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ARTICLE *in* SURFACE AND COATINGS TECHNOLOGY · AUGUST 2014

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Effects of nanoTiO₂–SiO₂ on the hydrophilicity/dyeability of polyester fabric and photostability of disperse dyes under UV irradiation



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ARTICLE INFO

Article history:

Received 22 January 2014

Accepted in revised form 12 May 2014

Available online 27 May 2014

Keywords:

TiO₂–SiO₂ nanoparticles

Polyester fabric

Hydrophilicity

Disperse dyeing

UV irradiation

Colour measurement

ABSTRACT

The aim of the presented work was to study the effects of TiO₂–SiO₂ nanoparticles on the hydrophilicity as well as colouration ability of polyester fabric during high-temperature disperse dyeing. Various analytical techniques were employed to characterize three TiO₂–SiO₂ dispersions with different SiO₂ weight percent. In addition, one-bath exhaustion procedure was accomplished by combining TiO₂ dispersions and three disperse dyes in two concentrations, respectively. Finally, the dyed/nano-upgraded samples were subjected to artificial UV light with the intention of establishing any undesired photo-fading behaviour of applied dyes on account of TiO₂ presence. The results provided evidence of enhanced wettability at low SiO₂ content, and on the other hand, pale depth of shade when the nanoTiO₂–hybrides were attended, regarding the type of dye and its concentration. Moreover, UV irradiation significantly influenced the hue, brightness, chroma, and colour strength, although the higher SiO₂ amount suppressed the photocatalytic activity of nanoTiO₂ and thus, diminished the oxidative dye-fading.

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1. Introduction

Polyethylene terephthalate (PET) occupies a leading position (by volume) amongst all the man-made synthetic fibres produced in the world, owing to its favourable properties such as durability, strength, dimensional stability during heat-setting, abrasion resistance, and resistance to sunlight, acids, alkalis, and bleaches [1]. Polyester (PES) fibres have very good crease recovery and are durable to washing. Because of these features, it is extensively used for different purposes including home furnishings, apparel fabrics, carpeting, automotive interior fabrics, and sewing threads. On the other hand, it is an exceedingly hydrophobic (non-polar) synthetic fibre in character, certainly in comparison with natural cellulose and protein fibres. This is a result of the benzene rings' prominence and the –CH₂CH₂– groups' presence [2]. PES is also a highly crystalline fibre that consists of tightly-packed, highly ordered polymer molecules, and with the absence of polar functional groups capable of forming hydrogen bonds with other molecules [3].

Herein, changing the water absorption properties and imparting/enhancing the fabrics' functional characteristics through the surface modification by integrating nanotechnology (TiO₂, silica, iron oxide, zinc oxide, silver, etc.) has become an attractive research field over the recent years providing new insights for scientists to develop high-added value products. Amongst the numerous nanoparticles, TiO₂ has been widely utilised for the functionalization of textile materials on account of its excellent optical properties, superior thermal stability,

long-term lifetime, lack of toxicity, and relatively low-cost, as quoted in [4–7]. Mihailović et al. [8] studied the functionalization of PES fabric by polysaccharide alginate as a surface modifier for the improvement of binding efficiency of colloidal TiO₂ nanoparticles, in order to engineer the multifunctional textile nanocomposite material with outstanding antibacterial activity, sufficient photocatalytic ability and UV protection efficiency after several consecutive laundering cycles. Bozzi et al. [9] investigated the self-cleaning ability of polyester textiles pre-treated with radio frequency plasma, microwave plasma, and vacuum/UV light irradiation, and subsequently treated by rutile TiO₂ nanoparticles according to the wet chemical technique. Luo et al. [10] summarised that PES/TiO₂ nanoparticle composites exhibit higher glass transition temperatures, higher flattened rubbery plateau modulus and better hydrophilicity, compared to the pure PES. The study realised by Harifi and Montazer [11] demonstrated an idea as to how the application of nanoTiO₂ as a pre-treatment procedure could lead to the augmented wettability and dyeability of polyester fabric during subsequent free-carrier dyeing at 100 °C. Moreover, according to the proposed method various desirable multi-functional features were conferred on the PES including hydrophilicity, self-cleaning and UV protection abilities, without any adverse effects on colour fastness properties.

Those systems where TiO₂ is associated with dye in one bath have been almost completely neglected by those researchers who were interested in the mechanisms of fabrics' TiO₂ functionalization processes; even though, it would be economically and ecologically convenient, if dyeing and TiO₂ modification could be accomplished in one step upon the same stipulations. However, the specific application and/or fixation conditions for the above-stated two processes could be mutual preclusive

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by destructively affecting the nanoparticle/dyestuff sorption, and consecutively, causing poor colouration equality and inconstant colour shades [12]. Moreover, owing to the formation of hydroxyl radicals when absorbing UV rays, catalyst TiO_2 is already being used for the effectual degradation and mineralisation of diversified synthetic dyes during wastewater treatment [13–16], as well as for the discolouration of various organic stains (red wine, coffee, red beet, etc.) including persistent pigments [4,7,9,17]. To minimize their photocatalytic activity, TiO_2 nanoparticles need to be surface coated with an inert material, such as silica (SiO_2).

Therefore, the purpose of this research was to investigate the compatibility of TiO_2 – SiO_2 core–shell nanoparticles with process regime of high-temperature disperse dyeing, and also to elucidate the role of TiO_2 – SiO_2 on the: i) colour characteristics (their impact on hue, brightness, and colour strength), and ii) hydrophilic features of polyester fabric as one of the important functional properties of clothes (improvement of antistatic behaviour, touch, and moisture transport). Although, it is well-known that silica coating suppressed the photocatalytic behaviour of TiO_2 nanoparticles [12], the emphasis was also placed on the possible UV-accelerated fading of applied disperse dyes on the surface of PES fabric in the presence or absence of selected nano-sized TiO_2 –hybrids.

2. Experimental

2.1. Materials

A series of experiments were conducted using an industrially-bleached plane-weave 100% polyester fabric (PES) with a mass/unit area of 163 g/m^2 , warp density of 20 threads/cm and weft density of 17 threads/cm, and fineness of 36.6 tex. The source fabric was washed at 40°C for 20 min using a neutral non-ionic washing agent, and afterwards rinsed in warm and then cold water, and dried at an ambient temperature.

Three commercially-interesting Terasil W (Ciba) disperse dyestuffs with azo type chromophores were used for the dyeing procedure, namely, Yellow W-6GS (C.I. Disperse Yellow 114 - DY114), Red W-4BS (C.I. Disperse Red 376 - DR376), and Navy W-RS (mixture of dyes - DNmix). The chemical constitution of DY114 is presented in Fig. 1, whilst the structures of the other two dyestuffs, i.e. DR376 and DNmix, are undisclosed by the producer.

