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The Effect of Inorganic Nanoadditives on the Thermal, Mechanical and UV Radiation Barrier Properties of Polypropylene Fibres

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ABSTRACT

The objective of this study of modified polypropylene (PP) fibres using nanoadditives (nano-$CaCO_3$ and Cloisite 30B) was to determine the influence of these additives on thermal and mechanical properties, but especially on the barrier properties of the nanocomposite fibres against UV radiation. The DSC data obtained from measurements of PP/$CaCO_3$ or PP/C30B nanocomposite fibres were used for determination of the constants n and K of the Avrami equation and in the estimation of other thermal properties of the fibres, such as their crystallization half-time $t_{1/2}$, rate of crystallization $\tau_{1/2}$, the necessary time for maximum crystallization t_{max} and free energy per unit area of surface in the lamella perpendicular to the axis of a high-molecular chain σ_e. The nano-$CaCO_3$ or Closite 30B fillers (pre-treated separately in three different solvents: glycerine, acetone and water) did not influence the melting temperatures but caused an increase in PP crystallization temperatures in comparison with the pure PP fibres. The pre-treatments of nanoadditives resulted in increase of n, K, $\tau_{1/2}$ values and decrease of $t_{1/2}$, t_{max} as well as the values of free surface energies per unit area of the modified PP fibres. There was also observed a decrease in the mechanical properties, however, there was an increase of barrier properties against UV radiation of nanocomposite PP fibres in comparison with neat PP fibres, which was one of the main objectives of the study.

Keywords: Polypropylene (PP) Fibres; Nano-$CaCO_3$; Cloisite 30B; Kinetics of PP Crystallization; Thermal; Mechanical and UV Radiation Barrier Properties

1. Introduction

One of the latest evolutionary ways of preparation of novel polymeric materials is the development of polymer/nanofiller materials with improved properties which allow their application in the manufacture of demanding equipment. The principle underlining the nanofiller effect on polymer matrix is based on the relatively high surface area of nanofiller particles and so possibility creating more intimate interactions with polymer chains. These can lead to crosslinks among polymer chains and throughout the physical polymer network. This effect of the nanofiller considerably influences the physical and mechanical properties of the polymer/nanofiller material. Therefore, incorporation of nanoadditives into a polymer matrix offers an attractive potential for diversification of conventional polymeric materials, such as iso-tactic polypropylene (PP) in various areas of technical application [1-5]. Nano-particles provide new application opportunities in plastic materials used in the areas of automotive, aerospace or electrical engineering industries. Thanks to the unique nano-size of primary filler particles, they offer some new properties such as transparency, improved abrasion resistance as well as unique colouristic effects. New generation of materials comprising nano-size particles with treated surfaces has resulted in a breakthrough in modification of thermosets and thermoplastics. A noteworthy advantage has already been realized from the use of nano-sized filler in that only a small addition of filler significantly increases impact strength as well as toughness of the polymer materials [6].

PP is an important commercial polymer with wide use in many areas such as packaging, automotive industry, fibres and textiles. Its wide use exhibits stems from an attractive combination of low cost, low weight, easy processibility, as well as desirable end-use properties [7]. The rapid growth of PP application in fibre form has lead to an increase in the production of non-woven materials by using spunbond and meltblown technologies. From the application standpoint there is still considerable interest in improving the properties of PP fibres.

It may be expected that the higher surface area of nano-particles could enhance further the crystallization rate of semicrystalline polymers. The type and content of crystallinity plays an important role in the properties of oriented fibers produced for textiles. It has been found that the use of nanoadditives having the proper morphology and particle size, when compounded with polypropylene (PP) fibres induce different behaviour of the polypropylene during crystallization, as well as on the crystallization conditions [1-5].

During crystallization of polymers from melt, one observes in the first step the formation of nucleation entities and in the second step the growth of these entities. These steps influence the kinetics as well as level of crystallization. The influence of clay nano-particles on the intercalated PP-clay nanocomposites was investigated by Yuan *et al.* [8], Al-Mulla *et al.* [9], Philips and Manson [10] and Di Lorenzo and Silvestre [11]. They stated that the surfaces of the filler particles act as nucleation sites for semi crystalline polymers. Perrin-Sarazin *et al.* [12] indicated that the kinetics of crystallization (crystallization temperature and rate) and structure of PP is not only related to clay content, but also depends on PP-clay interactions. In the absence of coupling agent, the crystallization from the melt of PP containing clay platelets occurred faster and at higher temperature than that of neat PP. The type and amount of crystalline phase in PP has a significant effect on the end-use properties of nano-filled fibres, such as thermal, mechanical as well as barrier properties against UV radiation.

