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Effect of Weave Structures and Zinc Oxide Nanoparticles on the Ultraviolet Protection of Cotton Fabrics

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Abstract
The protection provided by clothing against ultraviolet (UV) radiation has been the subject of considerable recent research. However, there is a lack of information concerned with the effect of weave structures and zinc oxide nanoparticles on these properties. A series of cotton fabrics differing in weave structure was produced and treated with zinc oxide nanoparticles. These fabrics were spectrophotometrically assessed and the UV protection factor calculated. It was found that while there was no significant difference in the Ultraviolet Protection Factor (UPF) in untreated samples, in samples treated with zinc oxide nanoparticles an increase was noticed in satin and granite weaves. There is no relationship between weave parameters and the UPF. Also between porosity and the UPF, no relationship was noticed. Thus the present study provides design guidelines for clothing manufacturers.

Key words: *UPF, spectrophotometric, weave factor, zinc oxide nanoparticles.*

List of abbreviations:

UPF - Ultraviolet protection factor
UVR - Ultraviolet radiation
UVA - Ultraviolet A
UVB - Ultraviolet B
UVC - Ultraviolet C
CFF - Crossing over firmness factor
FYF - Floating yarn factor
FFF - Fabric firmness factor
EPI - Ends per inch
PPI - Picks per inch
UV - Radiation is divided into three wavelength ranges
UVA - (315 - 400 nm) *
UVB - (280 - 315 nm) *
UVC - (100 - 280 nm) *

* The ranges adopted by various national standards for evaluating the UV protection of textile products.

UVC is characterised by higher energy and is extremely dangerous.

Introduction

Among the recent technologies for the surface treatment of textiles, the merits of the nano finishing method are considerable as it is a powerful technique to fulfill environmental requirements with very specific functions. Nanoparticles possess more surface than micrometer particles, leading to a change in properties. Moreover a small quantity can provide significant effects. l00 nm particles seem to give the best performance. Common nano finishing of textiles are hydrophilic, water and oil repellence, antibacterial, antistatic, pilling resistance, wrinkle resistance, mechanical resistance and UV protection [1].

Currently the incidence of skin cancer is on the increase, and about 60,000 people die from this every year. Exposure to UV radiation can cause cancer as it can penetrate the skin and damage cells [2]. Knowing the gravity of the situation, a number of authors such as Reichrath [1], Vanicek et al. [3], and Wyszecki and Stiles [4] Majumdar et al. [36] have dealt with this subject.

Saravanan [5] provided an excellent account of the UV protection of textile materials. Akgun [6], Arshia Hussain and Shahnaz Jahan [7], Kathirvelu *et al.* [8], and Yadav *et al*. [9] reported good work on UV protection. Stankovic *et al.* [10] and Wong *et al*. [11] found that yarn twist significantly affects UPF. Dubrovski and Golob [12] gave an excellent account of ultraviolet protection in which the effects of yarn twist, colour and fabric structure on ultraviolet protection were well covered. Yadav *et al.* [9] reported about 75% absorption of UV light by zinc oxide nanoparticles. Grancaric' *et al.* [13] studied the effect of the fluorescence of sun protected white cotton fabrics. The contributions made by Hatua *et al.* [38, 39], Majumdar *et al.* [33, 40], Vigneshwaran *et al.* [34] and Katja Jazbee *et al.* [35] are quite significant for UVP properties. Upasani *et al.* [41] have discussed the UV protection properties of polyester fabric following treatment with zinc oxide.

Dubrovski [14], Gambichler [15] and Paya *et al.* [16] suggested a new ultraviolet protection factor.

Dubrovski [37] predicted by means of genetic experiments.

Gambichler [32] used In vitro as instrumental radiometry.

Paya *et al.* [16] developed a new system consisting of three basic elements: a UV radiation lamp and a photo detector consisting of an photoelectric sensor that absorbs all the radiation emitted by the UV lamp.

Majumdar [40] reported a substantial improvement in the UPF with pore yarns in the fabrics.

A UPF range of 20 - 29 is considered to be in good accordance with the European standard EN-1358-2: 200-3 (Fabrics – Solar UV protective properties – classification and marking of apparel).

The range of UVR is also subdivided into UVA (400 - 315 nm), UVB (315 - 280 nm), and UVC (< 280 nm). UVB radiation causes most cancers, cataracts and sunburn. UVC radiation is extremely harmful, but it is completely absorbed in the atmosphere by the ozone layer before it reaches the earth's surface.