In the presented research, three neutral colloidal dispersions of TiO_2 – SiO_2 core–shell nanoparticles in the form of paste were utilised respectively. Each paste contained approximately 20% of rutile crystalline TiO_2 nanoparticles that were superficially coated by different concentrations of hydrated amorphous SiO_2 shell, i.e. 3, 5 or 10 wt.%. All the dispersions were industrially-produced and supplied by the Cinkarna, Metallurgical and Chemical Industry, Celje, Inc., Slovenia. Data about solid TiO_2 nanoparticles' concentrations and SiO_2 content within individual dispersions was procured by the producer. These, so-called TiO_2 –hybrids were synthesized via the sol–gel process from metatitanium acid, which is a by-product of the sulphate synthesis process during the TiO_2 pigment output of Cinkarna. The synthesis

procedure of rutile nanoparticles is fully described within patent SI 23218A, and the coating procedure of the synthesized rutile nanoparticles by SiO_2 within patent SI 23547A.

2.2. Combined dyeing and TiO_2 application procedure (exhaustion procedure)

Polyester fabric was treated according to the one-bath exhaustion procedure in a sealed, stainless-steel dye-pot of 250 cm^3 capacity, housed in a Turby (W. Mathis) laboratory-scale apparatus with 800 rpm bath circulation. The initial bath contained 0.1 or 0.5% owf (of weight of fabric) individual disperse dye (DY114 or DR376 or DNmix) and 9% owf of individual nano TiO_2 – SiO_2 colloidal dispersion, 1 g/L of dispersing agent (Kutregal OD), 1% of anionic levelling agent (Egasol SP), and 1 g/L of pH-regulator (Sandacid DSB) for pH 4.5–5 adjustment of the media. For a comparative study obtaining the reference samples, the dye-baths were composed of disperse dye (three types) in two concentrations, respectively, and the herein above auxiliaries, without the addition of TiO_2 paste.

The dyeing/ TiO_2 application procedure was started at 80°C , when the dyestuff, nano TiO_2 colloidal dispersion, and auxiliaries were added in a dye-pot together with a bleached fabric sample using a liquor-to-fabric weight ratio of 20:1 (190 mL of deionized water against 9.5 g of PES). Afterwards, the bath was heated-up to 130°C (2°C/min), maintained for 60 min, and then cooled-down to 70°C . At the end of this process, the polyester fabric was removed from the bath and rinsed thoroughly in warm and then cold water, neutralized, and dried at room temperature. In order to remove unfixed reactants, the treated samples were washed at 50°C for 5 min (bath-to-fabric weight ratio of 20:1) using 2 g/L of non-ionic wetting agent, rinsed in tap water, and finally dried at room temperature.

2.3. UV irradiation of dyed/ TiO_2 – SiO_2 treated samples

The dyed and dyed/ TiO_2 – SiO_2 treated samples were exposed to an artificial UV source for up to 24 h with the intention of evaluating possible fabric discolouration on account of the excessive photo-catalytic behaviour of TiO_2 . A photo-reactor (Luzchem) consisting of 6 combined overhead lamps was used for the photo-decomposition test; 3 UVA lamps emitted light within the range of 316–400 nm with the main peak at 350 nm and 52.7 mW/cm^2 intensity, and 3 UVB lamps emitted light within the range of 281–315 nm with the main peak at 313 nm and 35.3 mW/cm^2 intensity. The irradiated area of the textile samples in the photo-reactor was $8 \times 6 \text{ cm}$. The plausible time-dependent stabilities of the applied dyes towards UV-provoked fading in the presence or absence of TiO_2 dispersions were followed after 3, 6, 9, 12, 15, 18, 21, and 24 h of irradiation using a two-ray spectrophotometer Spectraflash SF600 Plus (Datacolor), as described in Section 2.4.3. Furthermore, the CIE total colour differences (ΔE^*) and K/S values were calculated according to Eqs. (3) and (4).

2.4. Analytical methods

2.4.1. Analysis of TiO_2 colloidal dispersions

Various analytical techniques were employed with the intention of characterizing the selected nano-sized TiO_2 colloidal dispersions, i.e. transmission electron microscopy (TEM), dynamic light scattering (DLS), and Zeta potential (ζ -potential) measurement.

TEM images were obtained by dropping an individual stable dispersion (of 1% concentration) on the Cu-grid, and thereafter dried and observed using a transmission electron microscope (TEM, Jeol 2100, 200 kV, LaB₆ as an electron source).

Dynamic light scattering (DLS) measurements were carried-out in order to determine the particles size distribution as a function of different inert shells formed around the TiO_2 . Analysis was performed by means of a Zetasizer Nano series HT (Malvern, UK), equipped with a

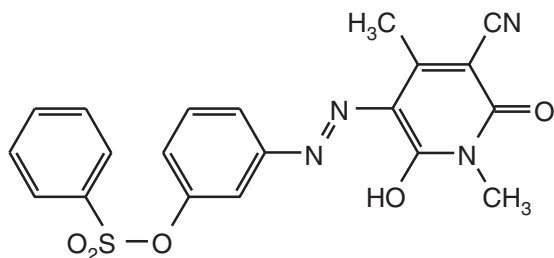


Fig. 1. The chemical structure of dyestuff C.I. Disperse Yellow 114.

light-scattering unit. Individual peaks were derived from the multi-modal correlation functions. The measuring temperature was fixed at $25.0 \pm 1^\circ\text{C}$.

The zeta-potential (ζ -potential) of the individual TiO_2 - SiO_2 dispersion was monitored in pH-adjusted deionized water (pH 3 by 0.1 M HCl, and pH 12 by 0.1 M NaOH) using laser-velocimetry Doppler utility on a Zetasizer Nano series HT (Malvern, UK). The electro-phoretic mobility data of the dispersions were transformed into ζ -potentials according to Eq. (1):

$$\zeta = \left[\frac{4\pi\eta\mu}{\varepsilon} \right] \quad (1)$$

where ε is a dielectric constant of the dispersing medium, η is a constant of the solvent viscosity, and μ is the electro-phoretic mobility.

2.4.2. Morphological analysis of PES surfaces

Dyed/nano TiO_2 modified PES fabrics were characterized by scanning electron microscopy (SEM) in order to elucidate the changes between the samples' surface morphologies. Approximately 1 cm^2 of the selected fabric sample was applied onto an adhesive carbon band fixed to a brass holder for the observation on a Zeiss Gemini Supra 35 VP Scanning Electron Microscope (Carl Zeiss NTS GmbH, Germany) with a maximum scan resolution of up to 1.5 nm at 20 kV .

