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Shielding Effect of Nanoadditives Against UV Radiation in Polypropylene Fibres

Abstract
The shielding effect of a nanoadditive ($CaCO_3$) against ultraviolet radiation (UVR) in polypropylene fibres was investigated. Unmodified and modified polypropylene (PP) fibres with different contents of the nanoadditive were prepared. It was investigated how the modified polypropylene fibres affect the transmission of UVR. The impact of nanoadditive treatment, the amount of nanoadditive in the fibre, and the fibre preparation was studied from the point of view of barrier properties against UVR. The different parameters which influence the transmission of UVR through fibres were observed. The thermal characteristics were evaluated by DSC measurement. The mechanical properties were also measured.

Key words: *polypropylene, nanocomposites, $CaCO_3$, ultraviolet radiation (UVR).*

Introduction

The fact that the sun's radiation can cause health problems such as sunburn or skin cancer is known in general. One possibility of how to protect our health against harmful ultraviolet radiation (UVR), mainly the skin, is to wear suitable clothes made of safety textile materials [1, 2]. The shielding properties of textile material depend on many factors that are either chemical (type, structure of fibre) or physical (warp and weft thread configuration in a given fabric) [3].

The chemical structure of fibres depends on the molecular, supermolecular and macromorphological structure. Chemical parameters also include the substances – additives, textile auxiliary agents, dyestuff etc. used in the finishing treatment [4]. In the case of dyed fibres, the absorbing properties depend on the hue of the dyes. Moreover, pigments like titanium dioxide cause opacity by scattering visible light, which is due to white pigment being able to bend light. The rest of the light is refracted, diffracted, or scattered. The greater the difference between the pigment's refractive index and that of the polymer matrix in which it is dispersed, the more the light is scattered. The refractive indexes of some additives increase in this order: calcium carbonate < clay < zinc oxide < TiO_2 [5]. The porosity, the warp and weft configuration of weave threads in a given fabric, the thickness and weight are included in the physical parameters describing fabric construction [3, 6]. These parameters are important in the case of non-dyed and unmodified fibres.

The modification of PP fibres by nanoparticles is possible to impart chemical as well as physical factors that influence their barrier properties against UVR. Chemical factors are related to the chemical structure of the nanoparticles used as well as their interaction with basic polymer and other additives. Physical factors are related to the size of particles and their dispersation in the polymer matrix, etc. To achieve suitable barrier properties against UVR, it is necessary to obtain well-dispersed nanoparticles in the PP matrix.

The ability of textile materials to protect the skin against UVR denotes the ultraviolet protection factor UPF - the higher the UPF the better barrier properties a textile material has against UVR [7]. The UPF, whose estimation is based on the measurement of the transmittance of UVR, is mostly reported for clothes and fabrics [8]. The UPF of fibres is also interesting to study. What is more, less fibre is needed for measurement of the transmittance. The preparation of knitted fabrics, woven fabrics or other textile materials is not necessary for the primary evaluation of fibres developed.

Many contemporary research works in the thermoplastic field deal with the modification of polymers by nanoadditives to improve their properties (barrier, mechanical or thermoplastics) [9 - 12]. The nanoadditives (TiO_2, $CaCO_3$, clay or ZnO) are supposed to improve barrier, mechanical and thermoplastics properties. Thus, it was interesting to modify polypropylene fibres with $CaCO_3$, which is the filler most often used, in large quantities, for the processing of PP in various applications. Besides $CaCO_3$, titanium dioxide (TiO_2) showed very good barrier properties in different materials (plastics, coatings) [13].

This work focuses on the influence of the nanoadditive $CaCO_3$ on the barrier and thermal properties of modified PP fibres. There are two different ways of preparing composite PP/$CaCO_3$ fibres. The influence of the preparation of modified PP fibres with the nanoadditive $CaCO_3$ and the content of the nanoadditive and compatibiliser in the fibre as well as in the masterbatch used for their preparation are compared in terms of the shielding effect of the nanoadditive. Therefore, the transmittance through the model fabrics was measured, and consequently the UPF, UVA and UVB were evaluated. Spectrophotometry was used as a method for measuring the transmittance. The mechanical and thermal properties of the polypropylene fibres modified were evaluated as well.

