Cellulose (2018) 25:4841–4858
https://doi.org/10.1007/s10570-018-1885-1

ORIGINAL PAPER

Crease resistance improvement of hemp biofiber fabric via sol–gel and crosslinking methods

Buket Arık · Ozan Avinc · Arzu Yavas

Received: 9 January 2018 / Accepted: 30 May 2018 / Published online: 9 June 2018

Abstract In this study, crease resistance finish with sol–gel method, crosslinking method and commercial crease resistant finish products were applied to hemp biofiber cellulosic fabrics and the effects of these studied methods on hemp fabrics were investigated by physical performance tests and characterization analyses. In addition, chitosan biopolymer was also studied to investigate its effects on performance properties of hemp cellulosic fabrics. It was determined that sol–gel method and crosslinking method could be used to improve crease resistance property of hemp fabrics. Both sol–gel and crosslinking methods exhibited comparable close results to studied commercial crease resistant finish products, but sol–gel method was found to be better than crosslinking method especially when tensile and tear strength values were considered. The crease recovery angle values of these two methods were found to be quite close to the values of commercial products, on the other hand, chitosan biopolymer addition was not observed to be efficient in terms of crease resistance and physical performance properties.

Keywords Hemp · Cellulosic fiber · Crease resistance · Sol–gel · Crosslinking · Chitosan · Wrinkle

B. Arık · O. Avinc · A. Yavas (✉)
Textile Engineering Department, Pamukkale University, Denizli 20160, Turkey
e-mail: aozerdem@pau.edu.tr

Introduction

Hemp as natural, eco-friendly, renewable, sustainable and biodegradable cellulosic fiber exhibits excellent strength and durability properties due to its high crystalline structure. Besides its good strength properties, hemp fiber also displays very good antistatic, antimicrobial, thermal, UV protection, water permeability properties and does not lead to any allergic reaction for human body (Kozlowski et al. 2005; Kostic et al. 2008; Pejic et al. 2008; Clarke 2010; Gedik et al. 2010; Shahzad 2011; Hwang and Ji 2012; Gedik and Avinc 2018; Liu et al. 2018; Ramesh 2018). In addition, hemp fiber plant is low-input crop and provides natural weed control and needs low fertilizer requirement in its plant agriculture contrary to cotton cultivation that needs high water and agricultural chemical consumption (Kozlowski et al. 2005; Clarke 2010; Gedik and Avinc 2018; Liu et al. 2018). However, hemp fibers which find applications in many different textile products tend to wrinkle like other cellulosic fibers during their use (Kozlowski et al. 2005; Shahzad 2011; Hwang and Ji 2012; Yu 2015; Ramesh 2018).

The reason of the crease or wrinkle formation on the cellulosic fibers is the existance of their free hydroxyl groups. When force is applied to the cellulosic fibers, these free hydroxyl groups form new hydrogen bonds with the adjacent polymer chain which then leads to wrinkles that affect the appearance properties of the cellulosic fabric (Carty and Byrne

1991; Fiscus and Grunenwald 1995; Perkins 1996; Sharpe and Mallinson 2003; Bilgen 2005; Ammayappan et al. 2013; Yu 2015; Arik 2015; Arik et al. 2017). Wrinkle-free (Crease-free) finish process is generally applied to fabrics to prevent wrinkling and to impart crease resistance by limiting the action of these functional groups and preventing new bond formation. There are two main mechanisms that ensure crease resistance as polymer structure like resin formation and covalent bond formation in free hydroxyl groups of cellulose (Needles 1986; Carty and Byrne 1991; Hill et al. 1993; Fiscus and Grunenwald 1995; Perkins 1996). Many studies have focused on crease resistance of cellulosic fabrics which is quite an important problem. The precursor studies were about the conventional methods and the mechanisms of crease resistance (Needles 1986; Carty and Byrne 1991; Hill et al. 1993; Fiscus and Grunenwald 1995; Perkins 1996) on the other hand subsequent studies investigated the new methods, developments and environmental factors (Lacasse and Baumann 2004; Zhou et al. 2004a; Harifi and Montazer 2012; Arik 2015; Arik et al. 2017).

Towards the end of the 1980s, it was understood that formaldehyde released from the first used wrinkle-free materials was not suitable for human health due to its carcinogenic effect. For this reason, the use of low formaldehyde-containing or formaldehyde-free cross-linkers has become prominent (Carty and Byrne 1991; Bajaj 2002; Sharpe and Mallinson 2003; Lacasse and Baumann 2004; Gürsoy et al. 2010; Harifi and Montazer 2012; Arik 2013; Dehabadi et al. 2013; Arik 2015; Arik et al. 2017). Of these cross-linkers, 1,2,3,4-butanetetracarboxylic acid (BTCA) has found a wider usage area than the others due to its more effective crease resistance procurement, quick fixation, resistance against multiple washes, non-malodor-occurence, and less yellowing effect (Perkins 1996; Bajaj 2002; Sharpe and Mallinson 2003; Bilgen 2005; Arik 2015). However, on the other hand, the high cost of BTCA, the harmful effect of the phosphorus-containing catalyst and the strength losses have also created problems for the BTCA usage (Perkins 1996; Sharpe and Mallinson 2003; Lacasse and Baumann 2004; Bilgen 2005; Arik 2013, 2015).

The sol–gel method is an increasingly important method for the modification of textile materials. This method is based on the hydrolysis and condensation of metal or semi-metal alkoxides and it is suggested that this method can also be used to obtain crease resistance (Schramm et al. 2005; Brzezinski et al. 2012; Arik 2013, 2015). In this method, the textile materials are padded with the hydrolyzed metal alkoxide solution and then dried and cured at certain temperatures. Thus, the surface of the applied textile materials is coated with a thin film coating and then the fiber surface is modified by silane-based coupling materials (Schramm et al. 2005; Roe 2008; Arik 2013, 2015; Onar et al. 2015; Onar and Mete 2016).

There are many studies in the literature about the usability of BTCA to provide crease resistance for different types of cellulosic fabrics such as cotton (Schramm et al. 2004; Hebeish et al. 2006; Lam et al. 2010), viscose (Sauperl and Stana-Kleinschek 2010) and ramie (Zhou et al. 2004b, 2007). Some researches also studied the effects of different curing conditions like microwave curing (Fouda et al. 2009), UV and high temperature curing (Nazari et al. 2009) or multifinishing formulations of BTCA with chitosan (Hebeish et al. 2011; Arik et al. 2017), titaniumdioxide (Lam et al. 2010) and silane coupling agents (Schramm et al. 2004). However, there is not much research done on the hemp fabric in this regard. Similarly, the sol–gel method has generally been applied to cotton fiber fabrics and has not been extensively used and investigated to impart functional properties to the bast fibers such as flax, hemp etc. There are some examples for sol–gel treatment on bast fibres to improve thermal stability (Alongi and Malucelli 2013), flame retardancy (Alongi and Malucelli 2013), abrasion resistance (Alongi and Malucelli 2013), UV protection (Vihodceva and Kukle 2011; Ibrahim et al. 2013), antibacterial activity (Ibrahim et al. 2013) and hydrophobicity (Rachini et al. 2012) however there is no published study to provide crease resistance on the bast fibers.

In the previous studies, to enable crease resistance on hemp fabrics, Li et al. 2010 studied liquid ammonia and then DMDHEU (crosslinking chemical with formaldehyde) treatment and improved the crease recovery, washing shrinkage, bending modulus and other appearance qualities of hemp fabrics (Li et al. 2010). Hwang and Ji 2012 investigated the effects of yarn number and liquid ammonia treatment on the physical properties of hemp woven fabrics and stated that the crease recovery of treated hemp fabric was improved up to 78% (Hwang and Ji 2012). So, this current (our) study will be the first extensive study

about triple comparison of crease resistance properties of hemp fiber fabrics in terms of application of sol–gel method, crosslinking finish with BTCA as non-formaldehyde chemical and application of commercial crease resistance products used for other cellulosic fabrics. In addition, crease resistance treatment trails were also carried out with the existence of chitosan biopolymer for hemp cellulosic fiber fabrics in order to investigate the final performance characteristics and their physical properties. Therefore, add-on value, crease recovery angle, bending length, color, tensile strength and tear strength properties of treated and untreated hemp biofiber fabrics were investigated. Moreover, the surface characterization properties of treated hemp fabrics were examined by Scanning Electron Microscopy (SEM) and chemical structure properties of treated hemp fabrics were examined by Fourier Transform Infrared-Attenuated Total Reflectance Spectroscopy [FT-IR (ATR)] Analysis and Energy Dispersive X-ray Analysis (EDX).

