Multifunctional Ultra-fine Silky PET Fabrics; Nanofunctionalization via an Ultrasound-assistant Nanocolloidal Preparation

Ozra Khanjarpanah, Roya Dastjerdi

Yazd University, Department of Textile Engineering, Yazd IRAN

Correspondence to:
Roya Dastjerdi email: nanobiotex.dastjerdi@yazd.ac.ir

ABSTRACT
Providing an even nano-finishing via pad-dry process as the simplest finishing method on ultra-fine silky PET fabrics is difficult due to low absorption potential, extremely low friction resulting in pad mangles and the low thickness. This research aims to develop a procedure of continuous nano-functionalization of ultra-fine silky PET fabrics and examines their properties. An as-prepared TiO_2 nano-colloidal solution was applied to fabrics by means of a continuous pad-dry process. To stabilize the nanostructures on the fabric surfaces, the samples were subjected to a simple and fast aftertreatment. The effects of this treatment were assessed on washing stability, water repellency (contact angle and droplet absorption time), handle (bending length), wrinkle resistance, UV protection properties and wear properties. An even nano finish on the ultra-fine silky PET fabric was confirmed by SEM micrographs with different magnifications. Results indicate an enhancement of water droplet absorption time as well as the contact angle of droplets on the treated samples which corroborates increased hydrophobicity. Additionally, the treatment enhanced softness, wrinkle resistance and particularly washing fastness of the nanofunctionalized fabrics. The results demonstrate that the functionalization improves the wear properties and the UV stability of the treated fabrics.

Keywords: Ultra-fine silky PET fabric, Titanium Dioxide, Wetting, Finishing, Multifunctional properties.

INTRODUCTION

Silky PET fabrics are used for women's fine clothes, curtains and etc. These fragile fabrics are difficult to wash due to their sensitivity to mechanical effects of washing. In the case of curtains, unlocking and refixing them is also very difficult and time-consuming. Therefore, the development of self-cleaning curtains that require fewer washings would be of interest. Curtain fabrics can provide an ideal substrate for growth of bacteria, especially due to humidity caused by changes in the temperature inside and outside of buildings and near windows. UV protection and UV irradiation stability are also very important charcteristices for this kind of application in sunlight. Nanotechnology can offer such multifunctional modifications for textiles [1-6].

Nanotechnology is concerned with materials displaying novel and improved physical, chemical, and biological properties or phenomena. This function is due to the nano-scale size of materials [7]. With the advent of nanotechnology, a new era has begun in the field of textile finishing [8-10]. In recent years, the use of metal oxide nanoparticles 1 to 100 nm in size has been a focus for researchers due to their unique properties. [11].

Titanium dioxide nanoparticles are of particular interest because of their compatibility with the environment, chemical structure stability, and electrical and physical properties [12-13]. They widely used in textile finishing due to their antimicrobial and photo-catalytic activities, and to develop controllable wetting features [1], protection against ultraviolet rays, self cleaning, antistatic and anti-wrinkle properties. Therefore, they are a good option for modification of silky PET fabrics. This paper reports the multifunctional properties of silky PET fabrics nanofunctionalized with TiO_2 and stabilized by methods presented in previous publications [14, 15].

EXPERIMENTAL

Materials

A silky PET fabric with a density of 35 warp yarns per cm and 37 weft yarns per cm was subjected to nano-finishing with titanium dioxide nano powder (TiO_2 P25). The nano powder was provided by Evonik Degussa Corporation. TiO_2 P25 contains an

80 wt% anatase and 20 wt% rutile structure and has a particle size of 25–30 nm. Polysiloxane CT 208 E emulsion was supplied by Wacker Finish.

Methods

Colloidal solution components were dispersed using ultrasound, and a proper colloidal solution of 5 wt% of inorganic nanoparticle powder was prepared. The experiments were performed on samples with dimensions of 9 cm × 20 cm. The pre-washed fabric samples were immersed in the bath of colloidal nanoparticles for 20 seconds and squeezed by a pad to a 100% wet pick-up. Then, the samples were dried at 150 ºC for three minutes. The after-treatment with cross-linkable polysiloxane (XPs), was performed under the same conditions but with a shorter fabric immersion time (three seconds).

The samples were washed with 5 g/L non-ionic detergent at 60 ºC in a liquor ratio of 40:1 for 30 minutes. They were then rinsed with tap water, thoroughly rinsed three times with deionized water at 40 °C for 10 minutes, and dried at room temperature. Each sample was marked with an identification code according to *Table I*.