One possibility for protecting against harmful ultraviolet radiation (UVR), mainly on the skin, is to wear suitable clothing made of safety textile materials [13,14]. The shielding properties of textile materials depend on their chemical and physical characteristics [15]. Nanoadditives, such as TiO_2, $CaCO_3$, clay or ZnO are intended to improve barrier properties as well as mechanical or thermoplastics properties in different plastic materials, like coatings, packaging, etc. [16]. Thus it seemed reasonable to modify the PP fibres by $CaCO_3$. These fillers are commonly used in large quantities in the processing of PP for various applications.

The larger surface area and dimensional aspect ratio of inorganic nanoadditives provides for more numerous nucleating sites for PP crystallization. Nanoclay Cloisite 30B-C30B consists of plate-shaped filler particles with high aspect ratio which produce more numerous nucleating sites for PP crystallization than do $CaCO_3$ nanoparticles, which have spherical particles and lower aspect ratio is [17]. The chemically modified $CaCO_3$ caused significant changes in the thermal behaviour mainly during PP crystallization. It affects the total degree of PP crystallinity, the crystallization rate and crystallization temperature. The mechanical properties of PP modified with nano-$CaCO_3$ have been increased, too [18]. So, the thermal and mechanical properties of conventional polymers can be significantly influenced using fillers that act as artificial nucleating agents [3]. However, inorganic nano-particles very easily agglomerate because of their large specific surface area and high surface energy and they show poor dispersability in nonpolar polymers like PP, resulting in poor mechanical properties [18].

On the basis of previously published work, we have chosen nanoadditives Cloisite 30B and $CaCO_3$ for modification of PP fibres and have examined their thermal, mechanical as well as barrier properties against UV radiation [19,20]. The advantage of both fillers, $CaCO_3$ and C30B, is that the products are dyeable, an important requirement of textile producers. Mechanical property measurements such as tenacity, modulus and elongation were carried out and thermal properties of the modified PP fibres were evaluated by DSC analysis. The barrier properties against UV radiation were determined by a spectrophotometric method, which provide a basis for evaluation of the shielding effect of fibres containing both nanoadditives: Cloisite 30B and $CaCO_3$.

2. Experimental

2.1. Materials

Polypropylene TG 920 (PP) with the melt flow index MFI = 10.5 g/10min, supplied by Slovnaft Corporation was used in the preparation of unmodified and modified PP fibres. Two types of nanoadditives (NA) with various aspect ratios and nanoparticle size were used. Nano-$CaCO_3$ filler (n$CaCO_3$) with the commercial name Socal U3 (Corporation Solvay) has mean particle diameter = 20 nm, free flowing density = 170 g/l and specific surface = 70 m^2/g. Cloisite 30B (C30B, from the corporation Southern Clay Products), Inc. is a natural montmorillonite modified with a quaternary ammonium salt. The chemicals used for nanofiller treatment were glycerine with the density of 1260 kg/m^3 and acetone with the density of 790 kg/m^3. Both liquids were analytically pure commercial products (fa Lachema, Czech Republic). The information of the used materials is available according to the Technical Data Sheet and Product Bulletin of the source corporations.

2.1.1. Pre-Treatment of Nanoadditives

Generally the preparation of polymer nanocomposites in systems involving polymers containing inorganic nanofiller is often accompanied by problems related to agglomeration of nanoparticles as well as negative influences on processability, thermal behavior and crystallization of the polymer matrix. These negative factors consequently also appear in the mechanical properties of the prepared polymer nanocomposite. In the search for a way

to decrease the agglomeration of nano-particles, we have explored the possibility of decreasing the natural polar interactions among the nanoparticles of the additives and so to decrease their agglomeration. Therefore, in this work we investigated pre-treatment procedures for the nanoadditives prior to the preparation of PP/inorganic filler nanocomposite. The pre-treatment procedures involved the combining of nanoadditives with the solvents glycerine or acetone, and subjecting the mixtures to a variety of conditions of mechanical stirring and ultrasonication in an effort to improve adsorption of the solvent molecules on the surface of the nano-particles and ultimately achieve a positive influence on the behavior of additive PP matrix.