Experimental

Material

In this study, desized plain woven fabric which is derived from 20/1 Nm 100% hemp fiber yarn was utilized. The weight of the fabric was 175 g/m^2. In bleaching process, hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH), wetting agent, anti foam agent, stabilizator; in sol–gel crease resistance finish, tetraethylorthosilicate (TEOS) [$Si(OC_2H_5)_4$] 98%, 3-glycidyloxypropyl trimethoxysilane (GPTMS) [$C_9H_{20}O_5Si$] 98%, hydrochloric acid (HCl) 37%, ethanol (C_2H_5OH) 96%; in crosslinking crease resistance finish, 1,2,3,4-Butanetetracarboxylic acid (BTCA) ($C_8H_{10}O_8$) 99%, sodiumhypophosphite (SHP) ($NaPH_2O_2$) 98–101%; in commercial crease resistance finish, two commercial products as crease resistant finish product with low formaldehyde content and formaldehyde free crease resistant finish product were used. These commercial products were supplied from BASF and Archroma. In addition, medium molecular weight chitosan ($C_{12}H_{24}N_2O_9$) with 200.000 cps viscosity and 85.5% deacetylation degree was added to the solutions and the effects were evaluated. TEOS, GPTMS, BTCA, SHP and chitosan were supplied from Aldrich, while the other chemicals were supplied from Merck.

Methods

Bleaching process

Since the bleaching of hemp fabric was quite difficult when compared to other cellulosic fabrics, two step process (pad-batch + exhaustion) was applied to desized hemp fabrics. The bleaching recipe for padding process is shown in Table 1.

Pad-batch bleaching process was carried out with the shown recipe (Table 1) with a 90% wet pick-up and then padded fabric was stored in ambient temperature for 18 h waiting time while rotating. In the second step of the bleaching process (exhaustion step) 0.4 g/kg stabilizator, 2 g/kg sodium hydroxide and 2 g/kg hydrogen peroxide were exhausted for 20 min at 95 °C. Then, the hemp fabric was washed at 95 °C and then neutralized by using acetic acid and finally flat-dried at room temperature.

Sol–gel crease resistance finish

In sol–gel crease resistance finish, four different recipes were applied (Table 2). In these recipes, only the concentration of silane coupling agent (GPTMS) was changed while the concentration of other chemicals were remained constant.

Prepared solutions, as shown in Table 2, were mixed for 24 h at room temperature and then diluted to the ratio of 1:10 with pure water. Diluted solutions were padded with a 90% wet pick-up, then hemp fabrics were dried at 100 °C for 2 min and cured at 150 °C for 30 min.

Table 1 Bleaching recipe of hemp fabric for padding process

Chemical agent	Concentration (g/kg)
Hydrogen peroxide	80
Sodium hydroxide	50
Wetting agent	5
Anti foam agent	3
Stabilizator	4

Table 2 Sol–gel crease resistance finish recipes of hemp fabrics

	GPTMS (mmol)	TEOS (mmol)	Ethanol (ml)	HCl (0.05 M) (ml)
S1	25	50	15	3.60
S2	50	50	15	3.60
S3	75	50	15	3.60
S4	100	50	15	3.60

Crosslinking crease resistance finish

In crosslinking crease resistance finish, four different recipes were applied, likewise the sol–gel method. The details of the recipes were given in Table 3.

The solutions were prepared with the given concentrations in Table 3, mixed until the complete dissolution of the chemicals achieved and then padded with the hemp fabric at a 90% wet pick-up. Then the fabrics were dried at 100 °C for 2 min and cured at 150 °C for 5 min.

Crease resistance finish by commercial products

Two different commercial crease resistant products (LF: commercial crease resistant finish product with low formaldehyde content and FF: Formaldehyde-free commercial crease resistant finish product) were selected and applied in their recommended concentrations by the supplier in order to compare their results with the results of sol–gel and cross-linking methods. The optimum recipes were prepared as LF (100 g/l commercial crease resistant finish product with low formaldehyde content and 20 g/l $MgCl_2$) and FF (200 g/l formaldehyde-free commercial crease resistant finish product) and padded at a 90% wet pick-up. Then the hemp fabrics were dried at 100 °C for 2 min and cured at 150 °C for 5 min.

Chitosan application

Chitosan (1% w/v) was dissolved in an acetic acid solution with a concentration of 2% (v/v) and 500 ml solution was prepared. Then 50 ml of this solution was added to each solution that prepared according to both sol–gel and crosslinking method. The chitosan solutions that were combined with sol–gel finish were called as KS1, KS2, KS3 and KS4; while chitosan solutions that were combined with crosslinking finish were called as KC1, KC2, KC3 and KC4. In addition, in order to see the effect of only chitosan application, chitosan solution was exclusively applied to hemp fabric as a control and this control was called as K.

Table 3 Crosslinking crease resistance finish recipes of hemp fabrics

	BTCA (%)	SHP (%)
C1	1	1
C2	2	2
C3	3	3
C4	4	4

Crease recovery angle measurement

The CRA (Crease Recovery Angle, °) values of the hemp fabric samples were measured for both warp and weft directions according to the TS 390 EN 22313 standard utilizing a SDL Atlas M003A Crease Recovery Tester.

Bending length measurement

The bending length values of the hemp fabric samples were measured according to the TS 1409 standard using a Shirley Stiffness Tester.

Color measurement

It is known that the crease resistance finish may cause color change and may lead to a yellowness effect on white fabrics. In order to investigate this fact, whiteness and yellowness index values of the hemp fabrics were measured using DataColor 600^{TM} Spectrophotometer and the results were given as Stensby and E313 Yellowness Index values, respectively.

Add-on calculation

The add-on values of the coated hemp fiber fabric samples were calculated according to Eq. 1.

$$W_{add-on}(\%) = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 is the weight of the untreated (just bleached) hemp fabric and W_2 is the weight of the treated (finished) hemp fabric. The add-on percentage values of hemp fabrics treated with the solutions were given at Table 4.

Tensile and tear strength measurement

The tensile strength and elongation at break values of the hemp fabric samples were measured according to the TS EN ISO 13934-1 standard using a Tinius Olsen H10 K Strength Testing Machine. Tear strength values of the hemp fabric samples were measured according to the ISO 13937-1 standard using an Elmendorf M008E Tear Strength Tester.

Characterization analyses

The surface morphologies of untreated and treated hemp fabrics were examined by using scanning electron microscopy (SEM, Zeiss EVO 40) with 2000× magnification range. Before the test, the samples were coated with a thin gold film layer to increase the conductivity. Energy dispersive X-ray

Table 4 CRA (crease recovery angle), BL (bending length), WI (whiteness index), YI (yellowness index) and Add-on values of the treated and untreated hemp fabrics

Application Type[a]	Crease Recovery Angle (CRA) (°)		Bending length (cm)		Whiteness index (Stensby)	Yellowness index (E313)	Add-on (%)
	Weft	Warp	Weft	Warp			
Untreated	77	79	4.37	5.90	71.54	11.70	–
S1	78	85	4.90	6.65	64.27	14.21	3.56
S2	82	91	5.00	6.67	63.41	16.02	4.18
S3	94	105	5.07	6.77	61.29	17.58	5.08
S4	111	114	5.47	6.95	60.19	18.35	9.97
C1	83	87	5.57	7.40	71.42	11.84	1.39
C2	99	99	5.77	7.42	70.54	12.03	4.10
C3	116	113	5.80	7.67	68.41	12.73	7.11
C4	125	114	5.80	7.90	68.32	12.82	9.21
K	50	54	9.97	11.15	67.82	12.82	3.01
KS1	81	85	7.40	10.05	66.14	14.00	3.50
KS2	89	91	7.60	10.10	66.10	14.36	3.52
KS3	99	97	7.65	10.75	65.86	15.16	4.60
KS4	114	106	7.70	10.80	64.97	15.31	5.99
KC1	60	59	9.10	11.72	68.24	12.02	3.36
KC2	68	65	9.37	11.82	67.19	12.11	3.61
KC3	79	72	10.02	12.37	66.22	13.14	4.00
KC4	80	76	10.25	12.70	65.07	13.34	7.06
LF	123	119	5.02	7.02	70.45	11.13	5.30
FF	105	111	5.15	7.00	70.58	11.04	7.23

[a]S1: 25 mmol GPTMS + 50 mmol TEOS; S2: 50 mmol GPTMS + 50 mmol TEOS; S3: 75 mmol GPTMS + 50 mmol TEOS; S4: 100 mmol GPTMS + 50 mmol TEOS; C1: 1% BTCA + 1% SHP; C2: 2% BTCA + 2% SHP; C3: 3% BTCA + 3% SHP; C4: 4% BTCA + 4% SHP; **K:** 1% Chitosan; KS1: 1% Chitosan + 25 mmol GPTMS + 50 mmol TEOS; KS2: 1% Chitosan + 50 mmol GPTMS + 50 mmol TEOS; KS3: 1% Chitosan + 75 mmol GPTMS + 50 mmol TEOS; KS4: 1% Chitosan + 100 mmol GPTMS + 50 mmol TEOS; KC1: 1% Chitosan + 1% BTCA + 1% SHP; KC2: 1% Chitosan + 2% BTCA + 2% SHP; KC3: 1% Chitosan + 3% BTCA + 3% SHP; KC4: 1% Chitosan + 4% BTCA + 4% SHP; LF: 100 g/l commercial crease resistant finish product with low formaldehyde content + 20 g/l $MgCl_2$; FF: 200 g/l formaldehyde-free commercial crease resistant finish product

analysis (EDX, Zeiss Supra 40 VP) was conducted to collect elemental information from hemp samples. Before EDX analysis, the samples were coated with a thin carbon layer to render them conductive. The infrared analysis was performed using a Perkin Elmer Spectrum Two^{TM} Infrared Spectrometer (FT-IR) with diamond universal ATR accessory in ATR mode, employing a diamond crystal giving an effective depth of penetration of 1 micron, and at a resolution of 4 cm^{-1}. The measurement was carried out in the region from 4000 to 650 cm^{-1} and recorded spectrum for each sample was the average of 4 scans.

