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# Evaluation of the Photocatalytic Properties of Textile Fabrics Modified with Titanium Dioxide of Anatase Structure

## Abstract

*The effect of surface modification with selected alkoxy silanes on the photocatalytic properties of TiO<sub>2</sub> used in the reaction of formaldehyde photodegradation to UV radiation was investigated. Titanium dioxide - Tytanpol® A-11, a pigment of anatase structure of the untreated surface, was used. Silane coupling agents were hydrolysed and then deposited directly on the surface of the TiO<sub>2</sub>. The alkoxy silanes - 3-methacryloxypropyltrimethoxysilane, vinyltrimethoxysilane or N-2-(aminoethyl)-3-aminopropyltrimethoxysilane were applied in the amounts of 0.5, 1 or 3 wt. parts per 100 wt. parts of TiO<sub>2</sub>. The unmodified and modified titanium dioxide were used for the dip-coating of textile fabrics, and their photocatalytic properties were tested using UV radiation with TiO<sub>2</sub> as a photocatalyst. The results proved the very good photooxidative activity of TiO<sub>2</sub> introduced into the structure of polyester fabric.*

**Key words:** titanium dioxide, anatase, silane coupling agents, surface functionalisation, photocatalytic properties, formaldehyde degradation.

## Introduction

The photocatalytic properties of titanium dioxide have recently become the subject of considerable interest. TiO<sub>2</sub> satisfies all the requirements of a photocatalyst as it is easily activated by UV radiation and is photostable and non-toxic [1]. Two structures of titanium dioxide are used in photocatalytic studies: rutile and anatase. In photocatalytic processes the more active form is anatase, although there are reports of the higher activity of rutile [2, 3].

Titanium dioxide is a non-toxic compound widespread in the earth's crust, characterised by high mechanical strength and photochemical stability. The degradation of impurities takes place by applying the TiO<sub>2</sub>/radiation system, at ambient temperature and under atmospheric pressure. The use of this system permits the elimination of any other chemical oxidants. The hydroxyl radical formed in the system as a result of photochemical processes is a reactive and non-selective oxidant of impurities. As a result of heterogeneous photocatalysis, it is possible to achieve the total mineralisation of a wide gamut of compounds (e.g. alkenes, alkynes, alcohols, ketones, dyes, pesticides and surfactants), including toxic and not biodegradable substances. The final products of such a process are carbon dioxide, water, and inorganic acids [4 - 8]. The main drawbacks of this process are low catalytic activity and low quantum yield of TiO<sub>2</sub> [9].

According to literature data on heterogeneous photocatalysis, TiO<sub>2</sub> in the water and gas phase is characterised by high photocatalytic activity [10 - 13].

The anatase structure, characterised by a high degree of surface hydroxylation and large surface area, was found to show the highest catalytic activity in UV radiation. The TiO<sub>2</sub> catalyst of a well-developed surface area has many active sites that can be engaged in the adsorption of reagents [11, 12]. Rutile is less effective as a photocatalyst despite the fact that it has a forbidden band narrower than anatase. The reason for this lower activity is a faster recombination of holes and electrons [14]. Moreover, rutile has a smaller number of active sites and hydroxyl groups on the surface than anatase [15 - 19]. The amorphous structure of TiO<sub>2</sub> is photocatalytically inactive [20].

Technologically advanced photocatalytic coats containing TiO<sub>2</sub> have strong self-cleaning, bactericidal, superhydrophilic, deodorising, antistatic, air cleaning and UV barrier properties [9].

The surface modification of nanoparticles is one of the most common methods to improve the dispersion stability of nanoparticles. The modification of oxide surfaces (e.g., silica, titania and zirconia) with silylation is a well-known method of altering the chemical and physical properties of ceramic substrates. However, for applications where organosilane molecules provide a specific functionality, multilayer coverage can be more appropriate [21]. Silane coupling agents, which have 1-3 alkoxy groups and 3-1

organic functional groups, have been used to modify oxide nanoparticle surfaces since the 1960s. The metal-OH group on the particle surface is used as a reaction site. The first purpose of the silane coupling agents was to improve the compatibility of a hydrophilic particle surface with a hydrophobic polymer surface by functionalising the particle with various organic groups. Since Plueddemann et al. reported the concept of silane coupling agents [22], numerous researchers have modified the particle surface to improve the compatibility of particle/polymer surfaces and the properties of composite materials [23, 24]. Chaimberg et al. reported that the amount of silane coupling agent chemisorbed on the oxide surface differs drastically depending on the surface modification procedures [25]. The type of solvents, pH and amount of water adsorbed on particles largely affected the chemisorbed content of silane coupling agents. Surface modification with mixed silane alkoxides is also a useful tool to improve the dispersion of particles in various types of solvents. For an example, Iijima et al. modified the surface of TiO<sub>2</sub> nanoparticles by mixing silane alkoxides with a hydrophobic group derived from decyltrimethoxysilane - DES and a hydrophilic group from 3-aminopropyltrimethoxysilane - APTMS [26]. When TiO<sub>2</sub> particles were modified by DES, they were only redispersible in low-polarity solvents such as toluene, but they could be dispersed in high-polarity solvents when treated with both DES and APTMS.

Taking into consideration the toxicity and exposure levels of formaldehyde, it

is necessary to reduce its concentrations. The most effective solution is air cleaning, which has recently become more popular. There are some general methods of air purification like the adsorption of formaldehyde on activated carbon or other adsorbents with functional groups reactive to formaldehyde (usually primary and secondary amine groups), and the alternative technique – oxidation, which includes heterogenous catalytic oxidation with air, photocatalytic degradation, and the oxidation of formaldehyde using potassium permanganate filters [27].

