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Surface modification of cotton fabrics treated with organic-inorganic nanocomposites

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Cotton fabrics have been treated with mixtures of hydrolysed organoalkoxysilanes and hydrolysed metal alkoxides to impart novel properties to the cellulosic material. For this purpose, the cotton samples are impregnated with aqueous solutions comprising various compositions of (3-glycidyloxy)propyltrimethoxysilane, tetraethoxysilane, (3-amino)propyltriethoxysilane, aluminium isopropoxide, titanium tetraisopropoxide, and zircon tetrabutoxide, and then dyed with the natural dyestuff alizarin, as the hydrolysed metal alkoxide acts as mordant. The physico-mechanical properties, such as crease recovery angle, tensile strength, stiffness, contact angle, and whiteness index (undyed fabric), are evaluated. The results show that the incorporation of tetraethoxysilane or (3-amino) propyltriethoxysilane causes an alteration in physico-mechanical properties. The treatment with metal alkoxides increases the contact angle. Dyeing with alizarin causes different color shades which are evaluated in terms of the colorimetric data, such as ΔL*, Δa*, Δb* and *K/S* values.

Keywords: Alizarin, Cotton, Crease resistance, Mordant dyeing, Organoalkoxysilanes, Sol-gel technique

1 Introduction

Various mechanical and chemical processes have been used on cellulose-based textile products in order to impart specific properties or functionalities to textile materials[1-3]. During the last decades, the sol-gel process has been intensively investigated in terms of its capability to modify the surface characteristics of cotton materials. The sol-gel technique follows an excellent synthetic route which consists of a two-step reaction (hydrolysis and condensation). For this type of reaction, silicon-based alkoxides act mainly as precursors. The acidic or alkaline catalyzed hydrolysis results in the formation of silanol groups, which react to siloxane groups via condensation reaction, thus forming a siloxane-based organic-inorganic hybrid network[4, 5]. The as-prepared coatings are capable of modifying the ordinary physico-mechanical characteristics of the cotton material, such as crease resistance[6, 7], abrasion resistance[8, 9], hydrophobicity[10], flame retardancy[11] and dye fastness[12, 13]. Cotton samples can also be dyed with natural dyestuffs, such as alizarin in combination with mordanting agents, to fix the natural dye on the fabric and to prevent the dye from washing out and fading when exposed to light. Metal salts are intensively used as mordants[14-16].

The study has been undertaken to evaluate the impact of treatment of combinations of (3-glycidyloxy)propyltrimethoxysilane (GPTMS) with the tetraalkoxysilane (TEOS) or the amino group-containing organotrialkoxysilane (3-amino) propyltriethoxysilane (APTES) on the physico-mechanical properties, such as add-on, wet crease recovery angle (WCRA), tensile strength, stiffness, contact angle, and whiteness index (WI) of the modified cotton fabrics. The presence of the metal alkoxide aluminium isopropoxide (AIP) is necessary to enhance wrinkle resistance to the cotton fabrics. Thus, the combination of AIP with the titanium tetraisopropoxide (TTP) and zircon tetrabutoxide (ZTB), respectively, has also been evaluated in terms of possible alterations in the physico-chemical properties. Since the hydrolysed metal alkoxides AIP, TTP, and ZTB act as mordanting agents, the organic-inorganic nanocomposite-modified cotton samples have been dyed with the natural dye alizarin and the possible changes with regard to the shade and color strength are also investigated.

2 Materials and Methods

2.1 Materials

Aluminium isopropoxide (98%) (AIP), titanium tetraisopropoxide (98 %) (TTP), zircon tetrabutoxide (80 % in 1-butanol) (ZTB), alizarin (dye content 97 %) and sodium acetate anhydrous (99 %) were purchased from Sigma-Aldrich, Vienna, Austria. (3-Glycidyloxy)propyltrimethoxysilane (GPTMS, 98%), tetraethoxysilane (TEOS, 98 %), (3-amino)

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propyltriethoxysilane (APTES, 100%) were procured from Wacker Chemie, Burghausen, Germany. All chemicals were applied as received without further purification. The structural formulae of the chemicals used are shown in Fig. 1. Deionized water (DI) was used throughout the study. Desized, scoured, bleached and mercerized 100% cotton fabric (109 g/m^2) was utilized throughout the study.

2.2 Preparation of Hydrolysed Alkoxide Solutions

The 11.27 mL (50 mmol) GPTMS and 2.70 mL HCl (conc = 0.5 mol/L) were added into 10 mL ethyl alcohol (EtOH). The solution was stirred for 3 h at 20°C. The metal alkoxide solutions were separately prepared using the recipes: AIP–(0.51 g, 2.5 mmol AIP, 5 mL isopropanol, 0.12 mL DI); TTP–(0.74 mL, 2.5 mmol TTP, 5 mL isopropanol, 0.18 mL DI); ZTB–(0.74 mL, 2.5 mmol ZTP, 5 mL 1-butanol, 0.18 mL DI). These solutions were also stirred for 6 h at 20°C. The finishing baths were prepared by mixing the corresponding components in a 100 mL volumetric flask which was filled to the mark with EtOH. The recipes of the finishing solutions are presented in Table 1. The codes refer to the cotton fabrics which have been modified with the corresponding hydrolysed mixture of the alkoxides.

