VTT Technical Research Centre of Finland

Pre-treatments of pre-consumer cotton-based textile waste for production of textile fibres in the cold NaOH(aq) and cellulose carbamate processes

Määttänen, Marjo; Gunnarsson, Maria; Wedin, Helena; Stibing, Sara; Olsson, Carina; Köhnke, Tobias; Asikainen, Sari; Vehviläinen, Marianna; Harlin, Ali

Link to publication

Pre-treatments of pre-consumer cotton-based textile waste for production of textile fibres in the cold NaOH(aq) and cellulose carbamate processes

Marjo Määttänen · Maria Gunnarsson · Helena Wedin · Sara Stibing ·
Carina Olsson · Tobias Köhnke · Sari Asikainen · Marianna Vehviläinen ·
Ali Harlin

Abstract Recycling of textiles is of importance due to the large amount of waste generated from the increasing consumption and use worldwide. Cotton-rich pre-consumer textiles are considered as potential raw material for production of man-made regenerated fibres, but demands purification from the blends with synthetic fibres as well as the dyes and finishing chemicals. In this study we explore the use of different pre-treatments of pre-consumer textiles to meet specific parameters for production of fibres in the cold NaOH(aq) or cellulose carbamate process. The pre-treatments consisted of different bleaching sequences and were performed on both uncoloured and coloured pre-consumer textiles. For the uncoloured textile, degree of polymerisation and amount of inorganic content was efficiently reduced making the material suitable for both the cold NaOH(aq) and the cellulose carbamate process. In case of the coloured textile, the pre-treatments were able to remove the dye and decrease the inorganic content as well as reduce the degree of polymerisation but only sufficiently enough for production of fibres in the cellulose carbamate process. The work was able to prove a fibre-to-fibre concept while further optimisation of the

Sara Stibing: Formerly Sara Olsson.

M. Määttänen (✉) · S. Asikainen
VTT Technical Research Centre of Finland,
Ruukinmestarintie 2, 02330 Espoo, Finland
e-mail: marjo.maattanen@vtt.fi

M. Gunnarsson · H. Wedin · S. Stibing
Research Institutes of Sweden, RISE Bioeconomy,
Drottning Kristinas väg 61, 114 28, Stockholm, Sweden

C. Olsson · T. Köhnke
Research Institutes of Sweden, RISE IVF, Bio-Based
Fibres, Argongatan 30, 431 53 Mölndal, Sweden

S. Asikainen
Fortum Power and Heat Oy, Keilalahdentie 2-4,
02150 Espoo, Finland

M. Vehviläinen
VTT Technical Research Centre of Finland, Visiokatu 4,
33720 Tampere, Finland

A. Harlin
VTT Technical Research Centre of Finland, Tietotie 4E,
02150 Espoo, Finland

🖄 Springer

regeneration steps is expected to improve the mechanical properties of the produced fibres in future studies.

Introduction

The consumption of textile fibres has increased from 78 million tons to more than 103 million tons during the last decade (The Fiber Year 2018). This trend is expected to continue due to demographic and economic development. Most of the growth has come from synthetic fibres, especially from polyester and polypropylene, but also the production of regenerated cellulosic fibres has increased. The global consumption of man-made cellulosic fibres (viscose, lyocell, cellulose acetate, cupro etc.) reached 6.6 million tons in 2017 but is said to continuously exhibit high growth rates (The Fiber Year 2018). In addition to this, the production of cotton is not considered sustainable due to its massive use of water in combination with the usage of pesticides and arable land, which instead could be used for food production (Chapagain et al. 2006; Tariq et al. 2007). According to a recent publication, textiles are today one of the most environmentally damaging products in our society (Ljungqvist et al. 2018). From the year 2016 EU legislation has denied the land fill of organic material including textile waste. This has aroused the need to develop and improve textile recycling process and opened for the possibility to use recycled cotton waste textiles as raw materials for man-made cellulosic fibres.

A major part of the cellulose-based man-made fibres is manufactured by the viscose method (The Fiber Year 2018), which is based on a carbon disulphide mediated derivatisation of cellulose to form the NaOH(aq)-soluble cellulose xanthogenate. Due to high toxicity of carbon disulphide and of hydrogen sulphide that is formed during the regeneration, the recovery of these chemicals is essential for the establishment of a safe process (Klemm et al. 1998). The concern of the safety and environmental issues and to some extent economics of the current man-made cellulosic fibre processes, have encouraged the development of new cellulose dissolution technologies.

One attractive cellulose dissolution chemical, in terms of sustainability and integration with existing processes for pulp and paper production, is aqueous sodium hydroxide (NaOH). In the 1920s, Lilienfeld discovered that low temperature in combination with certain NaOH(aq) concentrations facilitates the dissolution of cellulose (Lilienfeld 1924). The process utilises a non-derivatising mechanism where the optimal NaOH(aq) concentration was found to be from 7 to 10 wt.% and the temperature from -5 °C to $+1$ °C (Davidson 1934). Due to the narrow dissolution window, the process experiences some difficulties in terms of stability (i.e. the dope tends to gel) why additives most often are used (Davidson 1937; Budtova and Navard 2016).

Another way to obtain dissolution of cellulose is through modification. One of the interesting methods is the cellulose carbamate (CCA) process, which is based on the reaction between cellulose and urea, resulting in the formation of a cellulose carbamate product. The cellulose carbamate can subsequently be dissolved in NaOH(aq) and is, in contrast to cellulose xanthate, a stable derivative which therefore facilitates a safer process to handle.

Several studies have been published on how to utilise cotton waste materials for regeneration into new textile fibres (Asaadi et al. 2016; Negulescu et al. 1998; Haule et al. 2016) but the use of the cold NaOH(aq) as dissolving media have until today been unexplored. The inhomogeneous constitution of cotton-rich waste material demands both its purification and tuning of the properties for achieving dissolution. Target of the pre-treatments is to remove non-cellulosic substances such as metals, ash, dyes, and residues of textile finishing chemicals, and to adjust the degree of polymerisation (DP) of the cellulose chains (Määttänen et al. 2019). Thus, the quality of pre-treated cotton-rich material meets the properties of commercial dissolving pulps. The pre-treatment sequence includes chemical, enzymatic and/or mechanical stages that are selected based on the characteristics of the raw materials (i.e. the textile waste). Through both chemical and enzymatic pre-treatments, an increased cellulose reactivity towards the dissolving agents is achieved (Asikainen et al. 2013, 2017).

In this work, our hypothesis is that with a sequential pre-treatment procedure pre-consumer waste cotton materials can be purified and the properties turned to achieve dissolution and regeneration of cellulose fibres using the cold NaOH(aq) or the cellulose carbamate processes.

Materials and methods

Raw materials

The raw materials used were pre-consumer cotton-based textile waste received from two textile companies. Uncoloured comber noil cotton (denoted Comber noil cotton), a by-product from yarn spinning, was delivered by SÖKTAŞ (Turkey) and a cotton fabric sample dyed with non-fixative reactive dyes (denoted Dyed cotton) was delivered by Tekstina (Slovenia). The textiles did not have any buttons, zips or other metal/plastic accessories.

The chemicals used in the pre-treatment stages, dissolution and fibre spinning are listed in the supplementary information. All chemicals were used as received without any further purification.

Pre-treatments

The raw materials were shredded with a hammer mill before the initial characterisation and the subsequent pre-treatments. The pre-treatment sequence used for the Comber noil cotton material was Ew-Z-P-A (as described below and in Fig. 1) without intermediate disk refining, whereas for the Dyed cotton material the same sequence was used with or without intermediated disk refining. The purpose of the disk refining was to open the textile and yarn structures of the Dyed cotton material. In the case when disk refining was used, alkaline washing was performed before the disk refining. The alkaline washing stage (Ew) was used to remove silicates originating from the raw materials as well as from the dyeing process. The intrinsic viscosity of the cotton materials was adjusted with the ozone (Z) and hydrogen peroxide (P) stages and the target viscosity level of each batch was selected based on the process to be used for dissolution. For the cold NaOH(aq) dissolution process the target viscosity level was 200–300 ml/g, and for the CCA processes it was 400–500 ml/g.