UVB radiation is more harmful than UVA due to its shorter wavelength, which is more energetic. The intensity of UVB radiation on the earth's surface is 5 W/m^2, while for UVA radiation it is 27 W/m^2.

In fact, 99% of the UVR that reaches the earth's surface is UVA radiation. However, in areas where the ozone layer is thinning, this is not the case. One of the most troublesome environmental problems faced by humans is the overall thinning of the ozone layer. This decrease in the thickness of the ozone layer causes an increase in the UVB radiation that reaches the earth's surface. A 1% decrease in the ozone layer will cause an increase in solar radiation at the earth's surface that could increase the number of cases of skin cancer by up to 2.3%.

The World Health Organization (WHO) recently recommended the use of textiles with high protection factors.

Most natural fibres transmit more UVR than synthetic ones. However factors such as the tightness of the weave (the more closely woven the fabric, the less UVR is transmitted), colour [12] [17] (light pastel shades of the same fabric type will transmit UVR more strongly than dark colours, and will consequently have lower UPFs), stretch (the greater the stretch, the lower the UPF rating), and finishing (UV absorbing chemicals improve UPF) [13] are also significant. The more the transmittance of the textile, the less its UPF value.

It is also known that worn and faded fabrics may have reduced UPF ratings after washing cotton and polyester fabrics. Because of fabric shrinkage, a slight improvement in UPF has been noticed.

UV protection is one of the most important functional finishes on textiles. Inorganic UV blockers are more preferable to organic ones as they are nontoxic and chemically stable under exposure to both high temperatures and UV. Inorganic UV blockers are usually certain semiconductor oxides, such as TiO_2, ZnO, SiO_2 and Al_2O_3. Among these oxides, zinc oxide (ZnO) and titanium oxide (TiO_2) are commonly used. It was found that nano-sized zinc oxide and titanium oxide were found to be more efficient at absorbing and scattering UV radiation than the conventional size and therefore block UV radiation more efficiently. Rayleigh's scattering theory stated that scattering was strongly dependent on the wavelength, which was inversely proportional to the wavelength to the fourth power. This theory predicts that in order to scatter UV radiation between 200 and 400 nm, the optimum particle size should be between 20 - 40 nm. A thin layer of zinc oxide is formed on the surface of the treated cotton fibre, which provides excellent UV [18, 19].

The spectrophotometric method is internationally accepted and is the most widely used due to its objectivity and reproducibility.

The measurement device consists of the following items: a UV source providing UVR throughout the wavelength range from 290 to 400 nm, an integrating sphere, a monochromator suited to measurements with a spectral bandwidth of 5 nm or less in the wavelength region 290 - 400 nm, and a UV transmitting filter, which transmits significantly only at a wavelength less than approximately 400 nm, and does not fluoresce.

$$UPF = \frac{\sum_{\lambda=290}^{\lambda=400} E(\lambda) \times \varepsilon(\lambda) \times \Delta(\lambda)}{\sum_{\lambda=290}^{\lambda=400} E(\lambda) \times T(\lambda) \times \varepsilon(\lambda) \times \Delta(\lambda)} \quad (1)$$

where, $E(\lambda)$ is the solar spectral irradiance in $Wm^{-2}nm^{-1}$, $\varepsilon(\lambda)$ the relative erythemal effectiveness, $\Delta(\lambda)$ the wavelength interval of measurement in nm, and $T(\lambda)$ is the average spectral transmittance at wavelength λ.

There are papers which report on the different ways to determine the UPF of fabrics [16]. Regarding UV protection, fabrics are classified as shown in ***Table 1***.

Table 1. *Criteria and evaluation of UV protection effectiveness according to AS/NZ standard.*

UPF range	Protection category	Effective UVR, transmission %	Rating
15 – 24	Good protection	6.7 and 4.2	15, 20
25 – 39	Very good protection	4.1 and 2.6	25, 30, 35
40 – 50 and more	Excellent protection	≤ 2.5	40, 45, 50, 50+

The AS/NZ 4399:1996 Standard is used for classification, which was first developed in Australia. This is meant to provide the consumer with information regarding protection against UVR. Some references are given.