2.3 Modification of Cotton Fabrics

The procedure for the chemical modification of the cellulosic specimens is presented in Fig. 2. The pre-weighed cotton samples were impregnated by dipping the cellulosic samples into the corresponding alkoxide solution twice. Subsequently, the as-prepared samples were dried at 20°C. The condensation process was conducted at elevated temperature (140°C) for 15 min in a lab dryer (LTE, W. Mathis AG, Switzerland). Then, the finished samples were washed (material-to-liquor ratio 1:50, temperature 50°C, and time 10 min, stirring) and dried at 105°C for 2 min.

2.4 Dyeing of Pre-treated Cotton Samples with Alizarin

The GPTMS/metal alkoxide-modified cotton samples were dyed as follows: Two hundred milligram (200 mg) of alizarin and 50 mg of sodium acetate were added to 150 mL of water in a beaker and heated until boiling. Then the cotton samples (5 g) were added to the solution and boiled for 15 min. The as-dyed samples were thoroughly washed under tap water until the wash water gets colourless and dried.

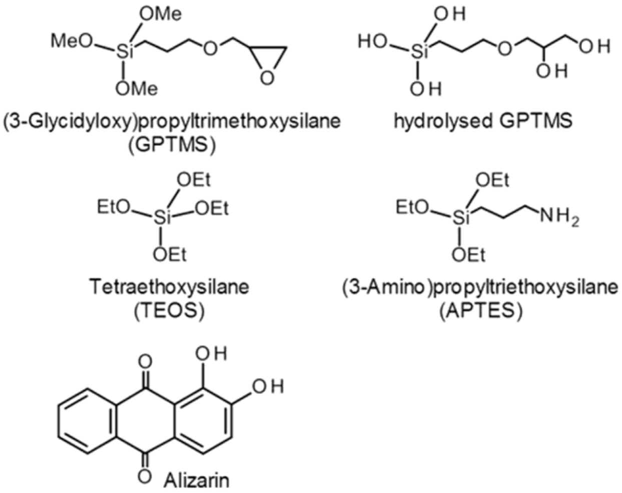

Fig. 1 — Chemical formulae of compounds

Table 1 — Components of nanosol solutions (100 mL) and codes of the cotton samples being treated with the corresponding solution

Code	GPTMS mmol	TEOS mmol	APTES mmol	AIP mmol	TTP mmol	ZTB mmol
RM (untreated)	-	-	-	-	-	-
GP-Al-2.5	25	-	-	2.5	-	-
GP-Al-5.0	25	-	-	5.0	-	-
GP-Al-TE-6.0	25	6	-	2.5	-	-
GP-Al-TE-12.0	25	12	-	2.5	-	-
GP-Al-AP-6.0	25	-	6	2.5	-	-
GP-Al-AP-12.0	25	-	12	2.5	-	-
GP-Al-Ti-1.25	25	-	-	2.5	1.25	-
GP-Al-Ti-2.50	25	-	-	2.5	2.50	-
GP-Al-Zr-1.25	25	-	-	2.5	-	1.25
GP-Al-Zr-2.50	25	-	-	2.5	-	2.50

GP – (3-Glycidyloxy)propyltrimethoxysilane, Al – Aluminium isopropoxide, TE– Tetraethoxysilane, AP – (3-Amino)propyltriethoxysilane, Ti Titanium tetraisopropoxide and Zr – Zircon tetrabutoxide.

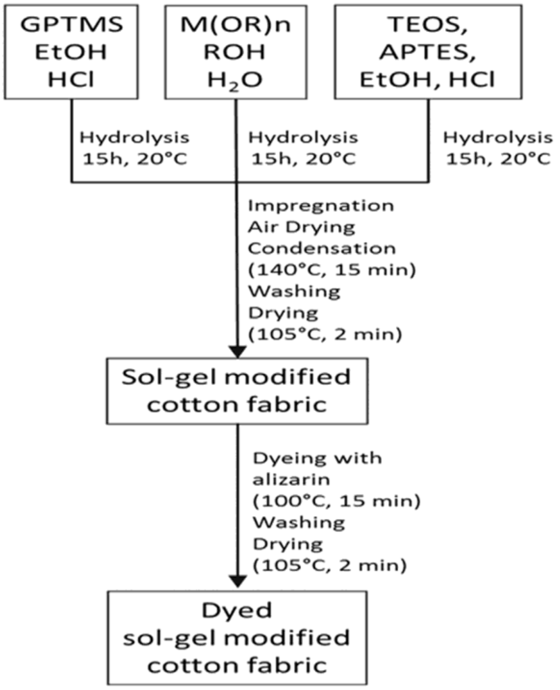

Fig. 2 — Finishing and dyeing procedure for cotton fabrics treated with hydrolysed GPTMS/metal alkoxide, GPTMS/TEOS/metal alkoxide and GPTMS/APTES/metal alkoxide solutions

2.5 Characterization

The add-on values of the cotton samples were calculated according to following equation:

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 treatment respectively.

