

Formaldehyde-free curing of cotton cellulose fabrics in anhydrous media

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ABSTRACT: The effect of formaldehyde-free curing on standard cotton cellulose fabrics in anhydrous media is studied. Different crosslinkers are applied via (1) a pad-cure-dry process (solid/liquid) and (2) in a vapor chamber (solid/gas). The performance of each crosslinker and set of conditions is assessed by measuring dry crease recovery angles, DCRA. We find that in control samples (treatment without crosslinker) the DCRA are altered depending on the solvent. Using DMF, carbonyldiimidazole shows the best DCRA (160.1°, 15° higher than the non-treated fabrics). In ethyl acetate, triglycidyl isocyanurate shows the highest DCRA (22° higher than the control). The most promising crosslinkers are applied with selected catalysts known from literature. Here, triglycidyl isocyanurate in combination with the superbase P4-*t*-Bu gives the best DCRA (35° higher than the control). Using the vapor-chemical finishing, divinylsulfone as crosslinker increases the DCRA to 162.7° (18° higher than non-treated fabrics). Hence, cotton cellulose fabrics can be successfully finished in anhydrous conditions. © 2019 The Authors. *Journal of Applied Polymer Science* published by Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2019**, 136, 48371.

Received 7 December 2018; accepted 21 July 2019

DOI: 10.1002/app.48371

INTRODUCTION

Textiles play an indispensable role in our everyday life and depending on the requirements are finished with non-slipping, antibacterial, antistatic, anti-pilling, flame-retardant, soil-repellent, or simply softening properties.¹ Yet, the most basic problems that are to be prevented with cellulosic cotton fabrics are wrinkling and shrinkage. Both phenomena occur due to the breaking of hydrogen bonds and swelling of the cellulosic fibers during a laundering process. To reduce these effects, cellulosic fibers are covalently crosslinked.² In the beginning of the 20th century, formaldehyde was introduced to the market as crosslinker converting free cellulosic hydroxyl groups into acetals.^{3–5} However, due to its toxicity it was soon replaced by urea-based crosslinkers, which showed equally good anti-creasing effects but reduced formaldehyde releases.⁶ In a pre-condensation step, urea is reacted with excess of formaldehyde to give hydroxymethyl-ureas **1** with a maximum of four hydroxymethyl groups installed (Scheme 1). The latter are now susceptible for condensation with cellulosic hydroxyl groups [Scheme 2(a)].⁷ As an alternative, melamine is hydroxymethylated with up to 6 mol of formaldehyde to deliver methylol-melamine derivatives of **2** (Scheme 1). Most commonly, trimethylol melamine **2a** and hexamethylol melamine **2b** (HMM) have been used in textile finishes. Compounds **1** and **2** are aminoplasts, since they serve as crosslinkers between adjacent polysaccharide chains and are able to self-condensate. This self-condensation results in intertwining polymer networks of aminoplasts and cellulose

chains adding higher stiffness to the fabric.⁸ In the 1950s, aminoplast crosslinkers were increasingly replaced by reagents based on cyclic ureas, as aminoplasts suffer from short shelf-life and the formaldehyde release in a moist atmosphere was still too high. The first developed cyclic urea is dimethylol ethylene urea **3a** (for X = H, Scheme 1).^{9,10} Due to its cyclic structure, the formaldehyde release is inhibited, at the same time the wrinkle recovery is increased with only marginal losses of mechanical strength of the fabrics. MgCl₂ or Zn(NO₃)₂ have been used as catalysts in the curing process.^{11,12} Further research in the field yielded dimethylol dihydroxyethyleneurea **3b** (DMDHEU, for X = OH, Scheme 1)^{13,14}—which has been applied in several processing methods^{15–17}—and dimethylol dimethoxyethyleneurea **3c** (X = OMe, Scheme 1).^{13,18} Though these surrogates are slightly less reactive, the formaldehyde release upon treatment of the fabrics is reduced to a minimum.^{18,19}

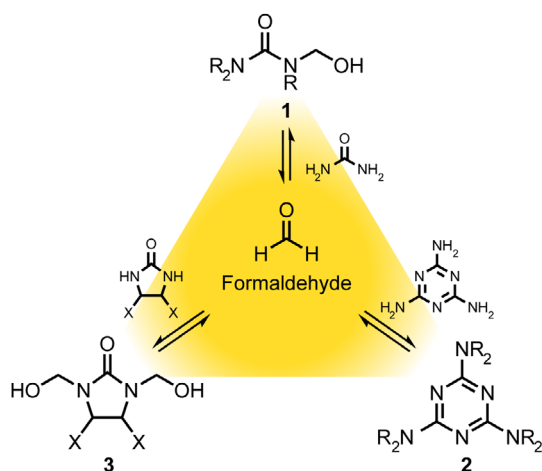
Up to now, it has been an ongoing challenge to completely cut the cord to formaldehyde-based curing agents for durable press finishes.²⁰ Additionally in 2014, formaldehyde has been reclassified as a carcinogen category 1B in the European Union leading to more stringent regulations and formaldehyde thresholds.²¹

In several studies, mostly combinations of ethylene ureas **3** and other crosslinking reagents are used to reduce cost and maintain efficiency of the procedures simultaneously reducing the formaldehyde release to a lowest possible level.^{22–25} Formaldehyde-free textile finishes

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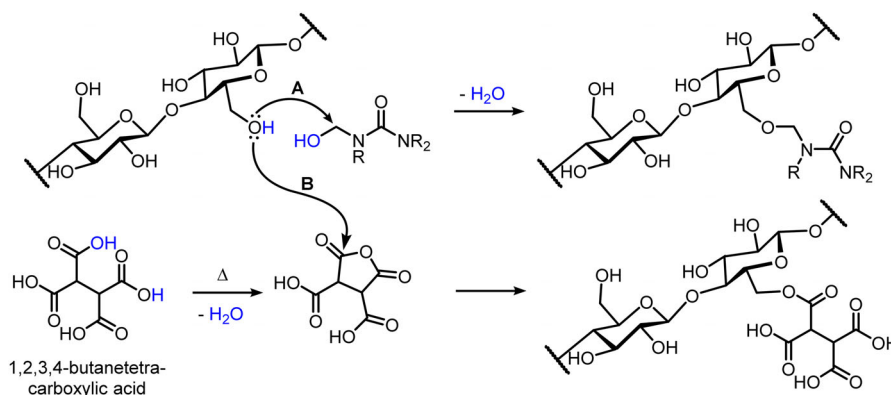
Scheme 1. Formaldehyde-containing crosslinking agents for cellulosic fabrics. Chemical structures represent varying degrees of methoxylation, being $R = H$ or CH_2OH . Compound **3** is synthesized from various ethylene urea derivatives being $X = H$ (**3a**), OH (**3b**), or OMe (**3c**). [Color figure can be viewed at wileyonlinelibrary.com]

involve polycarboxylic acids such as maleic acid,^{26–28} itaconic acid,²⁹ citric acid,³⁰ 1,2,3,4-butanetetracarboxylic acid,^{31–34} or others.³⁵ The crosslinking mechanism using polyacids relies on anhydrides as intermediate reagents. Upon heating of butanetetracarboxylic acid under weak alkaline conditions, a five-membered anhydride is obtained by cyclisation. Subsequent ring opening of this anhydride by a cellulosic hydroxyl group results in an ester bond between cellulose and crosslinker [Scheme 2(b)].^{36,37} Due to transesterification, polyacid-treated fabrics are re-curable³³ and weak bases like sodium monophosphate or sodium hypophosphite are used as catalyst.^{26,27,38} Further alternatives have been scarcely investigated and only dedicated reports explore optional compounds. McKelvey *et al.* studied cellulose–epoxide reactions as butadiene diepoxide is shown to react with cotton cellulose at room temperature in an alkaline environment.^{39–41} Treatments with epichlorohydrin⁴² or dihalohydrins as epoxide precursors⁴³ or other polyepoxides^{44,45} show similar promising effects on crease recovery angles of cotton cellulose fabrics. Besides, disulfide-based chemistry,⁴⁶ (hydroxyl)sulfones,^{47,48} divinylethers,^{49,50} or allyl and vinyl monomers^{23,50} as crosslinking agents for easy-care finishes of cotton cellulose fabrics have been