ASTMD 6544-00 (2007) Standard practice for preparation of textiles prior to ultraviolet (UV) transmission testing.

AS/NZS 4399 (1996) Sun protective clothing – evaluation and classification.

ASTMD 6603 – 07 (2007) Standard guide for labeling of UV – Protective Textile.

There are two principal methods of measuring UV protection in clothing: Vivo testing involves the determination of the minimal erythema dose for a test subject with and without fabric. However, cost and ethical considerations are the limitations in vivo test methods. The in vitro test method is based on determination of the UPF defined as the ratio of the effective UVR irradiance calculated for skin protected by the test fabric. This involves spectrophotometric measurement of UV transmission through fabrics, and the UPF calculation is done by using two weighting factors, namely the solar spectral irradiance and erythemal dose with and without textiles. It has been found that spectrophotometric assessment of the UV transmission through fabrics is an accurate and reproducible test method for determining the UPF.

The most detrimental effect of ultraviolet rays is sunburn, which is called erythema. Chronic sun damage leads to skin photo aging and non-melanoma and melanoma skin can be cancerous. There are several factors which determine UV protection. These are the fabric construction, cover factor and porosity. Stankovic *et al.* [10] found that yarn twist affects the UV protection properties of knitted fabrics. Porosity is found to affect UV protection, in that lower porosity leads to a higher UPF. Polyester fibres have a better UPF than that of cotton. Hustvedt and Cox [20] reported a high UPF for naturally pigmented cotton fabrics. According to the findings of other research workers, a reduction in pores after washing leads to a higher UPF. A recent paper by Taghipoor [21] discussed the effect of structural parameters on the UVR transmission of weft knitted fabrics. Some of their findings are in agreement with those of Wong [22].

Also the response of weave structures accompanied by zinc nanoparticles is expected to be different; and this information is desirable for consumers and manufacturers of fabrics.

A detailed review of the ultraviolet protection of weft-knitted fabrics has been published recently [23, 24]. Although some studies have already been reported on the effect of weave structures on UPF protection [25, 26], they did not characterise them to quantify the UPF values. Morino [27] and Milasius [28] characterised weave structures with the CFF, FYF and FFF. As pointed out by Wong *et al.* [23] in their recent review, to get a clearer picture of the contribution of the fabric sett alone to the UV protection of fabrics, fabrics should be prepared with a similar sett and with yarns of the same linear density. The aim of the study was to investigate the effect of both weave structures and zinc nanoparticles on ultraviolet protection.

Fabric specification

Fabrics were selected based on the work done by previous researchers [29]. Eleven fabric samples identical in warp and weft sett but differing in weave structure were woven on an automatic loom. Weave structures include plain, 4/1 sateen, 3/1 twill and 2/2 twill, sponge, special honey comb, dice huckaback, 9/1 sateen, granite and crepe weave. In the warp and weft, 40 Ne (14.76 tex) yarn was used.

Table 1 and ***Figure 1*** display their geometrical and constructional parameters.

Methodology

All the fabrics were bleached with 30% strength of hydrogen peroxide with an M:L ratio of 1:10, hydrogen peroxide concentration of 1.5%, caustic soda 1.2%, wetting agent 0.5%, lubricant oil 0.3% and stabilizer (sodium silicate) 0.2% at 90 °C for a duration of 45 min.

ZnO nanoparticles were applied on cotton using the pad-dry-cure method. The cotton fabric was cut into dimensions of 30 × 30 cm and immersed in a solution containing ZnO (2%) and acrylic binder (1%) for 5 min. It was then passed through a padding mangle running at a speed of 15 m/min with a pressure of 1.47 MPa to remove excess solution. A 100% wet pick-up was maintained for all the treatments. After padding, the fabric was air-dried and then cured at 140 °C for 3 min. The fabric was then immersed for 5 min in 2 gpl of sodium lauryl nanoparticles. Finally the fabric was rinsed at least 10 times to completely remove the soap solution and then air- dried.

The following weave parameters were used as they designate the fabric structure. Also they have good correlation with fabric properties (Morino *et al.* [27] and Milasius [28]).

The crossing over firmness factor CFF is defined as:

$$CFF = \frac{N_c}{N_i} \quad (2)$$

where, N_c = number of crossing over lines in the complete repeat and N_i = number of interfacing points in the complete repeat.

