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Asmaa Farouk[1,2], Torsten Textor[1], Eckhard Schollmeyer[1], Anita Tarbuk[3], Ana Marija Grancacic[3]

[1]German Textile Research Centre North-West e.V. (DTNW), D-47798 Krefeld, Germany
[2]National Research Center, Textile Research Division, Dokki, Cairo, Egypt
[3]Faculty of Textile Technology, University of Zagreb, Croatia

Abstract:

Despite the beneficial effects of ultraviolet (UV) radiation on the skin, radiation can cause sunburn, skin aging, allergies and even skin cancer. Textiles can provide effective protection against such damage. Unlike cosmetics, using textiles to protect the skin has only recently been researched. The design and modification of fabrics leading to a high protection against UV radiation is a relatively new application. It is important to consider the kinds of textiles to be used because most of the garments worn during summer, the time of highest exposure, are light and colourless materials that provide the lowest protection. Here, we report the synthesis and characterisation of nanosized zinc oxide particles known to absorb UV light. Sol-gel-based inorganic-organic hybrid polymers were modified with these particles and applied to cellulosic cotton (100%) and cotton/polyester (65/35%) fabrics. These modified inorganic-organic hybrids polymers were based on 3-GPTMS. The complete finishing sol prepared in this work has a marked long stability. The effectiveness of the novel finishing was determined by UV-visible spectroscopy to evaluate the UV protection factor. The influences of the finishing for general textile properties such as tensile strength, elongation, air permeability, degree of whiteness, wear resistance, stiffness and the durability of the treatments were investigated.

Key words:

Zinc oxide, ultraviolet protection, nanoparticles, sol-gel technique

Introduction

The solar radiation that reaches the Earth's surface ranges from 280 nm to 3000 nm and consists of ultraviolet (UV), visible and infrared radiation. The energy levels of UV radiation have been classified into three categories [1]:

a) Very high energy: UV-C rays (λ = 100 nm - 280 nm): Highly damaging to human skin, but filtered by the ozone layer, thereby not reaching the Earth's surface.
b) High energy: UV-B rays (λ = 280 nm-320 nm): Penetrating the skin to a depth of a few millimetres, such rays can induce the formation of stable pigments in the epidermis of the skin. Melanoma or skin cancer is increased considerably through the prolonged exposure to UV-B rays.
c) Low energy: UV-A rays (λ = 320 nm-400 nm): Penetrating the skin deeply, leading to premature aging. Acute effects are only temporary and of a short duration.

Although UV-B rays are only a small fraction (about 10%) of total UV radiation, they are dangerous since they are responsible for acute and chronic illnesses, including erythema (sunburn), suntanning, photo carcinogenesis and photoaging [2-8]. UV radiation is responsible for the generation of free radical species, which are supposed to participate in the development of various pathologies such as cancer, ageing, Alzheimer's disease, inflammatory disorders and several more [9-11].

Textiles are assembled to protect against environmental influences at all times. Textile garments will protect against the hazardous effects of UV radiation to a certain extent, but light and light-shaded clothing textiles provide insufficient protection. When direct light shines onto a textile, a part of the radiation is reflected. The material will absorb a certain amount but the remainder can reach the skin.

UV Protection Factor (UPF)

The UV protection properties of textiles are characterised by the so-called UPF value of a particular fabric [12, 13]. UPF shows how much longer a person wearing a particular garment can stay out in the sun before the onset of skin reddening compared with an unprotected person [12, 14]. The UPF is calculated by using the following equation [12, 13]:

$$UPF = \frac{\sum_{\lambda=280}^{400} E(\lambda)\cdot\varepsilon(\lambda)\cdot\Delta\lambda}{\sum_{\lambda=280}^{400} E(\lambda)\cdot\tau(\lambda)\cdot\varepsilon(\lambda)\cdot\Delta\lambda} \qquad (1)$$

where:
$E(\lambda)$ = the solar irradiance [$Wm^{-2}\ nm^{-1}$],
$\varepsilon(\lambda)$ = the erythema action spectrum,
$\tau(\lambda)$ = the spectral transmittance through specimens at wavelength λ,
$\Delta\lambda$ = the wavelength interval of the measurements [nm],

The UPF of a material is determined by the transmission of UV radiation through it [14]. The transmission of a given material depends on the:

- specific fibre material,
- structural characteristics of the fabric,
- moisture content,
- colour and dyeing intensity,
- presence of optical brightening agents,
- specific finishing products, e.g. UV absorbers,
- laundering conditions of the garment.

