CELLULOSE CHEMISTRY AND TECHNOLOGY

MULTIFUNCTIONALIZATION OF A CELLULOSIC MATERIAL BY MEANS OF A MULTIPLE-STEP COATING PROCESS APPLYING ORGANOTRIALKOXYSILANES

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The sol-gel process is an excellent process for coating various substrates and thus imparting new functionalities to the treated material. Cotton fabrics were finished with various silicon alkoxides: tetraethoxysilane, (3-triethoxysilylpropyl)succinic acid anhydride, and (3-glycidyloxy)propyltrimethoxysilane in a one-, two-, and three-step process, applying the pad-dry-cure method. The physico-mechanical parameters: dry crease recovery angle, tensile strength, flexural rigidity, air permeability, abrasion resistance, whiteness index (WI), and water vapor permeability of the as-prepared cotton samples were evaluated. In addition, the coated samples were analyzed by means of Fourier transform-infrared/attenuated reflection spectroscopy, thermal gravimetric analysis, and 3D laser confocal microscopy. To study the wettability, selected alkoxysilane-treated specimens were coated with octyltriethoxysilane. The impregnation with titanium tetraisopropoxide significantly increased the ultraviolet protection factor. The findings make evident that the wrinkle resistance could be improved.

Keywords: polysaccharide, cotton, surface modification, sol-gel process, alkoxysilanes

INTRODUCTION

Cotton is a natural fiber and an important resource for the apparel industry. The cotton fiber mainly consists of the natural raw material cellulose (>95%).[1,2] It has good strength and provides excellent comfort due to its ability to hold and release moisture. However, cotton material suffers from a few disadvantages, such as the tendency to wrinkle, poor dimension stability and high flammability. Consequently, after the pretreatment and coloration stage, cotton fabrics are subjected to various finishing processes to impart the final, customer-tailored properties to the textile material. These finishing processes can be conducted either under dry conditions, such as plasma treatment,[3,4] or under wet conditions.[5]

During the last two decades, the sol-gel process that takes place in an aqueous medium has attracted increasing interest in the modification of textile-based materials to convey novel functionalities to cotton fabrics.[6] The sol-gel technique is a synthetic route that involves acidic- or alkaline-catalyzed hydrolysis and a subsequent low-temperature condensation reaction of metal or semimetal alkoxides, the so-called precursors, in an appropriate solvent.[7,8] Various inorganic or organic substances can be incorporated into these precursor-containing nanosol solutions, which are applied to the textile surface by the pad-dry-cure method, thus making possible the formation of organic-inorganic hybrids.[9]

Multiple-step processes also enable the production of multi-functional textile surfaces. Colleoni *et al.* applied a multi-layer approach using tetraethoxysilane as precursor.[10] Cotton material was modified with layers consisting of SiO_2/TiO_2 at low temperature.[11] Cotton fabrics were treated in a two-step process, applying Zn(II)acetate and 1,4-benzenedicarboxylic acid to impart antibacterial properties.[12]

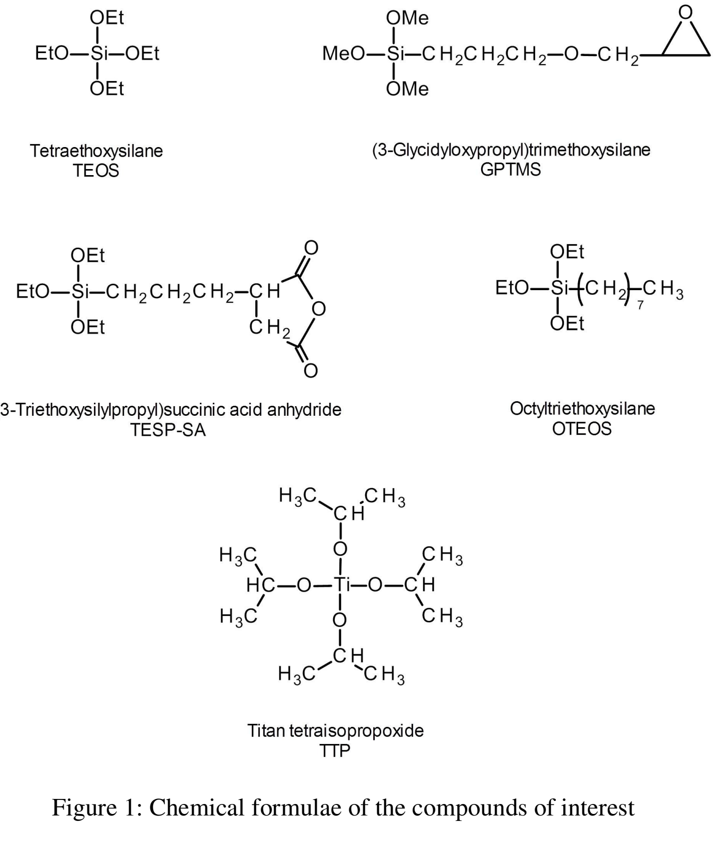
Most of the sol-gel based modification studies were focused on the improvement of the physico-mechanical functions, such as crease resistance,[13-16] flame retardancy,[17-19] UV protection,[20-22] hydrophobicity,[23-25] or self-cleaning.[26-29] The sol-gel method also was applied on textiles for various medical applications, such as drug release,[30,31] wound healing,[32] or antimicrobial finishing.[33-35] Efforts have been undertaken to produce smart textiles capable of reacting to environmental stimuli.[36,37] The sol-gel method is also used to improve the wash fastness of dyed cellulose-based fabrics.[38,39]

The present study was undertaken with a view of investigating the feasibility of carrying out multi-functional finishing of cotton fabric by multiple treatments of the cotton samples with different alkoxysilanes.

