Functionalization of Textile Materials by Nano-Titanium Dioxide

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1. Introduction

Intensive development of nanotechnology linked with generation of micro- and nano-structures offers great possibilities of creating modern multifunctional materials. Such materials based on textile substrates can have a very wide application due to new properties rendered to these substrates. Functionalization of textiles arouses interest of many research centres not only in Europe.

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 chemical substances photo-oxidation. Titanium dioxide and zinc oxide – micronized or in nanoparticle form – are used in cosmetics as substances absorbing UV radiation. Nano-crystals 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$_2$ nano-crystals, acting as photo-catalyst, are oxidized.

Photo-catalytic decomposition of air and water contaminants in the presence of semiconductive materials gives new, more efficient possibilities of contaminants removal. In photo-catalytic oxidation process organic impurities become mineralized to simple non-organic compounds: CO$_2$ and H$_2$O. Among many semiconductors such as ZnO, SnO$_2$, ZrO$_2$, Fe$_2$O$_3$ and TiO$_2$, titanium dioxide is the most useful in photo-catalytic process as it is chemically and thermally stable and it is a non-toxic product.

Titanium dioxide can occur in crystalline form as well as in amorphous state. Amorphous state is photo-catalytically inactive. 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. Alkoxide method known as sol-gel method allows to achieve more homogenous product at higher purity level.

Photo-catalytic properties of TiO$_2$ depend on its morphology, particle size, specific surface area and crystallographic form. From literature reports we know methods of producing coatings containing nano-titanium dioxide on ceramic and glass materials applied in building industry. In rooms where materials with nano-TiO$_2$ are used, from indoor air the smell of formaldehyde, ammonia or cigarettes is removed. It has been stated that nano-TiO$_2$ can be used in photo-catalytic 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 TiO$_2$ photo-catalyst. Challenging task for R&D centres is the development of methods introducing or incorporating nano-structural coatings onto textile substrates.

Development of a new generation of functional materials having photo-catalytic 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 covered the development of the methods of forming nano-TiO\textsubscript{2} coatings on selected textiles and the evaluation of achieved microstructures of modified materials applying high-resolution scanning microscopy. In our tests we used TiO\textsubscript{2} nano-particles obtained by sol-gel method from the precursor\textit{ Titanium tetraisopropoxide} using acid catalyzed hydrolysis and TiO\textsubscript{2} (titanium white) of defined microstructure and morphology as well as nano-TiO\textsubscript{2} modified with aminosilane.

**Experimental**

2. Methodology

2.1 Materials used in tests

2.1.1 Textile fabrics
- cotton woven fabric, chemically bleached, mass per unit area 140 g/m\textsuperscript{2}
- polyester nonwoven produced according to spunlace technique (water jet), mass per unit area 100 g/m\textsuperscript{2}

2.1.2 Chemical agents
- titanium dioxide –
  - Tytanpol R-003 (prod. Police Szczecin), average particle size 459nm, polydispersity = 0.239
  - Tytanpol R211 – presence of primary particles and agglomerates of average diameters 295 and 342 nm, polydispersity = 0.170
- modified titanium dioxide –
  - TK62: Tytanpol R003 + 1w/w N-2-(aminoethylo) 3-aminopropyltrimethoxysilane, presence of primary particles and agglomerates of average diameter 295 nm; polydispersity = 0.170
  - TK63: Tytanpol R003 + 3w/w N-2- (aminoethylo) 3-aminopropyltrimethoxysilane, presence of primary particles and agglomerates of average diameter 342 nm; polydispersity = 0.259
  - TK11: Tytanpol R211 + 1w/w 3-methacryloxypropyltrimethoxysilane, presence of primary particles and agglomerates of average diameter 615 nm; polydispersity = 0.194
  - TK12: : Tytanpol R211 + 3w/w 3-methacryloxypropyltrimethoxysilane, presence of primary particles and agglomerates of average diameter 396 nm; polydispersity = 0.183
  - TK17: Tytanpol R211 + 1w/w N-2-(aminoethylo) 3-aminopropyltrimethoxysilane, presence of primary particles and agglomerates of average diameter 342 nm; polydispersity = 0.161
  - TK18: Tytanpol R211 + 3w/w N-2-(aminoethylo) 3-aminopropyltrimethoxysilane, presence of primary particles and agglomerates of average diameter 342 nm; polydispersity = 0.227
- polyethylene glycol (PEG) - average molar mass 400 g/mol, Lipoxol 600 (prod. Sasol)
- hydroxyethylcellulose (HEC) – of low molar mass, Cellosize QP40 (prod. DOW)
- precursor TiO\textsubscript{2} \textit{Titanium tetraisopropoxide} 97% (TIPT) (prod. Aldrich)
- acetic acid 98% analytically pure (prod. POCh)
- hydrochloric acid 38% analytically pure (prod. POCh)
2.2 Methods of evaluation of modified textile fabrics

