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Modification of Textile Materials with Micro- and Nano-Structural Metal Oxides

Abstract
Nanotechnology offers the possibility of rendering textiles certain properties which protect humans and their natural environment. Nano-particles of metal oxides – titanium oxide (TiO_2) and zinc oxide (ZnO) – belong to a group of compounds showing photocathalytic properties i.e, the ability to absorb UV radiation and antibacterial properties. The aim of this research work, carried out by the Textile Research Institute, was the development of nano-structural textile composites with barrier properties. In the first stage of the research, the morphology and micro-structure of titanium dioxide before and after modification with aminosilane were determined at the Institute of Technology and Chemical Engineering at Poznań University of Technology. Further works focused on the development of: compositions of optimal dispersion containing ZnO and TiO_2 nano-particles and the methodology of nano-particle incorporation into selected textile substrates. Antibacterial properties were evaluated using the gram positive bacteria Staphylococcus aureus and the gram negative bacteria Escherichia coli. The evaluation also concerned the ability to block UV radiation by textile materials modified with nano-particles of metal oxides. The works performed proved the possibility of manufacturing a new generation of textile nano-composites with barrier properties against UV radiation and bacterial development.

Key words: *nano-oxides, textile substrates, UV barrier properties, antibacterial properties.*

Introduction

Novel materials, including textiles for specific applications, have to satisfy consumers' growing demands. Due to various applications, wearing and also economic aspects, it is necessary that a material should perform several functions. Intensive development of nanotechnology in the area of micro- and nano-structure generation offers the possibility of creating novel textile materials with protective properties for humans and their natural environment.

Nanoparticles of metal-oxides: titanium (TiO_2) and zinc (ZnO) belong to a group of compounds with photo-catalytic properties, which are able to absorb UV radiation (Wang R. et al. [1] ; Imai Hiroshi [2]) and provide an antibacterial barrier. Zinc oxide has been used in pharmacy for many years. It is a constituent of antiseptic pastes, ointments and dusting powders, where it has anti-inflammatory and anti-bacterial effects. Titanium dioxide and zinc oxide – micronised or in a nanoparticle form – are used in cosmetics as substances absorbing UV radiation. They provide a high level of blocking UV-A and UV-B radiation in a full wavelength from 290 to 400 nm. Nano-crystals of titanium dioxide have the ability to absorb ultraviolet range radiation, at the same time generating an energy which initiates chemical reactions. Particles of dirt of organic origin, which are present in the surroundings of TiO_2 nano-crystals, acting as a photo-catalyst, are oxidised.

In literature there are known processes of TiO_2 modification. Titanium white is subjected to surface processing in order to improve its insufficient refractoriness to weather conditions, as well as its whiteness and dispersion. The processing mainly includes stabilisation (Sales et al. [3], Pownceby et al. [4]), involving the introduction of other elements to its crystallic lattice (Tsuji et al. [5]), and surface modification (Esumi et al. [6, 7], Innocenzi et al. [8], Shirai et al. [9], Andrzejewska et al.[10], Jesionowski et al. [11-13]), aimed at altering its physicochemical properties. The most frequently applied modifiers include silane, titanate, and zirconate coupling agents, as well as fatty acids, their derivatives and surfactants.

In this research work we also performed TiO_2 modification. Modified TiO_2 was then incorporated into a textile substrate.

The functionalisation of textile fabrics has aroused the interest of many European research centres. A few publications indicate the possibility of rendering textile fabrics properties which protect against UV radiation, the growth of microorganisms and which offer photo-catalytic action by the modification process using nano-structural metal oxides (Beringer J. et al. [14], Daoud W.A. et al. [15], Reinert et al. [16]).

The main aim of these research works was the development of nano-structural textile composites with barrier properties, protecting against UV radiation and bacterial growth. In the first stage the works focused on:
- the development of suitable compositions of dispersions containing ZnO and TiO_2 nanoparticles,
- the process of TiO_2 modification with aminosilane,
- the methodology of nanoparticle incorporation into selected textile substrates.

