

Article

Washing Durability and Photo-Stability of NanoTiO₂-SiO₂ Coatings Exhausted onto Cotton and Cotton/Polyester Fabrics

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Abstract: The purpose of this study was to assess and compare the durability of TiO₂-SiO₂ coatings applied in three concentrations onto two lightweight cellulose-based fabrics diverse in the composition against two external factors, repeated washings and prolonged intensive UV irradiation, by observing the changes in surface morphology, investigation of optical properties, and identification of specific molecular vibrations. The scanning electron microscopy (SEM) micrographs, diffuse reflectance spectroscopy (DRS) profiles and fourier transform-infrared (FT-IR) spectra implied equal distribution of TiO₂-SiO₂ nanoparticles over the surfaces of both fabrics after exhaustion procedures, regarding the concentration of colloidal paste and the type of material used, followed by a slight reduction of nanoparticles after twenty washing cycles. Moreover, the newly gained, good to very good UV protective functionality proved the suitability of the employed procedure and the sufficient durability of the selected coatings. Additionally, UV irradiation mainly caused damages to the cotton. Cotton/polyester became yellower under UV, although the application of TiO₂-SiO₂ protected the material against yellowness.

Keywords: surface functionalization; cotton fabric; cotton/polyester fabric; nanoTiO₂-SiO₂; washing durability; photo-stability

1. Introduction

Cellulose fibers are well-known for comprehending imposing characteristics like biocompatibility, non-toxicity, high water absorbency, being safe and comfortable to wear and easy to dye [1]. Notwithstanding, textile fabrics based on cotton also have some undesirable features such as being easily soiling, easily wrinkled, having low strength, and an inclination towards microbial attack, supporting the growth of micro-organisms. This promotes the usage of cotton/polyester blends (Co/PES) of various ratios (25:75, 35:65, 50:50, etc., depending on the requirements of end-products) for short-sleeved sport shirts and summer blouses by assuring the required physical properties and comfort in wear [2]. However, lightweight non-colored or brightly-colored Co/PES garments, which are very popular for summer shirts, offer only low ultraviolet protection factor (UPF), less than 15; whilst the sufficient clothing UPF for outdoor wear should be at least 40 [3]. In order to enhance the UV protection, as well as to improve some other functional properties, numerous researchers have recently oriented their investigations towards the employment of various nano-sized particles during different steps of textile finishing [1,4–7]. Moreover, these novel nano-technological accessions seem to be a good alternative to the conventional harsh chemical treatments, and therefore, should offer desirable levels of material functionality even after prolonged usage and care.

Titanium dioxide (TiO_2) is among the highly desirable nanoparticles for surface modifications of numerous textiles, because of its superior chemical stability, non-toxicity, good heat resistance, excellent transparency for the visible light, and excellent photo-activity under UV radiation [8–10]. Herein, a limited number of studies have focused on both the evaluation of newly gained functional properties after several washings and the eventual side-effect after prolonged light exposure, like yellowness, bleaching, polymer degradation, reduction of newly-obtained functionalities, etc. Montazer et al. [11] studied the photo bleaching of wool using a nano TiO_2 catalyst, in order to decompose the naturally-occurring pigments. The obtained results confirmed excellent hydrophilicity and reasonable whiteness even after five washings, regarding the amount of applied TiO_2 , although the textile degradation was not investigated. In contrast, the study realized by Selishchev et al. [6] presented SEM pictures of the self-destruction of TiO_2 functionalized textiles under long-term UV irradiation. The same paper reported a reduction in material damages when nano TiO_2 was deposited by a silica (SiO_2) protective layer. Moreover, SiO_2 shell can also be used as a binder between nanoparticles and the textile surface, providing desired functionalities after laundering or extensive wearing.

The main goal of the presented research was, therefore, to examine the washing durability of nano TiO_2 - SiO_2 coatings, and consecutively, the influence of repeated launderings on the fabrics' newly obtained UV protective properties. TiO_2 - SiO_2 core-shell nanoparticles in the form of colloidal paste were applied in three concentrations onto two industrially bleached non-colored fabrics made from cotton and cotton/polyester fabric for summer clothes. Emphasis was also given to possible fabrics' self-destruction on a micro level under intensive UV-A and UV-B irradiation, as well as to the visually-perceivable changes in material whiteness/yellowness.

2. Experimental

2.1. Materials

Two woven fabrics in the form of strips (9.5 g) were selected for modification experiments. One fabric was made from cotton fibers (Co) in plane weave, with a mass of 110 g/m^2 , warp density of 41 threads/cm and weft density of 38 threads/cm, and yarn fineness of 20 tex. The other fabric was made from mixtures of cotton/polyester fibers (Co/PES) in a ratio of 70:30, with a mass of 105 g/m^2 , warp density of 34 threads/cm and weft density of 30 threads/cm, yarn fineness of 17 tex (from Co) in warp direction and yarn fineness of 20 tex (from mixture of Co/PES 50/50) in weft direction. Both fabrics were designed for summer shirts with high transparency, and consecutively, good air permeability. Moreover, both fabrics underwent the same industrially completed pre-treatment procedures without optical brighteners (preparation for dyeing). Before the TiO_2 - SiO_2 modification, the samples were washed for 20 min at $40 \text{ }^\circ\text{C}$ by a neutral non-ionic washing agent, in order to remove impurities that could influence the subsequent modification, and thereafter, thoroughly rinsed with warm and then cold water, and dried at an ambient temperature.

The commercially-available SiO_2 coated TiO_2 colloidal dispersion applied during this study was synthesized by the Cinkarna Inc., Metallurgical and Chemical Industry, Celje, Slovenia, in the form of paste via the sol-gel process from metatitanium acid, which is a by-product of the sulfate synthesis process. A detailed description of the surface treated pigmentary TiO_2 was disclosed [12]. According to the producer information, the dispersion contained approximately 20 wt.% of crystalline rutile TiO_2 nanoparticles and was precipitated with 3 wt.% of SiO_2 .