Results and discussion

CRA (crease recovery angle), BL (bending length), WI (whiteness index) and YI (yellowness index) values of the treated and untreated hemp fabrics are shown in Table 4 while tensile strength (N), elongation at break (%) and tear strength (N) values of the treated and untreated hemp fabrics are given in Table 5.

Crease recovery angle (CRA) evaluation

According to the measured results (Table 4), it is obvious that as the concentration of the chemical substances used in both the sol–gel and the cross-linking method increases, the crease recovery angle value increases leading to higher crease resistance levels. In the case of crosslinking method, it could be said that BTCA molecules could crosslink the hydroxyl groups of hemp fiber effectively, SHP catalyst accelerated the formation of anhydrides from BTCA and provided high CRA values which is in line with the previous study on cotton fiber fabric (Lam et al. 2010; Schramm and Rinderer 2015). For sol–gel method, the increase in the CRA values could be related to Si–O-cellulose bonds that occurred as a consequence of epoxide-ring opening of GPTMS and reaction with unreacted hydroxyl groups (–OH) of hemp fibers (Schramm et al. 2004; Schramm and Rinderer 2015). In terms of studied commercial crease resistant products, it was observed that the product with low formaldehyde content (LF) exhibited better crease resistant effect than the formaldehyde-free finish product (FF) (Table 4). When the results of the sol–gel and cross-linking methods were compared with the results of studied commercial crease resistant products, sol–gel method led to very close results with the formaldehyde-free finish product (FF) and on the other hand; the cross-linking method exhibited very close results to the result of the low formaldehyde content commercial crease resistant product (LF). When chitosan biopolymer is applied with cross-linking method, the crease recovery angle was adversely affected leading to significantly lower crease recovery angle results and thereby worse crease (wrinkle) resistance levels (KC1–KC4 vs C1–C4, Table 4). This fact was also observed in another study about the combined effect of chitosan and BTCA on the crease resistance of the nettle fiber fabric (Arik et al. 2017). When chitosan biopolymer is applied with sol–gel method, crease recovery angle levels slightly increased for the weft direction but on the other hand, crease recovery angle levels were either similar or slightly lower for the warp direction in the case of the chitosan biopolymer with sol–gel method application (KS1–KS4 vs S1–S4, Table 4). Overall, the application of chitosan biopolymer with sol–gel method resulted in close comparable results with the solely sol–gel application. Therefore, the application of chitosan biopolymer did not result in significant improvement in terms of crease resistance.

Bending length evaluation

It is earlier reported that crease resistance finish results in stiffer handle for cellulosic fabrics such as cotton and nettle fibers etc., in comparison to their un-treated counterparts (Arik 2015; Arik et al. 2017; Harifi and Montazer 2012; Bajaj 2002). Similar to these results, in this study, bending length values of all finished hemp fiber fabrics were found to be higher than those of un-treated hemp fiber fabrics leading to stiffer handle too (Table 4). Bending length values increased after both sol–gel and cross-linking methods (S1–S4 and C1–C4), but those measured values were close to the bending length results of commercial crease resistant products (LF and FF). Therefore, it could be stated that both sol–gel and cross-linking methods resulted in acceptable levels of bending length values. When the two methods (sol–gel and cross-linking methods) are compared with each other, the sol–gel method resulted in slightly lower bending length results leading to slightly better handle. The addition of chitosan biopolymer greatly increased the bending

Table 5 Tensile strength, elongation at break and tear strength values of the treated and untreated hemp fabrics

Application type[a]	Tensile strength (N)		Elongation at break (%)		Tear strength (N)	
	Weft	Warp	Weft	Warp	Weft	Warp
Untreated	734	681	30.01	7.00	40.64	40.29
S1	635	636	19.36	6.63	33.38	33.28
S2	619	608	19.54	6.46	26.70	30.68
S3	591	576	19.72	6.15	25.50	26.19
S4	553	535	21.41	5.80	19.19	25.20
C1	600	520	16.40	6.03	27.70	30.83
C2	491	468	16.60	5.46	19.91	27.71
C3	484	425	16.70	5.36	17.38	23.79
C4	452	405	17.50	4.87	15.18	23.61
K	695	593	15.78	5.74	39.83	33.23
KS1	572	569	15.24	6.38	35.37	37.23
KS2	554	566	15.83	6.13	28.35	32.87
KS3	550	559	15.98	6.03	27.86	28.32
KS4	541	516	16.00	5.40	26.85	27.37
KC1	615	595	15.26	6.00	31.16	32.28
KC2	601	472	13.06	4.80	23.43	29.52
KC3	505	439	12.58	4.68	19.00	25.67
KC4	454	424	11.78	4.60	17.56	25.16
LF	285	398	15.29	4.83	15.00	19.90
FF	539	512	17.55	5.30	22.56	29.70

[a]S1: 25 mmol GPTMS + 50 mmol TEOS; S2: 50 mmol GPTMS + 50 mmol TEOS; S3: 75 mmol GPTMS + 50 mmol TEOS; S4: 100 mmol GPTMS + 50 mmol TEOS; C1: 1% BTCA + 1% SHP; C2: 2% BTCA + 2% SHP; C3: 3% BTCA + 3% SHP; C4: 4% BTCA + 4% SHP; K: 1% Chitosan; KS1: 1% Chitosan + 25 mmol GPTMS + 50 mmol TEOS; KS2: 1% Chitosan + 50 mmol GPTMS + 50 mmol TEOS; KS3: 1% Chitosan + 75 mmol GPTMS + 50 mmol TEOS; KS4: 1% Chitosan + 100 mmol GPTMS + 50 mmol TEOS; KC1: 1% Chitosan + 1% BTCA + 1% SHP; KC2: 1% Chitosan + 2% BTCA + 2% SHP; KC3: 1% Chitosan + 3% BTCA + 3% SHP; KC4: 1% Chitosan + 4% BTCA + 4% SHP; LF: 100 g/l commercial crease resistant finish product with low formaldehyde content + 20 g/l $MgCl_2$; FF: 200 g/l formaldehyde-free commercial crease resistant finish product

length values of all hemp fabric specimens (KS1–KS4 and KC1–KC4 vs S1–S4 and C1–C4, respectively; Table 4), thus affecting the handles of the specimens in the negative direction leading to stiffer handle. The negative effect of chitosan biopolymer on handle properties of some textile fabrics was also reported in the previous studies (Bilgen 2005; Arik et al. 2017; Arik 2013).

Color change evaluation

Cellulosic materials may exhibit color change and mostly tend to turn yellow (yellowing effect) due to the presence of unsaturated conjugated groups in the cellulosic substrate and degradation processes especially in the curing step of crease resistant finish. Three reactions such as the hydrolysis of the glycosidic bond, the oxidation of the hydroxyl groups and the dehydration of the cellulose backbone can cause this yellowing effect and this undesired modification can rise because of the additive chemicals, high curing temperature and high curing time (Schramm and Rinderer 2015).

The application of both commercial crease resistant products (LF and FF) on hemp fabrics led to almost no change on color properties in respect of whiteness and yellowness (Table 4). On the other part, the application of both sol–gel and cross-linking methods (S1–S4 and C1–C4, Table 4) on hemp fabrics resulted in decrease on whiteness and increase on yellowness levels. When the two methods (S1–S4 and C1–C4) were compared with each other, the whiteness and

yellowness changes appear to be more pronounced in the case of sol–gel method in comparison with cross-linking method leading to yellower and less white appearance. The distinctive changes in the color in the sol–gel method were thought to be due to high curing time (30 min). On the one hand, the addition of chitosan biopolymer improved the whiteness levels in the case of sol–gel method; on the other hand, the addition of chitosan biopolymer slightly reduced the whiteness levels in the case of cross-linking method. However, these aforementioned differences, due to the presence of chitosan biopolymer, were not quite significant.

Add-on evaluation

All the crease resistance finishing processes gave rise to increase in the weight of the hemp fabrics in the range of 1.39–9.97%. It was observed that as the concentration of the crosslinking chemicals in the solution increased, the final fabric weight increased in line with this fact. For example, the highest add-on values were found to be in the hemp fabrics treated with the recipes S4 and C4 (9.97 and 9.21% respectively). When commercial products were considered, the add-on values of LF and FF were calculated as 5.30 and 7.23% respectively. So, it can be concluded that the values of both sol–gel and crosslinking methods were slightly higher than those of commercial finishes.