Experimental part

Methodology

Materials used in tests

Textile fabrics
- polyester woven fabric, mass per unit area = 100 g/m^2

- polyester woven fabric subjected to alkali pre-treatment, mass per unit area = 97 g/m^2
- cotton woven fabric, mass per unit area = 140 g/m^2
- polyester nonwoven produced according to the spunlace technique (water jet), mass per unit area = 100 g/m^2

Chemical agents

- zinc oxide – nanoparticles – average particle size = 60 nm – NANOX 200 (prod. Elementis Specialities)
- titanium dioxide – TYTANPOL R-003 (prod. Police S.A., Szczecin, PL), average particle size = 459 nm
- titanium dioxide modified by aminosilane – TK 62, average particle size = 295 nm
- polyethylene glycol (PEG), average molar mass = 600 g/mol, LIPOXOL 600 (prod. Sasol)
- hydroxyethylcellulose (HEC) – of low molecular mass, CELLOSIZE QP40 (prod. Dow)

Methods of evaluation of modified textile fabrics

* *Antibacterial activity assessment of textile fabrics* (according to the diffusion method AATCC test method 147 – 1998) In this research work bacterial test strains of *Staphylococcus aureus* ATCC 6538 and *Escherichia coli* ATCC 8739 were used. They were cultivated in a liquid Nutrient Broth for 24 hours at a temperature of 37 °C. The bacteria dispersion obtained was used in the assessment of the bactericidal activity of the above-mentioned samples of textile fabric. The antibacterial properties of the textile fabrics tested were evaluated by the diffusion method. On the surface of the agar medium, Nutrient Broth streak inoculation of the bacteria was performed (distance between streaks – 1 cm). Then, the textile samples (size 2.5 x 3.5 cm) were placed on the agar surface and incubated at a temperature of 37 °C for 24-49 hours. Evaluation of the antibacterial properties was made on the basis of:

- the presence and size of the inhibition zone of microorganism growth around the textile sample tested,
- bacterial growth in the contact zone of the textile sample tested with culture media (growth description: none, slight, moderate, heavy). The evaluation range of antibacterial performance is three rate: good effect, limited efficacy, insufficient effect.