TABLE I. The samples identification codes.

Sample ID	TiO_2	XPs	After-wash
C	-	-	-
TiO_2	*	-	-
TiO_2+Ps	*	*	-
W(TiO_2+ Ps)	*	*	*

Characterization

Morphological Properties

The SEM micrographs were obtained using a Vega 3, Tescan scanning electron microscope with different magnifications.

Water Droplet Absorption Time

The hydrophobicity of the samples was studied by measuring the time required for water droplets to be completely spread on the fabric surfaces. To that end, 10µL water droplets were dropped from a height of 1 cm on the fabric surface using a small syringe. The time for complete absorption of the water droplets on the fabric surfaces was measured for nine replicates at 28^{o}C and 30% relative humidity, and the average value was reported. This test was conducted for the treated fabrics before and after washing as well as for the untreated fabrics.

Contact Angle

The contact angle (CA) of a 10 µL distilled water droplet dropped from the distance of 1 cm was measured five seconds after being placed on the fabric surface. This measuremnt was done using a self-developed goniometer apparatus [16] equipped with a high-resolution camera and suitable lens. The average value of contact angle of drops, determined through MB-Ruler software, was calculated and reported as the CA of each sample.

Stiffness

The Shirley stiffness test was used as a standard for stiffness, and the bending length was reported for the test specimens cut in 25-mm-wide and 200-mm-long pieces parallel to the warp. Bending stiffness was calculated according to Eq. (1).

$$G = 0.10MC^3 \tag{1}$$

Where “C” and “M” are the values of bending length (cm) and fabric surface density (g/m^2) , respectively.

Modulus was calculated according to Eq. (2).

$$q = \frac{12G}{g^3} \times 10^{-6} \tag{2}$$

Where “G” and “g” are the values of bending stiffness (mg.cm) and thickness (cm), respectively.

Wrinkle Recovery Angle

Wrinkle recovery angle was determined by using a Shirley crease recovery tester based on the AATCC 66–2003 test method. For this test, the samples were cut into 40 mm × 15 mm pieces. The specimens are folded and compacted under2 Kg force for 5 min to obtain folded wrinkles. After suspending them for recovery, the wrinkle angle was recorded.

UV Protection Properties

UV stability of the fabrics was evaluated by measujring the color changes of wool fabrics colored with an extremely UV-sensitive dye (Methylene Blue) covered by different modified and unmodified samples after exposure to UV irraditation [17]. The specimens were exposed to sunlight in Yazd, Iran during July 2014 between 10 a.m. to 4 p.m for a total of 20 hours.

After UV irradiation, the color changes were studied based on the reflectance data using an x-rite sp62 Spectrophotometer. ΔE% was calculated according to Eq. (3).

$$\Delta E\,\% = \frac{\Delta E_C - \Delta E_T}{\Delta E_C} \times 100 \quad (3)$$

ΔE_C and ΔE_T are the color differences of each wool fabric supported by the control and treated samples, respectively. They were calculated according to Eq. (4).

$$\Delta E = \left[\left(L_{C,T} - L_0 \right)^2 + \left(a_{C,T} - a_0 \right)^2 + \left(b_{C,T} - b_0 \right)^2 \right]^{0.5} \quad (4)$$

Where "L", "a" and "b" are the values of lightness, redness–greenness, and yellowness–blueness, respectively determined by a computer color matching system. L_0, a_0 and b_0 refer to the dyed fabric samples before UV irradiations [17].

Washing Durability

Washing effluent was used to investigate the washing durability of the fabrics. TiO_2 concentration in the effluent was used to deteremine washing durability. This is believed to be the most precise method [15]. Wash fastness test was conducted on each of the samples after 40 laundering cycles using a Rotwash by AATCC test method 61(2A)-1996. Each cycle of laundering was performed at 40 °C for 45 minutes with 5 g/L standard soap, which is equal to five launderings at 38°C. The effluent of each washing cycle was collected. This method can be used for identification of TiO_2 by a particular absorption peak in the UV–vis spectrum [15, 18]. Accordingly, the mixed and diluted washing effluents were evaluated at a suitable ratio by UV–vis absorption [15].

Wear Properties

According to the ASTM (D 4966) standard test method, the abrasion properties of the fabrics were evaluated by using the Martindale machine (Shirley development LTD model).