2.4.3. Hydrophilic properties determination

In order to evaluate the effect of nano TiO_2 - SiO_2 hybrids on the hydrophilic properties of PES fabric by capillary rise method, dyed/ TiO_2 treated samples were cut into $2 \times 2\text{ cm}$ quadratic pieces and hung on the sample holder in the Tensiometer Krüss K12 apparatus. A total of 10 measurements were taken for each sample in order to obtain statistically significant results. Detailed description of capillary rise measuring procedure has been gathered in [18]. Briefly, the hydrophilic properties were determined by measuring the weight increase (m) during liquid (Milli-Q water) penetration due to capillary effect as a function of time (t). Additionally, the contact angle was calculated from the initial slope of the function $m^2 = f(t)$ according to the modified Washburn Eq. (2):

$$\cos\theta = \frac{m^2}{t} \cdot \frac{\eta}{\rho^2 \cdot \gamma \cdot c} \quad (2)$$

where θ ($^\circ$) is the contact angle between the solid and liquid phases, m (g) is the mass of the absorbed liquid, t (s) is the time, η (Pa s) is the liquid viscosity, ρ (g cm^{-3}) is the liquid density, γ (N m^{-1}) is the surface tension of the liquid, and c (cm^5) is a material constant.

2.4.4. CIE colour measurements

The diversely-treated samples were colourimetrically evaluated in order to examine the compatibility of the TiO_2 - SiO_2 nanoparticles with process parameters during disperse dyeing, and consecutively, colour shade and strength as well as colouration uniformity. CIE colour measurements were achieved within a spectral range of $400\text{--}700\text{ nm}$ wavelengths by means of a two-ray Spectraflash SF600 Plus spectrophotometer (Datacolor) under a standard illuminant D65 (LAV/Spec. Incl.), and a measuring geometry of $d/8^\circ$. The CIE total colour differences (dE^*) between the dyed samples (references) and dyed/ TiO_2 -treated samples were calculated from the coordinate differences in all three directions of the colour space, i.e. brightness L^* , red/green axis a^* , yellow/blue axis b^* , by following Eq. (3) [19]:

$$dE^* = \sqrt{(dL^*)^2 + (da^*)^2 + (db^*)^2} \quad (3)$$

where dE^* is the total colour differences, dL^* is the brightness differences, da^* is the differences at the red/green axis, and db^* is the differences at the yellow/blue axis.

The relative colour strength (K/S value) of individual sample was calculated from the reflectance curves at a wavelength of minimal reflectance for each dyeing, i.e. for yellow samples at 430 nm , for red samples at 530 nm , and for blue samples at 630 nm , using the Kubelka-Munk Eq. (4):

$$K/S = \frac{(1-R)^2}{2R} \quad (4)$$

where K is the absorption coefficient, S is the light-scattering coefficient, and R is the decimal fraction of the dyed sample's reflectance.

3. Results and discussion

This research work is set out to investigate the compatibility of diverse nano TiO_2 - SiO_2 dispersions with selected three disperse dyes and associated dyeing agents during one-bath high-temperature exhaustion procedure with the intention of highlighting the role of TiO_2 with different content of SiO_2 on the hydrophilic properties and colour characteristic of polyester fabric. SiO_2 has often been selected as inert shell to protect the textile from the high oxidation potential of irradiated TiO_2 nanoparticles as well as to augment binding ability of TiO_2 with textiles [7,12]; although, the large content of SiO_2 tends to reduce nano TiO_2 functional efficiency when applied on the material. Accordingly, three commercially-available TiO_2 - SiO_2 colloidal dispersions different in weight percent of SiO_2 shell were characterized and afterwards, the formation of core-shell nanoparticles together with an individual disperse dye on the PES fabric surface was examined closely by the SEM technique, and hydrophilicity of the surface by the capillary rise method. Colour of differentially dyed/treated samples was determined using spectrophotometry. Also, any possible UV-accelerated fading of the applied disperse dyes in the presence or absence of selected nano-sized TiO_2 -hybrides was emphasised. The representative results are gathered in images, diagrams and tables, along with their appropriate discussions, as follows.

3.1. Characterization of TiO_2 - SiO_2 core-shell colloidal dispersions

TEM images of three commercially-available TiO_2 core-shell colloidal dispersions at concentration of $0.01\text{ wt.}\%$ were taken, with the intention of studying the surface morphology of TiO_2 - SiO_2 nanoparticles for subsequent modification of PES fabric. Furthermore, DLS measurements were performed for determining the particles size distribution and the average particles size within individual dispersions, and the obtained results are presented in Fig. 2.

The TEM images in Fig. 2(a–c) clearly demonstrate the isotropic morphology of small non-spherical TiO_2 crystals of $>10\text{ nm}$ in length and ca. 5 nm in width that aggregated within individual (polycrystalline) TiO_2 non-spherical shaped nanoparticles of different sizes, which can thus be more precisely established from DLS diagrams. In addition, an amorphous phase between the crystals can be perceived that presumably belonged to hydrated titanium oxide or residual organic alkyl components originating during the preparation of nanoparticles, as also reported by Nimittrakoolchai and Supothina [20]. From the DLS plots in Fig. 2, it can be noticed that two TiO_2 dispersions with higher weight percentages of SiO_2 , i.e. TiO_2 -5% SiO_2 and TiO_2 -10% SiO_2 , contain exceedingly heterogeneous scattering populations. The wider peak in Fig. 2(b) (average particles' size of 552 nm) and in Fig. 2(c) (average particles' size of 580 nm) proves the presence of large agglomerates of size ca. 5000 nm , and for this reason these two colloidal dispersions are less suitable for fabrics' functionalization. On the other hand, the average size of the TiO_2 particles coated with $3\text{ wt.}\%$ SiO_2 in Fig. 2(a) was 165 nm , which indicates a lower agglomeration tendency in water compared to the above-mentioned dispersions.

