

Functionalization of textile materials by alkoxy silane-grafted titanium dioxide

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Abstract Modern materials, including textiles for specific applications, have to satisfy growing requirements. Regulations concerning man and natural environment protection against harmful substances emission, UV radiation, and electromagnetic field radiation become more and more stringent. Intensive development of nanotechnology offers great possibilities to create novel—conforming to the requirements—multifunctional materials based on textile substrates. Nanoparticles of metal oxides, e.g., titania (TiO_2), belong to a group of compounds having photocatalytic properties, which are able to absorb UV radiation and provide antibacterial barrier. The aim of research works was the modification of selected textiles using nanoparticles of metal oxides. Nano- TiO_2 and modified nano- TiO_2 with aminosilane were applied. In the first stage, the works concerned the methodology development of such nanoparticles incorporation onto selected textile substrates. Commonly used techniques, such as padding and spraying were used as well as sol–gel coating. The evaluation of microstructure of textile fabrics covered with nanostructural titanium dioxide was performed using high-resolution SEM

and TEM electron microscopes. Assessment of modified textiles pertained to the determination of protective properties against UV radiation and photocatalytic and antibacterial properties. Absorption spectra of textiles were determined using double beam type of UV–Vis Jasco V-550 with integrating sphere attachment. The same apparatus was used to determine ultraviolet protection factor (UPF) of textiles according to the standard EN 13758-1:2002. Textiles modified with nano- TiO_2 demonstrated high absorption of UV radiation in a full wavelength and their good photocatalytic properties were also confirmed.

Introduction

Intensive development of nanotechnology linked with generation of micro- and nanostructures offers great possibilities of creating modern multifunctional materials. Such materials based on textile substrates can have very wide applications due to the new properties rendered to these substrates. Functionalization of textiles arouses interest of many research centers in the world [1–3].

Nanoparticles of metal oxides such as: TiO_2 , ZnO , SiO_2 , MgO belong to a group of compounds exhibiting the properties of electric conductivity, UV absorption, and photooxidation. Titanium dioxide and zinc oxide—micronized or in nanoparticles form—are used in cosmetics as substances absorbing UV radiation. Nanocrystals of titanium dioxide have the ability to absorb ultraviolet range radiation generating at the same time the energy which initiates chemical reactions. Particles of organic origin, which are present in the surroundings of TiO_2 nanocrystals, acting as photocatalyst, are oxidized.

Photocatalytic decomposition of air and water contaminants in the presence of semiconductive materials gives

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new, more efficient possibilities of contaminants removal. In photocatalytic oxidation process, organic impurities become mineralized to simple nonorganic compounds: CO₂ and H₂O [4–8]. Among many semiconductors such as ZnO, SnO₂, ZrO₂, Fe₂O₃, and TiO₂, titanium dioxide is the mostly used in photocatalytic process as it is chemically and thermally stable and it is a nontoxic product [9–12].

Titanium dioxide can occur in crystalline form as well as in amorphous state. The noncrystalline state is photocatalytically inactive. The crystalline form occurs in three phases: anatase, rutile, and brookite. The methods of achieving crystalline form of titanium dioxide can be divided into dry ones, e.g., flame synthesis and into wet chemical methods, e.g., alkoxide method or precipitation [13–15].

Photocatalytic properties of TiO₂ depend on its morphology, particle size, specific surface area, and crystallographic form. From literature reports, methods of producing coatings containing nanotitanium dioxide on ceramic and glass materials applied in building industry are known. In rooms where walls are covered with materials with nano-TiO₂ the smell of formaldehyde, ammonia, or cigarettes is removed. It has been stated that nano-TiO₂ can be used in photocatalytic decomposition of volatile organic compounds such as: formaldehyde, benzene, toluene, trichloroethane, dimethylamine. Not only ceramic but also other materials including textile fabrics can be used as background material for TiO₂ photocatalyst. Challenging task for R&D centers is the development of methods introducing or incorporating nanostructural coatings onto textile substrates [16–22].

Development of a new generation of functional materials having photocatalytic and UV-barrier properties based on textile substrates was the primary aim of research work carried out by the authors. The first step of research work concerned the development of the methods of forming micro- and nano-TiO₂ coatings on selected textiles and the evaluation of achieved microstructures of modified materials applying high-resolution scanning microscopy. In our tests, we used TiO₂ particles obtained by sulfate method from the titanium sulfate precursor of defined microstructure and morphology as well as titanium dioxide modified with aminosilane or methacryloxysilane.

