SOL-GEL DERIVED INORGANIC-ORGANIC HYBRID POLYMERS FILLED WITH ZNO NANOPARTICLES AS ULTRAVIOLET PROTECTION FINISH FOR TEXTILES

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Abstract:

In spite of some beneficial effects of ultraviolet (UV) radiation on skin, radiation can cause sunburn, skin aging, allergies and even skin cancer. Textiles can provide effective protection against such damage of UV radiation. Unlike cosmetics, using textiles protecting the skin or at least enhancing protection 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 very important to consider the kind of textile to be used, most of the garments worn during summer, the time of highest exposition, are light and colourless materials and therefore provide the lowest protection. We report the synthesis and characterization of nanosized zinc oxide particles known to highly absorb UV light. Sol-gel based inorganic-organic hybrid polymers were modified with these particles and were applied to cellulosic cotton (100%) and cotton/polyester (65/35%) fabrics. These modified inorganic-organic hybrids polymers were based on 3-glycidyloxypropyltrimethoxysilane (GPTMS). Complete finishing sol prepared in this work has remarked long stability for further processing. The effectiveness of the novel finishing was determined by UV-Vis spectroscopy and by evaluation of the ultraviolet protection factor (UPF). The influences of the finishing for some general textile properties as e.g. tensile strength, elongation, air permeability, degree of whiteness, wear-resistance, stiffness as well as the durability of the treatments were investigated.

Key words:

Zinc oxide - ultaviolet protection - UPF - nanoparticles - sol-gel technique

Introduction

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

(a) Very high energy: UV-C rays (λ = 100 nm - 280nm): Highly damaging to human skin, but filtered by ozone layer, therefore 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 millimeters, induce the formation of stable pigments in the epidermis of the skin. Melanoma or skin cancer is increased considerably due to a 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 short duration.

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

Textiles are assembled for protecting against environmental influences all the times. Textile garment will protect against the hazardous properties effect of UV radiation to a certain extent, but the light and often light shaded clothing textiles preferably worn nowadays will only protect insufficiently. When direct light shines onto a textile, a part of the radiation is reflected, the material will absorb a certain amount and the remain transmit and can reach the skin.

Ultraviolet Protection Factor - UPF

In practice, the UV protection properties of textiles are characterized by the so called UPF value of a particular fabric [12, 13]. UPF is the abbreviation of the ultraviolet protection factor. It shows how much longer a person wearing the particular garment can stay out in the sun before the onset of skin reddening compared to an unprotected person [12, 14]. The UV protection factor 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(λ) = the solar irradiance [W m^{-2} nm^{-1}],
ε(λ) = the erythema action spectrum,
τ(λ) = the spectral transmittance through specimen at wavelength λ,
Δλ = the wavelength interval of the measurements [nm].

As described the UPF [14] of a textile material is determined by the transmission of the UV radiation through the textile material. Transmission of a given material is depending on:

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

UV absorbers are used to protect various substrates, e.g. tires, fabrics and polymers against decomposition for more than twenty years. The use of textiles as UV protecting material is not new but the specific modification of fabrics for improving the capability as UV protecting materials has been a topic of interest for only the last ten years [15]. Simultaneously the interest in the application of nanotechnology in the textile industry has increased rapidly and it has been the object of several studies aiming the development of new finishing approaches achieving a lot of new or improved properties. For example nanoparticles of natural zeolite led to better UV and antimicrobial protection of polyester and cotton fabrics [16-18], nano-Ag has been used for imparting antibacterial properties [19], nano-TiO2 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 more preferable than organic UV blockers [27,28], because the inorganic absorbers like 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. A proper dispersion and homogenous distribution in a coating layer yields a 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 appearance. If the employed particles exhibit particle sizes below 50 nm no light scattering within the coating occurs guaranteeing the mentioned 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, a homogeneous dispersion in different matrices is required. A number of synthetic strategies have been developed to prevent particle agglomeration and increase the stability of e.g. ZnO nanoparticles in various dispersions [36-41]. For application of ZnO as a UV-absorbing finishing it has to be incorporated in an adequate binder. Some previous work had been done by DTNW for preparing finishing sols based on ZnO and 3-glycidyloxypropyltrimethoxysilane (GPTMS) but the sols used showed only poor stability (less than 30 min). This paper describes the preparation of stable ZnO dispersions and the embedding of the ZnO into a hybrid polymer network, acting as a binder and following the finishing of cellulosic fiber. The aim was to develop a highly UV-absorbing system that can be applied to textiles using a simple pad-dry-cure.