UV absorbers have been used to protect various substrates (e.g. tyres, fabrics and polymers) against decomposition for more than 20 years. The use of textiles as UV-protecting materials is not new but the specific modification of fabrics to improve this specific capability has only been a topic of interest for the past 10 years [15]. Simultaneously, the interest in the application of nanotechnology in the textiles industry has increased rapidly and has been the subject of several studies aiming to develop new finishing approaches to improve properties. For example, the nanoparticles of natural zeolite have led to the better UV and antimicrobial protection of polyester and cotton fabrics [16-18], *nano-Ag* has been used to impart antibacterial properties [19], *nano-*TiO_2 is used for UV-blocking or self-cleaning properties [20-22] and *nano-ZnO* is used for antibacterial and UV-blocking properties [23-26]. Inorganic UV blockers are preferable to organic UV blockers [27, 28] because inorganic absorbers such as zinc oxide are non-toxic and chemically stable under exposure to both high temperatures and UV radiation. Nanoparticles have a large surface area-to-volume ratio. The proper dispersion and homogeneous distribution in a coating layer yields more effective UV blocking with less material than a coating modified with coarse particles [29]. Furthermore, these coatings are transparent/colourless, which is important for the product's appearance. If the employed particles exhibit particle sizes below 50 nm no light scattering within the coating occurs, guaranteeing transparency. Zinc oxide, especially doped zinc oxide, is widely used in different areas because of its unique photocatalytic, electrical, electronic, optical, dermatological and antibacterial properties [30-35].

For many applications of nanoparticles, homogeneous dispersion in different matrices is required. A number of synthetic strategies has been developed to prevent particle agglomeration and increase the stability of ZnO nanoparticles in various dispersions [36-41]. For the application of ZnO as a UV-absorbing finishing it has to be incorporated into an adequate binder. Previous work by the German Textile Research Centre has prepared finishing sols based on ZnO and 3-glycidyloxypropyltrimethoxysilane (GPTMS), but the sols used showed a poor stability (less than 30 min). This paper describes the preparation of stable ZnO dispersions and the embedding of ZnO into a hybrid polymer network, acting as a binder and following the finishing of cellulosic fibre. The aim was to develop a highly UV-absorbing system that could be applied to textiles using a simple pad-dry-cure.

Experimental

Materials

The coating experiments were carried out using cotton (100%) and cotton/polyester (65/35%) fabrics, and the specific data of the material are summarised in Table 1.

Table 1. Specifications of the textiles used for all experiments.

No.	substrate	weight (g/m^2)	threads/cm		thickness (mm)
			warp	weft	
I	Bleached CO (100%)	250	21	18	0.57
II	Bleached CO/PET(65/35%)	162	27	25	0.33

Chemicals

Zinc acetate dihydrate ($ZnAc.2H_2O$), lithium hydroxide monohydrate (98%) and 2-propanol were obtained from Merck and 3-GPTMS (98%) from ABCR. For catalysing the cross-linking reaction of the epoxy group of the GPTMS 1-methylimidazole (97%, Fluka) was used.

Preparation of zinc oxide nanoparticles

The preparation procedure was basically comparable to that of Spanhel [40]. The procedure consists of two major steps. First, the suspension of the precursor and second the hydrolysis of the precursor to form the zinc oxide nanoparticles. Zinc acetate and isopropanol were used to prepare the precursor before lithium hydroxide ($LiOH.H_2O$) was used to hydrolyse the precursor.