Experimental

Material used

In the preparation of the unmodified and modified PP fibres, the following materials were used: Polypropylene TG 920 (PP), MFI = 10.5 g/10 min (Slovnaft

Table 1. Composition of unmodified and modified polypropylene fibres; C - Compatibiliser.

Fibre	Content of NA in masterbatch, wt. %	Content of NA in fibre, wt. %	Content of C in fibre, wt. %
PP	0	0	0
$PP/CaCO_3/C$	5	1.5	0
		1.5	0,09
PP	0	0	0
$PP/CaCO_3$	15	1,5	0
		3,0	0

Co); $CaCO_3$ Socal U3 (NA), mean particle diameter (by permeability) = 20 nm, free flowing density = 170 g/l, specific surface = 70 m^2/g (Solvay Co), compatibiliser PP-g-MA – polypropylene grafted by maleic anhydride (Ciba Specialty), Glycerine (density = 1260 g/m^3), and acetone (density = 790 g/m^3).

Pretreatment of the nanoadditive

In order to disperse the NA in polypropylene, it was treated in a solution of glycerine and acetone with a ratio of 1:5. Then a beaker with the dispersion was put into water using ultrasound and simultaneously mixing with a stirrer. The ultrasound was supposed to help divide the aggregates of the nanoparticles.

Preparation of the masterbatch and modified fibres

The fibres modified by the nanoadditive $CaCO_3$ were prepared in two steps:

1. Preparation of masterbatches with the following contents of NA:
   - 5 wt. % of NA with/without a compatibiliser
   - 15 wt. % of NA without a compatibiliser

The masterbatches were prepared using a twin screw extruder of diameter ϕ = 16 mm. The extrusion temperature was 220 °C. Finally, the extrudates were cooled and pelletised, and the resulting pellets were mechanically mixed and used for the preparation of fibres.

2. Preparation of fibres:

The composite PP fibres modified by the nanoadditive $CaCO_3$ were prepared by melt spinning a polymer mixture of PP and the masterbatches. The mixtures were spun by a classical procedure using a laboratory pilot line with a single screw extruder of diameter ϕ = 16 mm, at a temperature of 240 °C and take up speed of 150 m. min^{-1}.

Undrawn fibres were drawn using laboratory drawing equipment at a temperature of 110°C. The composition of the fibre prepared is given in ***Table 1***. The linear density of the drawn multifilaments was T_{dt} = 21-22 dtex x f13.

Method used

Barrier properties of the unmodified and modified PP fibres

In the quantitative test spectrophotometry was used for the evaluation of the shielding effect of NA in the fibres. A Libra S12 spectrophotometer with a deuterium lamp was used for measuring the transmittance through a sample of fibre. Accordingly, the UPF factor, UVA and UVB transmittances were calculated using the Standard STN EN 13758-1:2001 for textile materials. In this case, this specification was adapted for fibres.

A sample of fibre was prepared for measurement of the transmittance in order to simulate fabric. Therefore, small frames (rectangular in shape) with an evenness of the cuts of 0.75 mm were made as a model for the preparation of model fabrics from fibres for the measurement of light transmittance. Then woven fabrics were made of fibres by hand and used as samples for measurement. When the fibre was reeled on the frame, UVR was able to go through it.

Each fibre was reeled on 7 frames, each of which was measured in 4 different vertical positions on the spectrophotometer. Statistical measurements were taken to assess the number of reelings and measurements [6].