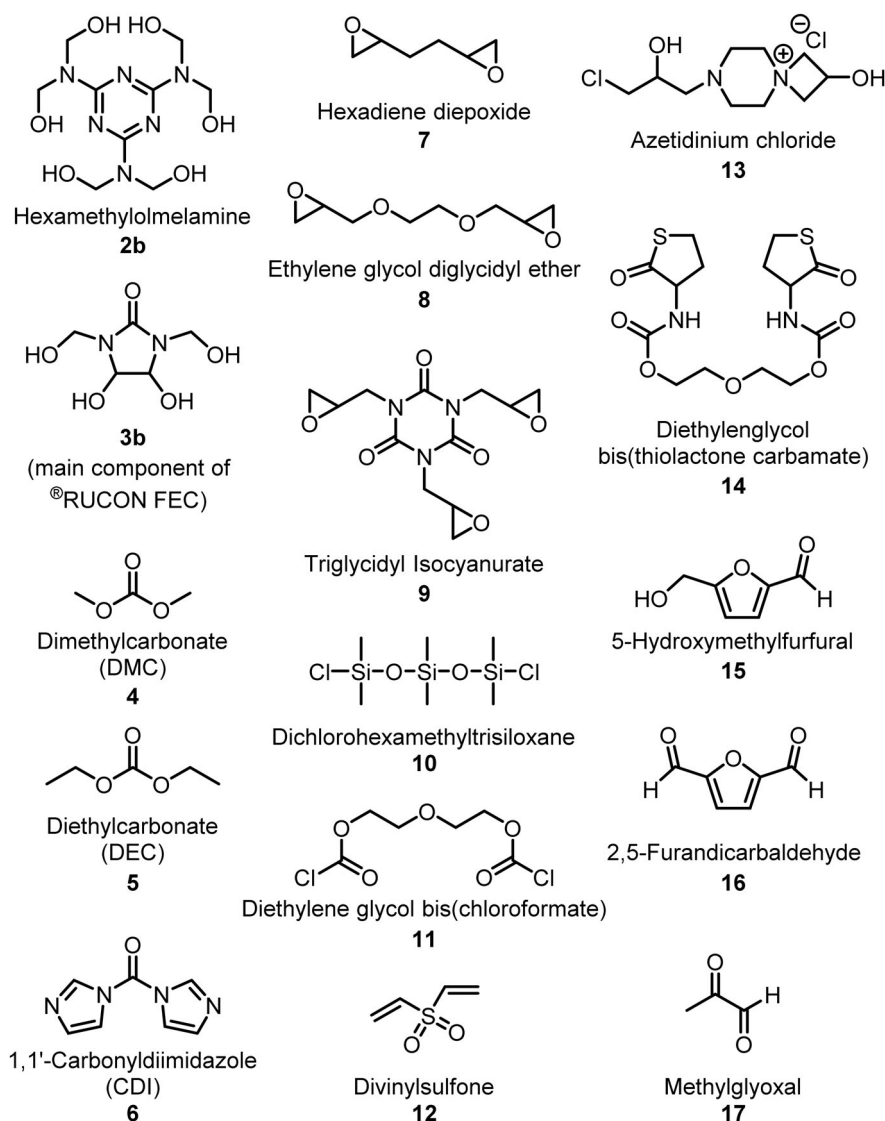
studied. Recent developments in the field have shown that alkaline pretreatment of the fabrics also known as mercerization facilitates subsequent crosslinking in the fibers of the cellulose fabrics.^{51–53} By treating the fabrics with either aqueous $NaOH$ or KOH solutions, the cellulose hydroxyl groups get partially deprotonated and the fibers swell due to anionic repulsion between the chains.⁵² Thus, the DCRA's depend on the degree of swelling during the crosslinking process and are significantly increased if pretreatments are applied.^{54–56}

All these procedures applied throughout the literature are mainly restricted on application in aqueous solution by padding the fabrics into a reagent bath with a subsequent curing process at elevated temperatures. Consequentially, the reactivity of every crosslinker is (1) strongly pH-dependent and (2) impeded by water as competitive reaction partner. All the crosslinking reactions occur in a heterogeneous environment, where the penetration of the curing agent into the fibers is strongly diffusion limited. Hence, the concurrent reactivity of the excess of water plays an important role that cannot be neglected. In this study, the first focus lies on the effect of organic solvents as medium for the durable press finishes of cotton cellulose fabrics. By processing the fabrics under anhydrous conditions, any disadvantageous effects of water are excluded. As a second focus, the majority of the chosen curing agents are formaldehyde-free and the functional groups span over a broad range of reaction mechanisms (Scheme 3). The easy-care finishes of cotton cellulose fabrics are carried out in dimethylformamide (DMF) and ethyl acetate (EA) via a pad-cure-dry process, where the reaction of crosslinker and cellulose fabrics takes place at the solid/liquid interface. The second procedure consists of a closed vapor chamber. Here, the volatile crosslinkers are evaporated to react with the fabrics at the solid/gas interface without the use of any solvent. Throughout this work, we renounce on any mercerization of the fabrics to concentrate on the main two parameters for a given procedure: solvent and crosslinker. Dry crease recovery angles are measured according to DIN 53890, compared between different crosslinkers as well as with DCRA's of:

- non-treated fabrics
- control fabrics, where the fabrics underwent the same finishing procedure without the use of a crosslinker.
- fabrics treated with RUCON FEC in different solvents according to our treatment protocol.



Scheme 2. Chemical reaction of cellulose with hydroxymethyl-urea based crosslinking agent (route A) and 1,2,3,4-butanetetracarboxylic acid as formaldehyde-free alternative (route B). [Color figure can be viewed at wileyonlinelibrary.com]



Scheme 3. Assembly of compounds evaluated as crosslinking agents of cotton cellulose fabrics to improve dry crease recovery angles.

- fabrics treated with RUCON FEC in water according to the industry treatment protocol.

The DCRA's help to rank the different crosslinkers as well as the methods and solvents used to finish the cotton cellulose fabrics. As the use of catalysts in durable press finishes is common practice, chosen crosslinkers were applied in conjunction with selected catalysts known from the literature. The effect of the catalysts become apparent when compared to non-catalyzed specimen.

EXPERIMENTAL

Materials

Ultrapure MilliQ water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$ was used for all experiments. Dimethylcarbonate (99%, Sigma-Aldrich, Darmstadt, Germany), diethylcarbonate (>98%, TCI Chemicals), 1,1'-carbonyldiimidazole (>97%, TCI Chemicals), 1,5-hexadiene diepoxide (>96%, TCI), triglycidyl isocyanurate (>98%, TCI Chemicals), 1,5-dichlorohexamethyltrisiloxane (95%, ABCR), diethylene glycol bis(chloroformate) (>95%, BASF), divinylsulfone

(>95%, ChemPUR), 2,5-diformylfuran (>98%, TCI chemicals), 5-hydroxymethyl-2-furaldehyde (>95%, TCI chemicals), methylglyoxal (~40% in H_2O , Sigma-Aldrich), and hexamethylol melamine (95%, BOC Sciences) were used without further purification. Unless otherwise indicated, all solvents were purchased from commercial sources and were used without further purification.

As a state-of-the-art curing agent that is currently in industrial use, RUCON FEC was obtained from the Rudolf Group (Geretsried, Germany). RUCON FEC is chemically based on DMDHEU and comes as an aqueous mixture (35 g L^{-1} substance). A volume of 100 mL of this aqueous mixture was lyophilized to obtain a yellow viscous oil. This oil was then used for the preparation of the 5 wt % finishing solutions and further tests to determine dry crease recovery angles.