The TEM and DLS results were supplementarily verified by electrochemical property determination (Table 1). Zeta-potential (ζ -potential)

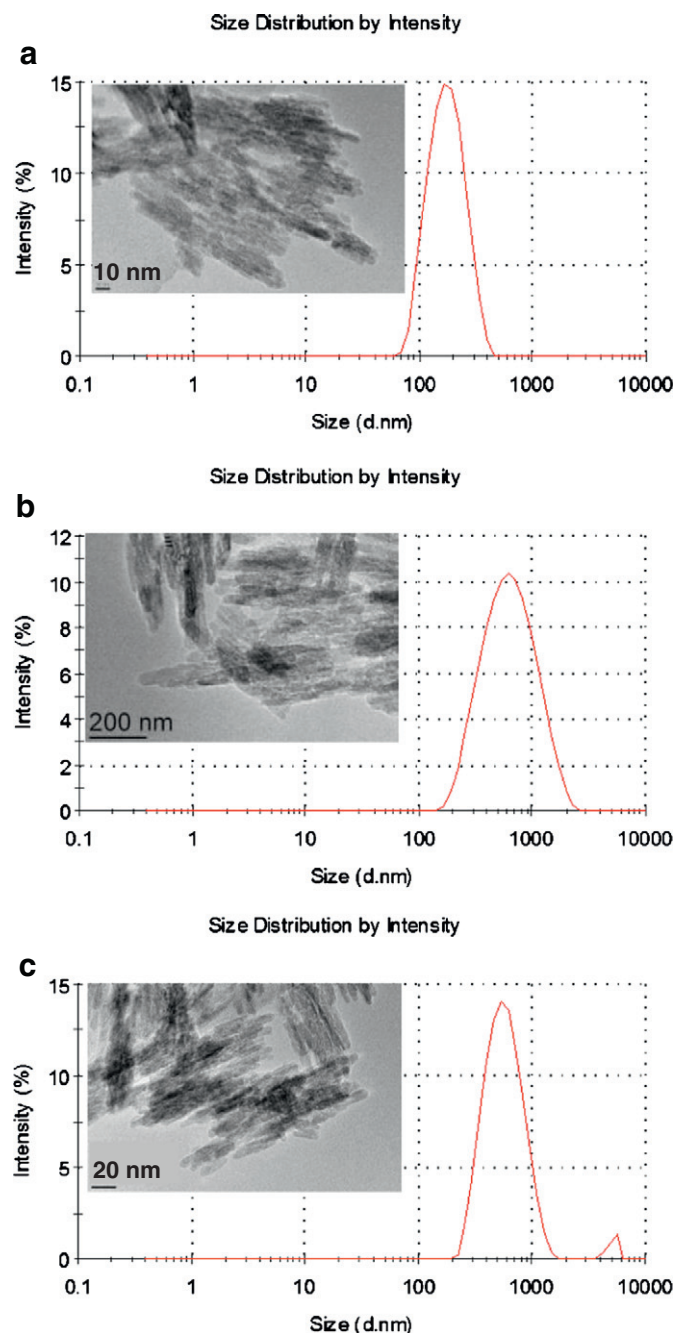


Fig. 2. DLS results and TEM images of nano-sized TiO_2 coated with: (a) 3 wt.% SiO_2 ; (b) 5 wt.% SiO_2 ; (c) 10 wt.% SiO_2 .

can be used as qualitative information of the particle surface charge, being the parameter that affects the dispersion stability [21].

It could be perceived from Table 1 that the surface-charge density of the TiO_2 - SiO_2 core-shell nanoparticles decreases as the pH of the colloidal dispersions decreases. Moreover, the zeta-potential measurements of TiO_2 - SiO_2 dispersions significantly depend on the amount of SiO_2

Table 1
Zeta-potential (ζ -potential) as a function of dispersion pH.

Sample	Zeta-potential (mV)		
	pH 3	pH 7	pH 12
TiO_2 -3% SiO_2	4.8	-51.4	-55.0
TiO_2 -5% SiO_2	-17.2	-44.7	-47.0
TiO_2 -10% SiO_2	-18.3	-41.6	-47.3

shell. The obtained results demonstrated the high stability of examined dispersions at pH 7, as the values of ζ -potential were higher than ± 30 mV thus confirming large repulsive electrostatic forces between the nanoparticles, which has been explained in detail elsewhere [17]. Consequently, TiO_2 - SiO_2 nanoparticles were uniformly distributed in deionized water with no tendency to form agglomerate structures even after six months of storage (data not shown). The dispersions were less stable at pH 3, on account of the reduced electrostatic interactions between nanoparticles implying the formation of larger aggregates of TiO_2 - SiO_2 . Rutile TiO_2 coated with 3% SiO_2 had an isoelectric point (IEP) between pH 5 and 6, which is consistent with the bibliographic data for TiO_2 nanoparticles (IEP near pH 7) and SiO_2 nanoparticles (IEP of around pH 2) [22]. The IEP was not reached when higher percentages of SiO_2 (5 and 10%) were coated on the surface of TiO_2 nanoparticles.

3.2. Morphological analysis of dyed/ TiO_2 - SiO_2 treated fabrics

The SEM images in Fig. 3 represent the surface morphologies of the selected PES fabrics that were one-bath dyed and TiO_2 - SiO_2 modified according to the exhaustion procedure using 0.1% owf of Disperse Yellow 114 dye and 9% owf of individual colloidal dispersion, as well as adequate auxiliaries.

Fig. 3(a) displays the more homogenous coating on the surface of the polyester fabric using TiO_2 -3% SiO_2 dispersion. It is evident from Fig. 3(b) that the application of TiO_2 -5% SiO_2 obviously did not cover the entire surface, and from Fig. 3(c) that the PES surface was covered by larger agglomerates of nanoparticles, as could be expected from the results obtained by TEM and DLS analyses of these two colloidal dispersions (Fig. 2(b) and (c)).

3.3. The effect of TiO_2 - SiO_2 nanoparticles on the wettability of PES fabric

PES is an exceedingly hydrophobic (non-polar) synthetic fibre in character [3]. The textiles hydrophobicity can result in unfavourable electrostatic charge, causing clothes to cling to each other. On account of extremely poor water and moisture absorption, PES is less desirable material in many textile applications, i.e. sportswear, under garment, and bedding. Therefore, adding the hydrophilic function to PES brings about an increased comfort for the end-users.

With the intention to elucidate the role of different nano TiO_2 -hybrids on the hydrophilic features of polyester fabric, dyed/ TiO_2 - SiO_2 treated samples were evaluated via capillary rise method using tensiometer, and the water contact angles were calculated according to Eq. (2). The obtained results are graphically presented in Fig. 4.

Fig. 4(a) depicts the results of water rise in differentially treated samples in terms of gained mass data versus time during tensiometry experiment. From the plotted curves it could be noticed that all samples adsorbed water, with the exception of sample dyed/treated with TiO_2 -10% SiO_2 dispersion (the highest SiO_2 content in present study), which was wetted merely 2–3 mm after 600 s. For this sample, both the mass of liquid uptake in the equilibrium and the water contact angle could not be determined. The extreme hydrophobicity can be attributed to the presence of larger nanoparticles agglomerates of size ca. 5000 nm in dispersion as obtained by DLS measurements – Fig. 2(c), and consecutively, on the fabric surface as perceived from SEM image in Fig. 3(c).

