

NUCLEATION AND CRYSTALLIZATION OF POLYPROPYLENE FILLED WITH BaSO₄

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Abstract

The influence of high concentration of BaSO₄ as nucleating agent on crystallization of fiber-forming polypropylene was studied by DSC. The work presents experimental and calculated values of melting and crystallization enthalpies of filled polypropylene and the influence on the formation of interface interactions between filler and polymers. These results show minimal interactions of components (BaSO₄ and polypropylene) under experimental conditions.

Keywords: crystallization, DSC, filled polypropylene, nucleation, structural modification

Introduction

The original purpose of adding mineral fillers to polymers up to high concentrations was one of cost reduction. The result of these works are often new polymeric materials with some very interesting physical and mechanical properties, as tenacity and impact strength [1-7], electrical properties [8] and absorption of radioactive radiation [9, 10].

The properties of dispersion systems are affected by a number of important parameters, that is the structure of particles, their concentration and magnitude as well as the average distance between particles [11, 12], character of the interface, morphology of the polymeric component and morphology of the surface layer [8, 13].

The filler significantly influences the crystallization kinetics, too, especially for polymers with a high crystallization ability (e. g. polypropylene). In addition to it it, this effect is multiplied by crystallization conditions, particularly by cooling rate of the melt. In cooling the melt by a lower rate, mainly stable α -modification with a melting point of about 438 K is formed. At a higher cooling rate (more than 50 K min⁻¹) and for fiber-forming polymers with melt flow index (MFI) from 8 to 30 g/10 min, other structural modifications are formed with melting points from 413 to 433 K and with a significant share of especially hexagonal β -modification [14, 15].

The crystallization rate for polypropylene can be increased by several orders of magnitude for certain crystallization modifications of solid particles, e.g. by

adding phthalocyanine pigments, phthalimide, some natural fillers (talc) etc. [16]. Interesting results were gained in selective β -nucleation of some organic solid particles, e.g. anthraquinone pigments [17]. These effects should be related to specific interactions on the interface: polymer-filler.

Very interesting surface-active components for filled polyolefins seem to be organometallic (Zr, Ti) compounds, which enable the preparation of highly concentrated polymeric dispersions with suitable rheological and processing properties [18].

In the present work, we have investigated the influence of high concentrations of BaSO₄ on crystallization of fiberforming polypropylene.

Experimental

Material

Polymer

Polypropylene PP TI 902 (Slovnaft, a.s.), melt flow index (MFI)= 27 g/10 min

Filler

Baryt, BaSO₄, from Moravske Chem. Zavody, Ostrava (CZ) H₂O-0.08%, Salt sol. in water 0.04% pH-9.0, rest on the sieve No 0.06–0.03%

Surface active compounds

Organotitanic comp., from Kenrich (USA), Plasticizer – from Structural (USA)

Preparation of samples

The filled polypropylene containing 30, 50, 60 and 70 wt. % of BaSO₄ was prepared by homogenization of necessary amounts of granulated PP TI 902 and powdered BaSO₄ with surface active particles at 503 K on a twin-screw extruder.

Model fibers were prepared from granulated filled polymer by a TSØ 16 mm extruder at 503 K. They were employed for thermoanalytical evaluation of the supermolecular structure.

Methods of measurement

Thermal properties of polypropylene filled with BaSO₄ were evaluated by DSC 7 apparatus (Perkin Elmer) using the following procedure: Sample of the

original fibre was heated by a rate of 10 K min^{-1} up to 513 K . Thus, a melting endotherm of the original sample with a melting point T_m and melting enthalpy ΔH_m was obtained. Then, the sample was cooled by a rate of 10 K min^{-1} and/or 50 K min^{-1} and the crystallization exotherm with crystallization temperature T_c and crystallization enthalpy ΔH_c was obtained. Subsequently, the sample was exposed to a second heating by a rate of 10 K min^{-1} and the endotherm with a melting point T_{mi} and enthalpy ΔH_{mi} was gained. In the measurements nitrogen atmosphere was used.