Tensile and tear strength evaluation

Both tensile and tear strength performances of hemp fabrics decreased after all studied crease resistant finish applications when compared to untreated hemp fabric (Table 5). This was an expected result and this determination was in line with the reported earlier studies about other cellulosic fabrics, mainly about cotton fiber fabrics (Arik 2015; Zhou et al. 2004a; Harifi and Montazer 2012; Bajaj 2002; Dehabadi et al. 2013; Hebeish et al. 2006). In general, it was observed that the loss of tensile strength in the cross-linking method was slightly higher than that of the sol–gel method. This fact was attributed to the acidity of the crosslinking finishing bath whose pH value was 3, while the pH value of sol–gel method was 5. Moreover, although the curing time was quite higher (30 min.) in sol–gel method than in crosslinking method (5 min.) the results were found to be quite good for sol–gel method. When studied commercial crease resistant products are taken into consideration, it is determined that commercial crease resistant finish product with low formaldehyde content (LF) resulted in considerable loss of tensile strength (61% in weft direction and 41% in warp direction) (Table 5). Actually this measured tensile strength loss and as well as the tear strength loss measured after the finishing with this product (LF) were the maximum strength losses in this study for both weft and warp directions. In this case, it is obvious that both methods (sol–gel and cross-linking methods) displayed lower strength losses than commercial crease resistant finish product with low formaldehyde content (LF). When formaldehyde-free commercial crease resistant finish product (FF) is compared with sol–gel and cross-linking methods, the sol–gel method is found to be better than this product (FF) from the tensile strength point of view; whereas, oppositely, the cross-linking method generally led to higher tensile strength and tear strength losses in comparison to this product (FF).

The addition of chitosan biopolymer reduced the tensile strength for the sol–gel method treated hemp fabrics and improved the tensile strength for the cross-linking method treated hemp fabrics. According to this, it could be said that chitosan biopolymer application for sol–gel method is not effective and beneficial from the tensile strength point of view. In the case of cross-linking method, chitosan biopolymer application seems to be beneficial for the hemp fiber fabric from the tensile strength point of view (Table 5). Similar determination was also reported in an earlier reported study (Arik et al. 2017) about the combined effect of chitosan and BTCA on the crease resistance of nettle fiber fabric and in the other study (Hebeish et al. 2011) about the combined effect of chitosan and BTCA on the easy care and antimicrobial properties of cotton fabric from the tensile strength point of view. Nevertheless it is the right spot to remind once more that chitosan biopolymer addition in the cross-linking method substantially affected the crease recovery angle in a negative way leading to less crease resistance performance (Table 4). Therefore, it could be stated that the addition of chitosan biopolymer for both sol–gel and cross-linking methods is not beneficial for crease resistance performance.

When the elongation at break results of hemp fabrics were examined (Table 5), it was observed that there was a general decrease on elongation, especially

in the weft direction, for all crease resistant finish treated hemp fabrics in comparison with the untreated hemp fabric. It was determined that the elongation at break values obtained from the hemp fabrics treated with both sol–gel and crosslinking methods could be at acceptable levels since these measured results were either very close to or sometimes even better than the elongation at break values obtained from the hemp fabrics treated with both commercial crease resistant products (LF and FF) (Table 5).

As in the case of tensile strength, there were also losses on tear strength values of the treated hemp fabrics (Table 5). In general, it was observed that both sol–gel and cross-linking methods resulted in comparable close values to those of hemp fabrics treated with commercial crease resistant products (LF and FF) leading to acceptable performance from the tear strength point of view (Table 5). When the two methods (sol–gel and cross-linking methods) are compared with each other, it is clear that the sol–gel method is slightly better, but with little difference, than cross-linking method in respect of tear strength performance. The addition of chitosan biopolymer played a role in increasing the tear strength in both the weft and warp directions for both sol–gel and cross-linking methods. However when all test results are considered, the addition of chitosan biopolymer for sol–gel method is not beneficial for crease resistance finish application mainly due to higher stiffness, lower tensile strength and lower elongation levels attained. Similarly, when all test results are considered, the addition of chitosan biopolymer for cross-linking method is not beneficial for crease resistance finish application mainly due to lower crease recovery angle, higher stiffness, less whiteness, higher yellowness and lower elongation levels attained.

Evaluation of the relation between crease recovery angle and tensile strength

The relation between crease recovery angle and tensile strength values of the hemp samples treated with sol–gel method is given in Fig. 1; the relation between crease recovery angle and tensile strength values of the hemp samples treated with crosslinking method is given in Fig. 2 and the relation between crease recovery angle and tensile strength values of the hemp samples treated with commercial crease resistant products (LF and FF) is given in Fig. 3.

When Figs. 1 and 2 were examined, measured strength losses in hemp fiber fabrics subjected to cross-linking method were found to be higher than those of the hemp fabric treated with sol–gel method. Both graphs clearly exhibited that tensile strength values decreased while crease recovery angle values increased. Moreover, the distance between the curves of crease recovery angles and tensile strength values was observed to be more in sol–gel method than in crosslinking method and this fact showed that sol–gel method was better than crosslinking method in terms of tensile strength in the same crease recovery angle.

When Fig. 3 was examined, it was clearly visible that higher strength loss was observed in the case of hemp fabric treated with commercial crease resistant finish product with low formaldehyde content (LF) in comparison to hemp fabric treated with formaldehyde-free commercial crease resistant finish product (FF) while they both exhibited similar comparable crease angle recovery levels. So, the strength loss caused by the increase in the crease recovery angle of the hemp fabrics subjected to the LF product is significantly higher than the strength loss caused by the similar level of increase in the crease recovery angle of the hemp fabrics subjected to the FF product.

Generally speaking, the result showed that the studied commercial crease resistant finish product with low formaldehyde content (LF) and cross-linking type crease resistance finish increased the crease resistance of hemp fiber fabric while decreasing their respective tensile strength values significantly. When the two studied crease resistance application methods were compared, sol–gel method was found to be more suitable with better tensile strength results than the crosslinking method in terms of crease resistance attainment on hemp fiber fabric.

Scanning electron microscopy (SEM) analysis

SEM images of the treated and un-treated hemp fiber fabric samples are given in Figs. 4 and 5. When these obtained images were observed, it can be clearly seen that un-treated hemp fibres possess nodal and rough surface structure. As seen in the images, crease resistance finish caused some deformation, cracking and even breakages at some zones on hemp fibre surfaces. When sol–gel and crosslinking finish were compared to each other, sol–gel method was found to be more suitable in terms of its less harmful effect than

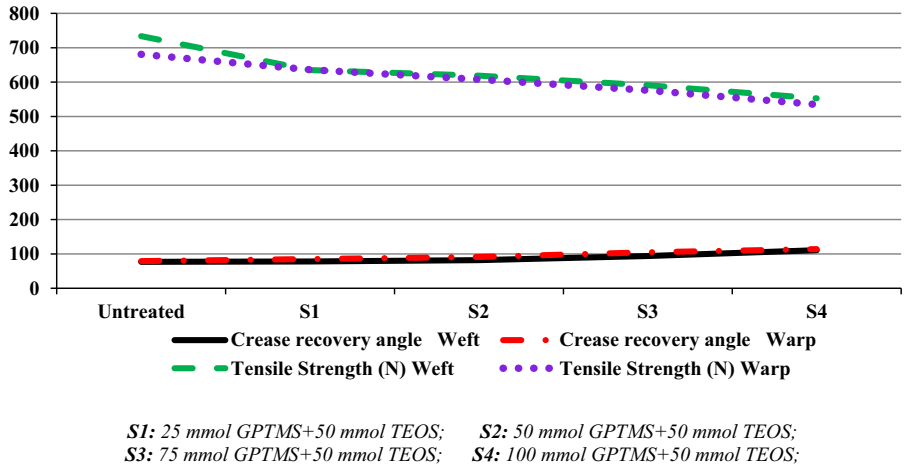


Fig. 1 The relation between crease recovery angle and tensile strength values of the hemp fabrics treated with sol–gel method

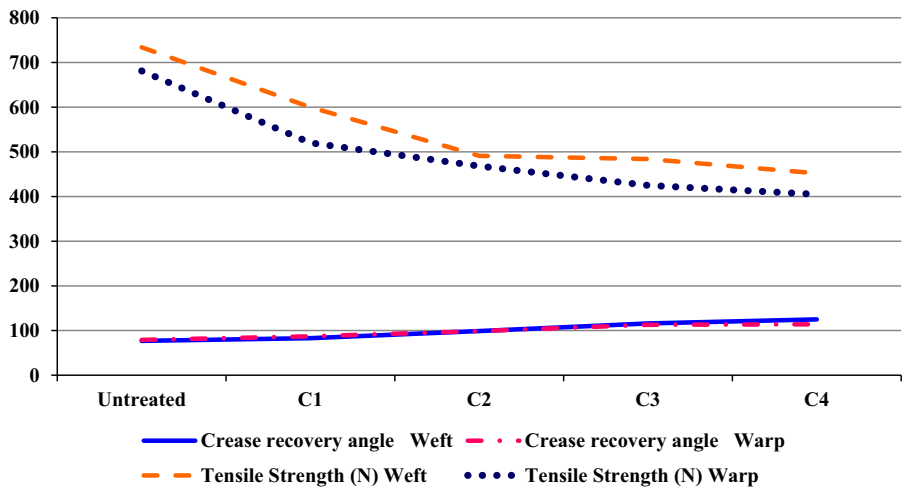


Fig. 2 The relation between crease recovery angle and tensile strength values of the hemp fabrics treated with crosslinking method

crosslinking method. In the case of chitosan biopolymer added treatments, chitosan application seems to form a thin film layer on the hemp fibre surface and it seems that this thin layer played a binding role on the deformed parts (Fig. 4). So, the previously measured improvement in tear strength performance after the chitosan application (Table 5) could be attributed to this fact. On the other hand, when commercial crease resistant finish products were considered, it was determined that formaldehyde-free commercial crease resistant finish product (FF) caused less deformation than commercial crease resistant finish product with low formaldehyde content (LF) and this fact could be attributed to more possible crosslink formation among hemp fibers due to formaldehyde presence and this may make fibers more brittle leading to decrease on tensile and tear strength values.