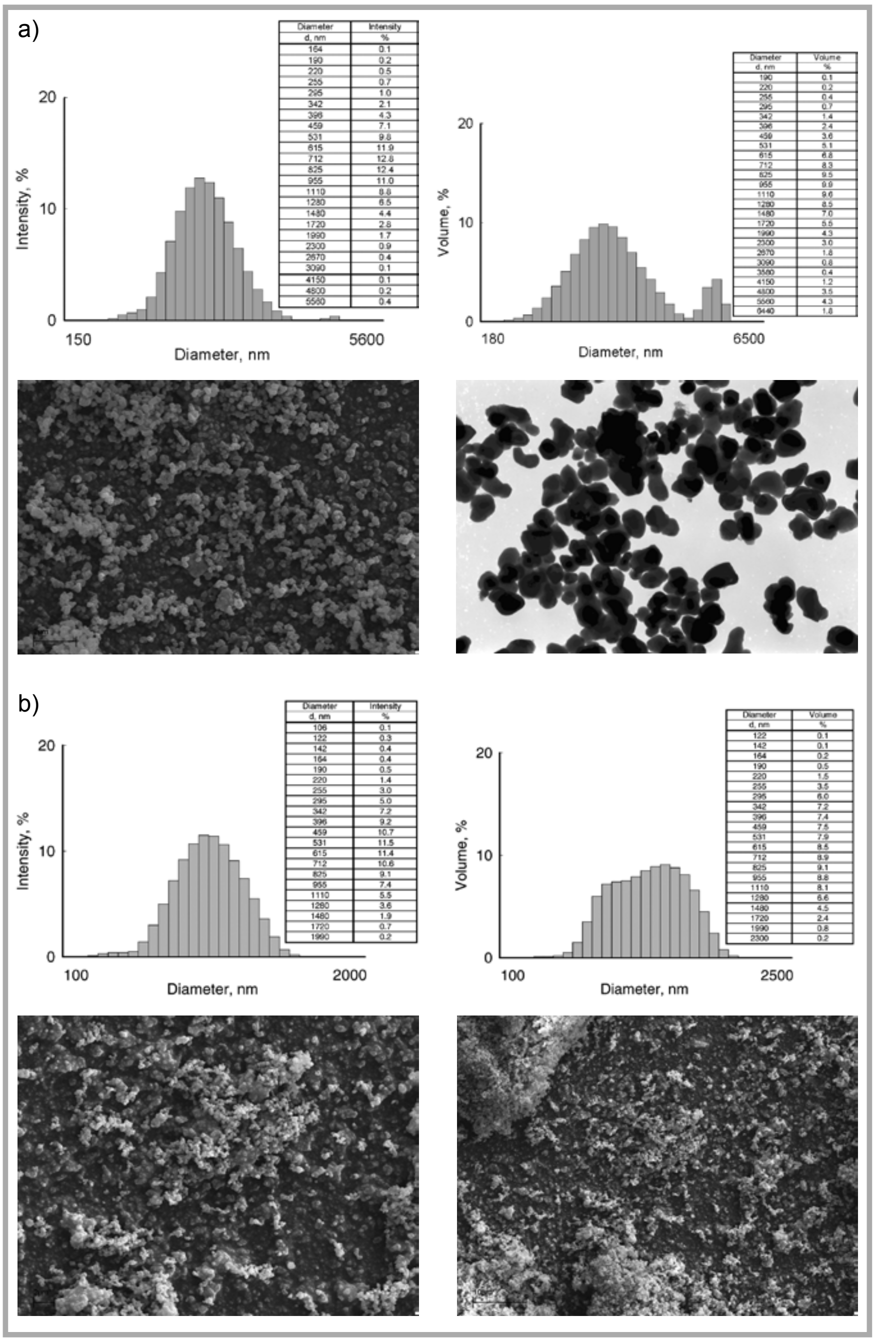

Figure 1. *Particle size distribution and SEM photos – a and b:* ***a.*** *TYTANPOL R- 003,* ***b.*** *TK.*

Microbiological tests were performed at the Institute of Fermentation Technology and Microbiology at the Technical University of Lodz.

* *Determination of the protective properties of textile fabrics against UV radiation*

- absorption spectra of the textile fabric samples were determined using the double beam type of UV-VIS Jasco V-550 (prod. Jasco, Japan) with integrating sphere attachement
- the same apparatus was used to determine the Ultraviolet Protection Factor (UPF) of textile fabrics, according to Standard: PN-EN 13758-1:2002

$$UPF = \frac{\sum_{\lambda=290}^{\lambda=400} E(\lambda)\varepsilon(\lambda)\Delta\lambda}{\sum_{\lambda=290}^{\lambda=400} E(\lambda)T(\lambda)\varepsilon(\lambda)\Delta\lambda} \quad (1)$$

where:

E (λ) – the solar irradiance,
ε (λ) – the erythema action spectrum,
Δ λ – the wavelength interval of the measurements,
T (λ) – the spectral transmittance at wavelength λ.

The UPF value of the textile fabric was determined as the arithmetic mean of the UPF values for each of the samples, reduced by the statistical value depending on the number of measurements performed, at a confidence interval of 95%

* *Microstructure evaluation of modified textile fabrics*

Evaluation of the microstructure of textile fabrics covered with nano-structural zinc oxide and titanium dioxide was performed using high-resolution scanning microscopy – Zeiss Leo 1530. This work was done at the Faculty of Materials Science and Engineering at Warsaw Technical University.