Additionally, the ozone and peroxide stages in combination with the alkaline washing stage were used to remove the colour from the cotton materials. The main metal management was done through acid washing (A) using sulfuric acid.

The pre-treatments were carried out in laboratory mixing reactors and the used processing conditions are presented in Tables 1 and 2. The alkaline washing treatments (Ew) were done in a 40 dm³ reactor having a combined anchor blade mixer. The reactor was heated by pressurised water in a heating mantel. The ozone treatment (Z) was performed in a 17 dm³ plastic flow-through reactor with medium concentration (12 wt.%) at pH 2 using oxygen as carrier gas. To calculate the total ozone consumption, the ozone content of the residual gas from the reactor as well as the ozone generation was analysed after the reached reaction time. The ozone formation and consumption were measured from the potassium iodide solution by titration with sodium thiosulfate. For the hydrogen peroxide (P) treatment and acid (A) washing, 15 or 40 dm³ laboratory reactors having an anchor mixer were used. The cotton material and most of the pre-heated dilution water were then mixed and the pH adjusted if needed, before adding the chemicals.

After each stage, a standard laboratory washing was performed: the pulp was diluted to 5 wt.% concentration with deionized water, having the same temperature as the preceding treatment stage, and dewatered. The materials were then washed two times with cold deionized water with an amount equivalent to ten times the absolute dry cotton amount. After the acid washing stage, the pulps were characterised. For the subsequent CCA process, several batches of material were prepared.

Preparation of cellulose carbamate

The pre-treated sample was dried using hot air to obtain dry content of 91–94%. Urea ($OC(NH_2)_2$, 11–12 wt.% based on cellulose) was dissolved in water with hydrogen peroxide (H_2O_2, 0.6–0.7% based on cellulose) and the mixture was introduced to the sample using a Forberg mixer. The obtained sample (dry weight 63%) was thereafter run six times through a specially designed pelletizer (Kahl) to homogenise and compact the structure. The cellulose-urea pellets were treated at 140 °C for 4 h during which the reaction between the urea and cellulose occurred and
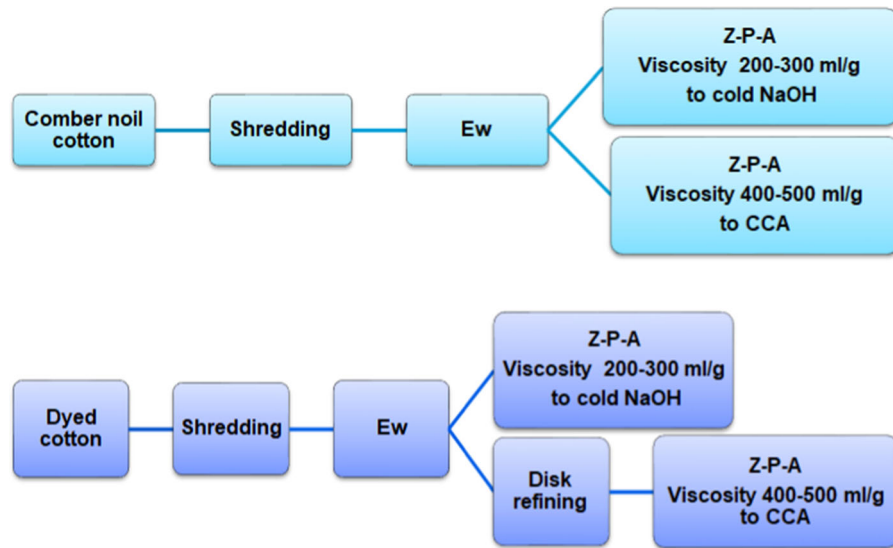
Fig. 1 The schematic description of the used pre-treatment procedures of Comber noil and Dyed cotton materials for cold NaOH and CCA dissolution and wet-spinning trials

Table 1 Pre-treatment conditions of Comber noil cotton material for the CCA and cold NaOH(aq) processes

Chemical dosages are wt.% of the used cotton amount

	Ew	Z (CCA)	Z (Cold NaOH)	P (CCA)	P (Cold NaOH)	A
NaOH (%)	2.7	–	–	3.2	3.2–3.5	
O$_3$ or H$_2$O$_2$ (%)	–	0.7	2–8	1.5	1.5–3.0	
H$_2$SO$_4$ (%)	–	0.82	0.74			5.9
Concentration (%)	10	12	12	10	10	2.5
Temperature (°C)	100	25	25	90	90	60
Time (min)	120	10	29–109	120	120	60

Table 2 Pre-treatment conditions of Dyed cotton material for the CCA and cold NaOH(aq) processes

Chemical dosages are wt.% of the used cotton amount

	Ew	Z (CCA)	Z (Cold NaOH)	P (CCA)	P (Cold NaOH)	A
NaOH (%)	36	–	–	1.1	3.5	
O$_3$ or H$_2$O$_2$ (%)	–	0.2	0.5	0.4	3.0	
H$_2$SO$_4$ (%)	–	0.5	0.65			4.9
Concentration (%)	10	12	12	10	10	2.5
Temperature (°C)	95	25	25	90	90	60
Time (min)	120	3	7.5	120	120	60

the final product was obtained as cellulose carbamate. Finally, the product was shredded to fine powder to facilitate the following dissolution.

Dissolution and spinning processes

Dissolution of pre-treated material in NaOH(aq)

Initially, pre-treated pre-consumer cotton materials were subjected to swelling in 6.7 wt.% NaOH(aq), at 10 wt.% cellulose for 16 h at a temperature slightly above 0 °C to increase the dissolution rate in cold NaOH(aq). Dissolution was then carried out by

filtering the swelled cotton materials and adding NaOH and water to reach a NaOH(aq) concentration of 6.9–8.6 wt.%. All batches contained ZnO at a concentration of 1.0–1.4 wt.%. The cellulose concentration was approximately 4.5 wt.% and the dissolution temperature ranged from − 5 to 5 °C. The time for dissolution was around 30 min or until a sufficiently low amount of particles or fibres could be observed in an optical microscope. The dissolved cellulose samples were thereafter stored at + 5 °C.

Wet-spinning of NaOH(aq) dope

Prior to the wet-spinning, the dope was filtered using a stack of 2×20 μm polypropylene non-woven filters and 1×5 μm metal fleece filter. The filtrated dope was deaerated under near vacuum for 10 min to remove air bubbles that could disturb the spinning process. Multifilament spinning was then performed in a bench scale spinning machine at 10 m/min linear extrusion speed through a 300×70 μm spinneret. The cellulose dope was coagulated in a spinning bath, an aqueous solution of 10% H_2SO_4 and 15% Na_2SO_4 at approximately 20 °C, and the newly formed fibres were stretched in hot water (80 °C) using a set of three godets. Fibres were collected on a second set of godets after the stretch bath. The maximum stretching of the fibres was determined by increasing the velocity of the take-up roll until the fibres broke. The take-up velocity was thereafter slightly decreased, the fibres guided once more through the spinning line and the fibre samples were collected. The final take-up velocity varied among the samples, and the final draw ratios are listed in Table 6. Finally, the fibres were thoroughly rinsed in fresh water at room temperature, soaked in a dilute solution of commercial fabric softener, cut, and dried in a convection oven at 60 °C.

Dissolution of carbamated pre-treated material

The carbamated pre-treated materials were dissolved in two steps as described previously (Valta et al. 2011) except zinc oxide was used as an additive. Initially, the carbamated pre-treated material was mixed with 3.5 wt.% NaOH(aq) containing 0.4 wt.% ZnO for 5 min at − 5 °C. Dissolution was then carried out by adding 18.6 wt.% NaOH(aq) containing 2.2 wt.% ZnO under mixing. The cellulose concentration was

from 5.5 to 6.5 wt.% and the dissolution temperature ranged from − 5 to 0 °C.