Energy dispersive X-ray (EDX) analysis

The atomic percentages of elements that appeared in hemp fiber fabric samples are shown in Table 6. Moreover, related EDX spectras are given in Fig. 6.

According to Table 6, C content was found to decrease after crease resistant finish treatments. The percentage amount of C content decrease was

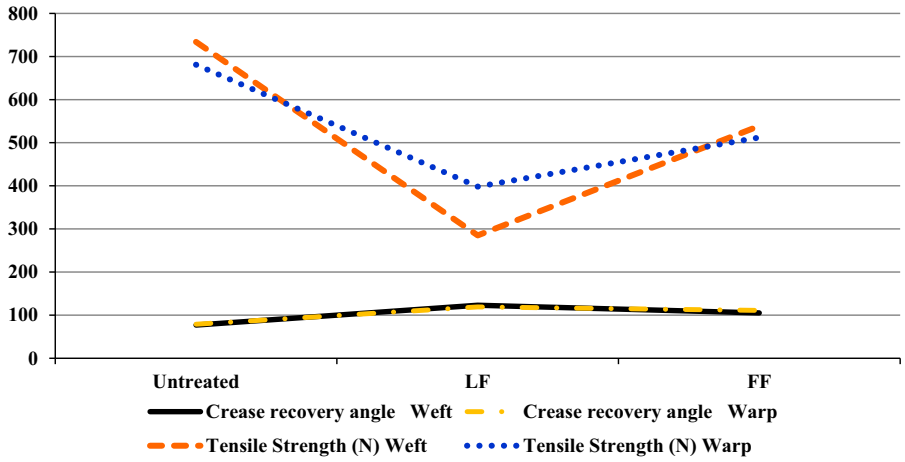


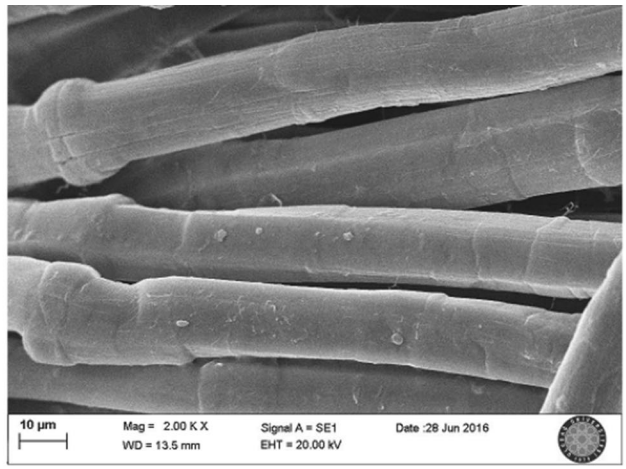
Fig. 3 The relation between crease recovery angle and tensile strength values of the hemp fabrics treated with commercial products

calculated as 2.59% for S4, 6.75% for C4, 4.77% for LF and 4.63% for FF. The maximum loss was observed in the sample that was treated by BTCA and SHP and this fact was attributed to the esterification between polycarboxylic acid and hemp cellulose structure. Esterification reaction involves formation of a five-membered cyclic anhydride intermediate and ester respectively and this fact causes carbonyls to be in three forms as intermolecular ester linkage, carboxyl and carboxylate (Yang 1991; Yang and Bakshi 1996; Yang and Wang 1996; Lewis and Voncina 1997; Lam et al. 2011). Contrary to decrease in the C content, O content was found to increase after crease resistant finish treatments as expected. The percentage amount of O content increase was calculated as 2.83% for S4, 9.64% for C4, 10.27% for LF and 14.63% for FF. The difference in the ranking of the treatments in terms of C and O content change was attributed to the presence of auxiliary agents in the finishing baths. For instance, data showed the presence of elements due to catalysts like SHP (small amount of Na and P recorded in C4) and $MgCl_2$ (small amount of Mg and Cl recorded in LF) in the finishing baths. The EDX results also proved the presence of Si element after sol–gel process (S4). These results were found to be in line with the previous studies (Lam et al. 2011; Brancatelli et al. 2011; Rachini et al. 2012; Gashti et al. 2012).

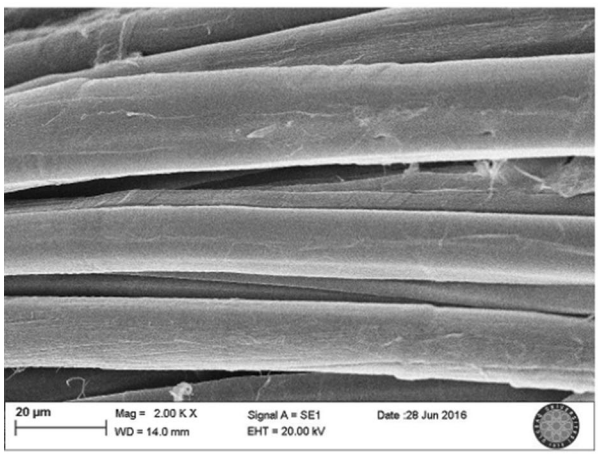
Fourier transform infrared spectroscopy (FT-IR) analysis

FTIR (ATR) spectra of the treated and untreated hemp fabric samples are given in Fig. 7.

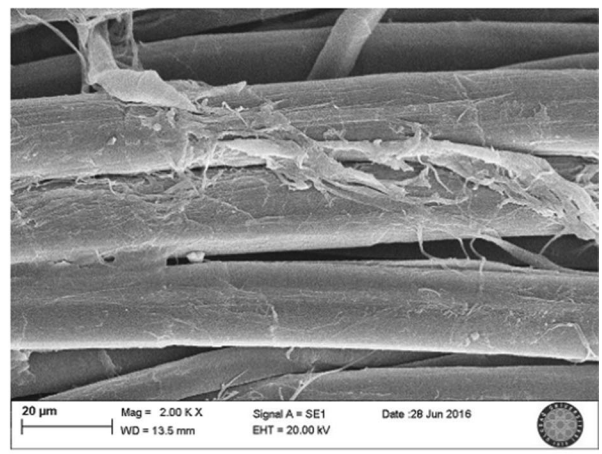
Similar to other lignocellulosic fibres, hemp fibres give certain peaks of cellulose and lignin combinations too. For instance, the wide peaks in 3410 and 3290 cm^{-1} belong to hydroxyl group (–OH) and short peaks in 2900 and 1430 cm^{-1} belong to methylene groups ($–CH_2$) of cellulose. The short peak in 1733 cm^{-1} is related to carbonyl group (C=O) composed from acetyl esther and carbonyl aldehyde groups; the medium peaks in 1160 and 1114 cm^{-1} are due to –C–O–C asymmetric bonding and the peak in 1058 cm^{-1} is due to –C–O– stretching in hemicellulose and lignin (Garside and Wyeth 2006; Ibrahim et al. 2010; Surina and Andrassy 2013; Zimniewska et al. 2012; Schramm and Rinderer 2015). It is already known that when cellulose fibres are treated with BTCA and SHP, ester bonds occur between cellulose and BTCA (Arik et al. 2017; Arik 2013; Sauperl and Stana-Kleinschek 2010; Schramm and Rinderer 2015; Zhou et al. 2004a). Therefore, it was clearly understood that the band in 1750 cm^{-1}, which appeared in crosslinking finish however similar peak did not exist in the untreated hemp, was originated from esther carbonyl group and verified covalent bonding. On the other hand, when the spectrum of sol–gel finish treated hemp sample compared to the spectrum of untreated



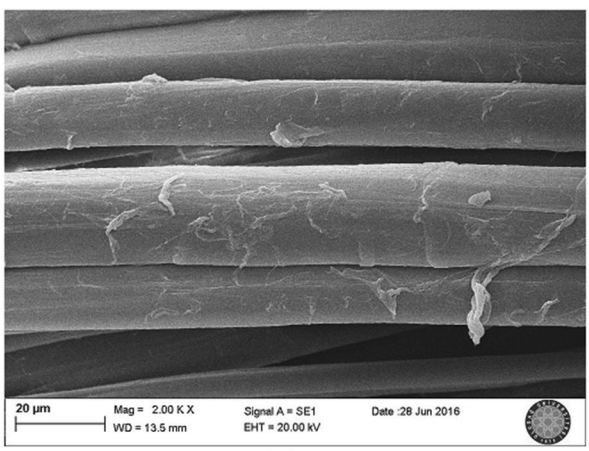
(a)



