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Self-cleaning and Handle Properties of TiO_2-modified Textiles

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Abstract: Self-cleaning surfaces based on photocatalysis are an extremely promising nano-technological field of extensive research and development. Recently comprehensive research work has been performed to evaluate the optical, photocatalytic and antimicrobial properties of TiO_2 nano-particles and composites thereof. The aim of this study was to obtain self-cleaning properties for regenerate cellulose surfaces by nano-modification, using TiO_2 nano-coating and to define the impact of the modification on fabrics end-use properties. Two different modified fabrics with self-cleaning effect were prepared and analysed, i.e. the modification efficiency was determined. In addition, the influence of fibre modification on several textile properties was determined. However, a soft handle, good appearance and some other surface properties accompanied by appropriate mechanical properties represent the basis for a high quality fabric therefore the influence of the modification procedure on textiles handle was studied.

Keywords: Self-cleaning, Nano-technology, Lyocell fibre, Low-stress mechanical property, Handle property

Introduction

Recently, the application of nano-technology in the textile processing has increased extensively due to its unique and valuable properties. By fibres' nano-modification textiles-properties are improved and new functionalities are created. The properties imparted to textiles using nano-technology include water repellence, soil resistance, wrinkle resistance, anti-bacteria, anti-static and UV-protection, flame retardation, dye-ability improvement, self-cleaning, etc. [1-3].

Self-cleaning effect of a textile material can be obtained by a photo-catalytically active (PCA) coating containing a photo-catalytically active oxide of a transition metal (MO) or (MO_2) such as titanium dioxide (TiO_2). Due to light absorption in the near UV, electrons are hoisted from the energy level of the valence band of TiO_2 into that of the conductive band, thus leaving a positively charged hole in the valence band. The separated electron/hole pair is called "exciton". The generation of excitons is the cause for the light induced semiconductor properties of TiO_2 [4]. Self-cleaning coatings react with and decompose organic compounds or pollutants, deposited on the textiles from the environment, under the effects of exposure to sunlight, particularly the ultraviolet radiation. The organic pollutants are decomposed to simple inorganic compounds such as CO_2 and H_2O and are removed under the effects of heat, wind and/or rain. The efficiency of the self-cleaning coating is dependent upon the photo-catalytic activity of the MO_2 catalyst, which is directly proportional to the total surface area of the MO_2 particles [5-7].

Besides on impurities the photo-activity of titania could have an oxidizing influence on textile substratum, and damage fibres. To avoid the negative impact of the coating on the fibre we developed a composite titanium-silica (TiO_2-SiO_2) coating.

The photo catalytic self-cleaning fabrics could be applied for sportswear, military uniforms, outdoor upholstery and carpets, as well as other upper clothes, e.g. women dresses. However, the realization of self-cleaning properties on textile surfaces by using the nano-technology includes a vast potential for the development of new products and applications for known materials. Furthermore, for garment production process it is important to know the effect of various treatments on fabric processing properties from point of view to assure appropriate three-dimensional form and comfort of clothes. Objective evaluation method of fabric handle was developed by Kawabata and Niwa [8,9]. The evaluation equations are used widely for various end-uses of men's or women's garments, such as light weight fabrics for women's garments [10,11]. Fabric handle is related to basic mechanical properties of fabrics, especially initial low-stress region of those properties. Fabric handle includes not only soft and/or smooth touch of fabrics, but also drape shape and/or appearance of fabrics and clothes, and comfortable feeling of clothes, in a broad sense [12].