Test fabrics were purchased from wfk Testgewebe GmbH (Brüggen, Germany). Standard Cotton (wfk code 10 A) was used with a width of 100 cm and an area weight of 170 g m^{-2} . The pick count was 270/270 (pick dm^{-1}) in a plain weave (1/1) with a yarn count of

295/295 (dtex). Sample fabrics were cut in warp and in fill direction with a size of approximately 5×20 cm. This way after the curing process, the fabrics (warp and fill, one each) were cut up in 10 separate sample specimens with dimensions of 5×2 cm.

Methods

Dry crease recovery angles were measured with a crease recovery workbench of Karl Schröder KG (Weinheim, Germany) using the DIN 53890. Each 5×2 cm specimen was loaded with a 1 kg weight for 30 min. After removal of the weight, the dry crease angles were measured after 5 and 30 min recovery time. Every crease angle is averaged over 10 specimens (warp and weft, each). The final values in the present manuscript for the dry crease angles are presented as sum of warp and fill ($W + F$) after 30 min recovery time.

All sample fabrics were pre-dried in the vacuum oven at 50°C overnight. In a pad-cure-dry process, sample fabrics were padded in a 1–5 wt % solution of the reagent in the designated solvent (DMF, EtOAc, or water). Fabrics were padded with reagent and—if used—catalyst to 100% wet pickup. Next, the wet fabrics were gently dab dried to remove excess of reagent solution prior to be put in the oven for curing. If not otherwise noted, the samples were cured for 3 min at 180°C . After the crosslinking process, the fabrics were dried in the vacuum oven at 50°C to remove residual solvents traces. Before the measurement of the dry crease angles was carried out, each fabric was conditioned for several hours in the climate room with 65% R.H. at 21°C .

For sample, **H₂O150-03** fabrics were treated with RUCON FEC in water according to the following industry treatment protocol: (1) 10 min slightly acidic solution using a foulard. (2) 5 s padding in a solution of RUCON FEC 35 g L^{-1} and 10.5 g L^{-1} MgCl_2 as catalyst using a foulard. (3) 1 min drying at 120°C , (4) 3 min drying at 150°C .

For the solid/gas setup, pre-dried fabrics were cut in separate sample specimen. The crosslinker (1 mL) was spread of the entire area of the storage vessel. On top of the porous sinter material, 20 sample specimens were equally allocated. The lid was put on top to close the vapor chamber. The entire device was put into the oven at 160°C with vacuum turned on. The curing process was carried out for 10 min. Afterward, sample specimens were dried in the vacuum oven at 50°C overnight. Before the measurement of the dry crease angles was carried out, all sample specimens were conditioned for several hours in the climate room with 65% R.H. at 21°C .

Infrared spectra were carried out on a ThermoNicolet FTIR Nexus spectrometer and are recorded between KBr disks or using an ATR unit (ThermoNicolet, Smart SplitPEA). Transmission maxima are reported in wavenumbers (cm^{-1}) and only selected intensities are reported.

RESULTS AND DISCUSSION

Scheme 3 depicts the crosslinkers that have been used throughout this work. Dimethylcarbonate **4** as well as diethylcarbonate **5** is known to act as electrophiles in substitution reactions. According to the hard and soft acid base principle, the carbonyl group is designated as a harder electrophile. This is due to the partial positive charge and the sp^2 hybridization of the carbonyl C atom. Hence, hard nucleophiles like cellulosic hydroxyl groups are able to add to

the carbonyl, eliminating methoxide or ethoxide, respectively.⁵⁷ Carbonyldiimidazole **6** has been an alternative reagent to phosgene and triphosgene-based chemistry for the synthesis of carbamates. Similar to **4** and **5**, the carbonyl acts as electrophile. Once the nucleophile is attached, imidazole groups are cleaved off.^{58,59} Beside carbonylation reagents, different polyepoxides were tested as crosslinking agents (**7**, **8**, and **9**, Scheme 3). Hexadiene diepoxide **7** and ethylene glycol diglycidyl ether **8** are bisepoxides, while triglycidyl isocyanurate **9** carries three oxiranes susceptible for ring-opening reaction. Dichlorohexamethyltrisiloxane **10** represents an inorganic crosslinker. Upon reaction with a nucleophilic cellulosic hydroxyl group, a new O—Si bond is formed. Diethylene glycol bis(chloroformate) **11** react in the same way, yet carbonate groups are formed. Divinylsulfone **12** has been shown to react with cellulosic cotton in earlier reports.⁴⁸ It reacts directly with hydroxyl groups via a oxo-Michael addition or as precursor for the formation of bis(hydroxyethyl)sulfone. The latter reacted with hydroxyl groups of the cotton cellulose in an etherification driven by the exclusion of water at higher temperatures (similar to methylol-based compounds).⁶⁰ Azetidinium chloride **13** is a coupling reagent elaborated and studied first in 2012.⁶¹ Upon reaction with a nucleophile, the 4-membered cycle will be opened simultaneously restoring a second azetidinium cycle by aminolysis of the chloromethyl group. This liberates a chloride ion that forms a stable salt with the new azetidinium cycle.⁶² Bis(thiolactone) **14** reacts similar to the polyepoxides via ring opening of the five-membered cycles. Nucleophiles provoke lysis of the thiolactone, which is in a strained ring conformation and an active ester at the same time.^{63,64} Upon ring-opening of the cycle, free thioethyl moieties are released that further support the crosslinking process via atmospheric oxidation of the thiols to disulfide bonds.⁶⁵ Finally, furan derivatives **15** and **16** represent formaldehyde-free aldehyde crosslinkers. Additionally both compounds are obtained from renewable resources (e.g., by dehydration of fructose).⁶⁶ As it is the case with formaldehyde, the cotton cellulose hydroxyl groups are able to react with the free aldehyde groups in **15** and **16** to form semi- or full acetals. Methylglyoxal **17** is a less reactive surrogate of glyoxal and is able to react with alcohols in the same way as other aldehydes to form acetals.⁶⁷ HMM has been used in the past as formaldehyde source or aminoplast crosslinker for cotton cellulose fabrics. Finally, RUCON FEC is applied as it represents a state-of-the-art curing mixture.

Sample fabrics are named according to the format **MediumXXX-YY-Z**. Medium either denotes a solvent (**DMF**; **EA**; water, **H₂O**) or measurements in vacuum (**Vac**). **XXX** describes the temperature at which the sample fabrics were treated (50, 150, 160, or 180°C), **YY** the crosslinker used (**2–18** or **Control**, if no crosslinker was used). **Z** describes either a nonstandard concentration or one of the catalysts used later on.

Wet-Chemical Application at the Solid/Liquid Interface

The first processing method involves a simple reagent bath, where the fabrics are soaked with the chemical reagent (Figure 1). However, prior to the finishing process, each fabric was dried in a vacuum oven at 50°C overnight. After the drying process, each fabric loses 4.5 ± 0.8 wt % water. The dried fabrics are both immersed 1 min up to 100% wet pickup in the reagent bath (20 mL solution).

