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 related either to chemical (type, structure of fibre) or physical (warp and weft configuration in a given fabric) properties [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 < TiO₂ [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 dispersion 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 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.

This work focuses on the influence of the nanoadditive CaCO₃ on the barrier and thermal properties of modified PP fibres. There are two different ways of preparing composite PP/CaCO₃ fibres. The influence of the preparation of modified PP fibres with the nanoadditive CaCO₃ 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.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Content of NA in masterbatch, wt. %</th>
<th>Content of NA in fibre, wt. %</th>
<th>Content of C in fibre, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PP/CaCO3/C</td>
<td>5</td>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>PP</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PP/CaCO3</td>
<td>15</td>
<td>1.5</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Co); CaCO₃ Socal U3 (NA), mean particle diameter (by permeability) = 20 nm, free flowing density = 170 g/l, specific surface = 70 m²/g (Solvay Co), compatibiliser PP-g-MA – polypropylene grafted by maleic anhydride (Ciba Specialty), Glycerine (density = 1260 g/m³), and acetone (density = 790 g/m³).

Preparation of the masterbatch and modified fibres

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, 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 Tₐₖ = 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 Tₘ and melting enthalpy ΔHₘ. The sample was then cooled at a rate of 10 °C.min⁻¹, and a crystallisation exotherm of the crystallisation temperature Tₖ and crystallisation enthalpy ΔHₖ 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 enthalpy of the melting point Tₘ and melting enthalpy ΔHₘ was determined. In all the
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 CaCO₃. 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 CaCO₃ of 15 wt. % was prepared without a compatibiliser. To improve the compatibility of hydrophobic PP and the inorganic nanoaditive, a compatibiliser was used in the next preparation of fibres. Thus, a masterbatch with a content of CaCO₃ of 5 wt. % and addition of a compatibiliser was prepared in order to obtain better mechanical properties, such as the better dispersion of CaCO₃ in polypropylene fibre and ultimately a better shielding effect of CaCO₃ against UVR. In the case of CaCO₃ of 15 wt. % in the masterbatch, fibres with a content of CaCO₃ of 1.5 and 3 wt. % were prepared. From the masterbatch with a content of CaCO₃ of 5 wt. %, only fibres with a maximum content of CaCO₃ of 1.5 wt. % could be prepared.

The shielding effect of the nanoaditives 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. CaCO₃ 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 CaCO₃ and on the quality of the dispersion of its particles. If the particles are more dispersed in the PP matrix, they can decrease UVA and UVB transmittances through textile materials. Moreover, a higher amount of CaCO₃ can form a more continuous layer in the PP matrix and increase the UPF of modified fibres. The UPF of modified fibres was also higher than that of unmodified PP fibres. The higher UPF of modified PP fibres also increased with a rise in CaCO₃ content in comparison with unmodified PP fibre.

![Figure 3. DSC thermograms of the unmodified and modified PP fibres from the 1st heating (a) and cooling (b), 5% MB – 5 wt. % CaCO₃ in the masterbatch, 15% MB - 15 wt.% CaCO₃ in the masterbatch, C – compatibiliser](image)

**Table 2. Melting (Tₘ) and crystallization (Tₜ) temperatures of unmodified PP and modified PP/CaCO₃ (with/without a compatibiliser) fibres obtained in the 1st heating (Tₘ₁), cooling and 2nd heating (Tₘ₂) - heating and cooling rates = 10 °C.min⁻¹, C – compatibiliser.**

<table>
<thead>
<tr>
<th>Composition of fibres</th>
<th>Content of CaCO₃ wt. % Tₘ₁, °C</th>
<th>Tₜ, °C</th>
<th>Tₘ₂, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP/CaCO₃</td>
<td>15.0</td>
<td>163.1</td>
<td>114.2</td>
</tr>
<tr>
<td>PP/CaCO₃+C</td>
<td>1.5</td>
<td>165.7</td>
<td>119.5</td>
</tr>
<tr>
<td>PP</td>
<td>3.0</td>
<td>164.7</td>
<td>121.3</td>
</tr>
<tr>
<td>PP/CaCO₃</td>
<td>0.0</td>
<td>161.8</td>
<td>114.8</td>
</tr>
<tr>
<td>PP/CaCO₃+C</td>
<td>1.5</td>
<td>160.0</td>
<td>164.8</td>
</tr>
<tr>
<td>PP</td>
<td>1.5</td>
<td>160.5</td>
<td>164.5</td>
</tr>
</tbody>
</table>

The higher UPF of modified PP fibres also increase with a rise in CaCO₃ 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 nanoaditives 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]. CaCO₃ induces an increase...
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 CaCO3 content. In contrast, a compatibiliser, which was added to modified PP/CaCO3 for the improvement of processability during fibre preparation, reduces the effect of CaCO3 on the crystallisation ability of PP (Table 3).