The most important problem of the study proved to be the photooxidative activity of TiO<sub>2</sub> with anatase introduced into the structure of polyester fabric. The photocatalytic activity of textile fabric coated with unmodified and modified titanium dioxide was evaluated using the test reaction of the photodegradation of formaldehyde by UV irradiation. Selected organic compounds were used in the functionalisation of the commercial titanium dioxide surface. The modified titanium dioxide was thoroughly characterised to determine the yield of functionalisation with silanes. The study was undertaken mainly to determine the effectiveness of surface character changes by dispersion, morphology, adsorptive and electrokinetic measurement (zeta potential) of the functionalised titanium dioxide.

## ■ Experimental part

### Substrates used:

- a) *Titanium dioxide of anatase structure:*
  - Tytanpol® A-11,
- b) *Silane coupling agents:*
  - 3-methacryloxypropyltrimethoxysilane (U-511),
  - vinyltrimethoxysilane (U-611),
  - N-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D),
- c) *Textile products:*
  - Polyester nonwoven fabric produced according to the spunlace technique (water jet), mass per unit area 100 g/m<sup>2</sup>,
- d) *Chemical agents used for dip-coating:*
  - Poly(ethylene glycol) (PEG) of 400 g/mol mean mass, Lipoxol 600 (made by Sasol),
  - Hydroxyethylcellulose (HEC) of low molar mass, Cellosize QP40 (made by DOW),

### e) *Chemical agents used for the determination of formaldehyde concentration in the air:*

- 0.05% water solution of 3-methyl-2-benzothiazolehydrazone – MBTH (absorbing solution),
- 3.2% sulphamide acid and 1% iron(III) chloride (oxidising solution),
- 50 mg of formaldehyde (126 µl 36% formalin solution) supplemented with water up to 100 ml (base solution),
- 1 ml of the base solution diluted to 500 ml with 0.05% MBTH (standard solution).

### Method of titanium oxide modification

The titanium dioxide sample was functionalised with selected alkoxy silanes to extend the spectrum of application and improve the affinity to textile fabrics.

To introduce functional groups facilitating bond formation with other active substances, selected alkoxy silanes, listed in **Table 1**, were purchased from UniSil.

The functionalisation of the TiO<sub>2</sub> product was performed by the so-called dry technique [28]. The surface modification of titanium dioxide was carried out in a reactor of 500 ml capacity. The silane coupling agents were hydrolysed in the methanol/water system (4/1 v/v), and from this solution they were deposited directly onto the surface of the titanium dioxide. The solution contained a given silane coupling agent in the amounts of 0.5, 1 or 3 wt. parts per 100 wt. parts of TiO<sub>2</sub>. Then the system was stirred for 1 hour to homogenise the sample with the solution of the modifying agent, after which the solvent was distilled off. The modified sample was dried at 105 °C in a stationary drier for 2 hours [29, 30]. The samples thus obtained were subjected to characterisation.

### Physico-chemical investigation of TiO<sub>2</sub> and its derivatives

The determination of certain physico-chemical parameters was undertaken to verify the effectiveness of the TiO<sub>2</sub> surface modification with alkoxy silanes.

**Table 1.** Alkoxy silanes used.

Silane coupling agents	Symbol	Chemical formula
3-methacryloxypropyltrimethoxysilane	U-511	CH <sub>2</sub> =C(CH <sub>3</sub> )COO(CH <sub>2</sub> ) <sub>3</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>
Vinyltrimethoxysilane	U-611	CH <sub>2</sub> =CHSi(OCH <sub>3</sub> ) <sub>3</sub>
N-2-(aminoethyl)-3-aminopropyl-trimethoxysilane	U-15D	H <sub>2</sub> N(CH <sub>2</sub> )NH(CH <sub>2</sub> ) <sub>3</sub> Si(OCH <sub>3</sub> ) <sub>3</sub>

The dispersive properties of the unmodified and modified titanium dioxide were assessed on the basis of particle size distributions and polydispersity index determination by the non-invasive back light scatter method using a Zetasizer Nano ZS made by Malvern Instruments Ltd. The surface morphology of the titanium dioxide was evaluated by the SEM (Zeiss VO40) and TEM (Jeol 1200 EX II) techniques. On the basis of nitrogen adsorption/desorption isotherms, the surface area (A<sub>BET</sub>), pore volume (V<sub>p</sub>) and average pore size (S<sub>p</sub>) were assessed using an ASAP 2020 (Micromeritics Instruments Co.). The pore size distributions were determined by the method of BJH (Barret, Joyner and Halenda). The crystallographic structure of the titanium dioxide was established by the WAXS method. X-ray diffraction measurements were performed using Cu Kα radiation and a fixed power source (30 kV, 15 mA). The sample was scanned at a rate of 0.04° over a angle range of 3 - 60°. The chemical composition of the modified TiO<sub>2</sub> was carried out using Elementar model Vario EL III apparatus. The effectiveness of the surface modification process was evaluated with selected alkoxy silanes on the basis of the zeta potential measurement. With the help of a Zetasizer Nano ZS equipped with an autotitrator (Malvern Instruments Ltd.), it was possible to measure electrophoretic mobility and the zeta potential indirectly using laser Doppler velocimetry (LDV). The electrokinetic potential was measured in the whole pH range, which permitted the determination of electrokinetic curves.