2.2. TiO_2 - SiO_2 Application Procedure

The aforementioned nano TiO_2 colloidal dispersion was applied on the two selected fabrics according to the industrially-acceptable exhaustion procedure, using liquor-to-fabric weight ratio of 20:1 (180 mL of deionized water against 9 g of Co or Co/PES fabric), within a sealed stainless-steel pot of 200 cm^3 capacity, housed within the laboratory apparatus Labomat (W. Mathis AG, Oberhasli, Switzerland) at a temperature of $60 \text{ }^\circ\text{C}$ for 110 min. The previously-optimized initial bath was

composed of 3%, 6% or 9% owf (of weight of fabric) of TiO₂-SiO₂ paste (meaning ca. 0.054 g, 0.108 g or 0.162 g of pure TiO₂), respectively, 30 g/L of NaCl, 5 g/L of NaHCO₃, 1g/L of leveling agent (Meropan OFS, CHT Switzerland AG, Montlingen, Switzerland), and 0.8 mL/L of NaOH (32%) for alkaline pH adjustment. The treated samples were rinsed in warm and then cold deionized water, and dried at room temperature.

2.3. Washing Procedure

In order to assess the washing durability of TiO₂ core-shell nanoparticles bonded onto cotton and cotton/polyester fabrics, all the samples were washed repeatedly up to 20 times in a Labomat (W. Mathis AG, Oberhasli, Switzerland), using a solution of 4 g/L of standard reference detergent without optical brighteners (the formulation is given in EN 20105-CO1:1993; Clause 4.2) at a temperature of 40 °C for 30 min, and a liquor-to-fabric weight ratio of 50:1. Thereafter, the samples were rinsed several times in deionized water, and then tap water for 30 min, and finally dried at a room temperature.

2.4. UV Irradiation

For the purpose of the fabrics' photo-stability evaluation, TiO₂-SiO₂ coated samples were irradiated with an artificial UV source for a prolonged time of up to 720 h. Those samples with an area of 8 cm × 5 cm were placed in a photo-reactor (Luzchem Research Inc., Ottawa, ON, Canada) equipped with six overhead UV lamps of which three lamps, providing UV-A light within the range of 316–400 nm and the main peak at 350 nm, and three lamps emitting mainly UV-B light within the range of 281–315 nm and the main peak at 313 nm. The UV luminance in the reactor was 18,600 Lux measured by a Digital Light Meter SLM-110, A.W. Sperry Instruments, Inc. (New Berlin, WI, US).

2.5. Characterization Methods

2.5.1. Analysis of Colloidal Dispersion

Three analytical techniques were employed, with the intention of analyzing the selected TiO₂-SiO₂ core-shell nanoparticles' dispersion, i.e., scanning electron microscopy (SEM), transmission electron microscopy (TEM), and ultraviolet-visible (UV-Vis) spectrophotometry. The sample for SEM analysis was prepared by drying a drop of water dilution of TiO₂-SiO₂ dispersion in a 0.1% concentration on adhesive carbon tape, which was placed on a brass holder for observation on a scanning electron microscope FE-SEM-ZEISS Gemini Supra 35 VP (Carl Zeiss NTS GmbH, Oberkochen, Germany). In addition, morphology analysis of the surface-treated TiO₂ was accomplished by dropping a watering colloidal dispersion of about 1% on the Cu-grid, dried at a temperature of 40 °C and thereafter observing the using a JEM-2100 transmission electron microscope (Jeol Ltd., Tokyo, Japan) with LaB₆ as an electron source. With the aim to establish the particles size distribution and average particle size, dynamic light scattering (DLS) analysis was accomplished, using a Zetasizer Nano HT (Malvern, UK), equipped with a light-scattering unit. The measuring temperature was fixed at 25 °C. Finally, the absorption spectra of TiO₂ dispersion (diluted in a deionized water at a concentration of 16 mg/L) was recorded throughout the UV-Vis spectrum from a wavelength of 200 up to 700 nm, by means of a Varian Cary 50 UV-Vis spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) using a 10 mm quartz cuvette.

2.5.2. Analysis of TiO₂-SiO₂ Coated Fabrics

Various analytical techniques were utilized, with the aim of exploring the washing durability of coatings (up to 20 washing cycles), as well as the photo-stability of modified fabrics under prolonged UV irradiation (up to 720 h), i.e., scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), Attenuated total reflectance-fourier transform infra-red (ATR-FTIR) spectroscopy, and UV transmittance spectrophotometry.

SEM images were obtained by attaching approximately 1 cm² of fabric samples onto an adhesive carbon band fixed to a brass holder and observed using a scanning electron microscope FE-SEM-ZEISS Gemini Supra 35 VP (Carl Zeiss NTS GmbH, Oberkochen, Germany).

The diffuse reflectance spectra (DRS) profiles of fabrics in the 220–400 nm wavebands were taken on a Lambda 900 UV-Vis-NIR spectrophotometer (Perkin Elmer, Waltham, MA, US) with an integrated sphere at a scanning speed of 450 nm per min. The tested samples were folded three times to obtain eight layers, so that the light could not be transmitted through the fabric.

Measurement of reflectance from wavelengths 400 up to 700 nm was accomplished for each sample at three different locations by means of a spectrophotometer SF 600 Plus (Datacolor, Luzern, Switzerland) under a standard illuminant/observer D65/10° (SAV/Spec. Incl.) and thereby, the average International Commission on Illumination (CIE) whiteness (W) and yellowness (YI) indices of samples were calculated using Equations (1) and (2), respectively:

$$W = Y + 800(x_n - x) + 1700(y_n - y) \quad (1)$$

where Y is the tristimulus value; x and y are the chromaticity coordinates of the observed white sample; and x_n and y_n are chromaticity coordinates of the completely opaque standardized white object.

$$YI = \frac{100 \cdot (1.3013 \cdot X - 1.1498 \cdot Z)}{Y} \quad (2)$$

where Y , X and Z are tristimulus values in CIE color space.

Infrared transmission absorbance spectra of selected samples were obtained using a spectrophotometer FTIR System Spectrum GX (Perkin Elmer, Waltham, MA, US) with a Golden Gate ATR attachment and a diamond crystal. The measurements were carried-out within the range of 4000–650 cm⁻¹, with 32 scans and a resolution of 4 cm⁻¹.