The additives *i.e.* nCaCO$_3$ or C30B in glycerine (C30B) or acetone in the ratio 1:5 (solid to liquid) were given pretreatments before mixing with PP. There were used three treatment methods: 1) mechanically mixing of NA particles in glycerine or acetone dispersion, 2) sonicating a beaker of the NA-liquid dispersion in the solvent which had been placed in a water bath of the ultrasonicator (U) and 3) sonicating while simultaneously mechanically mixing the beaker of dispersion of NA in solvent in the water bath of the sonicator (MU). The time of treatment of filler in all cases was 5 minutes. The dispersions were filtered, rinsed by deionized water and ethanol and dried at room temperature.

The literature describes similar ultrasound treatments of nanoparticles of various nanoadditives like nano zinc oxide or nCaCO$_3$ for improvement of their dispersability in polymers or polymer systems, to facilitate the preparation of polymer blends or emulsions [18,21,22].

2.1.2. Preparation of the PP/NA Masterbatch and Modified PP/NA Fibres

The fibres modified by nanoadditives nCaCO$_3$ or C30B were prepared in two steps:

1) Preparation of masterbatches contained 15 wt% of nCaCO$_3$ or C30B: The isotactic PP was mixed with the appropriate amount of modified nano-additive and melt-compunded in a twin screw extruder with diameter ϕ = 16 mm at extrusion temperature 493 K. Finally, the extrudate was cooled and pelletized. The resulting pellets of masterbatches containing 15 wt% of the additive (nCaCO$_3$ or C30B) were used for the preparation of PP/NA mixtures with required content of NA additives suitable for spinning.

2) Preparation of PP/nCaCO$_3$ or PP/C30B fibres. The pellets of 15 wt% masterbatch (of nCaCO$_3$ or C30B) were mixed mechanically with the appropriate amount of PP to obtain a mixture containing of 1.5 wt% nCaCO$_3$ or C30B in the fibre. The individual mechanically stirred mixtures were melt compounded and spun into fibres by classical procedure using a laboratory pilot line with a

single screw extruder having ϕ = 16 mm, and equipped with a nozzle containing 13 holes, at 513 K, with fibre take up speed of 150 m·min^{-1}. The resultant primary undrawn fibres were subsequently drawn using laboratory drawing equipment at 383 K. The linear density of the drawn multifilaments was T_{dt} = (21 - 22) dtex × f13.

2.2. Characterization Methods

2.2.1. Thermal Properties of Unmodified and Modified PP Fibres

The evaluation of thermal behaviour of unmodified PP and modified PP/nCaCO$_3$ or PP/C30B fibres in the form of heating or cooling programs was performed using a DSC apparatus (Perkin Elmer). The thermal behavior characteristics were estimated for the non-isothermal and isothermal processes.

The following typical procedure is presented for the non-isothermal analysis: A sample of the original fibre was heated at a rate of 10 K·min^{-1} from 343 K to 493 K, then the sample was isothermally held at 493 K for 5 minutes to remove the thermal history of the fibre preparation. Thus, a melting endotherm of the original sample with a melting temperature T_m and melting enthalpy ΔH_m was obtained. The sample was then cooled at a rate of 10 K·min^{-1} and the crystallisation exotherm with crystallisation temperature T_c and crystallisation enthalpy ΔH_c were determined. Subsequently, the sample was exposed to a second heating at a rate of 10 K·min^{-1} from 343 K to 473 K and the endotherm with a melting point T_m, and melting enthalpy ΔH_m was again determined. The actual melting enthalpy ΔH_{100} is related to enthalpy of weight fraction w of PP

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

where w is the weight fraction of PP in the modified PP/nCaCO$_3$ or PP/C30B samples. All measurements were carried out in nitrogen atmosphere.

The effect of nCaCO$_3$ or C30B on the non-isothermal crystallization behavior of PP in the modified PP/nCaCO$_3$ or PP/C30B isotropic blends was studied by evaluation of initial crystallization temperature T_{co}, peak temperature of crystallization T_{cp}, half height width of crystallization ΔW_c, temperature difference between T_{co} and T_{cp} ($\Delta T_c = T_{co} - T_{cp}$) [18] as well as by estimation of other thermal properties such as n and K from Avrami equation. Crystallization half-time $t_{1/2}$, rate of crystallization $\tau_{1/2}$, the necessary time for maximum crystallization t_{max} and free energy per unit area of surface in the lamella perpendicular to the axis of a high-molecular chain σ_e were also determined. These parameters were estimated using isothermal crystallization and non-isothermal processes at 5 different cooling rates (5, 10, 20, 30 and 50 K·min^{-1}).

