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Polypropylene Crystallisation in the Presence of Inorganic Additives

Abstract
The physical modification of polypropylene (PP) fibres with inorganic additives ensures more intense anchoring of PP fibres in constructional composites, which leads to great improvement of the function of PP fibres in relation to the transmission and absorption of deformation energy in the formation and loading of composites. This work focuses on the preparation of PP fibres modified with untreated and treated $CaCO_3$ and SiO_2 for constructional composites. It investigated the effect of inorganic additives on the thermal, thermo-mechanical and sorption properties of these fibres. Melting and crystallisation temperatures as well as the melting and crystallisation enthalpies of PP and modified PP fibres depend on the additives and conditions of preparation of PP fibres applied. A lower amount of inorganic additives improves and a higher amount of inorganic additives worsened the dimensional stability of the PP fibres observed. The addition of inorganic fillers increased the water vapour sorption of the modified PP fibres in comparison with the pure PP fibre.

Key words: *polypropylene (PP) fibres, inorganic additives, modification, crystallisation.*

Introduction

Unmodified short and long polypropylene (PP) fibres are standard materials used in constructional composites. The PP fibres used as reinforcement in construction composites induce the reduction of crack propagation, increase flexural and bending strength, and improve impact resistance. Their advantage is very good chemical resistance and low sensitivity to moisture [1]. On the other hand, their non-polar, hydrophobic physical and chemical inactive polyolephinic character does not allow the creation of chemical or physical intermolecular bonds between the concrete matrix and PP fibres and thus results in a low affinity of PP fibre to the cement matrix. The effects of PP fibres of various geometry on the compressive and bending strength of reinforced cement mortars were compared in [2]. PP fibres of various geometry do not affect the compressive strength, but a significant increase in the bending strength was observed for mortars reinforced with fibrillated fibres, a lower increase with a star cross section, and the increase in bending strength was very little for mortars reinforced with fibres of round shape. One of the disadvantages is mainly the decrease in the fibre's ability to absorb deformation energy during the loading of the concrete composite in flexure. The result is the increased release of fibres by detaching from concrete composites, instead of their deformation along with the composite matrix [3, 4]. Many methods of the surface treatment of polymer fibres exist at present which improve the bond strength with concrete matrix [5-9].

It was demonstrated on the basis of knowledge from literature that the nanoparticles added to concretes as active mineral additives affect their nucleation centers in the formation of hydration products, which helps to increase the strength and durability of construction materials [9-11]. An increase in the effectiveness of a dispersed PP fibre reinforcement in a concrete composite for mechanical parameters in the presence of nano-SiO_2 was also presented in literature [11].

One of the possible modifications of PP fibres for the improvement of the chemical and physical interaction between the fibres and concrete matrix is modification with nanoparticles of inorganic fillers [12]. If the particles are incorporated in the fibre surface, then the interactions between the inorganic particles in the fibre surface and inorganic concrete matrix would cause an increase in significantly stronger bonds. Some knowledge from the application of PP fibres in concrete composites with nano-SiO_2 particles is interesting. It was shown that the physical and chemical effects of nanoparticles are helping to reduce the amount of water film around PP fibres, and that nanofillers decrease porosity at the fibre/matrix interface. Results also showed that nano-SiO_2 improves the mechanical parameters of fibre-concrete composite [11].

The other disadvantage of PP fibres is also their low elasticity module as well as the significantly higher density in comparison with fresh concretes, which causes the imperfect dispersion of fibres in the composite volume. Special hy-

drophilic treatments of PP fibres can decrease these undesirable effects and provide more complete dispersion in a water environment. The modification of PP fibre surfaces leads to a very significant increase in their water absorbency [12].

PP is relatively highly brittle, and the addition of inorganic nanoadditives ($CaCO_3$, SiO_2 and TiO_2) also eliminates this property. The high agglomeration ability and worse dispersion of nanoparticles within the PP matrix is caused by the high surface energy of nanoparticles and the fact that improvement of their mechanical properties is very difficult. Therefore specific methods for the preparation of nanoparticle/polymer composites are used [13]. It was ascertained that even a small number of nanoparticles results in an effective increase in the flexural and bending strength, elastic module, and rigidity [14, 15]. Inorganic nanoadditives, as one of many additives (e.g. pigments [16], carbon nanotubes [17], montmorillonite [18, 19], wood or lignin fibres [20-23]) used for PP, commonly referred to as nucleating agents, affect the thermal and mechanical properties of filled PP significantly [24-29]. Nanoparticles acting as nucleating agents induce a change in the crystallisation behaviour of semicrystalline PP at crystallisation and increase the crystallisation rate and content of crystalline phase. Changes in the crystallisation behaviour of PP with inorganic nanoadditives are the cause of the final properties of PP fibres, e.g. mechanical and thermo-mechanical properties, sorption etc. [30]. Consequently the study of the crystallization behaviour of PP modified with nanoadditives is very difficult from the point of their preparation, required properties and further application. The crystallisation process of PP can be studied under isothermal or non-isothermal conditions [25, 28, 31-37].

In this work, the effect of two types of inorganic additives on the thermal properties of various masterbatches, as well as on the thermal, thermo-mechanical and mechanical properties and sorption of water of modified PP fibres with and without stabilisation was studied.

■ Experimental part

Materials used
Isotactic polypropylene TATREN HT 1810 (PP) (Slovnaft Corporation, Slovakia) with the melt flow index MFI = 20.6 g/10 min, supplied by the

Table 1. Characteristics of unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres. Note: C_A is the concentration of the additive, LN – the linear density, X – $CaCO_3$ or SiO_2, XP – $CaCO_3$ or SiO_2 treated with pimelic acid.