Experimental

Materials

Titanium dioxides

In our work, two types of titanium dioxide were applied, R003 and R211, both produced by ZCh POLICE S.A. using the sulfate technique. Modification of titanium white surface was conducted using selected alkoxysilanes

produced by Unisil: 3-methacryloxypropyltrimethoxysilane (U-511) and *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D).

Table 1 presents TiO₂ samples used for textile materials functionalization.

Dispersive properties of the titanium dioxide pigments are presented in Table 1, which are used to functionalize textile materials.

Textile fabrics

The textile materials functionalization was conducted using several materials: cotton woven fabric, chemically bleached, mass per unit area 140 g/m², and polyester nonwoven produced according to spunlace technique (water jet), mass per unit area 100 g/m².

Chemical agents

The following chemicals were used in tests: polyethylene glycol (PEG)—average molar mass 400 g/mol, Lipoxol 600 (Sasol), hydroxyethylcellulose (HEC)—of low molar mass, Cellosize QP40 (DOW), precursor TiO₂—titanium tetraisopropoxide 97% (TIPT) (Aldrich), acetic acid 98% analytically pure (POCh S.A.), hydrochloric acid 38% analytically pure (POCh S.A.).

Methods

Modification and examination of dispersive and morphological properties of titanium dioxide samples

The surface modification of TiO₂ was conducted by the so-called dry technique [23, 24], by applying 1.0 or 3.0 weight parts of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane or 3-methacryloxypropyltrimethoxysilane per 100 weight parts of SiO₂ (expressed in wt/wt). In order to avoid aging, the silanes were subjected to hydrolysis in a solution prepared directly before modification (methanol/water 4:1, v/v). The modification was performed in a specially constructed reactor [25] in 1 h and the solvent was distilled off.

Size of titanium white particles and the respective particle size distribution were determined using Zetasizer Nano ZS (Malvern Instruments Ltd.) using the non-invasive back light scattering method (NIBS). Particle size distribution permitted to establish polydispersity index (as a measure of uniform character of the pigment). The cumulants analysis gives a width parameter known as the polydispersity, or the polydispersity index (PDI). The cumulants analysis is actually the fit of a polynomial to the log of the *G*1 correlation function: $\text{Ln}[G1] = a + bt + ct^2 + dt^3 + et^4 + \dots$. The value of *b* is known as the

Table 1 Dispersive characteristics of unmodified and modified titania samples

Sample symbol	Titanium dioxide sample	Average particle size (nm)	Polydispersity index
R003	Tytanpol R003	459	0.239
R211	Tytanpol R211	295–342	0.170
TK11	Tytanpol R211 + 1 wt/wt 3-methacryloxypropyltrimethoxysilane	396	0.194
TK12	Tytanpol R211 + 3 wt/wt 3-methacryloxypropyltrimethoxysilane	396	0.183
TK17	Tytanpol R211 + 1 wt/wt <i>N</i> -2-(aminoethyl)-3-aminopropyltrimethoxysilane	342	0.161
TK18	Tytanpol R211 + 3 wt/wt <i>N</i> -2-(aminoethyl)-3-aminopropyltrimethoxysilane	342	0.227
TK62	Tytanpol R003 + 1 wt/wt <i>N</i> -2-(aminoethyl)-3-aminopropyltrimethoxysilane	295	0.170
TK63	Tytanpol R003 + 3 wt/wt <i>N</i> -2-(aminoethyl)-3-aminopropyltrimethoxysilane	342	0.259

second-order cumulant, or the z -average diffusion coefficient. The coefficient of the squared term, c , when scaled as $2c/b^2$ is known as the polydispersity.

The modified titania powders were also subjected to morphological and microstructural analysis using scanning electron microscopy (Zeiss VO 40) and transmission electron microscopy (Jeol 1200 EX 2).

In order to characterize adsorptive properties isotherms of nitrogen adsorption/desorption were determined and parameters such as specific surface area, pore volume, and average pore size were determined using ASAP 2020 instrument (Micromeritics Instruments Co.).

Elemental analysis of selected modified and unmodified titania samples was performed in Elementar Vario EL III apparatus.

Textile fabrics modification using TiO₂ and methods of evaluation of modified textile fabrics

In conducted tests, samples of polyester nonwoven were modified with nanostructural titanium dioxide. Dispersions of unmodified titanium dioxide (1 wt%) and of aminosilane-grafted TiO₂ (1 wt%) in water and in aqueous suspensions of PEG and HEC were introduced according to dip-coating method onto polyester nonwoven. Then the sample was squeezed (Benz automatic padding machine) at a nip pressure of 30 kG/cm² and dried at the temperature of 100 °C for 10 min. Depending on the type of dispersion, TiO₂ deposition level after sample drying was from 1.6 to 3.8 wt/wt.