EXPERIMENTAL

Materials

Tetraethoxysilane (98%, TEOS) and ethanol (>97%) were purchased from Fluka Chemie GmbH, Buchs, Switzerland. (3-Triethoxysilylpropyl)succinic acid anhydride (TESP-SA, 100%), (3-glycidyloxy)propyltrimethoxysilane (100%, GPTMS), and octyltriethoxysilane (100%, OTEOS) were donated by Wacker Silicone, Burghausen, Germany. Titanium tetraisopropoxide (98%, TTP) was purchased from Sigma-Aldrich, Vienna, Austria. The chemical formula of the substances can be seen in Figure 1. The chemicals were applied without further purification. Deionized water (DI) was used throughout the investigation. Desized, scoured, bleached 100% cotton fabric (weave type: plain, density warp: 52 yarn/cm, weft: 24 yarn/cm, weight: 109 g/m^2) was utilized throughout the study and is denoted as raw material (RM).



Tetraethoxysilane
TEOS

(3-Glycidyloxypropyl)trimethoxysilane
GPTMS

(3-Triethoxysilylpropyl)succinic acid anhydride
TESP-SA

Octyltriethoxysilane
OTEOS

Titan tetraisopropoxide
TTP

Figure 1: Chemical formulae of the compounds of interest

Preparation of the organotrialkoxysilane solutions

The finishing solutions were prepared as follows: 30 mmol of each of the alkoxysilanes (TEOS, GPTMS, TESP-SA,) were hydrolyzed in 30 mL DI and 5 mL HCl (c = 0.1 mol/L) at room temperature for 3 h under stirring in polypropylene beakers, which were sealed with a pierced parafilm (Bemis, Neenah, Wisconsin, USA). Subsequently, the volumes of the homogenous solutions were filled up to 100 mL with DI. 16 mL (50.34 mmol) of OTEOS were dissolved in 150 mL of ethanol. 3 mL of HCl (c = 0.1 mol/L) were added and the solution was stirred for 3 h at room temperature. The titanium dioxide-nanosol solution was prepared by mixing TTP (1%) with 100 mL of DI containing nitric acid (1%) under vigorous stirring for 48 h using a magnetic stirrer. After a certain period, a transparent, yellowish solution was obtained.[20]

Preparation of the cotton samples

The pre-weighed cotton samples were impregnated with the corresponding alkoxide solutions, applying a two-roll laboratory padder (HVL 500 Mathis AG, Niederhasli, Switzerland; air pressure 1 bar, rotary speed 3 m/min). The samples were dried at 105 °C for 2 min in a lab dryer (LTE, W. Mathis AG, Switzerland). The condensation reaction was conducted at 160 °C for 10 min. The scheme of preparation is shown in Figure 2.

The as-prepared cotton specimens are coded as follows: the terms TE, GP and TS refer to the cotton samples treated with TEOS, GPTMS and TESP-SA, respectively. The coding of the multiple-treated samples is explained in terms of an example: TE-GP-TS denotes the sample that was firstly treated with TEOS, subsequently with GPTMS, and finally with TESP-SA.

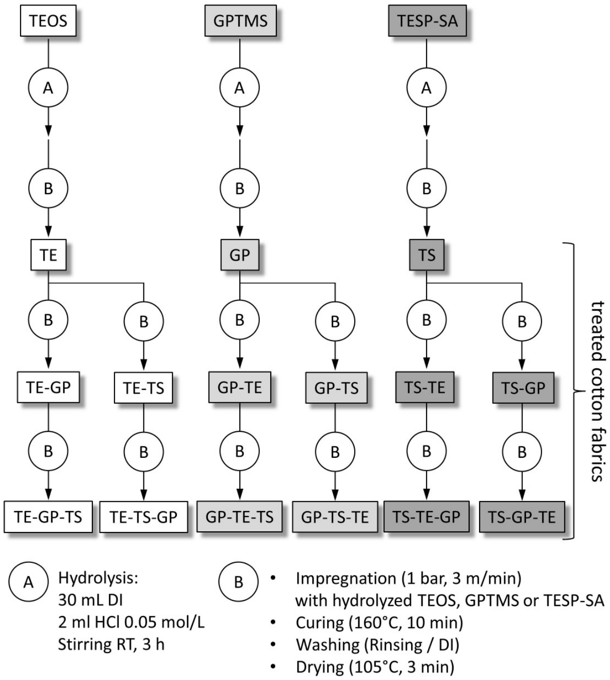


Figure 2: Modification scheme for the multiple-step preparation of the nanosol-modified cotton samples

Prior to the contact angle measurements, the cotton samples were immersed for 1 h into the OTEOS-containing solution, dried for 12 h at room temperature, and cured for 15 min at 150 °C.

To impart UV protection properties, the cotton samples were impregnated with titanium dioxide-nanosol, applying the two-roll laboratory padder, and cured for 15 min at 150 °C.