2.2.2. Mechanical Properties of Composite PP Fibres Modified by nCaCO₃ or C30B

The apparatus, Instron 1122, was used for the estimation of the tenacity, Young's modulus as well as elongation of the modified PP/nCaCO₃ or PP/C30B fibres in accordance with standard testing procedures (Standard ISO 2062:1993).

2.2.3. Barrier Properties of Unmodified and Modified PP Fibres

A quantitative spectrophotometric test was used for quantitative evaluation of the ultraviolet shielding effect of nCaCO₃ or C30B modified PP fibres. A spectrophotometer, Libra S12 with deuterium lamp was used for measuring the transmittance through a sample of reeled fibre. Accordingly, the ultraviolet protective factor (UPF) was calculated using the standard specification STN EN 13758-1:2001 for textile materials. In this case, this specification was adapted for fibres [19]:

$$UPF = \frac{\sum_{290}^{400} E(\lambda) \times \varepsilon(\lambda) \times \Delta(\lambda)}{\sum_{290}^{400} E(\lambda) \times T(\lambda) \times \varepsilon(\lambda) \times \Delta(\lambda)} \qquad (2)$$

where $E(\lambda)$—relative erythermal spectral effectiveness (W/m²·nm), $\varepsilon(\lambda)$—solar spectral irradiance (Melbourne), $T(\lambda)$—spectral transmittance of the sample (%), $\Delta\lambda$—bandwidth (nm), λ—wavelength (nm).

3. Results and Discussion

### 3.1. Thermal Properties of PP/nCaCO₃ and PP/C30B Nanocomposite Fibres

It is known that nanofillers influence the characteristics of polymer/filler nanocomposite melt (e.g. viscosity), but also the process of formation of supermolecular morphology during the crystallization occurring in the cooling of melt, as well as the end-use properties of prepared fibre materials [20,23]. It follows from this, that the spinning process and drawing of the resultant fibres of the systems polypropylene—PP/CaCO₃ or PP/C30B will be affected too. Therefore the modification of PP fibres with special additives like nano-particles of inorganic origin allows for the preparation of new fibre materials with improved properties and with potentially quite new applications [20，23-25].

Melting behaviour of modified PP/nCaCO₃ and PP/C30B fibres was studied at a heating rate of 10 K·min⁻¹ (**Figures 1** and **2**). At the first heating for the anisotropic as well as at the second heating for the isotropic PP/nCaCO₃ and PP/C30B fibres containing various pre-treated nanoadditives, the peaks with the melting temperatures from 434,3 to 438,5 K were determined (**Figures 1**, **2**;