### Evaluation of the number of surface functional groups

The number of surface functional groups N<sub>R</sub> in nm<sup>-2</sup>, which shows the density of the modifier on the TiO<sub>2</sub> surface, was calculated from the results of elemental analysis and BET measurement. N<sub>R</sub> is defined as the number of methacryloxy, vinyl, propyl, amino ethyl or amino propyl groups on the TiO<sub>2</sub> surface per 1 nm<sup>-2</sup> and is expressed using equation (1) below.

$$N_R = \frac{C \times N_A}{12 \times n \times 100 \times S}, m^{-2} \quad (1)$$

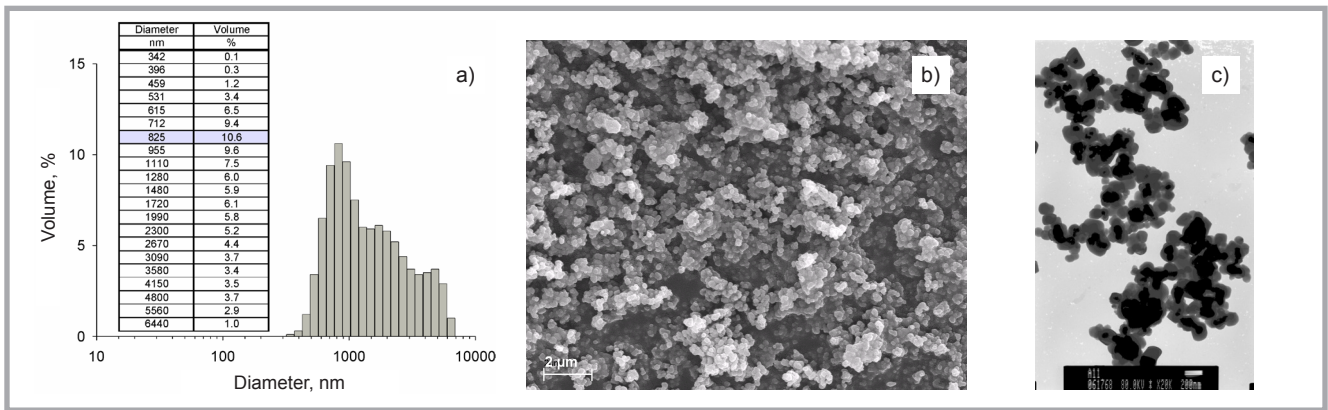


Figure 1. a) Particle size distribution by volume, b) SEM and c) TEM microphotographs of titanium dioxide (sample A-11).

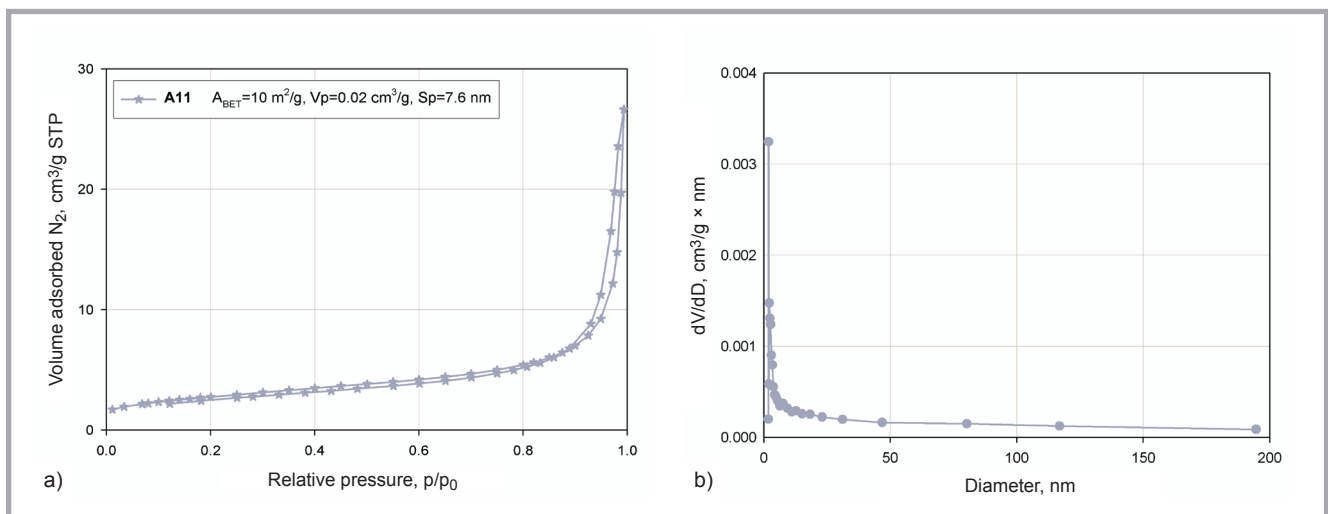


Figure 2. a)  $N_2$  adsorption/desorption isotherm and b) pore size distribution for  $TiO_2$  particles (sample A-11).

In which  $C$  is the carbon content obtained from the result of elemental analysis,  $n$  – the number of carbon in the silane coupling agents, except methoxy groups,  $N_A$  – Avogadro's number, and  $S$  is the surface area [31].

### Dip-coating of nonwoven polyester fabric with a water dispersion containing $TiO_2$

The incorporation of  $TiO_2$  particles into the structure of nonwoven polyester fab-

ric was realised by dip-coating the fabric with a water dispersion containing 3% wt. of unmodified or modified  $TiO_2$ , poly(ethylene glycol) as a wetting agent in the amount of 10% wt. and hydroxyethylcellulose as a thickening agent

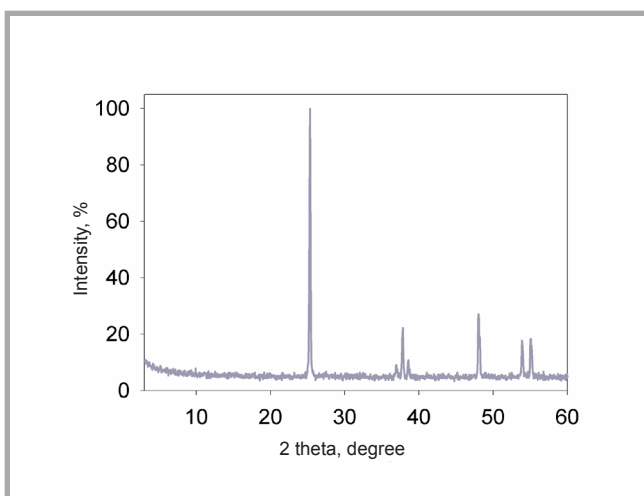


Figure 3. WAXS pattern of  $TiO_2$  (sample A-11).