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

No	Substrate	Weight (g/m^2)	Tthreads/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

Experimental

Materials

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

Chemicals

Zinc acetate dihydrate (ZnAc.2H2O), lithium hydroxide monohydrate (98%) and 2-propanol were obtained from Merck, (3-Glycidyloxypropyl) trimethoxysilane (GPTMS, 98%) from ABCR. For catalysing the cross-linking reaction of 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 [37]. 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 hydrolyze the precursor.

A two neck round bottom distillation flask was used to suspend 2.8 g of ($ZnAc._2H_2O$) in 100 ml 2-propanol by reflux heating for three hours. 0.75 g lithium hydroxide was dissolved in 100 ml isopropanol at room temperature by magnetic stirring. The ZnAc suspension was cooled down to 0 °C before the lithium hydroxide solution was added drop wise under vigorous stirring. The mixture was treated in an ultrasonic bath at room temperature for about 2h. The resulting sol theoretically contains 0.675 wt. % ZnO. Higher amounts of ZnAc and lithium hydroxides were used (using constant amounts of solvent) to prepare colloidal solution of higher concentration.

Characterization of ZnO nanoparticles:

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

Preparation of a GPTMS sol:

10 ml GPTMS are dissolved in 100 ml isopropanol before hydrolysis using (1.22 ml) 0.01M hydrochloric acid. The resulting sol is stirred for at least 3h to form the basis sol (concentration of GPTMS sol 9,1 vol.%).

Coating process

Before finishing of textiles the zinc oxide and the GPTMS sol were mixed in different ratios and 1-methylimidazol (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 by a pad-cure-method. The coating was carried out by a padding process with a laboratory padder to a wet pick up of 100%. After padding samples were dried in a labcoater at 130 °C for 30 min.

Characterization of coated fabrics

Investigation of the coated textiles was carried out by means of the following procedures:

- Investigation of the mechanical properties (tensile strength and elongation) was carried out according to DIN 53857 1 using a Zwick 1445 Testing System.
- Air permeability was tested using air permeability tester (21443, FRANK) according to DIN 53887.
- Treated fabrics were analyzed by scanning electron microscopy (SEM), Topcon-Microscope (ATB-55) to investigate morphological changes of the surface structure.
- 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 5 washing cycles using standard ECE detergent without FWA's.
- Wear resistance was investigated by a Martindale test (James H. Heal & company limited) 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 is given according to Berger (light source D65/10).
- Stiffness of the fabric was tested using Shirley stiffness tester according to DIN 53362.
- Turbidimeter measurements were measured by Model 2100N laboratory Turbidimeter (HACH).

Results and discussion

The synthesis of ZnO nanoparticles basically described by Spanhel(38) lead 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. The picture shown in Figure 1 shows a corresponding sol after more than ten weeks indicating the stability and the absence of any precipitation.

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

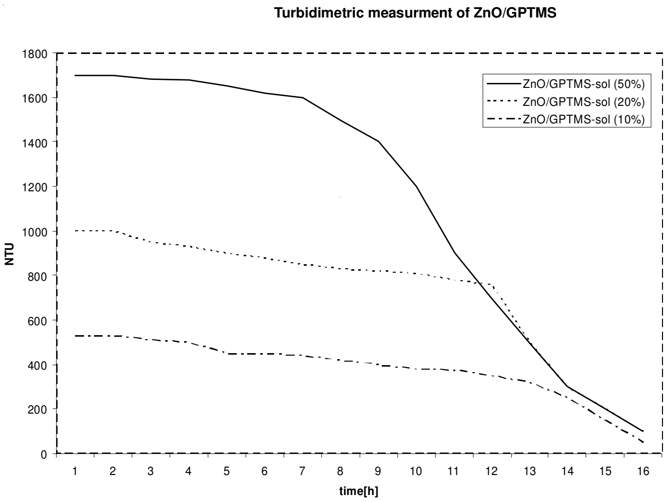


Figure 2. Stability of different ZnO /GPTMS sols according to turbidimetric measurements (NTU...Normal-Turbidity-Unit).

Figure 2 shows the stability of different concentrations of complete finishing prepared ZnO /GPTMS sols measured by turbidimetric measurements (NTU...Normal-Turbidity-Unit). From the figure we can see that higher concentration of ZnO-nano is more turbid and still stable till nearly 8 hours, but lower concentrations of ZnO-nano show more stability nearly till 12-13 hours.