Tests of cotton woven fabric and polyester nonwoven were also performed with nano-TiO₂ obtained by sol-gel method. To produce TiO₂, ca. 80 g/dm³ of precursor TIPT were used in hydrolysis carried in acid environment. Transparent solution was introduced onto textile substrate according to padding-squeezing method in Benz horizontal padding machine. The samples were then dried at the temperature of 80 °C for 10 min and heated up at 100 °C for 60 min.

Absorption spectra of textile fabric samples were determined using double beam type of UV-vis Jasco V-550

(Jasco) with integrating sphere attachment. The same apparatus was used to determine ultraviolet protection factor (UPF) of textile fabrics, according to the standard PN-EN 13758-1:2002.

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

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

where $E(\lambda)$ is the solar irradiance, $\varepsilon(\lambda)$ the erythema action spectrum, $\Delta\lambda$ the wavelength interval of the measurements, and $T(\lambda)$ the spectral transmittance at wavelength λ .

The analysis of color change of red wine stains allowed to assess photocatalytic properties of TiO₂ coatings. Samples of textile substrate were stained on the whole surface with red wine drops and dried at room temperature. The color was measured using spectrophotometer Spectraflash 500 (Data-color Int.) according to PN-EN ISO 105-J01:2002. Then, the samples were exposed to intensive light—UV-vis range in weathering test instrument. The color was measured after 3, 9, and 15 h of light exposure. Weathering chamber was equipped with two VIS lamps and two UV lamps, irradiance energy 6.76 J/min cm². Changes in colors were determined according to PN-EN ISO 105-J03:2000.

The evaluation of microstructure of textile fabrics covered with titanium dioxide was performed using high-resolution scanning microscopy—Zeiss Leo 1530.

Results and discussion

Dispersive and morphological characteristics of titanium dioxide

In the particle size distribution for R211 titania, which took into account band intensity (Fig. 1a), two bands were

noted. The more intense band within the range of 142–1,280 nm, with maximum intensity of 14.4% for particles of 342 nm in diameter, was linked to the presence of particles and primary agglomerates. On the other hand, the second band reflected the presence of secondary agglomerates in the range of 3,090–5,560 nm in diameter (maximum intensity of 0.5% corresponded to agglomerates of 4,800 and 5,560 nm in diameter). The polydispersity amounted to 0.17. The respective SEM image (Fig. 1b) demonstrated the presence of spherical particles with low diameter and few clumps. The TEM image (Fig. 1c) documented coating of titanium dioxide with aluminum and silica oxides, used for surface modification.

