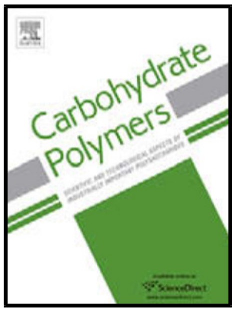
Accepted Manuscript



Title: Non-formaldehyde, crease resistant agent for cotton
fabrics based on an organic-inorganic hybrid material

Author: Christian Schramm Beate Rinderer Richard Tessadri

PII: S0144-8617(14)00072-1
DOI: http://dx.doi.org/doi:10.1016/j.carbpol.2014.01.063
Reference: CARP 8527

To appear in:

Received date: 30-9-2013
Revised date: 16-1-2014
Accepted date: 19-1-2014

Please cite this article as: Schramm, C., Rinderer, B., & Tessadri, R.,Non-formaldehyde, crease resistant agent for cotton fabrics based on an organic-inorganic hybrid material, *Carbohydrate Polymers* (2014), http://dx.doi.org/10.1016/j.carbpol.2014.01.063

Non-formaldehyde, crease resistant agent for cotton fabrics based on an organic-inorganic hybrid material

Christian Schramm (corresponding author)

Research Institute of Textile Chemistry and Textile Physics, University Innsbruck

Höchsterstrasse 73, A-6850 Dornbirn, Austria

Phone: ++43(0)5572 28533 582

Fax: ++43(0)5572 28629

E-Mail: christian.schramm@uibk.ac.at

Beate Rinderer

Research Institute of Textile Chemistry and Textile Physics, University Innsbruck

Höchsterstrasse 73, A-6850 Dornbirn, Austria

Phone: ++43(0)5572 28533 582

Fax: ++43(0)5572 28629

E-Mail: beate.rinderer@uibk.ac.at

Richard Tessadri

Institute of Mineralogy and Petrography, University of Innsbruck, Bruno-Sander-Haus, Innrain 52, A-6020 Innsbruck, Austria

Phone: +43(0)512 507 5509

Fax: +43(0)512 507 2926

E-Mail: richard.tessadri@uibk.ac.at

Abstract

1,2,3,4-Butanetetracarboxylic acid (BTCA) was reacted with (3-aminopropyl)triethoxysilane (APTES) to a poly(amic)acid (PAA). The molar ratios of BTCA and APTES were 1/1 (B/A-1/1), 1/2 (B/A-1/2), 1/3 (B/A-1/3), and 1/4 (B/A-1/4). The as-prepared precursor solution was applied to cotton substrates. After thermal treatment (180°C) the physical-mechanical properties of the cotton samples were tested by means of dry crease recovery angle and tensile strength. For B/A-1/1 treated fabrics a significant improvement of the crease resistance was observed. FT-IR spectra revealed the formation of an imide group and an ester linkage, indicating the cross-linking of the cellulosic material. SEM images showed a smooth surface. As evidenced by TGA data the thermal stability of the cotton samples was not increased. No hydrophobicity could be observed. For B/A-1/3 and (B/A-1/4) modified cotton samples no crease resistant properties were detected. However, enhanced contact angle values were measured. A reaction mechanism for the formation of the ladder-like polysilsesquioxane and the cross-linking reaction is proposed.

Keywords

Cotton, crease resistance, polyimide, organic-inorganic hybrid, sol-gel

1. Introduction

Cellulosic material is chemically modified in an attempt to impart specific properties to cotton fabrics or garments. Thus, cotton textiles are reacted with crease resistant finishing agents, which react with the hydroxyl groups of the cellulose to improve the wrinkle resistance and the dimensional stability. As a consequence the mechanical strength is decreased. The most widely used crease resistant finishing agent is dimethyloldihydroxyethyleneurea (DMDHEU), since this finishing chemical is very effective and inexpensive. However, DMDHEU tends to release the potential human carcinogen formaldehyde during the curing process, the storage and the consumer use (Bajaj, 2002; Hewson, 1994). Polycarboxylic acids, such as 1,2,3,4-butanetetracarboxylic acid (BTCA) or citric acid (CA) in conjunction with sodium hypophosphite (SHP) as appropriate catalyst are considered to be capable of replacing DMDHEU. At elevated temperatures (180°C, 90s) the carboxyl groups of BTCA react with the hydroxyl groups of the cellulose via a five-membered cyclic anhydride forming an ester linkage (Harifi & Montazer, 2012; Welch, 1990; Welch & Andrews, 1989).

Different approaches have been used to substitute SHP as catalyst due to its adverse impact to the environment (Choi, Li, Goodin & Pratt, 1994; Choi, 1993). A reduction of the phosphorus-containing catalyst was obtained using nano-TiO_2 as co-catalyst (Nazari, Montazer, Rashidi, Yazdanshenas & Anary-Abbasinejad, 2009; Yuen, Ku, Kan, Cheng, Choi & Lam, 2007).

To produce a novel formaldehyde-free crease resistant finishing agent BTCA was reacted with APTES. The latter had been subjected to a hydrolysis reaction according to the sol-gel process. In general, the sol-gel technology is based on the hydrolysis and the ensuing condensation of tetraalkoxysilanes $Si(OR)_4$, such as tetraethoxysilane ($R = CH_2CH_3$, TEOS) or of organotrialkoxysilanes $R^1Si(OR^2)_3$, such as methyltriethoxysilane ($R^1 = -CH_3$, $R^2 = CH_2CH_3$, MTEOS), thus forming a three dimensional siloxane network (Brinker & Scherer, 1990; Hench & West, 1990; Wright & Sommerdijk, 2001). This sol-gel method is also extensively applied to impart new properties to cotton textiles, such as antimicrobial function (Lee, Broughton, Akdag, Worley & Huang, 2007; Montazer & Afjeh, 2007), flame retardancy (Blanchard & Graves, 2002; Yang & Wu, 2003), water repellency (Gashti, Alimohammadi & Shamei, 2012; Wang, Ding, Xue, Wang & Lin, 2011) or other functional properties (Mahltig & Textor, 2008).

Various studies had been carried out to improve the non-formaldehyde crease resistant properties of cotton fabrics using sol-gel technology (Ibrahim, Refai, Ahmed & Youssef, 2005; Lam, Kan & Yuen, 2011; Schramm, Binder & Tessadri, 2004).

The major objective of this paper is to present the results that were obtained, when cotton fabrics were treated with a BTCA/APTES solution. The as-treated cellulosic material was subjected to a curing process and subsequently evaluated in terms of crease resistant properties, hydrophobic behavior and thermal stability. This approach had been selected since a previous investigation has shown that the reaction of BTCA with APTES results in the formation of a poly(amic) acid, which gives rise to the formation of a cyclic imide when cured at elevated temperature (Schramm, Rinderer & Tessadri, 2012).

2. Experimental

2.1 Materials

Desized, scoured, bleached and mercerized 100% cotton fabric, weighing 109 g/m^2, was used throughout the investigation. The dyes: C.I. Reactive Red 141 and C.I. Reactive Black 5 (Fig. 1) as well as the textile auxiliaries were supplied by BEZEMA AG, Montlingen, Switzerland. 3-Aminopropyltriethoxysilane (100%, APTES, Fig. 1) was obtained from Wacker Silicone, Burghausen, Germany. 1,2,3,4-Butanetetracarboxylic acid (> 99%, BTCA) (Fig. 1), was purchased from Merck GmbH, Germany. Deionized water was used throughout the investigation. The chemicals were used without further purification.

2.2 Preparation of the precursor solution

The standard procedure for the synthesis of a BTCA/APTES solution (molar ratio 1/1) in an aqueous medium was as follows: APTES (7.07 mL, 30 mmol) was hydrolyzed with HCl (c = 0.05 mol/L, 2.70 mL) in deionized water (20 mL) under magnetic stirring (500 rpm) in a polyethylene beaker (100 mL) for 15 hours at room temperature (RT). Subsequently, 20 mmol of BTCA (7.02 g, 30 mmol) were added under vigorous stirring. Stirring was continued for 30 min and the solution was filled to 100 mL with deionized water.

2.3 Finishing of the cotton fabrics

The pre-weighed cotton fabrics (undyed and dyed) were impregnated with the corresponding BTCA/APTES solution applying a two-roll laboratory padder (HVL 500 Mathis AG, Niederhasli, Switzerland; air pressure 1 bar, rotary speed 3 m/min). After drying (5 min, 105°C) the as-treated fabric was cured in a lab dryer (LTE, W. Mathis AG, Switzerland) at a specified temperature and for a specified time.

2.4 Dyeing procedure

The dyeing process was conducted according to a standard dyeing procedure (Fig. 2). The dyes were used with 4% on weight of fabric (owf), mass-to liquor ratio 1:15 and 2 hr total dyeing time. After completion of dyeing, the fabrics were neutralized with acetic acid and after-treated with anion active soaping product. Standard textile auxiliaries were used for the process of dyeing: A: Meropan NX, Biavin 109; B: NaCl; C: Na_2CO_3 5.0 g/L, D: NaOH 38° Bé, E: acetic acid, F: Cotoblanc NSR.

2.5 Testing methods

Colorimetric data measurements were conducted with the Spectrophotometer CM-3610d from Konica Minolta, Japan. The color data software CM-S100w Spectra Magic NX V1.9 was used for data acquisition. The whiteness index (WI) was calculated according to CIE.

Dry crease recovery angle (DCRA) was measured according to ISO 2312: 10 test specimens were creased and compressed under controlled conditions of time and load. After removal of the creasing load the angle formed between the two limbs was measured. The DCRA values render possible the evaluation of a cross-linking reaction between a crease resistant finishing agent and the cellulosic material.