Values ΔH_{calc} and β_{calc} were calculated by the following relation

$$\Delta H_{\text{calc}} = \Delta H_{m(w=0)}(1-w) \quad (1)$$

and

$$\beta_{\text{calc}} = \beta/(1-w) \quad (2)$$

where w is the weight fraction of filler.

Melting and crystallization enthalpies (ΔH_m and ΔH_c) were determined from the surface of endotherm or exotherm, between two selected temperatures. The melting and crystallization temperatures (T_m and T_c) correspond with peaks on the DSC curve. All values gained by software DSC 7.

Results and discussion

A high content of BaSO_4 in polypropylene at relatively very good flow properties was achieved at optimal employment of surface active agents (organotitanic compounds) along with an efficient plasticizer. Flow properties of the polymer, containing up to 70 wt. % filler, enabled extrusion and preparation of polypropylene- BaSO_4 fibres by a classical procedure (melt spinning). Extraordinary good flow properties of the system polypropylene- BaSO_4 are, apart from other factors, the result of its microstructure and solid particles distribution,

Table 1 Melting and crystallization temperatures of polypropylene fibres filled with BaSO_4 at a cooling rate of 50 and 5 K min^{-1}

w	1. 50 K min^{-1}		2. heating		1. 5 K min^{-1}		2. heating	
	heating	crystall.	$T_{m1}/$	$T_{m2}/$	heating	crystall.	$T_{m1}/$	$T_{m2}/$
BaSO_4	K				K			
0.00	433.6	370.1	428.0	435.8	433.6	385.4	430.3	—
0.30	432.6	372.3	427.6	435.2	432.6	388.3	430.0	—
0.50	432.6	372.5	427.8	434.9	432.9	388.3	430.4	—
0.60	432.9	371.1	427.7	434.6	432.1	388.3	430.3	—
0.70	432.9	372.1	426.8	434.1	432.8	388.2	429.9	—

which can significantly influence especially the thermal properties of filled polymers.

Already the melting and crystallization temperatures (maxima of the endotherm and minima of the exotherm) (Table 1) demonstrate the small influence of filler on this parameter at the first heating T_m as well as the second heating- T_{m1} . This holds also in the case of splitting the endotherm into two maxima at foregoing crystallization of the sample at a cooling rate of 50 K min^{-1} (Fig. 1). The endotherm is not splitted after crystallization at a cooling rate of 5 K min^{-1} (Fig. 2). Crystallization temperatures T_c are significantly dependent only on the cooling rate (Table 1). Minimal changes in the plot of T_c vs. filler concentrations are the evidence of a very low nucleation effect of BaSO_4 in polypropylene and a negligible influence on supermolecular structure of