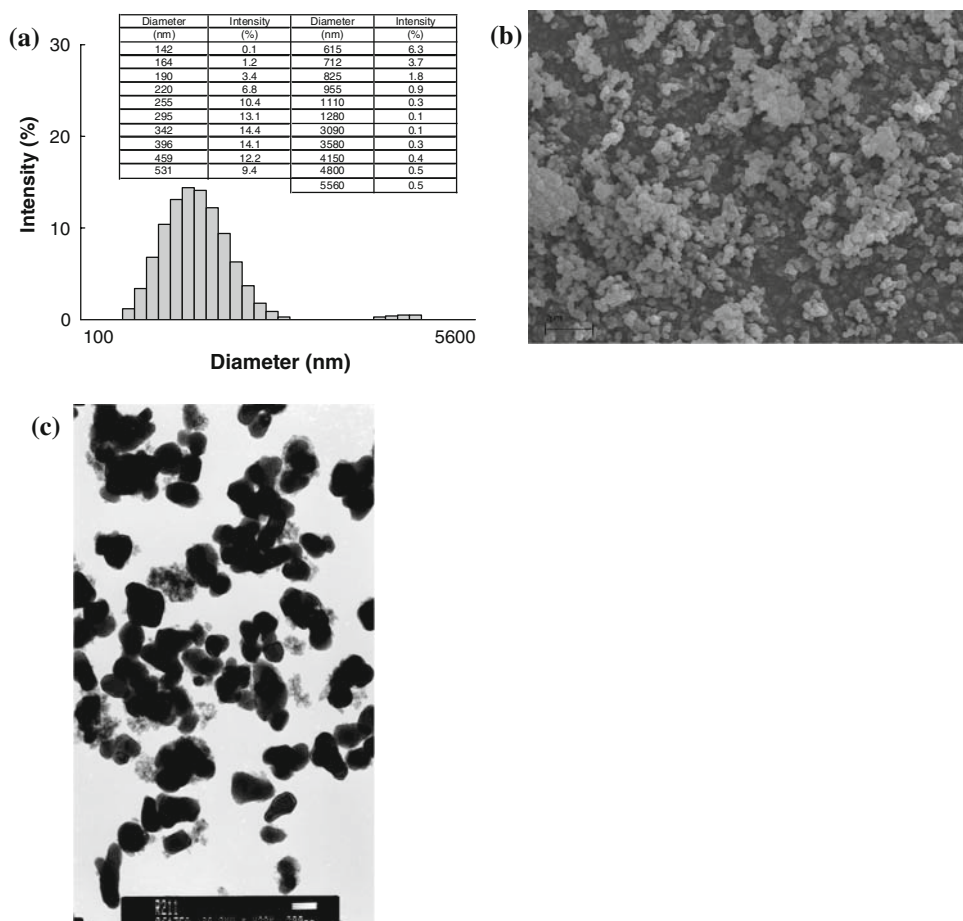
The particle size distribution paying appropriate attention to band intensity (Fig. 2a) for R211 titanium dioxide modified with 1 wt/wt of 3-methacryloxypropyltrimethoxysilane manifested two bands. The first band of a very high intensity was linked to the presence of primary particles and primary agglomerates in the range of 142–2,670 nm (with maximum intensity of 13.8 for the particles of 615 nm in diameters). The band in the range of 4,800–5,560 nm corresponded to secondary agglomerates (maximum intensity of 0.4 corresponded to the agglomerates in the range of 5560 nm in diameter). The polydispersity

amounted to 0.194. The SEM microphotograph (Fig. 2b) documented also the presence of spherical particles.

Particle size distributions taking into account band intensity and SEM microphotograph of R211 titanium white modified with 1 wt/wt of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane are presented in Fig. 3. The particle size distribution considering band intensity (Fig. 3a) demonstrated two bands. The intense band was linked to the presence of primary particles and primary agglomerates in the range of 164–955 nm (with maximum intensity of 18.7 for the particles of 342 nm in diameter). Polydispersity, which characterized scatter of particle diameters, amounted to 0.161 only. The other band of lower intensity in the range of 3,580–5,560 nm corresponded to secondary agglomerates (maximum intensity of 0.9 corresponded to the agglomerates of around 5,560 nm in diameter). The SEM microphotograph (Fig. 3b) confirmed the presence of spherical particles

The content of carbon and hydrogen permitted to determine the extent of modification of TiO₂ with 3-methacryloxypropyltrimethoxysilane (Fig. 4). Titania powders, which were not modified with organic compounds, demonstrated low content of carbon and hydrogen (R003: 0.22% C and 0.20% H; R211: 0.26% C and

Fig. 1 PSD by **a** intensity, **b** SEM, and **c** TEM images of TYTANPOL R211



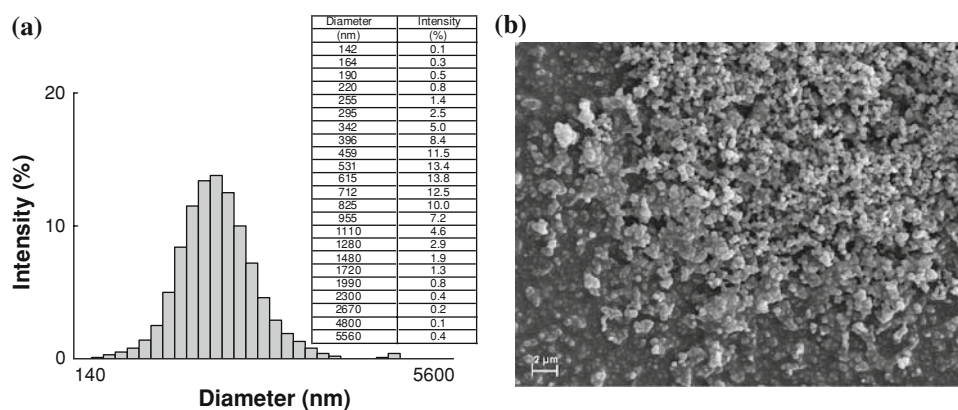


Fig. 2 PSD by **a** intensity and **b** SEM images of TYTANPOL R211 modified with 1 wt/wt of 3-methacryloxypropyltrimethoxysilane (TK11)