This was calculated using the following formula:

$$FYF = (Type_{1\text{-}1x} - 1) \times A/B \quad (3)$$

where, A - existing number of $type_{1\text{-}1x}$ in the complete repeat, B - number of interlacing points in the complete repeat.

This was computed using the formula provided by Milasius [28]. This parameter gives the weave structure taking into account six factors.

$$\varphi = \sqrt{\frac{12}{\pi}}\,\frac{1}{P^{1}}\sqrt{\frac{T_{average}}{\rho}}\; x\, S_2^{\frac{1}{1+2/3\sqrt{T_1}/T_2}}\, S_1^{\frac{2/3\sqrt{T_1}/T_2}{1+2/3\sqrt{T_1}/T_2}} \quad (4)$$

were, T_1, T_2 and T_{av} are the warp tex, weft tex and average tex. P^l is the Milasius weave factor, ρ the fibre density, and S_1 and S_2 are the ends and picks per dm.

The weave factor (P1) represents the number of interlacements of warp and weft which are obtained from the weave matrix. Since calculation of the weave factor is quite complicated, it was done using software found at the link, http://www.textuers.ktu.It/Pagr/En/Cont/pagrE, htm [42]. The values of weave parameters are given in ***Table 2***.

This was determined by the AATCC method 183-2014 transmittance of blocking of erythemally weighted ultraviolet radiation through fabrics.

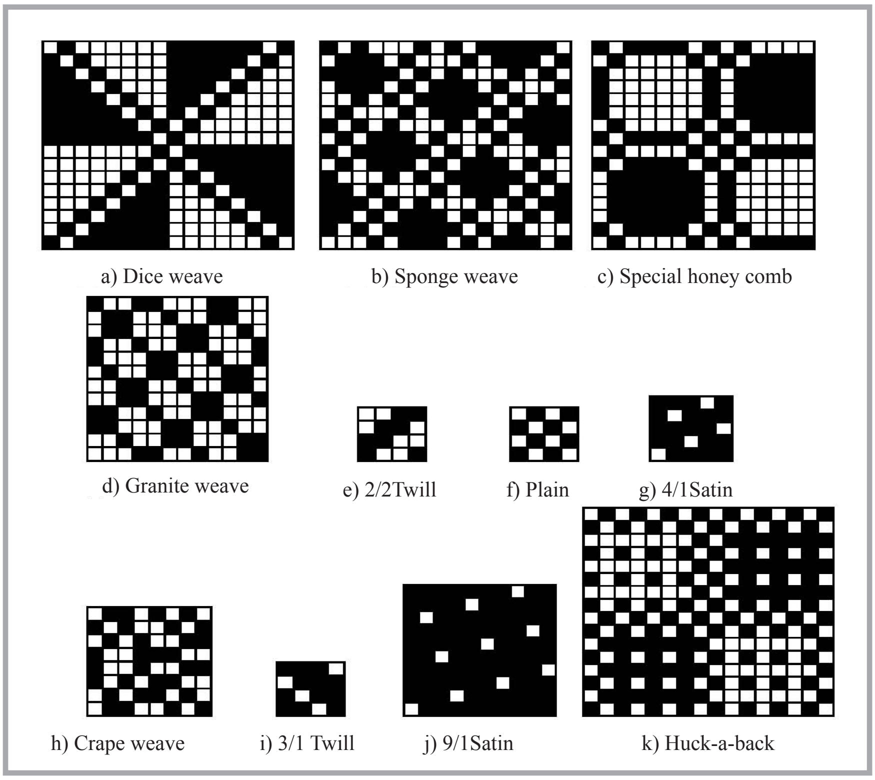


Figure 1. *Weave structures.*

Table 2. *Fabric specifications of bleached cotton woven fabrics, weave characteristics and values of UPF, UVA and UVB.*