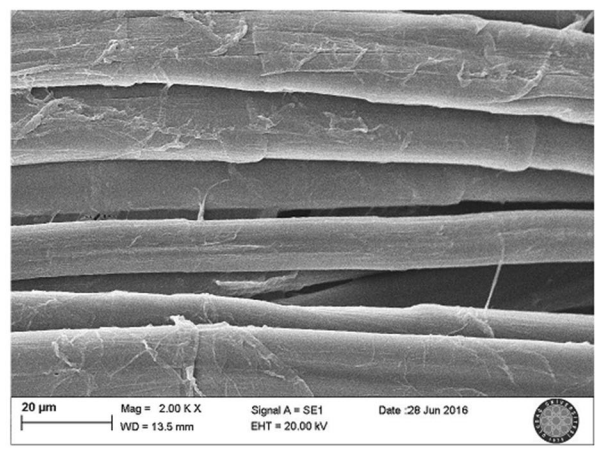
(b)



(c)

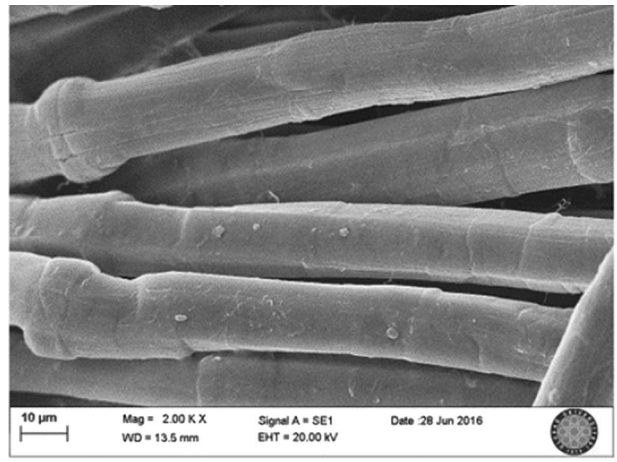


(d)

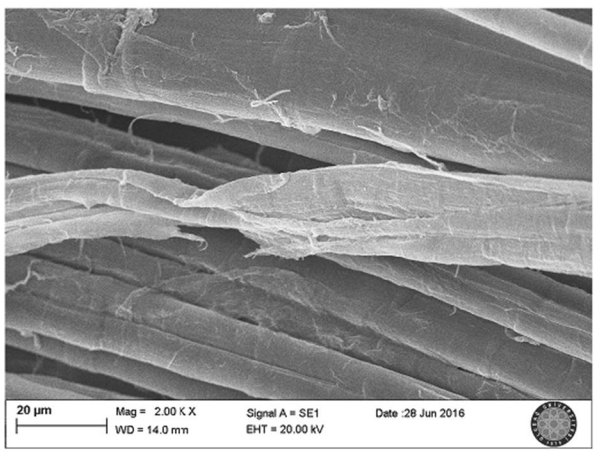


(e)

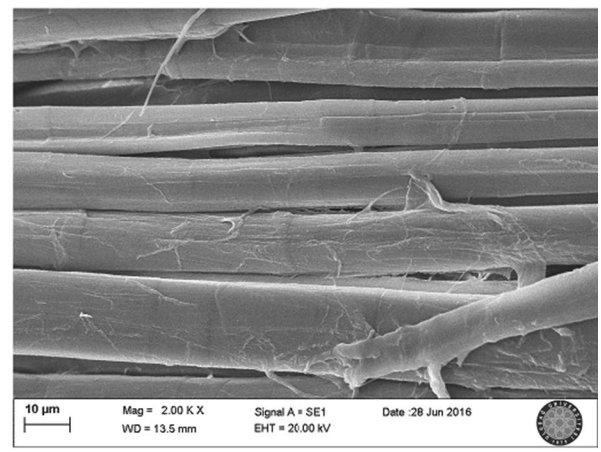
Fig. 4 SEM images of the hemp fabric samples—1 (Magnification range = ×2000). **a** Untreated hemp, **b** Sol–gel finish treated hemp (100 mmol GPTMS + 50 mmol TEOS), **c** crosslinking finish treated hemp (4% BTCA + 4% SHP), **d** Chitosan added sol–gel finish treated hemp (1% Chitosan + 100 mmol GPTMS + 50 mmol TEOS), **e** chitosan added crosslinking finish treated hemp (1% Chitosan + 4% BTCA + 4% SHP)



(a)



(b)



(c)

Fig. 5 SEM images of the hemp fabric samples—2 (Magnification range = ×2000). **a** Untreated hemp, **b** Hemp treated with the commercial crease resistant finish product with low formaldehyde content (100 g/l finish product with low formaldehyde content + 20 g/l $MgCl_2$), **c** hemp treated with the formaldehyde-free commercial crease resistant finish product (200 g/l formaldehyde-free finish product)

Table 6 The atomic percentage of different elements in crease-resistant-treated hemp fabrics

Finishing type	Elements (atomic %)						
	C	O	Si	Na	P	Mg	Cl
Untreated hemp	75.94	24.06	–	–	–	–	–
S4	73.97	24.74	1.29	–	–	–	–
C4	70.81	26.38	–	1.80	1.01	–	–
LF	72.32	26.53	–	–	–	0.55	0.60
FF	72.42	27.58	–	–	–	–	–

hemp sample, there was no significant change between both and no new peak formation were observed after the sol–gel finish. Only, due to silica content, some inconspicuous decreases in the levels of some bands occurred and this fact confirmed that Si–O-cellulose bonds did not cause prominent slippages or changes as

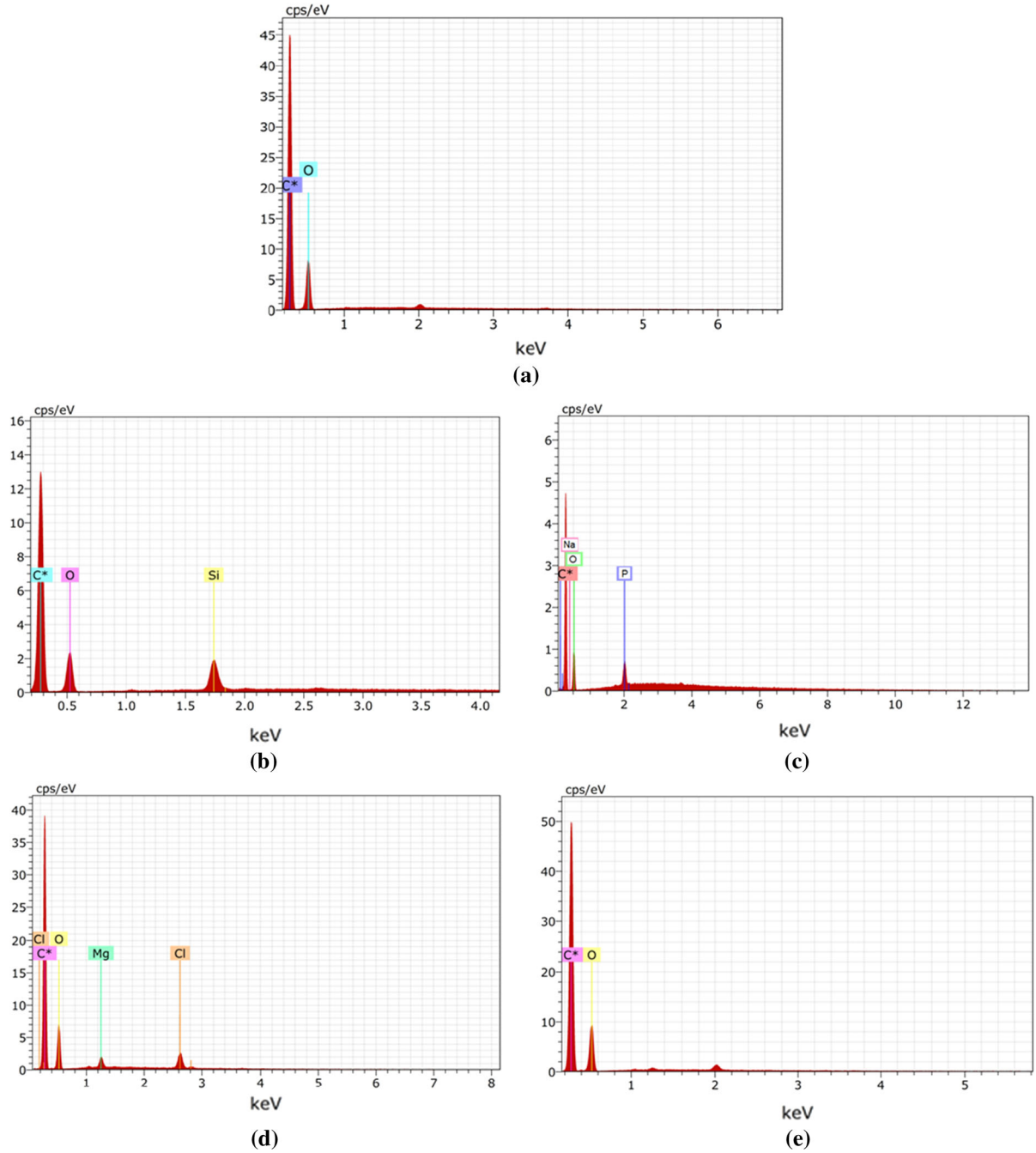


Fig. 6 EDX spectra of the hemp fiber fabric samples. **a** Untreated, **b** treated by recipe S4, **c** treated by recipe C4, **d** treated by recipe LF, **e** treated by recipe FF

reported in previous studies (Arik 2013; Li et al. 2008).