Thermal properties of the unmodified and modified PP fibres

The thermal characteristics of the unmodified and modified PP fibres were evaluated by DSC 7 apparatus (Perkin Elmer) using the following procedure: A sample of the original fibre was heated from 70 °C to 220 °C at a rate of 10 °C·min^{-1} and then isothermally kept at 220 °C for 5 minutes. Thus, a melting endotherm of the original sample was obtained with a melting temperature T_m, and melting enthalpy ΔH_m. The sample was then cooled at a rate of 10 °C.min^{-1}, and a crystallisation exotherm of the crystallisation temperature T_c and crystallisation enthalpy ΔH_c was obtained. Subsequently, the sample was exposed to a second heating at a rate of 10 °C.min^{-1} from 70 °C to 200 °C, and the endotherm of the melting point T_m and melting enthalpy ΔH_m was determined. In all the

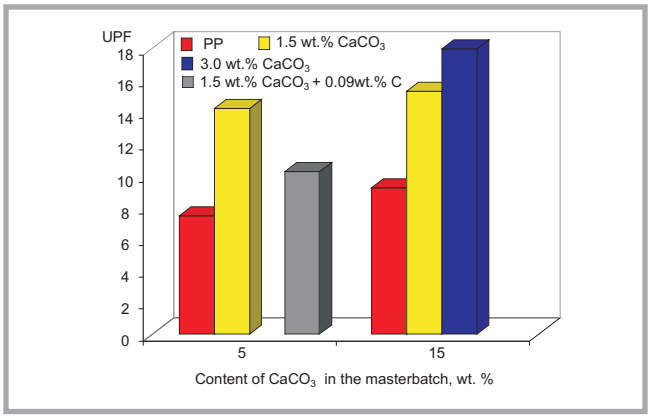

Figure 1. Dependence of UPF on the $CaCO_3$ content in masterbatches and in fibres, a comparison of fibres with/without a compatibiliser - C.

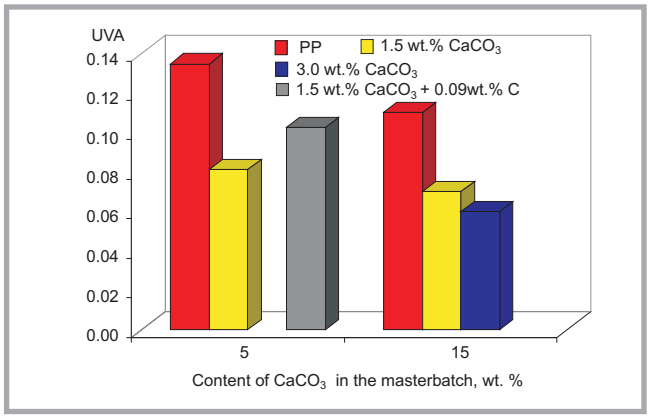

Figure 2. Dependence of UVA on the $CaCO_3$ content in masterbatches and in fibres, a comparison of fibres with/without a compatibiliser - C.

measurements, nitrogen atmosphere was used.

Mechanical properties of the unmodified and modified PP fibres

An Instron 1122 was used for evaluation of the tenacity, elongation and Young's modulus of the composite PP fibres modified with $CaCO_3$. A crosshead speed of 500 mm/min, a sample rate of 10 pts/sec and a clamping length of 12.5 cm were used in the calculation. Their coefficients of variation were calculated as well.

Results and discussion

Composite polypropylene fibres were prepared according to our previous experiments [14 - 16]. Firstly, a masterbatch with a content of $CaCO_3$ of 15 wt. % was prepared without a compatibiliser. To improve the compatibility of hydrophobic PP and the inorganic nanoadditive, a compatibiliser was used in the next preparation of fibres. Thus, a masterbatch with a content of $CaCO_3$ of 5 wt. % and addition of a compatibiliser was prepared in order to obtain better mechanical properties, such as the better dispersion of $CaCO_3$ in polypropylene fibre and ultimately a better shielding effect of $CaCO_3$ against UVR. In the case of $CaCO_3$ of 15 wt. % in the masterbatch, fibres with a content of $CaCO_3$ of 1.5 and 3 wt. % were prepared. From the masterbatch with a content of $CaCO_3$ of 5 wt. %, only fibres with a maximum content of $CaCO_3$ of 1.5 wt. % could be prepared.