Other two samples, i.e. dyed/treated with TiO_2 -3% SiO_2 or TiO_2 -5% SiO_2 dispersions, attained a plateau (max. water adsorption) after 190 and 110 s, respectively, presenting faster water adsorption compared to reference sample that reached the equilibrium after 443 s (Fig. 4(a)). Herein, the amounts of liquid uptake in equilibrium, which represent absorbency capacities, are almost the same for those three samples. On the other hand, the calculated average values of water contact angle significantly diminished for samples treated with TiO_2 -hybrids in comparison to reference, i.e. from 112.23° (reference) to 88.44° and 84.31° , depending on SiO_2 shell content, which is in

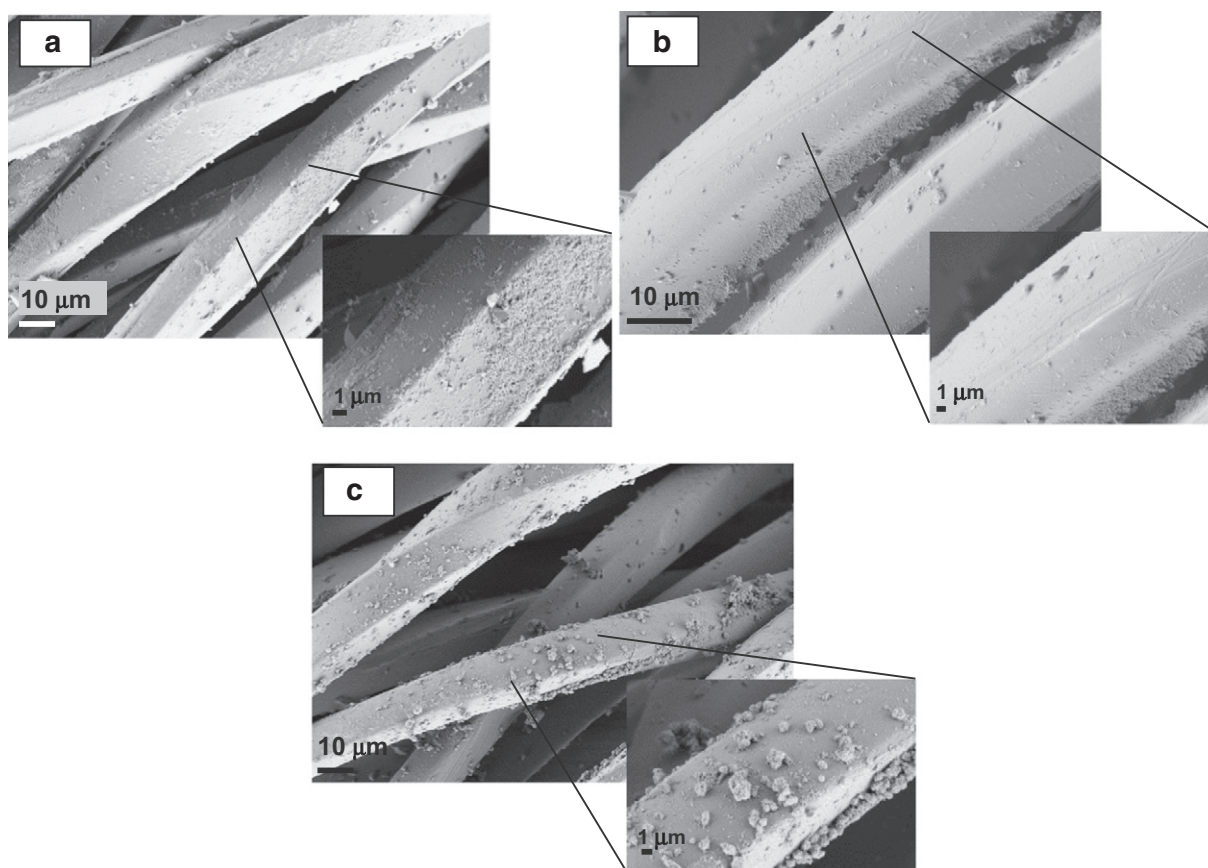


Fig. 3. SEM images of dyed/TiO₂-SiO₂ modified PES fabrics at different magnification using 0.1% owf of DY114 dye and 9% owf of: (a) TiO₂-3% SiO₂; (b) TiO₂-5% SiO₂; (c) TiO₂-10% SiO₂.

agreement with the results obtained by [7]. The lower the water contact angle, the higher the hydrophilicity of the PES fabric. The enlarged hydrophilicity on PES in the presence of silica can be explained by the higher surface acidity providing a higher concentration of -OH groups, due to the presence of Ti-O-Si linkages that appeared at 960 cm^{-1} in FTIR spectrum [7].

Meanwhile, Fig. 4(b) shows the slopes of curves in the first ten seconds of water uptake fitted by linear progressive curves, according to the modified Washburn equation. The velocity of mass increase at the beginning of sorption indicates that the imbibition of water was the fastest on the sample treated with TiO₂-5% SiO₂ (after 10 s it was $0.0332\text{ g}^2/\text{s}$), and rather low on the sample treated with TiO₂-10% SiO₂ (for the first 10 s it was only about $0.0004\text{ g}^2/\text{s}$), since this sample was not wetted fully as mentioned above.

3.4. The influence of TiO₂-hybrids application on the colouration of PES fabric

The dyeing of PES can be performed according to various procedures such as carrier dyeing at $100\text{ }^{\circ}\text{C}$, high-temperature pressure dyeing at $130\text{ }^{\circ}\text{C}$, and the pad-dry thermofixation "Termosol" process at $190\text{--}220\text{ }^{\circ}\text{C}$ [23]. In this study, polyester fabric was treated via a high-temperature one-bath exhaustion procedure at a temperature of $130\text{ }^{\circ}\text{C}$, when the tight physical structure of the polymer was temporarily loosened by thermal agitation, thus reducing the intramolecular bonding and facilitating entry of the molecules into the fibrous structure [2]. During this research, three disperse dyes at two concentrations were applied onto the PES fabric in combination with three nanoTiO₂-SiO₂ colloidal dispersions, whilst in parallel trials without

the nanoparticles' addition (reference samples). As a result, a series of 24 samples was prepared.

Various colour characteristics were determined or calculated (Eqs. (3) and (4)) with the intention of studying the effects of TiO₂-SiO₂ as a surface functionalization substance on the colouration of PES. The colour strengths (K/S values) and CIE $L^*a^*b^*$ colour coordinates of the samples, i.e. brightness (L^*), red-green axis (a^*) and yellow-blue axis (b^*), and colour differences, i.e. differences in brightness (dL^*) and total differences (dE^*), between the dyed (reference samples) and dyed/TiO₂-SiO₂ modified PES fabrics, are displayed in Table 2.