Samples	C_A, wt%	$CaCO_3$		SiO_2	
		λ_{max}	LN, dtex	λ_{max}	LN, dtex
PP	0	5.1	136	5.1	136
X	1	4.2	125	4.5	107
X	3	3.8	184	3.3	165
X	5	3.0	157	2.6	254
XP	1	3.8	126	4.5	124
XP	3	2.4	217	2.2	319
XP	5	2.4	135	2.2	318

Slovnaft Corporation, was used in the preparation of unmodified and modified PP fibres with inorganic additives. The polypropylene TATREN HT1810 was used for the preparation of short fibres for reinforced cement constructional composites. Two types of inorganic additives in the modified PP fibres were used: $CaCO_3$ (Ca) additive particles with the commercial name SOCAL U3 (Solvay Corporation, USA) with a diameter = 20 nm, free flowing density = 170 g·l^{-1} and specific surface = 70 m^2·g^{-1}; and SiO_2 (Si) additive particles with the commercial name SIPERNAT 22S (Evonik Industries AG, Germany) with a diameter = 13.5 nm, free flowing density = 90 g·l^{-1} and specific surface = 190 m^2·g^{-1}. Acetone (AC) (Lachema, a.s., Czech Republic) with a density of 790 kg.m^{-3} and pimelic acid (PA) with a melting temperature of 376.1-378.1 K (Merck, Germany) were used for the treatment of inorganic additives.

Preparation of PP Fibres modified with $CaCO_3$ or SiO_2
The $CaCO_3$, SiO_2 and pimelic acid were dried in a vacuum at room temperature. Multiple blends of $CaCO_3$, SiO_2 with PA and AC were used, respectively. at a concentrated ratio of $CaCO_3$: PA : AC = 5 : 1 : 20 (CaP) and SiO_2 : PA : AC = 5 : 1 : 50 (SiP). These blends were mixed for 1 h with a mechanical stirrer in the water bath of a ultrasonicator. After treatment of the inorganic additives, acetone from the blends prepared was evaporated at room temperature for 6 h.

PP/Ca or PP/Si modified fibres were prepared in two steps – preparation of PP/Ca, PP/CaP, PP/Si and PP/SiP masterbatches and of modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres. PP masterbatches were prepared with 5 and 10 wt% of inorganic additives. Isotactic PP was compounded with various amounts of

untreated ($CaCO_3$ – Ca or SiO_2 – Si) and treated (CaP or SiP) inorganic additives in a twin-screw extruder from LabTech Engineering Company Ltd., with a diameter of φ = 16 mm at an extrusion temperature of 513 K. The extrudate was the cooled and pelletised.

The pellets of 10 wt% masterbatches were mechanically mixed with the PP so that mixtures with required concentration of additives in the modified PP/Ca, PP/CaP, PP/Si or PP/SiP fibres (1, 3 and 5 wt% additive in fibres) were obtained. Undrawn modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres were prepared from individual mixtures by classical spinning using a laboratory pilot line with a single screw extruder of φ = 16 mm, equipped with a nozzle containing 13 holes, at a spinning temperature of 523 K with a fibre take-up speed of 150 m.min^{-1}. The undrawn fibres were drawn using laboratory equipment at 395 K with the maximum drawing ratio.

Characteristics of the unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres prepared are summarised in *Table 1*.

Methods used for characterisation
Differential scanning calorimetric (DSC) measurement
DSC 7 apparatus from Perkin Elmer was used for evaluation of the thermal properties of the unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP masterbatches and fibres.

Isothermal crystallisation tests of the unmodified PP and PP/Ca, PP/Ca, PP/CaP, PP PP/Si and PP/SiP masterbatches modified with various amounts of inorganic additives were performed at 403.1 K. The samples were heated from 323.1 K to 493.1 K at a rate of 10 K·min^{-1}. At 493.1 K the samples were isothermally held for 5 minutes and cooled down to the crystallisation temperature afterwards at a rate

of 200 K·min^{-1}. The dependencies of heat flow on time obtained that were used for determination of the crystallisation enthalpy and kinetics of crystallisation were evaluated using the Avrami equation.

Non-isothermal analysis of the unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP masterbatches and fibres was performed. A sample of the original fibre was heated from 323.1 K to 493.1 K at a rate of 10 K·min^{-1}. At this temperature (493.1 K) the sample was isothermally held for 5 minutes to remove the thermal history of the fibre preparation. Then the sample was cooled from 493.1 K to 323.1 K at a rate of 10 K·min^{-1} (plus 5, 20, 30 and 50 K·min^{-1} for the masterbatches). Subsequently the sample was exposed to a second heating from 323.1 K to 473.1 K at a rate of 10 K·min^{-1}. All measurements were carried out in a nitrogen atmosphere. From the melting endotherms of the 1st and 2nd heating, the melting temperatures (T_m) and enthalpies (ΔH_m) as well as the crystallisation temperatures (T_c) and enthalpies (ΔH_c) from the crystallisation exotherms were determined. The actual melting enthalpy ΔH_{100} is related to the enthalpy of the weight fraction w of PP *Equation (1)*:

$$\Delta H_{100} = \frac{\Delta H_{exp(w)}}{w} \qquad (1)$$

where, w is the weight fraction of PP in the modified PP samples.

The crystallinity (β) of PP in the unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP masterbatches and fibres was calculated from the *Equation (2)* given below:

$$\beta = \frac{\Delta H_{PP}}{\Delta H_{PP}^o} \qquad (2)$$

where, ΔH_{PP} is the experimental melting enthalpy of PP in unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP masterbatches and fibres, and ΔH_{PP}^o is the melting enthalpy of completely crystalline PP. This is a theoretical value obtained from literature (209 J·g^{-1}).

