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Treatment of 1,3-dimethylol-4,5-dihydroxyimidazolidine-2-one finished cellulosic material with tetraethoxysilane or glycidyloxypropyl-trimethoxysilane solutions

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DMDHEU (dimethyloldihydroxyethylene urea, 1,3-dimethylol-4,5-dihydroxyimidazolidin-2-one)-treated cotton fabrics were coated with hydrolyzed TEOS- or GPTMS-solutions in an attempt to reduce the release of the potential human carcinogen formaldehyde (two stage process). In addition, cotton fabrics were cured with solutions consisting of combinations of DMDHEU and TEOS or GPTMS in a one stage process. ATR-FTIR was used to investigate the coated cotton samples. The formaldehyde release as well as the textile physical properties (dry crease recovery angle, tensile strength, tear strength and whiteness index) of the fabrics were measured. To evaluate the properties of the coating material, pure xerogels of the treatment solutions were produced and tested by means of XRD and solid state ^{29}Si spectroscopy. The findings clearly give evidence that a reduction of the formaldehyde release is obtained when the cotton fabrics were treated with GPTMS-solutions. The hydrolyses of GPTMS in presence of DMDHEU results in a reaction of the epoxide group of GPTMS and the hydroxymethyl group of DMDHEU, consequently no durable press effect could be observed. SEM micrographs revealed that no microporous xerogel was produced when Triton X-100 was incorporated into the sol solution.

1. Introduction

Textile systems are treated with various chemical agents to obtain novel surface properties. For this purpose, numerous chemical or physical procedures are applied in order to fix these chemicals on the fabric. The sol-gel technology has attracted much attention to modify textile materials [1–3]. The sol-gel process is based on the hydrolysis and condensation of metal or semimetal alkoxides, such as tetraethoxysilane (TEOS) or glycidyloxypropyl-trimethoxysilane (GPTMS) (Fig. 1).

The reactions of these silicon alkoxides that are performed at relatively low temperatures (chimie douce) result in the formation of an amorphous three-dimensional silicon oxide network (Fig. 2) [4, 5].

Textile materials can be impregnated with the hydrolyzed metal alkoxide solution. Subsequently, the samples are annealed at a specified temperature. As a result, new or improved surface properties can be obtained.

DMDHEU is the most applied durable press agent that imparts crease resistance and dimensional stability to textile fabrics which consist of cotton or cotton/polyester blends (Fig. 1). However, this finishing reagent tends to continuously release the potential human carcinogen formaldehyde during durable press finishing, subsequent storage of the treated fabric,

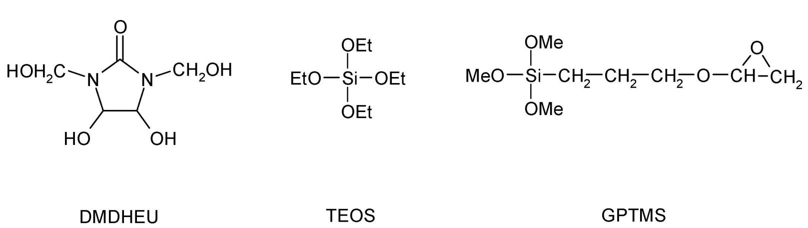

Figure 1 Formaldehyde releasing DMDHEU (1,3-dimethylol-4,5-dihydroxyimidazolidin-2-one) crosslinking agent, and the silicon alkoxide precursor tetraethoxysilane (TEOS) and glycidylpropyloxytrimethoxysilane (GPTMS).

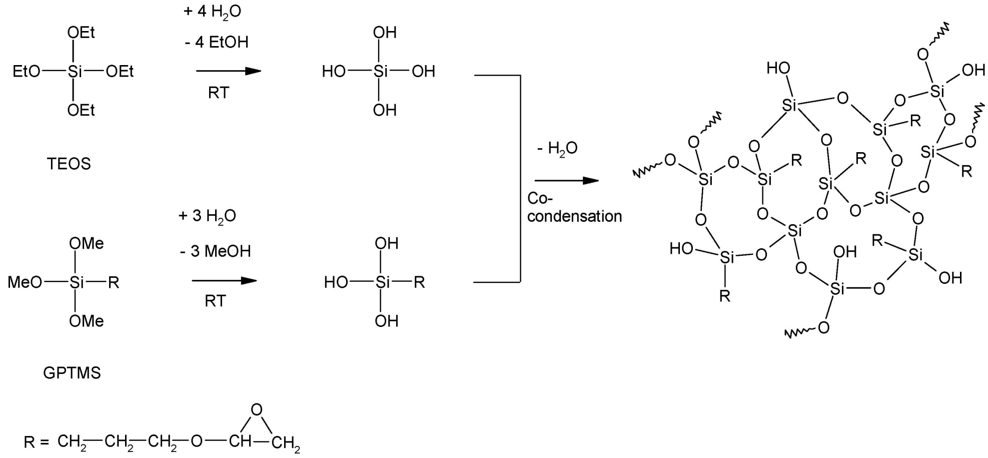

Figure 2 The hydrolysis and co-condensation reaction of TEOS and GPTMS results in the formation of a silicon oxide network.

manufacture of the garment, and finally during use by the consumer. Consequently, numerous attempts were undertaken in order to minimize the release of formaldehyde [6, 7].

The objective of the present paper is to investigate the impact of the sol-gel treatment with TEOS- and GPTMS-solutions on the release of formaldehyde and the on the textile physical performance of the cotton material. In addition, xerogels were prepared containing TEOS or GPTMS in combination with DMDHEU in order to study the properties by means of XRD (X-ray diffraction), ATR-FTIR (attenuated total reflection fourier transform infrared spectroscopy), solid state ^{29}Si MAS NMR (magic angle spinning nuclear magnetic resonance) spectroscopy and SEM (scanning electron microscopy).