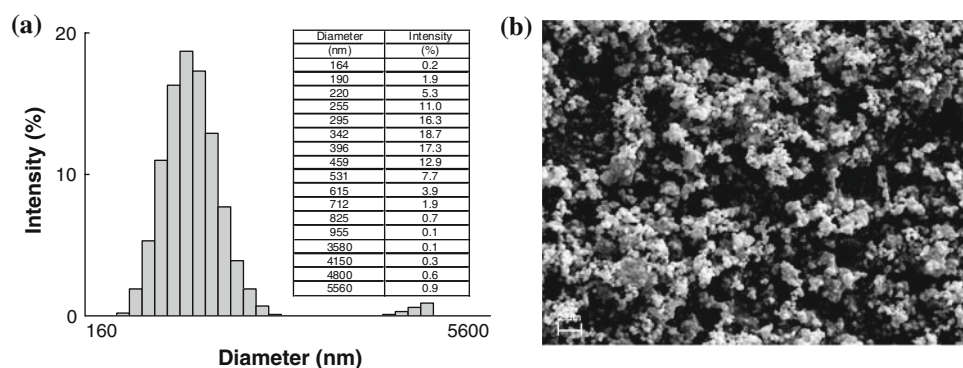


Fig. 3 PSD by **a** intensity and **b** SEM photograph of TYTANPOL R211 modified with 1 wt/wt of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (TK17)

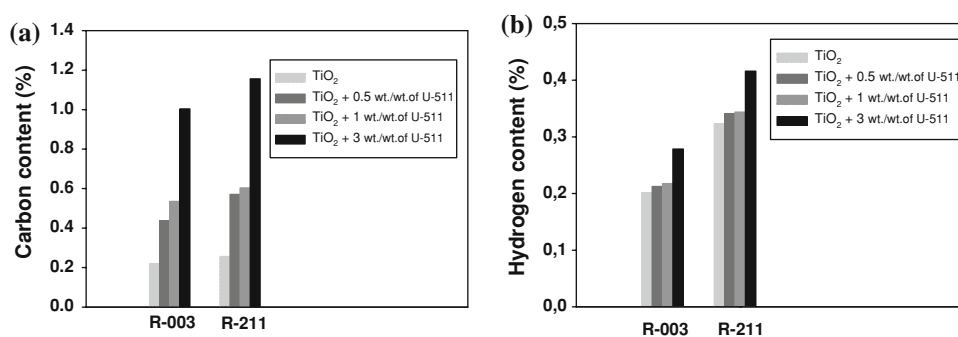


Fig. 4 Comparison of carbon (**a**) and hydrogen (**b**) contents in samples of titanium white modified using 3-methacryloxypropyltrimethoxysilane

0.32% H). The effect of the amount of organic coupling agent on content of carbon and of hydrogen in titanium dioxide samples could be observed in results of elemental analysis. The modification of TiO₂ samples yielded best results in the case of R211 powder. Contents of carbon and hydrogen increased, respectively, in R211 modified with 1 wt/wt of 3-methacryloxysilane to 0.60% C and 0.34% H and in R211 modified with 3 wt/wt of 3-methacryloxysilane to 1.16% C and 0.42% H.

Adsorption studies were also performed, which permitted to estimate BET specific surface area as well as size and

total volume of pores in titanium white samples. They determined suitability of titanium dioxide as a filler and a pigment. The highest adsorptive abilities were manifested by R211 titania, for which the range of hysteresis loop spanned relative pressures of 0.6–1.0 (Fig. 5). BET specific surface area for R211 white amounted to 24.9 m²/g, while pore diameter and total pore volume were 9.0 nm and 0.06 cm³/g, respectively. In the case of titanium white R003 titania; on the other hand, the hysteresis loop spanned a small compartment of 0.8–1.0 in relative pressures, and the respective low activity was confirmed by the low specific