Final evalution of overall study and optimum chemical concentrations and obtained results are summarized in Table 7. According to Table 7, the best crease resistance performance was achieved by crosslinking method and whiteness/yellowness index values of hemp fabric treated with this crosslinking method were quite close to commercial products. On the other hand, in terms of tensile/tear strength and

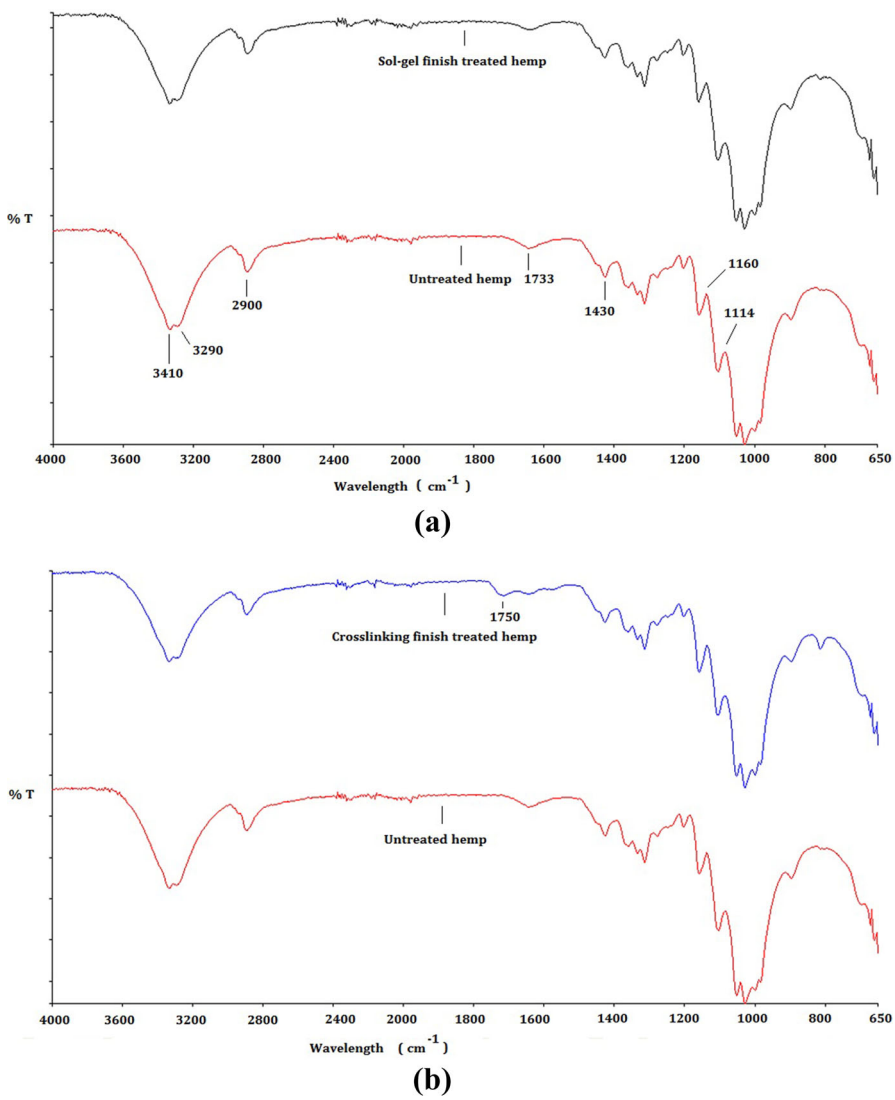


Fig. 7 FT-IR spectra of the hemp fabric samples. **a** Untreated hemp and sol–gel finish treated hemp (100 mmol GPTMS + 50 mmol TEOS). **b** Untreated hemp and crosslinking finish treated hemp (4% BTCA + 4% SHP)

bending length values, sol–gel method was found to be better than crosslinking method. When all data were considered, the results of the sol–gel method could be suggested as quite acceptable.

Conclusion

In this study, sol–gel and crosslinking methods as alternative crease resistance finish methods were studied on hemp cellulosic fabrics and the results were compared with commercially available crease resistant finish products. Two different commercial products (formaldehyde-free commercial crease resistant finish product and commercial crease resistant finish product with low formaldehyde content) were applied for this purpose. In addition, the effect of chitosan biopolymer on crease resistance and other physical performance properties of hemp cellulosic fabrics were investigated. According to all results of the study, it was determined that both two studied methods exhibited comparable close results to used commercial products, but sol–gel method was found to be better than crosslinking method especially when tensile and tear strength values were considered. Chitosan application did not cause significant changes on fabric performance properties and chitosan biopolymer addition seems to be useless for crease

Table 7 Final evalution of overall study and optimum results of applied crease resistance finish methods for hemp fabric

Application method	Applied chemicals	Crease recovery angle (°)		Tensile strength (N)		Tear strength (N)		Bending length (cm)		Whiteness index (Stensby)	Yellowness index (E313)
		Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp		
Untreated	–	77	79	734	681	40.64	40.29	4.37	5.90	71.54	11.70
Sol–Gel method	100 mmol GPTMS + 50 mmol TEOS	111	114	553	535	19.19	25.20	5.47	6.95	60.19	18.35
Crosslinking method	%4BTCA + %4 SHP	125	114	452	405	15.18	23.61	5.80	7.90	68.32	12.82
Low formaldehyde product Finish[a]	100 g/l finish product + 20 g/l $MgCl_2$	123	119	285	398	15.00	19.90	5.02	7.02	70.45	11.13
Formaldehyde-free product finish[b]	200 g/l finish product	105	111	539	512	22.56	29.70	5.15	7.00	70.58	11.04

[a]Commercial crease resistant finish product with low formaldehyde content (LF)

[b]Formaldehyde-free commercial crease resistant finish product (FF)

resistance finish applications. The deformations on hemp cellulosic fibre structure after the crease resistance finish and certain peaks of hemp fibres were clearly observed in SEM images and FTIR (ATR) spectra, respectively. In addition, EDX data showed the presence of elements in the hemp fiber fabric samples after the related crease resistance finishing treatments.

Acknowledgment This study was supported by PAUBAP with the Project Number 2014BSP017.

References

Alongi J, Malucelli G (2013) Thermal stability, flame retardancy and abrasion resistance of cotton and cotton-linen blends treated by sol-gel silica coatings containing alumina micro- or nano-particles. Polym Degrad Stab 98:1428–1438

Ammayappan L, Nayak LK, Ray DP, Das S, Roy AK (2013) Functional finishing of jute textiles—an overview in India. J Nat Fibers 10:390–413

Arik B (2013) Investigation of chitosan applicability in medical textiles by using different application methods (Ph.D. thesis). Ege University Graduate School of Natural and Applied Science, Izmir, Turkey

Arik B (2015) Latest developments on crease resistance processes for cellulosic fabrics. Pamukkale Univ J Eng Sci 21(7):296–305

Arik B, Yavas A, Avinc O (2017) Antibacterial and wrinkle resistance improvement on nettle biofiber using chitosan and BTCA. Fibres Text East Eur 3(123):106–111

Bajaj P (2002) Finishing of textile materials. J Appl Polym Sci 83:631–659

Bilgen M (2005) Wrinkle recovery for cellulosic fabric by means of ionic crosslinking (M.Sc. Thesis). Graduate Faculty of North Carolina State University, North Carolina, USA

Brancatelli G, Colleoni C, Massafra MR, Rosace G (2011) Effect of hybrid phosphorus-doped silica thin films produced by sol-gel method on the thermal behavior of cotton fabrics. Polym Degrad Stab 96:483–490

Brzezinski S, Kowalczyk D, Borak B, Jasiorski M, Tracz A (2012) Applying the sol-gel method to the deposition of nanocoats on textiles to improve their abrasion resistance. J Appl Polym Sci 125:3058–3067

Carty P, Byrne MS (1991) The chemical and mechanical finishing of textile materials, 2nd edn. Newcastle upon Tyne Polytechnic Products Ltd, Newcastle

Clarke RC (2010) Traditional fiber hemp (Cannabis) production, processing, yarn making, and weaving strategies—functional constraints and regional responses. Part 1. J Nat Fibers 7:118–153

Dehabadi VA, Buschmann HJ, Gutmann JS (2013) Study of easy care and biostatic properties of finished cotton fabric with polyamino carboxylic acids. J Text Inst 104(4):414–418

Fiscus G, Grunenwald D (1995) Textile finishing a complete guide, 1st edn. Editions High Textil, Sausheim