A two-neck round-bottomed distillation flask was used to suspend 2.8 g of $ZnAc.2H_2O$ in 100 ml 2-propanol by reflux heating for 3 h. 0.75 g lithium hydroxide was dissolved in 100 ml isopropanol at room temperature by magnetic stirring. The ZnAc suspension was cooled to 0°C before the lithium hydroxide solution was added dropwise under vigorous stirring. The mixture was treated in an ultrasonic bath at room temperature for about 2 h. The resulting sol theoretically contained 0.675 wt. % ZnO. Higher amounts of ZnAc and lithium hydroxides were used (using constant amounts of solvent) to prepare a colloidal solution of a higher concentration.

Characterisation of ZnO nanoparticles

The size of the ZnO nanoparticles was measured by dynamic light scattering using a Zetasizer, Nano-S, produced by Malvern.

Preparation of a GPTMS sol

10 ml GPTMS was dissolved in 100 ml isopropanol before hydrolysis using 1.22 ml 0.01 M hydrochloric acid. The resulting sol was stirred for at least 3 h to form the basic sol (concentration of GPTMS sol 9.1 vol.%).

Coating process

Before finishing textiles the zinc oxide and GPTMS sol were mixed in different ratios and 1-methylimidazole (0.5 ml/10 ml GPTMS) was added as a catalyst for the cross-linking reaction of the epoxy group of the GPTMS.

The final formulation was applied to the fabrics using a pad-cure method. The coating was carried out by a padding process with a laboratory padder to a wet pick up of 100%. Afterwards, padding samples were dried in a labcoater at 130(C for 30 min.

Characterisation of coated fabrics

The investigation of the coated textiles was carried out using the following procedures:

- The mechanical properties (tensile strength and elongation) were investigated according to DIN 53857-1 using a Zwick 1445 testing system.
- Air permeability was tested using an air permeability tester (21443, FRANK) according to DIN 53887.
- Treated fabrics were analysed by scanning electron microscopy (SEM), with a Topcon-Microscope (ATB-55) used to investigate the morphological changes of the surface structure.
- The transmissions of UV radiation were measured according to AS/NZS 4399:1996 - Sun Protective Clothing - Evaluation and Classification using a Cary 50 Solarscreen transmission spectrophotometer. UPF values were calculated automatically according to [1] and classified according to Table 2 [13].

Table 2. UV protection and classification according to AS/NZS 4399:1996.

UV protection	UPF classification	Transmitted UV radiation
excellent	40, 45, 50, 50+	≤ 2.5%
very good	25, 30, 35	4.1–2.6%
good	15, 20	6.7–4.2%
non-rateable	0, 5, 10	> 6.7%

- Laundering was performed in a laboratory washing machine (Linitest, ATLAS) according to 6330:2000 for five washing cycles using standard ECE detergent without FWAs.
- Wear resistance was investigated using a Martindale test (James H. Heal & Co. Ltd.). Tests were carried out according to DIN EN ISO 12947-3.
- Changes in the degree of whiteness of the treated fabrics were evaluated with a Datacolor spectrophotometer 3880 (cocos Manual Version 2, 3). The degree of whiteness was given according to Berger (light source D65/10).
- The stiffness of the fabric was tested using a Shirley stiffness tester according to DIN 53362.
- Turbidimeter was measured using a Model 2100N laboratory turbidimeter (HACH).

Results and discussion

The synthesis of ZnO nanoparticles basically described by Spanhel [40] leads to the formation of colloidal ZnO particles with a comparably homogenous distribution and an average particle size of 30-60 nm. The ZnO-sols show no significant precipitation for weeks. Figure 1 shows a corresponding sol after more than 10 weeks, indicating the stability and absence of any precipitation.

Figure 1. Image of a ZnO-sol taken 10 weeks after synthesis. The absence of any precipitation proves the excellent stability of the colloidal solution.