	EPI	PPI	Mass, g/m^2	Thickness, mm	Porosity, %	CFF	FFF	UPF	UVA	UVB
Plain	135	71	135	0.995	85	2.00	0.68	10.73	13.19	8.15
4/1 Satin	138	72	129	1.175	88	0.8	0.46	10.42	14.33	8.29
3/1 Twill	146	70	133	0.89	84	1.0	0.53	11.58	13.42	7.3
2/2 Twill	146	70	147	1.091	87	1.0	0.55	11.06	13.61	7.8
Sponge	138	72	138	1.06	88	1.25	0.58	11.16	13.53	7.6
Special honey comb	140	69	140	0.787	80	0.84	0.48	11.24	14.26	7.43
Dice	135	71	131	1.012	89	0.88	0.44	9.74	14.97	8.98
Huckaback	140	70	139	0.95	85	1.44	0.61	11.78	13.28	7.17
9/1 Satin	134	70	138	0.913	85	0.4	0.34	10.55	14.52	8.04
Granite	136	70	136	0.838	84	1.0	0.54	10.05	16.22	9.8
Crepe	142	70	141	1.133	89	0.38	0.61	10.21	14.49	8.52

Table 3. *Fabric specifications of zinc nano treated cotton fabrics, weave characteristics and values of UPF, UVA and UVB.*

Weave	EPI	PPI	Mass, g/m^2	Thick-ness, mm	Porosi-ty, %	CFF	FFF	UPF	UVA	UVB	UVB_{nt}/ UPF_{bl}
Plain	135	71	133	0.821	86	2.0	0.68	18.86	9.17	4.63	1.757
4/1 Satin	138	72	136	1.051	93	0.8	0.46	23.68	8.22	3.73	2.270
3/1 Twill	146	70	139	0.984	90	1.0	0.53	20.35	9.43	4.21	1.757
2/2 Twill	146	70	154	1.114	91	1.0	0.55	19.84	9.17	4.5	1.793
Sponge	138	72	141	0.965	92	1.25	0.58	20.42	9.02	4.29	1.829
Special honey comb	141	71	147	0.797	88	0.84	0.48	15.91	11.43	5.28	1.415
Dice	135	71	141	1	91	0.88	0.44	16.25	10.14	5.41	1.668
Huckaback	140	70	140	0.859	91	1.44	0.61	23.19	8.59	3.7	1.968
9/1 Satin	134	70	142	0.843	88	0.4	0.34	17.45	10.2	4.99	1.654
Granite	136	70	137	0.814	88	1.0	0.5	28.26	7.63	3.05	2.881
Crepe	142	70	147	1.061	91	1.38	0.6	18.63	9.43	4.68	1.824

Table 4. *Percentage of reduction in UVA and UVB components.*

Weave	UVA control	UVA treated	% UVA reduction	UVB control	UVB treated	% UVB reduction
Plain	13.39	9.17	31.51	8.15	4.63	43.1
4/1 Satin	14.33	8.22	42.63	8.29	3.73	55
3/1	13.42	9.43	29.73	7.3	4.21	42.32
2/2	13.61	9.17	32.62	7.8	4.5	43.31
Sponge	13.53	9.02	33.33	7.6	4.29	43.55
SHC	14.26	11.43	19.84	7.43	5.28	28.9
Dice	14.97	10.14	32.26	8.98	5.41	39.75
Huckaback	13.28	8.59	35.31	7.17	3.7	48.39
9/1	14.52	10.2	30.16	8.04	4.99	37.93
Granite	16.22	7.63	52.95	9.8	3.05	68.87
Crepe	14.49	9.43	34.92	8.52	4.68	45.1

Porosity was determined using ***Equation 5***:

$$\text{Porosity} = 1 - \frac{\rho_{Fab}}{\rho_{Fib}} \times 100, \quad (5)$$

where ρ_{Fab} is the bulk density in g/cm^3 and ρ_{Fib} is the fibre density in g/cm^3.

ρ_{Fab} is calculated using the ***Equation 6***:

$$\rho_{Fab} = \frac{\text{G Square cm}}{\text{Thickness in cm}} \quad (6)$$

Another formula is

$$\text{Porosity \%} = \frac{100\left(AT - \frac{W}{D}\right)}{AT} \quad (7)$$

where A is the area of the sample in m^2, W = weight of the sample in g, T = thickness of the sample in cm, D = density of fibre in g/cm^3, and bamboo density is 0.8 g/cm^3.

Fabric porosity refers to the portion of pores in woven fabrics. While woven fabric could be treated as a two or three dimensional form, the terms open porosity and volume porosity are distinguished. Open porosity indicates the percentage of the macropore area in the fabric area unit, which is calculated on the basis of the fabric cover factor or on the number of macropores and the area of the macropore cross section according to ***Equations 9*** and ***10***, respectively.