- Determination of protective properties of textile fabrics against UV radiation

  - Absorption spectra of textile fabric samples were determined using double beam type of UV-VIS Jasco V-550 (prod. Jasco, Japan) 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%.

\[
UPF = \frac{\sum_{\lambda=400}^{\lambda=290} E(\lambda) \varepsilon(\lambda) \Delta\lambda}{\sum_{\lambda=400}^{\lambda=290} E(\lambda) T(\lambda) \varepsilon(\lambda) \Delta\lambda}
\]

where: 
- \(E(\lambda)\) – the solar irradiance,
- \(\varepsilon(\lambda)\) – the erythema action spectrum,
- \(\Delta\lambda\) - the wavelength interval of the measurements,
- \(T(\lambda)\) – the spectral transmittance at wavelength \(\lambda\).

- Assessment of photo-catalytic properties of modified textiles

The analysis of colour change of red wine stains allowed to assess photo-catalytic properties of nano-TiO\(_2\) coatings. Samples of textile substrate were stained on the whole surface with red wine drops and dried at room temperature. The colour was measured using spectrophotometer Spectraflash 500 (Datacolor 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 colour was measured after 3, 9 and 15 hours of light exposure. Weathering chamber was equipped with 2 VIS lamps and 2 UV lamps, irradiance energy 6.76 J/min cm\(^2\). Changes in colours were determined according to PN-EN ISO 105-J03:2000.

- Microstructure evaluation of modified textile fabrics

The evaluation of 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.

2.3 Titanium white (TiO\(_2\)) – morphology and microstructure study

- The assessment of TiO\(_2\) dispersion was done using transmission electron microscope (TEM) – type JEM 1200 EX2 (prod. Japan). Particle size distribution was established using
Zetasizer Nano ZS (Malvern Instruments Ltd.) using non-invasive back scattering method (NIBS). This instrument allows to determine molecular mass of nano-particles.

- The measurement of BET specific surface area of selected titanium whites was performed on the basis of N₂ adsorption. For this purpose the apparatus ASAP 2010 (Micrometrics Instruments Corporation) was used.

2.4 Elemental analysis of titanium white – modified and unmodified

The elemental analysis of the selected modified and unmodified titanium whites was performed in the Elementar Vario EL III apparatus.

2.5 Textile fabrics modification using aminosilane modified TiO₂

In lab tests samples of polyester nonwoven were modified with nano-structural titanium oxide.

Dispersions of non-modified titanium dioxide (1%) and of aminosilane modified TiO₂ (1%) 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 minutes. Depending on the type of dispersion TiO₂ deposition level after sample drying was from 1.6 to 3.8 % ww.

Lab tests of cotton woven fabric and polyester nonwoven were also performed with nano-TiO₂ obtained by sol-gel method. To produce TiO₂ circa 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 minutes and heated up at 100°C for 60 minutes.