Washing tests were conducted in accordance with the AATCC Method 61-2009. Abrasion tests were performed according to DIN EN ISO 12947-3 (Martindale method).

Tensile strength (TS) was determined with the Material Testing System Z010 (Zwick/Roell, Ulm, Germany) according to DIN EN ISO 13934.

FT-IR spectra were recorded with a Bruker Vector 22 spectrometer using a DTGS detector. Since the FT-IR/ATR technique provided poor spectra, the KBr method was applied. Prior to the preparation of the KBr pellets the cotton samples were cut into small pieces and ground with a rotor mill ZM-1 (Retsch, Haan, Germany). The spectra were the result of 200 scans. The spectral resolution was 4 cm^{-1}.

TGA measurements were conducted in air with the thermogravimetric analyzer Linseis STA PT1000 (heating rate = 10°C/min; scan range = 40°C to 900°C).

The contact angles were measured using a home-made contact angle measuring instrument, which consists of a digital microscope camera (DigiMicro 2.0 Scale; dnt GMBH, Dietzenbach, Germany). The data acquisition had been performed by means of the software Microcapture. A water droplet (15 µL) was deposited on the cotton sample by means of a microliter syringe (Hamilton, Bonaduz, Switzerland), being placed on a glass slide, which was mounted on a microscope stage equipped with a double side holder.

The precise contact angle measurement had been conducted using the software ImageJ (Research Services Branch of the National Institute of Mental Health, Bethesda, Maryland, USA), and the plugin Drop Analysis (Biomedical Imaging Group, Ecole Polytechnique Federale de Lausanne, Switzerland) (Stalder, Kulik, Sage, Barbieri & Hoffmann, 2006).

3. Results and discussion

The organotrialkoxysilane APTES contains the aminopropyl functionality as well as three ethoxy groups. The latter is capable of reacting with water. As a result, ethanol is released and silanol groups are formed which condensate to a siloxane network (Brinker & Scherer, 1990). The amino group of APTES can react with the carboxy groups of BTCA thus forming a PAA. Since BTCA contains vicinal carboxyl groups a thermal treatment of the PAA results in the formation of a cyclic imide. This latter functionality can be readily determined by means of FT-IR (Ahmad, Al Sagheer, Al Arbash & Ali, 2009; Schramm, Rinderer & Tessadri, 2012; Snyder, Thomson, Bartges, Czerniawski & Painter, 1989; Sroog, 1967). The aqueous reaction mixtures of BTCA and APTES (molar ratio 1/1 and 1/4) were applied to cotton materials and treated at elevated temperatures in an attempt to evaluate the surface modification in terms of the crease resistant properties of the as-treated cotton samples.

3.1 Application of APTES solution to cotton fabrics

For comparison purposes, the cotton raw material had been impregnated merely with a solution containing pre-hydrolyzed APTES (30 mmol/2.7 ml HCl/20 ml deionized water). Thereafter the samples were cured at various elevated temperatures (110°C, 160°C, 180°C, 200°C, and 220°C) for 5 min. The findings are presented in Table 1. The denotations of the samples are as follow: A-110-5 indicates the cotton samples which had been impregnated with an APTES solution and which were treated at 100°C for 5 min.

Compared to the untreated cotton fabric no significant improvement of the DCRA values for the APTES-treated cotton specimens can be observed. The tensile strength is moderately decreasing as the temperature increases. A significant reduction of the WI can be observed when the curing temperature increases. This phenomenon can be attributed to decomposition products originating from the organic group of APTES. The data presented reveal that the application of APTES to cotton fabrics has no effect on the crease resistant parameters. No experimental runs had been performed with respect to BTCA, since previous investigations already have given evidence that the treatment with BTCA solutions without an appropriate catalyst is not effective in terms of crease resistant properties (Welch, 1988).

3.2 Application of BTCA/APTES solution to cotton fabrics

In an attempt to evaluate the impact of the curing temperature as well as of the curing time on the physical properties cotton fabrics were impregnated with finishing solutions consisting of BTCA and APTES with molar ratios of 1/1, 1/2, 1/3 and 1/4. The impregnated cotton samples were subjected to a drying process (100°C, 3 min) to remove the excess of water and ethanol which were released during the hydrolysis of APTES. Subsequently, the as-prepared samples were cured at 110°C, 160°C, 180°C, 200°C and 220°C each for 5 min and 15 min, respectively. The results of the physical tests (DCRA, TS and WI) are shown in Table 1. The denotations of the samples are as follow: B/A-1/x-110-5 indicates the cotton samples which had been impregnated either with an equimolar solution of BTCA and APTES (x = 1) or a BTCA/APTES solution with a molar ratio of 1/2, 1/3, 1/4 (x = 2, 3, 4). The second and third term indicate the curing temperature 100°C and the curing time 5 min.

Compared to the cotton raw material the DCRA values of B/A-1/1-110-5 as well as of B/A-1/1-110-15 are almost at the same level, indicating that no cross-linking reaction has occurred. These findings are confirmed by the TS data which have nearly the same values as the untreated cotton fabrics. These phenomena can also be observed with respect to the other cotton samples (x = 2, 3, 4). The WI values are moderately lowered when BTCA and APTES were reacted at the molar ratio of 1/2, whereas a significant reduction of the WI values is obtained in the case of B/A-1/3-110 and B/A-1/4-110.

An increase of the curing temperature gives rise to a significant improvement of the DCRA values for cotton fabrics having been treated with B/A-1/1 solutions. This phenomenon indicates that a cross-linking reaction has taken place under the curing conditions chosen. The DCRA values of the B/A-1/2 samples are remarkably reduced, whereas the B/A-1/3 and B/A-1/4 specimens show almost no increase in the DCRA values. The opposite tendency can be observed with respect to the TS data. The values for the B/A-1/3 and B/A-1/4 fabrics are very close to those of the raw material. The same trend can be noticed with respect to the WI values, which were significantly reduced when the curing temperature was increased.

An extension of the curing time from 5 to 15 min brings about a very moderate enhancement of the DCRA values. The TS values are slightly lower. The same trend applies to the WI values.

The decrease of the WI is presumably due to the thermo-oxidative instability of the PAA. It is suggested that the scission of the amide bond results in the formation of species containing the amine functionality. Under the thermo-oxidative conditions given the latter can be converted into various organic compounds, such as imines, imides, aldehydes, alkenes etc (El-Mazry, Ben Hassine, Correc & Colin, 2013; Richaud, Diogo, Fayolle, Verdu, Guilment & Fernagut, 2013).

B/A-1/1-180-15 had been subjected to a washing test. Five washing cycles had been performed. Compared to the unwashed specimen the DCRA values were reduced by 5.2 %. The tensile strength maintained at the same level, indicating that the wrinkle resistance withstands several washing treatments. The abrasion test was conducted in comparison to the raw material. After 10000 cycles the B/A-1/1-180-15 modified cotton samples showed deterioration (hole formation) whereas the raw material was destroyed after 12000 cycles. These findings give evidence that the chemical modification of the cotton fabric by means of B/A-1/1 results in a decrease of the abrasion resistance.

To confirm the formation of the imide group the normalized FT-IR spectra of B/A-1/1-180-15 (3a), B/A-1/1-220-15 (3b), and B/A-1/4-220-15 (3c) were recorded (Fig. 3). A comparison of the normalized spectra 3a-3c at 1771 cm^{-1} (asymmetric carbonyl stretching mode of imide group, Imide I) and at 1721 cm^{-1} (symmetric carbonyl stretching mode of imide group, Imide I) make evident that an imide functionality is present in B/A-1/1-180-15 as well as in B/A-1/1-220-15. In this region no absorption band can be observed for B/A-1/4-220-15, indicating that no cyclic imide ring had been formed during the curing process at 220°C. The spectra 3a as well as 3b show a shoulder at 1739 cm^{-1} which can be assigned to a stretching vibration of an ester carbonyl bond, which proves the cross-linking reaction of the hydroxyl groups of the cellulose and the carboxyl groups of the organic-inorganic hybrid. An inspection of the spectrum of B/A-1/4-220-15 (3c) reveals that no absorption band can be observed at 1739 cm^{-1}, indicating that no ester bond was built.

All the findings mentioned above clearly make evident, that the B/A-1/1 formulation is capable of endowing cotton fabrics with excellent crease resistant properties. The results of the physical-mechanical measurements undoubtedly reflect that a cross-linking reaction had occurred between the cellulose material and the organic-inorganic hybrid. The inspection of the FT-IR spectra confirms that the cross-linking reaction is obtained by ester linkages.

No crease resistant performance could be achieved through applying a finishing bath containing BTCA and APTES with the molar ratio of 1/3 and 1/4. This fact will be explained in a later section (Mechanism of the cross-linking reaction).

3.3 Morphology of the BTCA/APTES treated cotton fabrics

The morphological structure of cellulose samples which had been treated with BTCA/APTES solutions were observed using SEM (Fig. 4). Fig. 4a shows the image of untreated cotton material (4a) for comparison purposes. Fig. 4b shows the morphological characteristics of B/A-1/1-220-15 and those of BA-1/4-220-15 (4c). The scanning electron micrograms of the B/A treated cotton samples show that the most part of the surface is smooth. No obvious difference in shape between the cotton fabric before and after sol-gel treatments can be observed. No thin coating can be observed on the surface or in the interstices of the cotton fibers. Therefore, it can be concluded that the PAA having been formed through the reaction of BTCA with APTES in the finishing solution has penetrated into the cotton fibers. Upon heating the as-prepared cotton specimen the cross-linking reaction occurred between the cellulose and the cross-linking agent.