Mechanical properties

The tenacity (σ), elongation (ε) at break and Young's modulus (E), representing the mechanical properties of unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres, were evaluated by Instron 3343 equipment (USA). Measuring conditions were as follows: the clamping length of fibre – 125 mm and rate of clamp – 500 mm·min^{-1}. Mechanical characteristics of the PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres observed were determined in accordance with the standard (Standard ISO 2062:1993). The thermal parameters were determined with an error of 1.5%.

Thermo-mechanical properties

Thermo-mechanical characteristics of the unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres were measured by Schimadzu TMA-50 (Japan) equipment. The deformation (extension or shrinkage – Δl, %) and temperature of the first distortion of the fibres (T_D) were measured. The fibre was heated in the temperature range from room temperature to 383 K, at a heating rate of 5 K·min^{-1}, fibre length of 9.8 mm and at a constant load; the dependence of the dimensional stability of the fibre on the temperature was obtained, from which the thermo-mechanical characteristics were determined. The deformation (shrinkage – Δl, %) and temperature of the first distortion of the fibres (T_D) were determined with errors of 0.5 or 1.8%.

Water vapour sorption

Gravimetric analysis was used for evaluation of the water vapour sorption (WVA) of the unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres. Samples were dried at 353.1 K for 1 h in a drying chamber. Next the samples were put into glass vessels with a saturate solution of NH_4NO_3 (relative humidity above this solution was 65% at 293.1 K) for 96 h. After this period, the samples were weighed. Afterwards they were dried in a drying chamber at 378.1 K for 3 h and weighed again. The content of water vapour (C_{WV}) sorption was calculated using *Equation (3)*:

$$\beta = \frac{\Delta H_{PP}}{\Delta H_{PP}^o} \qquad (3)$$

where, m is the weight of the fibre with water vapour sorption in a equilibrium state (after 96 h) and m_o that of the fibre after drying. The water vapour sorption was determined with an error of 1.2%.

Results and discussion

Isothermal crystallisation kinetics

A significant amount of heat is released in the crystallisation of PP from melting. The heat released during the crystallisation allows for determination of the relative degree of crystallinity (X(t)) in the given period of time. The isothermal crystallisation of PP and PP masterbatches modified with $CaCO_3$ or untreated SiO_2 or SiO_2 treated with pimelic acid was performed at 403.1 K for the evaluation of crystallisation kinetics using the Avrami method [25]. The most commonly used analysis of the isothermal crystallisation of PP is evaluation using the Avrami method. This method describes the dependence of the relative degree of crystallinity (X (t)) on the crystallisation time (t):

$$X(t) = 1 - e^{-kt^n} \text{ or } X(t) = 1 - e^- \qquad (4)$$

where, *n* is the Avrami exponent, which is a function of the nucleation process, and *k* the growth function, which is dependent on the nucleation and crystal growth. If the Avrami index *n* is about 3, then heterogeneous nucleation with tridimensional spherulitic growth in a spherical form is characteristic of polymer crystallisation [38]. Primary crystallisation is characterised by the prevalence of nuclei and relatively faster growth of lamellar crystals, while a secondary crystallisation process is the result of the crystallisation of a component with different modification and/or by an increment in the perfection of existing crystallites [38, 39]. If the value of *n* is about 2, then it is possible

Table 2. Results of Avrami analysis for isothermal crystallisation of PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP masterbatches. Note: 5, 10 is the concentration of additive in wt %, Ca – CaCO$_3$, Si – SiO$_2$, CaP – CaCO$_3$ and SiP is SiO$_2$ treated with pimelic acid.

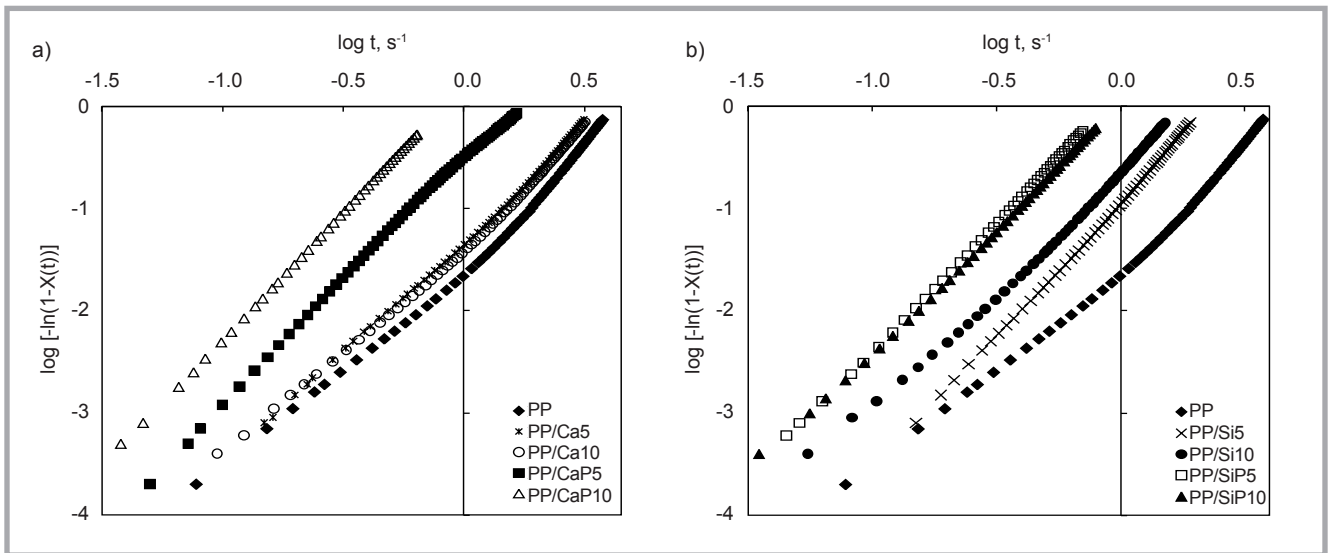|	*n*	*k*, min^{-n}	*t$_{1/2}$*, min	$\sigma \cdot 10^{-3}$, J·m^{-2}	$\sigma_e \cdot 10^{-1}$, J·m^{-2}	φ	*K*, min^{-1}
PP	2.20	0.030	4.23	-4.16	4.22	–	0.201
PP/Ca5	2.22	0.049	3.30	-4.10	4.02	0.92	0.256
PP/Ca10	2.18	0.046	3.49	-4.0	3.70	0.81	0.242
PP/CaP5	2.36	0.310	1.41	-4.05	3.07	0.70	0.608
PP/CaP10	2.48	1.590	0.72	-4.12	2.79	0.65	1.205
PP/Si5	2.65	0.116	1.96	-4.79	2.63	0.82	0.443
PP/Si10	2.34	0.222	1.63	-4.22	2.74	0.67	0.525
PP/SiP5	2.50	1.293	0.78	-4.05	2.51	0.56	1.108
PP/SiP10	2.35	0.946	0.88	-3.59	2.23	0.40	0.977