UV Irradiation Stability

In order to quantify the UV stability of the fabric samples, the wear resistance was measured according to the ASTM D4966 after 100 and 160 hours of exposure to sunlight in Yazd, Iran during July 2014 between 10 a.m. to 4 p.m [19] .

RESULTS AND DISCUSSION

Morphological Properties

A scanning electron microscope (SEM) was used to observe the particle dispersion on the treated samples. From *Figure 1*, observation of different magnifications showed the nanoparticles had good dispersibility and comfirmed that an even coating was formed on the fiber surfaces.

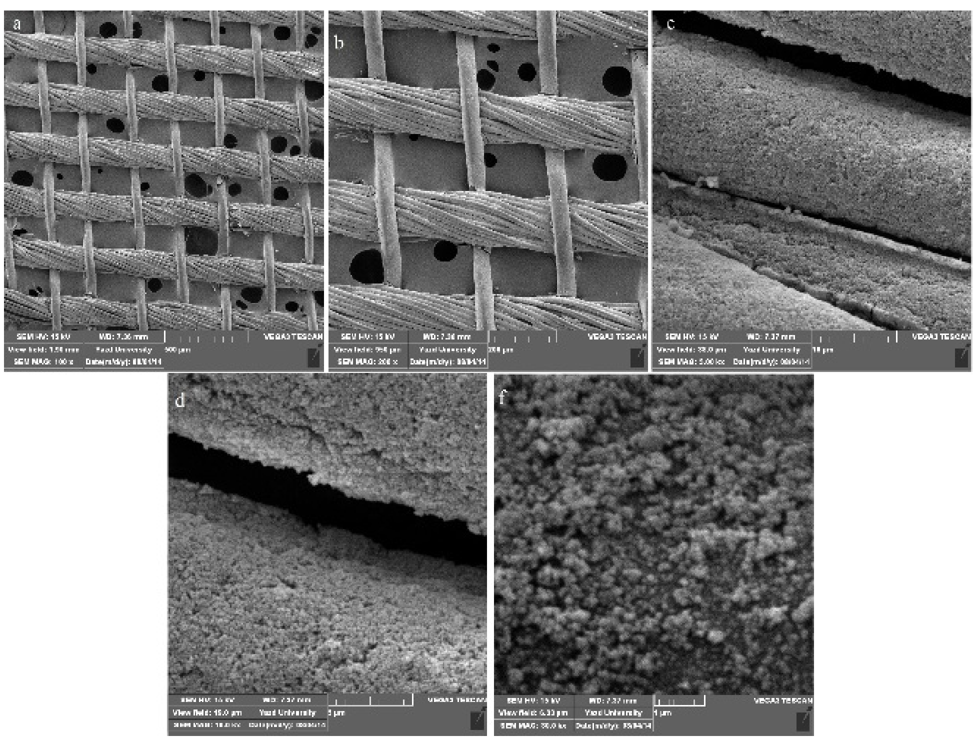

FIGURE 1. SEM micrographs of the treated fabric surface.

Water Droplet Absorption Time

The hydrophobicity of the samples was studied by measuring the time required for water droplet absorption by the fabric samples. This test was performed before and after washing. The results are reported in *Table II*. The recorded time of absorption by the untreated fabrics was very short. The results show that the water droplet absorption time was increased nearly 300 times following TiO_2 functionalization. The hydrophobicity of the treated sample increased after washing due to the removal of Ps emulsifiers [16].

TABLE II. Wetting properties of treated and untreated fabrics.

Samples	(s)Water droplet absorption time	
	Before washing (CV%)	After washing (CV%)
C	15 (6.66)	17 (3.33)
TiO_2	8 (6.93)	11 (5.41)
TiO_2+Ps	4114 (4.02)	4361 (5.63)

Droplet Contact Angle

The contact angles of the control samples as well as TiO_2-treated samples without XPs were both less than 90° and the droplets were immediately absorbed into the fabrics (*Figure 2*). The contact angle of samples coated with XPs increased to 141.9° (*Figure 2*).

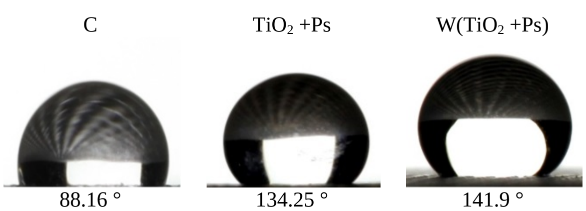

FIGURE 2. Contact Angle (CA) on different samples.