Apparatus and methods

The add-on of the fabric weight was calculated as follows: add-on (%) = $[(W_2 - W_1)/W_1] \times 100$; where W_1 and W_2 are the weights of the fabric specimens before and after the treatment, respectively. Dry crease recovery angle (DCRA) was measured according to ISO 2312: 10 test specimens were creased and compressed under controlled conditions of time and load. After removal of the creasing load, the angle formed between the two limbs was measured. The DCRA values render possible the evaluation of a cross-linking reaction between a crease-resistant finishing agent and the cellulosic material. Tensile strength (TS) was determined with the Material Testing System Z010 (Zwick/Roell, Ulm, Germany) according to DIN EN ISO13934. The stiffness of the fabrics was determined by means of a Taber Stiffness Tester, Model 112, New York, USA, according to ASTM D 1388-R6. The flexural rigidity was calculated as described in ASTM D 1388-R6. Abrasion tests were performed according to DIN EN ISO 12947 (Martindale method): the circular sample was mounted on a specimen holder and subjected to a defined load (12 kpa). Then, it was rubbed against a standard fabric in a translational movement. The measurement of the air permeability was conducted according to DIN EN ISO 9237 using the air permeability tester Textest FX 3030 LDM, Textest Ldt, Zurich, Switzerland. The air flux (L/dm^2/min) that passes through the fabric was evaluated at a pressure difference of 100 Pa. Colorimetric data measurements were conducted with the Spectrophotometer CM-3610d from Konica Minolta, Japan. The color data software CM-S100w Spectra Magic NX V1.9 was used for data acquisition.

The water vapor permeability was studied gravimetrically by placing disks covered with the cellulosic specimens in a desiccator at air humidity of 100%, at 23 °C for 96 h. The WVP rate was measured gravimetrically using the water method, following ASTM E96. A plastic cup (4 cm diameter, 2.5 cm height, 25 mL) was partially filled with DI (11 mL). A hole (1.5 cm diameter) in the lid of the cup was sealed with the circular test specimen. This cup assembly was placed in a desiccator filled with silica gel. The initial weight of the assembly was taken and it was reweighed after 96 h.

FT-IR/ATR spectra were recorded with a Bruker Vector 22 spectrometer using a DTGS detector. The spectra were the result of 50 scans. The spectral resolution was 4 cm^{-1}. A PIKE MIRacle TM ATR accessory, equipped with a diamond ATR crystal, was used. The surface morphology was studied by means of a 3D laser confocal microscope (Keyence VK-X150, Osaka, Japan). TG measurements were conducted with the thermogravimetric analyzer TGA 2 (Mettler-Toledo GmbH, Vienna, Austria) in air, using a heating rate of 10 °C/min and a scan range of 40-800 °C.

The contact angle values were assessed using a home-made contact angle measuring device, which consisted of a digital microscope camera (DigiMicro 2.0 Scale, Software Microcapture; dnt GmbH, Dietzenbach, Germany). Precise contact angle measurements were conducted using the IMAGEJ software (Research Services Branch of the National Institute of Mental Health, Bethesda, MD, USA) and the plug-in Drop Analysis (Biomedical Imaging Group, Ecole Polytechnique Federale de Lausanne, Switzerland).[40] The UV protection efficiencies of the treated fabrics were quantified according to the Australian/New Zealand Standard AS/NZS 4399:1999, applying a Specord 50 UV-VIS spectrophotometer, equipped with a photometer sphere (Analytik Zeiss-Jena, Jena, Germany).

RESULTS AND DISCUSSION

Different chemical agents are applied to convey novel properties to the surface of polysaccharide-based materials. For this purpose, precursors, such as TEOS, GPTMS, and TESP-SA, are subjected to acidic- or alkaline- catalyzed hydrolysis, thus forming a homogenous, aqueous nanosol solution comprising reactive silanol groups. The latter are capable of reacting with the hydroxyl groups of the polysaccharide at elevated temperatures, resulting in a permanent attachment to the textile substrate. Also, the functional groups of the organic unit of the precursors can react with the polysaccharide. Usually, the materials are chemically modified applying a single step. The present study aims to reveal the impact that is exerted on the properties of a polysaccharide-based, textile material treated by means of a three-step sol-gel process.

Physico-mechanical properties of the fabrics

In the first step of the coating process, cotton fabrics were impregnated with finishing baths containing either the hydrolyzed alkoxides TEOS, GPTMS or TESP-SA (30 mmol/100 mL). The as-prepared specimens were coated with a second and third layer, as presented in Figure 2. Subsequently, the physico-mechanical characteristics were evaluated. The experimental results are summarized in Table 1.

Add-on

The add-on values indicate the portion of the chemical agent that is attached to the cotton material and hence increases the weight of the fabric, which in turn influences the physico-mechanical properties.

The add-on values of the first coating step can be ranked as follows: TE < GP < TS. The add-on values of TE-GP and GP-TE are about 6%, those of TE-TS and TS-TE are about 9%. The three-step coating process provides add-on values in the range from 12% to 15%. These observations can be explained by the fact that the epoxide group of GPTMS is hydrolyzed to a diol functionality, whereas the anhydride unit of TESP-SA is converted into two carboxyl groups. As a result, the number of the reactive sites for the interaction with the cellulosic material is enhanced.