Acetonitrile was considered initially as solvent; however, its solvation capability for the chosen crosslinkers was quite limited. DMSO was

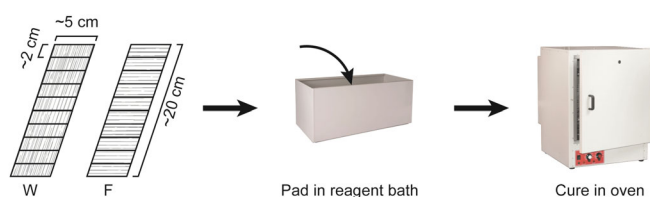


Figure 1. Pad-cure-dry process scheme for the treatment of cotton cellulose fabrics at the solid/liquid interface. [Color figure can be viewed at wileyonlinelibrary.com]

avoided as solvent, since its boiling point is higher than the actual curing temperature in the applied finishing process. Every source of protons is avoided; therefore, methanol and ethanol were not suitable. Hence, DMF is first chosen as solvent to study easy-cure finishes in water-free conditions, since it has a polarity close to water, a boiling point below curing temperature and is of aprotic nature. Each compound is dissolved in 20 mL DMF at a concentration of 5 wt %. For this initial experiment, the temperature for the curing process is chosen to be 50 °C for 1 h. To get a first assessment on crosslinkers with a wider variety of reactive groups RUCON FEC with **3b**, active ester **6** and **11** as well as bis(epoxide) **8** and dichlorosiloxane **10** are tested at these conditions (Table I). Control sample **DMF50-Control** shows that the fabric treatment in DMF at 50 °C without any crosslinker decreases the DCRA to 107.5° in comparison to the non-treated WFK fabrics with a DCRA of 145.0°. With use of crosslinkers **3b**, **6**, **8**, **10**, and **11** the DCRA increases again (Figure S1). Yet only **DMF50-06**—treated with carbonyldiimidazole **6**—shows a slight increase in dry crease recovery angles above the value of the non-treated fabrics (Table I). Surprisingly, crosslinker **3b** did not lead to a DCRA above the value of the non-treated fabrics (133.5°). If we compare this value to DCRA values obtained from the same crosslinker in the literature, the values are in a similar range. In a study from 2008, Namligöz *et al.* apply a DMDHEU **3b** to linen specimen and obtain increased DCRA of ~128°. ⁵⁴ In 2017, Manian *et al.* apply the same crosslinker to lyocell fabrics. After the finishing process, DCRA of approximately 116° is measured. ⁵⁶ Even though the increased DCRA values we observed indicate that a chemical reaction took place the overall results show that compared to the non-treated fabric, dry crease recovery angles have deteriorated upon treatment at 50 °C. Hence, soaking the fabrics in DMF for 1 h at 50 °C has a negative effect on the mechanical properties of the fabrics. In previous reports, the cotton cellulose fabrics were mostly treated for 3 min at 160 °C ^{18,22,25}; however, more recent publications suggest that with increasing temperatures up to 180 °C higher crease angles are obtained. ^{27,36} Therefore, the second approach involves the curing of the fabrics at 180 °C for 3 min. It is anticipated that with the high temperature a reaction is coerced on the fabrics simultaneously reducing the soaking time of the fabrics in DMF dramatically. In addition to **3b**, **6**, **8**, **10**, and **11**, crosslinkers **2b**, **13**, and **14** were investigated, too. Compound **13** and a derivative of **14** have been previously converted with amines at mild temperatures (25–40 °C) for the synthesis of polyamines and polyamides, respectively. ^{62,63} Thus, they are expected to show reactivity toward cellulose at higher temperatures. Fabric **DMF180-Control** shows that the change in conditions (reducing the reaction time) slightly increases the DCRA from 107.5° (**DMF50-Control**) to 123.8° (**DMF180-Control**, Table I). Still, the obtained DCRA is lower than the DCRA of

non-treated fabrics (145.0°), which confirms that DMF as solvent has a negative effect on the mechanical properties of the fabrics. Comparing the DCRA values of samples treated with crosslinkers with the control sample **DMF180-Control** shows a positive increase (Figure 2).

If ranked according to their Δ DCRA in the figure, the quality of the crosslinkers follows the trend: ethyleneglycol diglycidyl ether **8** (having no effect) < azetidinium chloride **13** < HMM **2b** < bis(chloroformate) **11** < bis(thiolactone) **14** < dichlorohexamethyltrisiloxane **10** < the company mixture comprising **3b** < carbonyldiimidazole **6**. The highest DCRA value is obtained by use of carbonyldiimidazole **6** as crosslinker (160.1°). Its DCRA is 36.3° higher than the DCRA of **DMF180-Control** and 15° higher than the DCRA of non-treated fabrics. Crosslinker **6** performs better than RUCON FEC in DMF (**DMF180-03** with 149.9°). Sample **DMF180-10** with dichlorohexamethyltrisiloxane **10** as crosslinker shows an improved DCRA of 142.8° (being below the DCRA of non-treated fabrics). Compared to HMM, carbonyldiimidazole **6** shows a considerably better performance and is the only crosslinker that noticeably increases DCRA values above those of non-treated fabrics. Benchmarked against a sample specimen that has been treated according to the industry standard (149.8, **H₂O150-03**) the treatment with carbonyldiimidazole **6** yields an improved DCRA (160.1°, **DMF180-06**).

With regard to the crosslinking process, the increased DCRA values compared to the control sample demonstrate that the treatment of the cotton cellulose is successfully carried out in a nonaqueous medium. However, the solvent itself has a crucial effect on the fabrics' DCRA. DMF is well known to dissolve cellulose when mixed with LiCl salt. ⁶⁸ Thus, we anticipate that DMF itself and even without LiCl is likely to have a strong impact on the microstructure of the material under this short but harsh thermal treatment. From the obtained DCRA values, it seems that DMF partially dissolves amorphous and crystalline domains of the cellulose. Hydrogen bonds are broken to the expense of crystallinity of the cellulose, thus, reducing the overall strength and stiffness of the textile fabrics (without addition of any crosslinker). In the next approach, we looked for a more benign solvent that would not deteriorate the mechanical properties of the fabrics in the first place. Knowing that a less polar solvent would likely not be able to dissolve all crosslinkers, we sought the compromise between mild impact on the fabrics and acceptable solvency power and chose EA. First, a control fabric is subjected to the pad-cure-dry procedure. Later on, solutions of each crosslinker in 20 mL of solvent with a concentration of 5 wt % are prepared. The curing process is again maintained at 180 °C for 3 min. Tested crosslinkers that are soluble in EA are compounds **4–12**, **15**, and **16**. For HMM, a saturated solution is prepared (below 5 wt %). Crosslinkers **13**, **14**, and [®]RUCON FEC containing **3b** were completely insoluble in EA, while reagent **17** only comes in an aqueous solution. Thus, these crosslinkers had to be excluded from the textile treatments in EA. However, resulting DCRA values were compared with non-treated fabrics (145.0°, Table I), control fabrics (144.7°, **EA180-Control**, Table II), and fabrics treated according to industry protocol (149.8°, **H₂O150-03**, Table I). The small difference of DCRA for non-treated fabrics and **EA180-Control** (145.0° vs. 144.7°) indicates that EA is a gentle

Table I. DCRA of Cotton Cellulose Fabrics Treated with Solutions of Different Crosslinkers in DMF

| Fabric | Crosslinker | Oven temperature | Curing time | Dry crease recovery angles | | |
|------------------------------|-------------|------------------|-------------|----------------------------|------------|--------------|
| | | (°C) | (min) | Warp (°) | Fill (°) | (W + F)° |
| Non-treated | – | – | – | 71.8 | 73.2 | 145.0 |
| H₂O150-03 | 03 | 120/150 | 1/3 | 73.6 ± 2.7 | 76.2 ± 5.6 | 149.8 |
| DMF50-Control | – | 50 | 60 | 51.5 ± 2.7 | 56.0 ± 2.6 | 107.5 |
| DMF50-03 | 3b | 50 | 60 | 64.2 ± 1.5 | 69.3 ± 2.2 | 133.5 |
| DMF50-06 | 6 | 50 | 60 | 73.1 ± 3.8 | 75.4 ± 3.5 | 148.5 |
| DMF50-08 | 8 | 50 | 60 | 58.3 ± 2.2 | 59.8 ± 3.6 | 118.1 |
| DMF50-10 | 10 | 50 | 60 | 67.3 ± 1.6 | 70.7 ± 4.3 | 138.0 |
| DMF50-11 | 11 | 50 | 60 | 61.8 ± 2.8 | 65.6 ± 1.6 | 127.4 |
| DMF180-Control | – | 180 | 3 | 61.4 ± 2.2 | 62.4 ± 3.0 | 123.8 |
| DMF180-02 | 2b | 180 | 3 | 67.0 ± 2.4 | 68.2 ± 2.5 | 135.2 |
| DMF180-03 | 3b | 180 | 3 | 71.0 ± 3.1 | 78.9 ± 3.7 | 149.9 |
| DMF180-06 | 6 | 180 | 3 | 75.6 ± 2.0 | 84.5 ± 4.8 | 160.1 |
| DMF180-08 | 8 | 180 | 3 | 61.4 ± 4.3 | 61.2 ± 2.6 | 122.6 |
| DMF180-10 | 10 | 180 | 3 | 67.5 ± 2.8 | 75.3 ± 1.5 | 142.8 |
| DMF180-11 | 11 | 180 | 3 | 67.4 ± 2.5 | 69.2 ± 2.8 | 136.6 |
| DMF180-13^a | 13 | 180 | 3 | 62.3 ± 1.3 | 65.6 ± 2.2 | 127.9 |
| DMF180-14 | 14 | 180 | 3 | 68.3 ± 2.2 | 71.8 ± 3.5 | 140.1 |

The bold numbers give sum of warp and fill.