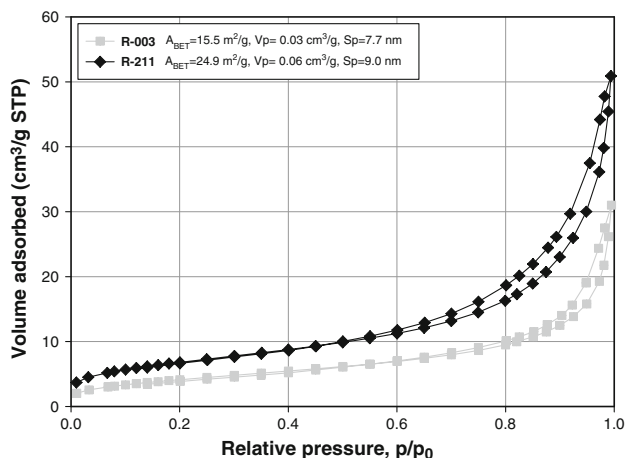


Fig. 5 N₂ adsorption/desorption isotherms of titanium dioxides

surface area of 15.5 m²/g. Shape of nitrogen adsorption/desorption isotherms (arms of the isotherms did not rise until relative pressures of over 0.6 were reached) as well as pore diameter and total pore volume of 7.7 nm and 0.03 cm³/g, respectively, were typical for mesoporous adsorbent.

Protective properties against UV radiation

The polyester nonwovens padded with aqueous dispersions containing 1% of titanium dioxide (Tytanpol R211 and Tytanpol R003) or 1 wt% of aminosilane modified TiO₂ (TK11, TK12 or TK17, TK18) demonstrated—characteristic of TiO₂ nanoparticles—spectrophotometric spectrum exhibiting very low transmittance of UV. On the basis of transmittance value (at the wavelength of λ 290–400 nm) calculated according to the Formula 1, UPF is above 50 for TiO₂ modified tested samples.

Figure 6 presents spectrophotometric transmittance spectrum in the wavelength λ = 290–400 nm of polyester nonwoven samples modified with: TiO₂ or aminosilane modified TiO₂. Very good barrier properties against UV radiation were obtained for polyester nonwoven samples modified with nano-TiO₂ (aminosilane modified)—TK11, TK12.

Microstructure of TiO₂-grafted fiber

The samples of raw polyester nonwoven and of modified—padded with aqueous dispersions of TiO₂ and with nano-TiO₂—were examined.

Figure 7 presents SEM microstructure of nonwoven samples. Figure 7a presents polyester nonwoven—unmodified with TiO₂. The fibers have circular cross-section, diameter ca. 10–12 nm. Their surface is smooth, partly covered with small objects, probably impurities.

In Fig. 7b, the polyester nonwoven after TiO₂ modification (Tytanpol R211) is shown. Single fibers have

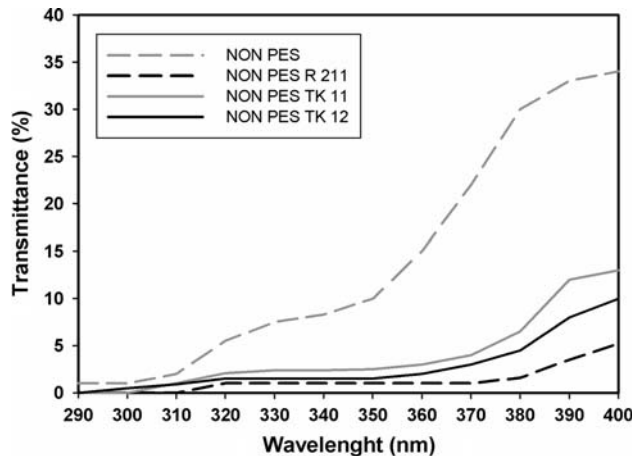


Fig. 6 Transmittance spectrum in the range of λ 290–400 nm—samples of polyester nonwoven fabrics modified with TiO₂

identical parameters as the fibers in a raw, reference nonwoven sample. Their smooth surface is covered by finely dispersed TiO₂. The particles of titania have the size ca. 100 nm. In some places agglomerated, larger structures, are also observed. The sample is covered with TiO₂ on its surface as well as in the volume of the nonwoven.

Figure 7c–f present polyester nonwoven samples treated with nano-TiO₂ (aminosilane-modified: TK11, TK12, TK17, TK18). The observations indicate that the surface quality of individual nonwovens has not changed when compared to the reference sample (raw polyester nonwoven). However, it seems that the fibers are covered more uniformly when compared to nonwoven sample modified with TiO₂—Tytanpol R211. Moreover, the powder particles of TiO₂ (TK11 and TK17) are less agglomerated than in case of the nonwoven samples treated with TiO₂—Tytanpol R211. Figure 7f shows an individual agglomerate of titanium dioxide nanopowder (TK18), deposited on the polyester nonwoven.

Photocatalytic properties

Table 2 presents test results on color changes—after 3, 9, and 15 h exposition to light in weathering test instrument of—cotton woven samples unmodified and modified with TiO₂ and their effect on red wine stains distribution.