The level of the fabrics' shielding capability against harmful UV rays is usually expressed by the ultraviolet protection factor (UPF). UPF was calculated from the fabrics' UV-A and UV-B transmittance values, which were recorded according to the Australian/New Zealand Standard (AS/NZS 4399-1996) [9] over the ultraviolet spectral region of 280–400 nm wavelengths using a solar-screen Varian Cary 50 spectrophotometer (Agilent Technologies, Santa Clara, CA, US), fitted with an integrated sphere accessory and a fabric holder accessory.

3. Results and Discussion

3.1. Colloidal Dispersion Analysis

In order to study the surface morphology of TiO₂-SiO₂ colloidal dispersion for the subsequent functionalization of Co and Co/PES fabrics, SEM and TEM micrographs were taken, and presented in Figure 1. Furthermore, the size distribution of nanoparticles was presented on Figure 2.

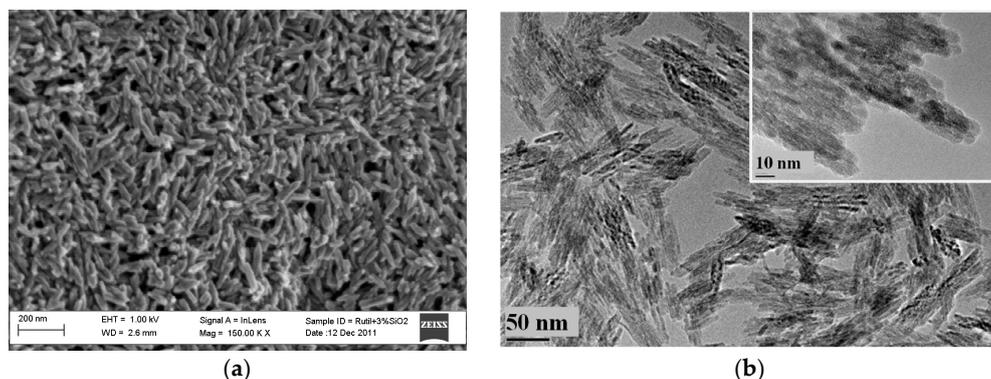


Figure 1. (a) SEM image; and (b) TEM image of used TiO₂-SiO₂ nanoparticles at different magnifications.

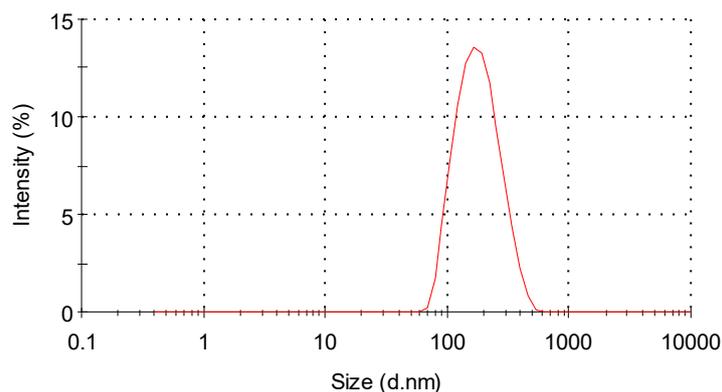


Figure 2. Size distribution plot of TiO₂-SiO₂ colloidal dispersion.

From the SEM image in Figure 1a, non-spherically shaped nanoparticles of ca. 167 nm in length and ca. 30 nm in width could be unequivocally perceived, which was also confirmed by dynamic light scattering (DLS) measurement (Figure 2). Further, the isotropic morphology of very small non-spherical TiO₂ crystals of >10 nm in length and ca. 4–5 nm in width was exposed by TEM (Figure 1b), which aggregated into an individual (polycrystalline) nanoparticle. These nanoparticles were coated with amorphous SiO₂ (white areas). The formation of SiO₂ shell in selected colloidal dispersion was depended above all on the reactions involved during industrial synthesis procedure as well documented [12].

In addition, the UV-Vis absorbance curve of TiO₂-SiO₂ paste dispersed in water within a concentration of 16 mg/L was recorded from a wavelength of 200 up to 700 nm, and shown on Figure 3, in order to elucidate the role of TiO₂ nanoparticles on the UV-blocking properties of modified Co and Co/PES fabrics.

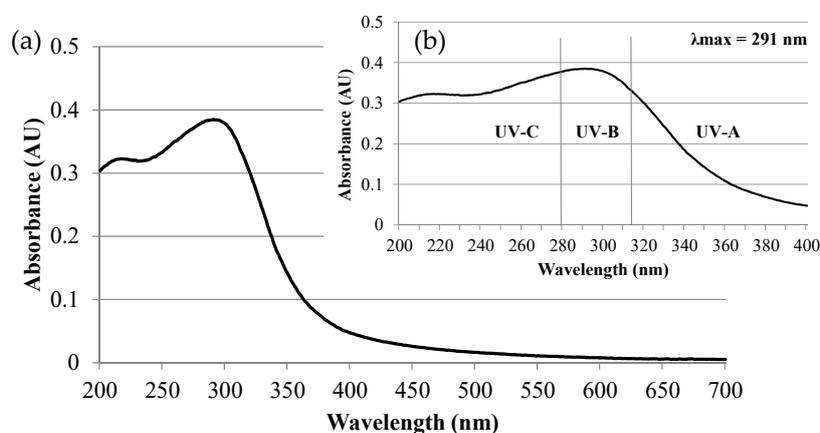


Figure 3. UV-Vis spectrum of mightily diluted colloidal dispersion.

It could be concluded from Figure 3a that the employed nanoparticles have prominent UV-shielding characteristics since they absorb the damaging UV light within a spectral range of between 200 and 400 nm at an exceedingly low concentration of TiO₂-SiO₂ colloidal dispersion, with an absorbance maximum (λ_{\max}) at a wavelength of 291 nm (Figure 3b). It should also be mentioned that a higher TiO₂ content in dispersion (in our case was approximately 20% regarding the producer information) indicates a higher absorbance within the UV region as demonstrated by Ojstršek et al. [9], which consequently influences the higher UV-protection ability of TiO₂-modified fabric at the same operational parameters during the TiO₂ application procedure.