Dubrovski and Brezocnik [14]

$$P_o = (100 - K) \cdot 100\% \quad (8)$$

$$P_o = N_p \cdot A_p \cdot 100\% \quad (9)$$

$$P_o = (10 - d_1G_1)(10 - d_2G_2).100 \quad (10)$$

where, P_o is the open porosity in percentage, K the fabric cover factor in percentage, Np the number of pores in pores per cm^2, A the area of the macropore cross section in cm, and G is the actual thread density in threads per cm. Air permeability values can also provide information on porosity, which is affected by the fabric structure. An examination of fabrics through light can also be used to find the porosity; this method has been used by some research workers. This is termed as optical porosity, and is the void between yarns and fabrics. This can be determined by Motu image software.

Results and discussion

In contrast to SEM images of untreated cotton fibres, the surface of the treated fibre is rougher and zinc nanoparticles are clearly seen on the fibre (***Figure 5***). The micrographs show that zinc oxide nanoparticles are well distributed on the cotton fibre surface. It is also seen that the size of the zinc oxide nanoparticles was in the nano-scale range. The size of the nano particle is 50 nm. SEM images were used to investigate the formation of ZnO nanoparticles on the cotton fibre surface. SEM photographs of the control and zinc oxide nanoparticles treated are shown in ***Figure 5***.

Tables 2, 3 and ***4*** present data on the UPF, UVA and UVB of eleven fabric samples. It is noticed that, following treatment with zinc oxide nanoparticles, there is a significant improvement in UPF values, ranging from 41.5% to as much as 187.2%. The largest improvement occurred in granite and 5-end satin weaves. These are in agreement with the indings of earlier researchers [14]. It is also noticed that there is no relationship between CFF and UPF. The reduction in

UVA and UVB is shown in ***Table 4***. That there is a significant reduction in UVB is noticeable, which is an important finding, as a reduction is desirable in UVB to avoid cancer. There is no relationship between the FFF and UPF. Furthermore no correlation is noticed between porosity and the UPF. This is contradictory to the findings of Taghipoor *et al*. [20]. According to Taghipoor *et al*. [21], as the porosity increases, UPF transmission increases. The correlations between CFF and UPF and FFF and UPF are 0.158 and 0.098, respectively. It is clear that there is no relationship between either weave characteristics or geometrical properties with the UPF before treatment. Only after applying zinc nanoparticles is there a change in the UPF. With the exception of granite weave, the improvements are marginal. This may be due to long floats in the weaves. The UPF value represents how much longer one can be exposed wearing clothing vis-à-vis not wearing it until the skin develops reddening.

It was found that weave structures have no influence on the UPF, and that the cloth cover factor has a major effect. Since the same fabric sett was used in this work, the question of the cover factor does not arise.

The differences observed are attributed to floats present in the fabrics. The presence of nano particles blocks ultraviolet light.

UV light passes direct through the macropore or fabric open area (direct UV transmittance) and also through yarns, which changes direction before leaving the fabric (scattered UV transmittance fabric mass porosity and fabric thickness affect UVP.

Figures 2 - 4 illustrate the effect of bleaching and zinc oxide nanoparticles on the UPF, UVA and UVB.

Satin and granite weaves show a substantial improvement in ultraviolet protection as the ratios of UPF_{nf}/UPF_{bl} get higher (***Table 3***).

The lowest value is recorded for the special honey comb weave.

It is noticed that the reduction in UVB is greater than that of UVA, which is desirable (***Table 4***).