2. Experimental

2.1. Materials

Glycidylpropyloxytrimethoxysilane (GPTMS) (98%) was obtained from Aldrich Chemical Company Inc., Milwaukee; USA. Tetraethoxysilane (TEOS) (98%), Triton X-100 (polyoxy-ethylene octyl phenyl ether), and magnesium dichloride hexahydrate $MgCl_2{\cdot}6H_2O$ were supplied from Fluka Chemie GmbH, Buchs, Switzerland. Fixapret CP konz. (DMDHEU solution) was supplied from BASF, Ludwigshafen, Germany.

2.2. Preparation of the silicon alkoxides solutions and the xerogels

2.2.1. Pure TEOS-GPTMS- and DMDHEU solution

The sol solutions for the impregnation of the cotton fabrics as well as for the production of the xerogels were synthesized according to Fig. 3. 11.46 mL (50 mmol) TEOS were hydrolyzed with 3.60 mL (200 mmol) HCl ($c = 0.05$ mol/L) in 15 mL ethanol (EtOH) or deionized water under vigorous magnetic stirring (500 rpm) in a PE beaker for 24 h at room temperature. For the hydrolyses of the GPTMS-solution 11.26 mL (50 mmol) GPTMS and 2.70 mL HCl ($c = 0.05$ mol/L) were used. The DMDHEU solution was prepared by mixing 6.00 g (9.00 g) of DMDHEU solution and 1.80 g (2.70 g) $MgCl_2{\cdot}6H_2O$ in 100 mL of deionized water. Prior to impregnation of the cotton fabrics, the solutions were diluted to 100 mL. For the two stage process these TEOS- or GPTMS-solutions were diluted (1:1 and 1:10 v/v) with EtOH or deionized water. The formulations containing Triton X-100 were prepared by adding 2 mL of the surfactant prior to hydrolysis (TEOS- and GPTMS-solutions) or dilution (DMDHEU solution). In order to produce the xerogels the solvent was removed under reduced pressure and the liquid, thus obtained, was subjected to a thermal treatment (80 and 150°C) for 3 h. Sample identifications are given in Fig. 3 and in the tables.

2.2.2. Mixed solution of TEOS (GPTMS) and DMDHEU

To the aforementioned hydrolyzed TEOS- or GPTMS-solution 6.00 g DMDHEU and 1.80 g $MgCl_2{\cdot}6H_2O$ were added. Vigorous stirring was continued for 4 h at room temperature. Subsequently, the solutions were diluted to 100 mL with ethanol or deionized water.

2.3. Fabric treatment

The pre-weighed cotton fabrics (109 g/cm^2) were impregnated with a treatment bath containing the DMDHEU—or the sol solution. If not otherwise

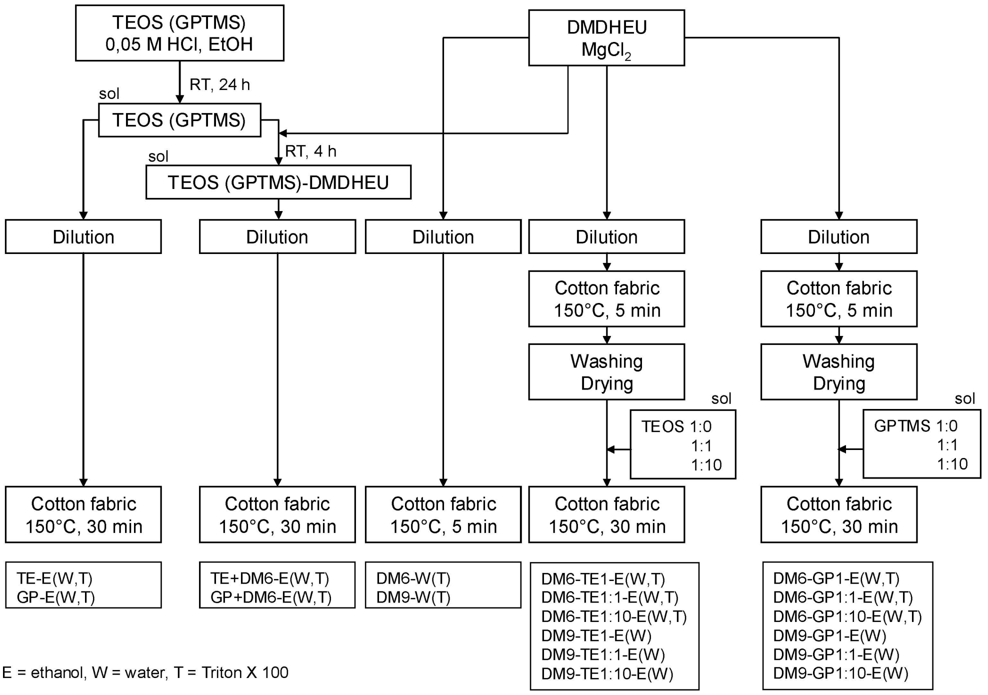

Figure 3 Scheme of the preparation of the sol solutions and of treatment of the cotton fabrics. The sol solution was prepared in ethanol (E), in water (W) or in water containing the surfactant Triton X-100 (T).

stated, no softener was applied. Subsequently, the cotton sample (30 cm × 50 cm) was passed through a two-roll laboratory padder (HVL 500 Mathis AG, Niederhasli, Switzerland; air pressure 1 bar, fabric speed 3 m/min). This treatment gave a wet pickup of about 70–80% weight of fabric (owf). After drying (2 min, 100°C) the fabric was cured for a specified time (3 or 30 min) at 150°C in a labdryer (LTE, W. Mathis AG, Switzerland)—washed with occasional stirring (1 g/L Na_2CO_3, 10 min, 50°C, 1000 mL) and finally dried again (3 min, 80°C).

2.4. Analytical methods

ATR-FTIR spectra of the finished fabrics were recorded with a Bruker Vector 22 spectrometer using an MCT detector. The ATR accessory used was a Miracle. A diamond crystal was applied as internal reflectance element. Single beam spectra were the result of 200 scans. The spectral resolution was 4 cm^{-1}. The absorption spectra of the xerogels were recorded as KBr pellets.