3.2. Washing Durability and UV Photo-Stability of Nano-Modified Textiles

With the intention of evaluating the washing durability of TiO₂-SiO₂ coatings, and therein, the suitability of bath composition, as well as the operational parameters of the exhaustion procedure, several approaches/techniques were used on the unwashed reference and the washed coated samples, including:

- examination of surface morphology by means of SEM;
- investigation of optical properties by measuring the fabrics' UV transmittance and UV/Vis reflectance, followed by the calculation of the ultraviolet protection factor (UPF), CIE whiteness degree and yellowness index, respectively, and
- identification of molecular vibrations through recording the infrared transmission absorbance by FTIR spectroscopy.

Veronovski et al. [12] explicated that like most organic materials, TiO₂-coated textiles meant that the outdoor wearer was inclined towards ageing under the influence of external conditions (sunlight). This can lead to changes in the coatings' appearances, changes in physical and chemical properties, as well as to the reduction of materials' functional properties. Moreover, nano-sized TiO₂ exhibited strong photo-catalytic activity under UV radiation, generating powerful oxidative intermediates (hydroxyl radicals) that can decompose or degrade various organic compounds [6,8]. Therefore, in order to evaluate the changes in coating appearance, as well as the photo-stability of the modified fabrics, the above-mentioned analytical techniques were employed on reference and UV irradiated samples. The results are evidently presented over seven figures in association with adequate discussions as follow.

3.2.1. Fabric Surface Morphology

With the aim of visually establishing the effect of repeated washings (up to 20 washing cycles) as well as intensive UV irradiation (up to 30 days) on the durability/stability of TiO₂-SiO₂ coatings and possible fabric damages, the surface morphologies of selected samples at the micrometer level are disclosed in Figure 4.

Representative SEM images in Figure 4 demonstrated the different coating morphologies regarding the used material, i.e., cotton (left column) or cotton/polyester (right column) as well as employed (post)treatment procedure, i.e. untreated, untreated and 30 days UV irradiated samples, modified by 9% owf of TiO₂-SiO₂ colloidal dispersion, TiO₂-SiO₂ modified and ten times washed, and TiO₂-SiO₂ modified and 30 days UV irradiated samples. Co fibers' morphological structure show regular helical longitudinal profile in comparison to the PES uniaxial structural symmetry. In the case of TiO₂-SiO₂ modified Co, slightly thicker coatings with higher nanoparticle content could be observed over complete fibers' surfaces as compared to the Co/PES. This is presumably on account of free hydroxyl groups on Co surface, which could interact with silanol groups of core-shell nanoparticles, forming covalent bonds, and thus, ensuring a strong adhesion between the coatings and the fiber surface [13]. On the other hand, PES fibers do not possess hydroxyl groups on the surface, therefore, only a weak physical adhesion occurs between the PES surface and nanoparticles, causing impaired adhesion of the coating. After 20 washing cycles, using standard washing procedure at a temperature of 40 °C, the amount of nanoparticles was reduced on both materials, and less uniform distribution was achieved. Thus, 720 h of intensive artificial UV-A/UV-B irradiation caused minor injuries and a decrease in the smoothness, not only on both modified fabrics, but also on unmodified ones; especially cotton fibers that are prone to the self-degradation under UV rays. Moreover, nanoparticles are agglomerated on the coated surfaces and in some degree flattened along the fibers. However, in order to evaluate the decreasing of nanoparticles over the entire fabrics' surfaces, and consecutively, the deterioration of materials' functional properties, further analyses are needed.