Wet-spinning of CCA dope

Prior to the wet-spinning the cellulose carbamate dope was filtered through absolute-rated pleated polypropylene filter cartridges (50 μm, 20 μm, 10 μm). The filtrated dope was deaerated by lowering the pressure inside the tank below 150 mbar for the next day. Temperature of the dope was maintained at 10 °C or at 15 °C. Multifilament spinning was carried out in laboratory scale wet spinning machine at 20–30 m/min using spinnerets of 1000–2100×50 μm. The coagulation bath contained 7–10 wt.% H_2SO_4, 8–10% Na_2SO_4 and 8–10% $Al_2(SO_4)_3$. The target linear density (titre) of the fibres was either 1.7 or 2.0 dtex. The desired capacity of gear pump was calculated as described in Vehviläinen et al. (2008). The coagulated fibres were guided through three godets to the fibre collector. The maximum stretching of the fibres was set by decreasing the velocity of the first godet until the fibres broke. The velocity was there after slightly increased, the fibres guided once more through the line and the sample collected. The fibres were cut manually to 55 mm length and washed with tap water until the pH settled around pH 7. Finally, the fibres were treated with ethanol and dried freely. The ethanol treatment was performed to prevent the fibres to attach to each other while drying.

Characterisation

Characterisation of raw materials and pre-treated materials

The raw materials as well as the pre-treated materials were characterised as follows: viscosity (ISO 5351:2010), brightness (ISO 2470-1:2009, from splitted sheet), ash content at 525 °C (ISO 1762:2001). In addition to this, metal content was determined through wet combustion and ICP-AES where the samples were dissolved in nitric acid in a microwave oven before the analysis. Molar mass distributions for both the raw materials and the pre-treated materials were determined by size exclusion chromatography (SEC). The solid samples were dissolved in DMAc/8% LiCl according to the solvent exchange method described by Berthold et al. (2001). The method includes

activation of the sample with water, solvent exchange with methanol and DMAc. Two parallel samples (a and b) of each cellulose sample were dissolved. After complete dissolution, the samples were diluted with DMAc providing final LiCl concentration of 0.8% as in the eluent. The elution curves were detected using Waters 2414 Refractive index detector. The molar mass distributions (MMD) were calculated against $8 \times$ pullulan (6100–708,000 g/mol) standards, using Waters Empower 3 software.

Characterisation of the cold NaOH(aq) dopes

The dissolved state of the cold NaOH(aq) dopes, both before and after filtration, was evaluated using an optical microscopy equipped with cross polarised plates, which can distinguish crystalline structures i.e. non-dissolved parts. A few samples were also analysed using a particle counter (Beckman Coulter Multisizer 4e) which gives a measure of undissolved materials, determining particle size from 10 to 2000 µm.

Additionally, the dopes were analysed with a CS Rheometer (Bohlin Instruments, Cirencester, UK) equipped with a 25 mm/5° cone and plate measuring system, to ensure that no gelling had occurred since the consequence of gelling is a dope that cannot be spun into fibres.

Characterisation of the cellulose carbamate and dopes

The cellulose carbamates were characterised by measuring the nitrogen content (Kjeldahl), limiting viscosity (ISO 5351:2010) and purity, where purity is defined as the share of cellulose carbamate after removing the unreacted urea by washing with hot water.

The cellulose carbamate dopes were characterized by measuring falling ball viscosity (ASTM D 1343-86) and CCA content. The CCA content was determined by coagulating a known amount of dope into a film, which was washed, dried and weighted. Additionally, one of the dopes was characterised by microscopic studies using an Olympus BH-2 light microscope with phase contrast mode, and by measuring the particle size distribution using a PAMAS S4031 particle counter equipped with HCB-LD-25/25 laser-based sensor.

Characterisation of fibres

The dried fibres were conditioned at a relative humidity of $65 \pm 4\%$ and temperature of 20 ± 2 °C for at least 24 h. The mechanical properties of the fibres were then determined as an average of 10 or 20 measurements according to the ISO 1973 and ISO 5079 standards using a testing machine for individual fibres (Vibroskop—Vibrodyn, Lenzing Instruments for cold NaOH(aq) fibres and Favegraph, Textechno GmbH for CCA fibres). The tests included linear density (dtex), tenacity (cN/dtex) and elongation (%). The test speed was 20 mm/min and gauge length 20 mm.

The surface and cross section structures of fibres were studied by scanning electron microscope (SEM) (JSM-6360LV, JEOL). The samples for cross section studies were prepared by breaking the fibres in liquid nitrogen. All the samples were coated with gold (Balazers SCD 050 Sputter Coater) and secondary electron images taken using 10 kV.

Results and discussion

Pre-treatments of pre-consumer cotton-based waste materials

The aim of the pre-treatment was to remove non-cellulosic substances like metals, ash, dyes, and residues of textiles finishing chemicals, and thus upgrade the quality of material prior to the dissolution and fibre spinning steps. The pre-treated materials were characterised by measuring their limiting viscosity, brightness and metal content (Tables 3, 4). The limiting viscosity of the raw materials i.e. the Comber noil (uncoloured) cotton and of the Dyed cotton were 1900 ml/g and 900 ml/g, respectively. For the cold NaOH(aq) dissolution process the target viscosity level was 200–300 ml/g, and for the CCA processes it was 400–500 ml/g. Target viscosity values were achieved well although the initial viscosities were very high. The removal of colour was also successful (Fig. 2). Despite the original Dyed cotton material was very dark, the brightness after the pre-treatment procedure was about 80%. There were some variations in brightness between batches prepared for the subsequent CCA trials partly due to colour variation in the original Dyed cotton material. For the Comber noil

Table 3 Viscosity and brightness of Comber noil and Dyed textile materials before and after pre-treatments

Material	Pre-treatment sequence	Viscosity (ml/g)	Brightness (%)	Pre-treatment yield (%)
Comber noil material	Original	1900	54.7	
To cold NaOH	Ew-Z-P-A	170	91.4	86.0
To cold NaOH	Ew-Z-P-A	190	89.9	89.9
To cold NaOH	Ew-Z-P-A	320	91.4	86.0
To CCA[a]	Ew-Z-P-A	410–430	89.9–91.5	91.3–92.4
Dyed textile material	Original	900	23.6	
To cold NaOH	Ew-Z-P-A	230	81.7	91.1
To CCA[b]	Ew-disk refining-Z-P-A	430	77.8–80.6	89.8–91.6

[a]three batches; [b]four batches

Table 4 Metal and ash contents of Comber noil and Dyed textile materials before and after pre-treatments

Raw material	Al (mg/kg)	Ca (mg/kg)	Co (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Mg (mg/kg)	Si (mg/kg)	Ti (mg/kg)	Ash (%)
Comber noil cotton material									
Original	21	773	< 0.1	1	19	724	41	< 10	1.6
Pre-treated	< 3	17	< 0.5	0.6	3.6	1.9	< 10	< 0.5	0.01
Dyed cotton material									
Original	22	66	0.2	4	< 10	37	676	128	1.7
Viscosity 230	4.9	9.6	< 0.5	< 0.5	5.3	1.8	14	14	0.05
Viscosity 430	16.6	9.2	< 0.5	0.75	11.2	< 1	37	0.69	< 0.01
Commercial dissolving pulp (Sixta 2006)	15–100	0.1		2.5–3.5	2–8	220	50–65		∼ 0.1

Ash was measured at 550 °C

cotton material a brightness level typical for dissolving pulps was achieved i.e. higher than 90%. Material losses caused by the pre-treatments were from 7.5 to 14%.