Bending Length, Bending Stiffness And Bending Modules

Fabric stiffness is a factor that relates to handle. Therefore, bending length was measured as an indicator of fabric softness [14]. The results are reported in *Figure 3* and *Table III*. As can be seen, the polysiloxane resin improved the handle and softness of the samples. After treatment of the fabrics with the colloidal solution of TiO_2 nanoparticles, the stiffness of increased (*Figure 3* and *Table III*). Finishing with polysiloxane also improved the softness, and as a result, drapability and formability of the treated fabrics over the control samples. These features are very important for curtain fabrics and women's fine clothes. Drapability is especially important in creating suitable forms in these applications.

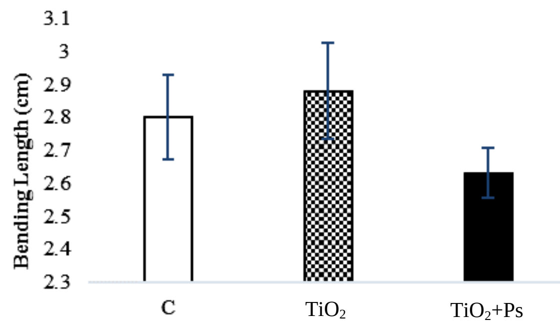

FIGURE 3. Bending length of different samples.

TABLE III. Bending stiffness and modulus of different samples.

Samples	Bending stiffness (% CV) (mg.cm)	Modulus (kg/cm^2) (CV%)
C	86.9 (8.9)	380.2 (8.9)
TiO_2	110.2 (9.5)	482.1 (9.5)
TiO_2+Ps	75.2 (5.8)	329.0 (5.8)

Wrinkle Recovery Angle

Treating fabrics with a colloidal solution of TiO_2 nanoparticles without XPs causes the wrinkle recovery angle (WRA) to decrease more than 20% compared to the control (WRA) (*Figure 4*). However, following the polysiloxane-based treatment the WRA increases to a value that is over 20% higher than that of the control. Therefore, polysiloxane treatment stabilizes particles and can be useful in compensating for such adverse side effects [14]. The positive effect of XPs is likely due to the fact that a network-like layer of polysiloxane forms on the fabric surface. XPs can also allow easier movement of polymer chains due to a plasticizing effect which results in easier polymer chain movement and crease recovery [16]. Wrinkle recovery angle is especially important in garment applications of silky PET fabrics. Wrinkles also cause an undesirable appearance on women's fine clothes and ironing of these delicate fabrics is difficult.

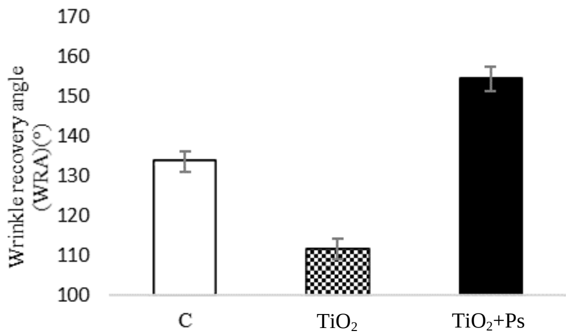

FIGURE 4. Wrinkle recovery angle (WRA) (°) of different samples.

UV Protection Properties

The UV protection properties of the samples are presented in *Table IV*. The table provides the data on attributes L, a, b of the UV-sensitive sensors, as well as ΔE. It can be concluded that improvement of less than 10% in UVP was caused by the treatment of the samples with TiO_2 nanostructures as well as TiO_2+Ps. The large fraction of pores in the structure of thin silky PET fabrics make it difficult to control the passage of UV rays. Considering *Figure 1*, the fibers cover only about 50% of the fabric area, and the rest consists of pores.

TABLE IV. Reflection data of different samples.