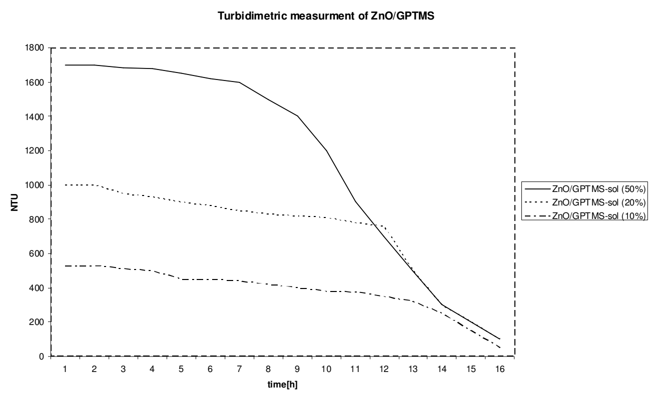


Figure 2. Stability of different ZnO /GPTMS sols according to turbidimetric measurements (NTU, normal turbidity unit).

Figure 2 shows the stability of different concentrations of complete finishing prepared ZnO /GPTMS sols measured by turbidimetric measurements (NTU). From the figure we can see that a higher concentration of ZnO-nano is more turbid and still stable for nearly eight hours, but lower concentrations of ZnO-nano show more stability (nearly 12-13 hours).

The sol-gel finishing of cellulosic fabrics (cotton 100% and CO/PET blend) markedly decreases the transmission of UV radiation compared with the untreated cellulosic fabrics. Figure 3 shows the UV transmission spectra of the cotton fabric before and after treatment with the hybrid polymer based on GPTMS and nano-sized ZnO. Different amounts of ZnO are shown. The relative amounts of ZnO correspond to the amounts of GPTMS in the final sol used for application (10% means 1 g ZnO/10 g GPTMS). The spectra show a significantly decreased transmission for all samples. The influence of the total amount of ZnO seems to be comparably low; nevertheless, a slight decrease in transmission can be observed with an increasing ZnO content.

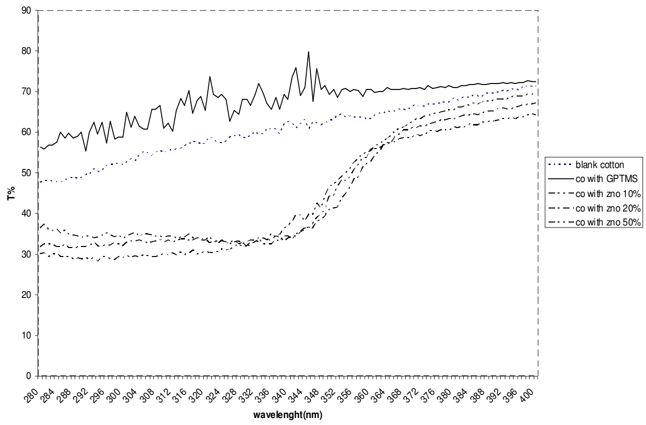


Figure 3. Comparison of the UV spectra of blank cotton fabrics and fabrics treated with ZnO-modified GPTMS sols.

Table 3. Effect of increasing the concentration of ZnO-sol on the UV protection properties of the cotton and cotton blend fabric samples after treatment.

Substrate		UPF value	τ_{UVA}	τ_{UVB}	UV protection	
Untreated	Cotton	21	7.355	3.629	20	good
	CO/PET	19	14.758	3.206	15	good
Treated with GPTMS	Cotton	19	15.846	2.643	15	good
	CO/PET	16	12.659	1.877	15	good
Treated with ZnO in GPTMS sol (10%)	Cotton	78	3.429	0.744	50+	excellent
	CO/PET	37	10.704	1.227	35	very good
Treated with ZnO in GPTMS sol (15%)	Cotton	147	2.201	0.451	50+	excellent
	CO/PET	47	7.662	1.199	45	excellent
Treated with ZnO in GPTMS sol (20%)	Cotton	150	1.606	0.416	50+	excellent
	CO/PET	49	6.988	1.153	45	excellent
Treated with ZnO in GPTMS sol (30%)	Cotton	163	1.574	0.331	50+	excellent
	CO/PET	45	8.583	1.187	45	excellent
Treated with ZnO in GPTMS sol (50%)	Cotton	177	0.795	0.293	50+	excellent
	CO/PET	48	7.677	1.168	45	excellent