Figure 1. Avrami plots of log[-ln(1-X(t))] vs. log t for isothermal crystallisation at 403.1 K of PP and modified PP/Ca (a), PP/CaP (a), PP/Si (b) and PP/SiP (b) masterbatches.
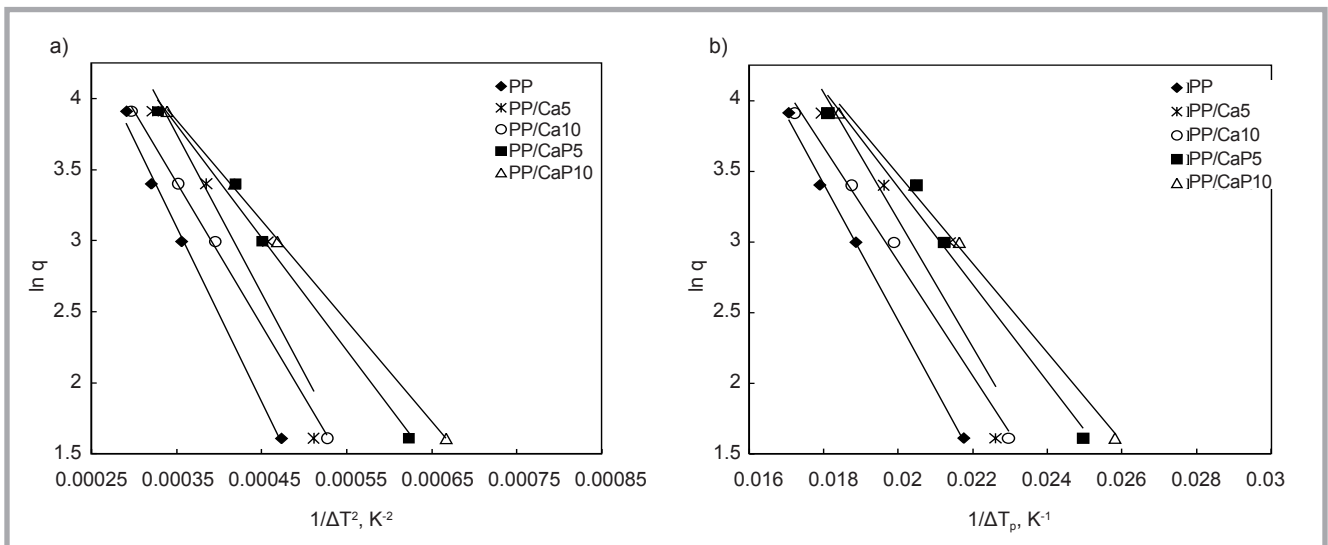

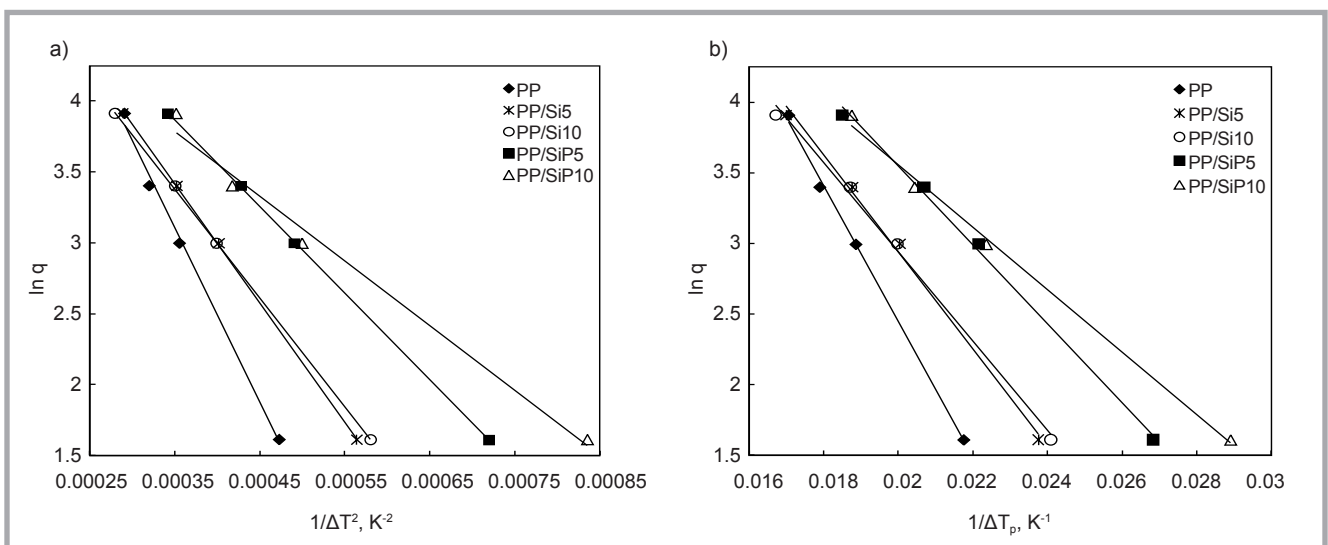*Figure 2. Dependencies of ln q on 1/ΔT² (a) and 1/ΔTₚ (b) of PP and modified PP/Ca and PP/CaP masterbatches.*