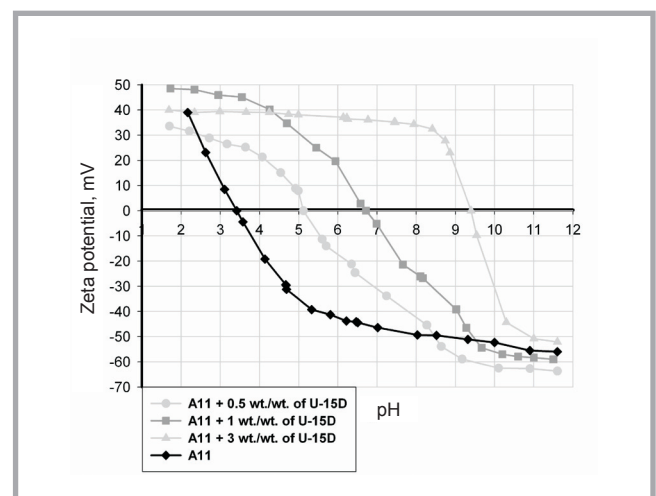
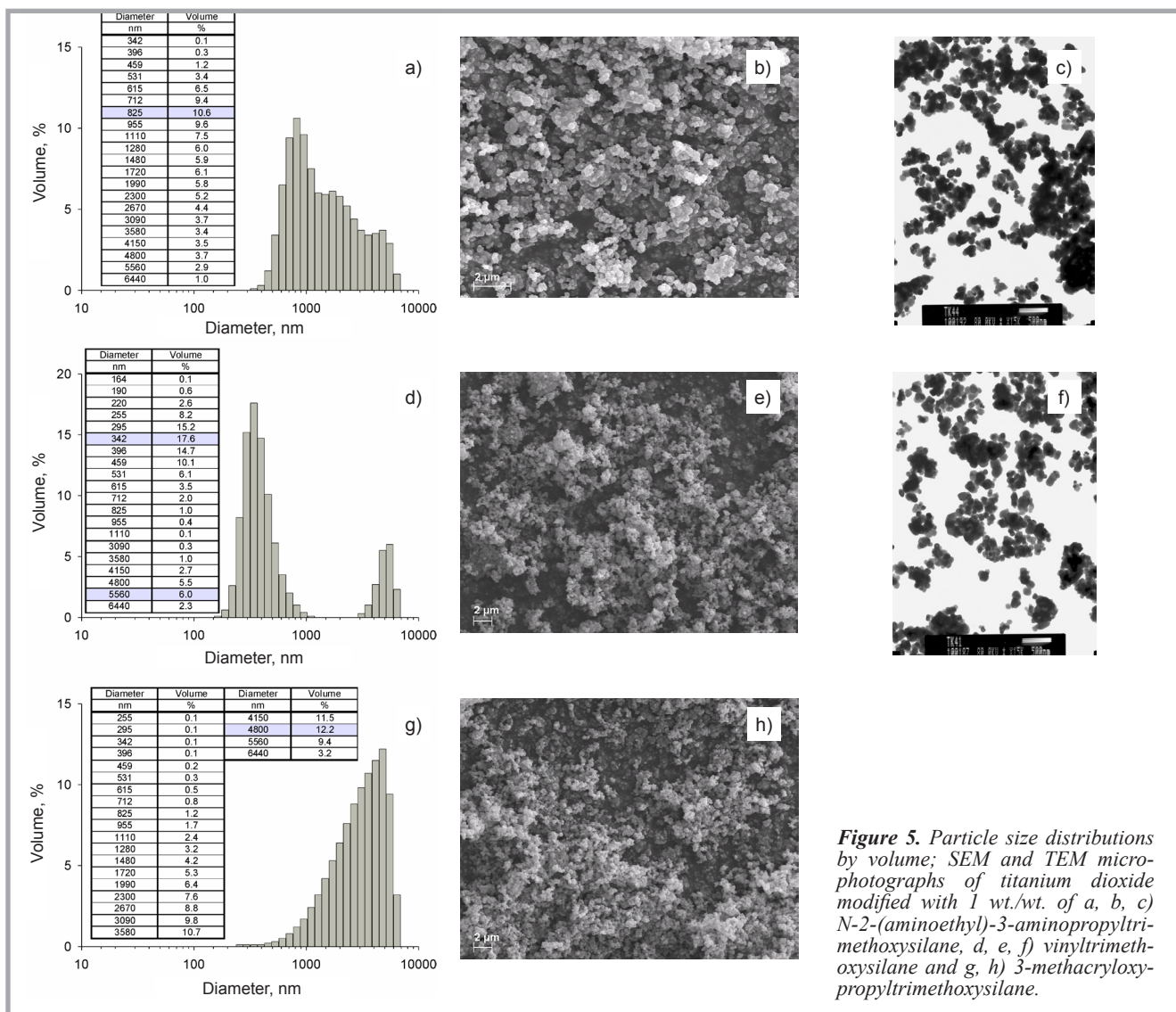


Figure 4. Electrokinetic curves of A-11 modified with 0.5, 1 and 3 wt./wt. of  $N$ -2-(aminoethyl)-3-aminopropyltrimethoxysilane (in the presence of 0.001 M NaCl electrolyte).