Table 1). These temperatures correspond to the melting temperature of the α-modification of PP. The type and manner of pre-treatment of nanoadditives differently affect the formation of super-molecular structure, which is characterized by the various peak shapes on the DSC
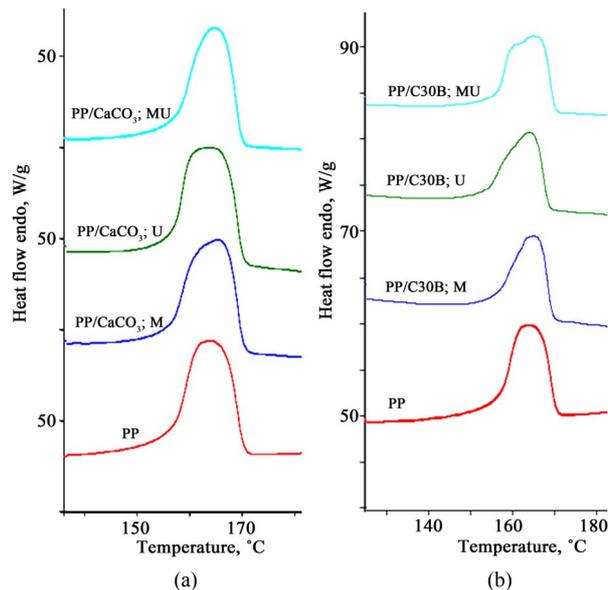
Figure 1. Nonisothermal endotherms of PP and composite PP fibres containing nCaCO₃ (a) and C30B (b) with the various pre-treatment of nanoadditives obtained at the heating rate of 10 K·min⁻¹ for the 1ˢᵗ heating (M—mechanical mixing, U - ultrasound, MU—simultaneously mechanical mixing and ultrasound).
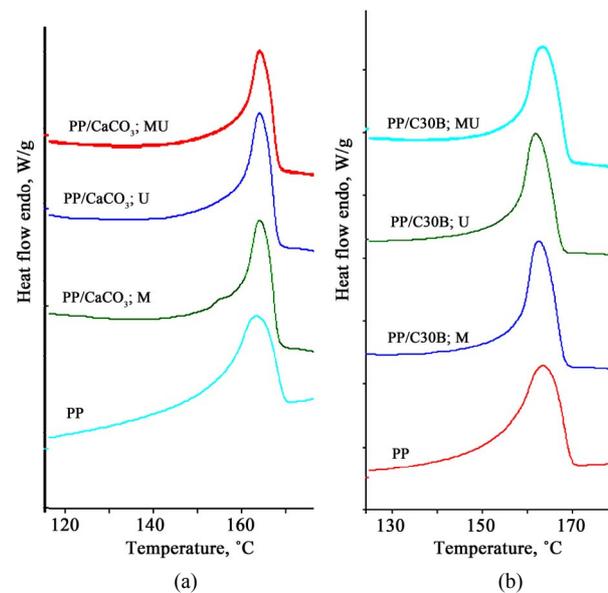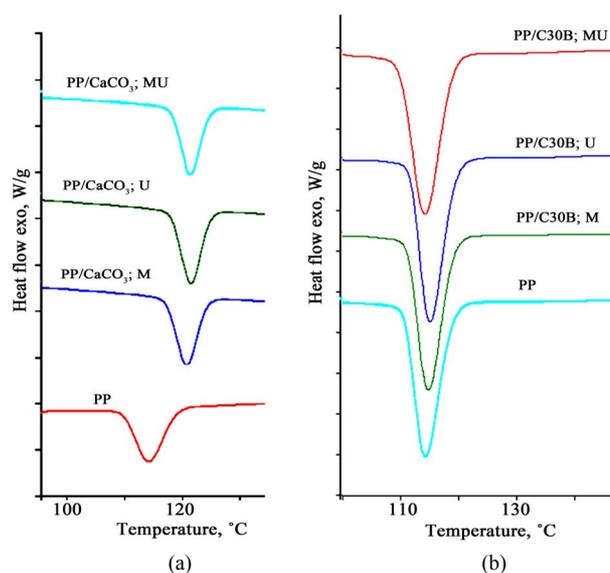

Figure 2. Nonisothermal endotherms of PP and composite PP fibres comtaining nCaCO₃ (a) and C30B (b) with the various pre-treatment of nanoadditives obtained at the heating rate of 10 K·min⁻¹ for the 2ⁿᵈ heating (M—mechanical mixing, U—ultrasound, MU—simultaneously mechanical mixing and ultrasound).

thermograms. The first heating of anisotropic PP/nCaCO₃ fibres containing nCaCO₃ produced DSC thermograms with wide and flat peaks. PP containing anisotropic PP/C30B-based fibres crystallized in the modified morphological structure characterized by narrow and sharp peaks on the thermograms. The peak at the endotherm reflects the thermal history of fibre preparation and indicates PP crystallization during the spinning and drawing of the fibres in the presence nanoadditives. During the second heating, isotropic PP/nCaCO₃ and PP/C30B systems show endotherms with narrow peaks for both nanoadditives (**Figure 2, Table 1**). The melting temperatures of the PP crystallites in the PP/nCaCO₃ composite are higher than the melting temperatures of PP in PP/C30B systems. This can be attributed to the chemical modification of C30B particles with organic quartery alkylammonium salt by the commercial producer. The purpose of the quaternary salt additives is for the improvement of affinity to the hydrophobic chains of the polypropylene which can restrain formation of PP crystallized phase. In the case of nCaCO₃ particles which were not chemically modified, one observes the formation of PP crystallites with larger sizes.

Another observation was noted during the crystallization of these materials after holding them isothermally for 5 min at 493 K (**Figure 3**, **Table 1**). The PP melt containing nCaCO₃ starts to crystallize at a higher temperature than in the blend containing C30B or in the pure PP. All three methods of the pre-treatment of nanoadditives incorporated into the PP matrix did not show any differences in crystallization temperatures. However, the rate of PP crystallization in the fibres containing nCaCO₃ is higher than for C30B at the same cooling rate, which demonstrates the decrease of ΔT_c or ΔW_c, mainly in the case of the nCaCO₃—based composite [17]. This means that at these conditions, the C30B does not behave like a nucleating agent. Only the use of mechanical mixing or ultrasound on C30B is the nucleation effect increased,

but not at the level of the nCaCO₃ system (**Table 1**).