Modification of titanium white (TiO_2)

The surface modification of TiO_2 was conducted by the so-called dry technique, by applying 0.5, 1.0 or 3.0 weight parts of *N*-2-(aminoethyl)-3-aminopropyltrimetho-xysilane, prepared in methanol/water solution (4:1), for a 40 g sample of titanium dioxide. The samples obtained in this way were dried at a temperature of 105 °C in order to evaporate the solvent.

Titanium white (TiO_2) – morphology and microstructure study

The dispersion analysis of unmodified and silane-functionalised TiO_2 involved the determination of particle size – a parameter of principal importance for definition of the activity of the powders obtained. The assessment of TiO_2 dispersion was done using SEM and a transmission electron microscope (TEM) – type JEM 1200 EX2 (prod. Japan).

Particle size distribution was established using Zetasizer Nano ZS (Malvern Instruments Ltd.) using the non-invasive back scattering method (NIBS). Particle size distribution was performed with reference to intensity and volume – see ***Figure 1a and b*** (see page 113). The particle size distribution permitted us to determine polydispersity as an exponent of the uniformity of titanium dioxide.

The modification of textile fabrics using nano-structural oxides of zinc and titanium (ZnO and TiO_2)

Laboratory tests of modifying polyester woven, nonwoven fabrics and cotton woven fabric with nano-structural zinc and titanium oxides were carried out. Aqueous suspensions containing 1 part by weight of hydroxyethylcellulose (HEC) and 10 parts by weight of polyethylene glycol (PEG) were prepared using a homogenizer (mixing rate: 20000 rpm, time: 60 s). In such a medium 10 or 15% of the nano-ZnO was suspended.

Aqueous suspensions of PEG and HEC of nano-ZnO were introduced onto selected textile substrates by the dip-coating method. Then the samples were squeezed by rollers at a nip pressure of 30 kG/cm and dried at a temperature of 100 °C for 10 minutes. Depending on the type of textile substrate, the level of nano-ZnO deposition after sample drying was from 4.2 to 11.6% ww. for polyester and from 8.8 to 13.8% ww. for cotton.

Dispersions of non-modified titanium dioxide and modified aminosilane TiO_2 (1%) in aqueous suspensions of PEG and HEC (prepared in a similar way to the dispersions above) were introduced according to the dip-coating method onto polyester nonwoven and onto polyester woven fabric after alkali pre-treatment.

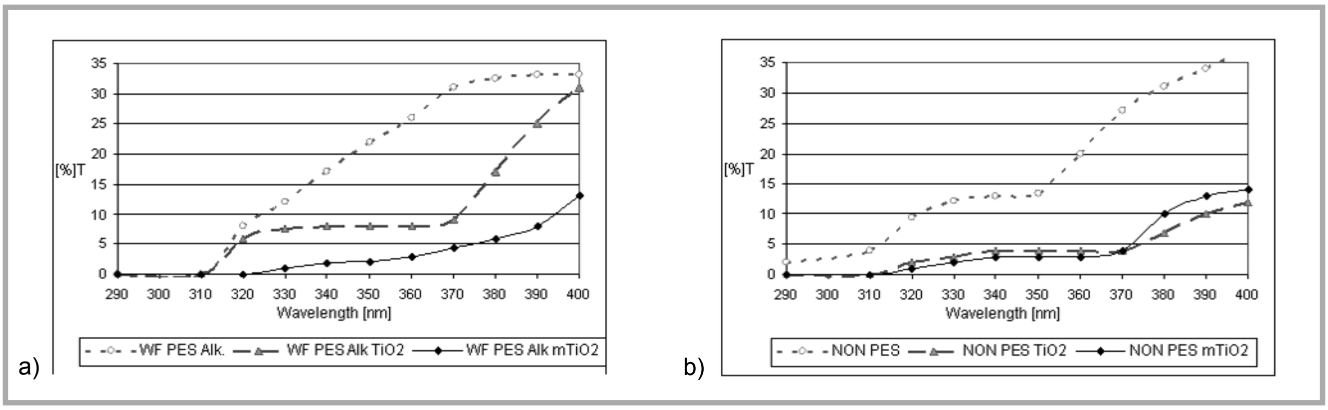

Figure 2. *Transmittance spectrum in the range λ = 290-400 nm – samples of polyester woven (a) and nonwoven fabrics (b) with TiO_2 incorporated.*