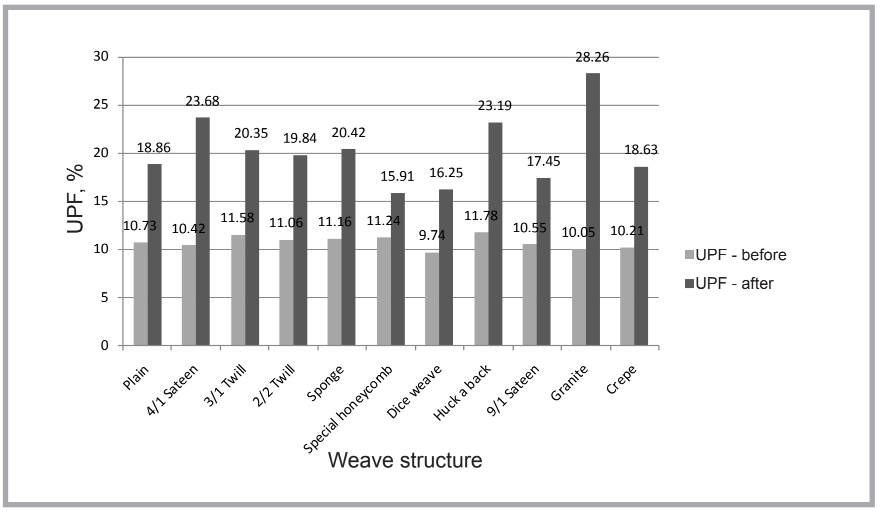


Figure 2. Values of UPF before and after treatment.

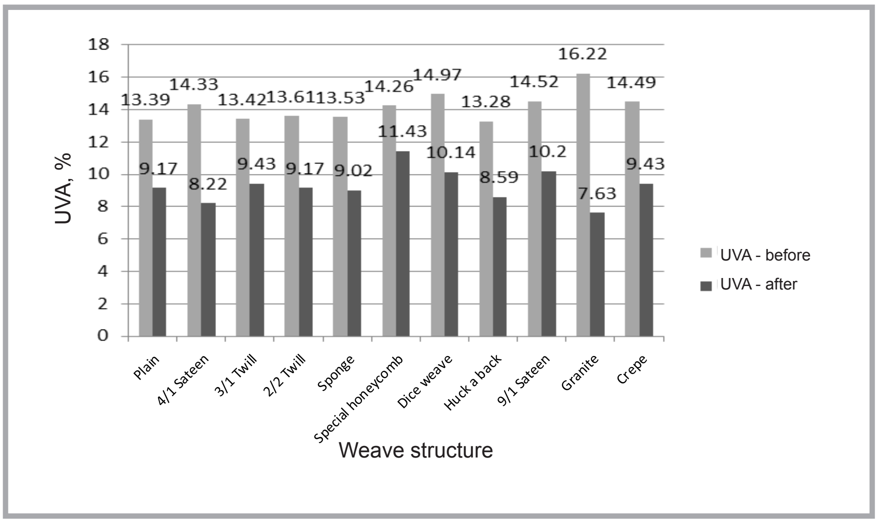


Figure 3. Values of UVA before and after treatment.