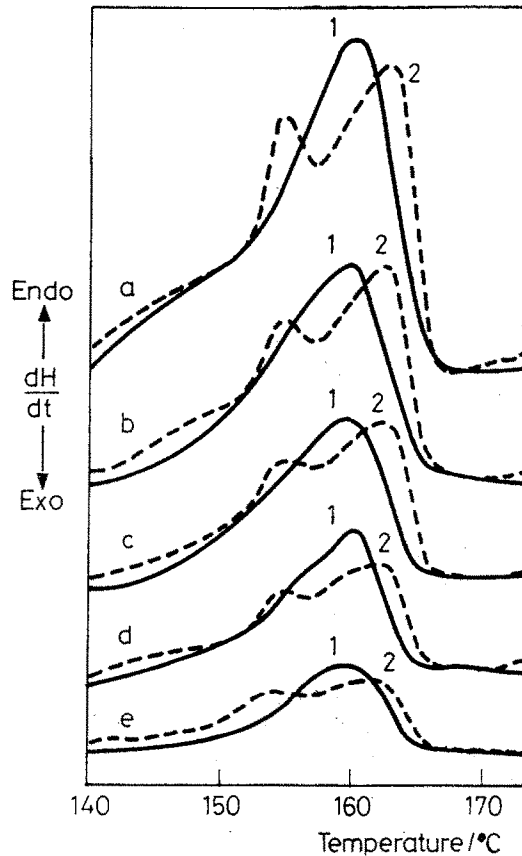


Fig. 1 The DSC endotherm of polypropylene filled with BaSO_4 at various concentrations of filler and a cooling of rate 50 K min^{-1} . a – unfilled polypropylene, b – 30 wt. % BaSO_4 , c – 50 wt. % BaSO_4 , d – 60 wt. % BaSO_4 , e – 70 wt. % BaSO_4 , 1 – original sample, 2 – second heating.

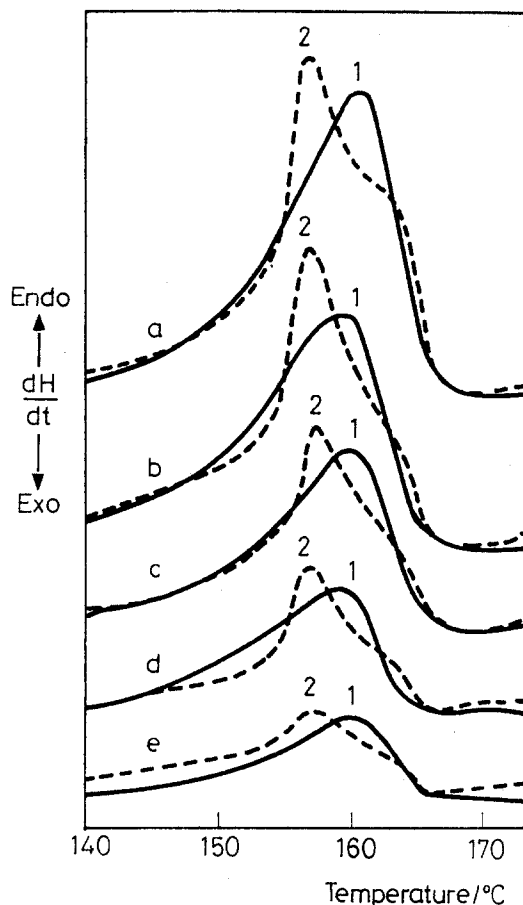


Fig. 2 The DSC endotherm of polypropylene filled with BaSO₄ at various concentrations of filler and a cooling rate of 5 K min⁻¹. a – unfilled polypropylene, b – 30 wt. % BaSO₄, c – 50 wt. % BaSO₄, d – 60 wt. % BaSO₄, e – 70 wt. % BaSO₄, 1 – original sample, 2 – second heating

polypropylene in the investigated concentration range (30–70 wt.%) (Figs. 1, 2).

The DSC analysis of melting and crystallization enthalpies of the filled polypropylene confirms the 'independence' of the formation of polypropylene structure from the filler concentration (Tables 2–4). In Tables 2 and 3 are displayed melting enthalpies for the cycle: melting 1/crystallization/melting 2. From these results it follows that both ΔH_m and crystallinity β , expressed as $\beta = \Delta H_m / \Delta H_m^0$ (in with $\Delta H_m^0 = 142.6 \text{ kJ kg}^{-1}$ is a value related to 100 wt. % of the crystallized polymer [18]) practically do not depend on structure forming conditions, shape of the endotherm (splitting) and BaSO₄ concentration (up to 50 wt.%). A significantly lower crystallinity of polypropylene (25–28 wt.%)