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

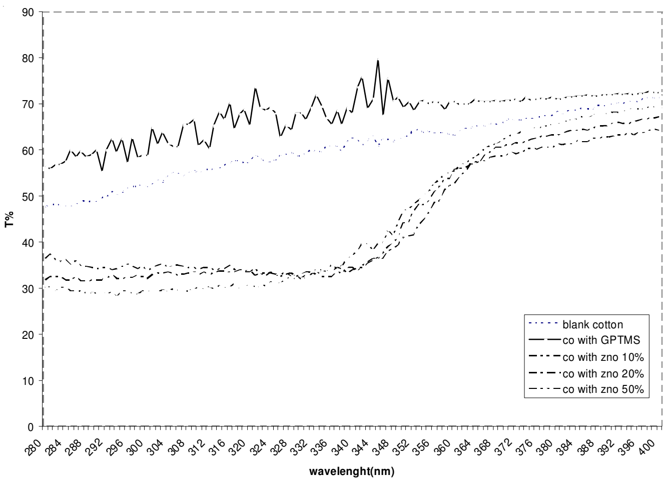


Figure 3. Comparison of UV-spectra of blank cotton fabrics and fabrics treated with ZnO modified GPTMS sols.

To investigate the durability of the treatments 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 investigated again. The corresponding data for selected fabrics are summarized in tables 3 and 4, and Figure 4 indicating only slight changes in the absorption characteristics which expressed as UPF value.

Table 3. Effect of increasing the concentration of ZnO-sol on the UV-protection properties of 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

Table 4. Effect of increasing the concentration of ZnO-sol on the UV-protection properties of cotton and cotton blend fabric samples after treatment and 5 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

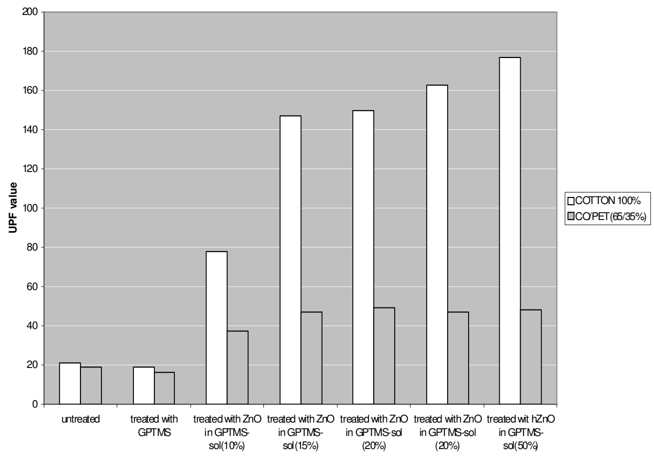
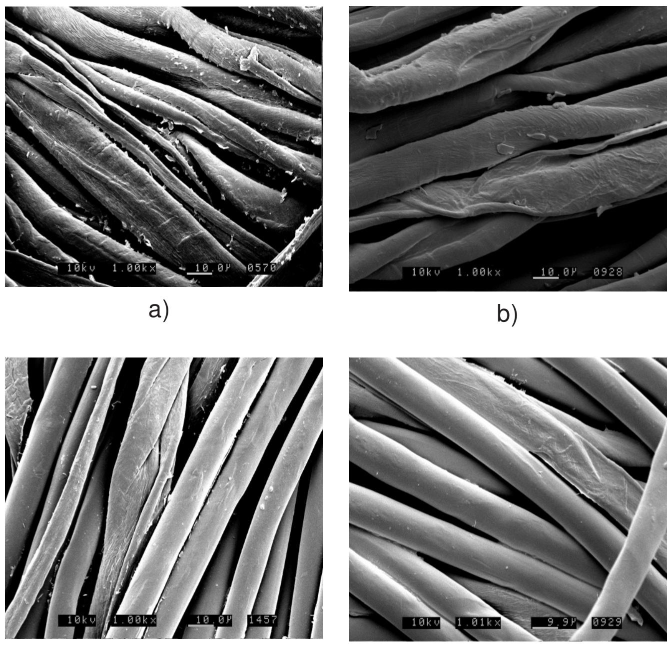


Figure 4. UPF value of Cotton and CO/PET substrates treated with different conditions.

Based on its aromatic backbone polyester fibre 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 as well as untreated cotton fabric. Treatment with GPTMS results in equally good UV protection. Results presented in tables 3 and 4, as well as in Figure 4, show the increment of UV protection ability with the increment of concentration of ZnO-sol on the both treated fabrics - cotton and cotton/polyester. All cotton fabrics give off excellent UV protection, as well as the most of cotton/polyester fabrics. The only exception is Cotton/Polyester fabric treated with 10 % ZnO nanoparticles in GPTMS-sol that gives off very good protection.