To investigate the durability of the treatments a laundry test were carried out. All samples were exposed to five washing cycles (40(C, 20 min, washing agent 1 g/l) before the UV transmission was reinvestigated. The corresponding data for selected fabrics are summarised in Tables 3 and 4, and Figure 4 indicates only slight changes in the absorption characteristics expressed as UPF value.

Table 4. Effect of increasing the concentration of ZnO-sol on the UV protection properties of the cotton and cotton blend fabric samples after treatment and five laundering cycles.

Substrate		UPF value	τ_{UVA}	τ_{UVB}	UV protection	
Untreated	Cotton	22	7.957	3.119	20	good
	CO/PET	18	7.365	3.614		good
Treated with GPTMS	Cotton	20	8.577	3.881	15	good
	CO/PET	17	13.980	3.469		good
Treated with ZnO in GPTMS sol (10%)	Cotton	76	7.563	0.409	50+	excellent
	CO/PET	38	10.398	1.121	35	very good
Treated with ZnO in GPTMS sol (15%)	Cotton	146	1.723	0.373	50+	excellent
	CO/PET	48	7.982	1.244	45	excellent
Treated with ZnO in GPTMS sol (20%)	Cotton	152	6.035	0.321	50+	excellent
	CO/PET	48	5.395	1.014	45	excellent
Treated with ZnO in GPTMS sol (30%)	Cotton	162	4.336	1.021	50+	excellent
	CO/PET	47			45	excellent
Treated with ZnO in GPTMS sol (50%)	Cotton	179	1.255	0.397	50+	excellent
	CO/PET	49	4.010	1.362	45	excellent

Based on its aromatic backbone, polyester fibres should absorb certain amounts of UV radiation. Nevertheless, from the tables it can be seen that blended with cotton the grey fabric yields only good UV protection just as the untreated cotton fabric. Treatment with GPTMS provides equally good UV protection.

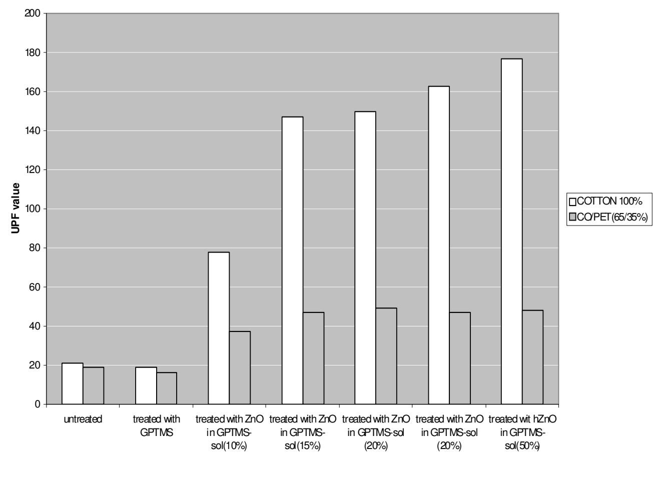


Figure 4. UPF values of cotton and CO/PET substrates treated with different conditions.

The results presented in Tables 3 and 4, as well as in Figure 4, show the increment of UV protection with the increment of the concentration of ZnO-sol on both treated fabrics. All cotton fabrics have excellent UV protection as do most cotton/polyester fabrics. The only exception is the cotton/polyester fabric treated with 10% ZnO nanoparticles in GPTMS sol that has only very good protection.