Figure 3. Dependencies of ln q on 1/ΔT² (a) and 1/ΔTₚ (b) of PP and modified PP/Si and PP/SiP masterbatches.

Table 3. *Melting temperatures (T_m), melting enthalpies (ΔH_m) and crystallinity (β) of unmodified PP and modified PP/Ca and PP/CaP fibres with various amounts of inorganic additive $CaCO_3$ obtained in the 1st heating.* **Note:** *C_A is the concentration of the additive, Ca – $CaCO_3$, and CaP is $CaCO_3$ treated with pimelic acid.*

Samples	C_A, wt%	T_{m1}, K	T_{m2}, K	T_{m3}, K	ΔH_m, J/g	ΔH_{mv}, J/g	β
PP	0			441.6 446.8	90.5	90.5	0.43
PP/Ca	1			440.3 444.8	94.9	95.8	0.46
	3	430.3		444.0 446.4	95.9	98.9	0.47
	5	432.8		438.6 441.6 446.8	83.3	87.7	0.42
PP/CaP	1	430.0	435.6	444.3	97.2	98.2	0.47
	3			439.9 442.6	88.4	91.1	0.44
	5		434.5 436.3	439.9 444.0	90.4	95.1	0.46

Table 4. *Melting temperatures (T_m), melting enthalpies (ΔH_m) and crystallinity (β) of unmodified PP,and modified PP/Si and PP/SiP fibres with various amounts of inorganic additive SiO_2 obtained in the 1st heating.* **Note:** *C_A is the concentration of the additive, Si – SiO_2, and SiP is SiO_2 treated with pimelic acid.*

Samples	C_A, wt%	T_{m1}, K	T_{m2}, K	T_{m3}, K	ΔH_m, J/g	ΔH_{mv}, J/g	β
PP	0			441.6 446.8	90.5	90.5	0.43
PP/Si	1			446.6	97.6	98.6	0.47
	3		433.4	441.6 444.8	88.6	91.3	0.44
	5			440.4 442.7	88.6	93.3	0.45
PP/SiP	1	430.6		445.6 446.8	95.8	96.7	0.46
	3			438.6	83.9	86.5	0.41
	5			439.6	84.2	88.6	0.42

Table 5. *Melting temperatures (T_m), melting enthalpies (ΔH_m) and crystallinity (β) of unmodified PP and modified PP/Ca and PP/CaP fibres with various amounts of inorganic additive $CaCO_3$ obtained in the 2nd heating.* **Note:** *C_A is the concentration of the additive, Ca – $CaCO_3$, and CaP is $CaCO_3$ treated with pimelic acid.*

Samples	C_A, wt%	T_{m1}, K	T_{m2}, K	T_{m3}, K	ΔH_m, J/g	ΔH_{mv}, J/g	β
PP	0	422.6	435.2	441.8	79.9	79.9	0.38
PP/Ca	1	422.2	433.7 436.0		91.0	91.9	0.44
	3	423.0	434.7	441.9	83.8	86.4	0.41
	5	423.1	436.7	442.5	79.0	83.2	0.40
PP/CaP	1	424.0	435.3	442.1	112.6	113.8	0.54
	3	424.3	437.7	442.0	104.5	107.7	0.52
	5	424.8	438.2	442.3	99.4	104.6	0.50

Table 6. *Melting temperatures (T_m), melting enthalpies (ΔH_m) and crystallinity (β) of unmodified PP and modified PP/Si and PP/SiP fibres with various amounts of inorganic additive SiO_2 obtained in the 2nd heating.* **Note:** *C_A is the concentration of the additive, Si – SiO_2, and SiP is SiO_2 treated with pimelic acid.*

Samples	C_A, wt%	T_{m1}, K	T_{m2}, K	T_{m3}, K	ΔH_m, J/g	ΔH_{mv}, J/g	β
PP	0	422.6	435.2	441.8	79.9	79.9	0.38
PP/Si	1	422.7	436.8		87.8	88.7	42.4
	3	422.9	437.0	442.1	80.6	83.1	39.8
	5	422.9	436.6	442.5	84.6	89.0	42.6
PP/SiP	1	423.1	436.8	442.3	89.7	90.6	43.3
	3	424.5	437.5	441.1	96.1	99.0	47.4
	5	424.1	434.7	441.1	100.1	105.3	50.4

to indicate the growth of bidimensional crystallites. Polymer crystallisation with bidimensional crystal growth in the form of a disk is predicted.