A Bruker-AXS D8 was used for X-ray powder diffraction (parallel beam optics, Cu-target, scintillation counter, sampler changer with rotation). The samples were run with 40 kV, 40 mA, 2–60° theta/2 theta, 0.01° step size and 5 s counting time.

Solid State NMR measurements were performed using a Bruker DRX-400 operating ^{29}Si-nucleus at 79.5 MHz. Powdered samples (about 200 mg) were filled into 4 mm zirconia rotors and spun at 6000 Hz. The measurements were performed using the single-pulse modus with an excitation pulse (^{29}Si) of 1.6 micro seconds. The relaxation time between the pulses was 180 s, which proved sufficient to obtain the necessary signal to noise ratio.

SEM micrographs were recorded with a FEI SEM XL30 ESEM FEG.

2.5. Textile testing methods

Formaldehyde was determined according to Japanese Law 112 in duplicate. The relative standard deviation varies from 0.4 to 3.4%. This colorimetric method allows the determination of any free or liberated formaldehyde in textile materials and is based on the reaction of formaldehyde, that was extracted by means of distilled water, with acetylacetone to form 3,5-diacetyl-1,4-dihydrolutidine which is measured photometrically at 412 nm. Dry crease recovery angle (DCRA) was measured according to ISO 2312: 10 test specimens are creased and compressed under controlled conditions of time and load. After removal of the creasing load the angle formed between the two limbs is measured. The DCRA values render possible the evaluation of a crosslinking reaction between a durable press finishing agent and the cellulosic material (relative standard deviation: 1.1 to 3.7%). Tensile strength was determined according to DIN EN ISO 13934 (relative standard deviation: 2.5 to 7.5%) and tear strength (Elmendorf) according DIN EN ISO 13937 (relative standard deviation: 1.4 to 5.0%). Fabric whiteness measurements were taken three times with the Chroma Meter CR 210 from Minolta, Japan.

3. Results and discussion

The treatment of cellulosic material with hydrolyzed metal alkoxide solutions is an excellent tool to convey new properties to polymer surfaces, particularly if organic components are incorporated into the formulation. To test the impact of TEOS or GPTMS-solutions in combination with DMDHEU on different textile properties cotton fabrics were finished with various amounts of DMDHEU (β = 6 and 9 g/100 mL) and subsequently treated with hydrolyzed TEOS- and GPTMS-solutions of different concentrations. Furthermore, TEOS and GPTMS were hydrolyzed in presence of DMDHEU and the solutions thus obtained were applied to cotton fabrics.

3.1. Application of TEOS- and GPTMS-solutions in ethanol to DMDHEU-treated fabrics

To evaluate the influence of TEOS- and GPTMS-solutions on the release of formaldehyde of DMDHEU-treated fabrics TEOS and GPTMS were hydrolyzed in EtOH under acidic conditions. EtOH was chosen as solvent, since both components the silicon alkoxide as well as water are completely soluble in EtOH. In addition, the DMDHEU-treated cotton samples were impregnated and cured with diluted solutions of TEOS and GPTMS (1:1 and 1:10 v/v) to study the change of the effectiveness in relation to the concentration of the hydrolyzed silicon alkoxide. Furthermore, DMDHEU was combined with TEOS and GPTMS prior to the hydrolysis reaction in order to investigate possible interactions of TEOS or GPTMS with DMDHEU. As can be seen in Fig. 4 the hydroxyl groups of DMDHEU can react with the hydroxyl groups of the cellulose (Fig. 4b) or $\mathrm{Si(OH)}_n(\mathrm{OEt})_{4-n}$ or $\mathrm{R\text{-}Si(OH)}_n(\mathrm{OMe})_{3-n}$ (Fig. 4e) during the condensation process thus forming C—O—Si bonds. The epoxide group of GPTMS also can react with the hydroxyl groups of DMDHEU (Fig. 4d). This reaction is catalyzed by basic compounds [8, 9]. In addition, possible hydrogen bridge bonding may be formed (Fig. 4c). In addition the formation of poly(ethylene) oxide must be taken into considerations (Fig. 4f) as well as the reaction of the cyclic epoxide group with GPTMS (Fig. 4a). All these interactions may lead to a decrease of the formaldehyde release. Cotton fabrics were treated with the pure chemicals TEOS, GPTMS and DMDHEU for comparison purposes.

The results are listed in Table I. Concerning the formaldehyde emission the raw material as well as those cotton fabrics that had been treated with the pure chemicals (*TE-E*, *GP-E*) are containing no formaldehyde. *DM6-E* and *DM9-E* were not included in this investigation, because DMDHEU is normally applied in aqueous media. *DM6-W* and *DM9-W* show values which are expected under the curing conditions given. When *DM6-W* was treated with different TEOS-solution no change of the amount of released formaldehyde can be observed. In contrary, the treatment with different GPTMS-solutions results in a remarkable decrease of released formaldehyde. As expected, an increase of the portion of DMDHEU from $\beta = 6$ g/100 mL to 9 g/100 mL causes an increase of the formaldehyde emission. The application of GPTMS, however, also gives rise to a reduction of the formaldehyde values. This phenomenon can be explained on the bases of the fact that the epoxy group reacts with the N-methylol groups of DMDHEU that are linked to the cellulosic material via a single linkage as shown in Fig. 4d. Consequently, the liberation of formaldehyde is decreased.