Sample	L	a	b	ΔE	ΔE%
C	46.67	-6.84	-3.94	24.63	-
TiO_2	45.65	-7.29	-6.13	22.18	9.94
TiO_2+Ps	45.26	-7.16	-5.72	22.41	9.01

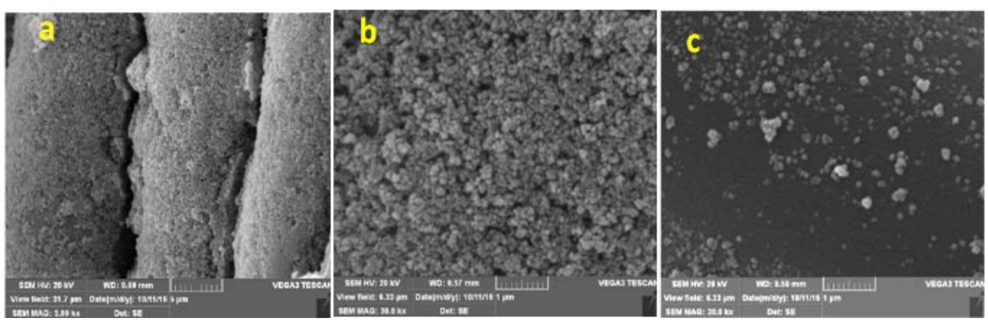

FIGURE 5. The SEM micrograph of 40-times washed samples; a and b TiO_2+Ps, and c TiO_2 sample.

Washing Durability

The TiO_2 concentration in the effluent can be used to quantify washing durability [19]. The amounts leached out TiO_2 in polysiloxane-treated samples compared to that of TiO_2-treated samples without polysiloxane is recorded in *Table V*. The amount of leached out TiO_2 is 76.2% to 94.6% lower in the polysiloxane treated samples, indicating significantly higher wash fastness of the modified nanoparticles. The cross-linked polysiloxane layer can act as a supporting layer at the surfaces of textiles, preventing nanostructures from being leached out [16].

TABLE V. Absorbance of washing effluents for various samples.

Wash Cycles	Sample type	Absorption
1-5	TiO_2	2.123
	TiO_2+Ps	0.1145
	Changes percentage	94.60%
5-10	TiO_2	1.088
	TiO_2+Ps	0.0932
	Changes percentage	91.43%
10-15	TiO_2	0.4403
	TiO_2+Ps	0.0442
	Changes percentage	90.00%
15-20	TiO_2	0.1654
	TiO_2+Ps	0.0348
	Changes percentage	79.00%
20-25	TiO_2	0.1287
	TiO_2+Ps	0.0251
	Changes percentage	80.49%
25-30	TiO_2	0.1325
	TiO_2+Ps	0.0288
	Changes percentage	78.26%
30-35	TiO_2	0.1601
	TiO_2+Ps	0.0381
	Changes percentage	76.20%
35-40	TiO_2	0.1864
	TiO_2+Ps	0.0409
	Changes percentage	78.05%
1-40	TiO_2	4.4244
	TiO_2+Ps	0.3264
	Changes percentage	93.00%

Figure 5 shows the SEM micrographs of washed samples after 40 laundering cycles. As shown in *Figures 5a* and *5b*, a complete and even nano-coating remains on sample "TiO_2+Ps" after the 40 cycles. *Figure 5c* shows that only a small number of nanoparticles can be detected on the sample "TiO_2". Some interfacial nanoparticles could partially diffuse into the surface of the fine thermoplastic yarns during the heating process, allowing them to survive washing. However, the majority of particles have removed from the untreated TiO_2 sample after washing.

Wear Properties

In *Figure 6*, weight reduction is plotted against number of abrasion cycles. The number of cycles to achieve the yield point (where the slope change occurs) and end point of the weight reduction curve and the number of rubs at the breaking point can be extracted from this figure. These two factors are direct indicators of fabric wear resistance [19]. From *Figure 6*, it is notable that the yield point of the curve occurs at about 100 cycles for the control sample, about 200 cycles for the sample containing the untreated TiO_2 and at about 250 cycles for the polysiloxane treated sample. From Table 6, the non-UV exposed control sample breaks after 172 cycles, the TiO_2 sample breaks after 255 cycles and the polysiloxane treated sample breaks after 279 cycles. Thus the polysiloxane treated sample improves wear properties of the fabrics by over 60 percent.

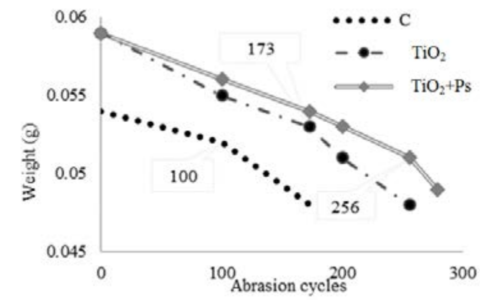

FIGURE 6. The weight reduction versus number of rub cycles.