Dry crease recovery angle measurements

Cotton-based fabrics exhibit the undesired propensity to wrinkle.[41] Therefore, cotton fabrics are finished with chemical agents resulting in a cross-linking reaction between the cellulosic chains. However, the most effective and low-cost cross-linking agent, dimethyloldihydroxyethyleneurea (DMDHEU) releases the potential human carcinogen formaldehyde.[42] Various studies have been undertaken to establish non-formaldehyde, crease-resistant finishing agents.[41,43] To evaluate the wrinkle-resistant properties, the DCRA values are measured.[44]

Table 1
Physico-mechanical properties of the alkoxysilane-modified cotton samples

Code	Add-on (%)	DCRA (w+f) (%)	Tensile strength (%)	Flexural rigidity (%)	Air permeability (%)	WI (%)
RM		100.0	100.0	100.0	100.0	100.0
TE	1.7	90.5	100.6	105.9	88.3	82.7
TE-GP	6.0	138.3	83.0	107.4	81.5	70.5
TE-GP-TS	13.3	151.6	85.5	154.4	78.8	64.1
TE-TS	8.5	136.8	48.0	108.8	81.5	63.6
TE-TS-GP	13.7	149.6	24.6	252.9	85.9	56.9
GP	4.2	129.0	100.2	101.5	84.6	74.4
GP-TE	6.0	147.6	82.8	139.0	92.2	63.5
GP-TE-TS	12.7	153.2	81.4	157.4	84.1	60.9
GP-TS	11.0	160.7	88.7	123.5	83.7	61.6
GP-TS-TE	12.6	160.9	73.2	125.7	81.0	63.2
TS	7.4	162.4	68.9	97.8	81.7	80.3
TS-TE	9.1	145.3	44.5	159.6	84.9	64.3
TS-TE-GP	14.6	154.8	40.8	210.3	91.0	53.9
TS-GP	11.4	165.7	72.5	175.7	84.4	66.4
TS-GP-TE	12.9	181.9	57.7	181.6	79.5	60.8

The results of the DCRA measurements are shown in Table 1. TE shows poor crease-resistance, whereas the DCRA value of GP is increased. A significant improvement of the crease-resistant properties can be observed for TS. These results make evident that TESP-SA is the most effective durable press agent due to the adjacent carboxylic groups, which are capable of reacting with the hydroxyl groups of the cellulosic material. TE-TS, TE-GP, TS-TE and GP-TE also give rise to enhanced DCRA values (136% to 148%). However, a remarkable increase can be detected for GP-TS and TS-GP. The three-step treatment results in excellent crease recovery properties (150-182%). The best value can be observed for TS-GP-TE. These findings confirm that the first treatment with TESP-SA results in a noteworthy improvement of the DCRA values.

Tensile strength

The DCRA values prove that the application of the alkoxysilanes causes a crosslinking reaction between the cellulose chains. Therefore, the relative movement of the chains is restricted; consequently, the distribution of the stress exerted on the individual chain cannot take place.[45] This phenomenon also influences the tensile strength. The findings in Table 1 reflect that the values of the tensile strength are reduced in comparison with the sol-gel untreated RM. The highest reduction can be noticed for the cellulosic specimens that were subjected to a three-layer coating process starting with TESP-SA (40-47%).

The cotton samples that were firstly treated with a GPTMS-containing formulation exhibit a moderate decrease. The values for TE and GP reached the same level as RM. The values are consistent with those found for the DCRA values.

Flexural rigidity

When multifunctional chemical agents react with a textile material, an increase in the weight as well as a crosslinking reaction takes place, thus causing an alteration in the stiffness properties of the textile fabric. The stiffness properties are reflected by the flexural rigidity (FR). The results are given in Table 1. TS, GP, and TE show a moderate increase in the FR values, whereas the two-step treated specimens have significantly higher values. The highest values can be observed for the samples treated with TESP-SA in the first step (TS-TE, TS-GP). The inspection of the stiffness properties of the three-step treated cellulosic fabrics makes it evident that TS-GP-TE, TS-TE-GP, and TE-TS-GP reach the highest levels. The findings are consistent with the results of the add-on measurements.

Air permeability

The air permeability is an important parameter of a woven material and it is mostly governed by the fabric's weight, thickness and porosity.[46] The coating material may block the voids, which are produced between the interlaced yarns, thus influencing the air permeability. Compared to

RM, the air permeability of all chemically modified samples is reduced (78.8% to 92.2%). The highest decrease in air permeability can be observed for the samples subjected to the three-step coating process (TE-GP-TS, TS-GP-TE, GP-TS-TE).

Abrasion resistance

Wear and maintenance processes have a significant influence on the abrasion performance of a textile material. This is also true for the finishing agent applied to the fabric to modify the surface properties. Therefore, the abrasive properties of the prepared cotton specimens were evaluated. The abrasion characteristics of RM and the modified cotton samples are presented in Figure 3 (Fig. 3a: fabrics coated in the first step with TEOS; Fig. 3b: fabrics coated in the first step with GPTMS; Fig. 3c: fabrics coated in the first step with TESP-SA). The findings of the abrasion experiments make it evident that RM suffers the lowest loss of mass. The abrasion curves of TE, GP and TS show a moderate increase in weight loss in comparison with RM. A further enhancement of the weight loss can be observed for the two-step treated samples. A significant weight loss is detected for the three-step treated samples, especially for those which were firstly treated with TESP-SA, as can be seen in Figure 3c.

Whiteness index

The treatment of polysaccharide-based material at elevated temperatures usually results in the formation of unsaturated conjugated groups, thus causing a yellowing effect. The decomposition reactions of the cellulosic material, as well as of the finishing agents, may be due to this phenomenon.[47] The results of the WI evaluation are shown in Table 1 and make it evident that, compared to RM, all nanosol-modified samples show reduced WI values. The highest decrease can be detected for TS, GP and TE. These phenomena may be due to the fact that the carboxylic groups present in TESP-SA and the vicinal diol group in GPTMS are decomposed during the heating process. A lower yellowing effect can be observed for the two-step treated and some three-step treated samples. The best protection against yellowing is given for TS-GP-TE, TS-TE-GP, and TE-TS-GP.