Wet crease recovery angle (WCRA) was measured according to ISO 2313; 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 WCRA values render possible 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. 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 whiteness index (WI) was calculated according to CIE. Prior to measurements, the test samples were preconditioned at 20°C and 65 % relative humidity for 12 h. Washing tests were carried out according to AATCC Method 61-2009.

FTIR spectra were recorded with a Bruker Vector 22 spectrometer using a DTGS detector. Since the FTIR /ATR technique provided poor spectra, the KBr method was applied. Prior to the preparation of KBr pellets, the cotton samples were cut into small pieces and ground with a rotor mill ZM-1 (Retsch, Haan, Germany). The spectra were the result of 50 scans. The spectral resolution was 4 cm^{-1}. The contact angles were measured using a home-made contact angle measuring instrument, which consists of a digital microscope camera (DigiMicro 2.0 Scale; dnt GMBH, Dietzenbach, Germany). The data acquisition was performed by means of the software Microcapture. A water droplet (15 µL) was deposited on the cotton sample by means of a microliter syringe (Hamilton, Bonaduz, Switzerland), being placed on a glass slide, which was mounted on a microscope stage equipped with a double side holder. The precise contact angle measurement was done using the software ImageJ (Research Services Branch of the National Institute of Mental Health, Bethesda, Maryland, USA), and the plugin Drop Analysis (Biomedical Imaging Group, Ecole Polytechnique Federale de Lausanne, Switzerland)[17]. The surface morphology was studied by means of a 3D laser confocal microscope (Keyence VK-X150, Osaka, Japan).

3 Results and Discussion

When GPTMS is subjected to an acid or base-catalyzed hydrolysis reaction, the ethoxysilane groups (SiOEt) are converted into silanol groups (Si-OH). Simultaneously, the epoxide ring reacts to diol functionality. The as-prepared homogenous nanosol solution can be applied to cotton substrates. The thermal treatment of the impregnated cotton samples results in the conversion of silanol groups into siloxane units (Si-O-Si) which are forming a polymeric network. This modification of the cotton surface enables the alteration in chemical and physical properties of the textile substrate. Various hydrolysed GPTMS/AIP-based nanosol solutions are prepared (Table 1). The cotton samples are impregnated with the finishing baths, dried and cured at elevated temperature. The physico-mechanical characteristics (add-on, wet crease recovery angle, tensile strength, stiffness, contact angle and whiteness index) are measured.

3.1 Physico-mechanical Properties of Modified Cotton Fabrics

3.1.1 Incorporation of TEOS and APTES

Table 2 presents the add-on and the data of the physico-mechanical measurements of those cotton fabrics which are treated with different finishing solutions containing GPTMS, AIP and either TEOS or APTES. For comparison purposes, RM, GP-Al-2.5 and GP-Al-5.0 are included into the investigation.

3.1.2 Add-on

The add-on values provide information on the amount of supplied chemicals added onto the fabric during the finishing process. Table 2 shows that doubling the AIP concentration results in a significant increase in add-on value, whereas the incorporation of TEOS or APTES causes only a moderate enhancement of the weight gain. The doubling of the concentration of TEOS and APTES slightly increases the add-on values.

3.1.3 Wet Crease Recovery Angle

Cotton fabrics possess the tendency to wrinkle. Consequently, cellulosic materials are treated with crease-resistant agents. The ability to recover from creasing is specified in terms of the crease resistance angle and can be explained by a cross-linking reaction, which is accomplished between the cellulosic chains[18]. The values of the WCRA measurements are presented in Table 2. An increase in the AIP concentration results in a significant improvement in CRA value, indicating the cross-linking reaction between the cellulosic chains. When TEOS is added to the finishing bath, the WCRA value is decreased. The same tendency can be observed for the APTES-based cotton samples, indicating that the incorporation of TEOS or APTES hinders the cross-linking reaction between the cellulose chains.

3.1.4 Tensile Strength

The GP-Al-5.0 fabric exhibits the lowest tensile strength (TS) value, due to the crosslinking reaction. The TS values of the other modified cotton samples are only slightly decreased. These TS values show similar trend as found for the WCRA values.

3.1.5 Stiffness

The stiffness of a fabric can be evaluated by measuring the bending length of fabric being bent in one plane under the force of gravity[19, 20]. The results are presented in Table 2. A moderate increase in the stiffness can be observed for GP-Al-TE-6.0, GP-Al-TE-12.0, GP-Al-Ti-1.25, and GP-Al-Ti-2.5, whereas the stiffness values of the other cotton samples are significantly increased.