Similar results were also obtained in the evaluation of the isotropic PP/CaCO3 system in the 2nd heating.

The physical-mechanical properties, such as the tenacity, elongation and Young’s modulus of PP/CaCO3 fibres, are shown in Table 4. The increase in the crystallisation ability of PP due to the change in the supramolecular structure also influences the physical-mechanical properties of the fibres observed. The higher the content of CaCO3 the lower the tenacity and elongation of the fibres. The positive effect of a compatibiliser on the processability of the fibres was confirmed by the tenacity of the PP/CaCO3 fibres obtained when compared with the tenacity of PP fibres. It was found that the Young’s modulus of PP/CaCO3 fibres does not decrease even after one addition of 1.5% wt. of CaCO3 without a compatibiliser.

All the properties of PP/CaCO3 fibres prepared from masterbatches with 5 wt. % CaCO3 are better than those of PP/CaCO3 fibres prepared from masterbatches with 15 wt. % CaCO3. The shielding effect of the nanoadditive CaCO3 was also confirmed in the fibres. In the conditions of preparation used, a lower amount of CaCO3 would be better for the preparation of masterbatches and resulting fibres.

**Summary**

1. From the results obtained we can state that the nanoadditive CaCO3 has a positive effect on the UPF of modified PP fibres in comparison with unmodified PP; the higher content of CaCO3, the better the shielding effect of fibres.
2. The nanoadditive CaCO3 increases the crystallisation temperature of the fibres modified, which correlates with the UPF of these fibres.
3. CaCO3 increases the crystallisation ability of PP in the PP fibres modified in comparison with unmodified polypropylene.
4. A compatibiliser improves the physical-chemical parameters of modified PP/CaCO3 fibres as well the processability and dispersion 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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**Table 3.** Melting enthalpies of unmodified PP and modified PP/CaCO3 (with/without a compatibiliser) fibres obtained in the 1st ($\Delta H_m1$) and 2nd ($\Delta H_m2$) heating - heating and cooling rates = 10°C.min$^{-1}$, C - compatibiliser.

<table>
<thead>
<tr>
<th>Composition of fibres</th>
<th>Content of CaCO3, wt. % in masterbatch</th>
<th>Content of CaCO3, wt. % in fibre</th>
<th>$\Delta H_m1$, °C</th>
<th>$\Delta H_m2$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>0</td>
<td>99.3</td>
<td>100.9</td>
<td></td>
</tr>
<tr>
<td>PP/CaCO3</td>
<td>15</td>
<td>99.7</td>
<td>105.9</td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>3.0</td>
<td>100.6</td>
<td>96.5</td>
<td></td>
</tr>
<tr>
<td>PP/CaCO3</td>
<td>5</td>
<td>96.5</td>
<td>95.6</td>
<td></td>
</tr>
<tr>
<td>PP</td>
<td>0</td>
<td>106.7</td>
<td>107.1</td>
<td></td>
</tr>
<tr>
<td>PP/CaCO3</td>
<td>1.5</td>
<td>102.3</td>
<td>94.2</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.** Mechanical properties – tenacity, elongation and Young’s modulus - of unmodified and modified PP/CaCO3 fibres, C - compatibiliser.

<table>
<thead>
<tr>
<th>Composition of fibres</th>
<th>Content of CaCO3, % wt. in masterbatch</th>
<th>Tenacity, cN/tex</th>
<th>Elongation, %</th>
<th>Young’s Modulus, N/tex</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>0</td>
<td>24.3</td>
<td>163</td>
<td>1.9</td>
</tr>
<tr>
<td>PP/CaCO3</td>
<td>15</td>
<td>22.1</td>
<td>146</td>
<td>2.3</td>
</tr>
<tr>
<td>PP</td>
<td>3.0</td>
<td>20.1</td>
<td>102</td>
<td>2</td>
</tr>
<tr>
<td>PP/CaCO3</td>
<td>5</td>
<td>25.1</td>
<td>151</td>
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<tr>
<td>PP/CaCO3</td>
<td>1.5</td>
<td>24.1</td>
<td>122</td>
<td>2.5</td>
</tr>
<tr>
<td>PP/CaCO3</td>
<td>1.5</td>
<td>25.2</td>
<td>153</td>
<td>2</td>
</tr>
</tbody>
</table>

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**References**


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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.

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 or 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 Palczyńska, 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)
- 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 Biopolymers and Chemical Fibres

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