The shielding effect of the nanoadditives in modified PP and unmodified polypropylene fibres was evaluated according to the standard specification for textile materials [7]. Instead of textile material, fibre was used for measurement of the transmittance of ultraviolet radiation. The main advantage of using fibres is that less fibre is needed for measurement - it is not necessary to prepare knitted or woven fabric, or other textile material. The number of measurements for one sample was estimated statistically.

The values of UPF and UVA measured are shown in ***Figures 1*** and ***2***. $CaCO_3$ can inhibit the transmission of radiation through textile material in various ways: The radiation can be absorbed, refracted, diffracted or scattered depending on the chemical structure of the $CaCO_3$ and on the quality of the dispersion of its particles. If the particles are more dispersed

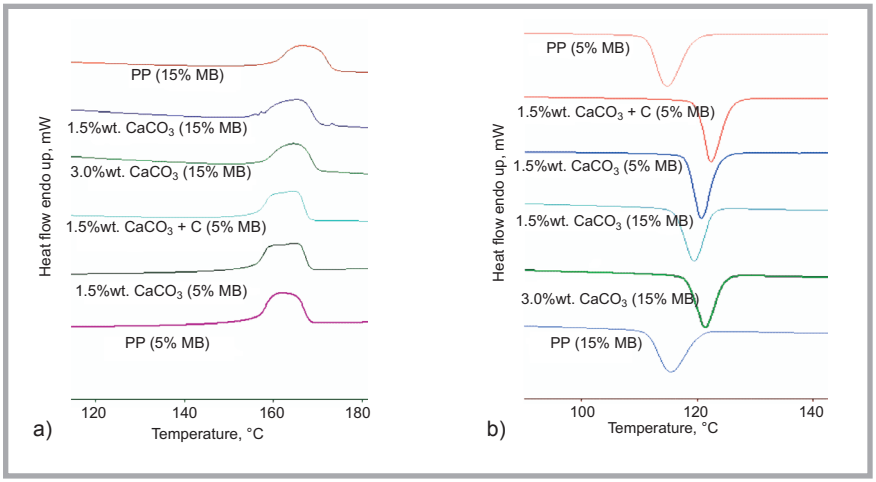

Figure 3. *DSC thermograms of the unmodified and modified PP fibres from the 1st heating (a) and cooling (b), 5% MB – 5 wt. % $CaCO_3$ in the masterbatch, 15% MB - 15 wt.% $CaCO_3$ in the masterbatch, C – compatilbiliser.*

Table 2. *Melting (T_m) and crystallization (T_c) temperatures of unmodified PP and modified PP/$CaCO_3$ (with/without a compatibiliser) fibres obtained in the 1st heating (T_{m1}), cooling and 2nd heating (T_{m2}) - heating and cooling rates = 10 °C.min^{-1}, C - compatibiliser.*

Composition of fibres	Content of $CaCO_3$, wt. %		T_{m1}, °C	T_c, °C	T_{m2}, °C
	in masterbatch	in fibre			
PP	15	0	163.1	114.2	162.9
PP/$CaCO_3$		1.5	165.7	119.5	163.9
		3.0	164.7	121.3	164.2
PP	5	0	161.8	114.8	162.0
PP/$CaCO_3$		1.5	160.0 164.8	120.6	163.5
PP/$CaCO_3$+C		1.5	160.5 164.5	122.5	163.9

in the PP matrix, they can decrease UVA and UVB transmittances through textile materials. Moreover, a higher amount of $CaCO_3$ can form a more continuous layer in the PP matrix of fibres and increase the UPF of modified fibres. The UPF (relating to UVA, UVB) of PP fibres modified by $CaCO_3$ and prepared from a masterbatch with different $CaCO_3$ contents is higher than that of unmodified PP fibres. The higher UPF of modified PP fibres was also due to the higher $CaCO_3$ content. The different $CaCO_3$ contents in the masterbatch (5 or 15 wt. %) from which modified PP fibres with the same content of $CaCO_3$ were prepared do not affect the UPF or UVA (***Figures 1, 2***). In contrast, the addition of a compatibiliser, which improved the processability of modified PP fibres, decreases the UPF (but increases the transmissions of UVA and UVB).