3.1.6 Contact Angle

The wettability properties of a textile material can be evaluated in terms of the contact angle (CA) (hydrophilic CA < 90°, hydrophobic CA < 90° and super-hydrophobic surface CA ≥ 150°). The hydrophilicity of cotton fabrics can be modified by applying functional hybrid materials to the cotton fabric. However, since cotton fabrics have a rough surface, increased CA values are measured, as shown by the theory of Wenzel[21], Cassie and Baxter[22], and Kwok and Neumann[23]. The CA values of the cotton fabrics having been treated with various nanosol solutions are shown in Table 2. The findings make it evident that the treatment with the hydrolysed metal alkoxides leads to an enhancement in hydrophobicity of the cotton textile. Cotton samples that are finished with an APTES-containing recipe show remarkably

Table 2 — Physico-mechanical properties of alizarin-dyed cotton samples

Code	Add-on, %	WCRA, deg	Tensile strength, %	Stiffness, %	Contact angle (CA), deg	WI[a]
RM		203.6	100.0	100.0	Not measurable	71.5
GP-Al-2.5	7.6	236	94.3	77.4	138	55.0
GP-Al-5.0	14.5	279	73.1	181.0	138	56.3
GP-Al-TE-6.0	8.7	251	97.2	98.8	Not measurable	54.8
GP-Al-TE-12.0	10.2	259	93.0	110.7	135	54.4
GP-Al-AP-6.0	9.1	233	98.9	169.0	106	35.8
GP-Al-AP-12.0	13.3	243	97.6	171.4	Not measurable	9.1
GP-Al-Ti-1.25	8.6	229	99.4	138.1	137	31.1
GP-Al-Ti-2.5	9.3	240	90.7	138.1	138	45.4
GP-Al-Zr-1.25	8.9	230	95.4	176.2	142	52.4
GP-Al-Zr-2.5	10.4	238	95.6	200.0	139	51.0

[a] Undyed.

reduced CA values, indicating that the amino-groups decrease the surface tension of the as-treated cotton samples. Figure 3 shows the water droplet deposited on GP-Al-2.5, GP-TE-6.0, GP-AP-6.0, and GP-Al-Ti-2.5. GP-Al-2.5, GP-TE-6.0, GP-AP-6.0 and GP-Al-Ti-2.5 have been subjected to washing procedure. In comparison to the unwashed samples, the CA values of washed samples are found to decrease by 10.3%.

3.1.7 Whiteness Index

The nanosol solutions are applied to the cotton substrates which are subjected to treatment at elevated temperatures in an attempt to promote the formation of siloxane groups as well as the reaction of silanol groups with hydroxyl groups of the cellulose. This procedure usually causes various types of reactions of the cellulose as well as the chemical agents applied, thus producing functional groups which give rise to the yellowing of the cotton samples[24-27]. Therefore, the WI values of the undyed and thermally treated samples are evaluated (Table 2). As compared to the WI of RM, all the finished cotton samples exhibit a pronounced yellowing tendency, indicated by the depletion of WI values. A significant reduction in WI can be observed, when the cotton samples (GP-Al-AP-6.0, GP-Al-AP-12.0) are finished with an APTES-containing solution. This observation can be explained by the fact that amino groups tend to react with carbonyl moieties to imine groups which act as a chromophore. The carbonyl groups in the cellulosic material are formed due to oxidation reactions at elevated temperatures[28, 29].

3.1.8 Application of Mixed Catalysts

GPTMS in combination with AIP are applied onto cellulosic material to modify the surface properties. Crease resistance and hydrophobicity could be improved. In an attempt to increase the performance of AIP, the addition of TTP and ZTB has also been tested. The results of the physico-mechanical measurements are presented in Table 2. No significant increase in weight gain is observed. This is due to the use of the lower amount of TTP and ZTB. In comparison to GP-Al-2.5, no significant enhancement of the DCRA is detected after addition of TTP and ZTB. The tensile strenght values also attain almost the same level as the raw material. The stiffness is remarkably increased in the case of GP-Al-Zr-2.5. The hydrophobicity as well as the WI are reaching the same level. The findings obtained show that the incorporation of TTP or ZTB does not significantly influence the performance of GPTMS/AIP system.

3.2 Dyeing Properties of Fabrics

Cellulosic samples have been chemically modified by means of the effective crosslinking system GPTMS/AIP. In addition, TTP or ZTB are incorporated to evaluate their capability to act as a catalyst. AIP, TTP as well as ZTB contain a metal atom which can be attached to the cellulosic material. Because metal salts act as mordant in the dyeing process with natural dyes, the GPTMS/metal alkoxide treated fabrics are dyed with anthraquinone-based alizarin. The colorimetric data of the alizarin-dyed fabrics, evaluated in terms of the ΔL*, Δa* and Δb* values, are listed in Table 3. In the CIE Lab space, the a* axis runs from left to right. A color measurement movement in the +a direction depicts a shift toward