Tables 3 and 4 show that sol-gel treatment has a high durability since the five washing cycles have no effect on the UPF values of the fabrics. Therefore, the UV protection levels of the treated fabrics are excellent even after laundering, except for the cotton/polyester treated with ZnO in GPTMS sol (10%), which remains very good.

SEM Investigations

SEM investigations were carried out to investigate topographical changes. The corresponding SEM micrographs are shown in Figure 5. The surfaces of the untreated fibres are comparably rough, whereas the surfaces of the treated fibres appear much smoother because the coatings obviously lead to a flattening of the fibre surface. In the micrograph, no agglomerated particles are visible on the surface, which indicates a homogeneous distribution of the ZnO in the coating layer and the absence of unwanted agglomeration during the formation of the resulting coatings.

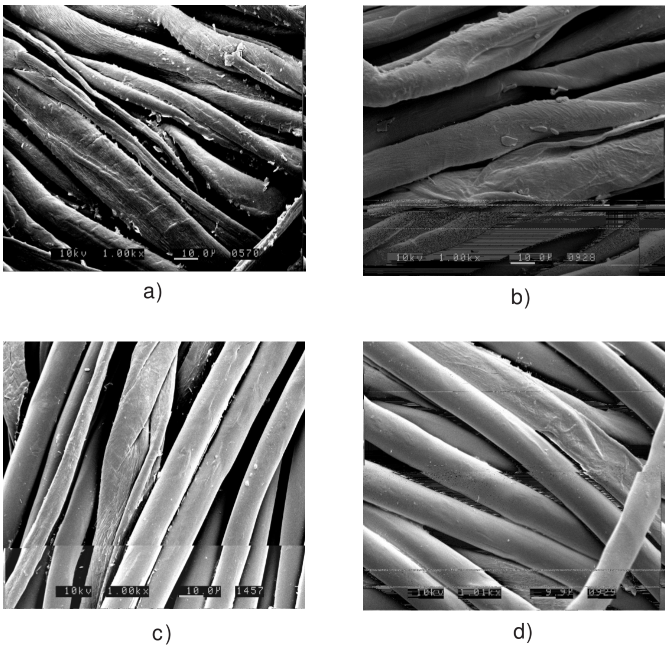


Figure 5. SEM micrographs of: (a) blank cotton fabric, (b) cotton fabric treated with 20% nano-ZnO, (c) blank cotton/polyester fabric and (d) cotton/polyester fabric treated with 20% nano-ZnO.

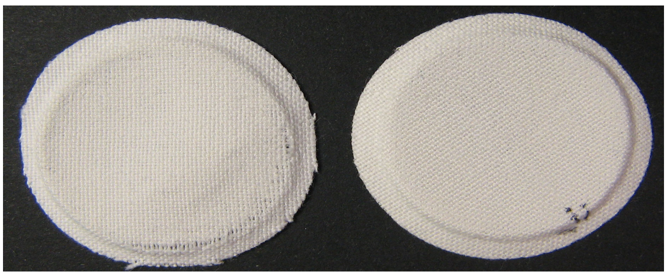
The mechanical data of the treated and untreated samples and the influence of the sol treatment for the degree of whiteness and for the air permeability were investigated (Table 5). The tensile strength of the coated cotton and the coated cotton blend fabrics slightly decreased. The whiteness of the fabrics also slightly decreased but to a tolerable degree. The decrease for cotton was between 3.8 and 6.4%, whereas the decrease for CO/PET was only between 3.2 and 6.6%. Air permeability is an important factor in the performance of textile materials and is used to indicate the breathability of coated fabrics. Table 3 shows that there is no worsening in air permeability and indeed a slight improvement (up to 6%). The

Table 5. Effect of increasing the concentration of ZnO-sol on some performance properties of the cotton and cotton blend fabric samples.