The presence of certain inorganic compounds such as silicates, calcium salts, and catalytically active transition metal ions are shown to impair the filterability and spinnability of a viscose spinning dope (Sixta 2006). In addition, pulp contamination with inorganic compounds leads to a gradual clogging of the spinnerets, and this alters the uniformity of fibre titre (Lenz 1981). Fe(II) ions also promote light-induced yellowing, and are together with Cu(II) involved in detrimental reactions in the presence of hydrogen peroxide for example in the carbamation process. Although some of the initial values were at high level, such as calcium, magnesium, silicate and ash content, the removal of metals by the pre-treatment sequences was effective (Table 4). Due to the higher silicate content of Dyed cotton fabric, a stronger alkaline treatment compared to Comber noil cotton was performed. High calcium and magnesium contents probably originate from the water used in textile production and the silicate content in the used dyes.

The molar mass distribution curves show that degradation due to pre-treatments occurred rather evenly (Fig. 3). The average molar mass and polydispersity values of pre-treated cotton materials decreased as the viscosity of the material decreased
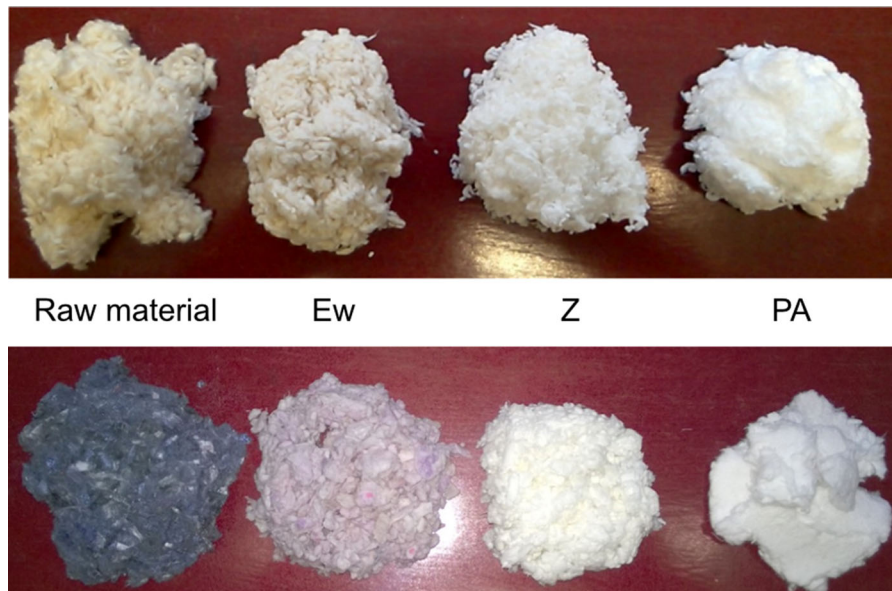
Fig. 2 Development of brightness of Comber noil materials and Dyed textile materials during pre-treatments
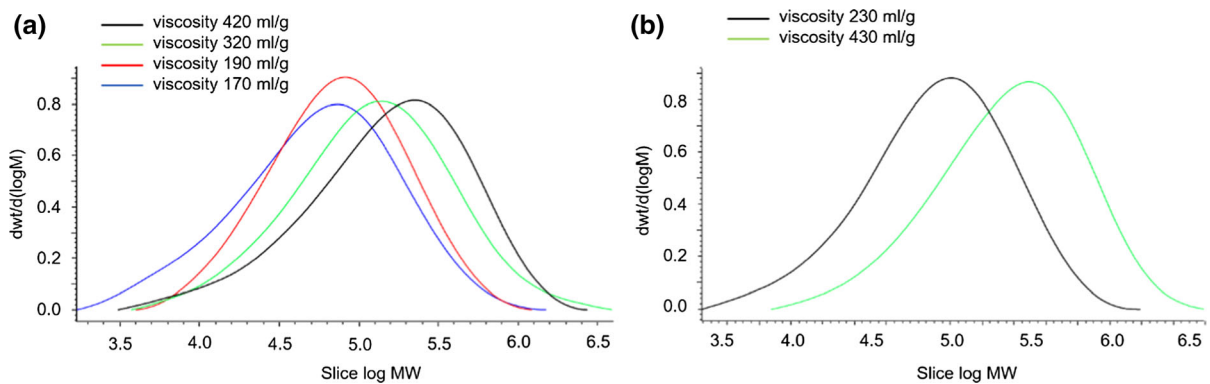

Fig. 3 Molar mass distributions for **a** pre-treated Comber noil cotton material and **b** pre-treated Dyed cotton material

Table 5 Molar mass and polydispersity values of pre-treated Comber noil and Dyed textile materials in different viscosity levels

Pre-treated cotton material	Viscosity (ml/g)	Mn (kDa)	Mw (kDa)	Mz (kDa)	MP (kDa)	Polydispersity
Comber noil	420	82	321	568	235	3.9
	320	58	203	534	134	3.5
	190	38	112	242	80	3.0
	170	30	101	237	74	3.3
Dyed cotton	430	108	347	786	266	3.3
	230	45	131	271	99	2.9

in the course of pre-treatments (Table 5). At the viscosity level of 400 ml/g the molar mass (Mw) was over 300 kDa and polydispersity over 3 whereas at the viscosity level 200 ml/g values were around 100 kDa and near 3, respectively.

Dissolution and spinning of pre-treated cotton material in the NaOH(aq) process

Preparation of spinning dopes in the cold NaOH(aq) process

Several spinning dopes were prepared from the pre-treated Comber noil cotton materials using the cold NaOH(aq) dissolution process (Table 6). Unfortunately, no spinning dopes could be prepared from the Dyed cotton material due to insufficient dissolution with large amount of undissolved fibres. Some fibres were shown more or less unaffected by the dissolution process, which indicates that the fibres have decreased accessibility for the solvent. The reason for this could be a macromolecular alteration in the fibres induced either by the dying treatment or during the removal of the dye which is not in favour for the dissolution process in NaOH(aq). Moreover, the solution showed gel tendencies although the viscosity was measured as being very low (see Figure S1 in SI). This behaviour has previously been observed and explained as the formation of new compact agglomerates that are induced by the initial presence of interagglomerate interactions in the solution (Roy et al. 2003).

The dissolution efficiency for the pre-treated Comber noil cotton materials before the filtration step can be seen in the micrographs presented in Fig. 4. As expected, the sample with the lowest limiting viscosity (170 ml/g) gave the solution with the least optically observable particles and fragments. All other dopes showed undissolved particles and fragments in the micrographs before filtration. Furthermore, the spinning dopes were analysed in terms of viscosity to evaluate eventual gelation, which influences the spinnability of the dope (Fig. 5). The viscosity measurements showed that the samples with higher

limiting viscosity (320 ml/g) to a higher extent exhibited shear thinning behaviour, which indicates a tendency for gelation. This applied for sample S4 that had higher cellulose concentration than S3 and lower ZnO concentration than S5, and thereby implies the importance of choosing the right dissolution conditions even though an optical observation with low amount of particles and fragments in the dope suggests efficient dissolution.

Wet-spinning of the cold NaOH(aq) dopes

Fibres were spun into an acidic coagulation bath. During the spinning, some clogging of the spinneret was observed, which could be correlated to the gelation tendency observed in the viscosity measurement or indicate that all impurities were not removed. The mechanical properties of the fibres together with their tactile sensation are presented as average values from ten measurements in Table 7. In general, the fibres spun from the pre-treated Comber noil material with a low limiting viscosity (170–190 ml/g) became brittle in their appearance, with low dry tenacity. The sample showing the highest tendency of gelation in the viscosity measurement (S4) did also display poor spinnablility. Its highest possible draw ratio was well below one, and consequently the dope produced low quality fibres. The gelation as such may prevent the polymeric chains from becoming oriented in the axial direction during the spinning process leading to weaker secondary interactions between the chains. The Young's modulus (YM) and elongation at break can be seen as a direct consequence of the draw ratio.