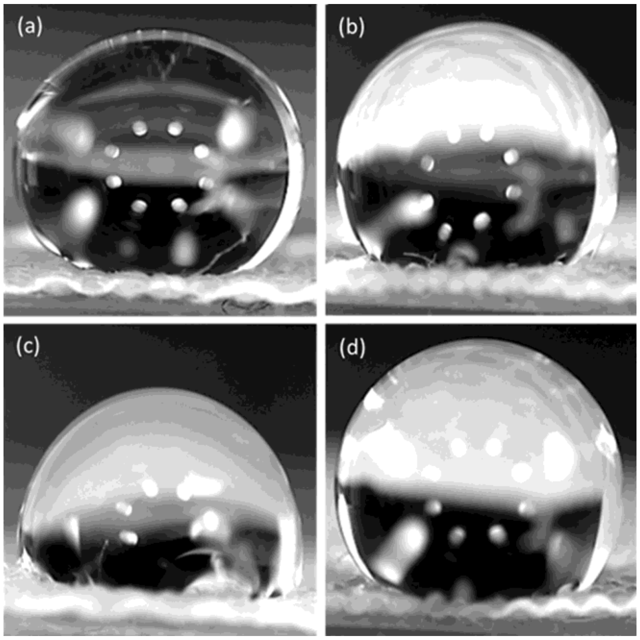

Fig. 3 — Water droplets deposited on (a) GP-Al-2.5, (b) GP-TE-6.0, (c) GP-AP-6.0, and (d) GP-Al-Ti-2.5 for contact angle measurements

Table 3 — Colorimetric data of the alizarin-dyed cotton samples

Code	ΔL*	Δa*	Δb*	ΔE*
GP-Al-2.5	33.1	32.3	12.4	-
GP-Al-5.0	30.9	27.3	12.8	5.5
GP-Al-TE-6.0	36.5	33.6	9.0	5.0
GP-Al-TE-12.0	43.5	31.2	6.1	12.2
GP-Al-AP-6.0	29.0	33.4	10.6	4.6
GP-Al-AP-12.0	38.2	34.4	9.9	6.1
GP-Al-Ti-1.25	38.9	41.6	16.1	11.6
GP-Al-Ti-2.5	37.6	40.4	15.1	9.6
GP-Al-Zr-1.25	27.5	29.8	-2.3	15.9
GP-Al-Zr-2.5	26.5	25.9	-5.2	19.9

ΔE* calculated in relation to GP-Al-2.5.

red. Along the b* axis, +b movement represents a shift toward yellow. The center L* axis shows L = 0 (black or total absorption) at the bottom. At the center of this plane it is neutral or gray[30, 31].

3.2.1 Colorimetric Data

The findings show that an increase in AIP concentration results in almost no change in colorimetric data. The incorporation of TEOS gives rise to an increase in ΔL* value. The addition of APTES causes a moderate change in colorimetric parameters, which is confirmed by the ΔE* values. A significant alteration of the coloristic behavior can be observed in this case, when ZTB is incorporated into the recipe. The ΔL* values are reduced. The same phenomenon can be detected in respect to the Δa* as well as Δb* values. As a consequence, the ΔE values are reaching the highest level.

3.2.2 Color Strength

The relation of absorption and scattering behavior of incident light of an opaque material can be expressed by the Kubelka-Munk equation[32, 33]. Figure 4(a) presents the reflectance spectra of GP-Al-2.5, GP-Al-5.0, GP-Al-TE-6.0, GP-Al-TE-12.0, GP-Al-AP-6.0, and GP-Al-AP-12.0. A comparison of the spectra of GP-Al-2.5 and GP-Al-5.0 makes it evident that the doubling of AIP concentration has no influence on the color strength. The incorporation of 6 mmol TE results in a decrease in *K/S* value. The addition of 12 mmol TE gives rise to a further decrease in the *K/S* value. When 6 mmol APTES are incorporated into the finishing bath an increase in *K/S* value can be observed. The addition of 12 mmol APTES into the finishing bath results in a reduction of the color strength. The incorporation of TEOS and APTES also causes an increase in the wavelength of absorption. Figure 4(b) presents the *K/S* values of GP-Al-Ti-2.5 and GP-Al-Zr-2.5. The color strength of GP-Al-Ti-2.5 is significantly increased.

3.3 FTIR Study

Figure 5 shows the FTIR spectra of GP-Al-5.0, GP-Al-TE-12.0, and GP-Al-AP-12.0. The bands which can be observed in the region 3600 to 3000 cm^{-1} are ascribed to the O-H vibrations. The broad bands at 2890 cm^{-1} are due to the C-H stretching vibrations of the methylene groups. Adsorbed water causes the peak at 1645 cm^{-1}. The C-H wagging vibration mode (in-plane bending) can be seen at 1430 cm^{-1}. The bands at 1364 cm^{-1} and 1312 cm^{-1} are assigned to the C-H bending (deformation stretch) and the CH wagging vibrations, respectively. A noteworthy aspect is that no peak can be observed at 1255 cm^{-1}, indicating that no epoxide ring is present[34]. The bands appearing in the region 1155 cm^{-1} - 900 cm^{-1} are the characteristics of asymmetric stretching vibrations of the bridge C–O–C and the siloxane (Si-O-Si) group.