Thermal characteristics were evaluated to establish any correlation between the UPF and the crystallinity/melting enthalpy. The thermal behaviour of semicrystalline modified PP fibres depends on the $CaCO_3$ additive used as well as on the conditions of their preparation or treatment. All the endotherms of un-modified and PP fibres modified by $CaCO_3$, obtained in the first heating (break up of the anisotropic system), have one remarkable wide peak at a melting temperature of about 164 - 165.7 °C (***Figure 3.a***). These temperatures correspond to the melting temperature of the α–modification of pure PP formed during the spinning and drawing processes, which is the most stable modification (***Tables 2, 3***). The crystallisation temperatures of modified fibres also increase with a rise in $CaCO_3$ content in comparison with unmodified PP fibre.

The crystallisation ability of PP is usually influenced by a change in preparation conditions as well as by the compounds added, such as modifiers, pigments, stabilisers, etc. An increase or decrease in the crystallisation ability of PP can be due to the chemical structure, the size of particles or the quality of their dispersion in the PP matrix. The nanoadditives currently used for the modification of polymers to improve their various properties still have a more special and complicated effect on the crystallisation of PP [10,17]. $CaCO_3$ induces an increase

Table 3. *Melting enthalpies of unmodified PP and modified PP/$CaCO_3$ (with/without a compatibiliser) fibres obtained in the 1st (ΔH_{m1}) and 2nd (ΔH_{m2}) heating - heating and cooling rates = 10°C.min-1, C - compatibiliser.*

Composition of fibres	Content of $CaCO_3$, wt. %		ΔH_{m1}, °C	ΔH_{m2}, °C
	in masterbatch	in fibre		
PP	15	0	99.3	100.9
PP/$CaCO_3$		1.5	99.7	105.9
		3.0	100.6	96.5
PP	5	0	96.5	95.6
PP/$CaCO_3$		1.5	106.7	107.1
PP/$CaCO_3$+C		1.5	102.3	94.2

Table 4. *Mechanical properties – tenacity, elongation and Young's modulus - of unmodified and modified PP/$CaCO_3$ fibres, C - compatibiliser.*

Composition of fibres	Content of $CaCO_3$, % wt.		Tenacity, cN/tex	Elongation, %	Young's Modulus, N/tex
	in masterbatch	in fibre			
PP	15	0	24.3	163	1.9
PP/$CaCO_3$		1.5	22.1	146	2.3
		3.0	20.1	102	2
PP	5	0	25.1	151	2
PP/$CaCO_3$		1.5	24.1	122	2.5
PP/$CaCO_3$+C		1.5	25.2	153	2

in the crystallisation ability of PP in anisotropically modified PP fibres without a compatibiliser. This is confirmed by the higher melting enthalpies of PP in these systems, which grow with an increase in $CaCO_3$ content. In contrast, a compatibiliser, which was added to modified PP/$CaCO_3$ for the improvement of processability during fibre preparation, reduces the effect of $CaCO_3$ on the crystallisation ability of PP (***Table 3***).

Similar results were also obtained in the evaluation of the isotropic PP/$CaCO_3$ system in the 2nd heating.

The physical-mechanical properties, such as the tenacity, elongation and Young's modulus of PP/$CaCO_3$ fibres, are shown in ***Table 4***. The increase in the crystallisation ability of PP due to the change in the supermolecular structure also influences the physical-mechanical properties of the fibres observed. The higher the content of $CaCO_3$ the lower the tenacity and elongation of the fibres. The positive effect of a compatibiliser on the processability of the fibres prepared was confirmed by the tenacity of the PP/$CaCO_3$ fibres obtained when compared with the tenacity of PP fibres. It was found that the Young's modulus of PP/$CaCO_3$ fibres does not decrease even after one addition of 1.5% wt. of $CaCO_3$ without a compatibiliser.

All the properties of PP/$CaCO_3$ fibres prepared from masterbatches with 5 wt. % $CaCO_3$ are better than those of PP/$CaCO_3$ fibres prepared from masterbatches with 15 wt. % $CaCO_3$. The shielding effect of the nanoadditive $CaCO_3$ was also confirmed in the fibres. In the conditions of preparation used, a lower amount of $CaCO_3$ would be better for the preparation of masterbatches and resulting fibres.