It is evident from Table 2 that the more significant changes in colour (a^*-b^* axes) and the lowest differences in brightness (dL^*) occurred when 0.1% of the DY114 dye was used, irrespective of the applied TiO₂-SiO₂ dispersion. Moreover, the total colour differences (dE^*) are extremely high, i.e. 5.38, 4.60, and 6.11, as the permitted value is <1 . Meanwhile, all the red and navy samples had similar a^* and b^* values implying similar hue and higher L^* values – all the samples were brighter compared to the references. It could also be noted that the higher weight percent of SiO₂ inert shell led to elevated dL^* as well as to reduced colour strengths (K/S values), regarding the type of the dye and its concentration. The paler depths of shade determined on dyed/TiO₂-upgraded samples could be elucidated in terms of interactions between TiO₂-SiO₂ and disperse dyes or incompatibility between the TiO₂ colloidal dispersions and the employed auxiliaries, on account of the opposite charges tending to an undesirable TiO₂-SiO₂ agglomeration on the fabric's surface, as perceived in Fig. 3(c). Lower dyeing depth and brighter colouration of the samples upon the TiO₂ nanoparticles' application were in agreement with the result obtained by the one-bath reactive dyeing of cotton under varied dyeing regimes [12], as well as during the free-carrier dyeing of PES at $100\text{ }^{\circ}\text{C}$ [11].

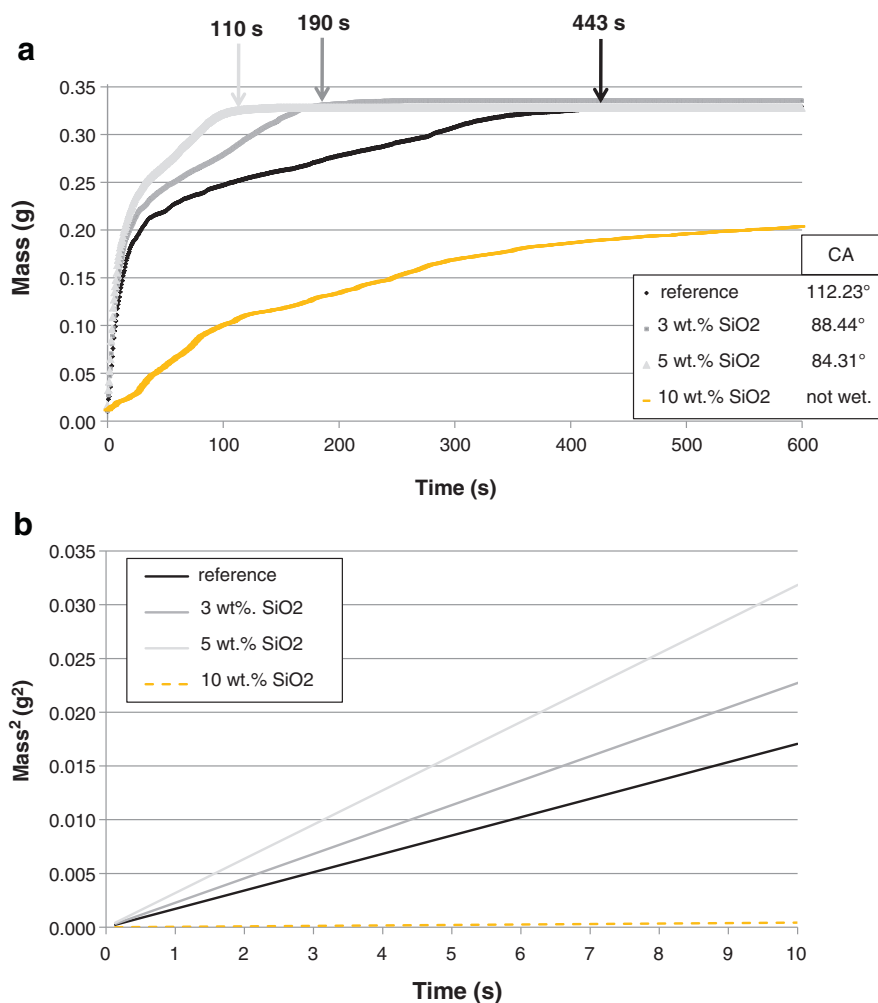


Fig. 4. Hydrophilicity determination of differentially treated PES samples: (a) water rise on samples and time to reach equilibrium; (b) fitted square mass data of water rise versus time.

3.5. Photostability of disperse dyes in the presence of TiO₂ catalyst under UV irradiation

Since TiO₂ nanoparticles have a relatively large surface area per unit mass and volume, under UV rays with higher energy than their band gaps (3.2 eV), pairs of negative electrons (e⁻) and positive holes (h⁺) are produced [6]. These holes can react with water molecules and generate powerful oxidative intermediates, such as hydroxyl radicals. These free radicals can further participate in various chemical reactions with the latent capability of decomposing/degrading numerous organic pigments [4,7–9,17].

For the dyeing of polyester fibres, disperse dyes are commonly used in the form of fine aqueous dispersion, because they have relatively low aqueous solubility [2]. Disperse dyes are required to be relatively small, planar non-ionic molecules to allow the dyes to penetrate between the polymer chains and into the bulk of the fibre. The dye-fibre's affinity is generally considered to involve a combination of Van der Waals' and dipolar forces, and hydrogen bonding. The disperse dyes of azo type chromogen, as employed in this study (Fig. 1), were capable of exhibiting azo-hydrazone tautomerism [24]. It is believed that the hydrazone form was more prone to the photodegradation caused by the TiO₂ catalyst.

In order to investigate the possible photo-oxidative degradations of the selected disperse dyestuffs in the presence of the TiO₂-SiO₂ nanoparticles, the treated samples were irradiated with a combination of artificial UVA and UVB rays over a time period of 3 to up to 24 h. The influences of different variables were studied, such as the ratio of SiO₂

to TiO₂, the type of dye and its concentration, as well as the time of irradiation. CIE colour differences, i.e. differences in brightness (dL^*), differences at the red/green axis (da^*), differences at the yellow/blue axis (db^*), total differences (dE^*), and K/S differences, between the non-irradiated and 24 h-irradiated samples, and K/S values of samples after 24 h of UV irradiation, are displayed in Table 3.

The total colour differences (dE^*) versus time of the UV light exposure are gathered in Fig. 5, separately for each dye and dye concentration.