On the basis of achieved results of color change and W value for cotton woven fabric stained with red wine before and after irradiation in weathering chamber, it can be stated that TiO₂ coating introduced onto textile fabric by sol–gel method has poor photocatalytic properties. In case of unmodified woven sample, the longer the irradiation time the higher the W value—relative degree of staining. In case of irradiation time (15 h), protective activity is the highest.

Table 3 presents test results on color changes—after 3, 9 and 15 hours exposition to light in weathering test

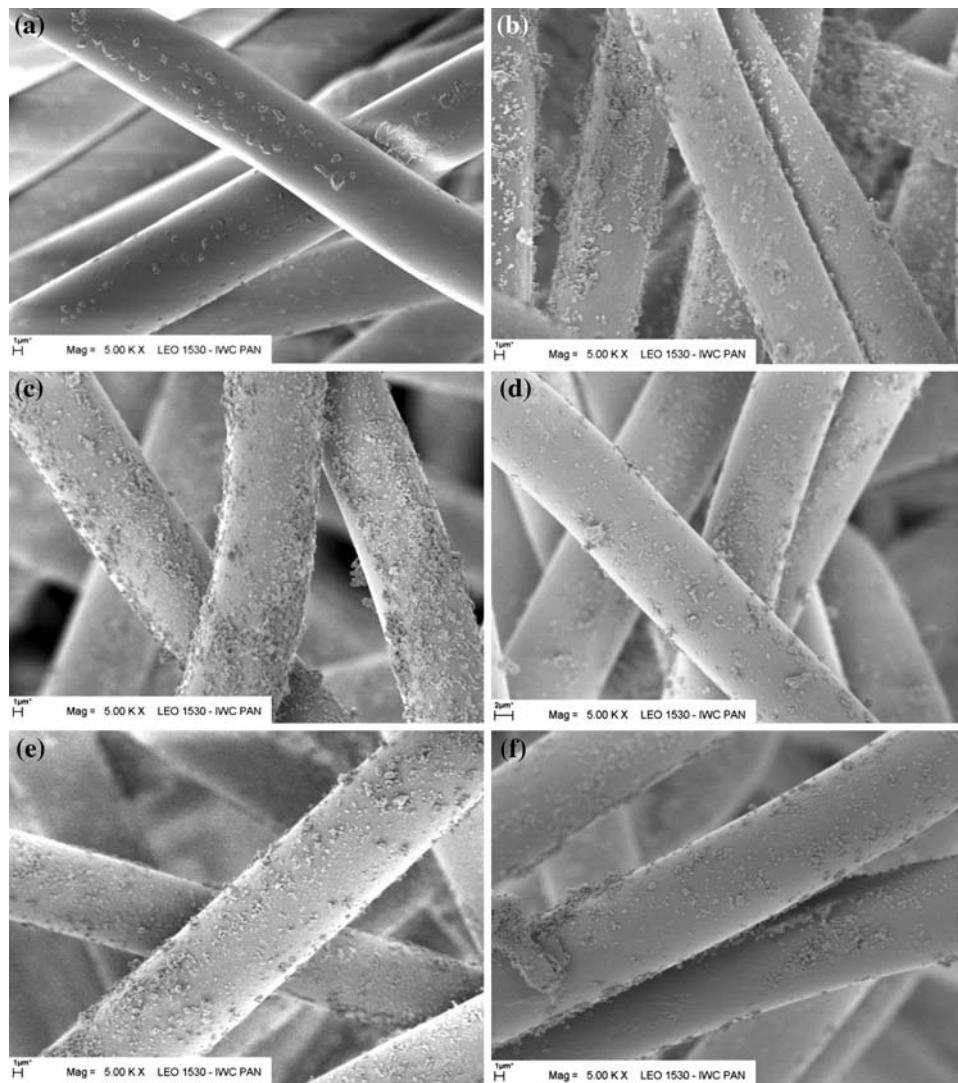


Fig. 7 SEM microstructures of the nonwoven samples: **a** polyester nonwoven—reference sample—untreated, images **b–f**: polyester nonwoven, modified with TiO₂: **b** R211, **c** TK11—Tytanpol R211 + 1 wt/wt *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane, **d** TK12—

Tytanpol R211 + 3 wt/wt 3-methacryloxypropyltrimethoxysilane, **e** TK17—Tytanpol R211 + 1 wt/wt *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane, **f** TK18—Tytanpol R211 + 3 wt/wt *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane

instrument—of polyester nonwoven samples unmodified and modified with nano-TiO₂ (aminosilane modified) and their effect on red wine stains distribution.