3. Results and discussion

In order to obtain information on dispersion, particle morphology, structure of individual particles of titanium dioxide and on the character of its agglomerations, tests on morphology and microstructure were performed using scanning microscopy SEM 515 (prod. Philips). In this way it was possible to get images of the surfaces of obtained titanium whites. Research works indicated that the better adsorption ability has had titanium white Tytanpol R211 than Tytanpol R003. The value of BET specific surface area of Tytanpol R211 – reached 24.9 m²/g while for Tytanpol R003 it reached 15.5 m²/g.

Out of all applied silanes for titanium white modification the best turned out to be 3-methacryloxypropyltrimethoxysilane and then N-2-(aminoetylo)3-aminopropyltrimethoxysilane. Applied surface modification based on silane coupling agents increased the content (%) of carbon, hydrogen in the samples of titanium dioxide – this was confirmed by the results of elemental analysis:
Protective properties against UV radiation

Polyester nonwovens padded with aqueous dispersions containing 1% of titanium dioxide (Tytanpol R211 and Tytanpol R003) or 1% of amonosilane modified TiO₂ (TK11, TK12 or TK17, TK18) demonstrated - characteristic of TiO₂ nano-particles – spectrophotometric spectrum, very high absorption of UV radiation in the whole wavelength and the value of UPF above 50 units.

Figure 1 presents spectrophotometric spectra 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.

Micro-structural analysis of obtained materials was performed using high-resolution scanning microscopy - Zeiss Leo 1530. Samples of raw polyester nonwoven and of modified – padded with aqueous dispersions of TiO₂ and with nano-TiO₂ – were examined. Photo “0” presents polyester nonwoven – unmodified with TiO₂. Fibres have circular cross-section, diameter ca. 10-12 nm. Their surface is smooth, partly covered with small objects, probably impurities.

Photo “a” – presents polyester nonwoven after TiO₂ modification (Tytanpol R211). Single fibres have identical parameters as fibres in a raw nonwoven sample. Smooth surface is covered by finely dispersated TiO₂. The particles of titanium oxide have the size ca. 100 nm, observed are also agglomerated – bigger structures. Nonwoven sample is covered with TiO₂ on its surface as well as in its inner part.

Photos “b” to “e” present polyester nonwoven samples treated with nano-TiO₂ (aminosilane modified: TK11, TK12, TK17, TK18). Observations indicate that the surface quality of individual nonwovens have not changed when compared to control sample – raw polyester nonwoven. It seems that the fibres are covered more uniformly when compared to nonwoven sample modified with TiO₂ – Tytanpol R211. Moreover, powder particles of TiO₂ (TK11 and TK17) - although are also agglomerated yet to a smaller degree than in case of nonwoven samples treated with TiO₂ – Tytanpol R211. Samples treated with TK12 and TK18 differ in the degree of powder distribution on nonwoven sample and in powder amount.

Photo “e” (TK18) presents individual, big structures made of titanium dioxide deposited on polyester fibrils.

Photo-catalytic properties

Table 1 presents test results on colour changes - after 3, 9 and 15 hours exposition to light in weathering test instrument - of cotton woven samples unmodified and modified with nano-TiO₂ (obtained by sol-gel method) and their effect on red wine stains distribution.
Table 1
Influence of nano-TiO\textsubscript{2} modification of cotton woven fabric onto the distribution of red wine stains after defined irradiation in weathering chamber

<table>
<thead>
<tr>
<th>No.</th>
<th>Textile fabric</th>
<th>Sample symbol</th>
<th>W Relative degree of staining [%]</th>
<th>Colour change</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>DE</td>
</tr>
<tr>
<td>1</td>
<td>Cotton woven fabric - modified</td>
<td>Ew5</td>
<td>100.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew5/3h</td>
<td>98.1</td>
<td>10.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew5/9h</td>
<td>94.9</td>
<td>15.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew5/15h</td>
<td>97.3</td>
<td>17.07</td>
</tr>
<tr>
<td>2</td>
<td>Cotton woven fabric - unmodified</td>
<td>Ew9</td>
<td>100.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew9/3h</td>
<td>111.2</td>
<td>16.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew9/9h</td>
<td>121.5</td>
<td>23.42</td>
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<tr>
<td></td>
<td></td>
<td>Ew9/15h</td>
<td>165.3</td>
<td>27.48</td>
</tr>
</tbody>
</table>