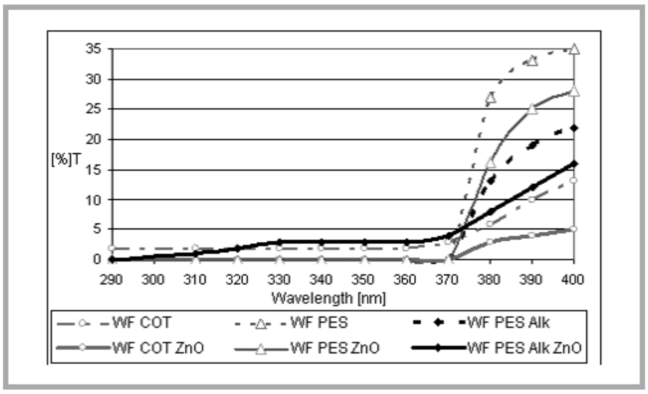

Figure 3. *Transmittance spectrum in the range λ=290-400 nm – samples of woven fabrics made of cotton or polyester fibers with nano-ZnO incorporated.*

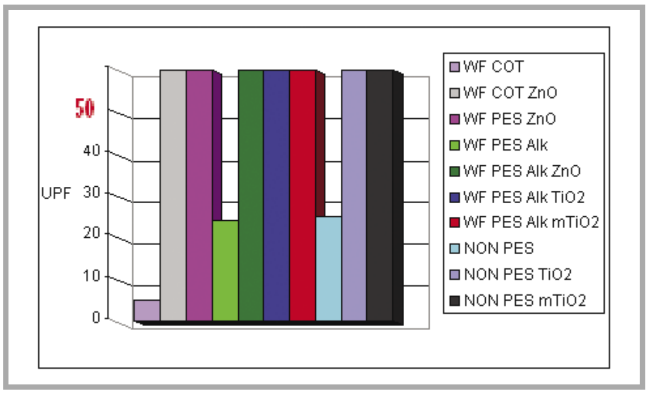

Figure 4. *UPF values of woven and nonwoven fabric samples with TiO_2 and nano-ZnO incorporated.*

Then the samples were squeezed by rollers at a nip pressure of 30 kG/cm and dried at a temperature of 100 °C for 10 minutes. Depending on the type of textile substrate, the level of TiO_2 deposition after sample drying was from 0.3 to 1.6% ww.

Results and discussion

The padding of ZnO and TiO_2 nanostructural forms onto polyester and cotton textiles decreases the transmittance values of the samples in the UV range when compared to control samples (without modification).

Figures 2 and 3 compare transmittance spectra of woven (cotton and polyester) and nonwoven (polyester) textiles: ZnO and TiO_2 modified with those non-modified. Nanostructural forms of compounds padded onto a sample surfaces strongly absorb UV radiation, which, as a consequence, causes low transmittance of UV radiation observable on the spectra of modified samples.

Samples modified with nanoZnO and TiO_2 obtain a UPF value > 50 ***(Figure 4)***, calculated on the basis of transmittance measurements for λ = 290-400 nm (according to Formula 1). This result indicates that the modification performed imparts proper barrier properties against UV radiation according to PN-EN 13758-1:2002.

The highest absorption of UV radiation was observed in polyester woven fabric after alkali pre-treatment, modified using nano-structural ZnO and modified aminosilane TiO_2.