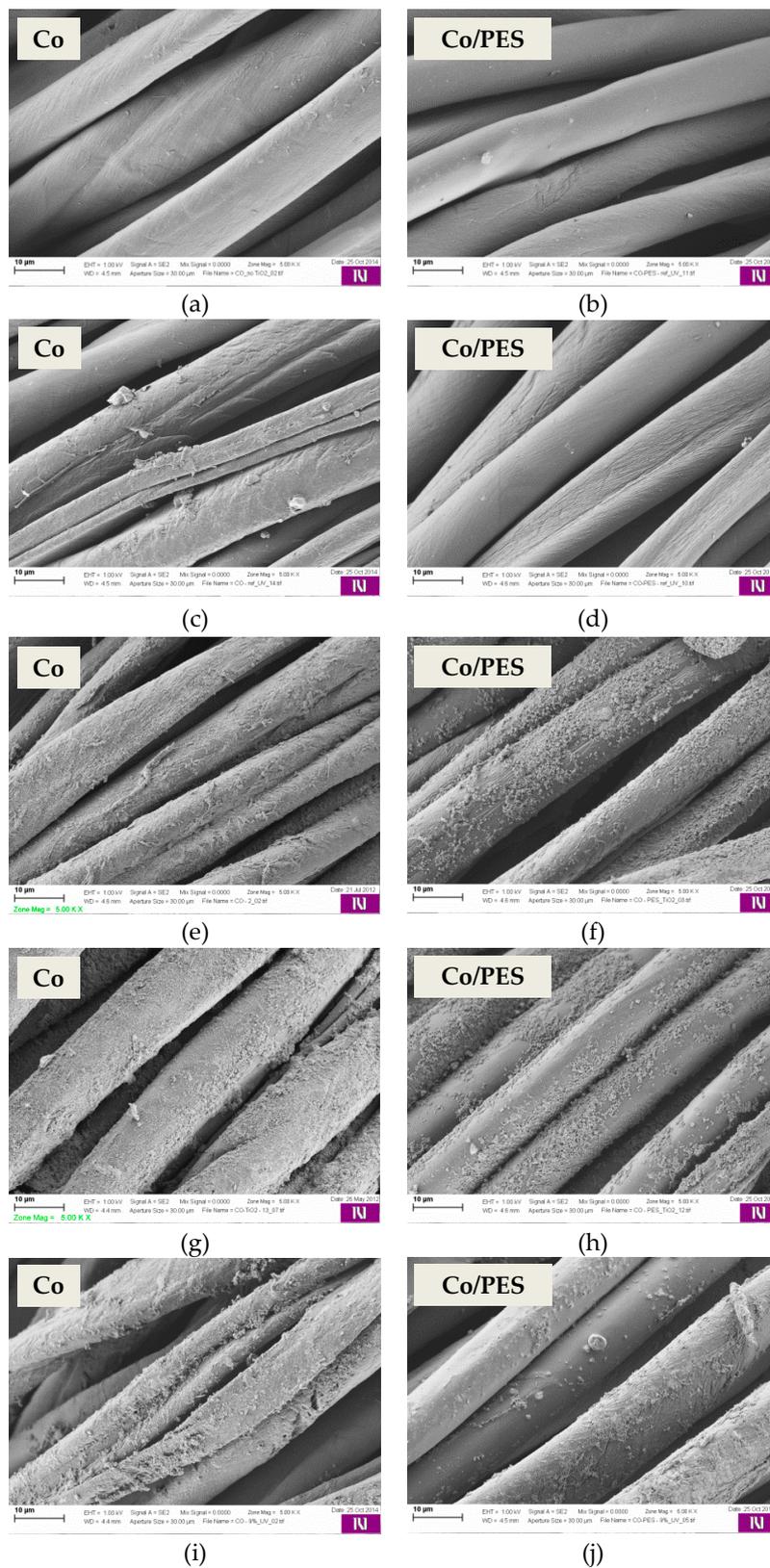


Figure 4. Selected SEM microphotographs of untreated and modified cotton (Co) and cotton/polyester blend (Co/PES) fabrics further washed and UV irradiated at 5000× magnification. (a,b) Reference; (c,d) Reference/UV irradiated; (e,f) TiO₂-SiO₂ modified samples; (g,h) TiO₂-SiO₂ modified/20× washed samples; (i,j) TiO₂-SiO₂ modified/UV irradiated samples.

3.2.2. Diffuse Reflectance Spectra (DRS)

The DRS profiles within the UV region are presented and compared in Figure 5 between TiO₂-SiO₂ modified cotton and cotton/polyester fabrics, with the emphasis on the stability of TiO₂-SiO₂ nanoparticles application after 20th washing cycles and after long-time UV exposure.

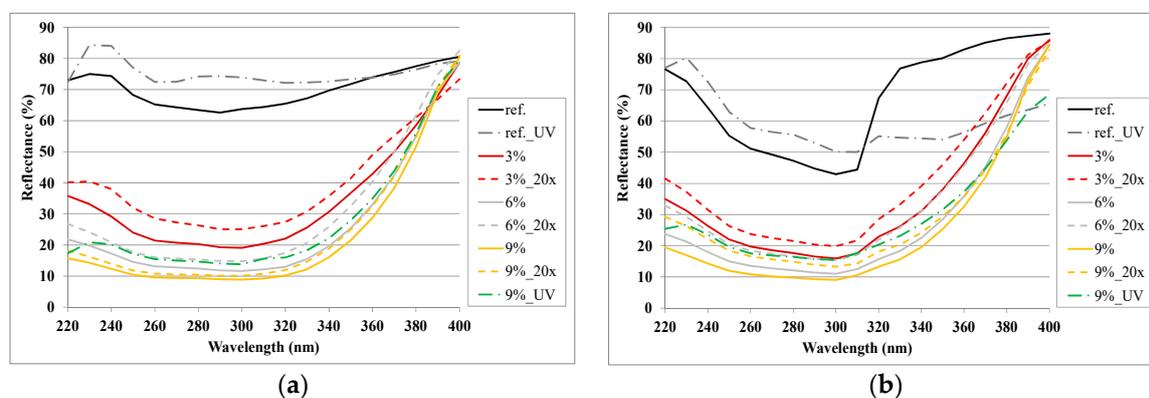


Figure 5. DRS profiles of: (a) Co; and (b) Co/PES; un-modified (ref.), un-modified/UV irradiated (ref._UV), nano-TiO₂ modified by 3%, 6% or 9% owf of TiO₂ paste, nano-TiO₂ modified/20× washed fabrics, and 9% owf nano-TiO₂ modified/UV irradiated sample.

Figure 5 shows the differences between the DRS curves of the non-modified Co and Co/PES fabrics as expected on account of the higher UV absorbance capacity of the PES fibers in comparison to the Co fibers. The employment of nano-sized TiO₂ exceedingly diminished the reflectance curves on both graphs; enlarged the UV absorption ability, as also presented by Zhang and Zhu [14]. Moreover, the higher the paste concentration on the fabric, the lower the reflectance values were in the spectrum' UV region, implying superior UV-rays blocking properties of the TiO₂-modified fabrics. The obtained results also indicated somewhat increased reflectance curves after twenty washing cycles, irrespective of the material used, which was more explicit at a lower amount of applied TiO₂-SiO₂ colloidal dispersion, i.e., 3% owf. Notwithstanding, we can deduce satisfying durability of the exhausted nanoparticles. These results were in good agreement with the calculated fabrics' UPFs.

Exposure to UV lightness significantly changed the courses of the reflectance curves of the untreated Co/PES sample. The reflectance values were approximately 20% lower within the UV-A region, indicating higher UV absorption ability, and consecutively, a higher UPF as compared to the non-irradiated one, which was further proven by transmittance measurement.

3.2.3. ATR-FTIR Spectroscopy

The FTIR spectra of reference (untreated) and modified Co and Co/PES samples before and after several washings, and after intensive UV irradiation were recorded within the region of 4000–650 cm⁻¹ and presented in Figure 6, in order to examine the binding efficiency between the fibers and applied TiO₂-SiO₂ colloidal dispersions, and also to study the possible fiber degradation. All spectra were normalized at a chosen wavenumber of 1200 cm⁻¹, which remained unaffected during surface modification.