On the bases of plots of log[-ln(1-X(t))] vs. log t (*Equation (4)*) for isothermal crystallisation at 403.1 K of PP and modified PP/Ca, PP/CaP, PP/Si or PP/SiP masterbatches, Avrami values *n* and *k, K* were calculated (*Figure 1* and *Table 2*). During PP crystallisation in the various masterbatches in the presence of inorganic nanoadditives, heterogeneous nucleation with bidimensional crystal growth was observed. The addition of treated $CaCO_3$ in the PP masterbatch increases the Avrami index *n* in comparison with the Avrami index *n* of pure PP as well as with those of PP with untreated $CaCO_3$ in masterbatches with both $CaCO_3$ concentrations. The treated SiO_2 decreases the Avrami index *n* in comparison with the Avrami index *n of* untreated SiO_2 mainly at a lower SiO_2 concentration in masterbatches, while the Avrami index of PP masterbatches with treated SiO_2 is higher than that of pure PP. The Avrami values (*n, k, K* and $t_{1/2}$) confirm the increased nucleation effectiveness of treated $CaCO_3$ and untreated SiO_2 for PP crystallization in the form of bidimensional crystals in comparison with the untreated $CaCO_3$ and treated SiO_2.

The secondary nucleatio Laurtintzen--Hoffman theory [25, 36, 37] was used for the calculation of σ and $σ_e$, which are the side surface (lateral) and fold surface (end) free energies, which are a measure of the work required to create a new surface, as well as for the calculation of nucleation activity (ϕ) (*Figures 2 & 3* and *Table 2*). The addition of inorganic additives to PP causes a decrease in the free energy in crystal creation as opposed to that in unmodified PP. In PP crystallisation in the presence of inorganic additives, the creation of crystallites is faster and simpler in comparison with pure PP. The nucleation activity (ϕ) can take values between 0 and 1. If the value of nucleation activity is equal to 1, then the inorganic additive is inactive in the crystallisation of PP; conversely, if the value is equal to 0, then the inorganic additive is extremely active. The treatment of inorganic additives ($CaCO_3$, SiO_2) with pimelic acid increases the nucleation activity of these additives for PP crystallisation (*Table 2*). Higher nucleation activity is observed at their higher content in the PP masterbatches.
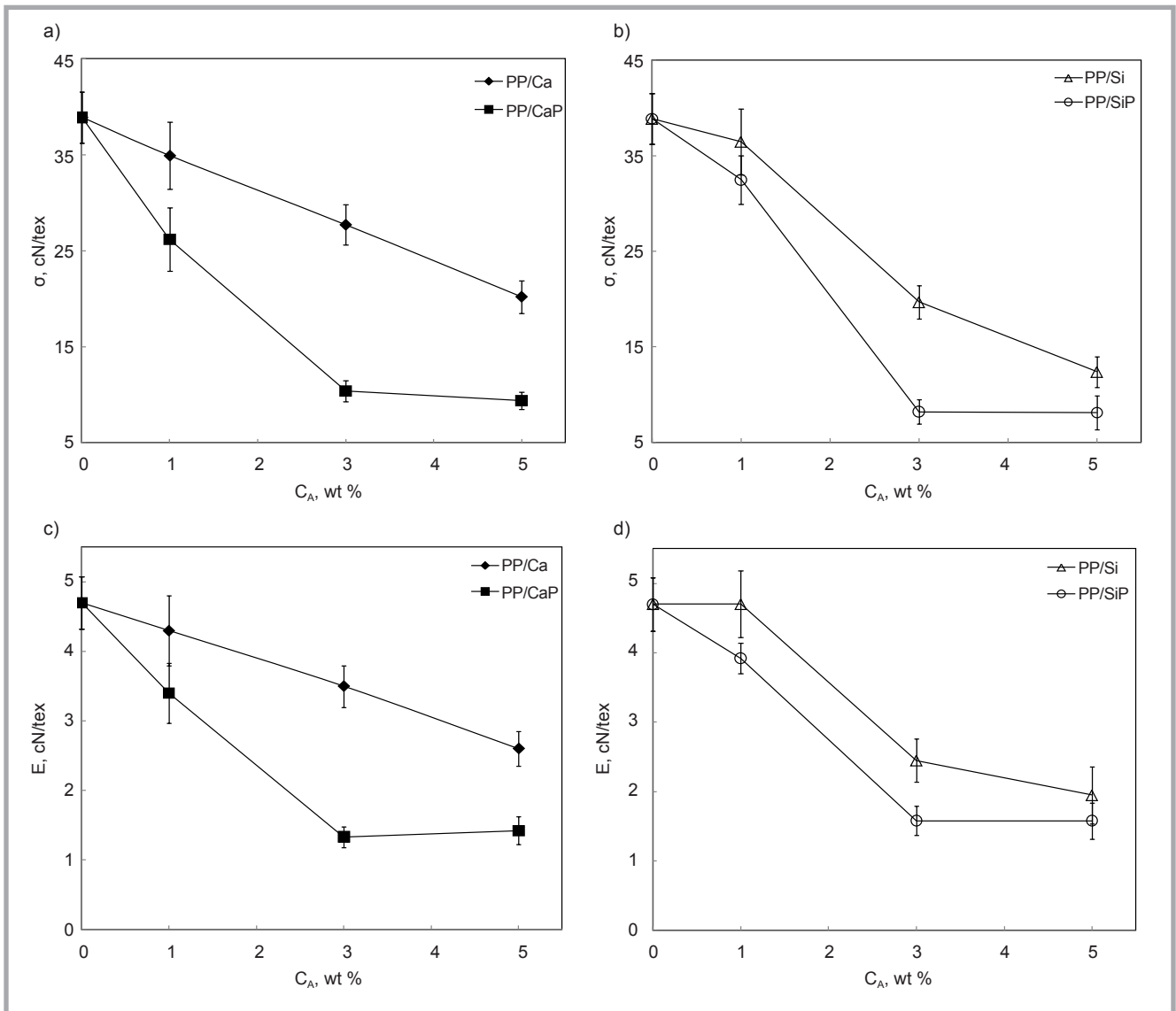
Figure 4. *Dependencies of tenacity at break – σ (a, b) and Young's modulus – E (c, d) on the concentration (C_A) of $CaCO_3$ and SiO_2 of modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres.*