3.4 Thermostability of the BTCA/APTES treated cotton fabrics

Cotton is regarded to be one of the most flammable fibers. Therefore, intensive investigations have been undertaken in an effort to improve the flame retardancy of cellulosic-based materials, since they are widely used for apparel (protection clothing), home furnishing (cover fabrics, upholstery) and technical textiles (Horrocks & Anand, 2004; Tesoro, 1978). Cotton substrates had been coated with novel materials which were produced by means of the sol-gel process to improve the thermal stability (Alongi, Ciobanu & Malucelli, 2011).

Since PI materials are well known for their outstanding properties at elevated temperatures, the B/A-treated cotton fabrics were tested in terms of their thermal stability by means of thermogravimetric analysis, which has proven as an excellent analytical tool to estimate the thermal behavior of materials (Simkovic, 2012; Zhu, Sui, Wang, Sun & Sun, 2004).

Fig. 5 shows the thermograms as well as the corresponding DTG curves of the cellulosic raw material (TG: 5a, DTG: 5d), B/A-1/1-220-15 (TG: 5b, DTG: 5e), B/A-1/4-220-15 (TG: 5c, DTG: 5f). An inspection of the curves makes evident, that the treatment of the cotton samples with a BTCA/APTES solution does not result in an improvement of the thermal stability of the cotton material. A comparison of the DTG curves of B/A-1/1-220-15 (5e) and of the untreated cotton fabric (5d) reveals that the DTG maxima temperature of B/A-1/1-220-15 is reduced. No pristine BTCA is present on the fabric, since no DTG peak at 311°C is visible.

3.5 Contact Angle of the BTCA/APTES treated cotton fabrics

The possibility of imparting multifunctional features to a fabric represents one of the main goals that the researchers aim to achieve. Therefore, the impact of the BTCA/APTES treatment on hydrophobicity had been investigated by measuring the contact angle, since various investigations have shown that cotton material can be endowed with hydrophobicity using different methods (Bae, Min, Jeong, Lee, Jang & Koo, 2009; Bhat, Netravali, Gore, Sathianarayanan, Arolkar & Deshmukh, 2011; Gashti, Alimohammadi & Shamei, 2012; Liu, Chen & Xin, 2008). Fig. 6 shows the water droplet which was deposited on a cotton fabric treated with B/A-1/4 solution at 220°C for 15 min. Measurable values only could be obtained when the cotton samples were treated with B/A-1/4 (Table 2). The other cotton samples showed no improved contact angle values compared to the raw material. This phenomenon can be explained by the fact that all the carboxyl groups of the BTCA had been converted into amide groups.

3.6 Dyeing properties of the BTCA/APTES treated cotton fabrics

A previous study revealed that the application of tetraethoxysilane, triethoxypropylsuccinic anhydride or APTES did not cause a change of the color properties of cotton samples having been dyed with C.I. Reactive Red 141 or C.I. Reactive Black 5 (Fig. 1). (Mahltig & Textor, 2006; Schramm & Rinderer, 2011)

To evaluate the impact of the BTCA/APTES treatment on the properties of dyed cotton fabrics, cotton samples were dyed with 2% owf and 4% owf C.I. Reactive Red 141 (Red) and 2% owf and 4% owf C.I. Reactive Black 5 (RBlack), respectively. Subsequently, all dyed cotton samples were treated with a B/A-1/1 solution at 180°C for 15 min. The samples are denoted as follow: RBlack-2-B/A-1/1 indicates the sample having been dyed with 2% owf C.I. Reactive Black 5. Subsequently, the sample was treated with an equimolar BTCA/APTES solution and cured at 180°C for 15 min.

The cotton samples were tested with respect to the colorimetric data ! L*, ! a*, ! b* and the color difference DE* (Table 3). The dyed and untreated samples were applied as references. Almost no alteration can be observed, when the cotton samples were dyed with C.I. Reactive Red 141 and C.I. Reactive Black 5. These results give clear evidence that no interaction of the dyestuffs with the components of the precursor solution takes place during the curing process at elevated temperatures.

3.7 Successive application of BTCA and APTES to cotton fabric

Firstly, cotton samples were impregnated with a solution containing BTCA and dried at 100°C for 3 min. Subsequently, prehydrolysed APTES solutions (molar ratio B/A-1/1, and B/A-1/4) were applied to the as-prepared cotton fabrics. The latter were dried again and cured at 180°C for 15 min. The findings of the physical tests are presented in Table 4 and reveal that the DCRA values are much lower than those which had been measured when BTCA and

APTES were applied in a combined solution (Table 4). The higher TS values also confirm the moderate effect of that treatment. The WI values are almost the same.

These experimental runs make evident that no cross-linking occurs when BTCA and APTES are applied sequentially.

3.8 Mechanism of the cross-linking reaction

Crease resistant chemicals which are capable of cross-linking cellulose can be divided into two categories: the reactants which predominately cross-link with the cellulose forming a covalent bond with the hydroxyl group of the cellulose and the self-cross-linker which primarily self-polymerize thus forming a three-dimensional network (Harifi & Montazer, 2012).

The present, novel crease resistant agent can be assigned as a reactant, since B/A-1/1 contains vicinal, free carboxyl groups, as shown in a previous study (Schramm, Rinderer & Tessadri, 2012). These carboxyl groups are capable of reacting with the hydroxyl groups of the cellulosic material via a five-membered cyclic anhydride intermediate (Gu & Yang, 2000; Yang, 1993).

Fig. 7 describes the reaction mechanism. APTES is hydrolyzed in an aqueous medium. As a consequence the ethoxy groups are converted into silanol groups. The addition of a solution containing an equimolar amount of BTCA results in the formation of an amide functionality. The as-prepared finishing solution is applied to the cotton fabric. At elevated temperature the silanol groups condense to siloxane units.

Based on the results which are presented in a previous paper, it can be concluded that a ladder-like polysilsesquioxane is produced (Schramm, Rinderer & Tessadri, 2012). The thermal treatment at 220°C results in the production of an imide group as well as of cyclic, five-membered anhydride functional groups. The latter are assumed to react as an intermediate with the hydroxyl groups of the cellulosic material thus forming an ester linkage which leads to the cross-linking of the cellulose (Gu & Yang, 2000).

When BTCA reacts with APTES at a molar ratio of 1/3, three carboxylic groups of BTCA are converted to amide functionalities. At a molar ratio of 1/4 all four carboxylic functionalities of BTCA react to an amide group. As a consequence no imide groups and no cyclic, five-membered anhydride moieties can be formed. However, the generation of cyclic anhydrides is necessary to obtain an ester linkage between the ladder-like polysilsesquioxane and the cellulosic material. This phenomenon explains why B/A-1/3 or B/A-1/4 treated cotton samples possess very poor crease resistant properties.

Fig. 8 demonstrates potential cross-linkage of the polysilsesquioxane and the hydroxyl groups of the cellulosic material. The formation of the cross-link as shown in Fig. 8a seems rather unlikely since the silanol groups will be converted into siloxane entity during the curing process. The cross-link depicted in Fig. 8b takes into account the formation of a siloxane network but still contains unreacted, vicinal carboxyl groups, which are capable of reacting with the hydroxyl groups of the cellulose. Therefore, it can be assumed that each entity containing vicinal carboxyl groups will be converted to an ester linkage as shown in Fig. 8c.

4. Conclusions

Cotton fabrics were impregnated with various solutions containing BTCA and APTES using different molar ratios (1/1, 1/2, 1/3 and 1/4). The as-treated samples were cured at 110°C, 160°C, 180°C, 200°C and 220°C for 5 min and 15 min, respectively, and evaluated in terms of DCRA, TS and WI. The findings give clear evidence that an improvement of the DCRA values can be observed when BTCA and APTES were used in the molar ratios of 1/1 and 1/2 and cured at elevated temperatures. An increase of the curing periods resulted in a moderate improvement of the DCRA values. The increase in the DCRA values resulted in a decrease in the TS values and WI. In contrast, the B/A-1/3 and B/A-1/4 treated samples showed no improved crease resistant properties compared to the untreated cotton fabric. TG measurements revealed that no improvement of the thermal stability could be obtained. B/A-1/4 treated cotton samples were endowed with enhanced hydrophobicity. No phosphorus-containing catalyst, such as SHP, was applied to impart crease resistant performance.

5. Acknowledgements

The authors would like to thank the Testing Institute of the HTL Dornbirn (Austria) for making available textile-physical devices.

6. References

Ahmad, Z., Al Sagheer, F., Al Arbash, A., & Ali, A. A. M. (2009). Synthesis and characterization of chemically cross-linked polyimide-siloxane hybrid films. *J. Non-Crystall. Solids, 355*(8), 507-517.

Alongi, J., Ciobanu, M., & Malucelli, G. (2011). Novel flame retardant finishing systems for cotton fabrics based on phosphorus-containing compounds and silica derived from sol–gel processes. *Carbohydrate Polymers, 85*(3), 599-608.

Bae, G. Y., Min, B. G., Jeong, Y. G., Lee, S. C., Jang, J. H., & Koo, G. H. (2009). Superhydrophobicity of cotton fabrics treated with silica nanoparticles and water-repellent agent. *J. Colloid Interface Sci, 337*(1), 170-175.

Bajaj, P. (2002). Finishing of textile materials. *Journal of Applied Polymer Science, 83*(3), 631-659.

Bhat, N., Netravali, A., Gore, A., Sathianarayanan, M., Arolkar, G., & Deshmukh, R. (2011). Surface modification of cotton fabrics using plasma technology. *Textile Research Journal, 81*(10), 1014-1026.

Blanchard, E. J., & Graves, E. E. (2002). Polycarboxylic acids for flame resistant cotton/polyester carpeting. *Textile Research Journal, 72*(1), 39-43.

Brinker, C. J., & Scherer, G. W. (1990). *Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing*. Academic Press, San Diego.