These results show that the presence of additives in the PP fibres, *i.e.* PP/nCaCO₃ and to a lesser extent PP/C30B, produced increased melting and/or crystallization enthalpies, mainly at the first heating. This became most evident with the pre-treatment using ultrasound and also with simultaneous mechanical mixing with ultrasound (US) (**Table 2**). But in the presence of C30B, very little decrease of ΔT_c and ΔW_c were obtained. This is related to the inability of C30B to promote nucleation of crystallization in PP. This observation indicates that pre-treatment of nanoparticles of both types of nanofillers (nCaCO₃ and C30B) contributes some influence on the thermal behavior of PP nanocomposite fibres.

Figure 3. Nonisothermal enxotherms of PP and composite PP fibres containing nCaCO₃ (a) and C30B (b) with the various pre-treatment of nanoadditives obtained at the cooling rate of 10 K·min⁻¹ (M—mechanical mixing, U - ultrasound, MU—simultaneously mechanical mixing and ultrasound).

Table 1. Melting temperatures obtained during 1ˢᵗ (T_{m1}) and 2ⁿᵈ (T_{m2}) heating and crystallization temperature (onset T_{co}, peak T_{cp}), $\Delta T = T_{co} - T_{cp}$, half height width of crystallization (ΔW) of PP, PP/nCaCO₃ and PP/C30B fibres (M—mechanical mixture, U—ultrasound, UM—both simultaneously).

Type and content of nanoadditives in PP fibres	Treatment of nanoadditives	T_{m1} K	T_{m2} K	T_{co} K	T_{cp} K	ΔT K	ΔW K
PP fibres (0.0 wt%)	-	436.0	435.9	391,8	387.2	4.6	5.0
	M	438.5	437.2	397.3	393.8	3.5	3.9
nCaCO₃ (3.0. wt%)	U	437.0	437.0	397.9	394.5	3.4	3.8
	UM	437.7	437.2	397.7	394.3	3.4	3.7
	M	438.3	435.5	392.5	388.1	4.3	4.5
C30B (3.0. wt%)	U	437.0	434.7	392.1	387.8	4.3	4.5
	UM	438.3	436.4	391.9	387.3	4.6	4.9

Melting and crystallization enthalpies of PP in the PP/C30B anisotropic or isotropic systems are lower than for pure PP. The highest effect on the PP crystallization from the standpoint of pre-treatment of nanoadditives before their incorporation into the polymer/fibres has been achieved by using mechanical mixing with simultaneous application of ultrasound (**Table 2**). This method probably promotes improved dispersion of the nanoadditive particles.

As it is generally known, the crystallization process of polymers such as PP is complex and depends on temperature. The relative degree of crystallinity increases with an increase in crystallization time t, as is described by the Avrami equation [26,27]:
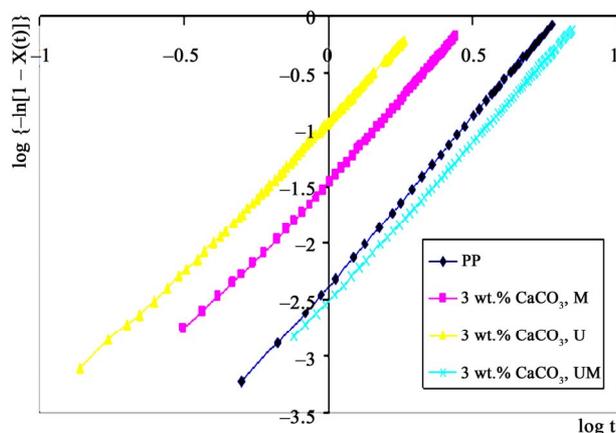
$$X_c = 1 - e^{-K \cdot t^n} \tag{3}$$

The parameters n and K determined from double logarithmic plots (**Figures 4** and **5**) are shown in **Table 3**. The Avrami parameter n is in the range from 2.6 to 4.8, depending on type or pre-treatment of nanoadditives