UV Irradiation Stability

Figure 7a and *Figure 7b* show the abrasion resistance behavior of pure and treated samples after 100 hours and 160 hours of UV irradiation. Weight diminutions of the samples during the abrasion test were recorded in this figure. The number of rubs at the breaking point are reported in *Table VI*.

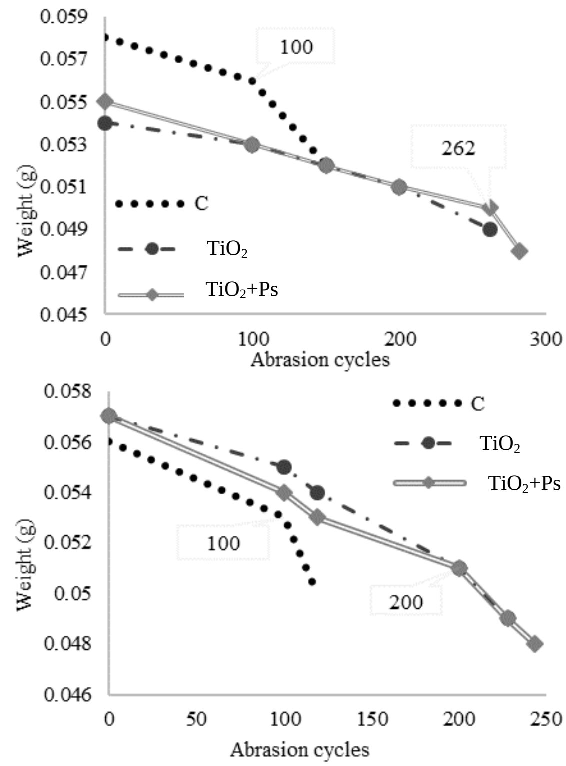

FIGURE 7. The weight reduction versus number of rub cycles after a) 100 h and b) 160 h UV irradiation.

TABLE VI. Numbers of rub cycles at the breaking points.

Irradiation time (h)	0 (CV%)	100 (CV%)	160 (CV%)
C	172 (4.52)	150 (2.35)	119 (4.75)
TiO_2	255 (2.49)	261 (1.89)	228 (1.85)
Enhanced wear properties(%)	48	74	48
TiO_2+Ps	279 (1.52)	282 (1.50)	243 (2.61)
Enhanced wear properties(%)	62	87	51

At each stage of UV exposure, the treated samples showed significantly improved wear properties as compared to that of the control, with cycles to break of the polysiloxane treated samples approximately twice those required to break the control sample. The breaking point of the treated samples is essentially unaffected after 100 hours and at 160 hours it is reduced 13%, while the breaking point of the control Is reduced by 31 percent.

CONCLUSION

In this research, the effect of nanocolloidal treatment on multifunctional properties of fine silky PET fabrics was investigated. The results showed that finishing of silky PET fabrics increases the water droplet absorption time. Polysiloxane treatment on the surface of samples functionalized by titanium dioxide nanoparticles has also a positive effect on bending stiffness, and increases softness and resistance to wrinkles. This provides formability for fabrics and is very important for such applications as women's fine clothes, curtains, etc. The nano-finishing process improves the abrasion resistance of fabrics. The data indicates that the finish serves as a protective layer against the damaging effects of sunlight on fabrics. The results of the study also suggest that XPs treatment has a major effect on the wash fastness of the fabrics based on significantly lower TiO_2 leaching after 40 wash cycles. Consequently, this research provides an easy, available and cost-effective TiO_2 nano-functionalization process for silky PET fabrics via a continuous pad-dry process and overcomes many challenges associated with the sensitivity of these fragile fabrics in applications like such as fine clothes and curtains.

REFERENCES

[1] Dastjerdi, R, Montazer, M, "A Review on the Application of Inorganic Nano-structured Materials in Modification of Textiles: Focus on Anti-microbial", *Colloids and Surfaces B: Biointerfaces*, 79, 2010, 5.

[2] Sundarrajan, S, Chandrasekaran, A.R, Ramakrishna, S, "An Update on Nanomaterials-Based Textiles for Protection and Decontamination", *J. Am. Ceram. Soc*, 93, 2010, 3955.

[3] Bhat, G, Hegde, R.R, Kamath, M.G, Deshpande, B, "Nanoclay Reinforced Fibers and Nonwovens", *Journal of Engineered Fibers and Fabrics*, 3, 3. 2008, 22.