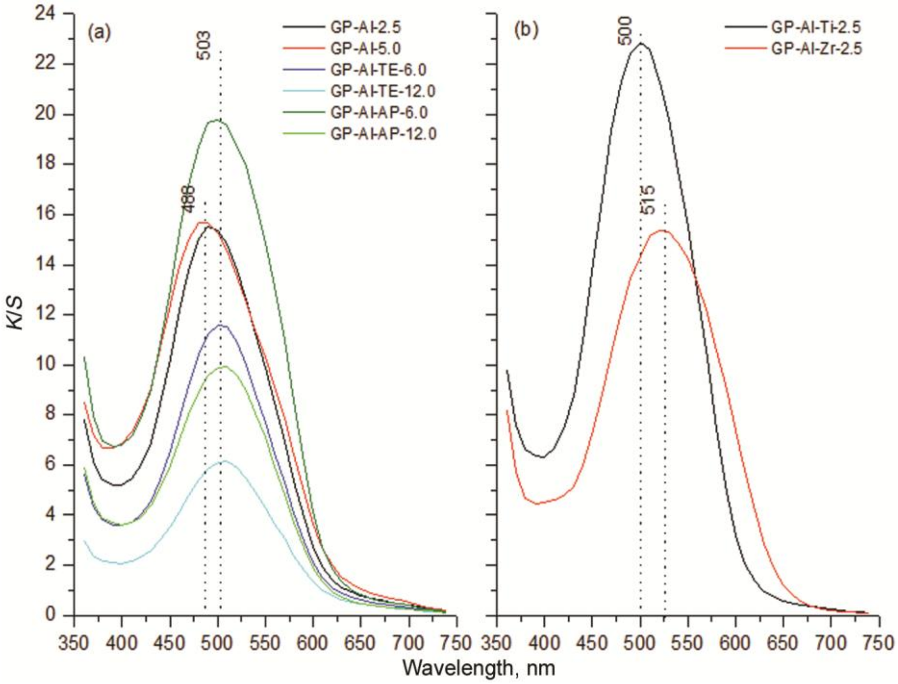

Fig. 4 — Color strength of alizarin-dyed cotton samples

3.4 Morphology

Figure 6 shows the images of raw material, GP-Al-5.0, GP-Al-TE-12.0, and GP-Al-AP-12.0, which have been recorded by means of confocal laser microscopy. In comparison to the raw material, the images clearly make evident that the depositions being attached to the fibre surface can be observed.

3.5 Reaction Mechanism

Figure 7 presents a tentative reaction mechanism. GP **(a)**, AIP **(c)** and TEOS **(e)** are hydrolyzed such forming the corresponding silanol compounds **(b)**, **(f)** and aluminium trihydroxide **(d).** Cotton samples were treated with a mixture of these solutions. Figure 7**(g)** suggests a possible structural arrangement of the reaction products.