DSC was used for non-isothermal measurement of the thermal properties of pure PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres (**Tables 3**, **4**). Results of the thermal properties of anisotropic pure PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres obtained in the first heating show that the creation of these fibres' supermolecular structure (expressed as crystallinity β) is simultaneously affected by preparation conditions (spinning and drawing) as well as the presence of inorganic additives. Several peaks corresponding to the melting temperatures of various crystal modifications created in the preparation of these fibres were obtained. Modifications with the melting temperature corresponding to a blend α-β-modification (T_{m1}, T_{m2} = 429.1-436.1 K) that correspond to the melting temperature of α-modification (T_{m3} = 438.1-446.1 K)

were also obtained. A higher melting temperature of the α-modification created in the modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres points towards the formation of more perfect crystals in the presence of untreated and treated inorganic additives. These additives increase the crystallisation ability of PP in modified fibres in comparison with pure PP.

The resultant samples of pure PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres obtained in the second heating describe the supermorphological structure created without strength in the spinning and drawing processes. The structure created in the cooling of isotropic pure PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP systems after the first heating and isothermal holding for 5 minutes to remove the thermal his-

tory of the fibre preparation only includes the effect of inorganic additives on PP crystallisation (**Tables 5, 6**). The addition of inorganic additives encourages the creation of crystal modifications with various melting temperatures; however, the crystal modifications with higher melting temperatures did not create multipeaks.

Changes in the creation of the supermolecular structure towards thermal behaviour of PP in the PP/Ca, PP/CaP, PP/Si and PP/SiP systems are affected by the presence of inorganic additives, but mainly by the spinning and drawing conditions. The supermolecular structure of fibre created in the spinning and drawing processes is the basis for their thermo-mechanical, mechanical and other useful properties.
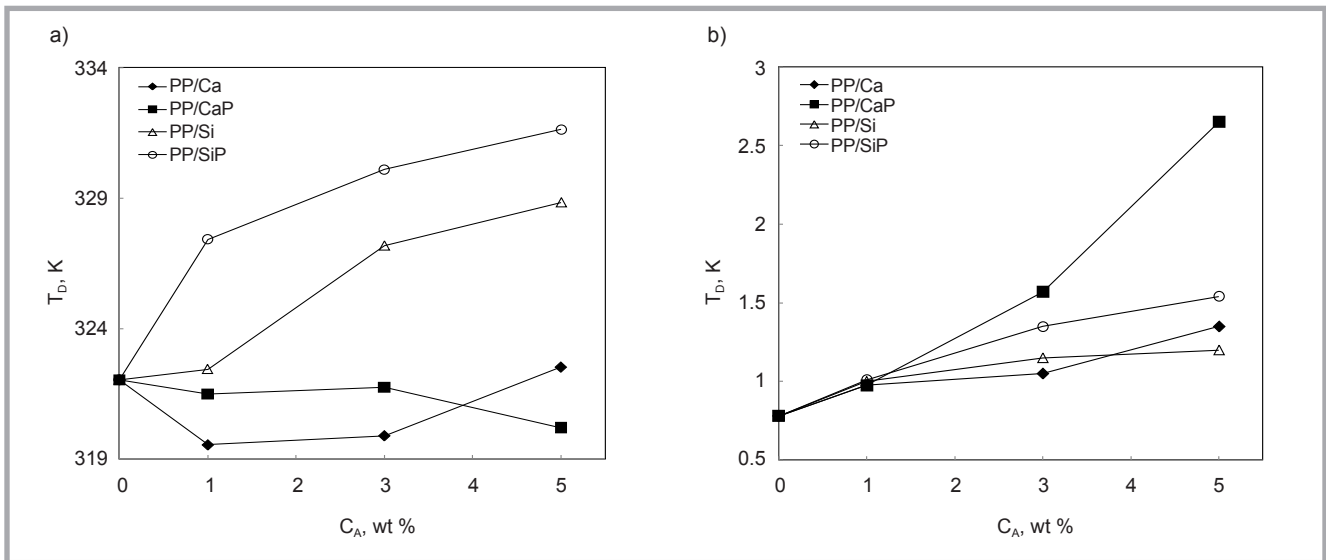
Figure 5. *Dependencies of the heat distortion of the fibres (T_D) (a) and water vapour sorption (WVS) (b) on the concentration (C_A) of CaCO$_3$ and SiO$_2$ of unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres.*

Table 7. *Elongation at the break (ε) and shrinkage (Δl) of unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres with various amounts of inorganic additives CaCO$_3$ or SiO$_2$. Note: C_A is the concentration of additives, X – CaCO$_3$ or SiO$_2$, and XP is CaCO$_3$ or SiO$_2$ treated with pimelic acid.*