DCRA is reduced when *DM6-W* is finished with TEOS-solutions, whereby an increase of dilution results in an increase of DCRA. When GPTMS was used a remarkable improvement of DCRA can be observed. These findings give evidence that GPTMS forms a poly(ethylene)oxide (Fig. 4e) or crosslinks the cellulose chains via a ring opening of the epoxide groups (Fig. 4f). In this case DMDHEU may function as basic catalyst. Similar tendencies can be observed for those cotton samples which were treated with DMDHEU ($\beta = 9$ g/100 mL). A comparison of the tensile strength indicates that no significant changes take place. Compared to the GPTMS-treated fabrics the application of TEOS causes a higher decrease of the tear strength. With respect to the whiteness index (WI) one can note that the additional coating process with TEOS or GPTMS results in a decrease of the WI, whereby the values of the GPTMS-treated fabrics are lower than those of the TEOS-treated samples.

TABLE I Formaldehyde emission and textile physical properties of cotton fabrics that were treated with TEOS- GPTMS nanosol solutions prepared in EtOH

	β(DMDHEU) (g/100 mL)	Sample ID	Formaldehyde (μg/mg)	DCRA (w + f)[a](°)	Tensile strength (%)	Tear strength (%)	WI
Raw material			0.1	191	100.0	100.0	63.6
TEOS		TE-E	5.4	170	102.8	78.1	57.3
GPTMS		GP-E	1.2	216	107.4	124.8	54.8
DMDHEU	6.0	DM6-W	73.9	254	83.0	86.7	59.1
	9.0	DM9-W	126.1	274	85.2	78.1	60.6
DMDHEU → TEOS	6.0	DM6-TE1-E	74.2	234	79.6	51.4	56.0
DMDHEU → TEOS 1:1	6.0	DM6-TE1:1-E	77.8	246	79.6	54.3	56.9
DMDHEU → TEOS 1:10	6.0	DM6-TE1:10-E	69.2	252	77.0	60.0	57.0
DMDHEU → GPTMS	6.0	DM6-GP1-E	35.0	279	84.3	77.1	51.0
DMDHEU → GPTMS 1:1	6.0	DM6-GP1:1-E	37.6	285	81.9	76.2	52.3
DMDHEU → GPTMS 1:10	6.0	DM6-GP1:10-E	37.6	289	80.0	73.3	55.6
DMDHEU → TEOS	9.0	DM9-TE1-E	100.7	255	77.6	40.0	56.3
DMDHEU → TEOS 1:1	9.0	DM9-TE1:1-E	94.5	255	75.3	46.7	56.8
DMDHEU → TEOS 1:10	9.0	DM9-TE1:10-E	87.4	271	75.0	54.3	56.9
DMDHEU → GPTMS	9.0	DM9-GP1-E	52.1	308	78.0	66.7	50.4
DMDHEU → GPTMS 1:1	9.0	DM9-GP1:1-E	49.4	295	72.7	63.8	52.4
DMDHEU → GPTMS 1:10	9.0	DM9-GP1:10-E	53.3	300	75.7	61.0	51.9
TEOS + DMDHEU	6.0	TE+DM6-E	72.5	281	62.5	36.8	64.7
GPTMS + DMDHEU	6.0	GP+DM6-E	32.2	214	101.3	83.2	61.4

[a] Warp and fill.

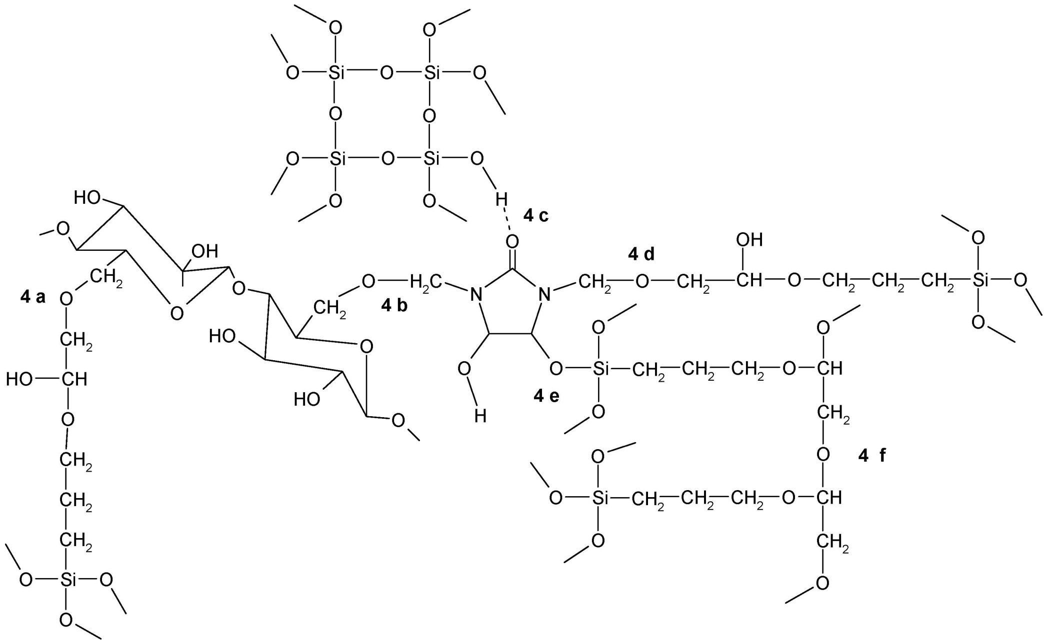

Figure 4 Possible interactions of TEOS and GPTMS with DMDHEU during the condensation and annealing process.