Figure 6a depicts a FTIR pattern with typical peak positions for cotton including free hydroxyl groups at 3500–3200 cm⁻¹, water molecules at ~1640 cm⁻¹, O–H, C–O, C–H and C–O–C vibrations within the glucose ring at 1500–800 cm⁻¹, as also fully interpreted in [3,5]. In Figure 6b, some typical peaks of polyester were observed, i.e. characteristic stretching vibration band of the ester carbonyl group in conjugation with an aromatic ring at 1716 cm⁻¹, asymmetric C–C–O vibrations at 1242 cm⁻¹, and aromatic C–H wagging at 719 cm⁻¹ [15], accompanied by some typical cotton peaks as the above-named. Although, the absorption peaks of all the obtained spectra are quite similar on an individual graph, some characteristic absorption bands are evidently recognized for the TiO₂-SiO₂

modification of both Co and Co/PES fabrics, i.e. the peak around 1100 cm^{-1} corresponded to stretching vibrations and around 800 cm^{-1} to the bending vibration modes of the Si–O–Si bonds, peak at 985 cm^{-1} related to Ti–O–Si linkages, and around 670 cm^{-1} corresponded to the symmetric stretching vibrations of O–Ti–O bands [3,16]. After repeated washings those peaks were slightly reduced on both diagrams, but did not disappear, confirming good durability of the selected coatings against washing as could be expected from SEM and DRS results. UV irradiation, on the other hand, caused damage to the material, and consecutively, some peaks became expanded or intensified like peaks at 1716 and 1242 cm^{-1} (Co/PES), on account of the larger amount of degradation products on the surface containing –CO group (ketones, carboxylic acids and esters), and peaks at 3324 and 1633 cm^{-1} (Co), due to the enlarged free hydroxyl groups and water molecules.

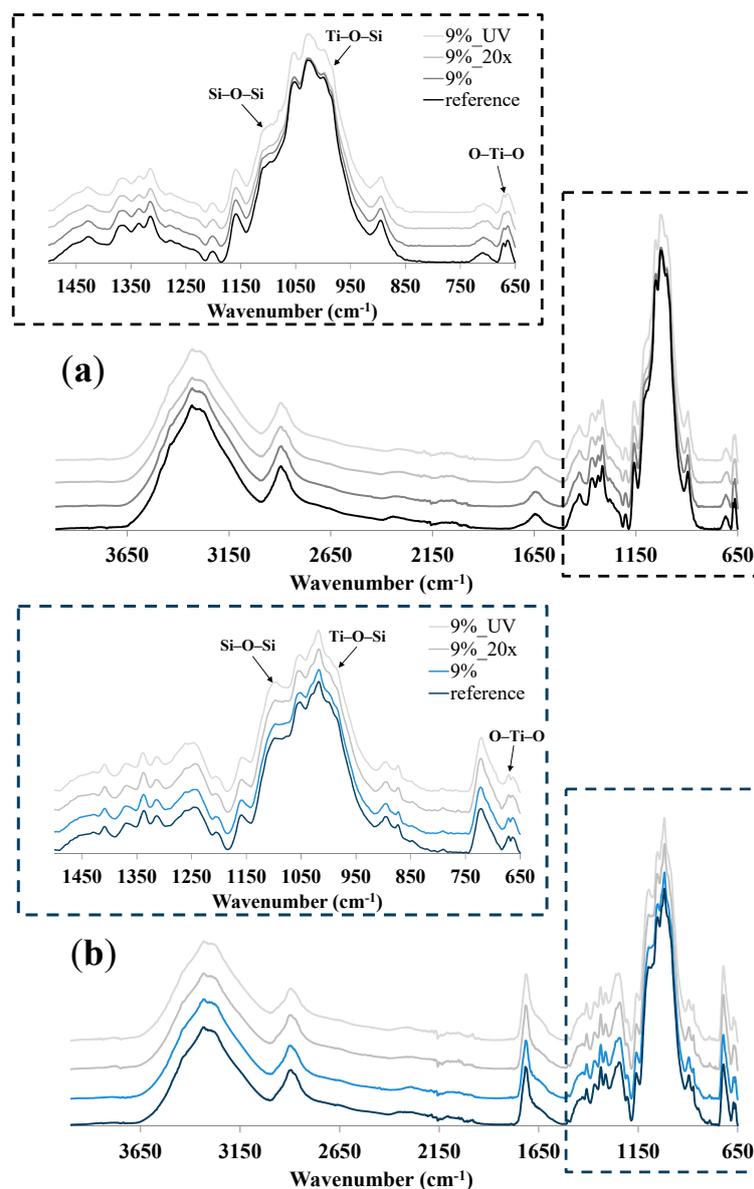


Figure 6. Normalized FTIR spectra (at 1200 cm^{-1}) of: (a) Co; and (b) Co/PES samples modified by 9% of nano-TiO₂-SiO₂ before and after 20th launderings, and after UV irradiation.

3.2.4. CIE Whiteness and Yellowness Index

Based on the presumption that TiO₂ is a white organic pigment, and thus, applied on the material's surface in an adequate concentration producing a white color, the influence of selected TiO₂-SiO₂

coatings and subsequent washing on the changes of the samples' whiteness degree was given by CIE whiteness (W) and yellowness index (YI) calculated according to Equations (1) and (2). The gained results are graphically shown in Figure 7.

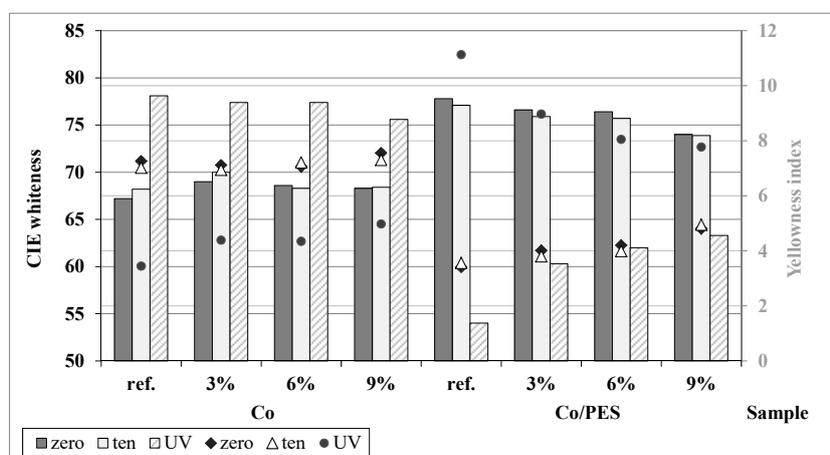


Figure 7. CIE whiteness (left axis) and yellowness index (right axis) of untreated samples (ref.), and TiO₂-modified samples (3%, 6% and 9%) before and after 20 washing cycles, and after 720 h of UV irradiation.