The fibres produced from the 320 ml/g-dope with 1.4 wt.% ZnO had the highest draw ratio (1.21) in the spinning line that translated to the highest mechanical properties and the soft appearance of the fibres (Figs. 6,

Table 6 Properties of Comber noil spin dopes in cold NaOH(aq) process

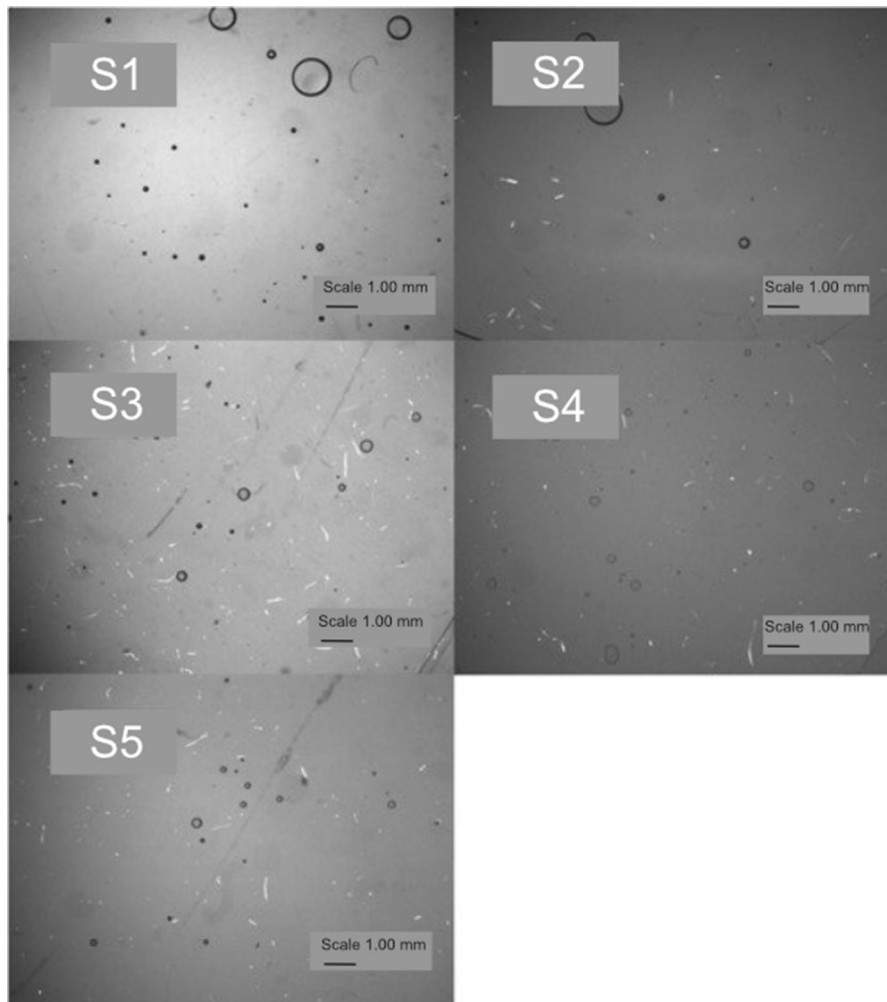| Sample	Limiting viscosity number (ml/g)	NaOH (wt.%)	Cellulose (wt.%)	ZnO (wt.%)	Particle size mean/median (Multisizer, μm)
S1	170	7.3	4.3	1.2	n.a
S2	190	7.3	4.3	1.2	n.a
S3	320	7.3	4.0	1.2	10.5/8.2
S4	320	7.3	4.3	1.2	9.0/7.9
S5	320	7.3	4.3	1.4	n.a

Fig. 4 Micrographs of the cold NaOH(aq) Comber noil spin dopes before filtration. Scale bar is 1 mm. S1 represents 170 ml/g, S2 190 ml/g and S3, S4 and S5 represent 320 ml/g
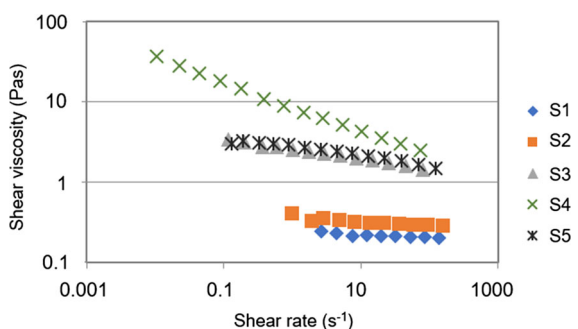

Fig. 5 Viscosity curves of the Comber noil dopes before filtration. S1 represents 170 ml/g, S2 190 ml/g and S3, S4 and S5 represent 320 ml/g

7). The high draw ratio and mechanical properties indicate better orientation of the cellulose chains in the fibre compared to the fibres with lower or no stretching. The dry tenacity reached 1.4 cN/dtex is moderate compared to commercial viscose fibres, however, it is important to notice that no attempts were made to optimise the spinning process.

Preparation of cellulose carbamate (CCA)

The pre-treated Comber noil and Dyed textile materials were used as starting materials in the cellulose carbamate process. Two batches were carbamated from the pre-treated Comber noil with slightly different peroxide charge, and one batch from the pre-

Table 7 Mechanical properties of fibres produced in the cold NaOH(aq) process from Comber noil

Sample	Draw ratio	Titer (dtex)	Elongation (%)	Dry tenacity (cN/dtex)	YM 1% (cN/dtex)	Comment
S1	1.01	1.3	10	1.1	48.9	Very brittle
S2_a	1.00	1.8	15	1.0	42.4	Brittle
S2_b	1.14	1.6	7	1.2	54.5	Brittle
S3	0.74	2.3	16	1.2	40.2	Soft and easy to separate
S4	0.55	3.2	20	0.7	30.4	Feels dry and brittle
S5_a	0.96	2.0	20	1.3	47.8	Soft and smooth to handle
S5_b	1.21	1.5	12	1.4	56.9	Soft and smooth to handle

Samples marked with *a* is the undrawn fibre and samples marked with *b* is the drawn fibre

Fig. 6 Filaments from spinning S5 (Comber noil, limiting viscosity 320 ml/g)

treated Dyed textile. The amounts of hydrogen peroxide added together with urea in the carbamation reaction and the characteristics of the obtained CCA samples are listed in Table 8.

The aim of the hydrogen peroxide addition was to decrease the limiting viscosity of the carbamated material to be suitable for the following dissolution process. The effect of the hydrogen peroxide is related to the activated derivatives formed, which will attack the cellulose backbone. The amount of hydrogen peroxide used in the carbamation reaction was determined based on previous experiments with similar kind of materials (unpublished results) and on the limiting viscosity of pre-treated material. The limiting viscosity obtained for the carbamated Comber noil material in the first batch was optimal for the following dissolution process. However, only slightly decreased hydrogen peroxide charge in the second batch resulted in significantly higher viscosity which was not
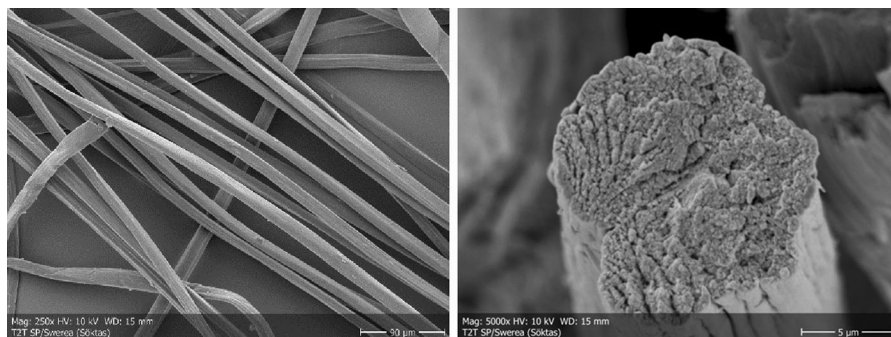