^a Azetidinium **13** was dissolved in 20 mL dimethylsulfoxide (DMSO) as it was insoluble in DMF. DMSO is considered to have the same polarity as DMF.

solvent, which preserves the internal microstructure of the cotton cellulose fibers during the finishing process.

The difference of DCRA of samples and control (Δ DCRA) is presented in Figure 3. A negative effect for the Δ DCRA is observed for

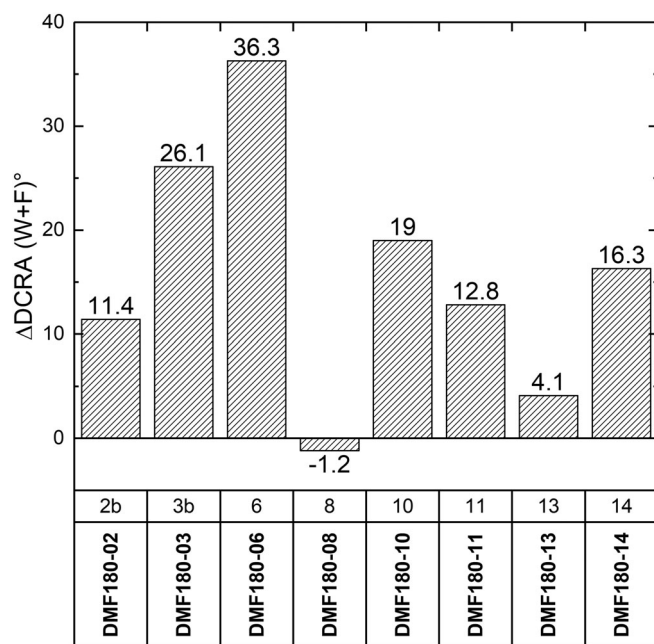


Figure 2. Cotton cellulose fabrics treated with different crosslinkers in DMF at 180 °C. Difference of DCRA and the control value.

dimethylcarbonate **4** and 5-hydroxymethylfurfural **15**. Within the limit of the usual standard deviations, diethylene carbonate **5**, divinylsulfone **12**, 2,5-furandicarbaldehyde **16**, and HMM **2b** have little to no effect on the Δ DCRA values (Figure 3). Improvements for the DCRA are achieved with the following crosslinkers in the order: 5.9° (ethylene glycol bis(chloroformate) **11**) < 9.7° (ethyleneglycol diglycidyl ether **8**) < 10.6° (hexadiene diepoxide **7**) < 12.9° (dichlorohexamethyltrisiloxane **10**). By use of triglycidyl isocyanurate **9** (**EA180-09**), the best DCRA is obtained being 22° higher than for the control value **EA180-Control** (Table II, Figure 3). This value (166.7°) is again higher than **H₂O150-03** (149.8°, Table I) and those obtained for DMDHEU **3b** in an (alkaline) aqueous finishing process reported in literature.^{54,56} To assess concentration influences, crosslinkers **5**, **6**, **8**, **10**, and **11** are exemplarily used in 1 wt % solutions (instead of 5 wt %). The reduction of reagent weight concentration from 5 to 1 wt % results in reduced Δ DCRAs (Figure S2). As expected, with less reagent being present, a smaller degree of crosslinking is obtained after the curing process (**EA180-YY-1** wt %, see Table S1). Only for fabrics **EA180-06-1** wt %, DCRA is higher than for **EA180-06** with a concentration of 5 wt %.

In summary, crosslinkers **7–11** show moderate to good increase of DCRA, while other crosslinkers had little to no effect. Although crosslinkers **10** and **11** deliver fabrics with increased DCRA, these crosslinkers cause yellow staining of the fabrics. The staining is due to the release of hydrochloric acid from the reagents upon curing and could damage the cellulose on a molecular level. For the catalyst approach, these crosslinkers are therefore excluded.

In the catalyst approach, polyepoxides **7–9** and divinylsulfone **12** are tested with selected catalysts that have been used in the literature. The

Table II. DCRA of Cotton Cellulose Fabrics Treated with Solutions of Different Crosslinkers in Ethyl Acetate (EA)

| Fabric | Crosslinker | | Dry crease recovery angles | | |
|----------------------|-------------|------------------------|----------------------------|------------|--------------|
| | | Concentration (wt %) | Warp (°) | Fill (°) | (W + F)° |
| EA180-Control | – | 0 | 72.3 ± 3.2 | 72.4 ± 4.4 | 144.7 |
| EA180-02 | 2b | Saturated ^a | 71.4 ± 2.5 | 74.5 ± 3.6 | 145.9 |
| EA180-04 | 4 | 5 | 66.1 ± 1.6 | 70.8 ± 2.6 | 136.9 |
| EA180-05 | 5 | 5 | 70.8 ± 2.4 | 74.3 ± 2.5 | 145.1 |
| EA180-06 | 6 | 5 | 69.0 ± 3.0 | 73.5 ± 2.5 | 142.5 |
| EA180-07 | 7 | 5 | 75.2 ± 2.6 | 80.1 ± 3.7 | 155.3 |
| EA180-08 | 8 | 5 | 75.6 ± 1.9 | 78.8 ± 3.6 | 154.4 |
| EA180-09 | 9 | 2.5 ^b | 81.9 ± 3.1 | 84.8 ± 2.2 | 166.7 |
| EA180-10 | 10 | 5 | 73.4 ± 4.4 | 84.2 ± 4.5 | 157.6 |
| EA180-11 | 11 | 5 | 74.2 ± 2.4 | 76.4 ± 2.1 | 150.6 |
| EA180-12 | 12 | 5 | 70.5 ± 2.5 | 74.1 ± 2.3 | 144.6 |
| EA180-15 | 15 | 5 | 65.3 ± 1.9 | 70.5 ± 3.1 | 135.8 |
| EA180-16 | 16 | 5 | 70.1 ± 3.1 | 74.0 ± 3.0 | 144.1 |

The bold numbers give sum of warp and fill.

Curing conditions: 3 min at 180 °C.

^a For Hexamethylol melamine **18**, a saturated solution was prepared, since the solubility of **18** in EtOAc is limited.^b

^b For the treatment with triglycidyl isocyanurate **9**, only 2.5 wt % solutions in EtOAc were applied due to the low solubility of **9** in EtOAc.

catalyst concentration is always maintained at 5 mol %. The concentration of the crosslinkers is set to 5 wt %. For the polyepoxides, tetrabutylammonium bromide (TBAB) and tetrabutylphosphonium bromide (TBPB) are used. Both are known to stabilize the partially negative oxygen atom of epoxide rings. This way, a nucleophile is triggered to open the epoxide ring. The third candidate as catalyst for the ring-opening of epoxides is the polyaminophosphazene P4-*t*-Bu. Polyaminophosphazenes are neutrally charged, sterically hindered compounds that are extremely basic but only weakly nucleophilic. For divinylsulfone **12**, a different set of catalysts is tested.