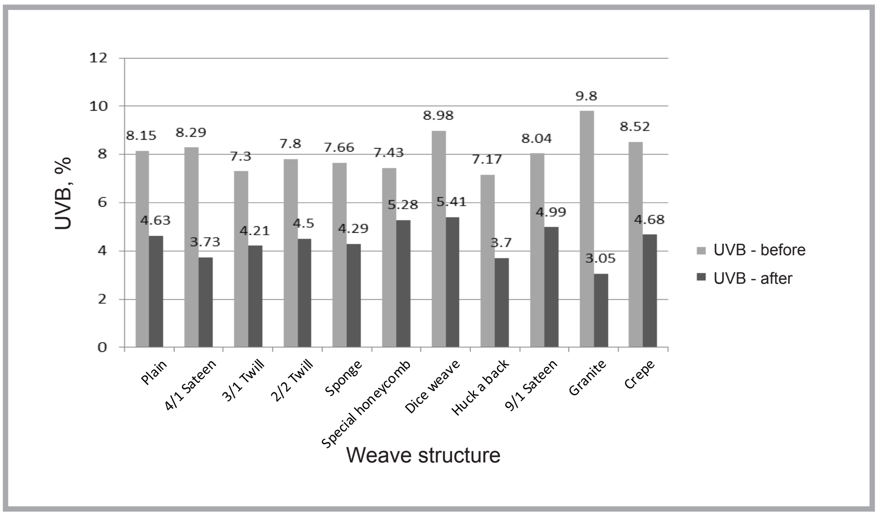
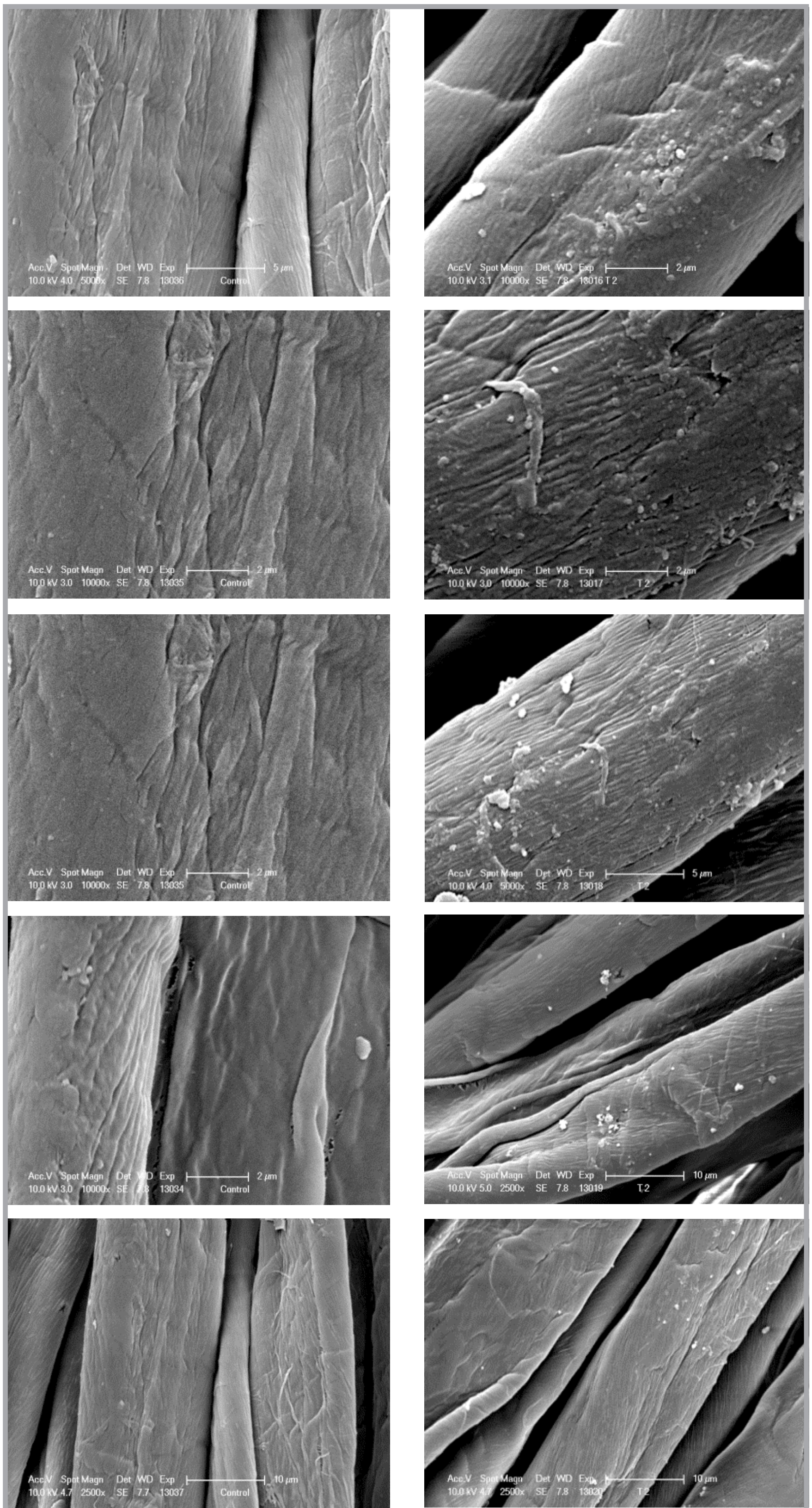


Figure 4. Values of UVB before and after treatment.

Conclusion

In this study, the UV protection properties of eleven cotton fabrics both in untreated bleached and treated with zinc oxide nanoparticles are discussed. The fabrics selected were identical in all respects, except that they differed



a) control, *b) zince oxide nanoparticle treated.*

***Figure 5.** SEM image of a) control and b) zinc oxide nanoparticle treated fabric.*

in weave structure. The results show that UV protection properties are unaffected by the weave structure and fabric geometrical properties of fabrics in a bleached control state. However, 4/1 satin, 3/1 twill, sponge, huckaback and granite weaves show a higher UPF following treatment with zinc oxide nanoparticles. UPF values of fabrics before treatment show no change at all. As expected, UVA and UVB show a decrease following treatment with zinc oxide nanoparticles, and the reduction is higher in UVB.

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