In our previous research, the influence of photocatalytic activity of TiO_2 on applicable properties of cellulose fibres was determined. Tenacity of TiO_2-coated fibres after 44 days of exposure to direct daylight was reduced for ~22 %. In the meantime, the tenacity of TiO_2-SiO_2 coated fibres was almost unchanged, since the presence of SiO_2 nanoparticles limited the influence of TiO_2 nanoparticles on cellulose fibres. Therefore, in this research two different self-cleaning coatings, i.e. a TiO_2 coating and a composite TiO_2-SiO_2 coating on regenerated cellulose fibres were prepared. Some researchers used two different precursors for formation of TiO_2 and SiO_2 nanoparticles, meanwhile we developed the process for making composite TiO_2-SiO_2 coatings directly

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on the fibres surface using commercial TiO_2 P25 nanoparticles, known as the best photocatalyst, and precursor tetraethy ortosilicate (TEOS), which was used as a binder for TiO_2 P25 nanoparticles and as protection against high oxidizing power of TiO_2. As a result of surface nanomodification, the surface structure of coated fibres changed significantly and consequently, the properties related to the handle changed, too. For this reason, the effect of coatings on fabrics' handle was determined, since the handle of textiles plays an important role. That kind of research hasn't been reported yet.

Experimental

Material and Samples Preparation

For the study Lyocell fabric in 2/1 twill weave with S twill line was used. Two different methods for the TiO_2 coating preparation were involved, i.e. previously formed nano TiO_2 particles were used and bound by SiO_2 nano-coating on the fibre surface and TiO_2 nano-particles were produced directly on the fibre surface by sol-gel procedure, respectively. For the first modification method the sol-gel deposition technique for SiO_2 coating from precursor Tetraethyl ortosilicat, TEOS with incorporated TiO_2 nanoparticles was used (TiO_2-SiO_2 coating) and therefore Lyocell fabrics were treated using TiO_2 P25 nanoparticles (Degussa), Tetraethyl ortosilicat TEOS, 98 % (Merck), ammonia solution, 25 % (Merck) as a catalyst and ethanol, 96 % (Riedel-de Haën) as a solvent, in a small amount of distilled water (Method 1; Sample 2). Secondly, the sol-gel deposition technique from precursor Titanium (IV) isopropoxide, TIP was involved for fibre TiO_2 nanomodification. For the nano-coating's preparation Titanium (IV) isopropoxide (TIP), 97 % (Aldrich) as a precursor, ammonia, 25 % (Merck) as a catalyst and ethanol, 99 % (Merck) as a solvent, in a small amount of distilled water (Method 2, Sample 3) was used. Ultrasound stirring of the mixture was performed using an Elma ultrasonic cleaning bath for sixty minutes after addition of the precursor at 60°C. Samples were dried at room temperature during the night and thermally treated at 105 °C for 15 minutes. Basic properties of the untreated and surface treated fabrics are listed in Table 1.

Table 1. Basic properties of the untreated and treated samples

Sample	Weight per unit area (gm^{-2})	Yarn density	
		Warp (Yarns/ cm)	Weft (Yarns/ cm)
Sample 1 untreated	155.63	40	30
Sample 2 (Method 1): TiO_2/SiO_2 composite nano-coating	162.97	40	30
Sample 3 (Method 2): TiO_2 nano-coating	159.86	40	30

Analytical Methods

SEM (Scanning Electron Microscopy)

Coating morphology was observed on scanning electron microscope images, which were obtained on a Scanning Electron Microscope Zeiss Gemini Supra 35 VP.

Self-cleaning Test

Self-cleaning test was performed by observing the photo-degradation oxidation of organic dye solution, which was spoiled on the treated fabric. Red beet sap was used for staining samples, however the same results were obtained if any other stain was analysed, e.g. wine -stain. Samples were exposed to day light for 32 days. Colour changes of the stain were followed visually and colorimetric using a Datacolor international Microflash 200d apparatus.

Low-stress Mechanical Properties

The Kawabata Evaluation System for fabrics (KES-FB) was used for measuring the low-stress mechanical properties of the untreated and treated samples, including tensile, shear, bending, compression and surface properties. Furthermore, primary hand values (HV) were calculated by equations of Kawabata [8] for estimation of the treated samples' handle. The examined HV for category women's thin dress fabrics KN-202-LDY were Koshi (stiffness), Hari (anti-drape stiffness), Shinayakasa (flexibility with soft feeling), Fukurami (fullness and softness), Shari (crispness) and Kishimi (scroopy felling) [9].