It could be observed from Table 3 that 24 h UV irradiation significantly influenced the hue, brightness, chroma and colour strengths (K/S) of the exposed samples, the dyed (reference) as well as the dyed/TiO₂-SiO₂ treated, depending on the type and concentration of the applied dyestuff; in essence, the samples dyed with DY114 were darker, reddish and bluer, the samples dyed with DR376 were brighter, greener and more yellow, whilst the samples dyed with DNmix were brighter, greener and more yellow, in comparison with the non-irradiated samples. Moreover, all the UV-ray treated samples were less saturated with declining colour strengths. The K/S values were gradually reduced during the irradiation time for 3.6% (3 h) to 9.8% (24 h) at 0.1% dye concentration, and for 5% (3 h) to 20% (24 h) at 0.5% dye concentration. Several factors may affect the photo-oxidation stability of a dye such as the nature of the light source, the absorption characteristic of a dye, the lifetimes of the excited states, the nature of the substrate, the environmental conditions, and the presence of a catalyst.

It could be deduced from the curves presented in Fig. 5 that the total colour differences (dE^*) increased with increasing time of UV

Table 2CIE colour coordinates, *K/S* values and CIE colour differences.

Sample dye/dye conc.	Disp. type	Disp. conc.	CIE values			CIE differences		K/S
			L*	a*	b*	dL*	dE*	
DY114								
0.1%	–	–	89.23	–9.68	63.65			3.01
0.5%	–	–	87.31	–8.30	84.38			10.07
0.1%	3 wt.%	9%	89.32	–9.65	58.27	0.08	5.38	2.33
0.5%	SiO ₂	9%	87.86	–8.47	85.30	0.55	1.09	10.23
0.1%	5 wt.%	9%	89.74	–9.73	59.07	0.50	4.60	2.37
0.5%	SiO ₂	9%	88.05	–8.57	83.86	0.75	0.95	9.32
0.1%	10 wt.%	9%	89.41	–9.49	57.55	0.17	6.11	2.22
0.5%	SiO ₂	9%	88.07	–8.41	84.15	0.76	0.80	9.02
DR376								
0.1%	–	–	60.16	36.66	–5.34			1.88
0.5%	–	–	43.55	46.71	–3.16			7.77
0.1%	3 wt.%	9%	60.92	36.74	–5.66	0.76	1.36	1.79
0.5%	SiO ₂	9%	44.55	46.18	–3.51	0.99	1.18	7.07
0.1%	5 wt.%	9%	61.13	36.55	–5.34	0.98	0.98	1.76
0.5%	SiO ₂	9%	45.72	46.28	–3.64	2.18	2.27	6.48
0.1%	10 wt.%	9%	61.35	36.02	–5.76	1.19	1.42	1.71
0.5%	SiO ₂	9%	45.87	45.94	–4.19	2.32	2.66	6.32
DNmix								
0.1%	–	–	61.34	–7.05	–15.18			1.55
0.5%	–	–	38.70	–5.71	–20.51			8.36
0.1%	3 wt.%	9%	61.80	–6.99	–13.10	0.45	2.13	1.48
0.5%	SiO ₂	9%	39.26	–6.02	–20.46	0.56	0.65	8.21
0.1%	5 wt.%	9%	62.81	–7.40	–14.12	1.47	1.84	1.82
0.5%	SiO ₂	9%	41.03	–6.85	–19.66	2.33	2.73	7.30
0.1%	10 wt.%	9%	65.20	–7.66	–14.56	3.86	3.96	1.20
0.5%	SiO ₂	9%	41.25	–6.35	–20.09	2.55	2.67	7.07

irradiation, irrespective of the dye-bath composition. The poorest stability was attained when using both, DR376 and DNmix dyes in regard to the dye concentration and the type of TiO₂–SiO₂ paste present. In addition, the SiO₂-coated TiO₂ had a positive influence on the retardation of the oxidative dye-fading, preferentially when using 10 wt.% SiO₂. This phenomenon could be interpreted as a reduction

in the effective surface area of the TiO₂ catalyst that influences the suppressed photocatalytic activity of the nano-sized TiO₂ under UV light. This conclusion has arisen out of several studies [16,21], although it was demonstrated in the present research that the structure of the used dye had been a decisive parameter, which mostly affected the photo-fading mechanism. In such a manner, the TiO₂

Table 3CIE colour differences, *K/S* values and *K/S* differences (in %) after 24 h of UV irradiation.

Sample dye/dye conc.	Disp. type	Disp. conc.	CIE differences after 24 h UV irradi.				K/S	dK/S (%)
			dL*	da*	db*	dE*		
DY114								
0.1%	–	–	–0.1615	0.4554	–1.5805	1.65	2.76	8.01
0.5%	–	–	–0.2481	0.5723	–1.3734	1.51	8.94	8.03
0.1%	3 wt.%	9%	–0.4208	0.6642	–1.5010	1.69	2.13	5.69
0.5%	SiO ₂	9%	–0.3853	0.7942	–1.2621	1.54	9.48	7.13
0.1%	5 wt.%	9%	–0.5767	0.9730	–1.4758	1.86	2.26	4.07
0.5%	SiO ₂	9%	–0.5068	0.8321	–1.3660	1.68	8.70	6.40
0.1%	10 wt.%	9%	–0.3064	0.6140	–1.2912	1.46	2.90	5.73
0.5%	SiO ₂	9%	–0.4357	0.7527	–0.8957	1.25	8.34	5.04
DR376								
0.1%	–	–	0.8738	–2.1715	1.7080	2.90	1.71	9.57
0.5%	–	–	1.0696	–1.7357	1.0969	2.32	6.59	11.96
0.1%	3 wt.%	9%	1.0885	–1.5961	2.8480	3.44	0.79	9.49
0.5%	SiO ₂	9%	1.9313	–1.6909	1.4546	2.95	6.40	13.57
0.1%	5 wt.%	9%	0.9203	–1.7863	1.4649	2.49	1.59	9.00
0.5%	SiO ₂	9%	1.3285	–1.8154	1.3978	2.65	5.79	13.05
0.1%	10 wt.%	9%	0.5686	–1.2504	1.0560	1.73	1.13	5.81
0.5%	SiO ₂	9%	0.8017	–1.2319	0.8228	1.68	5.81	11.92
DNmix								
0.1%	–	–	0.8274	–0.1938	2.2981	2.45	1.39	9.82
0.5%	–	–	2.1444	–0.5737	2.6331	3.44	6.41	19.93
0.1%	3 wt.%	9%	0.2855	–0.1155	2.1680	2.19	1.24	6.45
0.5%	SiO ₂	9%	1.6644	–0.3814	2.3947	2.94	5.75	16.81
0.1%	5 wt.%	9%	0.0695	–0.4090	2.0684	2.11	1.10	7.11
0.5%	SiO ₂	9%	1.7315	–0.3481	2.0250	2.69	6.13	13.21
0.1%	10 wt.%	9%	0.5210	–0.1637	1.8274	1.91	0.78	3.61
0.5%	SiO ₂	9%	1.2835	–0.2080	1.5688	2.04	6.23	18.26