Choi, H., Li, J. D., Goodin, R. D., & Pratt, T. D. (1994). Shade Changes in Dyed Cotton Treated with Nonformaldehyde-Nonphosphorus Durable Press Finishes. *Am. Dyest. Rep., 83*(2), 38-43.

Choi, H. M. (1993). Nonphosphorus Catalysts for Formaldehyde-Free DP Finishing of Cotton with 1,2,3,4-Butanetetracarboxylic Acid PartI: Aromatic N-Heterocyclic Compounds. *Textile Research Journal, 63*(11), 650-657.

El-Mazry, C., Ben Hassine, M., Correc, O., & Colin, X. (2013). Thermal oxidation kinetics of additive free polyamide 6-6. *Polymer Degradation and Stability, 98*(1), 22-36.

Gashti, M. P., Alimohammadi, F., & Shamei, A. (2012). Preparation of water-repellent cellulose fibers using a polycarboxylic acid/hydrophobic silica nanocomposite coating. *Surface & Coatings Technology, 206*(14), 3208-3215.

Gu, X., & Yang, C. Q. (2000). FT-IR Spectroscopy Study of the Formation of Cyclic Anhydride Intermediates of Polycarboxylic Acids Catalyzed by Sodium Hypophosphite. *Textile Research Journal, 70*(1), 64-70.

Harifi, T., & Montazer, M. (2012). Past, present and future prospects of cotton cross-linking: New insight into nano particles. *Carbohydrate Polymers, 88*(4), 1125-1140.

Hench, L. L., & West, J. K. (1990). The Sol-Gel Process. *Chem. Rev., 90*, 33-72.

Hewson, M. (1994). Formaldehyde in Textiles. *110*(4), 140-142.

Horrocks, A. R., & Anand, S. C. (Eds.). (2004). *Handbook of technical textiles*. Cambridge, England: Woodhead Publishing Ltd.

Ibrahim, N. A., Refai, R., Ahmed, A. F., & Youssef, M. A. (2005). New approach for improving UV-protecting properties of woven cotton fabrics. *Polymer-Plastics Technology and Engineering, 44*(5), 919-930.

Lam, Y. L., Kan, C. W., & Yuen, C. W. M. (2011). Wrinkle-resistant finishing of cotton fabric with BTCA - the effect of co-catalyst. *Textile Research Journal, 81*(5), 482-493.

Lee, J., Broughton, R. M., Akdag, A., Worley, S. D., & Huang, T. S. (2007). Antimicrobial fibers created via polycarboxylic acid durable press finishing. *Textile Research Journal, 77*(8), 604-611.

Liu, Y., Chen, X., & Xin, J. H. (2008). Hydrophobic duck feathers and their simulation on textile substrates for water repellent treatment. *Bioinspiration & Biomimetics, 3*(4), 046007.

Mahltig, B., & Textor, T. (2006). Combination of silica sol and dyes on textiles. *Journal of Sol-Gel Science and Technology, 39*, 111-118.

Mahltig, B., & Textor, T. (2008). *Nanosols and Textiles*. Singapore: World Scientific Publishing Co. Pte.Ltd.

Montazer, M., & Afjeh, M. G. (2007). Simultaneous X-linking and antimicrobial finishing of cotton fabric. *Journal of Applied Polymer Science, 103*(1), 178-185.

Nazari, A., Montazer, M., Rashidi, A., Yazdanshenas, M., & Anary-Abbasinejad, M. (2009). Nano TiO2 photo-catalyst and sodium hypophosphite for cross-linking cotton with poly carboxylic acids under UV and high temperature. *Applied Catalysis a-General, 371*(1-2), 10-16.

Richaud, E., Diogo, O. O., Fayolle, B., Verdu, J., Guilment, J., & Fernagut, F. (2013). Review: Auto-oxidation of aliphatic polyamides. *Polymer Degradation and Stability, 98*(9), 1929-1939.

Schramm, C., Binder, W., & Tessadri, R. (2004). Durable Press Finishing of Cotton Fabric with 1,2,3,4-Butanetetracarboxylic Acid and TEOS/GPTMS. *Journal of Sol-Gel Science and Technology, 29*, 155-165.

Schramm, C., & Rinderer, B. (2011). Dyeing and DP Treatment of Sol-gel Pre-treated Cotton Fabrics. *Fibers and Polymers, 12*(2), 226-232.

Schramm, C., Rinderer, B., & Tessadri, R. (2012). Sol-gel synthesis and characterization of polyimides based on the reaction of butane-1,2,3,4-tetracarboxylic acid with 3-aminopropyltriethoxysilane. *Journal of Applied Polymer Science, 125*, 1201–1206.

Simkovic, I. (2012). TG/DTG/DTA evaluation of flame retarded cotton fabrics and comparison to cone calorimeter data. *Carbohydrate Polymers, 90*(2), 976-981.

Snyder, R. W., Thomson, B., Bartges, B., Czerniawski, D., & Painter, P. C. (1989). FTIR studies of polyimides: thermal curing. *Macromolecules, 22*(11), 4166-4172.

Sroog, C. E. (1967). Polyimides. *J. Polym. Sci., Part C: Polym. Symp., 16*(2), 1191-1209.

Stalder, A. F., Kulik, G., Sage, D., Barbieri, L., & Hoffmann, P. (2006). A snake-based approach to accurate determination of both contact points and contact angles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *286*(1-3), 92-103.

Tesoro, G. (1978). Chemical Modification of Polymers with Flame-Retardant Compounds. *J. Polym. Sci: Macromol. Rev., 13*, 283-353.

Wang, H., Ding, J., Xue, Y., Wang, X., & Lin, T. (2011). Superhydrophobic fabrics from hybrid silica sol-gel coatings: Structural effect of precursors on wettability and washing durability. *Journal of Materials Research, 25*(07), 1336-1343.

Welch, C. M. (1988). Tetracarboxylic Acids as Formaldehyd-Free DP Finishing Agents. Part I: Catalysts, Additives and Durability Studies. *Textile Research Journal, 58*(8), 480-486.

Welch, C. M. (1990). Durable Press Finishing without Formaldehyde. *Textile Chemist and Colorist, 22*(5), 13-16.

Welch, C. M., & Andrews, B. K. (1989). Catalysts and Processes for Formaldehyde-Free Durable Press Finishing of Cotton Textiles with Polycarboxylic Acids. (Vol. US Patent 4,820,307 Apr.11, 1989).

Wright, J. D., & Sommerdijk, N. A. J. M. (2001). *Sol-Gel Materials Chemistry and Applications*. Gordon and Breach Science Publisher, The Netherlands.

Yang, C. Q. (1993). Effect of PH on Nonformaldehyde Durable Press Finishing of Cotton Fabric: FT-IR Spectroscopy Study Part II Formation of the Anhydride Intermediate Part I ? *Textile Res J, 63*(12), 706-711.

Yang, C. Q., & Wu, W. D. (2003). Combination of a hydroxy-functional organophosphorus oligomer and a multifunctional carboxylic acid as a flame retardant finishing system for cotton: Part I. The chemical reactions. *Fire and Materials, 27*(5), 223-237.

Yuen, C. W. M., Ku, S. K. A., Kan, C. W., Cheng, Y. F., Choi, P. S. R., & Lam, Y. L. (2007). Using nano-TiO2 as co-catalyst for improving wrinkle-resistance of cotton fabric. *Surface Review and Letters, 14*(4), 571-575.

Zhu, P., Sui, S. Y., Wang, B., Sun, K., & Sun, G. (2004). A study of pyrolysis and pyrolysis products of flame-retardant cotton fabrics by DSC, TGA, and PY-GC-MS. *Journal of Analytical and Applied Pyrolysis, 71*(2), 645-655.

7. Captions of Figures and Tables

Fig. 1	Formula of substances of interest.
Fig. 2	Dyeing procedure. A: Meropan NX, Biavin 109; B: NaCl; C: Na_2CO_3 5.0 g/L, D: NaOH 38° Bé, E: acetic acid, F: Cotoblanc NSR.
Fig. 3	FT-IR spectra of B/A-1/1-180-15 (3a), B/A-1/1-220-15 (3b), and B/A-1/4-220-15 (3c).
Fig. 4	SEM images of cotton raw material (4a), and BTCA/APTES treated cotton samples: B/A-1/1-220-15 (4b) and BA-1/4-220-15 (4c).
Fig. 5	TG and DTG curves of the cellulosic raw material (TG: 5a, DTG: 5d) and the BTCA/APTES treated cotton samples: B/A-1/1-220-15 (TG: 5b, DTG: 5e), B/A-1/4-220-15 (TG: 5c, DTG: 5f).
Fig. 6	Water droplet deposited on a cotton fabric treated with B/A-1/4 solution at 220°C for 15 min.
Fig. 7	Reaction scheme for the formation of the ladder-like polysilsesquioxane based on the reaction of APTES and BTCA at elevated temperature.
Fig. 8	Potential cross-linkage of the ladder-like polysilsesquioxane with the hydroxyl groups of the cellulose. (8a) single (8b) partial (8c) complete conversion of the vicinal carboxyl groups to ester linkages.

Table 1	Physical–mechanical properties of cotton fabrics treated with an APTES solution (A) and BTCA/APTES solution with different molar ratio (B/A-1/1, B/A-1/2, B/A-1/3 and B/A-1/4) at various curing temperatures and curing times.
Table 2	Contact angle values of B/A-1/4 treated at various temperatures.
Table 3	Colorimetric data of dyed fabric (C.I. Reactive Red 141: Red-2 and Red-4) and C.I. Reactive Black 5: RBlack-2 and RBlack-4) which had been treated with a B/A-1/1 solution at 180°C for 15 min.
Table 4	Physical–mechanical properties of cotton fabrics treated with B/A-1/1 and B/A-1/4 solutions – successive application of BTCA and APTES.