To evaluate the performance of the sol solution that contained both TEOS or GPTMS and DMDHEU, *TE + DM6-E* and *GP + DM6-E* were prepared by adding 6 g of DMDHEU to the hydrolyzed TEOS or GPTMS-solution. The results are listed in Table I. The formaldehyde values are reaching the same level as *DM6-TE1-E* and *DM6-GP1-E*. The DCRA value of *TE + DM6-E* shows excellent durable press properties (218°), whereas the value of *GP + DM6-E* (214°) is solely reaching the level of raw material. These findings clearly give evidence that no reaction occurs between the reactive groups of TEOS and DMDHEU during the hydrolysis step and the annealing procedure. Consequently, DMDHEU can crosslink with the cellulosic material. Furthermore, it can be concluded that the epoxide group of GPTMS preferably reacts with the hydroxyl groups of DMDHEU as shown in Fig. 4d. This assumption is additionally supported by Fig. 5 that demonstrates the FTIR spectra obtained from a GP-E (Fig. 5a) and a *GP + DM6-E* solution (Fig. 5b) which were stirred for 4 h at ambient temperature. The stretching vibration ν C—O—C of the epoxide ring at 910 cm^{-1} is still visible in Fig. 5a, whereas the analogous band completely disappears in Fig. 5b indicating the opening of the epoxide ring. The absorption band at 1707 cm^{-1} is ascribed to ν *C=O* of DMDHEU.

Fig. 6 shows the ATR-FTIR spectra of the raw material (Fig. 6a), *DM6-W* (Fig. 6b), *TE-E* (Fig. 6c), *DM6-TE1-E* (Fig. 6d) and *TE + DM6-E* (Fig. 6e). A comparison of the spectra reveals that those of the sol-treated fabrics are very similar to the spectra of the raw material. The bands in the range of 1500 to 1200 cm^{-1} can be ascribed to various stretching vibrations of ν_{as} Si—O—Si and ν_s Si—O—Si as well as ν C—O.

In Fig. 6b and 6d the stretching vibration of the carbonyl bond in DMDHEU can be observed at 1705 cm^{-1}. This frequency is increased in the case of *DM6 + TE-E* (Fig. 6e). The ν C=O of DMDHEU,

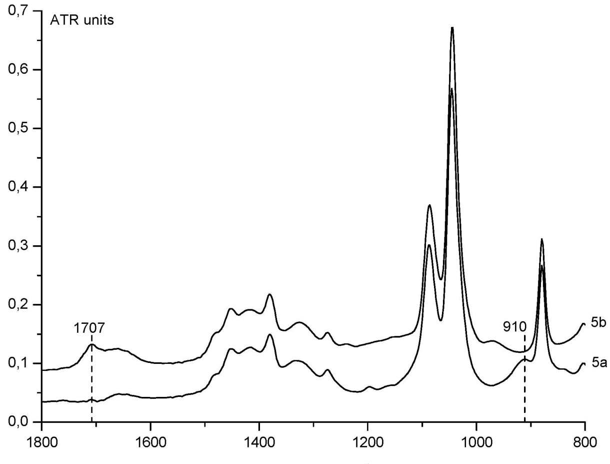

Figure 5 FTIR of the precursor solution of GP-E (5a) and GP+DM6 (5b) after 24 h in deionized water.

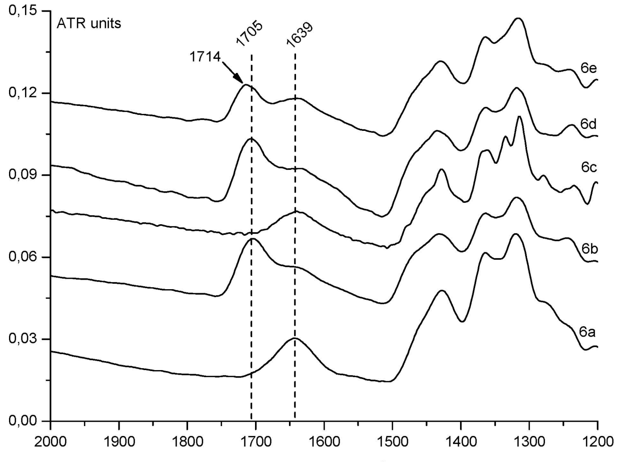

Figure 6 ATR-FTIR spectra of cotton raw material (6a), DM6-W (6b), TE-E (6c), DM6−TE-E (6d), and TE+DM6-E (6e).

however, in an aqueous solution (1 mL DMDHEU in 1 mL water, liquid plate insert for ATR) lies at 1690 cm^{-1} (spectrum not shown). This indicates a stronger interaction of DMDHEU with the silica gel network. The absorption band at 1639 cm^{-1} is due to the δ (H—O—H) vibration of adsorbed water.

The ATR-FTIR spectra of *DM6+GP1-E* (not shown) showed almost the same spectrum as *DM6+TE1-E* (Fig. 6e). The absorption of ν C=O is visible at 1706 cm^{-1}, but neither the absorption band at 910 cm^{-1} (ν C—O—C of the epoxide ring) nor the absorption band at 3050 cm^{-1} (ν C—H of the epoxide ring) can be observed. This may be due to the fact that nitrogen-containing organic compounds serve as catalysts in the ring opening reaction of epoxides, and as a result the epoxide ring was converted to glycolic groups [8, 9]. Furthermore, a shift of the ν C=O from 1706 to 1714 cm^{-1} is also evident for *DM6-GP1-E.*

3.2. Application of aqueous TEOS- and GPTMS-solutions to cotton fabrics

Alcohols are the preferred solvents for the hydrolysis of metal alkoxides since both reagents, the alkoxide precursor as well as water are completely soluble. However, ethanol is flammable (12°C), and therefore should be avoided in a technical process. Thus, the nanosol solutions were prepared in an aqueous solution under vigorous stirring. The findings are shown in Table II. Compared to the results in Table I the formaldehyde values are remarkably reduced when the DMDHEU-treated fabrics were coated with TEOS. The GPTMS-finished cotton samples show a moderate decrease. Similar effects are observed for the samples that were finished with DMDHEU ($\beta = 9$ g/100 mL). The values of the DCRA are reaching nearly the same level or are somewhat lower. A comparison of the tensile strength and the tear strength reveals that no significant change is obtained. The same tendency is true for the WI values.