Substrate		Tensile strength (daN)	Elongation (%)	Air permeability l/dm^2*min.	Degree of whiteness (Berger)	Bending stiffness ($cNcm^2$)
Untreated	Cotton	102.1	22.6	250.5	66.0	12.12 ±.028
	CO/PET	88.4	30.5	334.0	70.9	3.88 ±.023
Treated with ZnO in GPTMS sol (10%)	Cotton	97.5	22.9	258.8	56.1	13.46 ±.018
	CO/PET	85.6	32.3	350.7	68.3	5.23 ±.013
Treated with ZnO in GPTMS sol (15%)	Cotton	95.5	22.3	256.0	56.7	13.83 ±.025
	CO/PET	84.2	33.0	350.7	68.9	8.38 ±.014
Treated with ZnO in GPTMS sol (20%)	Cotton	98.2	20.8	254.6	56.9	15.21 ±.018
	CO/PET	84.4	32.6	355.2	69.2	9.65 ± 022
Treated with ZnO in GPTMS sol (30%)	Cotton	95.4	20.6	256.0	61.6	18.54 ±.017
	CO/PET	82.9	32.7	350.1	70.2	13.83 ±.026
Treated with ZnO in GPTMS sol (50%)	Cotton	96.2	21.3	258.8	62.2	20.81 ± .012
	CO/PET	82.6	31.6	352.2	70.6	15.19 ±.024

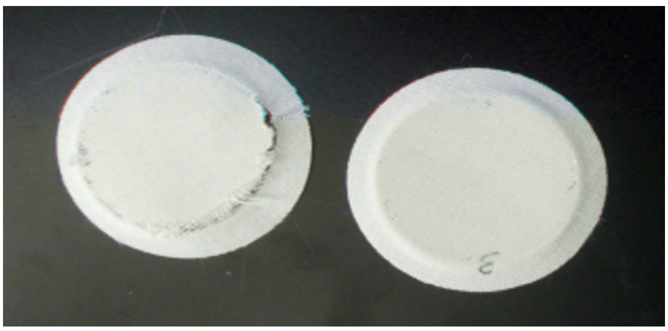
mentioned increase in the bending stiffness values recorded by increasing the concentrations of nano-ZnO could be explained by the higher uptake of inorganic-organic hybrids polymers on the cellulosic fabric surface, because of an increasing solid content for sol with a higher amount of ZnO. Some authors have stated that comparable hybrid polymers modified with alumina particles improve the wear resistance of treated fabrics [41]. Against this backdrop, Martindale tests were carried out. An exemplarily chosen pair of samples is shown in Figure 7. The picture shows an untreated and a treated sample after 20,000 scrubbing cycles. As can be clearly seen, the treated sample is still intact and shows no destruction, whereas the untreated one is already destroyed.

Cotton fabric (100%):



(a) untreated (b) treated

Cotton/polyester (65/35%) fabric:



(a) untreated (b) treated

Figure 7. Results of a Martindale test investigating the wear resistance of the treated samples after 20,000 scrubbing cycles compared with the untreated sample. Cotton fabric (100%) and cotton/polyester (65/35%) fabrics.

Conclusion

Nanosized zinc oxide particles were synthesised and applied to the preparation of functional coatings for inorganic-organic hybrid materials. Final coating solutions were stable for several hours showing minimal precipitation, which is sufficient for industrial applications. These hybrid materials can be applied to textile materials by using a simple pad-cure method - here shown for cotton (100%) and cotton/polyester (65/35%) fabrics. The resulting textile materials achieve significantly improved UV absorption with a high durability, without affecting the textile, changing air permeability or even improving wear resistance. The use of hybrid polymers modified with ZnO is, therefore, a promising approach for the development of highly UV-protecting textiles. The inorganic UV-absorber ZnO is highly stable against degradation and non-toxic. The sol-gel approach used here to prepare the coating materials guarantees a simple processing that can be easily transferred to the textile industry. Furthermore, the principles of the sol-gel technique allow the combining of additional properties in a single coating material. Future work on the topic of UV protection will not only further improve the UPF value but also use a combination of additional effects such as antimicrobial activity.

Acknowledgments

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