Results and Discussion

Fibres Morphology

Surface morphology of the untreated and different treated samples is demonstrated on Figure 1. A smooth surface of the untreated Lyocell fibre is shown on Figure 1a, however, using two different methods for nano-coating formation leads to significantly different fibre surface morphology. Nano-modification using TiO_2 P25 nano-particles embedded in SiO_2 coating (TiO_2-SiO_2 coating) resulted in a homogenous coating with an uniform particle distribution (Figure 1(b)), while a non-uniform TiO_2 nano-coating was formed when the preparation of the coating proceeded using TIP precursor (TiO_2 coating) (Figure 1(c)). The latter coating shows a cracked surface with the deposition of huge agglomerates, which are strongly bound also after intense fabric treatment. There are also differences in the thickness of the coating, i.e. TiO_2-SiO_2 coating is thicker when compared to the TiO_2 coating. The difference between the two coatings is confirmed by the fabrics surface mass increase. An increase of 4.72 % for the surface mass is observed after modification of Lyocell fibres by TiO_2-SiO_2 coating, while TiO_2 coating increases surface mass only for 2.72 %. The surface masses of the untreated and both treated samples are collected in Table 1. Yarn density remained unchanged after the nano-modification process.

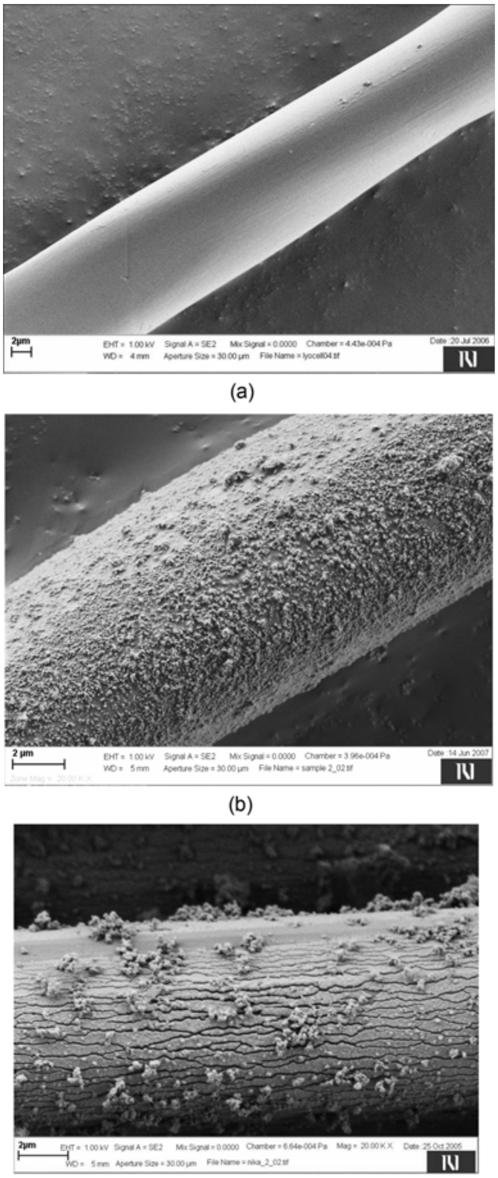

Figure 1. SEM images of surface morphology of Lyocell fibres - untreated (a) and under different conditions nanocoated Lyocell samples (b-sample 2) and (c-sample 3).

Self-cleaning Efficiency

The results of the self-cleaning test, which is based on the photo-catalytic degradation of the dye-solution dropped on the surface of the untreated, and under different conditions nano-coated Lyocell fabrics are demonstrated in Figure 2. No decolouration of the test dyestuff was observed when the untreated sample (a) was used. However, TiO_2 nanocoated Lyocell fabrics (b) and TiO_2-SiO_2 nanocoated Lyocell fabrics (c) display a self-cleaning effect.