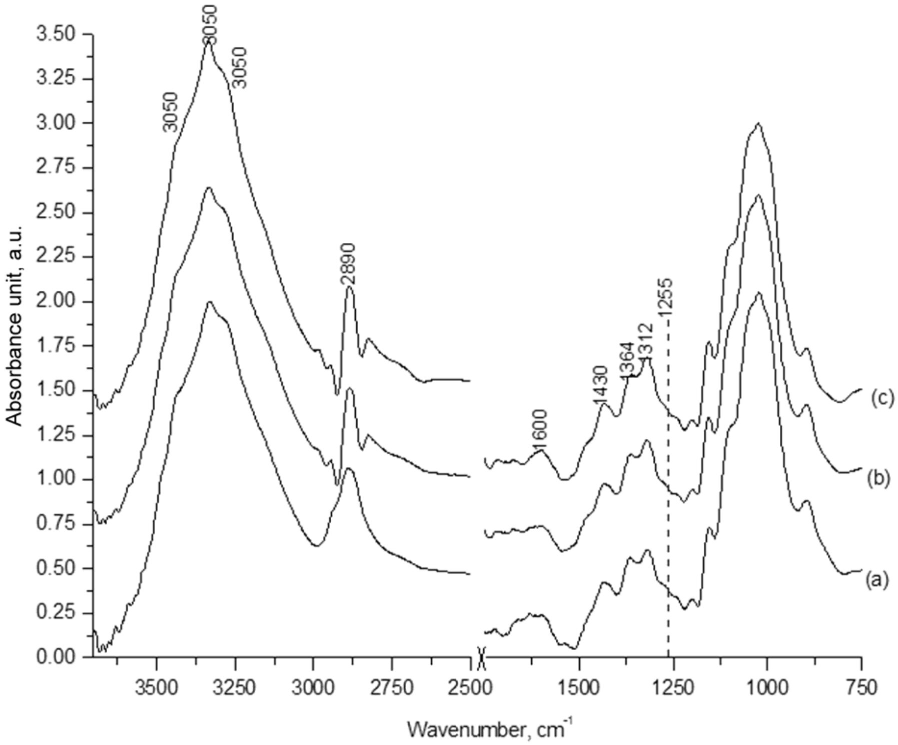

Fig. 5 — FTIR spectra of (a) GP-Al-5.0, (b) GP-Al-TE-12.0, and (c) GP-Al-AP-12.0

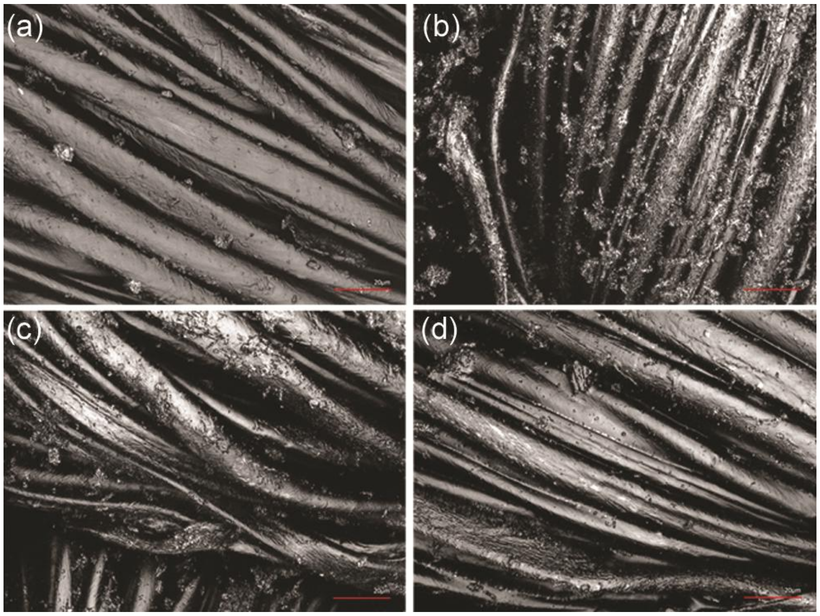

Fig. 6 — Confocal laser microscopy images of (a) raw material, (b) GP-Al-5.0, (c) GP-Al-TE-12.0, and (d) GP-Al-AP-12.0

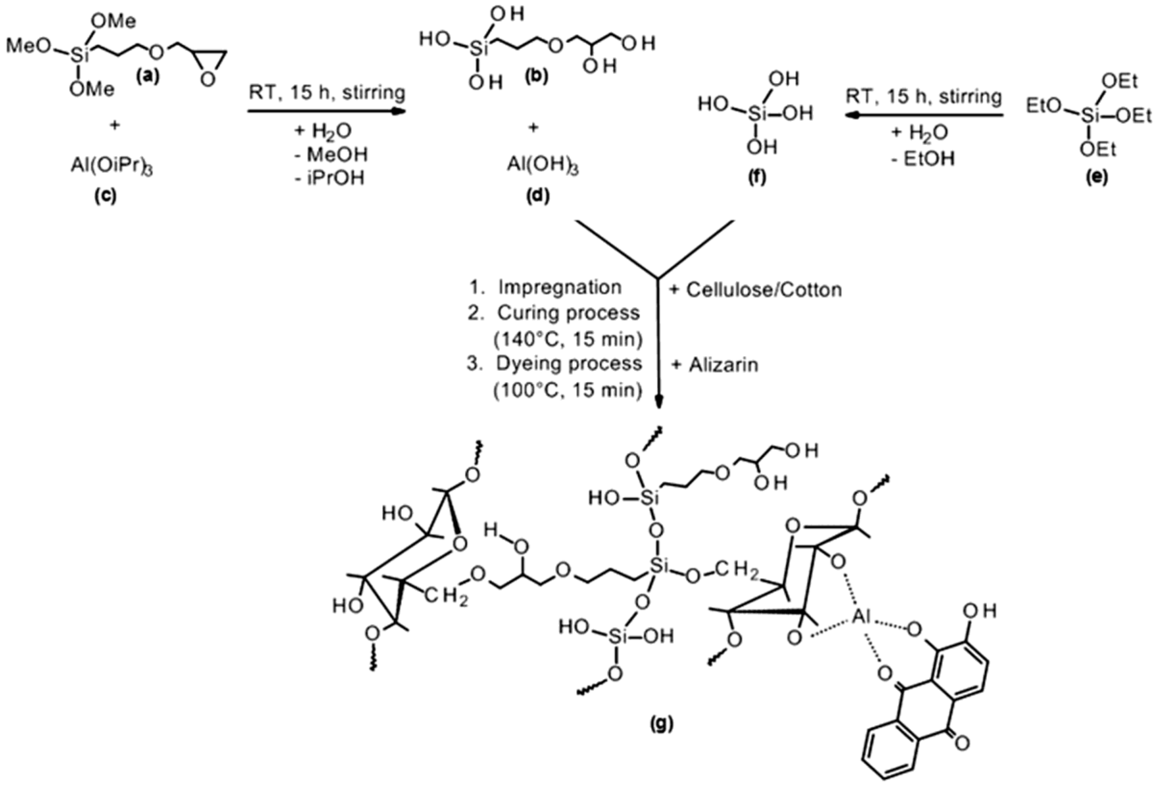

Fig. 7 — Tentative reaction mechanism of GPTMS, AIP and TEOS with cellulosic material (a) GPTMS, (b) hydrolyzed GPTMS, (c) AIP, (d) hydrolyzed AIP, (e) TEOS, (f) hydrolyzed TEOS, and (g) structural arrangement of the reaction products