Table 2 Melting enthalpy and crystallinity of polypropylene fibres filled with BaSO₄ (1) and after subsequent crystallization of sample at a cooling rate of 50 K min⁻¹ (2)

w	1.					2.				
	$\Delta H_m/$ J g ⁻¹	$\Delta H_{calo}/$ J g ⁻¹	$\beta/$ %	$\beta_{calo}/$ %	$\Delta H/$ %	$\Delta H_m/$ J g ⁻¹	$\Delta H_{calo}/$ J g ⁻¹	$\beta/$ %	$\beta_{calo}/$ %	$\Delta H/$ %
0.00	86.3	86.3	0.61	0.61	0.0	91.2	91.2	0.64	0.64	0.0
0.30	55.0	60.4	0.38	0.55	9.8	56.4	63.8	0.39	0.57	10.9
0.50	42.8	43.2	0.30	0.60	1.6	44.1	45.6	0.31	0.62	3.1
0.60	33.2	34.5	0.23	0.58	4.9	30.6	36.5	0.22	0.54	15.6
0.70	18.8	25.9	0.13	0.44	27.9	19.9	27.4	0.14	0.47	26.6

Table 3 Melting enthalpy and crystallinity of polypropylene fibres filled with BaSO₄ (1) and after subsequent crystallization of sample at a cooling rate of 5 K min⁻¹ (2)

w	1.					2.				
	$\Delta H_m/$ J g ⁻¹	$\Delta H_{calo}/$ J g ⁻¹	$\beta/$ %	$\beta_{calo}/$ %	$\Delta H/$ %	$\Delta H_m/$ J g ⁻¹	$\Delta H_{calo}/$ J g ⁻¹	$\beta/$ %	$\beta_{calo}/$ %	$\Delta H/$ %
0.00	81.0	81.0	0.57	0.57	0.0	82.9	82.9	0.58	0.58	0.0
0.30	54.0	56.7	0.38	0.54	5.3	54.0	58.0	0.38	0.54	6.9
0.50	48.3	40.5	0.34	0.68	-19.3	45.0	41.5	0.32	0.63	-8.6
0.60	31.4	32.4	0.22	0.55	3.5	30.2	33.2	0.21	0.53	8.6
0.70	18.5	24.3	0.12	0.43	24.6	22.3	24.9	0.16	0.52	10.3

calculated from melting enthalpy was obtained only at the highest concentration of filler (70 wt. %).

The assumption of 'amorphization' of a certain portion of polypropylene due to the influence of BaSO₄ (Tables 2 and 3) at a 50–70 wt. % concentration of filler excludes Table 4, where are listed crystallization enthalpies at a cooling rate of 50 and 5 K min⁻¹. The unambiguity of these results follows from the course of crystallization, in which the endotherm represents a process in a narrow temperature interval (Fig. 3). Experimental determined values of ΔH_c are practically coincident with calculated values and this holds also at the highest content of BaSO₄ in polypropylene. The difference between experimental and calculated values of crystallinity is within the error of measurement. The plot for enthalpy and crystallinity of filled polypropylene can be expressed by relations

$$\Delta H_c = \Delta H_{c(w=0)} \cdot (1-w)$$

and

$$\beta = \beta / (1 - w)$$

Results given in Table 4 reveal that the formation of the polypropylene structure does not depend on the presence of BaSO₄, even at extremely high concentrations. In terms of thermoanalytical evaluation, both components behave independently from each other. The absence of interactions on interface assumes a minimal thickness of the adsorbed polypropylene segments on the BaSO₄-particles surface, which is occupied by molecules of organotitanic compounds and a plasticizer. This assumption about the composition of surface (adsorption) layer at minimal interaction of polypropylene and filler agrees with the relative low viscosity of the melt of a highfilled polypropylene.