In addition to visual determination, colorimetric measurements using Datacolor international Microflash 200d apparatus were performed, Figure 3. To evaluate the photocatalytic activity of the coating, chroma (C^* component of CIELAB system) of the coloured stain was investigated. Both samples demonstrated photo-catalytic activity, however, higher degradation of organic dye was observed when using TiO_2-SiO_2 nanocoating when compared to TiO_2 coating. The longer the treated fabric was exposed to the daylight more intensive was the change of the stain. The most significant decrease of the chroma is observed in the first day of UV treatment, later on the stain decolouration is not so intensive.

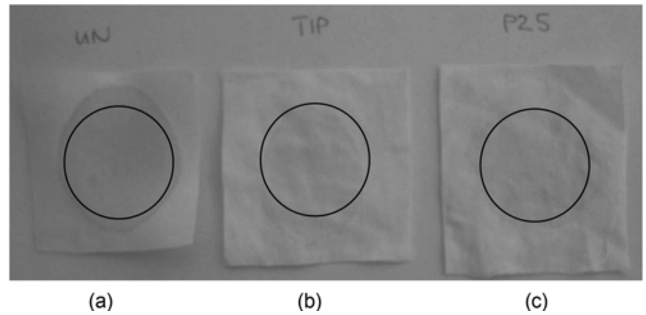

Figure 2. Untreated Lyocell fabric (a) and under different conditions nanocoated Lyocell samples (b-sample 3) and (c-sample 2) after the self-cleaning test performed by the organic dye solution.

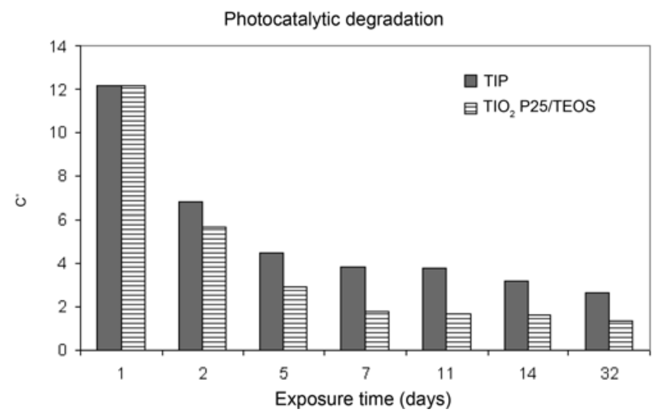

Figure 3. Chroma of the stain colour as the function of UV exposure time for which TiO_2 and TiO_2-SiO_2 modified Lyocell fabric, respectively, were UV treated.

Low-stress Mechanical Properties

The low-stress mechanical properties of the untreated and treated samples are presented in Table 2. Alterations (expressed as percentage) of the treated samples' low-stress mechanical properties when compared to the properties of unmodified fibres are presented in Table 2 in the round brackets.

The differences between differently treated samples are observed. The most expressive changes indicate bending, compression and surface properties, whilst the changes of the tensile and shear properties are smaller. A slight decrease