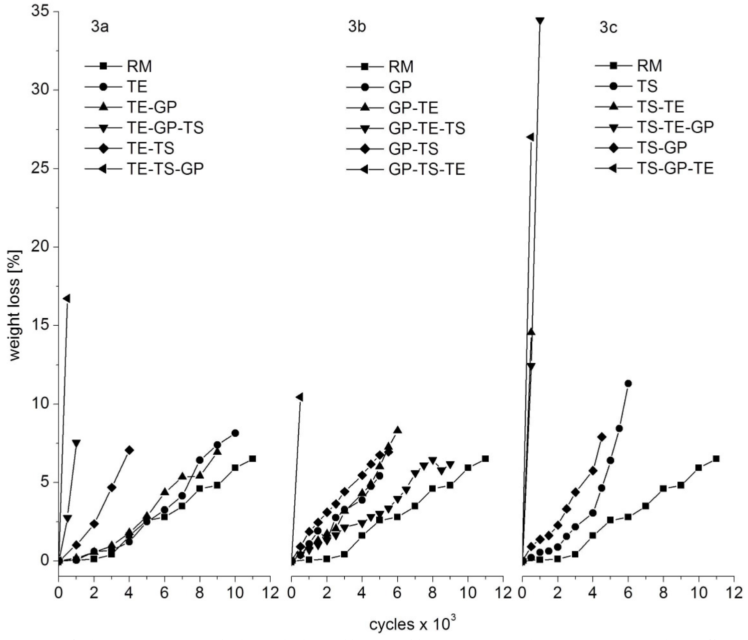


Figure 3: Abrasion curves of the raw material and the alkoxysilane-treated cotton samples: first treatment with TEOS (3a), first treatment with GPTMS (3b), first treatment with TESP-SA (3c)

Water vapor permeability

Water vapor permeability (WVP) of fabrics plays an important role in determining the wear comfort of clothing. The fabric that comes in close contact with the skin is able to wick the sweat and transport the moisture through the layer to the environment, thus producing a cooling and drying effect.[48,49] Therefore, it is of interest to study the interaction of the modified cotton fabrics with water vapor. For this purpose, the WVP values were measured. The findings presented in Figure 4 indicate that, compared to the raw material, the chemical modification results in enhanced WVP values. A low increase can be observed for the specimens treated with TEOS in the first step. An additional moderate increase can be detected for the samples finished with GPTMS in the first step. The samples that were firstly treated with TESP-SA show the highest WVP values. The sequence of the treatment with various organotrialkoxysilanes seems to have no influence on the water vapor transmission.

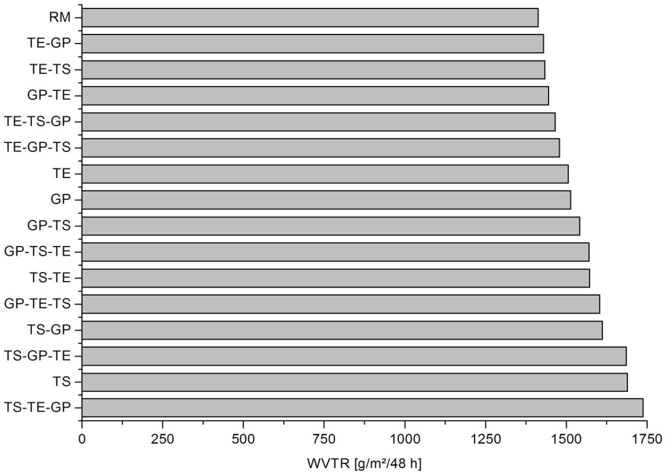


Figure 4: Water vapor permeability of the modified cotton samples after 48 h

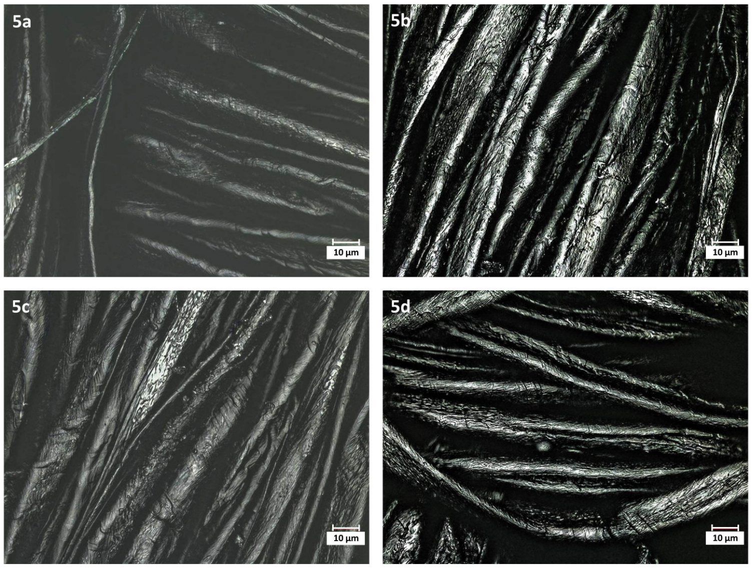


Figure 5: Confocal microscopy images of the raw material (5a), TE (5b); TE-GP (5c), and TE-GP-TS (5d)

Morphology of the surface

The surface morphology was studied by means of confocal laser microscopy. The images are presented in Figure 5: RM (Fig. 5a), TE (Fig. 5b) TE-GP (Fig. 5c) TE-GP-TS (Fig. 5d). The inspection of the figures makes it evident that no depositions can be observed on the surface of the treated fabrics. These facts indicate that no agglomeration took place in the course of the coating process. Therefore, it can be concluded that the nanosol solution of the alkoxysilanes penetrated into the cotton fibers, where the functional groups of the precursor reacted with the cellulose chains.