Microstructural assessment of nano-ZnO and TiO_2 modified textile fabrics was performed using SEM. SEM observation was also performed for all the control textile fabric samples (without modification) including polyester woven fabric without alkali pre-treatment and after alkali pre-treatment. This examination indicated that the structure of polyester woven fabric after alkali pre-treatment gets looser (mass loss) when compared to polyester woven fabric without alkali pre-treatment. This fact explains the higher ability to absorb nano-ZnO by polyester woven fabric after alkali pre-treatment, eg.:

dispersion: 10% nano-ZnO	level of nano-ZnO deposition
Woven fabric PES	4.63 % ww.
Woven fabric PES/alk	6.85 % ww.

dispersion:15% nano-ZnO	level of nano-ZnO deposition
Woven fabric PES	7.6 % ww.
Woven fabric PES/alk	10.82 % ww.

Higher penetration of nano-ZnO into polyester woven fabric after alkali pre-treatment was also observed ***(Figures 5, 6,*** see page 116).

The Photos ***(Figures 7, 8,*** se page 116) present polyester woven fabric modified with TiO_2 after alkali pre-treatment. These photos show the uniform covering of fibres by TiO_2. Fibres bonded with TiO_2 can be observed as well.

The impacts of modified textile fabric samples on bacteria *Staphylococcus aureus ATCC 6538* are presented in ***Table 1***, while ***Table 2*** presents the effects on *Escherichia coli ATCC 8739*.

Non-modified samples of polyester, cotton woven fabrics as well as polyester

Table 1. *Textile fabrics – evaluation of antibacterial activity towards Staphylococcus aureus ATCC 6538.*

Sample type	Evaluation of bacteria growth		Textile fabrics
	inhibition zone	bacterial growth under specimens	bio-active performance
Woven fabric PES/alk (control)	0	heavy	insufficient effect
Woven fabric PES/alk. 10% nano-ZnO	0	none	good effect
Woven fabric PES/alk. 15% nano-ZnO	4	none	good effect
Woven fabric PES (control)	0	heavy	insufficient effect
Woven fabric PES 15% nano-ZnO	0	none	good effect
Nonwoven PES (control)	0	heavy	insufficient effect
Nonwoven PES 10% nano-ZnO	0	none	good effect
Nonwoven PES 15% nano-ZnO	3	none	good effect
Woven fabric CO (control)	0	heavy	insufficient effect
Woven fabric CO 10% nano-ZnO	2	none	good effect
Woven fabric CO 15% nano-ZnO	5	none	good effect

Table 2. *Textile fabrics – evaluation of antibacterial activity towards Escherichia coli ATCC 8739.*

Sample type	Evaluation of bacteria growth		Textile fabrics
	inhibition zone	bacterial growth under specimens	bio-active performance
Woven fabric PES/alk (control)	0	heavy	insufficient effect
Woven fabric PES/alk. 10% nano-ZnO	3	none	good effect
Woven fabric PES/alk. 15% nano-ZnO	5	none	good effect
Woven fabric PES (control)	0	heavy	insufficient effect
Woven fabric PES 15% nano-ZnO	2	none	good effect
Nonwoven PES (control)	0	heavy	insufficient effect
Nonwoven PES 10% nano-ZnO	2	none	good effect
Nonwoven PES 15% nano-ZnO	4	none	good effect
Woven fabric CO (control)	0	heavy	insufficient effect
Woven fabric CO 10% nano-ZnO	3	none	good effect
Woven fabric CO 15% nano-ZnO	5	none	good effect