Summary

1. From the results obtained we can stated that the nanoadditive $CaCO_3$ has a positive effect on the UPF of modified PP fibres in comparison with unmodified PP; the higher content of $CaCO_3$, the better the shielding effect of fibres.
2. The nanoadditive $CaCO_3$ increases the crystallisation temperature of the fibres modified, which correlates with the UPF of these fibres.
3. $CaCO_3$ increases the crystallisation ability of PP in the PP fibres modified in comparison with unmodified polypropylene.
4. A compatibiliser improves the physical-mechanical parameters of modified PP/$CaCO_3$ fibres as well the processability and dispersation of NA in the PP matrix.

Acknowledgments

The support of the National Grant Agency of Slovakia APVV-20-011401 is greatly appreciated.

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Received 27.03.2008 Reviewed 02.12.2008

Institute of Biopolymers and Chemical Fibres

Biocomposites Containing Feather Keratin




A Scientific Team from the Institute of Biopolymers and Chemical Fibres in Łódź, Poland, used chicken feathers to produce modern composite materials of a wide application spectrum. The invention is protected by the following patent and patent application:

- Polish Pat. PL 193736: **Method for the Manufacture of Fibres, Films, Fibrids and Other Microcrystalline Products from Feathers**.
- Polish Pat. Appl. 386 554 (20.11.2008): **Paper-like Products Made from Chicken Feathers Keratin**.

One group of biocomposites is **modified with feather keratin fibrous materials** in the form of **fibres** and **sponges** made of chitosan, cellulose and alginate. Keratin-enriched biocomposites have better sorptive and biostatic properties, however they do not have irritating no allergenic properties.

The other especially interesting group are novel **paper-like keratin/cotton composites** produced by paper processing methods.

The main properties of the composite are as follows:

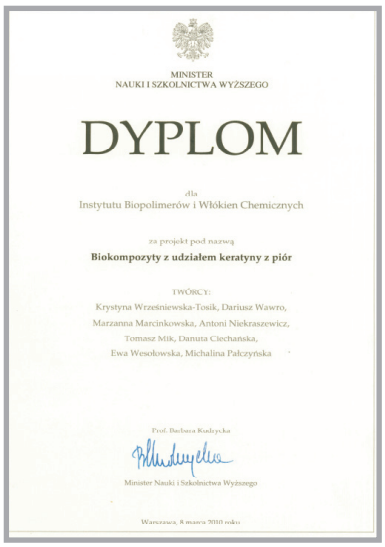
- made of natural raw materials (chicken feather, cotton)
- made of waste not managed until today
- indicates pH 7
- resistant to the action of water
- biodegradable
- bioactive
- lower flammability

Applications of "keratin paper":

- base for artistic painting
- base for surface coating (with resin, varnish, paint)
- shoe insoles
- printing paper
- photocopying paper
- producing different paper products
- available in every grammage

For the invention entitled "**Biocomposites Containing Feather Keratin**", the authors of which are **Krystyna Wrześniewska-Tosik, Dariusz Wawro, Marzanna Marcinkowska, Antoni Niekraszewicz, Tomasz Mik, Danuta Ciechańska, Ewa Wesołowska and Michalina Pałczyńska**, the Scientific Team received the following prestigious awards and distinctions:

- Gold Medal - The Belgian And International Trade Fair For Technological Innovation, BRUSSELS INNOVA 2009
- Gold Medal - The 6th Taipei International Show & Technomart (Taipei INST 2010, Sep. 30 - Oct. 3)
- Bronze Medal - CONCOURS LEPINE LE SALON INTERNATIONAL DE L'INVENTION DE PARIS "CONCOURS – LEPINE" 2010, Paris
- Award of the Minister of Science and Higher Education, Warsaw 2010
- Prize of Paul Magnette, Belgian Minister of Climate and Energy, BRUSSELS INNOVA 2009 Institute of Biopolimers and Chemical Fibres



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