**Figure 5.** Particle size distributions by volume; SEM and TEM microphotographs of titanium dioxide modified with 1 wt.% of a, b, c) N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, d, e, f) vinyltrimethoxysilane and g, h) 3-methacryloxypropyltrimethoxysilane.

in the amount of 1% wt. The dispersion was vigorously stirred by a homogeniser, working at a rate of 20 000 r.p.m for 60 s. Then the sample was squeezed (Benz automatic padding machine) at a nip pressure of 30 kG/cm<sup>2</sup> and dried at a temperature of 100 °C for 3 min. Then the samples were dried for 3 minutes in a coating-heating machine of the type KTF-350-S, made by Mathis, and heated at the same temperature for 10 minutes [32 - 34].

### Evaluation of the photocatalytic properties of textile products modified with titanium dioxide of anatase structure

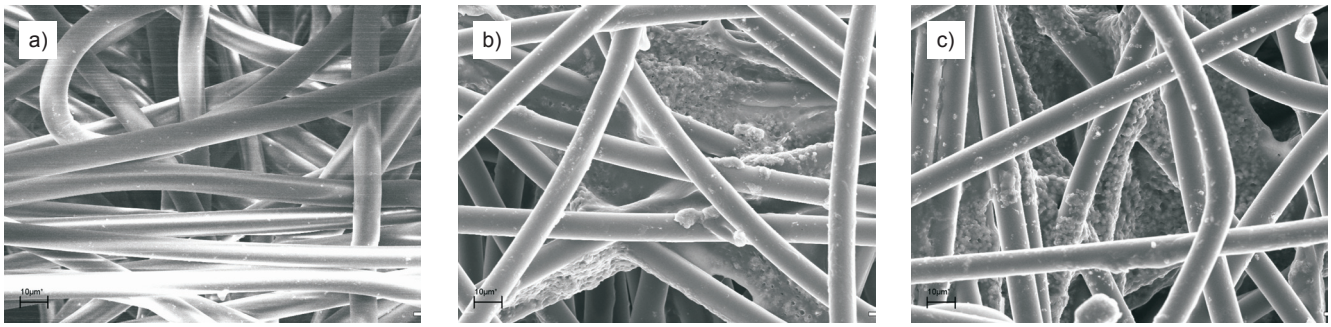
In the experiment the possibility of the removal of organic impurities (formaldehyde) from the air in a closed system with the help of UV radiation and titanium dioxide as a photocatalyst was tested. A sample of the textile product tested was introduced into a reactor containing

a 1.8% water solution of formaldehyde at the bottom. This sample had earlier been subjected to UV<sub>ABC</sub> radiation of 500 W/m<sup>2</sup> intensity at room temperature for 1.5 hours. After the irradiation, the polyester fabric, with an area of 120 cm<sup>2</sup> and mass of about 1.6 g, was kept in the reactor in air containing formalde-

hyde for 2 hours. During these 2 hours, a certain constant pressure of formaldehyde vapour was produced in the reactor. After these 2 hours, the air from the reactor was pumped into a scrubber with porous glass and an absorbing solution of MBTH. Then the concentration of formaldehyde in the air was determined by

**Table 2.** Dispersive characteristics of TiO<sub>2</sub> samples modified with different silane coupling agents (sample A-11).

Modifying agent	Amount of modifying agent, wt./wt.	Particle size distribution by volume in nm and maximum volume contribution in %	Polydispersity
U-511 silane	0.5	122-6440 (5560 nm – 12.0)	0.244
	1	255-6440 (4800 nm – 12.2)	0.319
	3	255-6440 (4800 nm – 19.1)	0.429
U-611 silane	0.5	142-6440 (5560 nm – 11.8)	0.398
	1	164-1110; 3090-6440 (342 nm – 17.6; 5560 nm – 6.0)	0.157
U-15D silane	3	122-1720; 2300-6440 (342 nm – 5.1; 5560 nm – 16.7)	0.437
	0.5	255-6440 (825 nm – 11.3)	0.224
	1	164-6440 (5560 nm – 13.5)	0.237
	3	459-6440 (4800 nm – 24.1)	0.403



**Figure 6.** SEM microphotographs of polyester nonwoven: a) unmodified, b) modified with A-11, and c) modified with 1 wt./wt. of N-2-(aminoethyl)-3-aminopropyltrimethoxysilane.

the colorimetric method for evaluation of the aliphatic aldehydes based on the use of MBTH. Aliphatic aldehydes react with MBTH in the presence of iron(III) chloride and sulphamide acid to give a blue-coloured compound with a maximum absorption at 630 nm [35, 36]. The concentration of formaldehyde in the reactor (X) was calculated from equation (2):

$$X = \frac{C \times 10}{V \times 5}, \frac{\mu\text{l}}{\text{ml}} \quad (2)$$

In which C is the amount of formaldehyde in  $\mu\text{g}$  in a sample volume of 5 ml; V – volume of air pumped out in ml, 10 – total volume of absorbing solution in ml, and is the volume of the solution collected for determination in ml.

On the basis of the measurements, the amount of formaldehyde absorbed by the absorbing solution and the efficiency of formaldehyde decomposition in the solution in which the modified fabric sample was kept were determined and compared with the results for the unmodified fabric sample. Measurements were performed for polyester fabric containing  $\text{TiO}_2$  particles of an anatase structure. The source of  $\text{TiO}_2$  was titanium dioxide Tytanpol® A-11, unmodified or functionalised with selected alkoxy silanes.

## Results and discussion

At first, the  $\text{TiO}_2$  pigment of an anatase structure was subjected to morphologi-

cal and dispersion analysis. The particle size distribution according to the volume contribution shows a single band (**Figure 1.a**) covering a range of particle diameters of 342 - 6440 nm. The maximum volume contribution of 10.6% corresponds to aggregates of 825 nm in diameter, whose polydispersity index is 0.218. According to the dispersion analysis, aggregates comprise 41.1% and agglomerates - 58.9% of the material studied. SEM and TEM microphotographs reveal the presence of particles of spherical shape with high homogeneity, showing a small tendency to agglomeration (**Figure 1.c** and **1.d**).