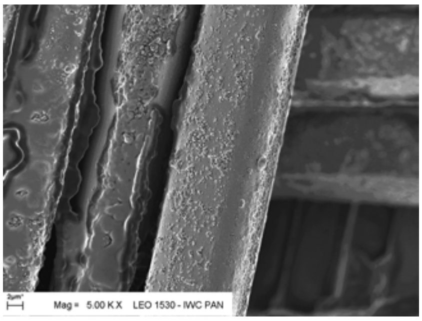

***Figure 5.** Polyester woven fabric after alkali pre-treatment – modified with nano-ZnO.*

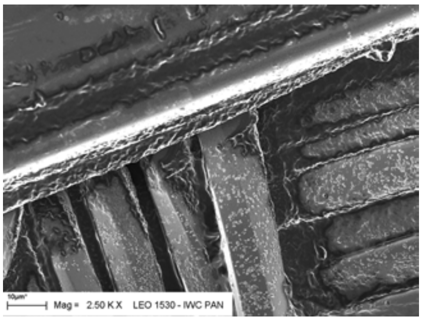

***Figure 6.** Polyester woven fabric – modified with nano-ZnO.*

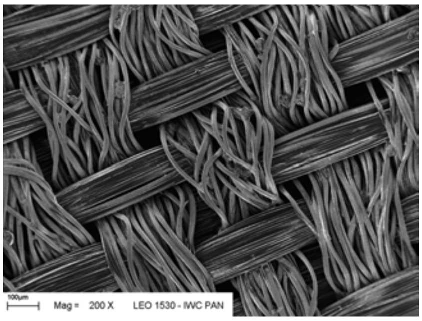

***Figure 7.** Polyester woven fabric after alkali pre-treatment – modified with TiO_2; magnification x 200.*

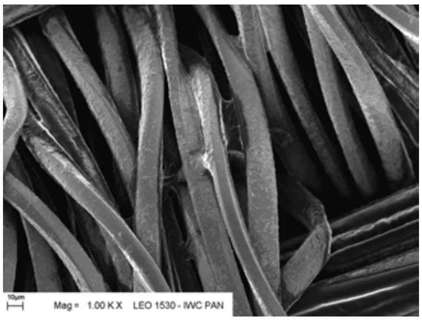

***Figure 8.** Polyester woven fabric after alkali pre-treatment – modified with TiO_2; magnification x 1,000.*

nonwoven did not inhibit the growth of gram positive *Staphylococcus aureus ATCC 6538* nor that of gram negative *Escherichia coli ATCC 8739* neither around the samples nor in the contact zone with the culture media. Antibacterial activity was demonstrated by the modified samples – padded with suspensions containing 10 or 15% nano-ZnO. A higher ability to inhibit the bacterial growth of *Staphylococcus aureus* and *Escherichia coli* was exhibited by the samples padded with suspensions containing 15% nano-ZnO.

Inhibition zones of bacterial growth of 2-5 mm and no bacterial growth in the samples tested confirmed this observation. The highest antibacterial activity was observed in cotton woven fabric and polyester woven fabric subjected to alkali pre-treatment – both fabrics were modified with nano-structural zinc oxide (15% nano-ZnO).

Conclusions

- Alkali pre-treatment of polyester woven fabric provides a higher ability to incorporate nano-ZnO or TiO_2.
- Textile fabrics modified with ZnO and TiO_2 nanoparticles demonstrated a high absorption of UV radiation in a full wavelength. Very good barrier properties against UV radiation were observed in:
  - polyester woven fabrics after alkali pre-treatment – modified with nano-ZnO and in
  - polyester woven and nonwoven fabrics modified with modified aminosilane TiO_2.
- The samples of textile fabrics obtained good antibacterial properties after the introduction of nano-structural zinc oxide. They showed better antibacterial activity towards gram-negative *Escherichia coli ATCC 8739* than towards gram-positive *Staphylococcus aureus ATCC 6538*.
- The highest antibacterial activity towards both strains, i.e. *Escherichia coli ATCC 8739* and *Staphylococcus aureus ATCC 6538* showed those modified with aqueous dispersion containing 15% of nano-ZnO:
  - polyester woven fabric after alkali pre-treatment and
  - cotton woven fabric.
- Modification with nano-structural ZnO allows to obtain textile fabrics with barrier properties against UV radiation and microorganism growth.
- Modification with TiO_2 allows textile fabrics to effectivley absorb UV-A and UV-B radiation. Further study will focus on the testing and application of photo-catalytic properties of titanium dioxide.
- An important issue for further studies will be the determination of the durability of barrier properties of modified textiles.

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