Highlights

A novel non-formaldehyde crease resistant agent has been applied to cotton fabrics

The finishing agent consists of an organic-inorganic hybrid which is prepared by sol-gel process

No phosphorous containing catalyst is necessary

The treated cotton fabrics show good crease resistant properties.

	DCRA (w+f) [°]					Tensile strength [%]					Whiteness index	
molar ratio		1/1	1/2	1/3	1/4		1/1	1/2	1/3	1/4		1/1
raw material	190.8					100.0					62.4	
A-110-5	204.4					98.7					54.4	
A-160-5	197.8					97.6					34.2	
A-180-5	191.8					96.6					9.9	
A-200-5	184.6					94.8					-16.6	
A-220-5	194.0					91.7					-32.6	
B/A-1/x-110-5*		214.6	226.8	210.4	175.0		95.9	99.4	98.4	95.9		65.0
B/A-1/x-110-15		216.2	227.2	214.8	165.2		97.9	98.3	93.5	108.0		65.2
B/A-1/x-160-5		258.4	252.3	218.3	180.8		92.5	93.8	94.5	90.7		50.1
B/A-1/x-160-15		271.4	260.1	215.3	174.8		85.5	96.1	98.3	103.9		43.0
B/A-1/x-180-5		274.4	261.3	216.5	180.4		84.2	87.4	96.4	101.3		30.9
B/A-1/x-180-15		294.2	268.5	216.7	189.2		73.9	80.1	93.4	92.8		18.1
B/A-1/x-200-5		287.8	269.5	219.5	181.8		76.2	79.4	93.4	94.3		1.9
B/A-1/x-200-15		289.6	273.4	226.4	188.4		68.2	76.5	91.8	92.5		-6.3
B/A-1/x-220-5		289.4	269.3	225.3	197.8		63.3	75.4	91.6	99.7		-14.5
B/A-1/x-220-15		296.8	275.4	228.5	214.0		55.6	73.5	92.3	82.9		-22.4

* x = 1, 2, 3 or 4

table 2

	Contact angle [°]
B/A-1/4-110-5	122.9
B/A-1/4-160-15	126.2
B/A-1/4-180-5	123.3
B/A-1/4-180-15	114.8
B/A-1/4-200-5	121.4
B/A-1/4-200-15	123.4
B/A-1/4-220-5	125.6
B/A-1/4-220-15	118.2

	! L*!	! a*!	! b*!	DE*
Red-2-B/A	0.25	1.08	1.66	2.0
Red-4-B/A	0.27	0.19	1.70	1.7
RBlack-2-B/A	-0.93	0.67	-0.50	1.3
RBlack-4-B/A	-1.04	0.36	0.21	1.1

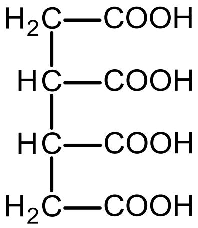
reference: dyed, untreated raw material

Table 3

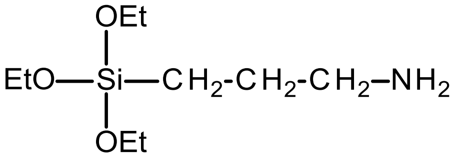
	DCRA (w+f) [°]	Tensile strength [%]	Whiteness index
raw material	190.8	100.0	62.4
B/A-1/1-180-15	243.6	78.5	17.1
B/A-1/4-180-15	146.6	99.5	1.7