Table 2. Low-stress mechanical properties

Properties	Symbols and units	Typical values	Sample 1	Sample 2		Sample 3	
Tensile properties							
Tensile energy	WT [N/m]	5-20	5.95	5.25	(-11.8 %)	5.69	(-4.4 %)
Tensile resilience	RT	55-70	51.98	57.70	(+11.0 %)	54.60	(+5.0 %)
Linearity	LT [-]	0.55-0.70	0.543	0.522	(-3.9 %)	0.554	(+2.0 %)
Extensibility (warp)	EM1 [%]	3-5	3.03	3.00	(-1.0 %)	2.88	(-5.1 %)
(weft)	EM2 [%]	More than 4	5.71	5.20	(-8.9 %)	5.49	(-3.9 %)
Shear properties							
Shear rigidity (warp)	G1 [N/(m·1 °)]	0.6-0.9	0.37	0.34	(-8.1 %)	0.37	(0.0 %)
(weft)	G2 [N/(m·1 °)]	0.6-0.9	0.34	0.33	(-2.9 %)	0.33	(-2.9 %)
Shear stress at 0.5 °	2HG [N/m]		0.42	0.27	(-35.7 %)	0.32	(-23.8 %)
Shear stress at 5 °	2HG5 [N/m]	1-3	1.41	1.03	(-27.0 %)	1.07	(-24.1 %)
Bending properties							
Bending rigidity (warp)	B1 [$\times 10^{-4}$ N·m]	0.04-0.10	0.090	0.059	(-34.4 %)	0.075	(-16.6 %)
(weft)	B2 [$\times 10^{-4}$ N·m]	0.04-0.10	0.052	0.042	(-19.2 %)	0.059	(+13.5 %)
Bending moment	2HB [$\times 10^{-2}$ N]	0.015-0.50	0.043	0.014	(-67.4 %)	0.024	(-44.2 %)
Compression properties							
Compression energy	WC [N/m]	0.1-0.5	0.135	0.135	(0.0 %)	0.101	(-25.2 %)
Compression resilience	RC [%]	35-60	40.85	47.29	(+15.8 %)	51.37	(+25.8 %)
Linearity	LC [-]		0.265	0.301	(+13.6 %)	0.337	(+27.2 %)
Fabric thickness at 49 N/m^2	T_0 [mm]		0.332	0.396	(+19.3 %)	0.270	(-18.7 %)
Fabric thickness at 4900 N/m^2	T_m [mm]		0.130	0.216	(+66.2 %)	0.150	(+15.4 %)
Surface properties							
Coefficient of friction	MIU [-]	0.15-0.30	0.173	0.351	(+202.9 %)	0.280	(+61.9 %)
Mean deviation of MIU	MMD [-]	0.010-0.05	0.0121	0.0148	(+22.3 %)	0.0157	(+29.8 %)
Geometrical roughness	SMD [mm]	2-15	2.855	3.421	(+19.8 %)	3.298	(+15.5 %)

of the extensibility for both warp (EM1) and weft (EM2) direction, as well as for the tensile energy (WT) appears when the surface treatments were used. However, the extensibility and tensile energy satisfy good fabric handle and garment production process demands.

The shear rigidity (G) of a fabric depends on the flexibility of cross threads at the intersection points, which depend on the weave, yarn diameter and the surface characteristics of the both fibre and yarn [13]. Nano-coatings slightly decrease the shear rigidity (G), Table 2. However, the shear rigidity is very low for the untreated and treated samples, due to the elastic behaviour of those fabrics. It is well known that different final treatments affect fabrics' shear properties intensely. Namely, final treatments influence stress relaxation and diminish fabric's internal pressures, consequently, a decrease in the G and 2HG appears. This phenomenon is observed also when textiles are nano-coated, especially a greater decrease in hysteresis of shear force at 0.5 degree (2HG) and 5 degree (2HG5) was detected. The low value of the shear hysteresis (2HG) has an advantage influence on handle and expresses greater softness of the fabric, respectively, while the value of (2HG5) influence on the fabric fitting and appearance of the garment or other 3D textile products.

Surface treatments significantly decrease bending rigidity (B), especially, when the TiO_2-SiO_2 treatment is used, Table 2. The low value of bending rigidity, which results from the reduction of the friction forces between the fibres, influences the handle and flexibility of the fabrics. Because of the low value of the bending rigidity the fabrics tend to the folding. A higher decrease was observed for sample modified by the composite TiO_2-SiO_2 coating, which is in the warp direction 34.4 % and 19.2 % in the weft direction. A decrease of the bending moment (2HB) was also observed when the treatments were performed. It is well known that bending behaviour has a very good correlation with the fabric handle [13]. The low bending rigidity is one of the most desirable properties to achieve better handle properties, and higher Total Hand Value (THV), respectively. Therefore, we can suppose that both surface treatments affect superior soft and flexible fabric handle.

Compressibility provides a feeling of bulkiness and spongy properties in the fabric [13]. A higher compressibility is usually characteristic of thicker fabrics, and mainly depends on yarn packing density and yarn spacing in the fabric. It is obvious that surface treatments increase the fabric thickness T_m, measured at 4900 N/m^2 pressure. We found that the compression energy (WC) is decreased for TiO_2 surface treated fabric therefore the lower fullness of this fabric is achieved. Generally, compression energy is low for untreated and treated samples, which is distinctive for thin fabrics.

