

The induction period t_0 of crystallization process is defined as proportional to the time needed for critical nucleus formation and depends both on filler and crystallization temperature. The t_0 results are shown in Fig. 8. The presence of talc and carbon black crystals reduces both the work required to create a new surface (decreasing $\sigma\sigma_e$) and the nucleus size for crystal growth (decreasing t_0).

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

$$v = v_0 \exp[-(\Delta G^* + \Delta G_\eta)/kT_c] \quad (3)$$

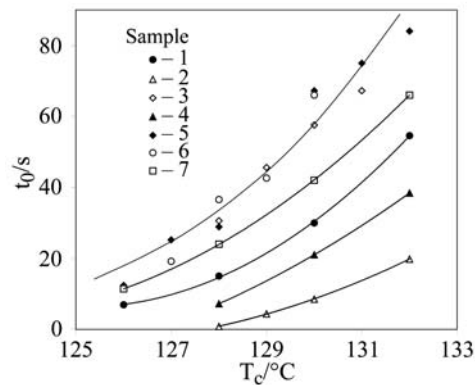


Fig. 8 Induction period of IPP crystallization vs. T_c for various samples no. 1–7

where v is the growth rate, v_0 the preexponential factor, ΔG^* the free enthalpy of nucleation of a nucleus of critical size, ΔG_η the free enthalpy of activation of molecular diffusion across the phase boundary and k is the Boltzmann constant.

For a secondary or heterogeneous nucleation, the ΔG^* value can be presented as follows:

$$\Delta G^* = 4\sigma\sigma_e b_0 T_m / \Delta h_f \rho_c \Delta T \tag{4}$$

where ΔG^* remains inversely proportional to supercooling $\Delta T \Delta T = T_m - T_c$, T_m^0 is the equilibrium melting temperature, b_0 the single layer thickness taken here as $4.65 \cdot 10^{-10}$ m, $\Delta H_f = \Delta h_f \rho_c = 1.98 \cdot 10^8$ J m⁻³ the enthalpy of melting [1], σ , σ_e the specific side surface (lateral) and fold surface (end) free energies which measure the work required to create a new surface.

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

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

$$\ln t_{0.5} = \text{const} + \Delta G^* / kT_c \tag{5}$$

However, ΔG_η should be dependent on an impurity (additive) content at constant temperature.

Dependence of half time of crystallization $t_{1/2}$ on crystallization temperature T_c of the samples is shown in Fig. 9. The difference in $t_{1/2}$ values decreases with lowering the crystallization temperature and becomes very close to each other at about $T_c = 122^\circ\text{C}$.

From the slopes of the straight lines $\{\ln t_{0.5} = f[1/(T_c \Delta T)]\}$ presented in Fig. 10 the $\sigma\sigma_e$ values are calculated. A clear tendency to decrease $\sigma\sigma_e$ is observed in the case of nucleating

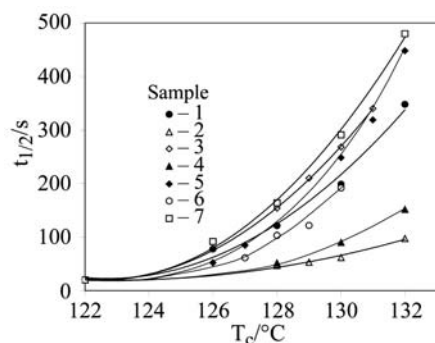


Fig. 9 Half time of crystallization $t_{1/2}$ vs. crystallization temperature for samples no. 1–7

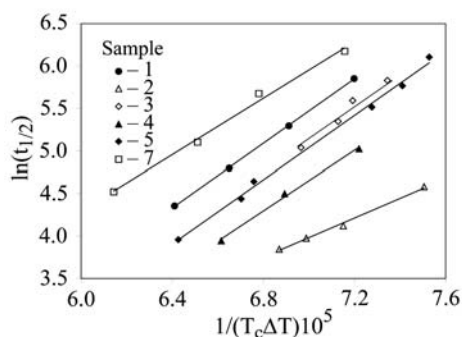


Fig. 10 $\ln t_{1/2}$ vs. $1/T_c \Delta T$ (ΔT – supercooling) for pure IPP (curve 1) and filled with various fillers (samples no. 2–7)

fillers as compared to pure polypropylene which is equal to $\sigma\sigma_e = 6.4 \cdot 10^{-4} \text{ J}^2 \text{ m}^{-4}$ to about $\sigma\sigma_e = 4.0 \cdot 10^{-4} \text{ J}^2 \text{ m}^{-4}$ for talc filled IPP. Other fillers do not change $\sigma\sigma_e$ in a visible way.

Conclusions

Some additives in polymer become a nucleation center leading to an increase of crystal growth in the crystallization process of the polymer. A foreign surface reduces the nucleus size needed for crystal growth since the creation of the interface between polymer crystal and substrate. It may be less hindered than formation of the corresponding free polymer crystal surface. The important effect of such nucleation is a modification of polymer morphology which can result even in a total collapse of its spherulitic structure [24] and possible change of crystallographic form [25].