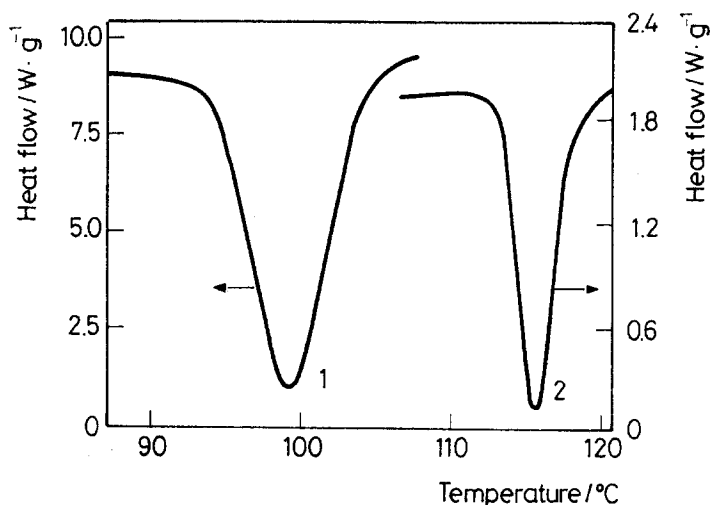


Fig. 3 The exotherms of crystallization of polypropylene filled with BaSO₄ (30 wt.%) at a cooling rate of 50 K min⁻¹ (1) and 5 K min⁻¹ (2)

Table 4 Crystallization enthalpy and crystallinity of polypropylene fibres filled with BaSO₄ at a cooling rate of 50 K min⁻¹ (1) and 5 K min⁻¹ (2)

w	50 K min ⁻¹					5 K min ⁻¹				
	$\Delta H_c /$ J g ⁻¹	$\Delta H_{\text{calc}} /$ J g ⁻¹	$\beta /$ %	$\beta_{\text{calc}} /$ %	ΔH_c %	$\Delta H_c /$ J g ⁻¹	$\Delta H_{\text{calc}} /$ J g ⁻¹	$\beta /$ %	$\beta_{\text{calc}} /$ %	$\Delta H_c /$ %
0.00	86.1	86.1	0.60	0.60	0.0	93.9	93.0	0.66	0.66	0.0
0.30	63.5	60.3	0.45	0.64	-6.7	69.7	65.7	0.49	0.70	-6.0
0.50	43.5	43.1	0.31	0.61	-1.7	46.7	46.9	0.33	0.65	1.5
0.60	33.9	34.4	0.24	0.59	1.7	38.0	37.6	0.27	0.66	0.0
0.70	24.8	25.8	0.17	0.58	3.3	30.8	28.2	0.22	0.72	-9.1

Table 5 Mechanical properties of polypropylene fibres filled with BaSO₄

w	T_d	σ	ε	$T_{d\text{calc1}}$	σ_{calc}	$\Delta\sigma_1$	$\Delta\sigma_2$
BaSO ₄	dtex	cN·dtex ⁻¹	%	dtex	cN·dtex ⁻¹	cN·dtex ⁻¹	cN·dtex ⁻¹
0.00	235.0	0.85	28.6	235.0	0.85	0.00	0.00
0.30	250.0	0.87	58.3	175.0	1.24	0.39	0.37
0.50	282.5	0.60	64.7	141.3	1.20	0.35	0.60
0.60	375.0	0.30	34.0	150.0	0.75	-0.10	-0.45
0.70	567.5	0.19	26.4	170.3	0.63	-0.22	-0.44

Supermolecular and morphological structure of the oriented fiber system directly influences especially its basic mechanico-physical properties. Table 5 shows that the tenacity of fiber indirectly proportionally falls off with the filler loading (>30 wt. %). If the tenacity of fiber is related only to the polymer component σ_{calc} , then, the influence of filler on this value is positive at 30–50 wt. % and negative over 50 wt. % of solid particle. The elongation of fiber at high concentration of filler is on the unfilled polypropylene level. Higher elongation at 30–50 wt. % of BaSO₄ are due to the influence of modification agents.

Basing on thermoanalytical evaluation of BaSO₄-filled polypropylene, the high level of filling is conditioned by interface between filler and polymer with minimal mutual interactions of components. This condition is assured by modification agents (polyorganotitanic compounds) and a suitable plasticator.

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