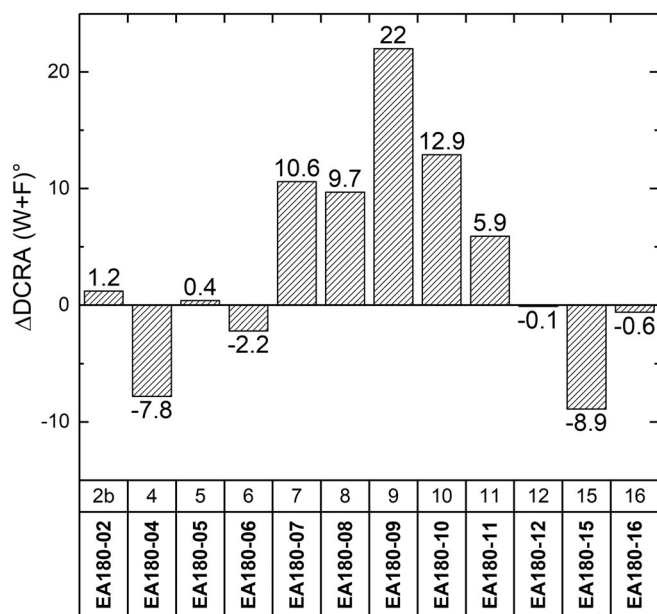


Figure 3. Cotton cellulose fabrics treated with different crosslinkers in EtOAc. Difference of DCRA and the control value.

Triphenylphosphin (TPP), 4-dimethylaminopyridine (DMAP), and 1,4-diazabicyclo[2.2.2]octane (DABCO) were recently shown to promote the oxa-Michael addition of alcohols to divinylsulfone in step-growth polyadditions.⁶⁹ Fabrics treated with hexadiene diepoxide **7** show the best increase of DCRA if the catalyst TBPB is employed. A total DCRA of 158.5° is reached (**EA180-07-TBPB**, Table III). For ethylene glycol diglycidyl ether **8** the trend is similar. **EA180-08-TBPB** shows the highest DCRA (167.4°). For triglycidyl isocyanurate **9**, fabrics **EA180-09-P4tBu** catalyzed by P4-*t*-Bu show the highest DCRA (180.2°). Compared to the polyepoxides, the effect of divinylsulfone is less pronounced. Here, the highest DCRA is obtained for divinylsulfone **12** in combination with DMAP as catalyst (**EA180-12-DMAP**, 166.3°, Table III). If the differences ΔDCRA (referred to control fabrics **EA180-Control**) are calculated and the results are compared to the non-catalyzed sample fabrics **EA180-07**, **EA180-08**, **EA180-09**, and **EA180-12** it becomes clear that depending on the system even in nonaqueous media the choice of the catalyst or base may be crucial for the reaction progress and crosslinking of the cotton cellulose (Figure 4). If compared to the sample treated according to the industry procedure (149.8°, **H₂O150-03**) the obtained DCRA in EA for triglycidyl isocyanurate (180.2°, **EA180-09-P4tBu**) is increased.

For crosslinker **7**, the use of catalyst TBAB shows a lower ΔDCRA (+6.1°) than without the use of a catalyst (**EA180-07**, +10.6°, Figure 4). Use of TBPB or P4-*t*-Bu slightly increase the ΔDCRA compared to the non-catalyzed sample fabrics **EA180-07**. A stronger effect is observed for crosslinker **8** (Figure 4). TBAB again shows a decrease in ΔDCRA compared to the non-catalyzed fabrics (**EA180-08-TBAB** vs. **EA180-08**). The treatment with P4-*t*-Bu has no effect (**EA180-08-P4tBu** vs. **EA180-08**). The catalyst TBPB in combination with **8** has the largest impact on the ΔDCRA as demonstrated for fabrics **EA180-08-TBPB** (increase of 22.7°, Figure 4). Triglycidyl isocyanurate **9** is able to deliver a high ΔDCRA value of

22° (EA180-09) even without the use of a catalyst. The catalyst TBAB does not change this status quo (22.1° for EA180-09-TBAB). Meanwhile, the use of TBPB lowers the Δ DCRA value as is seen for fabrics EA180-09-TBPB (only +11.7°). For crosslinker **9**, the best Δ DCRA is obtained with P4-t-Bu as catalyst and amounts to +35.5° (EA180-09-P4tBu). The DCRA value of 180.2° is significantly higher than those reported in literature where DMDHEU **3b** is used in an aqueous environment (116°–128°) and the sample treated according to industry procedure H₂O150-03 (149.8°, Table I). While divinylsulfone **12** as crosslinker shows no significant increase in DCRA (EA180-12, Figure 4), its performance is strongly dependent on the used catalyst. TPP as catalyst leads to an increase in Δ DCRA of +3.4° (EA180-12-TPP). DABCO-catalyzed fabrics EA180-12-DABCO show a gain in Δ DCRA of +11.2°. The highest Δ DCRA is obtained if DMAP is used as catalyst (EA180-12-DMAP). Here the Δ DCRA value is doubled and amounts to +21.6° above control fabrics EA180-Control.

As an exemplary proof, the fabrics of sample EA180-09-P4tBu were examined via FTIR spectroscopy. However, before the IR spectrum was acquired, the sample was immersed in pure EA and stirred for 20 min at room temperature to remove every excess of crosslinker, which may have adsorbed to the fibers of the sample fabrics. To compare and superimpose spectra, also IR samples of pure triglycidyl isocyanurate **9** and the non-treated fabrics were measured separately (Figure 5). In the spectrum of triglycidyl isocyanurate **9**, the amide I vibration band at 1691 cm⁻¹ and the amide II vibration band at 1468 cm⁻¹ appear as sharp strong signals. If we look at the spectrum of the non-treated fabrics, no such bands are detectable. Compared to the FTIR spectrum of the treated fabric, the spectrum of the non-treated fabric shows a strong band at 3334 cm⁻¹ for the hydroxyl band and the contained water. As the treated fabric has been dried twice—before and after the finishing, the water content and thus the band at 3334 cm⁻¹ is much weaker. However, the decisive difference between the spectra of the non-treated fabrics and

EA180-09-P4tBu is the amide I vibration band of crosslinker **9**. The band is clearly seen in spectrum of EA180-09-P4tBu, whereas for the spectrum of the non-treated fabrics it is not visible. This brings evidence that the crosslinker not only adsorbed on the sample fabric but also clearly reacted in a covalent manner (Figure 5). To sum up, triglycidyl isocyanurate **9** as crosslinker, catalyzed with 5 mol % of the superbases P4-t-Bu in EA shows the best results. With regard to the non-treated fabrics, an increase in DCRA of +35.2° is obtained.

For comparative reasons, crosslinkers **6** and **8** were examined in water, since they both showed a good performance in DMF and EA. The control value shows a DCRA of 153.2°, which is slightly higher than the value for the raw non-treated fabrics with 145.0°. Other than in DMF, if cellulose fibers are exposed to high temperatures in an aqueous environment for short time, it is assumed that the cellulose backbone gets quickly rehydrated, annealed, and thus can partially reform hydrogen bonding between adjacent polymer chains. As a result, the mechanical properties of the fabrics are slightly improved. Unfortunately, the treatments with the chosen crosslinkers show only negative results for the Δ DCRA (as compared to the control sample, Table S2 and Figure S3). The best result for the treatment in water is obtained with RUCON FEC (H₂O180-03, using our method), where only a decrease of -0.9° is measured. The absolute value of this sample amounts to 152.3°. Though this value is higher than what was obtained for the non-treated fabrics (145.0°), it seems that the effect of the solvent on the fabrics—in this case water 153.2°—has again been completely neglected. The attained results raise the question whether carrying out finishing processes without solvents could be a solution to this negative impact caused by the treatment in media.