table 4

Fig 1

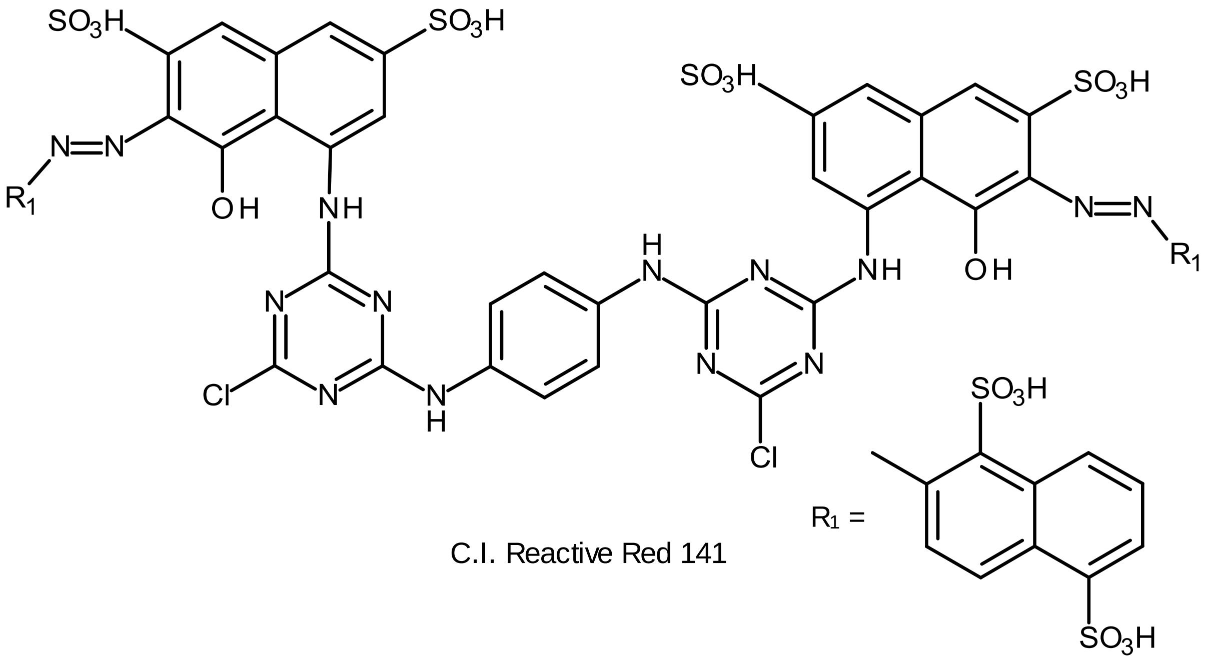


BTCA

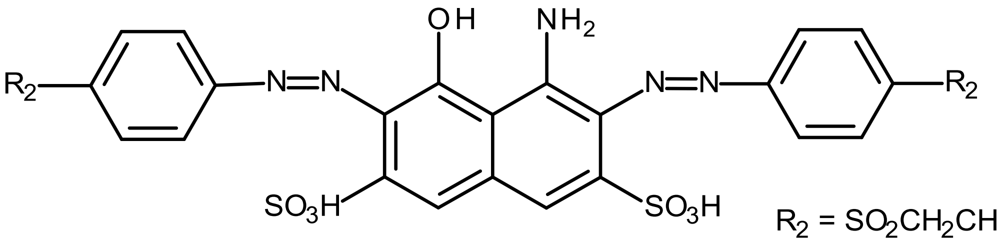


$$EtO-\overset{OEt}{\underset{OEt}{Si}}-CH_2\text{-}CH_2\text{-}CH_2-NH_2$$

APTES



C.I. Reactive Red 141



$R_2 = SO_2CH_2CH_2OSO_3Na$

C.I. Reactive Black 5

Fig 2

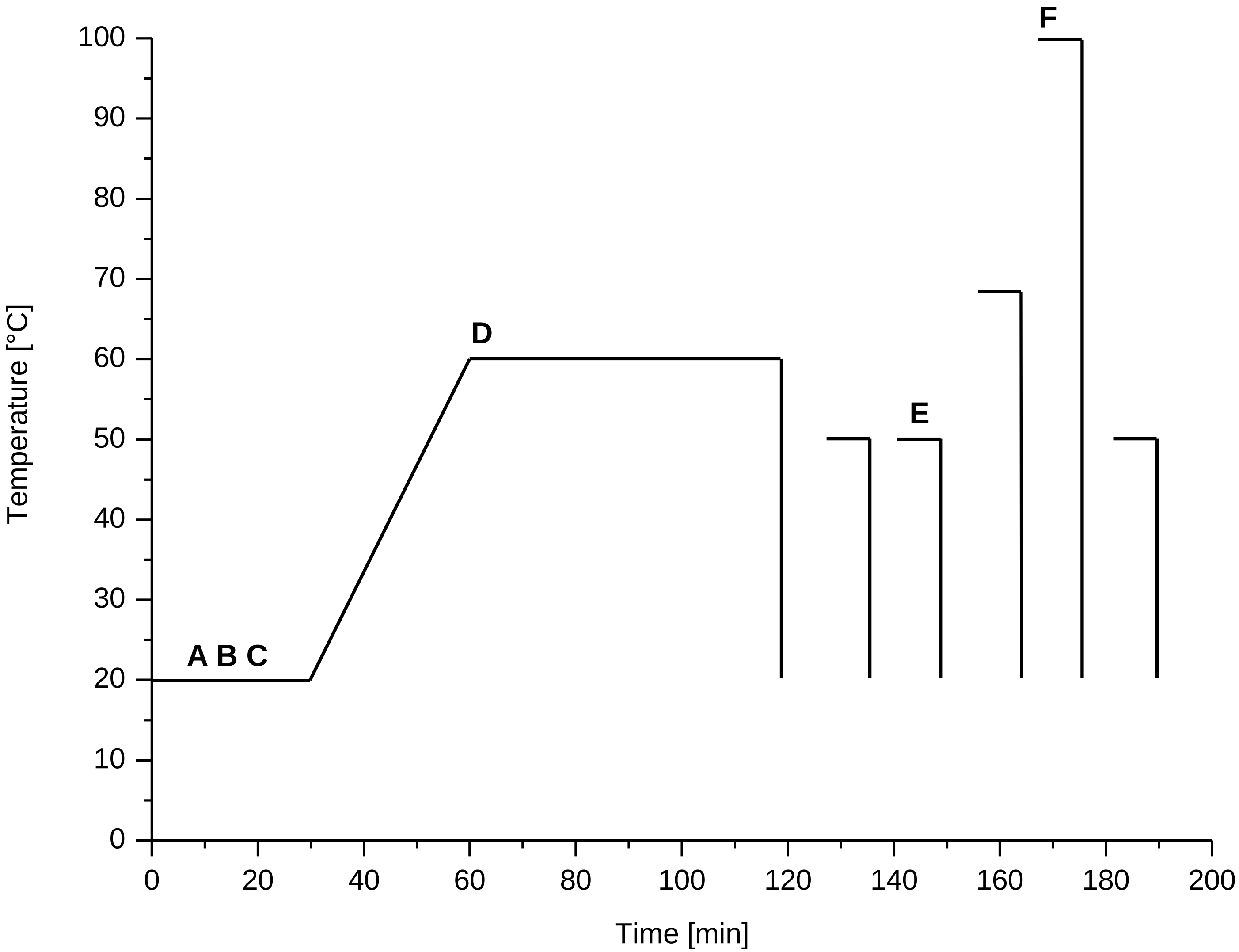
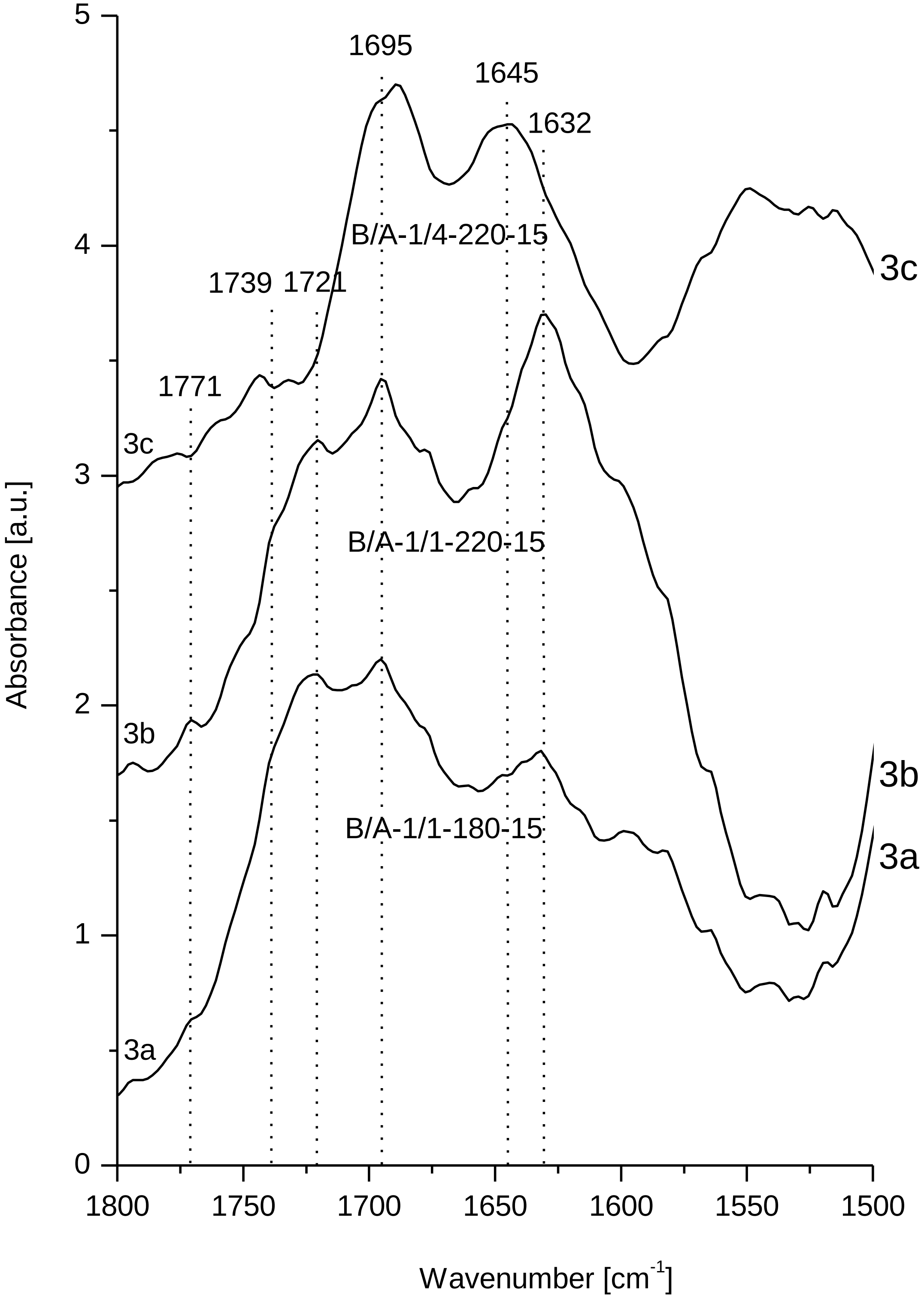
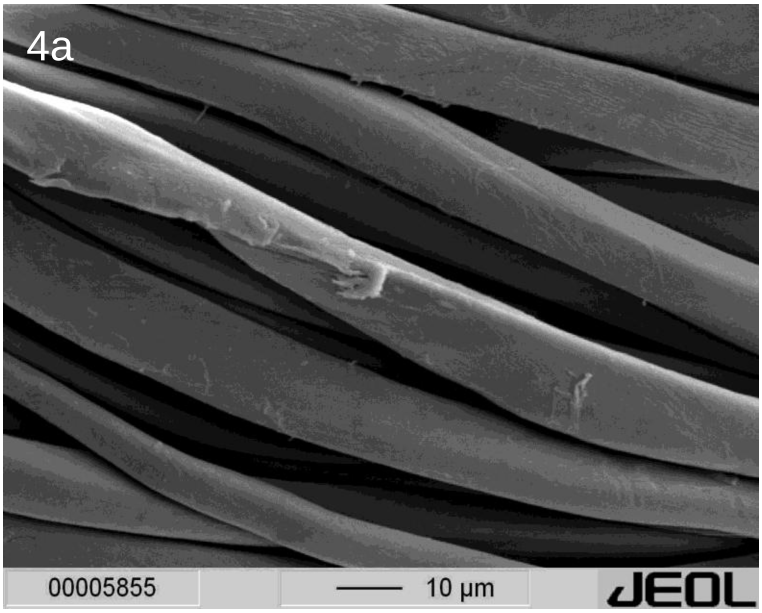

F
D
E
A B C
100
90
80
70
60
50
40
30
20
10
0
Temperature [°C]
0
20
40
60
80
100
120
140
160
180
200
Time [min]

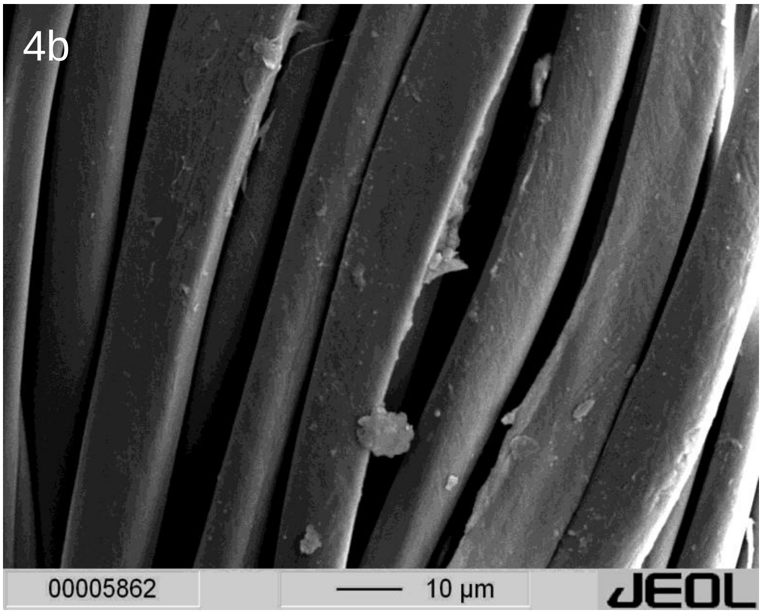
Fig 3



5
4
3
2
1
0
Absorbance [a.u.]
1800
1750
1700
1650
1600
1550
1500
Wavenumber [cm^{-1}]
1695
1645
1632
1739
1721
1771
B/A-1/4-220-15
B/A-1/1-220-15
B/A-1/1-180-15
3c
3b
3a
3c
3b
3a