Fig. 7 Surface (left) and cross section (right) SEM images of the S5 fibres (Table 6) obtained in the cold NaOH(aq) process (320 ml/g-dope with 1.4 wt.% ZnO) from pre-treated Comber noil cotton material

Table 8 Characteristics of carbamated samples

Starting material	Pre-treatment sequence	Limiting viscosity of pre-treated sample (ml/g)	Carbamation			Carbamated sample		
			Batch	H_2O_2 ($\%^a$)	Reaction time (h) and temperature (°C)	Nitrogen content (%)	Purity (%)	Limiting viscocity (ml/g)
Comber noil cotton material	Ew-Z-P-A	410–430	1	0.70	4/140	1.19	93.1	230
			2	0.65	4/140	1.00	93.7	280
Dyed cotton material	Ew-disk refining-Z-P-A	430	1	0.60	4.5/140	1.09	93.7	180

[a]Based on cellulose

expected. On the other hand, the viscosity of carbamated Dyed textile material was lower than expected, regardless the same viscosity level of the pre-treated materials and the slightly lower peroxide charge during the carbamation. This large variation gives an indication of the sensitivity of hydrogen peroxide to degrade the cellulosic material under the carbamation reaction and emphasises the need for more careful experimental studies to clarify all the affecting parameters. However, the higher susceptibility of the pre-treated Dyed material could be due to the initially harsher processes of original starting material (dyeing, weaving) and of the pre-treatment (Ew stage) which might have increased the reactivity of it. On the other hand, the Dyed material had higher iron content after the chemical pre-treatments compared to the Comber noil or commercial reference; which might have enhanced the effect of peroxide via so-called Fenton reactions. However, this has not been studied here.

Dissolution and spinning of cellulose carbamate

Preparation of the CCA spinning dopes

The dopes were prepared by using the previously developed two-step dissolution technique (Valta et al. 2011) with the addition of zinc oxide in sodium hydroxide. Zinc oxide has shown significantly to increase the solubility of cellulose (Davidson 1937; Yang et al. 2011), modified cellulose (Davidson 1937; Kihlman et al. 2013) and enzyme-treated cellulose (Vehviläinen et al. 2015) in NaOH-based systems. The zinc oxide is suggested to affect the intermolecular

hydrogen bonds of cellulose (Yang et al. 2011) and to charge up the cellulose (Kihlman et al. 2013) that would benefit its dissolution in alkaline media. Moreover, Fu et al. have successfully dissolved cellulose carbamate in sodium zincate and regenerated cellulose membranes (2014a) and filaments (2014b) from the solution.

In this work, three spinning dopes were prepared; Dopes 1 and 2 from carbamated Comber noil cotton materials and Dope 3 from carbamated Dyed cotton material. The parameters and characteristics of the dopes are given in Table 9. The Dope 3 was studied under microscope before and after filtration (Fig. 8), and its particle size distribution was measured after filtration (Fig. 9).

The targeted CCA content of Dope 1 was 5.5% that produced solution with low viscosity (falling ball time 10 s). The low viscosity improved filterability of the Dope 1 but might have had negative effect on spinning performance. The targeted CCA content of Dope 2 was also 5.5%, but due to the higher limiting viscosity of CCA (280 ml/g) compared to Dope 1 CCA (230 ml/g) it was expected that the falling ball time of Dope 2 would also be higher. Interestingly, the time was in the same range (12 s), which is very low considering the high limiting viscosity of 280 ml/g. The result could be partly explained by the thixotropic nature of the dope if the viscosity was measured too quickly after pouring the dope in the test tube (Vehviläinen et al. 2015). However, this kind of shear thinning cannot fully explain the result and thus it is plausible that the sample for limiting viscosity measurement was not representative. Due to the low

Table 9 Characteristics of the dopes

Parameter	Comber noil-1 Cotton/Dope 1	Comber noil-2 Cotton/Dope 2	Dyed Cotton/Dope 3
Limiting viscosity of CCA (ml/g)	230	280	180
Targeted CCA concentration of dope (wt.%)	5.5	5.5	6.5
NaOH of dope (wt.%)	8.6	8.6	8.6
ZnO of dope (wt.%)	1.0	1.1	1.1
Filtration rate	50 μm + 10 μm	50 μm + 10 μm	50 μm + 20 μm
Deaeration T (°C)	10	15	10
Falling ball time (s/20 cm)	10	12	60[a]
Dope T in falling ball measurement (°C)	20	18	20
Measured CCA content after filtration (wt.%)	5.6	5.5	6.4

[a]After first filtration stage (50 μm)
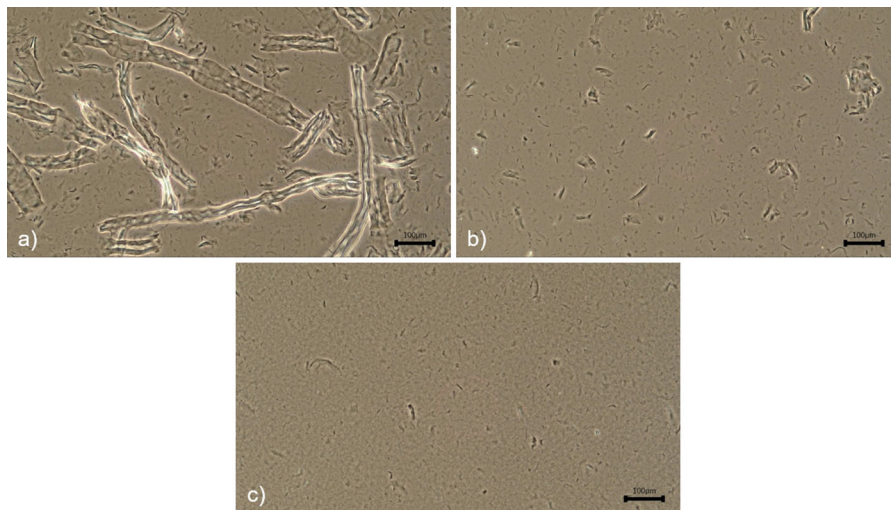
Fig. 8 Phase contrast microscope images of dope prepared from Dyed cotton: **a** before filtration, **b** after first filtration stage (50 μm) and **c** after second filtration stage (50 μm + 20 μm)
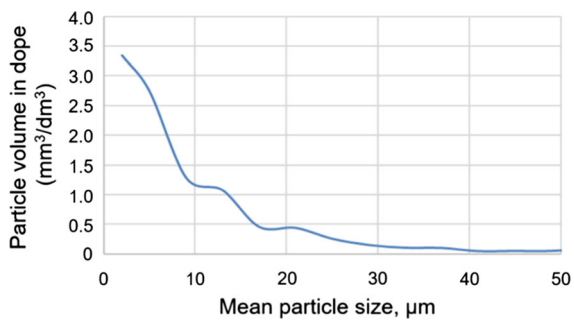
Fig. 9 Mean particle size distribution of filtrated spinning dope prepared from carbamated Dyed cotton material

falling ball time the Dope 2 was also effectively filtered through the 50 μm and 10 μm cartridges.

Targeted CCA content of the Dope 3 from the Dyed cotton CCA material was significantly higher (6.5 wt.%) than that of the previous dopes (5.5 wt.%) since the limiting viscosity of CCA was only 180 ml/g. In this case, the falling ball time of the dope was higher than desired and made the dope slightly instable. It was noticed that part of the 50 μm-filtered dope formed gel in the storage tank and it was necessary to discharge this portion from the next filtration stage. The unfiltered dope contained a lot of large undissolved and only partly swollen fibres as

well as small undissolved fibre fragments that were visible in the microscopic study (Fig. 8). The filtration stage removed the large fibres, but some of the small fragments were not captured by filters as confirmed by the average particle size distributions. (Fig. 9).