(nCaCO$_3$, C30B). These values indicate heterogeneous nucleation with the creation of two- and three-dimensional diffusion-controlled growth of spherulites. All pretreatment methods applied to nCaCO$_3$ additives indicated mainly two-dimensional growth. The various kinds of pre-treatments for C30B additives support a different nucleation mechanism for PP. Small variations of the Avrami index n can result from experimental and specific errors of the Avrami model [26], as well as by the existence of both primary and secondary crystallization in the material [28]. Also, the kinetics of PP crystallization is influenced by the type of pretreatment applied to the nanoadditives (**Table 3**). The most rapid PP crystallization was observed in the presence of nCaCO$_3$ pretreated by ultrasound (the highest of K, $\tau_{1/2}$ and lowest $t_{1/2}$, t_{max}). The end surface free energy needed for the creation of new crystalline surfaces in the crystallites during this heterogeneous nucleation is lowest, as well. The values of K, $\tau_{1/2}$ and lowest $t_{1/2}$, t_{max} confirm the lower PP crystallization rate in the presence of C30B in comparison with nCaCO$_3$ (**Table 3**).

Table 2. Melting (experimental-ΔH_m and calculated-ΔH_{mcalc}) and crystallization (ΔH_c) enthalpies for the 1st (1) and 2nd (2) heating and crystallization of PP, PP/nCaCO$_3$ and PP/C30B fibres (M—mechanical mixture, U—ultrasound, UM—both simultaneously).

Type and content of nanoadditives in PP fibres	Treatment of nanoadditives	ΔH_{m1} J·g^{-1}	ΔH_{m1calc} J·g^{-1}	ΔH_c J·g^{-1}	ΔH_{m2} J·g^{-1}	ΔH_{m2calc} J·g^{-1}
PP fibres 0.0 wt%	-	99.3	99.3	113.5	100.9	100.9
	M	99.6	102.7	110.8	103.5	106.7
nCaCO$_3$ 3.0.wt%	U	100.8	104	112.7	106.6	109.9
	UM	100.6	103.8	109.8	96.5	99.5
	M	85.4	88.0	100.3	88.4	91.1
C30B 3.0. wt%	U	88.1	90.8	102.5	89.6	92.4
	UM	92.0	94.8	105.1	81.4	94.2

Figure 4. Plots of log{−ln[1 − X(t)]} versus log t for isothermal crystallization at 403 K of PP/nCaCO$_3$ fibre with content of 3 wt% nCaCO$_3$ with various pre-treatment methods.
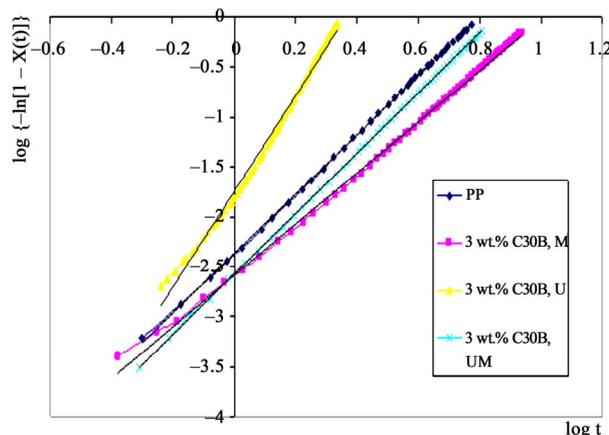
Figure 5. Plots of log{−ln[1 − X(t)]} versus log t for isothermal crystallization at 403 KC of PP/C30B fibre with content of 3 wt% C30B using various pre-treatment methods.

3.2. Mechanical Properties of PP/nCaCO₃ and PP/C30B Nanocomposite Fibres

Generally, any amount of solid particles (micro- or nano-) incorporated into a polymer, decreases the orientation of an anisotropic system of fibres or films. The solid particles impede drawingability of fibre-forming polymers during their production. The lower drawingability of PP decreases the orientation of the PP matrix of the fibres as well as their mechanical properties (**Table 4**). The data show that the mechanical properties (mainly tenacity and elongation at the break) of PP/nCaCO₃ and PP/C30B fibres are lower than for neat PP fibres.