4 Conclusion

Cotton fabrics were treated with finishing baths containing hydrolysed GPTMS/AIP solutions. As a consequence, the crease resistant properties of the as-treated fabrics are found to improve. To evaluate the influence of addition of TEOS and APTES on the physico-mechanical and dyeing properties of the fabrics, 6 mmol and 12 mmol of TEOS or APTES were added to the GPTMS/AIP-based finishing bath. Combinations of GPTMS/AIP with the metal alkoxides TTP and ZTB are also applied onto cotton fabrics to evaluate the effect on the fabric properties. The results show that TEOS and APTES cause an alteration of the physico-mechanical properties and thus can be used to tune the properties of the finished fabrics. The application of the metal alkoxides TTP and ZTB gives rise to an increase in the color strength.

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References

1 Mahbubul Bashar M & Khan M, *J Polym Environ,* 21 (2013) 181.
2 Horrocks A R & Anand S, Handbook of Technical Textiles (CRC Press/Woodhead Publications, Boca Raton, FL), 2000.
3 Scott R A, Textiles for Protection (CRC Press/Woodhead Publications, Boca Raton, FL), 2005.
4 Brinker C J & Scherer G W, *Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing* (Academic Press, San Diego), 1990.
5 Hench L L & West J K, *Chem Rev,* 90 (1990) 33.
6 Schramm C, Binder W & Tessadri R, *J Sol-Gel Sci Technol,* 29 (2004) 155.
7 Schramm C & Rinderer B, *Cellulose,* 22 (2015) 2811.
8 Brzezinski S, Kowalczyk D, Borak B, Jasiorski M & Tracz A, *J Appl Polym Sci,* 125 (2012) 3058.
9 Brzezinski S, Kowalczyk D, Borak B, Jasiorski M & Tracz A, *Fibres Text East Eur,* 19 (2011) 83.
10 Xu L, Zhuang W, Xu B & Cai Z, *J Text Inst,* 103 (2012) 311.
11 Zhang M & Wang C, *Carbohydr Polym,* 96 (2013) 396.
12 Aksit A C & Onar N, *J Appl Polym Sc,i* 109 (2008) 97.
13 Schramm C & Rinderer B, *Fibers Polym,* 12 (2011) 226.
14 Schweppe H; Handbuch der Naturfarbstoffe (ecomed Verlagsgesellschaft, Landsberg / Lech), 1993.

15 Bechtold T & Mussak R, *Handbook of Natural Colorants* (Wiley, Chichester), 2009.

16 Manian A P, Paul R & Bechtold T, *Color Technol,* 132 (2016) 107.

17 Stalder A F, Kulik G, Sage D, Barbieri L & Hoffmann P, *Colloids Surf, A,* 286 (2006) 92.

18 Huang K S, Hwang M C, Chen J S, Lin S J & Wang S P, *J Text Inst,* 98 (2007) 169.

19 Ghosh T K, Batra S K & Barker R L, *J Text Inst,* 81 (1990) 245.

20 Hu J L, Lo W M & Lo M T, *Text Res J,* 70 (2000) 237.

21 Wenzel R N, *Ind Eng Chem* 28 (1936) 988.

22 Cassie A B D & Baxter S, *Trans Faraday Soc,* 40 (1944) 546.

23 Kwok D Y & Neumann A W, *Adv Colloid Interface Sci,* 81 (1999) 167.

24 Albeck M, Ben-Bassat A, Epstein J A & Lewin M, *Text Res J,* 35 (1965) 836.

25 Albeck M, Ben-Bassat A & Lewin M, *Text Res J,* 35 (1965) 935.

26 Fromageot D, Pichon N, Peyron O & Lemaire J, *Polym Degrad Stabil*, 91 (2006) 347.

27 Urreaga J M & de la Orden M U, *Eur Polym J,* 42 (2006) 2606.

28 Matías M C, De La Orden M U, Sánchez C G & Urreaga J M, *J Appl Polym Sci*, 75 (2000) 256.

29 De La Orden M U, Matías M C & Martínez Urreaga J, *J Appl Polym Sci*, 92 (2004) 2196.

30 Gulrajani M L, *Colour Measurement* (Woodhead Publishing Limited, Cambridge), 2010.

31 Xin J H; *Total Colour Management in Textiles* (Woodhead Publishing Limited, Cambridge), 2006.

32 Convert R, Schacher L & Viallier P, *Text Res J*, 69 (1999) 357.

33 Hongying Yang, Sukang Zhu & Ning Pan, *Text Res J,* 80 (2010) 263.

34 Carboni D, Pinna A, Malfatti L & Innocenzi P, *New J Chem,* 38 (2014) 1635.