Vapor-Chemical Application in Solid/Gas Interface

Reviewing the previous findings clarifies that besides curing temperature, catalyst, and the general process set-up, the effect of the

Table III. DCRA of Cotton Cellulose Fabrics Treated with Solutions of Different Crosslinkers and Catalysts in Ethyl Acetate

| Fabric | Crosslinker | Catalyst | Dry crease recovery angles | | |
|----------------|-------------|----------|----------------------------|------------|--------------|
| | | | Warp (°) | Fill (°) | (W + F)° |
| EA180-07-TBAB | 7 | TBAB | 73.9 ± 2.7 | 76.9 ± 1.4 | 150.8 |
| EA180-07-TBPB | 7 | TBPB | 79.7 ± 5.6 | 78.8 ± 2.8 | 158.5 |
| EA180-07-P4tBu | 7 | P4-t-Bu | 78.8 ± 3.0 | 79.0 ± 4.4 | 157.8 |
| EA180-08-TBAB | 8 | TBAB | 72.2 ± 4.3 | 75.0 ± 3.0 | 147.2 |
| EA180-08-TBPB | 8 | TBPB | 84.2 ± 3.9 | 83.2 ± 3.2 | 167.4 |
| EA180-08-P4tBu | 8 | P4-t-Bu | 75.5 ± 2.2 | 78.9 ± 2.8 | 154.4 |
| EA180-09-TBAB | 9 | TBAB | 81.5 ± 3.8 | 85.3 ± 4.3 | 166.8 |
| EA180-09-TBPB | 9 | TBPB | 76.2 ± 2.1 | 80.3 ± 3.0 | 156.4 |
| EA180-09-P4tBu | 9 | P4-t-Bu | 89.4 ± 1.7 | 90.8 ± 2.8 | 180.2 |
| EA180-12-DABCO | 12 | DABCO | 75.6 ± 1.5 | 80.3 ± 4.0 | 155.9 |
| EA180-12-DMAP | 12 | DMAP | 80.8 ± 3.9 | 85.5 ± 2.9 | 166.3 |
| EA180-12-TPP | 12 | TPP | 73.6 ± 2.2 | 74.5 ± 1.9 | 148.1 |

The bold numbers give sum of warp and fill.

Crosslinker concentration is 5 wt %, catalyst concentration is 5 mol % referred to the amount of crosslinker. Curing conditions: 3 min at 180 °C.

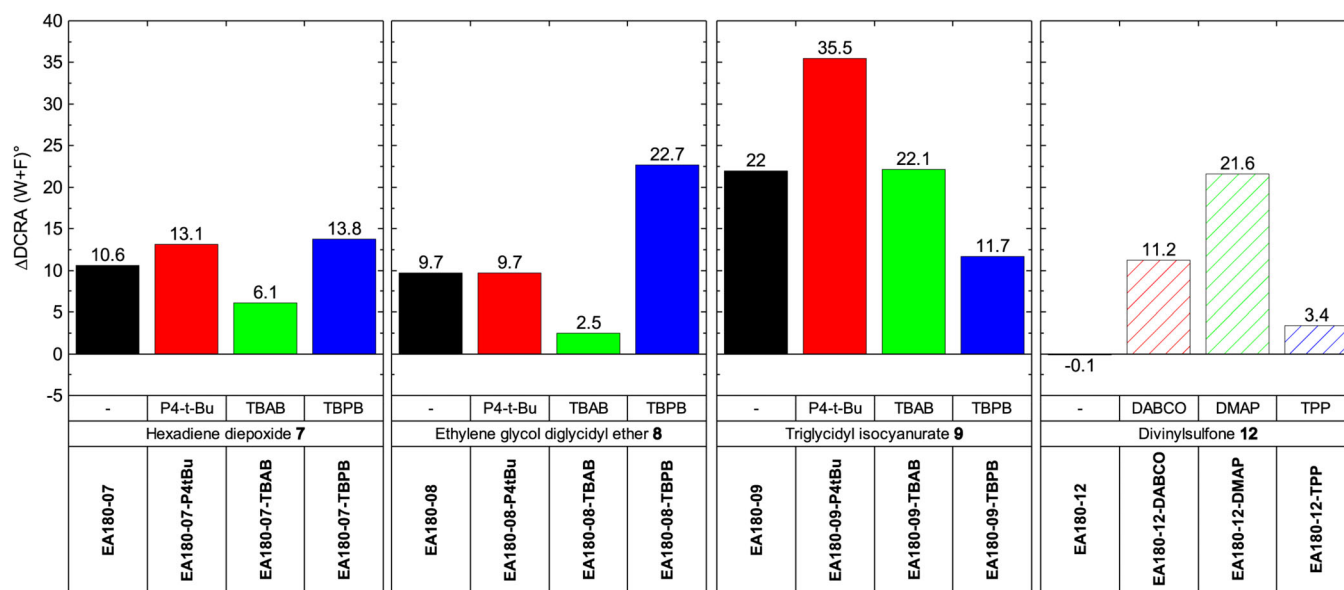


Figure 4. Cotton cellulose fabrics treated with different crosslinkers and catalysts in EtOAc. Difference of DCRA to the control value. [Color figure can be viewed at wileyonlinelibrary.com]

solvent is not to underestimate when applying easy-care finishes to textile fabrics. While for carbonyldiimidazol **6** in DMF good DCRA were reached, in EA triglycidyl isocyanurate **9** is the best reagent to use. With the conditions and reagents tested in water, no positive effect was observed. In the present section, a reaction setup has been developed to conduct the treatment at the solid/gas interface of the fibers without the use of any solvent. The raw non-treated but dried fabrics are reacted with crosslinkers in a vapor atmosphere at elevated temperatures. This way, the effect of the solvent was eliminated from the procedure. The only limitation for this process is that the reagents used for this procedure

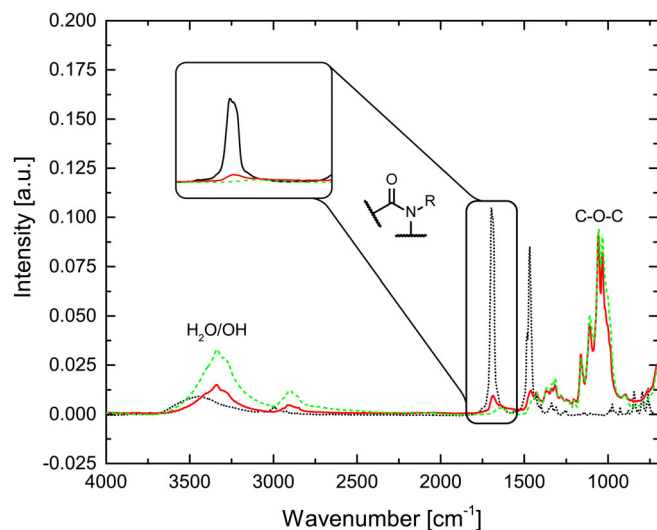


Figure 5. FTIR spectra of triglycidyl isocyanurate **9** (dotted line), the non-treated cotton cellulose fabrics (dashed line) and the treated cotton cellulose fabric **EA180-09-P4tBu** (solid line). Inset graph shows a magnification of the isocyanurate amide band at 1698 cm⁻¹. [Color figure can be viewed at wileyonlinelibrary.com]

need to be volatile at ambient pressure or in vacuum. This includes dimethylcarbonate **4**, diethylcarbonate **5**, hexadiene diepoxide **7**, ethylene glycol diglycidyl ether **8**, dichlorohexamethyltrisiloxane **10**, and divinylsulfone **12**. Due to the geometrical dimensions of the vapor chamber used, the size of the to-be-treated specimen differs in this reaction setup (Figure 6). Prior the processing, the two sample fabrics (warp and fill) are cut into 10 equal fabric strips. Meanwhile, the reagent is filled and spread in the low-level storage vessel of the vapor chamber (step 1, - Figure 6). After a porous sintering material is inserted to cover the storage vessel (step 2), the strips are equally placed on the sintering material (step 3). Now the vapor chamber cover lid is put onto the lower half of the metal chamber (step 4). The lid is connected via two outlets and a T-joint to the vacuum line. The closed vapor chamber is put into the oven at 160 °C for the curing process to start (step 5). Once the vapor chamber has reached temperature, the reagent is allowed to evaporate by applying vacuum (step 6, Figure 6). After the treatment (10 min), the reagent has been evaporated, and the sample fabrics are dried separately at 50 °C prior to measurements of the dry crease recovery angles.