FT-IR/ATR measurements

The FT-IR/ATR method is an excellent tool to study the functional groups present on the surface of sol-gel modified cotton material.[50,51]

Figure 6a shows the spectrum of the sol-gel untreated RM. The group of spectra (Fig. 6b-6f) presents the spectra of the cellulosic material treated with TEOS in the first step (6b: TE; 6c: TE-GP; 6d: TE-GP-TS; 6e: TE-TS; 6f: TE-TS-GP). The spectra 6g-6k were obtained when GPTMS was the starting material for the modification process (6g: GP; 6h: GP-TE; 6i: GP-TE-TS; 6j: GP-TS; 6k: GP-TS-TE). The application of TESP-SA as starting material provided the spectra shown in the third group of spectra 6l-6p (6l: TS; 6m: TS-TE; 6n: TS-TE-GP; 6o: TS-GP; 6p: TS-GP-TE).

The bands observed in region I (800-1200 cm^{-1}) are assigned to the vibration modes deriving from the siloxane group and the C-O-C unit.[52,53] Thus, the weak vibration mode at 898 cm^{-1} can be ascribed to the asymmetric out-of-plane ring stretch of the β-glycosidic bond. The band appearing at 1028 cm^{-1} is due to the C-O stretching vibration, whereas the band that is observed at 1161 cm^{-1} is associated with the asymmetric C-O-C vibration mode.

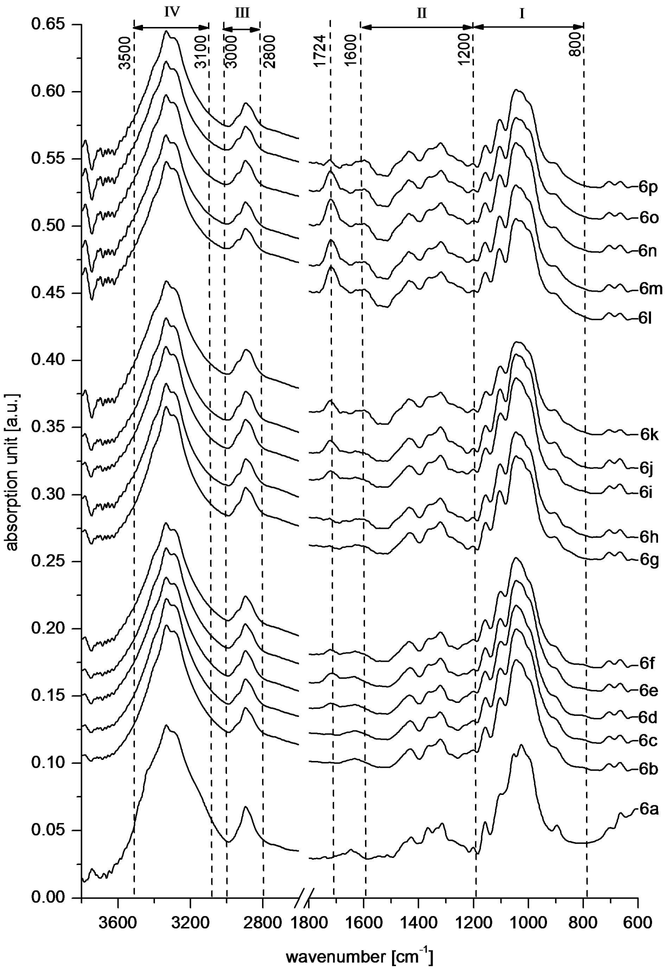


Figure 6: FT-IR spectra of 6a: RM; treated with TEOS in the first step: 6b: TE; 6c: TE-GP; 6d: TE-GP-TS; 6e: TE-TS; 6f: TE-TS-GP; treated with GPTMS in the first step: 6g: GP; 6h: GP-TE; 6i: GP-TE-TS; 6j: GP-TS; 6k: GP-TS-TE); treated with TEOS in the first step: 6l: TS; 6m: TS-TE; 6n: TS-TE-GP; 6o: TS-GP; 6p: TS-GP-TE

In region II (1200-1600 cm^{-1}), the bands of the bending vibration modes of C-H and O-H groups are visible. The band at 1319 cm^{-1} can be ascribed to the CH wagging bands. The band at 1367 cm^{-1} is due to the OH in-plane bending and the one at 1435 cm^{-1} can be assigned to CH wagging (in-plane). The band at 1640 cm^{-1} stems from the OH stretching vibration of adsorbed water.