To characterise the adsorptive properties of  $\text{TiO}_2$  pigment, the nitrogen adsorption/desorption isotherms were estimated and their surface area, pore volume and diameter determined. According to these parameters, Tytanpol® A-11 was found to show low adsorption activity. The isotherms evaluated for  $\text{TiO}_2$  pigment of an anatase structure were classified as type IV, indicating a mesoporous character of the samples. The surface area (BET) is  $10 \text{ m}^2/\text{g}$ . In the relative pressure range  $p/p_0 = 0 - 0.8$ , the amount of nitrogen adsorbed slowly increases; at higher relative pressures it rapidly increases, reaching  $26 \text{ cm}^3/\text{g}$ . For sample A-11 the pore diameter is 7.6 nm, and the total pore volume -  $0.02 \text{ cm}^3/\text{g}$ , as shown in **Figure 2.a**. **Figure 2.b** presents the pore size distribution for sample A-11, which reveals a single narrow band, indicating the high homogeneity of this sample.

The crystallographic structure of the  $\text{TiO}_2$  samples studied was verified by the WAXS method. Titanium dioxide of an anatase structure is characterised by the presence of maxima at  $2\theta$  of 25, 32, 33, 33.5, 48, 54 and 55. **Figure 3** presents the WAXS pattern for  $\text{TiO}_2$  sample studied, confirming its anatase type structure [37].

**Table 3.** Adsorptive properties of the modified  $\text{TiO}_2$ .

Modifying agent	Amount of modifying agent, wt./wt.	$A_{\text{BET}}$ , $\text{m}^2/\text{g}$	$V_p$ , $\text{cm}^3/\text{g}$	$S_p$ , nm
-	-	10.0	0.020	7.60
U-511 silane	0.5	8.47	0.001	5.79
	1	8.19	0.002	4.98
	3	7.05	0.005	2.99
U-611 silane	0.5	9.02	0.004	2.01
	1	8.58	0.004	1.86
	3	7.36	0.004	1.58
U-15D silane	0.5	5.60	0.004	2.99
	1	5.39	0.004	2.87
	3	4.91	0.004	3.01

**Table 4.** Degree of surface coverage of the modified  $\text{TiO}_2$  (sample A-11).

Modifying agent	Amount of modifying agent, wt./wt.	Elemental analysis, %			$N_R$ , $\text{nm}^{-2}$
		N	C	H	
-	-	-	0.024	0.014	-
U-511 silane	0.5	-	0.216	0.117	1.83
	1	-	0.295	0.122	2.60
	3	-	0.816	0.136	8.30
U-611 silane	0.5	-	0.055	0.008	1.53
	1	-	0.075	0.009	2.20
	3	-	0.173	0.012	5.90
U-15D silane	0.5	0.068	0.181	0.032	4.03
	1	0.114	0.283	0.057	6.60
	3	0.341	0.825	0.186	21.10

At the next stage of the experiment, the titanium dioxide sample was functionalised with selected alkoxysilanes to extend the spectrum of application and improve the affinity to textile fabrics. The main aim of the study was to evaluate the efficiency of the process of the functionalisation of commercial titanium dioxide and to determine the effect of this process on the fundamental physico-chemical properties of the systems obtained. Samples of TiO<sub>2</sub> functionalised with alkoxysilanes were subjected to morphological and dispersive characterisation. **Table 2** presents the dispersive characteristics of the modified TiO<sub>2</sub> samples.

The modification of the TiO<sub>2</sub> samples with selected modifying agents of different amounts had a significant effect on the dispersive parameters of the final products.

The dispersive characteristics (**Table 2**) show that noticeable changes in the particle size of the modified TiO<sub>2</sub> appear irrespectively of the type and amount of the modifying agent. The functionalisation of A-11 with 3-methacryloxypropyltrimethoxysilane resulted in an increase in the polydispersity index and the domination of agglomerates compared to those in sample A-11. For the majority of samples, the modification of the surface of titanium dioxide A-11 with selected silanes resulted in the considerable agglomeration of particles, manifested as a significant increase in the volume contribution of secondary agglomerations.

**Figure 5** presents selected particle size distributions as well as SEM and TEM microphotographs of TiO<sub>2</sub> samples functionalised with different silanes, confirming the data presented in **Table 2**.

At the next stage of the study, the adsorption abilities of the modified titanium dioxide samples were characterised. The fundamental parameters determining the surface activity of the modified samples, surface area (BET) and pore size distribution are given in **Table 3**.

Analysis of the data from **Table 3** shows that the greater the amount of the modifying agent, the smaller the surface area (BET). Most probably it is a consequence of blocking the active centres on the surface of the TiO<sub>2</sub> (Ti-OH groups) by the modifier molecules. A considerable decrease in the surface area compared to that of the unmodified sample

**Table 5.** Electrokinetic properties of A-11 functionalised with selected alkoxysilanes.

Modifying agent	Amount of modifying agent, wt./wt.	IEP
-	-	3.42
U-511 silane	0.5	3.21
	1	3.30
	3	3.63
U-611 silane	0.5	3.42
	1	3.22
	3	4.75
U-15D silane	0.5	5.12
	1	6.72
	3	9.40

was observed for all modified samples. The effect of modification with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D) produced a surface area much greater than that of the sample modified with U-511 and U-611 silanes. The addition of any of the modifiers resulted in a decrease in the pore diameters, irrespectively of the modifier amount, compared to those of the unmodified TiO<sub>2</sub>. In contrast to the results of the dispersion analysis, the determination of the adsorption properties proved the effectiveness of the modification and revealed that the modification induced changes in the character of the sample surfaces.