3.3. Application of aqueous TEOS-, GPTMS-solutions in combination with DMDHEU and Triton X-100 to cotton fabrics

Several investigations have demonstrated that the incorporation of a surfactant into a precursor solution significantly influences the structure of the metal alkoxide network [10, 11]. This procedure renders possible the formation of mesoporous materials therefore, the impact of the non-ionic surfactant Triton X-100 on the formaldehyde release and on the textile physical properties was investigated. The findings presented in Table III demonstrate that the emission of formaldehyde was dramatically increased when Triton X-100 was present during the hydrolysis process of TEOS and GPTMS. In addition, all cotton fabrics (*DM6-TE1-T, DM6-GP1:10-T, DM6-GP1:10-T*) that were treated by means of a two step process show almost identical values of formaldehyde release. The application of GPTMS does not result in a reduction of these values. However, *TE+DM6-T* as well as *GP+DM6-T* gives rise to a decrease of the formaldehyde emission.

The values of the textile physical properties (DCRA, tensile strength, tear strength, WI) show no remarkable alterations compared to the cotton samples whose sol solutions were prepared either in ethanol (Table I) or in deionized water (Table II). The DCRA of *GP+DM6-T* does not indicate any improvement. Tensile strength as well as tear strength are solely slightly reduced compared to raw material. These data unambiguously reveal that a reaction occurs between the epoxide group of GPTMS and the hydroxymethyl group of DMDHEU during the hydrolysis step.

TABLE II Formaldehyde emission and textile physical properties of cotton fabrics that were treated with TEOS- GPTMS nanosol solutions prepared in deionized water

	β(DMDHEU) (g/100 mL)	Sample ID	Formaldehyde (μg/g)	DCRA (w + f)[a](°)	Tensile strength (%)	Tear strength (%])	WI
Raw material			0.0	191	100.0	100.0	63.6
TEOS		TE-W	6.9	186	101.8	81.0	57.9
GPTMS		GP-W	6.1	214	98.2	85.7	48.8
DMDHEU	6.0	DM6-W	63.9	254	83.0	86.7	59.1
	9.0	DM9-W	126.1	274	85.2	78.1	60.6
DMDHEU → TEOS	6.0	DM6-TE1-W	41.2	251	77.7	58.1	55.5
DMDHEU → TEOS 1:1	6.0	DM6-TE1:1-W	45.4	257	82.0	61.9	53.3
DMDHEU → TEOS 1:10	6.0	DM6-TE1:10-W	39.7	273	73.5	74.3	54.6
DMDHEU → GPTMS	6.0	DM6-GP1-W	36.8	272	41.0	68.4	48.3
DMDHEU → GPTMS 1:1	6.0	DM6-GP1:1-W	30.2	280	82.0	61.2	42.8
DMDHEU → GPTMS 1:10	6.0	DM6-GP1:10-W	30.9	277	75.3	74.3	53.6
DMDHEU → TEOS	9.0	DM9-TE1-W	67.6	247	63.0	51.4	57.0
DMDHEU → TEOS 1:1	9.0	DM9-TE1:1-W	59.3	253	67.9	53.3	57.2
DMDHEU → TEOS 1:10	9.0	DM9-TE1:10-W	60.3	261	65.7	65.7	51.3
DMDHEU → GPTMS	9.0	DM9-GP1-W	49.4	269	64.3	59.0	51.3
DMDHEU → GPTMS 1:1	9.0	DM9-GP1:1-W	43.0	285	94.7	67.6	53.5
DMDHEU → GPTMS 1:10	9.0	DM9-GP1:10-W	56.6	283	88.0	75.2	56.5
TEOS + DMDHEU	6.0	TE+DM6-W	106.9	289	39.8	41.6	61.5
GPTMS + DMDHEU	6.0	GP+DM6-W	69.2	223	100.7	84.0	56.2

[a] Warp and fill.

TABLE III Formaldehyde emission and textile physical properties of cotton fabrics that were treated with TEOS- GPTMS nanosol solutions prepared in deionized water and Triton X-100

	Sample ID	Formaldehyde (μg/mg)	DCRA (w + f)[a](°)	Tensile strength (%)	Tear strength (%)	WI
Raw material		0.1	191	100.0	100.0	63.6
TEOS	TE-T	0.3	154	95.9	75.4	55.1
GPTMS	GP-T	1.0	276	85.4	77.0	53.2
DMDHEU[b]	DM6-T	79.0	282	62.1	68.9	67.6
DMDHEU → TEOS	DM6-TE1-T	174.6	276	73.4	59.8	58.8
DMDHEU → TEOS 1:1	DM6-TE1:1-T	163.3	275	67.5	61.5	58.3
DMDHEU → TEOS 1:10	DM6-TE1:10-T	172.1	270	71.4	56.6	58.8
DMDHEU → GPTMS	DM6-GP1-T	168.0	307	75.5	76.2	45.0
DMDHEU → GPTMS 1:1	DM6-GP1:1-T	156.9	292	73.4	71.3	53.0
DMDHEU → GPTMS 1:10	DM6-GP1:10-T	176.2	289	67.7	73.0	52.6
TEOS + DMDHEU	TE+DM6-T	87.5	280	51.0	44.8	64.3
GPTMS + DMDHEU	GP+DM6-T	55.2	204	95.7	84.8	57.5

[a]Warp and fill, [b]b(DMDHEU) = 6.0 g/100 mL.

3.4. Investigation of the xerogels

When the cotton fabric is impregnated with a sol solution the wet pick up is about 70% owf. After the drying and annealing process the add-on is about 5% owf. This amount of xerogel on fabric is too less in order to conduct additional analytical measurements. Therefore, the pure xerogels have been prepared in ethanol, in deionized water and in deionized water with Triton X-100.