Fig 4


4a


4b

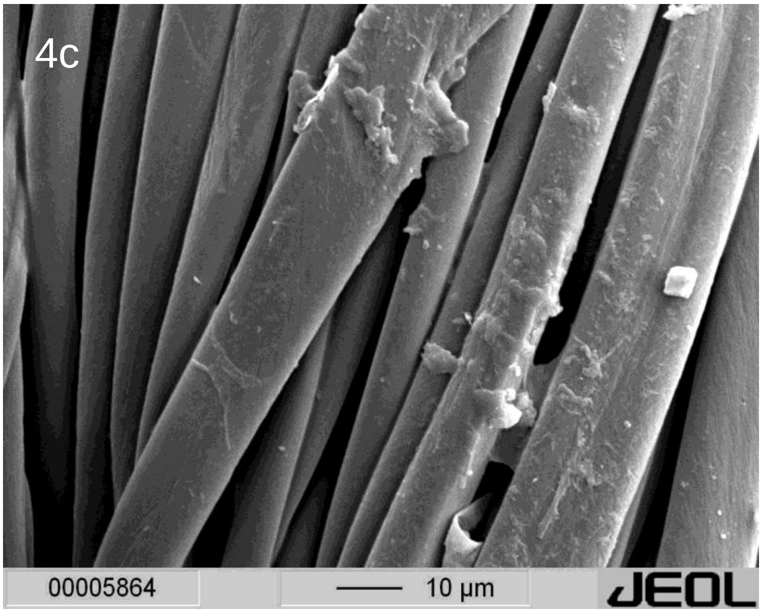
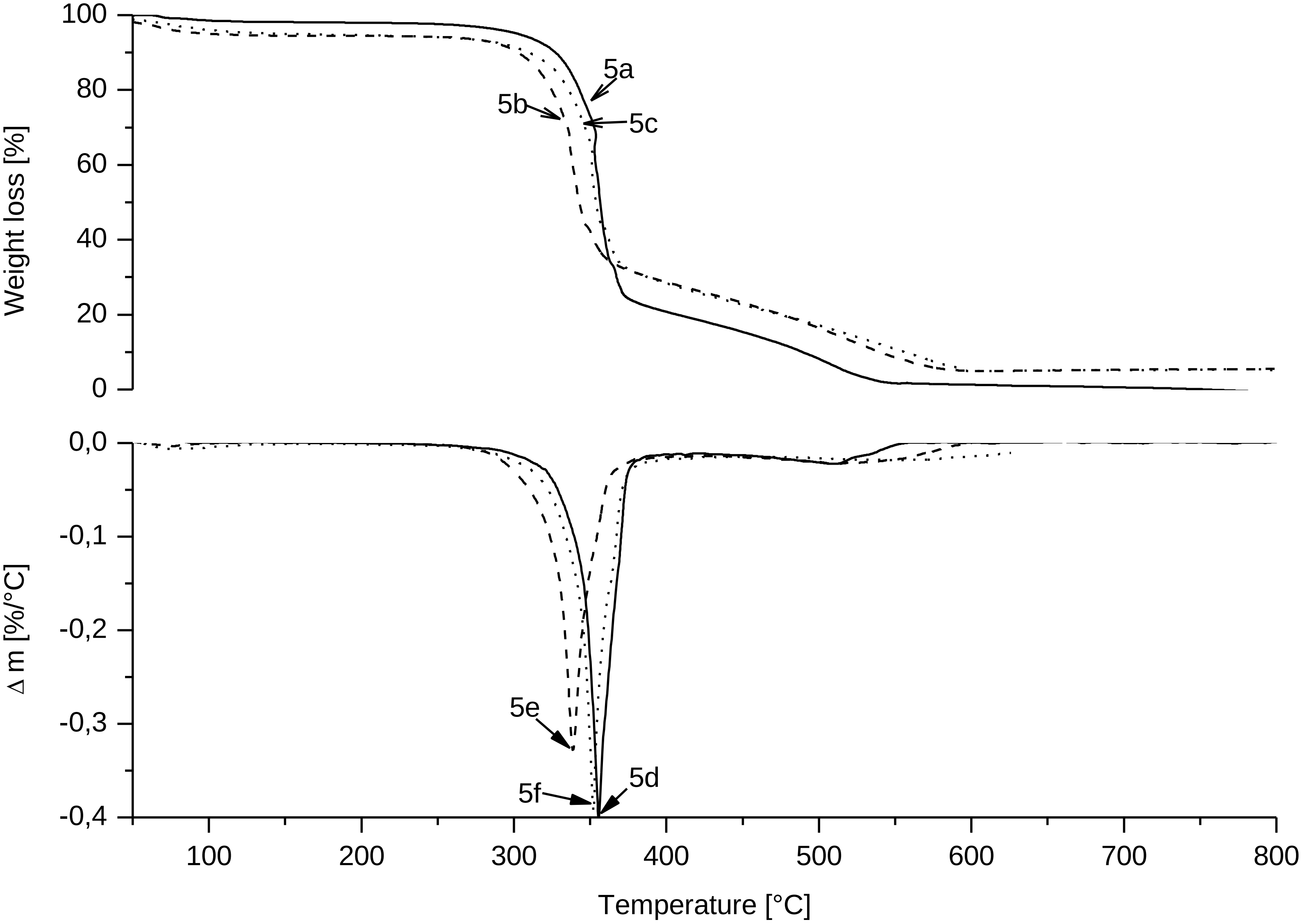

4c

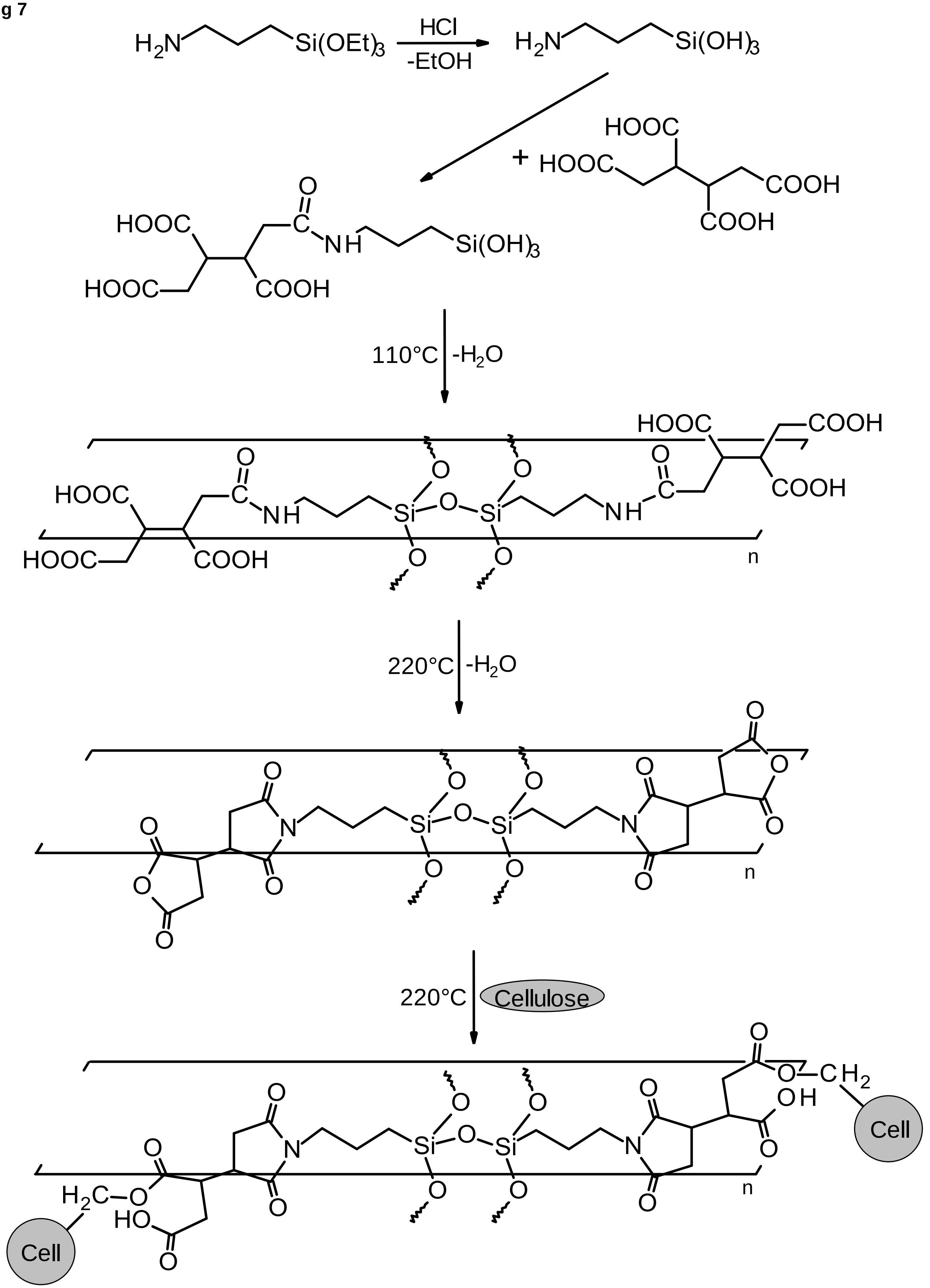
Fig 5



100
80
60
40
20
0
Weight loss [%]
5a
5b
5c
0,0
-0,1
-0,2
-0,3
-0,4
Δ m [%/°C]
5e
5f
5d
100
200
300
400
500
600
700
800
Temperature [°C]

Fig 6

Fig 7


HCl
-EtOH
H_2N
Si(OEt)3
Si(OH)3
HOOC
COOH
O
C
NH
110°C
-H_2O
220°C
-H_2O
Si
N
n
220°C
Cellulose
H_2C
CH_2
HO
OH
Cell