Presented studies of the isothermal crystallization of polypropylene by DSC enabled us not only to confirm the nucleating effect of various materials, but also to calculate some parameters, such as $\sigma\sigma_e$ which are helpful in explanation of the crystallization process. It was found that talc and carbon black acted as nuclei in IPP crystallization and in the case of talc $\sigma\sigma_e$ value decreased very clearly.

Chitosan or wood flour used as biodegradable fillers to synthetic polymers have a hydrophilic character. Thus the polypropylene molecules are not adsorbed on the foreign surfaces. The fillers form amorphous inclusions in IPP matrix. Their presence hinders a diffusion of IPP macromolecules in the crystallization process and also disturbs the creation of IPP spherulitic structure.

In general, it was shown here that all fillers even as their content is low (equal to 5% by mass) caused visible changes of the crystallization rate of IPP.

References

- 1 B. Wunderlich, *Macromolecular Physics*, Academic Press, New York 1976, Vol. 2.
- 2 J. R. Foks, *Crystallization of Polymers*, Kluwer Academic Publ., Netherlands 1993, Vol. 405.
- 3 J. H. Magill, *J. Mat. Science*, 36 (2001) 3143.
- 4 Z.-G. Wang, R. A. Phillips and B. S. Hsiao, *J. Polym. Sci. B: Polym. Phys.*, 38 (2000) 2580.
- 5 E. P. Collar, C. Marco, S. Areso and J. M. Garcia-Martinez, *J. Macromol. Sci. Phys.*, B40 (2001) 369.
- 6 M. A. Lopez Manchado, J. Biagiotti, L. Torre and J. M. Kenny, *J. Therm. Anal. Cal.*, 61 (2000) 437.
- 7 H. Harel and G. Maron, *Acta Polym.*, 49 (1998) 583.
- 8 J. Ma, S. Zhang, Z. Qi, G. Li and Y. Hu, *J. Appl. Polymer Sci.*, 83 (2002) 1978.
- 9 M. Avella, E. Martuscelli, M. Raimo, R. Partch, S. C. Gangolli and B. Pascucci, *J. Mater. Sci.*, 32 (1997) 2411.
- 10 M. Mucha, J. Marszałek and A. Fidrych, *Polymer*, 41 (2000) 4137.
- 11 M. Raimo, E. Cascone and E. Martuscelli, *J. Mater. Sci.*, 36 (2001) 3591.
- 12 M. Arroyo, M. A. Lopez-Manchado and F. Avalos, *Polymer*, 38 (1997) 5587.
- 13 N. S. Otsuda, Y. Nishida, M. Shimizu, T. Takeda and S. Yumitori, *J. Mater. Sci. Lett.*, 14 (1995) 1234.
- 14 D. Campbell and M. M. Qayyum, *J. Polymer Sci. Polymer Phys. Ed.*, 18 (1980) 83.
- 15 A. M. Chatterjee, F. P. Price and S. Newman, *J. Polymer Sci. Phys. Ed.*, 13 (1975) 2369.
- 16 M. Mucha, *J. Polymer Sci., Polymer Symp.*, 69 (1981) 79.
- 17 J. Varga, *J. Mat. Sci.*, 27 (1992) 2557.
- 18 Z. Bartczak, A. Gałęski and E. Martuscelli, *Polym. Eng. Sci.*, 24 (1984) 1155.
- 19 Quijada-Garrido, J. M. Barrales-Rienda, J. M. Perena and G. Frutas, *Polymer*, 38 (1997) 5125.
- 20 H. N. Beck, *J. Appl. Pol. Sci.*, 11 (1967) 673.
- 21 F. L. Binsbergen, *Polymer*, 11 (1970) 253.
- 22 J. Varga, *J. Thermal Anal.*, 35 (1989) 1891.
- 23 B. Lotz, *Polymer*, 39 (1998) 4561.
- 24 Y. Yang, *J. Appl. Polymer Sci.*, 85 (2002) 333.
- 25 F. Rybnikow, *J. Appl. Polymer Sci.*, 38 (1989) 1479.
- 26 M. Fujiyama, *Int. Polym. Process.*, 8 (1992) 84.
- 27 K. Mai, K. Wang, Z. Han and H. Zeng, *J. Appl. Polymer Sci.*, 83 (2002) 1643.
- 28 L. Finelli, N. Lotti and A. Munari, *Eur. Polym. J.*, 37 (2001) 2039.
- 29 M. Mucha and Z. Królikowski, *Macromolecular Symposia 2002*, in press.
- 30 T. Starzyński, M. Lambla, F. Georgi and H. Thomas, *Int. Polym. Process.*, 12 (1997) 64.
- 31 X. Zhang and G. Shi, *Thermochim. Acta*, 235 (1994) 49.
- 32 J. Varga and A. Menyhard, *J. Therm. Anal. Cal.*, 73 (2003) 735.