Fouda MMG, El Shafei A, Sharaf S, Hebeish A (2009) Microwave curing for producing cotton fabrics with easy care and antibacterial properties. Carbohyd Polym 77:651–655

Garside P, Wyeth P (2006) Identification of cellulosic fibres by FTIR spectroscopy differentiation of flax and hemp by polarized ATR FTIR. Stud Conserv 51(3):205–211

Gashti MP, Alimohammadi F, Shamei A (2012) Preparation of water-repellent cellulose fibers using a polycarboxylic acid/hydrophobic silica nanocomposite coating. Surf Coat Technol 206:3208–3215

Gedik G, Avinc O (2018) Bleaching of hemp (*Cannabis Sativa* L.) fibers with peracetic acid for textiles industry purposes. Fibers Polym 19(1):82–93

Gedik G, Avinç OO, Yavaş A (2010) Hemp fiber properties and its advantages in textile industry. Electron J Text Technol 4(3):39–48

Gürsoy NÇ, Armağan OG, Şahin UK, Gül M (2010) Effects of alternative pre-treatments on performance of durable press finished fabric. J Text Appar Tekst Konfeks 20(4):336–342

Harifi T, Montazer M (2012) Past present and future prospects of cotton cross-linking: new insight into nanoparticles. Carbohyd Polym 88:1125–1140

Hebeish A, Hashem M, Abdel-Rahman A, El-Hilw ZH (2006) Improving easy care nonformaldehyde finishing performance using polycarboxylic acids via precationization of cotton fabric. J Appl Polym Sci 100:2697–2704

Hebeish A, Abdel-Mohdy FA, Fouda MMG, Elsaid Z, Essam S, Tamam GH, Drees EA (2011) Green synthesis of easy care and antimicrobial cotton fabrics. Carbohyd Polym 86:1684–1691

Hill DJ, Hall ME, Holmes DA, Lomas M, Padmore K (1993) An introduction to textiles volume IV textile wet processing. Comett Eurotex, Bolton

Hwang MS, Ji DS (2012) The effects of yarn number and liquid ammonia treatment on the physical properties of hemp woven fabrics. Fibers Polym 13(10):1335–1340

Ibrahim NA, Hashem MM, Eid MA, Refai R, El-Hossamy M, Eid BM (2010) Eco-friendly plasma treatment of linen-containing fabrics. J Text Inst 101(12):1035–1049

Ibrahim NA, Eid BM, Abd El-Aziz E, Abou Elmaaty TM (2013) Functionalization of linen/cotton pigment prints using inorganic nano structure materials. Carbohyd Polym 97(2):537–545

Kostic M, Pejic B, Skundric P (2008) Quality of chemically modified hemp fibers. Biores Technol 99:94–99

Kozlowski R, Baraniecki P, Barriga-Bedoya J (2005) Bast fibres (flax, hemp, jute, ramie, kenaf, abaca). In: Blackburn RS (ed) Biodegradable and sustainable fibres, Chap 2. Woodhead Publishing, England, pp 36–86

Lacasse K, Baumann W (2004) Textile chemicals environmental data and facts, 1st edn. Springer, Heidelberg

Lam YL, Kan CW, Yuen CWM (2010) Wrinkle-resistant finishing of cotton fabric with BTCA: the effect of co-catalyst. Text Res J 81(5):482–493

Lam YL, Kan CW, Yuen CWM (2011) Physical and chemical analysis of plasma-treated cotton fabric subjected to wrinkle-resistant finishing. Cellulose 18:493–503

Lewis DM, Voncina B (1997) Durable press finishing of cotton with polycarboxylic acids. II. Ester crosslinking of cotton with dithiosuccinic acid derivative of S-Triazine. J Appl Polym Sci 66:171–177

Li F, Xing Y, Ding X (2008) Silica xerogel coating on the surface of natural and synthetic fabrics. Surf Coat Technol 202:721–4727

Li J, Feng J, Zhang H, Zhang J (2010) Wear properties of hemp, ramie and linen fabrics after liquid ammonia/crosslinking treatment. Fibres Text East Eur 18(5):81–85

Liu L, Li B, Xiang Y, Zhang R, Yu J, Fang B (2018) Effect of growth period and sampling section on the chemical composition and microstructure of raw hemp fibers. BioResources 13(1):1961–1976

Nazari A, Montazer M, Rashidi A, Yazdanshenas M, Anary-Abbasinejad M (2009) Nano TiO_2 photo-catalyst and sodium hypophosphite for cross-linking cotton with poly carboxylic acids under UV and high temperature. Appl Catal A 371:10–16

Needles HL (1986) Textile fibers dyes finishes and processes a concise guide, 1st edn. Noyes, New Jersey

Onar N, Mete G (2016) Development of water repellent cotton fabric with application of ZnO Al_2O_3 TiO_2 and ZrO_2 nanoparticles modified with ormosils. J Text Appar Tekst Konfeks 26(3):295–302

Onar N, Mete G, Aksit A, Kutlu B, Çelik E (2015) Water- and oil-repellency properties of cotton fabric treated with silane, Zr, Ti based nanosols. Int J Text Sci 4(4):84–96

Pejic BM, Kostic MM, Skundric PD, Praskalo JZ (2008) The effects of hemicelluloses and lignin removal on water uptake behavior of hemp fibers. Biores Technol 99:7152–7159

Perkins WS (1996) Textile coloration and finishing, 1st edn. Carolina Academic Pres, North Carolina USA

Rachini A, Troedec ML, Peyratout C, Smith A (2012) Chemical modification of hemp fibers by silane coupling agents. J Appl Polym Sci 123:601–610

Ramesh M (2018) Hemp, jute, banana, kenaf, ramie, sisal fibers. In: Handbook of properties of textile and technical fibres (2nd edn). A volume in The Textile Institute Book Series, vol 9, pp 301–325

Roe BG (2008) Durable non-fluorine water-repellent fabric finishing: surface treatment using silica nanoparticulates and mixed silanes (M.Sc. Thesis). Graduate Faculty of North Carolina State University, Raleigh, North Carolina, USA

Sauperl O, Stana-Kleinschek K (2010) Differences between cotton and viscose fibers crosslinked with BTCA. Text Res J 80(4):383–392

Schramm C, Rinderer B (2015) Non-formaldeyhde crease-resistant modification of cellulosic material by means of an organotrialkoxysilane and metal alkoxides. Cellulose 22:2811–2824

Schramm C, Binder WH, Tessadri R (2004) Durable press finishing of cotton fabric with 1234-butanetetracarboxylic acid and TEOS/GPTMS. J Sol-Gel Sci Technol 29:155–165

Schramm C, Rinderer B, Binder WH, Tessadri R, Duelli H (2005) Treatment of 1,3-dimethylol-4,5-dihydroxyimidazolidine-2-one Finished cellulosic material with tetraethoxysilane or glycidyloxypropyl-trimethoxysilane solutions. J Mater Sci 40:1883–1891

Shahzad A (2011) Hemp fiber and its composites: a review. J Compos Mater 46(8):973–986

Sharpe G, Mallinson P (2003) Easy-care finishing of cellulosics. In: Heywood D (ed) Textile finishing. Society of Dyers and Colourists, Hampshire

Surina R, Andrassy M (2013) Effect of preswelling and ultrasound treatment on the properties of flax fibers cross-linked with polycarboxylic acids. Text Res J 83(1):66–75

Vihodceva S, Kukle S (2011) Natural textile surface modification using sol-gel technique. Sci J Riga Tech Univ Mater Sci Text Cloth Technol 6:1–5

Yang CQ (1991) Characterizing ester crosslinkages in cotton cellulose with FTIR photoacoustic spectroscopy. Text Res J 61(5):298–305

Yang CQ, Bakshi GD (1996) Quantitative analysis of the non-formaldehyde durable press finish on cotton fabric: acid-base titration and infrared spectroscopy. Text Res J 66(6):377–384

Yang CQ, Wang X (1996) Formation of cyclic anhydride intermediates and esterification of cotton cellulose by multifunctional carboxylic acids: an infrared spectroscopy study. Text Res J 66(9):595–603

Yu C (2015) Natural textile fibres: vegetable fibres. In: Textiles and fashion. A volume in Woodhead Publishing Series in Textiles, Chap 2, pp 29–56

Zhou W, Yang CQ, Lickfield GC (2004a) Mechanical strength of durable press finished cotton fabric part V: poly (vinyl alcohol) as an additive to improve fabric abrasion resistance. J Appl Polym Sci 1(91):3940–3946

Zhou LM, Yeung KW, Yuen CWM, Zhou X (2004b) Characterization of ramie yarn treated with sodium hydroxide and crosslinked by 1234-butanetetracarboxylic acid. J Appl Polym Sci 91:1857–1864

Zhou LM, Yeung KW, Yuen CWM, Zhou X (2007) Effect of mercerization on the crosslinking of ramie fabric using 1234-butanetetracarboxylic acid: physical properties and crosslink distribution. Text Res J 72(9):795–802

Zimniewska M, Batog J, Bogacz E, Romanowska B (2012) Functionalization of natural fibres textiles by improvement of nanoparticles fixation on their surface. J Fiber Bioeng Inform 5(3):321–339