From the tables 3 and 4 it can be seen that sol-gel treatment have high durability since the 5 washing cycles have no effect on the UPF value of the fabric. Therefore, UV protection level of the treated fabrics is excellent even after laundering, except for Cotton/Polyester treated with ZnO in GPTMS-sol (10%), which remains very good.



a) b) c) d)

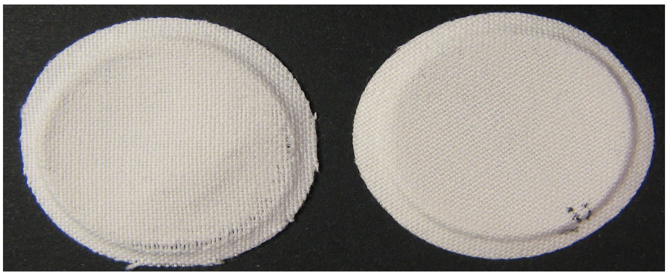
Figure 5. SEM micrographs of: (a) blank cotton fabric, (b) cotton fabric treated with 20% nano-ZnO, (c) blank cotton/polyester fabric, (d) cotton/polyester fabric treated with 20% nano-ZnO.

SEM Investigation

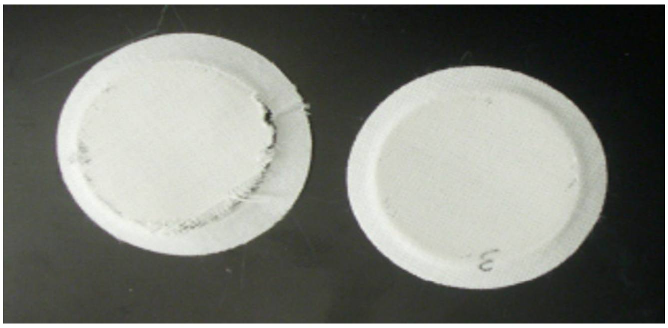
SEM investigations were carried out to investigate changes in the topography. The corresponding SEM micrographs are shown in Figure 5. The surface of the untreated fibers is comparably rough, the surface of the treated fibers appear much smoother, because the coatings obviously lead to a flattening of the fiber 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 formation of the resulting coatings.

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 and the corresponding data are given in Table 5. It can be determined that tensile strength of the coated cotton as well as the coated cotton blend fabrics is slightly decrease. Also the whiteness of the fabrics is slightly decreased, but in a tolerable degree. The decrease for cotton is between 3.8 to 6.4 % the decrease for CO/PET between 3.2 and 6.6 % only. Air permeability is an important factor in the performance of textile materials used to provide an indication of the breathability of coated fabrics, within the investigation summarized in Table 3 it can be seen that there is no worsening of the air permeability but at least a slight improvement of maximum 6 %. The mentioned increase of the bending stiffness values recorded by increasing the concentrations of nano ZnO could be explained by a higher up take of the inorganic-organic hybrids polymers on cellulosic fabric surface, due to an increasing solid content for sol with higher amount of ZnO.

It has been reported by some of the authors that comparable hybrid polymers modified with alumina particles will improve the wear-resistance of the treated fabrics [41]. Against this background 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 both after 20.000 scrubbing cycles. As can be clearly seen the treated sample is still intact showing no destruction while the untreated one is already destroyed.



Cotton fabric (100%):
(a) untreated (b) treated



Cotton/polyester (65/35%) fabric:
(c) untreated (d) treated

Figure 7. Results of a Martindale test investigating the wear resistance of the treated samples after 20.000 scrubbing cycles compared to the untreated sample. Cotton fabric (100%) and Cotton/polyester (65/35%) fabrics.

Conclusions

The nanosized zinc oxide particles were synthesized and applied for the preparation of functional coating for inorganic-organic hybrid materials. Final coating solutions were stable for several hours showing minimal precipitation which is sufficient for an industrial application. These hybrid materials can be applied to textile materials by a simple pad-cure method - here shown for cotton (100%) and cotton/polyester (65/35%) fabrics. The resulting textile materials achieve significantly

Table 5. Effect of increasing the concentration of ZnO-sol on some performance properties of 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

improved UV-absorption of high durability, without affecting the textile, changing air permeability and even improving the 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 it is non-toxic. The sol-gel approach used here for the preparation of the coating materials guarantees a simple processing easily transferred to textile industry. Furthermore the principles of sol-gel technique allow combining additional properties in a single coating material. Future work on the topic of UV-protection will not only direct on further improvement of the UPF value but also on the combination with additional affects as e.g. antimicrobial activity.

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