Spinning of the CCA dopes

The obtained dopes were spun into fibres by using coagulation baths containing sulphuric acid, sodium sulphate and aluminium sulphate in slightly different amounts from trial to trial. The temperature of the coagulation baths varied from ambient to + 5 °C (Table 10). The spinning parameters and characteristics of the fibres are given in Table 11.

The spinning variables in the trials were spin bath composition and temperature, number of spinneret orifices, targeted titre of the fibres as well as spinning velocity. The overall average mechanical properties of the fibres were low ranging from 0.7 to 1.0 cN/dtex with elongation (at break) from 7 to 16% (Table 11). Variation of the force–elongation curves from fibre to fibre were large leading to high standard deviations of average values (Fig. 10). Thus, it was not possible to draw any correlation between the spinning variables and the fibre properties. Instead, the effect of spinning

Table 10 Characteristics of the spinning baths

Parameter	Comber noil-1 Cotton/Dope 1	Comber noil-2 cotton/Dope 2	Dyed Cotton/Dope 3
Spinning bath content			
H_2SO_4 (wt.%)	7	10	7
Na_2SO_4 (wt.%)	8	10	8
$Al_2(SO_4)_3$ (wt.%)	8	10	8
Before spinning			
Specific gravity (g/l)	1.215	1.263	1.228
Temperature (°C)	21	10	5
After spinning			
Specific gravity (g/l)	1.202	1.251	1.223
Temperature (°C)	nd	15	10

Table 11 Spinning parameters and fibre properties of carbamated Comber noil cotton and Dyed cotton materials

Parameter	Comber noil-1 cotton		Comber noil-2 cotton				Dyed cotton	
	Fibre 1	Fibre 2	Fibre 1	Fibre 2	Fibre 3	Fibre 4	Fibre 1	Fibre 2
Targeted titre (dtex)	1.7	1.7	2	2	2	2	1.7	1.7
Spinneret (orifices)	2000	2000	1000	1000	2100	2100	1000	1000
Spinning velocity (m/min)	21	30	20	30	21	30	20	30
Stretching (%)	65	58	56	56	53	57	37	38
Spinneret draw	0.55	0.57	0.48	0.48	0.49	0.48	0.76	0.75
Characteristics of the fibres as average, standard deviation given in brackets								
Tenacity (cN/dtex)	0.9	0.9	1.0	0.7	1.0	1.0	0.9	0.7
Titre (dtex)	1.8	1.9	2.2	2.3	2.2	2.2	2.2	2.5
Elongation (%)	10	13	12	7	14	12	16	13
Characteristics of the strongest fibre								
Tenacity (cN/dtex)	1.1	1.5	1.3	1.3	1.3	1.4	1.3	1.0
Titre (dtex)	1.7	1.6	2.1	2.1	2.1	1.9	1.8	2.4
Elongation (%)	11	19	17	13	8	19	25	23

parameters was studied using the standard deviation i.e. the smaller the deviation the more stable the process. It seems that the lower spinning velocity enabled more stable spinning conditions for the dopes prepared from the carbamated Comber noil cotton materials, whereas the dope prepared from the carbamated Dyed cotton material was more stable at a higher velocity (SI Figure S2.). The observation is probably related to the dope viscosity. Due to the thixotropic behaviour of an alkaline cellulosic dope, the high spinning velocity thinned the low viscosity of the Comber noil cotton dopes too much for stable coagulation but affected the higher viscosity dope from the Dyed cotton material beneficially. The effect is seen in both the fibre tenacity and the elongation at break.

The maximum stretching of the fibres during the spinning is an important parameter that indicates the orientation of the fibre structure. Generally, the higher the stretching the higher the orientation and consequently the tenacity of the fibres. The stretching of fibres from carbamated Comber noil cotton dopes was around 60%, while the stretching of fibres from carbamated Dyed cotton dope was below 40%. Consequently, the tenacity of fibres regenerated from carbamated Comber noil cotton dopes was slightly higher than of the fibres regenerated from carbamated Dyed cotton dope. The reason for this is probably the higher limiting viscosity of the carbamated Comber noil cotton material (SI, Figure S3).

The SEM images (Figs. 11, 12, 13, 14) show that the fibres coagulated from the Comber noil cotton dopes have kink-like defects along the fibre axis while the fibres coagulated from the Dyed cotton dope are more even. The kinks are the result of an unstable coagulation of the fibres which might be due to clogging of the spinneret or changes in the flow velocity at the spinneret. In this case, it is suggested that the kinks are due to the low viscosity of the Comber noil cotton dope that was not able to hold the structure of as-formed fibres. The defects have a detrimental effect on fibre tenacity and are clearly one reason for the large variation in mechanical properties. All the fibres have longitudinal stripes on the surfaces that seem to continue across the fibre matrix. The stripes give serrated shape for the cross sections similar to viscose fibres. Also, the overall cross section shape mimics more viscose fibres than the round fibres coagulated using the NaOH(aq) process.

Fig. 10 Force–elongation curves of Comber noil-1, Fibre 3

Conclusions

Herein, we studied the possibilities to purify pre-consumer textile waste to raw material for production
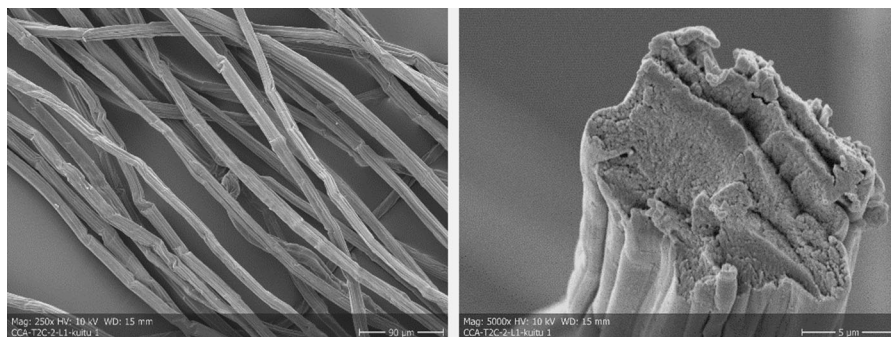

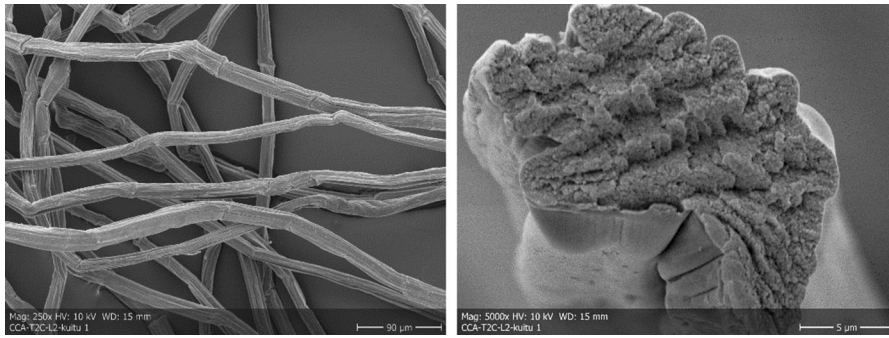Fig. 11 Surface and cross section SEM images of Comber noil-1 cotton, Fibre 1 (21 m/min, 2000×)

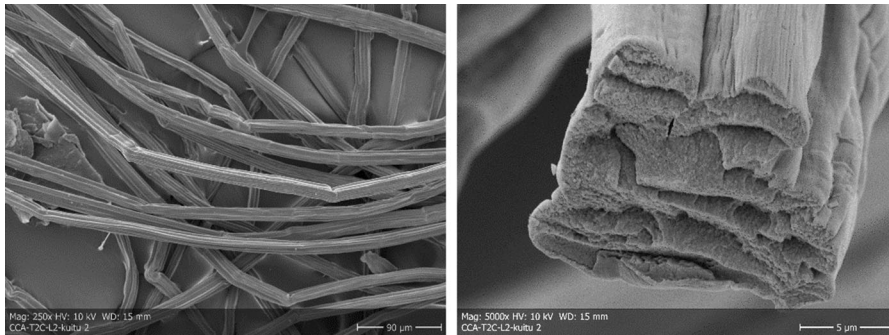**Fig. 12** Surface and cross section SEM images of Comber noil-2 cotton, Fibre 1 (20 m/min, 1000×)