The results of our research lead to the conclusion that nano-coatings positively influence tensile resilience (RT) and compression resilience (RC). When the treatments were performed the tensile resilience and, especially, compression resilience increased. Namely, these two properties reflect the fabric recoverability after tensile and compression deformation.

The surface characteristics of a fabric influence the handle, comfort and aesthetic properties of garments. The surface treatments significantly increase the friction coefficient of the fabrics' surface (MIU) and geometrical smoothness (SMD), which represents the geometrical roughness of the fabric surface. Increased surface friction and roughness is a result of the surface treatments, which actually shows Figure 1.

With our research greater changes in the low-stress mechanical properties are observed in the case of TiO_2-SiO_2 nanocoating, and greater decrease of the shear and bending properties and increase of the compression and surface properties is achieved with this treatment, respectively. Therefore, a greater flexibility, fullness and softness possess fabric treated TiO_2-SiO_2 nanocoating that which also reflects handle properties.

Handle Properties

Assuming that the analysed fabrics are designed for women's thin dresses, the primary hand values such as stiffness, anti-drape stiffness, flexibility, fullness and softness, crispness and scroopy feeling are estimated using the Kawabata system of regression equations for primary hand value estimation. These expressions are quantified and given on a 10-point scale, where 10 expresses the highest value of the particular property and 1 is its opposite. The results are collected in Table 3.

The results indicate that untreated and treated fabrics have low to medium stiffness, anti-drape stiffness, and flexibility, crispness and scroopy feeling, however, the primary hand values were slightly influenced by fabric' surface modifying by nano-coatings. The results show that surface treatments cause a slight increase in Koshi (stiffnes) and Shari (crispness) values. Koshi value is the feeling mostly related to the bending stiffness or elasticity when folding. Furthermore, it is dependent on shearing stiffness, and fabric weight and thickness. Supposing that in spite of the observed decrease of bending and shear rigidity of the surface treated fabrics, a slight increase of stiffness could be attributed to the increase of fabrics' weight and thickness. Shari value expresses the roughness of the fabric's surface, and stiffness and springy in bending properties. Therefore, the increase of geometrical roughness when surface treatments are used is the main reason for slight increase of crispness.

Table 3. Primary hand values for women's thin dress fabrics KN-202-LDY

Primary hand values	Sample 1	Sample 2	Sample 3
Koshi (stiffness)	3.57	3.83	4.12
Hari (anti-drape stiffness)	5.08	4.38	5.33
Shinayakasa (flexibility)	4.16	5.27	3.96
Fukurami (fullness and softness)	7.40	8.43	6.89
Shari (crispness)	3.46	3.88	4.38
Kishimi (scroopy feeling)	3.17	3.44	2.99

Based on the determined mechanical properties and evaluated primary hand values (HV) of the TiO_2 nano surface treated fabrics it could be concluded that no significant influence of the bending properties on stiffness and crispness is achieved. The results show significant interdependence between stiffness and weight and thickness, while crispness enhancement is conditioned by roughness increase due to the coating. Furthermore, the Hari value is defined by the bending hysteresis; i.e., a higher hysteresis enhances the anti-drape stiffness, moreover, it is also related to the surface properties, bending and shear rigidity. A decrease of this primary hand value is observed for Sample 2 owing to decrease in the bending and shear properties. Because the Hari value is increased for Sample 3, a main reasonable cause for this increase could be an increase of the bending rigidity in weft direction and increased roughness.