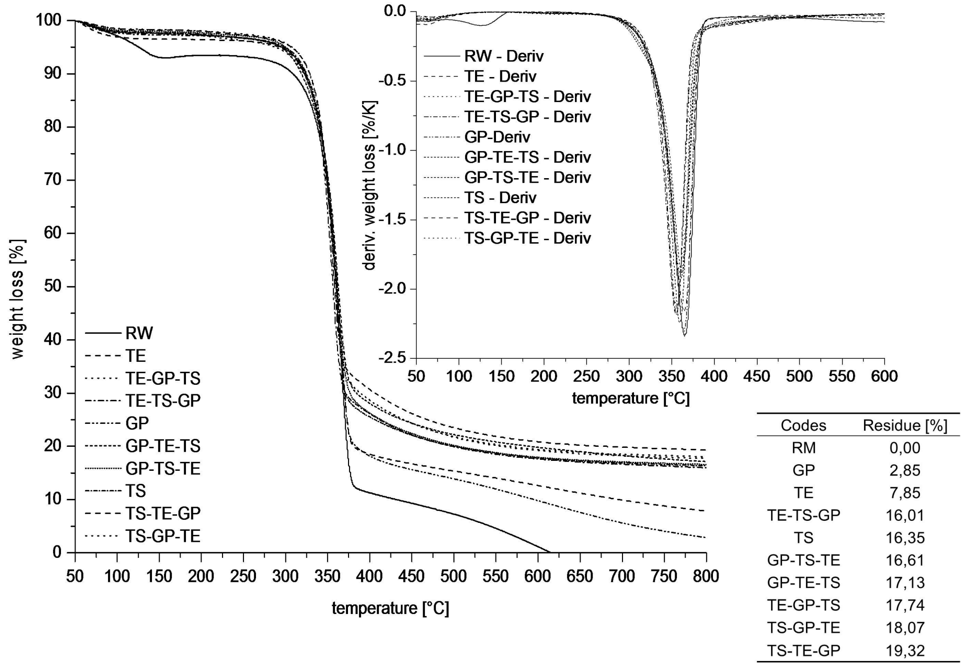
A noteworthy aspect of the spectra is that no absorption band can be observed at 1255 cm^{-1}, indicating that no epoxide ring is present in the cotton samples that were treated with GPTMS-containing finishing baths (Figs. 6c, 6d, 6f, 6g-6k, 6n-6p).[54] The band appearing at 1724 cm^{-1} is assigned to the stretching vibration mode of the carboxyl carbonyl group of TESP-SA (Figs. 6d-6f, 6i-6k, 6l-6p). The absorption bands in region III (2800-3000 cm^{-1}) are due to the -CH-stretching vibrations of the methylene groups of cellulose and the propyl unit of the organotrialkoxysilanes GPTMS and TESP-SA.

The vibration modes appearing in region IV (3100-3500 cm^{-1}) are assigned to H-bonded OH stretching vibrations. The OH absorption bands appearing at wavelengths higher than 3400 cm^{-1} are assigned to intramolecular hydrogen bonds, whereas the bands observed at wavenumbers lower than 3400 cm^{-1} are due to intermolecular hydrogen bonds.[55-57] Thus, the shoulder at 3440 cm^{-1} can be ascribed to the intramolecular hydrogen bonds, whereas the absorption bands at 3332 and 3283 cm^{-1} confirm the presence of intermolecular hydrogen bonds.

Thermogravimetric analysis

When polysaccharide-based materials, as well as other organic polymers, are subjected to thermal treatment at high temperatures, decomposition processes, such as depolymerisation, chain scission, oxidation, dehydration or decarboxylation, take place.[58,59] Therefore, it is of high importance to study the thermal behavior of the organotrialkoxysilane/polysaccharide hybrid.

The decomposition curves (TG and DTG) of RM, of the one-step treated and the three-step treated cotton samples are given in Figure 7. The curve of RM shows a moderate weight loss between 50-100 °C, which is due to the evaporation of absorbed water. The peak temperatures where the highest rate of decomposition is obtained are almost the same.



Codes	Residue [%]
RM	0,00
GP	2,85
TE	7,85
TE-TS-GP	16,01
TS	16,35
GP-TS-TE	16,61
GP-TE-TS	17,13
TE-GP-TS	17,74
TS-GP-TE	18,07
TS-TE-GP	19,32

Figure 7: TGA curves and derivative TGA curves of the raw material (RM), the one-step-coated and three-step coated cotton material (table shows the corresponding residues)

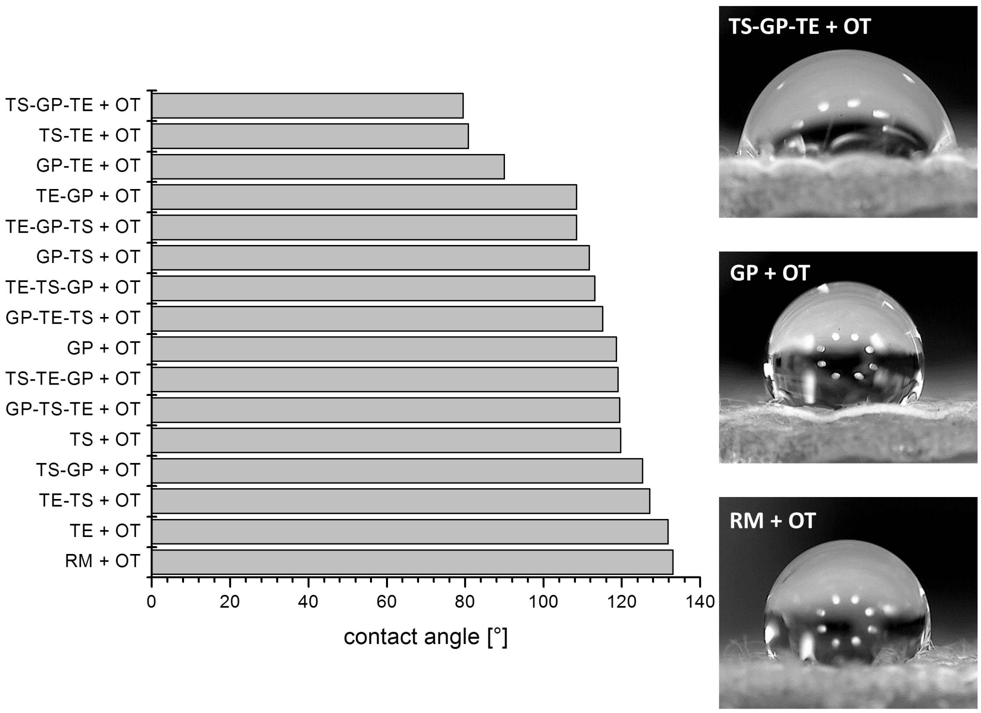


Figure 8: Contact angle values of all alkoxysilane-modified cotton samples coated with OTEOS