Direct evidence of the efficiency of the process of modification comes from the elemental analysis, whose results permitted the estimation of the degree of coverage of the TiO<sub>2</sub> samples with selected alkoxysilanes. **Table 4** gives the concentrations of modifiers as well as the results obtained from the elemental analysis and BET measurement. The contents of carbon, hydrogen and nitrogen increased and the surface area decreased with an increasing concentration of the modifier.

For the samples modified with U-15D silane, the C/N values, which were defined as the molar ratio of carbon to nitrogen, were close to 3, indicating that most of the methoxy groups in hydrolysed U-15D

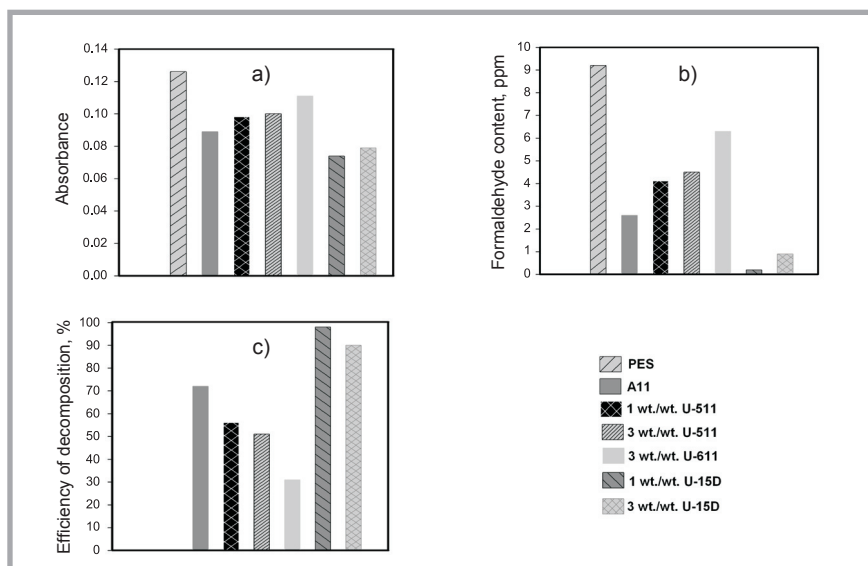
and the amino propyl groups remained on the TiO<sub>2</sub> surface. The N<sub>R</sub> of samples modified with U-15D increased up to 21, while that of samples modified with U-511 and U-611 increased up to 8 and 6, respectively. The N<sub>R</sub> value of the samples modified with U-15D was different from that of the samples modified with U-511 and U-611 at the same concentration of the modifier due to the different reaction mechanisms. It is well known that silane coupling agents are first hydrolysed to become silanols, and then condensation reactions between the silanols and surface hydroxyl groups on the substrate occur. However, a special interaction between the amino group and TiO<sub>2</sub> surface also takes place, which is responsible for the reactivity being higher than that of U-511 and U-611. Various types of interaction between aminosilane and the TiO<sub>2</sub> surface have been proposed in literature [38, 39]. Polyester nonwoven modified with TiO<sub>2</sub> functionalised with aminosilane contains amine groups which effectively remove formaldehyde [27].

The efficiency of the modification of inorganic oxides with selected organic compounds can be readily estimated by electrokinetic measurements, i.e. measurements of the zeta potential versus pH, which is why in the next step the samples of titanium dioxide functionalised with alkoxysilanes were studied for their electrokinetic properties. **Table 5** presents the IEP values recorded for titanium dioxide A-11 modified with selected alkoxysilanes.

The modification of a titanium dioxide surface A-11 with different amounts of *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D), see **Figure 4**, resulted in significant changes in the character of the electrokinetic curves. These plots differ considerably from the reference plot obtained for unmodified titanium dioxide – A-11 (whose IEP is 3.42 – Roessler et. al. [40] mentioned that the IEP's for anatase vary between 3 and 6.6.). After

**Table 6.** Photocatalytic properties of polyester nonwoven fabric dip-coated with unmodified or modified titanium dioxide (sample A-11).

Modifying agent	Amount of modifying agent, wt./wt.	Dry substance of TiO <sub>2</sub> on fabric samples, % wt.	Efficiency of formaldehyde degradation, %
-	-	4.0	72
U-511 silane	1	4.4	56
	3	4.4	51
U-611 silane	3	4.4	31
U-15D silane	1	4.0	98
	3	4.1	90



**Figure 7.** a) Absorbance, b) content of formaldehyde in air collected from the reactor, and c) efficiency of formaldehyde photodegradation in the reactor's air in the presence of different samples.

modifications with 0.5, 1 and 3 wt./wt. of U-15D silane, the isoelectric points were 5.12, 6.72 and 9.40, respectively; hence its value increased with an increasing amount of the modifying agent used for surface functionalisation. This significant increase in IEP values is attributed to the strong ionisation effect of  $-NH_2$  groups. The dissociation of these groups also plays an important role in changes in the surface charge of  $TiO_2$ . When the density of  $H^+$  ions is high,  $NH_3^+$  groups start forming, and hence a positive charge of the modified  $TiO_2$  is produced. With an increasing concentration of  $H^+$  ions, the process of dissociation gets restricted, and the surface charge decreases. For sample A-11 modified with U-15D silane, the zeta potential takes positive values in almost all the acidic pH range. Cai et. al. [41] confirmed that the isoelectric point of  $pH = 7$  for titanium film functionalised with (3-aminopropyl)-triethoxysilane was observed.

The modification of the surface of  $TiO_2$  of an anatase structure with the other two silanes studied did not result in considerable changes in the character of the relevant electrokinetic curves, which were similar to that recorded for the unmodified sample. This observation was confirmed by the isoelectric points of the modified samples. For A-11 modified with 0.5, 1 and 3 wt./wt. of U-511 silane, the IEP takes values of 3.21, 3.30 and 3.63, respectively, and for titanium dioxide modified with 0.5, 1 and 3 wt./wt. of U-611 silane the isoelectric points oc-

cur at a lower pH, that is, at 3.42, 3.22 and 4.75, respectively.