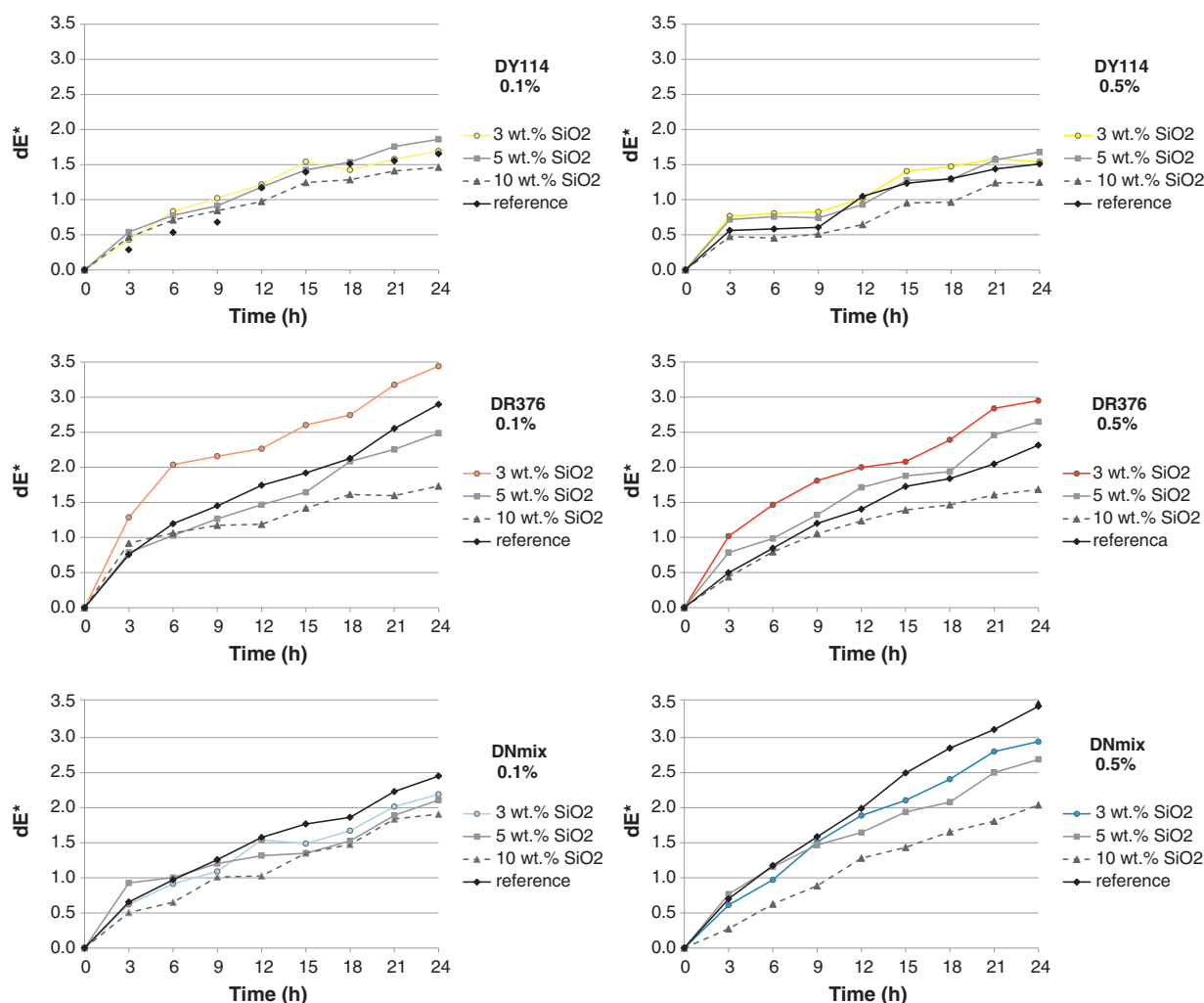


Fig. 5. Total colour differences (dE^*) of dyed (reference) and dyed/ TiO_2 treated samples as a function of irradiation time; 0.1% dye concentration (left diagrams) and 0.5% dye concentration (right diagrams).

surface covered by a moderate content of SiO_2 coating layers, i.e. 3 and 5 wt.%, could eventually cause catalytic fading of the red dyed samples in comparison with the reference samples, irrespective of the dye concentration, presumably on account of the minor DR376 stability towards photo-induced oxidation compared to the DY114 and DNmix dyes.

4. Conclusions

This research work characterized three different nano TiO_2 – SiO_2 colloidal dispersions, which were further applied onto polyester fabric together with disperse dyes.

SEM images of PES fabric revealed the most homogenous coating when utilising dispersion with the lowest SiO_2 content. Also, samples treated with TiO_2 –3% SiO_2 or TiO_2 –5% SiO_2 dispersions attained maximal water adsorption at shorter times as well as better hydrophilicity (lower contact angles) compared to reference sample. On the other hand, superior hydrophobic effect on the PES surface treated by TiO_2 –10% SiO_2 dispersion was attributed to the presence of larger nanoparticles agglomerates.

In addition, from the colour measurement data it could be concluded that the presence of TiO_2 – SiO_2 core–shell nanoparticles had a notable effect on the colour characteristic of the polyester fabric regarding the weight percent of SiO_2 , the type of dyestuff, and its concentration. In general, the TiO_2 nanoparticles had an influence on a declining dyeing depth and brighter colouration of the samples in comparison with the

dyed ones. In addition, the higher ratio of SiO_2 to TiO_2 implies elevated differences in brightness as well as reduced colour strengths. Furthermore, this research reported superior changes in the hue, brightness, chroma, and colour strength of all the samples, i.e. dyed and dyed/ TiO_2 treated, during 24 h of UV irradiation exposure depending on the structure and concentration of the applied dyestuffs. The SiO_2 -coated TiO_2 had a positive influence on the retardation of the oxidative dye-fading under UV light by reducing the effective surface area of TiO_2 nanoparticles and, thus, suppressing their photocatalytic activity.

Acknowledgement

The research leading to these results has received funding from the Slovenian Research Agency (ARRS) under a bigger applied project no. L2-4101 and a programme group for Textile Chemistry P2-0118.

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