The lowest decrease of tenacity was observed with the PP/nCaCO₃ fibres, where the additive nCaCO₃ was pre-treated simultaneously by mechanical mixing and ultra-sound. This agrees with the slowest rate of PP crystalli-zation in PP/nCaCO₃ fibres (**Tables 3** and **4**). Similar results were obtained with the PP/C30B fibres pre-treated by mechanical mixing and ultrasound, where a decrease of tenacity and Young's modulus were observed. The total decrease in mechanical properties of PP/C30B fi-bres is greater than PP containing nCaCO₃. Some de-crease of mechanical properties of PP/nCaCO₃ and PP/C30B fibres was expected because the nanocomposite

PP fibres were prepared without any compatibilizers, as is usually used [29,30]. But the limited decrease of me-chanical properties does not exclude the possibility for their practical use.

3.3. Barrier Properties against UV Radiation of PP/nCaCO₃ and PP/C30B Nanocomposite Fibres

The PP/nCaCO₃ and PP/C30B fibres were tested for the UPF parameter, which characterizes the ability of textile materials to protect human skin against UV radiation (**Table 4**). Because the nanoparticles of these additives improve the shielding properties of fibres by light beam reflection at their edges, it is expected that reduced pene-tration of harmful UV irradiation through the fibre can find practical use in certain environments. With simulta-neous pre-treatment by mechanical mixing and ultra-sonication, the nCaCO₃ nanoadditive could be converted into an effective dispersion of nanoparticles before their incorporation into the fibres. With higher content of nCaCO₃, the UV radiation beam reflection increased and so proportionally, also did the UV protection parameter. The more significant UV protection (higher UPF pa-rameter) of PP fibres was observed with the PP/nCaCO₃ fibres in comparison to PP/C30B fibres.

Table 3. Avrami parameters n, K, $t_{1/2}$, t_{max}, $\tau_{1/2}$ and end surface free energies (σ_e) of PP, PP/nCaCO₃ and PP/C30B fibres (M—mechanical mixture, U—ultrasound, UM—both simultaneously).

Type and content of nanoadditives in PP fibres	Treatment of nanoadditives	n	$K \cdot 10^3$ min^{-1}	$t_{1/2}$ min	t_{max} min	$\tau_{1/2}$ min	$\sigma_e \cdot 10^{-1}$ J·m^{-2}
PP fibres 0.0 wt%	-	2.99	4.2	5.48	5.41	0.18	23.4
nCaCO₃ 3.0.wt%	M	2.81	36.2	2.87	2.79	0.35	21.8
	U	2.65	119.2	1.91	1.85	0.52	20.3
	UM	2.84	2.9	7.00	6.82	0.14	25.0
C30B 3.0. wt%	M	2.57	2.6	8.57	8.19	0.12	25.8
	U	4.82	17.9	2.14	2.20	0.47	14.4
	UM	3.03	2.6	6.44	6.35	0.16	21.8

Table 4. Tenacity (σ) and elongation (ε) at the break, Young's modulus (E) and Ultraviolet protective factor (UPF) of PP, PP/nCaCO₃ and PP/C30B fibres (M—mechanical mixture, U—ultrasound, UM—both simultaneously).

Type and content of nanoadditives in PP fibres	Treatment of nanoadditives	σ cN·tex^{-1}	E N·tex^{-1}	ε %	UPF
PP fibres 0.0 wt%	-	24.3	2.00	163.2	9.25
nCaCO₃ 3.0. wt%	M	16.5	2.00	113.3	10.10
	U	16.8	1.76	75.4	14.47
	UM	20.1	2.00	101.5	17.98;
C30B 3.0. wt%	M	10.5	1.20	165.2	13.91
	U	12.0	1.30	31.4	8.99
	UM	12.9	1.80	55.3	12.58

4. Conclusions

- The melting temperatures for first and second heating of PP modified by C30B and nCaCO$_3$ and treated by various methods are the same as the melting temperature of pure PP fibre.
- The nCaCO$_3$ or C30B fillers pre-treated by all three methods influenced the increase of the PP crystallization temperatures in comparison with the pure PP fibres.
- The pre-treatment methods used on the nanoadditives influenced an increase of n, K, $\tau_{1/2}$ values and a decrease of $t_{1/2}$, t_{max} as well as the values of free surface energies per unit area of PP fibres modified with C30B and nCaCO$_3$.
- The use of nanofiller *i.e.* nCaCO$_3$, C30B in the fibres produced some decrease of mechanical properties of the prepared PP fibres in comparison with neat PP fibres but the decreases do not exclude the fibres from commercial use.
- Use of both, ultrasound or simultaneously mixing with ultrasound as pretreatments of the fillers gave the highest radiation barrier properties *i.e.* UPF in the fibres.

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