The synthesis of the xerogels *TE, GP, TE + DMx* ($x = 6, 9, 12$), and *GP + DM6* in ethanol as well as in water resulted in the formation of almost transparent solids. Xerogel *TE-E* and *TE-W* are very brittle, whereas *TE+DM6-E* shows no crack formation during condensation at room temperature (Fig. 7a). This fact lends support to the assertion, that DMDHEU acts as drying control chemical additive (DCCA). DCCA, such as formamide, dimethylformamide etc., change the structure of the xerogel via complex mechanisms, thus preventing the formation of cracks [12]. The incorporation of Triton X-100 into *TE+DM6* (*TE+DM6-T*) furnished a white opaque solid (Fig. 7b). The SEM micrographs of *TE+DM6-E* (Fig. 7c) and *TE+DM6-T* (Fig. 7d) indicate that no micropores were produced.

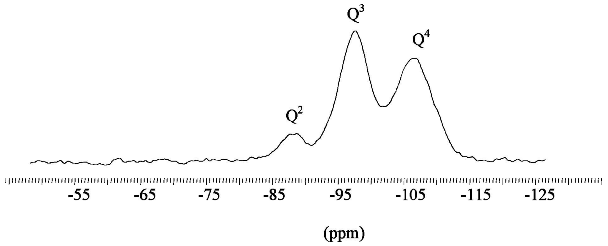

Figure 8 ^{29}Si CP-MAS NMR spectrum of TE+DM6-W (TEOS, 6 g/100 mL DMDHEU in deionized water).

3.4.1. Solid state ^{29}Si MAS measurements of the xerogels

Fig. 8 shows the spectra of *TE+DM9-W*. The peak at -86 ppm can be attributed to $\underline{\text{Si}}(\text{OSi})_2(\text{OR})_2$ (R = H,

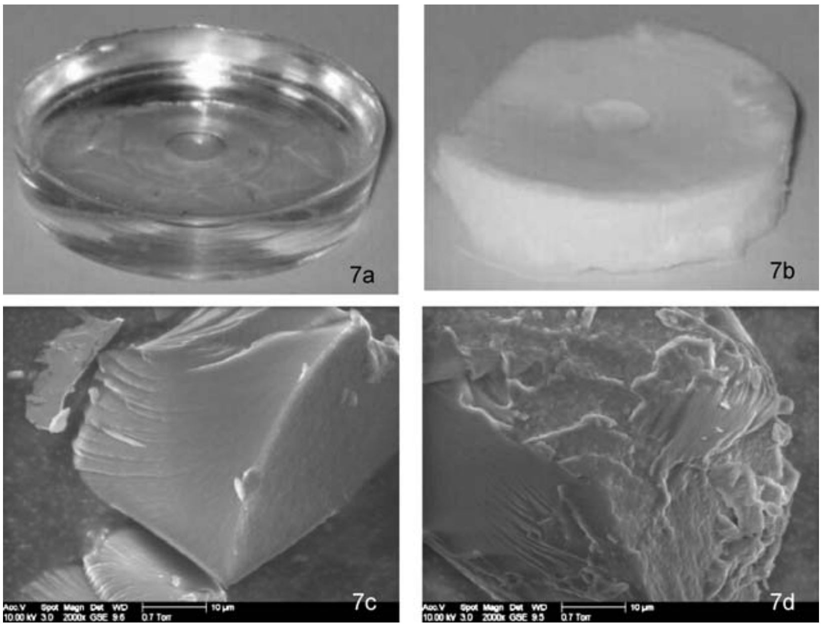

Figure 7 Xerogel of TE+DM6-E (7a) and TE+DM6-T (7b). The corresponding SEM micrographs are shown in (7c) and (7d).

TABLE IV

	b(DMDHEU) (g/100 mL)	Denotation	Line width Q^2 (Hz)	Line width Q^3 (Hz)	Line width Q^4 (Hz)	Relative intensity Q^2	Relative intensity Q^3	Relative intensity Q^4
TEOS		TE-W	220	507.0	610	1.0	9.6	6.3
TEOS + DMDHEU	6	TE+DM6-W	248	483.0	470	1.0	6.9	5.2
	9	TE+DM9-W	253	487.0	581	1.0	4.6	3.7
	12	TE+DM12-W	235	470.0	610	1.0	5.7	4.3

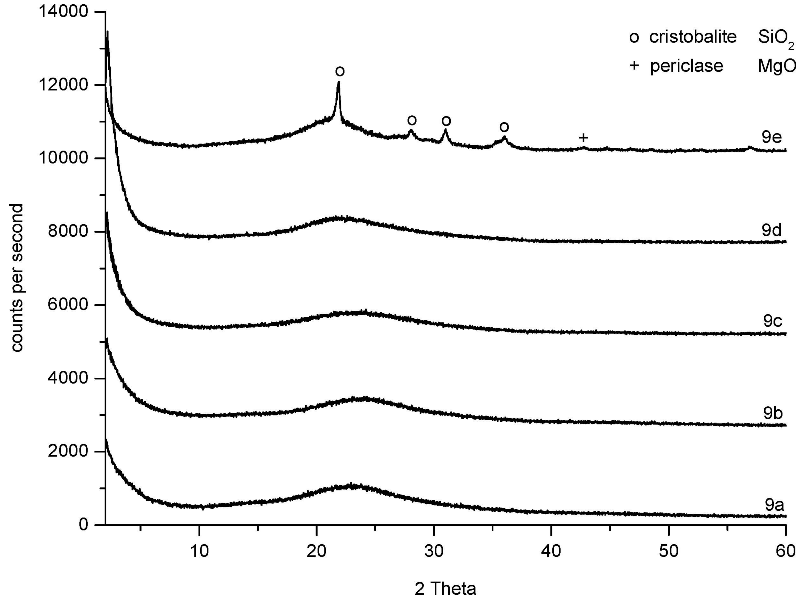

Figure 9 XRD patterns of TE+DM6-W annealed at various temperatures 150°C (9a), 250°C (9b), 500°C (9c), 750°C (9d) and 1000°C (9e).