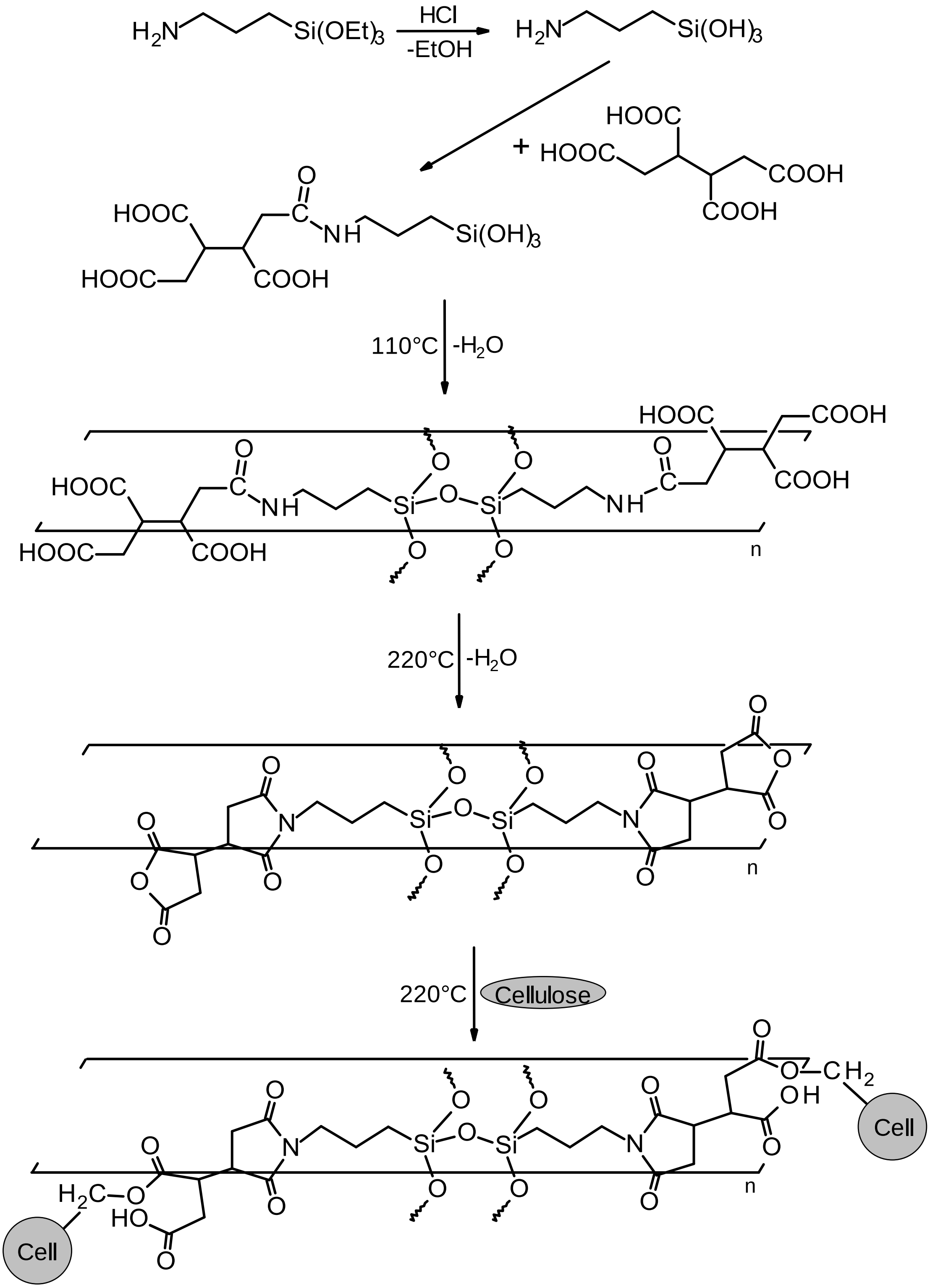
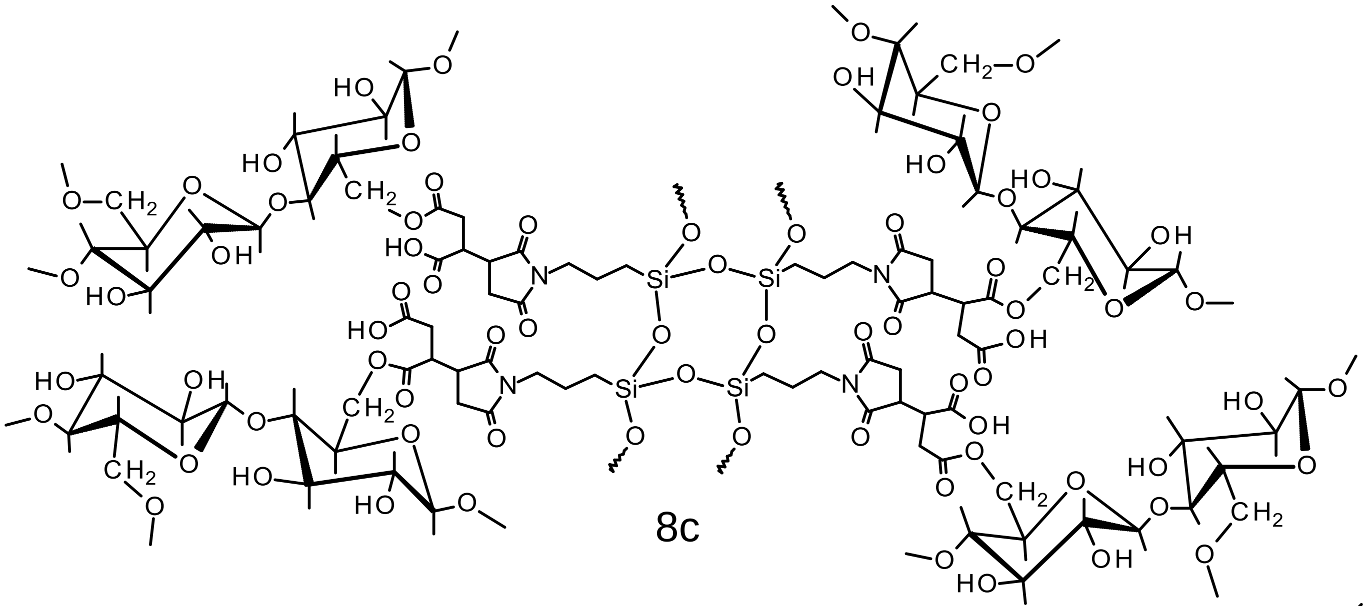
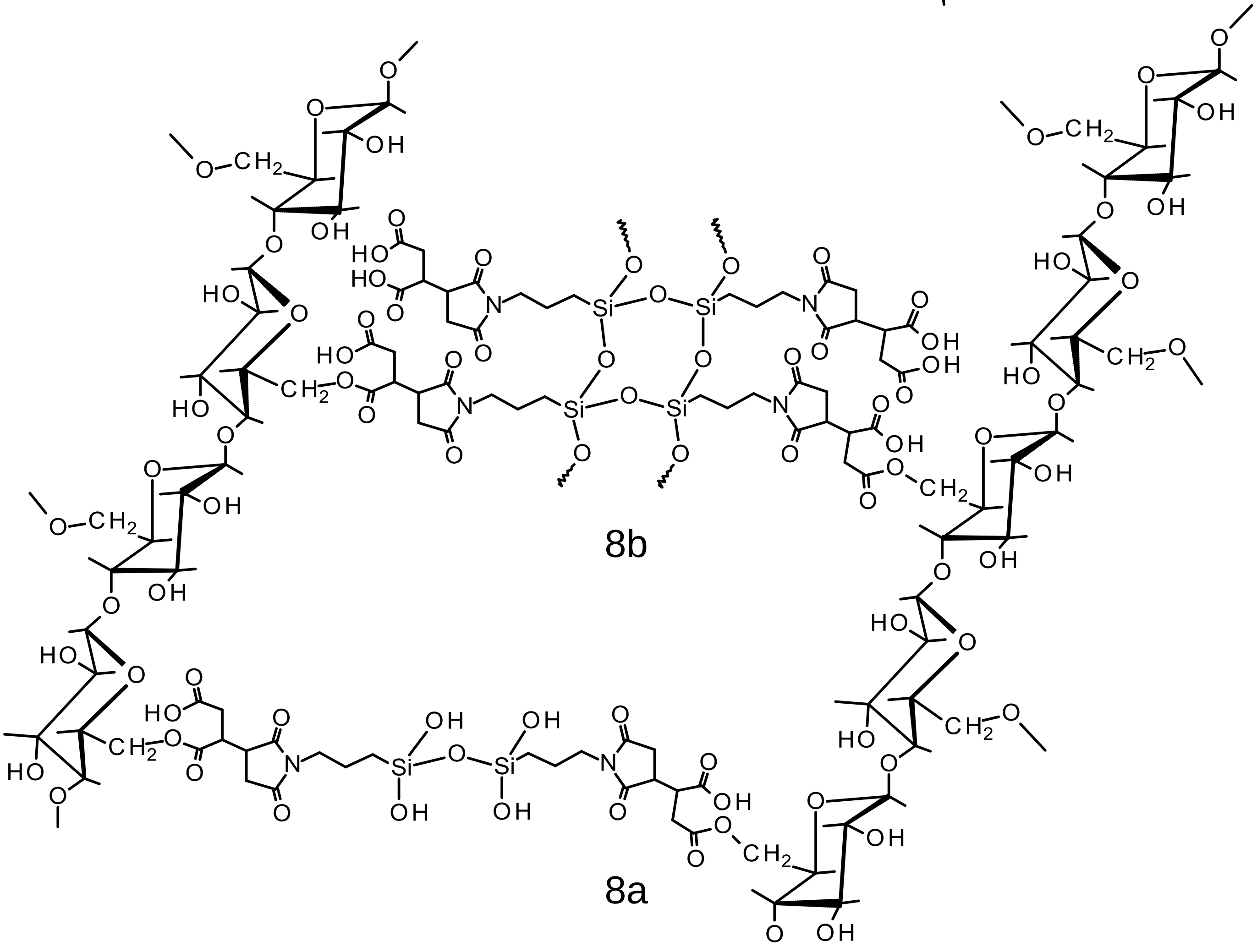
H2N
Si(OEt)3
HCl
-EtOH
Si(OH)3
+
HOOC
COOH
O
C
NH
110°C
-H2O
Si
O
n
220°C
-H2O
N
220°C
Cellulose
CH2
OH
H2C
HO
Cell

Fig 8



8c



8b

8a