Samples	C$_A$, wt%	CaCO$_3$		SiO$_2$	
		ε, %	Δl, %	ε, %	Δl, %
PP	0	37.1	**-2.54**	37.1	**-2.54**
X	1	24.6	-2.1	23.6	-2.03
X	3	29.3	-2.14	22.3	-1.87
X	5	47.5	-2.35	44.7	-2.75
XP	1	30.9	-1.82	24.6	-1.76
XP	3	52.1	-2.89	34.2	-2.58
XP	5	34.1	-2.28	47.3	-2.63

The mechanical properties of pure PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP PP fibres are shown in ***Table 7*** and ***Figure 4***. The tenacity at break (σ), Young's modulus (E) and elongation at break (ε) are affected by all additives, both untreated and treated CaCO$_3$ and SiO$_2$.

he tenacity at break (σ) and Young's modulus (E) decrease with an increase in the additive content in the fibres. A significant decrease is observed mainly at a content from 3 wt% of additives in modified PP fibres (***Figure 4***). The addition of 1 wt % untreated SiO$_2$ causes the insignificant growth of Young's modulus (E). The higher Young's modulus (E) of modified PP/Si fibres was caused by inorganic fillers, which act as a reinforcement additive. On the contrary, the inorganic filler induced a decrease in elongation of the modified PP fibre because the particles of the filler decrease the drawing ability of the polymer matrix (***Table 7***). This confirms the theoretical knowledge that the addition of micronised filler to the oriented anisotropic polymer matrix decreases its mechanical properties.

The size stability of fibres is a very important parameter from the viewpoint of their behaviour for the load of individual fibres as well as those in the concrete. Therefore the thermo-mechanical characteristics (the extension resp. shrinkage of fibre Δl, % and the heat distortion of the fibres T_D, K) were evaluated in the range from room temperature to 363 K, the results of which are presented in ***Table 7*** and in ***Figure 5a***. From the results obtained, the differences in the deformation of PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres were evident. The shrinkage of PP fibres is reduced by 2.54%. The addition of untreated as well as treated CaCO$_3$ or untreated SiO$_2$ improves the size stability of the fibres prepared. Treated SiO$_2$ has either a null or negative effect on the size stability of the fibres prepared (***Table 7***). On the other hand, the addition of untreated and treat-ed SiO$_2$ to PP fibres increases their heat distortion fibre (T_D) in comparison with pure PP fibres and PP fibres modified with untreated and treated CaCO$_3$ (***Figure 5a***).

For the improvement of PP fibre adhesion to the concrete matrix, the water vapour sorption (WVS, %) of CaCO$_3$ and SiO$_2$ of unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres (***Figure 5.b***) was evaluated. The water vapour sorption of unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres increases with an increase in filler concentration. The fibres prepared with inorganic additives treated with pimelic acid and those treated mainly with CaCO$_3$ showed a more significant increase in water vapour sorption.

■ Conclusions

In this work, crystallisation kinetics evaluated on the basis of the Avrami and Laurtintzen-Hoffman methods of isotropic PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP systems were investigated. The thermal, thermo-mechanical and mechanical properties and water vapour sorption of anisotropic PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres were studied as well.

The Avrami values (*n, k, K* and $t_{1/2}$) obtained for the PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP masterbatches confirm the increased nucleation effectiveness of treated CaCO$_3$ and untreated SiO$_2$ for PP crystallisation in the form of bidimensional crystals in comparison

with untreated CaCO$_3$ and treated SiO$_2$. The treatment of inorganic additives (CaCO$_3$, SiO$_2$) with pimelic acid increases the nucleation activity (from $\phi = 0{,}9$-$0{,}7$ to $\phi = 0{,}7$-$0{,}4$) of these additives for PP crystallisation. A higher nucleation activity is observed at their higher content in the PP masterbatches.

Results of the thermal properties of anisotropic pure PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres obtained in the first heating show that the creation of these fibres' supermolecular structure (expressed as crystallinity β) is simultaneously affected by the presence of inorganic additives as well as by the preparation conditions (spinning and drawing). In the spinning and drawing of the fibres observed, the singular crystal modification of PP is mainly formed. The second heating of pure PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres characterises the supermorphological structure created without strength in the spinning and drawing processes after removing the thermal history of the fibre preparation. The addition of inorganic additives encourages the creation of crystal modifications with various melting temperatures , but the crystal modifications with higher melting temperatures did not create multi-peaks.

The tenacity at break (σ) and Young's modulus (E) decrease with an increase inadditive content in the fibres mainly at a content from 3 wt% of additives in modified PP fibres. The inorganic fillers induced a decrease in the elongation of the modified PP fibres because the particles of the filler decrease the drawing ability of the polymer matrix.

The results of thermo-mechanical properties obtained show that the differences in the deformation of PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres were evident. The addition of untreated as well as treated CaCO$_3$ or untreated SiO$_2$ improves the size stability of the fibres prepared, and treated SiO$_2$ has a either null or negative effect on their size stability. But the addition of untreated and treated SiO$_2$ to PP fibres increases their heat distortion fibre in comparison with pure PP fibres and PP fibres modified with untreated and treated CaCO$_3$. The water vapour sorption of unmodified PP and modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres increases with an increase in filler concentration.

The results of this work show that untreated and treated inorganic additives change the supermolecular structure, thermo-mechanical and mechanical properties, and water vapor sorption of modified PP/Ca, PP/CaP, PP/Si and PP/SiP fibres. Untreated CaCO$_3$ and SiO$_2$ improve the size stability and increase the crystallinity but decrease the water vapour sorption properties. Treated CaCO$_3$ or SiO$_2$ significantly improve the water vapour sorption properties in particular. The better adhesion of PP fibres modified with CaCO$_3$ or SiO$_2$ treated with pimelic acid to concrete matrix can be predicted.

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