**Figure 6** presents SEM microphotographs of the polyester nonwoven samples and **Figure 6.a** - those of polyester nonwoven. The fibres have a circular cross-section, and their surface is smooth, partly covered with small objects, probably impurities. In **Figure 6.b**, polyester nonwoven after  $TiO_2$  modification (Tytanpol® A-11) is shown. Their smooth surface is covered by finely dispersed  $TiO_2$ . In some places agglomerated, larger structures are also observed. **Figure 6.c** presents polyester nonwoven samples treated with  $TiO_2$  functionalised with 1 wt./wt. of aminosilane. The observations indicate that the surface quality of individual nonwovens did not change when compared to the reference sample (raw polyester nonwoven). However, it seems that the fibres are covered more uniformly when compared to the nonwoven sample modified with  $TiO_2$ . Moreover, the powder particles of  $TiO_2$  functionalised with aminosilane are less agglomerated than in the case of nonwoven samples treated with A-11.

The textile products modified with titanium dioxide of an anatase structure are characterised by strong UV absorption. In view of the above, the photocatalytic properties of the textile fabrics dip-coated with unmodified or modified titanium dioxide were tested for their reaction to the photodegradation of formaldehyde by UV irradiation. **Figure 7.a** presents the absorbency of individual textile products

measured before and after dip-coating with unmodified or modified titanium dioxide. For the absorbency values measured, the corresponding concentration of formaldehyde was read off from the calibration curve. In this way we plotted the content of formaldehyde in the reactor's air corresponding to the presence of individual polyester fabric samples. The initial content of formaldehyde in the reactor into which the unmodified nonwoven polyester fabric was introduced was 9.2 ppm. When the polyester fabric contained in its structure  $TiO_2$  particles of an anatase structure, the content of formaldehyde decreased to 2.6 ppm. The greatest decrease in formaldehyde content was noted for nonwoven polyester fabric dip-coated with A-11 functionalised with U-15D. The content of formaldehyde was reduced to 0.2 and 0.9 ppm by the presence of nonwoven polyester fabric modified with 1 and 3 wt./wt. of aminosilane, respectively (**Figure 7.b**).

The efficiency of formaldehyde photodegradation in the presence of modified polyester fabric was measured with reference to that in the presence of unmodified polyester fabric. The measurements showed that titanium dioxide in an anatase form introduced into the structure of polyester fabric in the amount of about 4% wt. had very good photooxidation activity (**Table 6**).

The highest efficiency of formaldehyde degradation of over 90% was observed in the presence of polyester fabric dip-coated with  $TiO_2$  after surface functionalisation with U-15D, see **Figure 7.c** and **Table 6**. In the presence of polyester fabric coated with  $TiO_2$  modified with 1 wt./wt. of U-15D, the formaldehyde degradation efficiency reached 98%.

## Conclusions

According to the results discussed and presented above, the surface character of inorganic oxide systems like  $TiO_2$  can be modified by simple chemical methods, extending the spectrum of their application. The determination of the efficiency and stability of the inorganic oxide materials obtained is not a problem because there are many methods that can be used for this purpose.

For the majority of samples, the modification of titanium dioxide A-11 with selected silanes caused the significant agglomeration of particles of the samples,

manifested as a considerable increase in the volume contribution of secondary agglomerates.

In contrast to the results for dispersive characteristics, the determination of adsorptive properties proved the effectiveness of the modification and revealed that the modification induced changes in the character of the sample's surface. The surface area of TiO<sub>2</sub> modified with the silanes selected decreased with an increasing amount of the silane deposited. The smallest was the surface area of TiO<sub>2</sub> modified with aminosilane U-15D.

The efficiency of the adsorption of the alkoxy silanes selected was confirmed by elemental analysis, proving that the degree of surface coverage increases with increasing concentrations of the silanes used for inorganic surface functionalisation.

The zeta potential changes as a function of pH, and the IEP values of titanium dioxide strongly depend on the type and amount of alkoxy silane used. For the titanium dioxide samples modified with 3-methacryloxypropyltrimethoxysilane (U-511) and vinyltrimethoxysilane (U-611), the IEP values showed a tendency to shift towards lower pH values with an increasing amount of the modifying agent used. For the samples modified with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D), the reverse tendency was noted. The most pronounced changes in electrokinetic properties were observed for titanium dioxide modified *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane, which were attributed to the specific interactions of -NH<sub>2</sub> groups in acidic or alkaline environments, i.e. to their ability to attach or abstract potential forming ions, such as H<sup>+</sup>.

The efficiency of the process of modification was confirmed by the results of the elemental analysis, which permitted the estimation of the degree of surface coverage N<sub>R</sub>. The N<sub>R</sub> of samples modified with U-15D increased up to 21, while that of samples modified with U-511 and U-611 increased up to 8 and 6, respectively. A special interaction between the amino group and TiO<sub>2</sub> surface also happens, which causes a higher reactivity than in the case of U-511 and U-611.

The tests of formaldehyde photodegradation in the presence of titanium dioxide as a photocatalyst proved the very good photooxidation activity of TiO<sub>2</sub> in an anatase structure. The highest efficiency of formaldehyde degradation of

over 90% was obtained in the presence of polyester fabric dip-coated with TiO<sub>2</sub> and modified with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (U-15D). The results indicate the possibility of the degradation of organic compounds with the use of sunlight.

The research performed allows to state that textile products containing anatase titanium dioxide in their structure show very good photocatalytic activity as compared to organic compounds – formaldehyde. The materials modified can find application in building engineering, in rooms exposed to the presence of toxic organic compounds.

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