The obtained DCRA are shown in Table IV. Compared to the non-treated fabrics with DCRA = 145°, only the treatment with chlorosiloxane **10** gives lower angles (DCRA = 142.9°, **Vac160-10**). Fabrics **Vac160-04** and **Vac160-05** show an increase of the DCRA to 158.5° and 151.3°, respectively. Better results are achieved using diepoxides **7** and **8** for fabrics **Vac160-07** and **Vac160-08**, respectively. Here, the DCRA are almost 10° higher than for the non-treated fibers (154.5° and 154.7°, Table IV). The best result is obtained for divinylsulfone **12** as curing agent, as is shown for fabrics **Vac160-12**. The DCRA amounts to 162.7°, which is 17.7° higher than the non-treated fabrics. As RUCON FEC comes as a viscous yellow oil after lyophilization and is not volatile, it cannot be used in this procedure. The obtained value for **Vac160-12**, however, readily demonstrates that the DCRA is increased even though no solvent

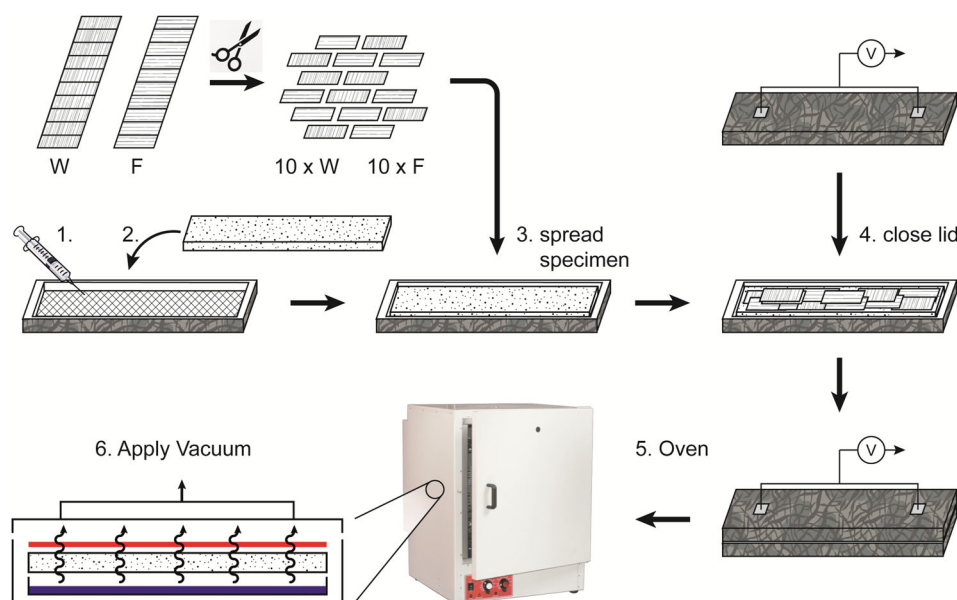


Figure 6. Vapor-chemical application setup for the treatment of cotton cellulose fabrics in a solid/gas interface. *In vacuo* (step 6), reagent (blue) evaporates through the sintering material and the fabrics (red). [Color figure can be viewed at wileyonlinelibrary.com]

Table IV. DCRA of Cotton Cellulose Fabrics Treated with Different Crosslinkers in the Vapor Chamber

| Fabric | Crosslinker | Dry crease recovery angles | | |
|-----------------------------|-------------|----------------------------|-------------|--------------|
| | | Warp (°) | Fill (°) | (W + F)° |
| Non-treated | - | 71.8 | 73.2 | 145.0 |
| H₂O150-03 | 3b | 73.6 ± 2.7 | 76.2 ± 5.6 | 149.8 |
| Vac160-04 | 4 | 76.7 ± 4.4 | 81.8 ± 3.6 | 158.5 |
| Vac160-05 | 5 | 76.0 ± 4.9 | 75.3 ± 3.9 | 151.3 |
| Vac160-07 | 7 | 77.7 ± 4.0 | 76.8 ± 4.7 | 154.5 |
| Vac160-08 | 8 | 76.6 ± 3.9 | 78.1 ± 4.7 | 154.7 |
| Vac160-10 | 10 | 72.4 ± 4.6 | 70.5 ± 10.3 | 142.9 |
| Vac160-12 | 12 | 79.3 ± 5.4 | 83.4 ± 9.3 | 162.7 |

The bold numbers give sum of warp and fill.

Curing conditions: 160 °C, vacuum (~20–40 mbar), 10 min.

was used. However, if compared to sample **H₂O150-03** (sample treated with RUCON FEC according to the industry procedure), sample **Vac160-12** yields increased DCRA values.

If we take the tentative experimental setup of this vapor chamber into account—including the dead volumes inside, irregular flow profiles, minor leakages, vacuum fluctuations—the obtained results are surely directional and trendsetting but not irrefutable. However, as a model and trial setup and procedure, the treatment of fabrics at the solid/gas interface may be a promising approach considering, that in terms of process control, there is no necessity for a solvent and the chemicals used may be recovered in a continuous flow cycle.

CONCLUSIONS

In this article, the effect of the curing of cellulose cotton fabrics under anhydrous conditions using two different processing methods was

investigated. Through excluding water from the crosslinking reactions, higher DCRA were achieved using a set of different crosslinkers. The first setup comprised a pad-cure-dry process. The treatment of cotton cellulose fabrics with polar solvents like DMF has a negative influence on the dry crease recovery angles of the sample fabrics. DMF reduces crystallinity of the fibers, hence, diminishing the DCRA. However, trends are observed using different crosslinkers. In DMF, carbonyldiimidazol **6** showed the best DCRA up to DCRA of 160.1°. It performed better than both comparisons **DMF180-03** and **H₂O150-03** (reaching 149.9°/149.8°). Using EA as solvent, an alteration of the microcrystalline structure of the cellulose cotton fabrics was not observed, as the corresponding control value and non-treated fabrics showed the same DCRA (145.0° and 144.7°, respectively). In EA, triglycidyl isocyanurate **9** showed the best DCRA (166.7°). As a supplemental parameter, different catalysts were introduced in the pad-cure-dry process with

EA. Here, literature-known catalysts were used and in general, DCRA's were increased by use of these catalysts. The best DCRA was obtained again for compound **9** with use of P4-t-Bu as catalyst and a DCRA of 180.2°. While the divinylsulfone treatment showed no effect without catalyst, the DCRA was raised to 166.3° by use of DMAP as catalyst (21.6° above the control value). To exclude the negative effects of the solvents on the fabrics, a reaction setup was developed, where the sample fabrics were treated in a vapor chamber. The results obtained for the treatments at the solid/gas interface of the fabrics all delivered increased DCRA's. The highest DCRA was obtained by use of divinylsulfone (162.7°). The obtained results highlight that the solvent plays an important role and without any crosslinker alters the mechanical properties of the fabrics. Furthermore, and despite this negative solvent effect, the water-free curing of cellulose cotton fabrics produces better DCRA's for the respective fabrics and therefore poses an attractive alternative to commonly used procedures in aqueous environment. Both methods used in this work represent promising approaches compared to conventional padding processes could be of high value for the further development of industrial processes.

ACKNOWLEDGMENTS

The authors thank Angelika Kaiser and Karen Hupfer-Kempkes for the measurement of dry crease angles. This study was performed in part by the Center for Chemical Polymer Technology (CPT), which is supported by the European Union and the Federal state of North Rhine-Westphalia (Grant No. EFRE 300088302). The authors acknowledge financial support for this study from the IGF 18882N grant agreement.

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