In addition, increased fabric flexibility and soft feeling (Shinayakasa), scroopy feeling (Kishimi), as well as fullness and softness (Fukurami) are observed for Sample 2 (TiO_2-SiO_2 coating), while TiO_2 coating (Sample 3) slightly reduces these hand characteristics. Due to the very complex structure of different hand characteristics, there are several parameters influencing positively and/or negatively the final hand value, therefore it is rather difficult to estimate exactly the origin of hand value changes. Shinayakasa value is influenced by bending, shear and compression properties. Therefore, the fabric flexibility- and soft feeling variation for Sample 2 arises from a significant decrease of shear and bending rigidity, and from an increase in compression resilience and fabric thickness when compared to the untreated sample. The decrease in Shinayakasa value for Sample 3 is mainly attributed to the decrease in fabric thickness T_0 and to the increase in weft bending rigidity. Furthermore, the Kishimi value, which expresses the scroopy and silk-like feeling, is influenced by fabric thickness and weight, as well as by tensile, shear and surface properties. The increase of fabric weight, thickness and surface characteristics when TiO_2-SiO_2 surface treatment is used are the main reasons for the scroopy feeling increase. We suppose that a slight decrease of the Kishimi value, which is observed for the TiO_2 coated fibre, is originating from the fabric thickness T_0 decrease and it is only to a small extent influenced by the weft bending rigidity increase. The most expressive hand for the analysed fabrics is Fukurami, which express fabrics' fullness and softness. A feeling comes from a combination of bulky, rich and well formed impressions and, a springy property in compression and thickness, accompanied by a warm feeling reflects this quality. Generally, we suppose, that the higher Fukurami value of the TiO_2-SiO_2 modified fabric arises from good compression resilience, accompanied by appropriate compression energy and thickness, which reflects spongy, bulky and rich feeling. By the TiO_2 coating a slight decrease of Fukurami value is observed due to the decrease of the fabric thickness T_0, however, this hand characteristic is still appropriate.

Conclusion

Two different procedures for nano TiO_2 coatings preparation were used for self-cleaning modification of textiles, i.e. the sol-gel deposition technique from precursor Tetraethyl ortosilicat with incorporated TiO_2 nanoparticles and the sol-gel deposition technique from precursor Titanium (IV) isopropoxide. Both methods demonstrated photocatalytic activity. Nanocoatings obtained by the TIP sol-gel treatment were unhomogeneous and several huge agglomerates were formed. The most uniform coating with the best particle distribution was obtained when using TiO_2-SiO_2 composite nanocoatings.

It was found that surface treatments can alter not only surface morphology, but also mechanical properties. The nano-coatings have the greatest influence on changes in the fabrics' bending, compression and surface properties. Surface treatments decrease the warp bending rigidity and bending moment, and increase the surface friction, geometrical roughness and fabrics' thickness T_m. Greater changes in the low-stress mechanical properties are observed in the case of TiO_2-SiO_2 nanocoating.

Furthermore, changes of the primary hand values were observed by surface treatments of the fabrics. An increase in stiffness of the surface treated fabrics is mainly influenced by changes in fabric weight and thickness, while an increase of the crispness mainly causes increased geometrical roughness. A decrease in anti-drape stiffness is achieved by TiO_2-SiO_2 composite fabric nano-coating and it is based on the decrease in the bending and shears properties, while an increase in anti-drape stiffness using TiO_2 nano-coating is attributed to the increase in weft bending rigidity and geometrical roughness. By using TiO_2-SiO_2 composite nano-coating an increase in fabric flexibility and soft feeling (Shinayakasa), scroopy feeling (Kishimi), as well as fullness and softness (Fukurami) is perceived, while TiO_2 nano-coating slightly reduces these hand characteristics. Increase in fabric flexibility and soft feeling (TiO_2-SiO_2 coating) is influenced by decreased fabric shear and bending rigidity and increased compression resilience and thickness, while an increase in scroopy and silk-like feeling causes increased fabric thickness, weight, fiction coefficient and geometrical roughness. The decrease in both fabric flexibility and scroopy feeling using TiO_2 nano-coating arise from the decreased thickness T_0 and from the increased weft bending rigidity. The fabric fullness and softness is increased on the basis of improved springy properties in compression and increased fabric thickness when TiO_2-SiO_2 composite nano-coating in used, while for TiO_2 fabric nano-modification a decrease in this hand characteristic, that mainly arises from a decrease in fabric thickness T_0, is characteristic.

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