Description:
W – relative degree of staining of samples after UV-VIS irradiation for 3, 9 and 15 hours

On the basis of achieved results of colour change and W value for cotton woven fabric stained with red wine – before and after irradiation in weathering chamber it can be stated that TiO\textsubscript{2} coating introduced onto textile fabric by sol-gel method has had photo-catalytic properties. In case of unmodified woven sample, the longer the irradiation time the higher is W value – relative degree of staining. In case of irradiation time – 15 hours, protective activity is the highest.

Table 2 presents test results on colour changes - after 3, 9 and 15 hours exposition to light in weathering test instrument - of polyester nonwoven samples unmodified and modified with nano-TiO\textsubscript{2} (aminosilane modified) and their effect on red wine stains distribution.

Table 2
Photo-catalytic properties assessment of polyester nonwovens modified with nano-TiO\textsubscript{2} after defined irradiation in weathering chamber

<table>
<thead>
<tr>
<th>No.</th>
<th>Textile fabric</th>
<th>Sample symbol</th>
<th>W [%]</th>
<th>Colour change</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>DE</td>
</tr>
<tr>
<td>1</td>
<td>Polyester nonwoven - TiO\textsubscript{2} (R003)</td>
<td>Ew121</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew121/3h</td>
<td>60.09</td>
<td>7.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew121/9h</td>
<td>52.13</td>
<td>9.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew121/15h</td>
<td>45.61</td>
<td>9.70</td>
</tr>
<tr>
<td>2</td>
<td>Polyester nonwoven TiO\textsubscript{2} (TK62)</td>
<td>Ew124</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew124/3h</td>
<td>71.56</td>
<td>8.40</td>
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<td></td>
<td></td>
<td>Ew124/9h</td>
<td>52.33</td>
<td>9.78</td>
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<td></td>
<td></td>
<td>Ew124/15h</td>
<td>46.21</td>
<td>9.78</td>
</tr>
<tr>
<td>3</td>
<td>Polyester nonwoven TiO\textsubscript{2} (TK63)</td>
<td>Ew126</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew126/3h</td>
<td>66.20</td>
<td>9.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew126/9h</td>
<td>50.17</td>
<td>10.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew126/15h</td>
<td>43.80</td>
<td>11.07</td>
</tr>
<tr>
<td>4</td>
<td>Polyester nonwoven - unmodified</td>
<td>Ew12</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew12/3h</td>
<td>89.64</td>
<td>10.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew12/9h</td>
<td>87.06</td>
<td>13.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ew12/15h</td>
<td>98.50</td>
<td>15.71</td>
</tr>
</tbody>
</table>
More efficient photo-catalytic 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

1. Better adsorption ability has titanium white Tytanpol R211 than Tytanpol R003. The value of BET specific surface area of Tytanpol R211 equals 24.9 m²/g.

2. Out of all applied silanes for titanium white modification the best turned out to be 3-methacryloxypropyltrimethoxysilane.

3. Applied surface modification based on silane coupling agents increased the content (in %) of carbon, hydrogen in the samples of titanium dioxide.

4. Textile fabrics modified with nano-TiO₂ demonstrated high absorption of UV radiation in a full wavelength.

5. Very good barrier properties against UV radiation were observed in polyester nonwoven fabrics modified with aminosilane modified TiO₂.

6. Performed tests confirmed photo-catalytic activity of nano-TiO₂. Samples of textile fabrics coated with TiO₂ (aminosilane modified) show the best photo-catalytic performance assessed on the basis of the efficiency of red wine stains degradation.

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Literature:
4. JP 11035412 Inorganic Antibacterial Agent
Photo “0” Polyester nonwoven – raw sample

Photos “a – e” Polyester nonwoven – TiO$_2$ modified

a) (R 211)

b) (TK 11)
c) (TK 12)

d) (TK 17)

e) (TK 18)