More efficient photocatalytic activity of polyester nonwoven modified with TiO₂ has been observed when compared to this effect obtained on cotton woven fabric modified with TiO₂ (sol–gel method). Substantially lower *W* value was determined for samples of modified polyester nonwoven after defined UV–vis irradiation in weathering chamber.

Conclusions

Performed study allows to state that modification of textile fabrics using titanium dioxide micro- and nanostructures

offers the possibility to render additional functions/properties to textiles, creating added-value textiles.

1. Textile fabrics modified with nano-TiO₂ demonstrate high absorption of UV radiation at a wavelength of λ 290–400 nm. On the basis of transmittance value calculated UPF is above 50 for TiO₂ modified fabrics.
2. Very good barrier properties against UV radiation were observed in polyester nonwoven fabrics modified with aminosilane modified TiO₂.
3. SEM observation analysis of polyester nonwovens (filled with TiO₂ or aminosilane-grafted TiO₂) showed that polyester fibers are covered more uniformly in case of nonwovens treated with aminosilane grafted TiO₂.

Table 2 Influence of nano-TiO₂ modification (sol–gel) of cotton woven fabric onto the distribution of red wine stains after defined irradiation in weathering chamber

No.	Textile fabric	Sample symbol	Relative degree of staining W^a (%)	Color change				
				ΔE	ΔL	Δa^*	Δb^*	ΔC
1	Cotton woven fabric—modified	Ew5	100.0	–	–	–	–	–
		Ew5/3 h	98.1	10.18	3.03	–1.23	9.64	6.50
		Ew5/9 h	94.9	15.16	5.00	–1.62	14.22	10.68
		Ew5/15 h	97.3	17.07	5.44	–1.72	16.09	12.46
2	Cotton woven fabric—unmodified	Ew9	100.0	–	–	–	–	–
		Ew9/3 h	111.2	16.59	3.28	–2.04	15.97	5.59
		Ew9/9 h	121.5	23.42	4.76	–2.29	22.59	11.55
		Ew9/15 h	165.3	27.48	2.89	–3.27	27.11	16.04

^a Relative degree of staining of samples after UV–VIS irradiation for 3, 9, and 15 h

Table 3 Photocatalytic properties assessment of polyester nonwovens modified with nano-TiO₂ (aminosilane-modified) after defined irradiation in weathering chamber

No.	Textile fabric	Sample symbol	Relative degree of staining W^a (%)	Color change				
				ΔE	ΔL	Δa^*	Δb^*	ΔC
1	Polyester nonwoven—TiO ₂ (R003)	Ew121	100	–	–	–	–	–
		Ew121/3 h	60.09	7.28	5.38	–2.06	4.45	3.56
		Ew121/9 h	52.13	9.52	6.94	–2.75	5.90	4.93
		Ew121/15 h	45.61	9.70	7.58	–3.20	5.13	4.14
2	Polyester nonwoven—TiO ₂ (TK62)	Ew124	100	–	–	–	–	–
		Ew124/3 h	71.56	8.40	4.85	–1.61	6.66	5.79
		Ew124/9 h	52.33	9.78	7.01	–2.89	6.18	5.18
		Ew124/15 h	46.21	9.78	7.51	–3.61	5.13	4.11
3	Polyester nonwoven—TiO ₂ (TK63)	Ew126	100	–	–	–	–	–
		Ew126/3 h	66.20	9.68	6.01	–2.08	7.29	5.97
		Ew126/9 h	50.17	10.90	8.02	–3.14	6.67	5.20
		Ew126/15 h	43.80	11.07	8.71	–3.76	5.71	4.18
4	Polyester nonwoven—unmodified	Ew12	100	–	–	–	–	–
		Ew12/3 h	89.64	10.30	3.71	–1.89	9.42	3.34
		Ew12/9 h	87.06	13.63	5.01	–2.31	12.47	5.83
		Ew12/15 h	98.50	15.71	4.48	–2.51	14.85	7.96

^a Relative degree of staining of samples after UV–VIS irradiation for 3, 9, and 15 h

4. Performed tests confirmed photocatalytic activity of nano-TiO₂. Samples of polyester nonwoven fabric coated with TiO₂ (aminosilane modified) show the better photocatalytic performance when compared to cotton woven fabric modified with TiO₂ (sol–gel method) assessed on the basis of the efficiency of red wine stains degradation.

Further studies will focus on the determination of durability of obtained effects of fabric modification after washing process.

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