The results in Figure 7 revealed higher whiteness of industrially pre-treated Co/PES reference sample (77.8) in comparison with the Co fabric (67.2), owing to the major brightness of PES fibers. The application of TiO₂ nanoparticles slightly changed the fabrics' whiteness degree and thus, yellowness index, which depended upon the type of material and TiO₂ concentration used. TiO₂-coated Co/PES were less white and more yellow compared to the reference sample and the opposite effect appeared on TiO₂-coated Co sample; although, the higher amount of TiO₂-SiO₂ colloidal dispersion worsened the whiteness degree of both materials. Subsequent washings also somewhat changed the calculated values, probably due to the fabrics' relaxation shrinkages and measuring uncertainties.

The biggest and most visually perceivable changes in whiteness originated on both materials after continuous 720 h of UV irradiation, regarding the composition of the textile and concentration of the applied paste. In the case of cotton fabric, UV rays influence the elevated whiteness (up to value 78.1), if compared with the whiteness of the non-irradiated samples. Although, Montazer et al. [17] studied the photo-catalytic activity of nanoTiO₂ causing decomposition of some cotton's naturally-originated/remained pigments under UV lightness, our study did not prove the bleaching action, probably due to the silica coated TiO₂. Just the opposite phenomenon could be comprehended from Figure 7; namely, the selected colloidal dispersion prevented yellowness of Co/PES fabric subjected to UV irradiation. The higher the concentration the lower the yellowness index was, i.e., 11.13 for the reference sample, and 8.97, 8.05 and 7.77 for the samples treated with 3%, 6% and 9% owf of TiO₂-SiO₂ dispersion, respectively.

3.2.5. UPF Measurement

The UV-A and UV-B transmittance of samples was spectrophotometrically characterized, and additionally, an ultraviolet protective factor (UPF) was calculated regarding the number of washing cycles, in order to evaluate the impact of repeated launderings on the fabrics' UV-blocking functionality, and thus, assessing the durability/bonding ability of TiO₂-coatings. Furthermore, the samples were UV irradiated, with the aim of studying the impact of a TiO₂ catalyst on the materials' newly-obtained functionality. The gained results are shown in the columns of Figure 8.

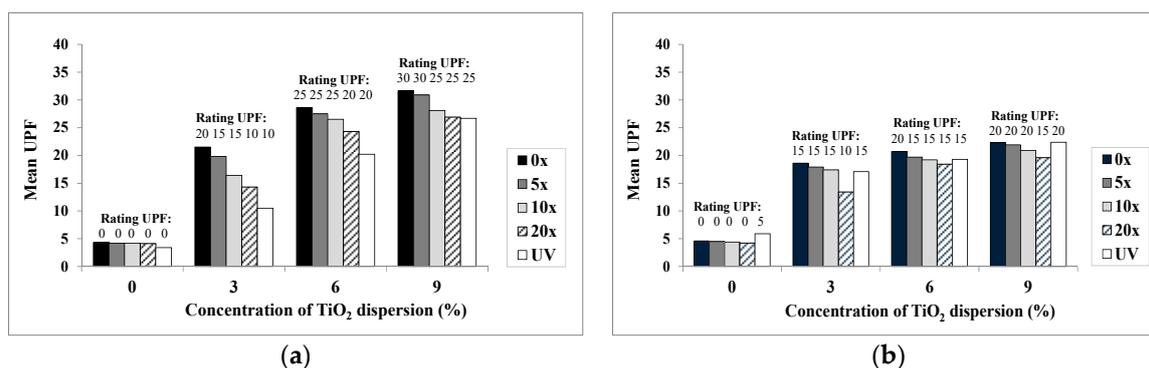


Figure 8. UPF values nano-TiO₂ functionalized: (a) Co; and (b) Co/PES fabrics before and after 5, 10 and 20 washing cycles, and after 720 h of UV irradiation.

It is evident from Figure 8 that both the untreated fabrics (Co and Co/PES) had almost the same UPF, i.e., 4.3 and 4.6, indicating a non-ratable UV protection level. After the application of 3%, 6% or 9% owf of TiO₂-SiO₂ paste, the fabrics' UPFs exceedingly but non-linearly increased as expected, i.e., for Co up to 21.5, 28.6 and 31.6, and for Co/PES 18.6, 20.7 and 22.3, respectively, meaning good to very good UV protective properties with regard to ASTM guidelines for labeling the sun protective clothing (ASTM D 6603) [9].

Measurements of UV transmittance also revealed that UPF values declined with any increase in washing cycles for both coated textiles, as well as for all the concentrations used. The highest reduction of UV factor was perceived after twenty washings when employing the lowest concentration of TiO₂ paste, i.e., for 33.5% (Co) and 28% (Co/PES), which is in good analogy with the above-presented DRS results (Figure 5). Nevertheless, the UPFs after washing were higher compared to the initial untreated samples, indicating the sufficient durability/bonding ability of TiO₂ nanoparticles with the cellulose fibers. Although the reached UPFs of all the TiO₂-modified/washed samples were lower than the value 55 (declared as UPF 50+), the gained results confirmed that nano-sized TiO₂ imparts the functionality to both fabrics against transmittance of harmful solar UV rays, particularly at higher concentrations of applied TiO₂. Further employment of dyestuffs/printing pigments and finishing agents could also improve the UPFs, as well-documented by Fakin et al. [8] and Wong et al. [18].

In addition, UV irradiation of modified samples contributed to enlarged UPF values of Co/PES and to a negligible reduction in Co fabrics' UPF; although UPF rating remained practically the same, thus meaning good photo-stability of applied coatings that were not inclined towards ageing under the influence of external conditions.

4. Conclusions

This paper evaluated the durability of TiO₂-SiO₂ coatings exhausted in three concentrations onto two non-colored light-weight cotton and cotton/polyester fabrics against repeated washings and prolonged intensive UV irradiation.