These findings are confirmed by the detailed information that can be extracted from the DTG curves. The table in Figure 7 indicates that the highest values for the residue are obtained for the three-step treated cotton samples. The highest values are obtained for TS-GP-TE and TS-TE-GP.

Incorporation of additives

Modification with OTEOS

Cellobiose, the constitutional repeating unit of the polysaccharide cellulose, is a hydrophilic material due to the six hydroxyl groups. To impart water-repellent properties to cotton material, the surface has to be modified with hydrophobic agents. For this purpose, hydrolyzed OTEOS is chemically attached to cotton material. Because of the hydrophobic character of the octyl group, OTEOS was hydrolyzed in an acidic ethanolic solution and applied to the corresponding cotton specimens by immersion. The as-prepared samples were dried at room temperature for 12 h and subsequently thermally treated at 150 °C for 15 min.

The contact angle was measured to evaluate the hydrophobic properties. The results are given in Figure 8. However, it has to be taken into consideration that the surface roughness increases the contact angle values, as described by the theories of Wenzel[60] and Cassie/Baxter.[61]

The results demonstrate that the application of OTEOS to the alkoxysilane-treated cotton fabrics results in a reduction in the CA values, compared to the OTEOS-treated raw material. This observation can be explained by the fact that the treatment of the textile material with the alkoxysilanes causes an increase in the number of hydrophilic functional groups (hydroxyl groups and carboxyl groups).

Modification with titanium dioxide

Skin has to be protected from excessive UV radiation, since UV radiation (UVA 315-400 nm, UVB 280-315 nm), being a component of the solar spectrum, has high skin damage potential.[62,63] One measure is to incorporate sun protection agents, such as the white, inorganic pigments titanium dioxide and/or zinc oxide, into human clothing. We applied a titanium dioxide-nanosol solution onto the cotton samples to impart UV blocking properties. The UPF values are presented in Figure 9.

The findings make it evident that the treatment with the alkoxysilanes moderately increases the UPF values, compared to the raw material. The incorporation of the titanium dioxide solution causes a significant improvement of the UV protection properties. The highest UPF values can be observed for the samples that have been treated with TESP-SA in the third step. This phenomenon may be due to the fact that the hydroxyl groups present on the surface of the titanium dioxide react via esterification with the carboxyl groups of the hydrolyzed TESP-SA, which is attached to the cotton material.

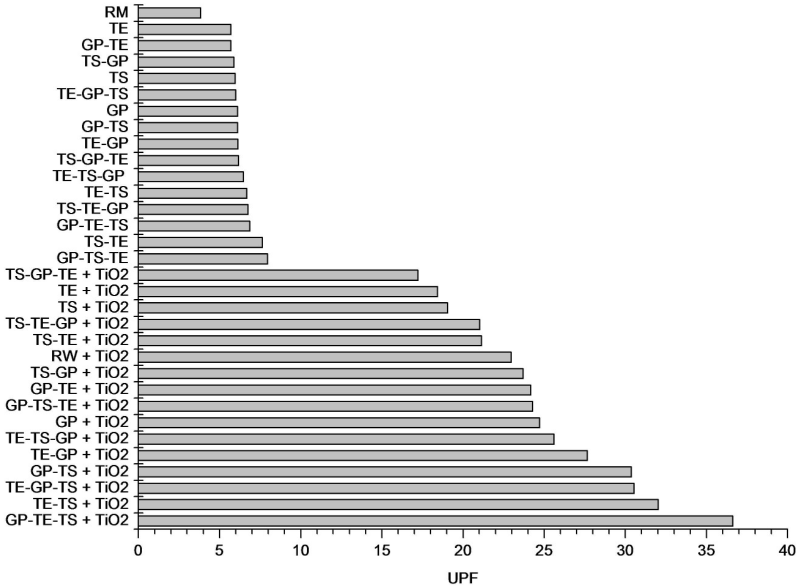


Figure 9: UPF values of the alkoxysilane-modified cotton samples treated with a TTP solution

CONCLUSION

Cotton-based material was chemically modified in a one-step process, two-step process and three-step process by means of nanosol-solutions containing various alkoxysilanes (TEOS, GPTMS, TESP-SA). The specimens were impregnated, dried and thermally treated at 140 °C for 20 min. The DCRA characteristics were improved. As expected, TS values were reduced. The flexural rigidity reached the highest level when the specimens were modified in the three-step process. The samples impregnated three times showed the lowest abrasion resistance. The thermal treatment caused a decrease in the WI values. The modification of the alkoxysilane-treated samples with OTEOS resulted in a moderate reduction in the contact angle values. In addition, the as-prepared samples were treated with a titanium dioxide solution to improve the UV-blocking properties. A significant increase in the UPF values can be observed for the samples that were treated with the three alkoxysilane solutions, whereby the third impregnation was performed applying a TESP-SA containing solution.

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