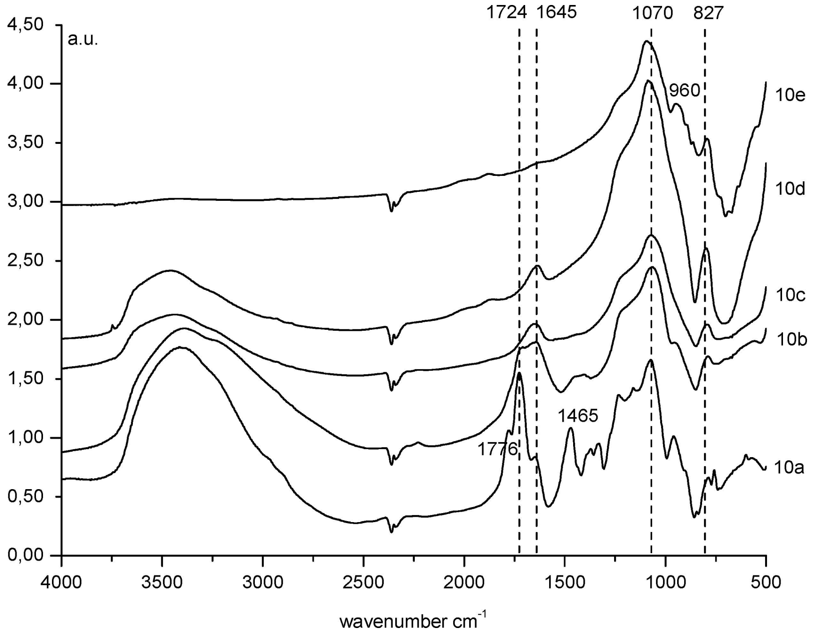

Figure 10 ATR-FTIR spectra of TE+DM6-W annealed at various temperatures 150°C (10a), 250°C (10b), 500°C (10c), 750°C (10d) and 1000°C (10e).

—CH_2—) moieties (Q^2). The signal that is observed at −97 ppm can be ascribed to $\underline{Si}(OSi)_3(OR)$ (R = H, —CH_2—)-moieties (Q^3) while the peak at −106 ppm. are attributed to $Si(OSi)_4$ (Q^4)-moieties.

Table IV shows the line widths and the relative intensities of the signals of *TE−W*, *TE+DM6-W*, *TE+DM9-W* and *TE+DM12-W*. The incorporation of DMDHEU only results in slight changes of the line width indicating a weak interactions between the silicon oxide cluster and DMDHEU. These findings were also found, when aldehydes were used as additives [13].

3.4.2. XRD measurements of the xerogels

DMDHEU is used as crosslinking agent for cellulosic materials in combination with magnesium dichloride hexahydrate as an appropriate catalyst. Therefore, this salt was incorporated in all formulations that contained DMDHEU. $MgCl_2·6H_2O$ dehydrates beyond 116°C to $MgCl_2·4H_2O$. The latter decomposes hydrolytically to MgO beyond 240°C. *TE+DM6-W* was annealed at various temperatures. The corresponding X-ray patterns: 150°C (Fig. 9a), 250°C (Fig. 9b), 500°C (Fig. 9c), 750°C (Fig. 9d) and 1000°C (Fig. 9e) are shown in Fig. 9. Fig. 9a–d indicate that no magnesium salts can be detected. Various peaks are observed when the *TE+DM6-W* samples were annealed at 1000°C for 3 h (Fig. 9c). The peaks can be assigned to cristobalite (high temperature form of quartz) and to some extent to periclase (MgO).

Fig. 10 shows the ATR-FTIR spectra of the *TE+DM6-W* annealed at temperatures mentioned above: 150°C (Fig. 10a), 250°C (Fig. 10b), 500°C (Fig. 10c), 750°C (Fig. 10d) and 1000°C (Fig. 10e). A comparison of the spectra in the region of 3600 to 3000 cm^{-1} reveals that the stretching vibrations of Si—OH, C—OH and H_2O are decreasing continuously as the temperature is increased. At 1000°C no band can be observed indicating that the organic components had been eliminated. The ν C=O vibrations of DMDHEU (1724 cm^1) disappears completely when the xerogel was annealed at 500°C indicating that the organic component was eliminated. The band at 1645 cm^{-1} (δ H—O—H adsorbed, SiO—H) also decreases with increase of temperature. This band disappears at 1000°C (Fig. 10e). The ν_s Si—O—Si at 1070 cm^{-1} is visible in all spectra. The absorption band at 960 cm^{-1} can be ascribed to the stretching vibration of ν Si—O.

4. Conclusions

Cotton fabrics were impregnated with the formaldehyde-releasing durable press finishing agent DMDHEU. To reduce the emission of formaldehyde the DMDHEU-treated cellulosic material was impregnated with nanosol solutions containing either TEOS or GPTMS in various concentrations. In addition the nanosol solutions were prepared in ethanol or deionized water or in an combination of deionized water and Triton X-100. Furthermore, raw cotton samples were treated with TEOS- or GPTMS-solutions containing DMDHEU.

When TEOS- or GPTMS solutions were applied to DMDHEU-treated fabrics in two steps no significant changes could be obtained in the case of TEOS, whereas the application of hydrolyzed GPTMS solutions resulted in a remarkable decrease of the formaldehyde release as well as in an enhancement of the DCRA values. The combination of the TEOS-solutions with DMDHEU gave rise to excellent durable press properties, whereas in the case of GPTMS only poor values were obtained indicating that GPTMS and DMDHEU undergo a reaction during the hydrolysis process.

When the same experimental runs were performed in aqueous solution the release of formaldehyde could be improved.

The incorporation of Triton-X 100 resulted in a significant increase of the formaldehyde emission of the DMDHEU-treated fabric samples.

The investigation of the xerogels by means of SEM demonstrates that DMDHEU acts as DCCA. The incorporation of Triton X 100 into the formulations results in the formation of an opaque material. Solid state ^{29}Si-MAS NMR spectra indicate a weak interactions between the silicon oxide and DMDHEU. XRD spectra support the assumption that MgO is produced during the annealing process at 1000°C.

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