The results obtained by surface morphology observation, investigation of optical properties, and identification of specific molecular vibrations of modified textiles demonstrated the equal distribution of TiO₂-SiO₂ core-shell nanoparticles on both fabrics. Consecutively, the fabrics' UV-shielding ability was exceedingly enlarged and, on the other hand, the fabrics' whiteness degree was reduced. After repeatedly accomplished standard washings, the amount of nanoparticles was slightly decreased, and less uniform distribution was achieved on both fabrics. Also, the newly obtained UV protective functionality declined with the increasing of washing cycles. Additionally, 720 h of intensive UV-A/UV-B irradiation caused minor damage and a decrease in the smoothness on both materials, as well as visually perceivable changes in whiteness; although TiO₂-SiO₂ protected the Co/PES against yellowness.

The newly gained good to very good fabrics' UV-rays shielding abilities, even after twenty washings and prolonged UV irradiation, proved the suitability of employed exhaustion procedure, the sufficient durability/bonding ability of the nanoparticles with the fibers, and good photo-stability of nano-modified fabrics.

Author Contributions: Conceptualization, A.O. and D.F.; Methodology, A.O. and D.F.; Formal Analysis, A.O.; Investigation, A.O.; Data Curation, A.O.; Writing—Original Draft Preparation, A.O.; Writing—Review and Editing, D.F.; Funding Acquisition, D.F.

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References

1. Singh, T.; Patnaik, A.; Gangil, B. Thermal stability analysis of nano-particulate-filled phenolic-based friction composite materials. *J. Ind. Text.* **2016**, *45*, 1335–1349. [[CrossRef](#)]
2. Burkinshaw, S.M.; Salihu, G. The wash-off dyeings using interstitial water. Part 4: Disperse and reactive dyes on polyester/cotton fabric. *Dye. Pigment.* **2013**, *99*, 548–560. [[CrossRef](#)]
3. Fakin, D.; Veronovski, N.; Ojstršek, A.; Božič, M. Synthesis of TiO₂-SiO₂ colloid and its performance in reactive dyeing of cotton fabrics. *Carbohydr. Polym.* **2012**, *88*, 992–1001. [[CrossRef](#)]
4. Fouda, M.M.G.; Abdel-Halim, E.S.; Al-Deyab, S.S. Antibacterial modification of cotton using nanotechnology. *Carbohydr. Polym.* **2013**, *92*, 934–954. [[CrossRef](#)] [[PubMed](#)]
5. Galkina, O.L.; Sycheva, A.; Blagodatskiy, A.; Kaptay, G.; Katanaev, V.L.; Seisenbaeva, G.A.; Kessler, V.G.; Agafonov, A.V. The sol-gel synthesis of cotton/TiO₂ composites and their antibacterial properties. *Surf. Coat. Technol.* **2014**, *253*, 171–179. [[CrossRef](#)]
6. Selishchev, D.S.; Karaseva, I.P.; Uvaev, V.V.; Kozlov, D.V.; Parmon, V.N. Effect of preparation method of functionalized textile materials on their photocatalytic activity and stability under UV irradiation. *Chem. Eng. J.* **2013**, *224*, 114–120. [[CrossRef](#)]
7. Dastjerdi, R.; Montazer, M.; Shahsavan, S. A new method to stabilize nanoparticles on textile surfaces. *Colloids Surf. A Physicochem. Eng. Asp.* **2009**, *345*, 202–210. [[CrossRef](#)]
8. Fakin, D.; Stana Kleinschek, K.; Kurečič, M.; Ojstršek, A. Effects of nanoTiO₂-SiO₂ on the hydrophilicity/dyeability of polyester fabric and photostability of disperse dyes under UV irradiation. *Surf. Coat. Technol.* **2014**, *253*, 185–193. [[CrossRef](#)]
9. Ojstršek, A.; Stana Kleinschek, K.; Fakin, D. Characterization of nano-sized TiO₂ suspensions for functional modification of polyester fabric. *Surf. Coat. Technol.* **2013**, *226*, 68–74. [[CrossRef](#)]
10. Alebeid, O.K.; Zhao, T. Anti-ultraviolet treatment by functionalizing cationized cotton with TiO₂ nano-sol and reactive dye. *Text. Res. J.* **2015**, *85*, 449–457. [[CrossRef](#)]
11. Montazer, M.; Morshedi, S. Photo bleaching of wool using nano TiO₂ under daylight irradiation. *J. Ind. Eng. Chem.* **2014**, *20*, 83–90. [[CrossRef](#)]
12. Veronovski, N.; Lešnik, M.; Vrhovšek, D. Surface treatment optimization of pigmentary TiO₂ from an industrial aspect. *J. Coat. Technol. Res.* **2014**, *11*, 255–264. [[CrossRef](#)]
13. Vasiljević, J.; Tomšič, B.; Jerman, I.; Simončič, B. Organofunctional trialkoxysilane sol-gel precursors for chemical modification of textile fibres. *Tekstilec* **2017**, *60*, 198–213. [[CrossRef](#)]
14. Zhang, H.; Zhu, H. Preparation of Fe-doped TiO₂ nanoparticles immobilized on polyamide fabric. *Appl. Surf. Sci.* **2012**, *258*, 10034–10041. [[CrossRef](#)]
15. Vijayakumar, S.; Rajakumar, P.R. Infrared spectral analysis of waste pet samples. *Int. Lett. Chem. Phys. Astron.* **2012**, *4*, 58–65. [[CrossRef](#)]
16. Pakdel, E.; Daoud, W.A.; Wang, X. Self-cleaning and superhydrophilic wool by TiO₂/SiO₂ nanocomposite. *Appl. Surf. Sci.* **2012**, *275*, 397–402. [[CrossRef](#)]

17. Montazer, M.; Morshedi, S. Nano photo scouring and nano photo bleaching of raw cellulosic fabric using nano TiO₂. *Int. J. Biol. Macromol.* **2012**, *50*, 1018–1025. [[CrossRef](#)] [[PubMed](#)]
18. Wong, W.; Lam, J.K.C.; Kan, C.; Postle, R. Influence of knitted fabric construction on the ultraviolet protection factor of greige and bleached cotton fabric. *Text. Res. J.* **2013**, *83*, 683–699. [[CrossRef](#)]



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