[4] Lam, G, Kan, R.R, Yuen, M.G, "Physical and Chemical Analysis of Plasma-Treated Cotton Fabric Subjected to Wrinkle-Resistant Finishing", *Cellulose*, 18, 2011, 493.

[5] Grace, M, Chand, N, Bajpai, S.K, "Copper Alginate-Cotton Cellulose (CACC) Fibers with Excellent Antibacterial Properties", *Journal of Engineered Fibers and Fabrics*, 4, 3. 2009, 24.

[6] Devaux, E, Aubry, C, Campagne, C, Rochery, M, "PLA/Carbon Nanotubes Multifilament Yarns for Relative Humidity Textile Sensor", *Journal of Engineered Fibers and Fabrics*, 6, 3. 2011, 13.

[7] Laforgue, A, Champagne, M.F, Dumas, J, Robitaille, L, "Melt-Processing and Properties of Coaxial Fibers Incorporating Carbon Nanotubes", *Journal of Engineered Fibers and Fabrics*, 7, 3. 2012, 118.

[8] Lam, Y.L, Kan, C.W, Yuen, C.W.M, "Effect of Concentration of Titanium Dioxide Acting as Catalyst or Co-catalyst on the Wrinkle-resistant Finishing of Cotton Fabric", *Fibers Polym*, 11, 2010, 551.

[9] Di, Y, Li, Q, Zhuang, X, "Antibacterial Finishing of Tencel/Cotton Nonwoven Fabric Using Ag Nanoparticles-Chitosan Composite", *Journal of Engineered Fibers and Fabrics*, 7, 2, 2012, 24.

[10] Dastjerdi, R, Montazer, M, "Nano-colloidal Functionalization of Textiles Based On polysiloxane as a Novel Photo-catalyst Assistant: Processing Design", *Colloids Surf., B: Biointerfaces*, 88, 2011, 381.

[11] Turker, A. R, "New Sorbents for Solid-Phase Extraction for Metal Enrichment", *Clean*, 35, 2007, 548.

[12] Linsebigler, A.L, Lu, G, Yates, J.T, "Photocatalysis on TiO_2 Surfaces: Principles Mechanisms, and Selected Results", *Chem. Rev*, 95, 1995, 735.

[13] Wongkalasin, P, Chavadej, S, "Thammanoon Sreethawong, Photocatalytic Degradation of Mixed Azo Dyes in Aqueous Wastewater Using Mesoporous-Assembled TiO_2 Nanocrystal Synthesized by a Modified Sol–Gel Process", *Colloids Surf., A: Physicochem. Eng. Aspects*, 384, 2011, 519.

[14] Dastjerdi, R, Montazer, M, Shahsavan, S., "A new Method to Stabilize Nanoparticles on Textile Surfaces", Colloids and Surfaces A: Physicochem. Eng. Aspects, 345, 2009, 202.

[15] Dastjerdi, R, Montazer, M, Shahsavan, S., "A Novel Technique for Producing Durable Multifunctional Textiles Using Nanocomposite Coating", Colloids and Surfaces B: Biointerfaces, 81, 2010, 32.

[16] Dastjerdi, R, Noorian, S. A, "Polysiloxane Features on Different Nanostructure Geometries; nano-wires and Nano-ribbons", *Colloids and Surfaces a: Physicochemical and Engineering Aspects*, 452, 2014, 25.

[17] Todorova, L, Vassileva, V, "A New Method of Determination of the UV Radiation Permeability through Cotton Cloth", *Fibers & Textiles in Eastern Europe*, 11, 2003, 21.

[18] Reddy, K.M, Gopal Reddy, C.V, Manorama, S.V, "Preparation, Characterization, and Spectral Studies, on Nanocrystalline Anatase TiO_2", *Journal of Solid State Chemistry*, 158, 2001, 180.

[19] Dastjerdi, R, Mojtahedi, M. R. M, "Multifunctional Melt-Mixed Ag/TiO_2 Nanocomposite PP Fabrics: Water Vapour Permeability, UV Resistance, UV Protection and Wear Properties", *Fibers and Polymers*, 14, 2013, 298.

AUTHORS' ADDRESSES

Roya Dastjerdi
Ozra Khanjarpanah
Yazd University
Department of Textile Engineering
Yazd P.O.BOX 89195-741
Yazd, 89195-741
IRAN