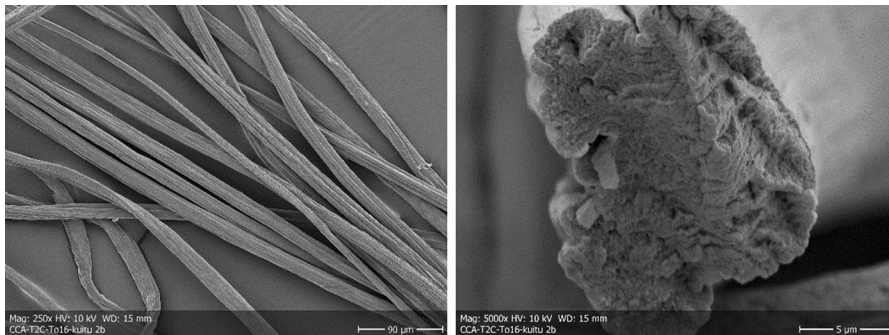**Fig. 13** Surface and cross section SEM images of Comber noil-2 cotton, Fibre 2 (30 m/min, 1000×)

Fig. 14 Surface and cross section SEM images of Dyed cotton, Fibre 2 (30 m/min, 1000×)

of new cellulose-based textile fibres in the cold NaOH(aq) and cellulose carbamate dissolution processes. Pre-treatments for de-dyeing and removal of inorganics was shown to be successful as all materials reached high brightness and decreased metal content. The pre-treatments were also effective in regulating the limiting viscosity of the materials, which is crucial for the subsequent dissolution and spinning steps. Dissolution of the pre-treated materials directly into sodium zincate (the cold NaOH(aq)) or after chemical

modification (the cellulose carbamate process) was shown to be efficient. The undissolved material was possible to remove by filtration which resulted in spinnable dopes. Based on the results obtained, it is suggested that the viscosity of the spinning dope largely influenced the spinnability as well as the mechanical properties of the obtained fibres. Altogether, the stated hypothesis, "with a sequential pre-treatment procedure pre-consumer waste cotton materials can be purified and the properties turned to

achieve dissolution and regeneration of cellulose fibres using the cold NaOH(aq)) or the cellulose carbamate processes", was proven to be true and we were able to demonstrate a fibre-to-fibre proof of concept by utilising pre-consumer textile waste as raw material to produce new textile fibres. It is important to stress that no attempts were made to optimise the spinning conditions to obtain improved mechanical properties, which leaves room for large improvements in the future work on the fibre-to-fibre concept.

Availability of data and materials　All data and produced materials supports our published claims and comply with field standards.

Compliance with ethical standards

Conflict of interest　Authors Määttänen, Asikainen, Vehviläinen and Harlin have made a patent related to pre-treatments of cotton waste materials before cellulose dissolution. FI 20175376 Treatment process for textile-based materials (filed 27.4.2017). Rights of the patent have been sold to third party.

References

Asaadi S, Hummel M, Hellsten S et al (2016) Renewable high-performance fibers from the chemical recycling of cotton waste utilizing an ionic liquid. ChemSusChem 9:3250–3258. https://doi.org/10.1002/cssc.201600680

Asikainen S, Määttänen M, Valta K, et al (2013) From recycled fibers to textile fibers. In: IFATCC 2013, 8–10 May 2013, Congress. Budapest

Asikainen S, Harlin A, Määttänen M, et al (2017) FI 20175376 Treatment process for textile-based materials. Accessed 27 April 2017

Berthold F, Gustafsson K, Sjöholm E, Lindström M (2001) An improved method for determination of softwood Kraft pulp molecular mass distribution. In: 11th ISWPC, vol 1, pp 363–366

Budtova T, Navard P (2016) Cellulose in NaOH–water based solvents: a review. Cellulose. https://doi.org/10.1007/s10570-015-0779-8

Chapagain AK, Hoekstra AY, Savenije HHG, Gautam R (2006) The water footprint of cotton consumption: an assessment of the impact of worldwide consumption of cotton products on the water resources in the cotton producing countries. Ecol Econ 60:186–203. https://doi.org/10.1016/j.ecolecon.2005.11.027

Davidson GF (1934) The Dissolution of chemically modified cotton cellulose in alkaline solutions. Part I—in solutions of sodium hydroxide, particularly at temperatures below the normal. J Text Inst Trans 25:T174–T196. https://doi.org/10.1080/19447023408661621

Davidson GF (1937) The dissolution of chemically modified cotton cellulose in alkaline solutions. Part 3—in solutions of sodium and potassium hydroxide containing dissolved zinc, beryllium and aluminium oxides. J Text Inst Trans 28:T27–T44. https://doi.org/10.1080/19447023708631789

Fu F, Yang Q, Zhou J, Hu H, Lia B, Zhang L (2014) Structure and properties of regenerated cellulose filaments prepared from cellulose carbamate-NaOH/ZnO aqueous solution. ACS Sustain Chem Eng 2:2604–2612

Fu F, Guo Y, Wang Y, Tan Q, Zhou J, Zhang L (2014a) Structure and properties of the regenerated cellulose membranes prepared from cellulose carbamate in NaOH/ZnO aqueous solution. Cellulose 21:2819–2830

Guldt A (2014) Tencel plant in Lenzing: positive scorecard in the six-month ramp-up phase. Lenzing, Austria

Haule LV, Carr CM, Rigout M (2016) Preparation and physical properties of regenerated cellulose fibres from cotton waste garments. J Clean Prod 112:4445–4451. https://doi.org/10.1016/j.jclepro.2015.08.086

Kihlman M, Medronho BF, Romano AL, Germgård U, Lindman B (2013) Cellulose dissolution in an alkali based solvent: influence of additives and pretreatments. J Braz Chem Soc 24:295–303

Klemm B, Philipp B, Heinze T et al (1998) Comprehensice cellulose chemistry. Wiley-VCH, Weinheim

Lenz J (1981) Der Einfluß der Begleitsubstanzen des Zellstoffs auf Verarbeitbarkeit und Fasereigenschaften im Viskoseprozeß. Lenzinger Berichte 51:10–13

Lilienfeld L (1924) Manufacture of cellulose solution

Ljungqvist H, Watson D, Elander M (2018) Developments in global markets for used textiles and implications for reuse and recycling

Määttänen M, Asikainen S, Kamppuri T et al (2019) Colour management in circular economy: decolourization of cotton waste. Res J Textile Apparel 23:134–152. https://doi.org/10.1108/RJTA-10-2018-0058

Negulescu I, Kwon H, Collier BJ et al (1998) Recyling of cotton from cotton/polyester fabrics. Text Chem Color 30:31–35

Roy C, Budtova T, Navard P (2003) Rheological properties and gelation of aqueous cellulose−NaOH solutions. Biomacromolecules 4:259–264. https://doi.org/10.1021/bm020100s

Sixta H (2006) Hanbook of pulp. In: Sixta H (ed) Wiley-VCH Verlag GmbH&Co. KGaA, Weinheim, pp 1009–1067

Tariq MI, Afzal S, Hussain I, Sultana N (2007) Pesticides exposure in Pakistan: a review. Environ Int 33:1107–1122. https://doi.org/10.1016/j.envint.2007.07.012

The Fiber Year (2018) The Fiber Year 2018

Valta K, Sivonen E, Malm T (2011) Method for preparing a cellulose carbamate solutions. US 8,066,903B2

Vehviläinen M, Kamppuri T, Rom M et al (2008) Effect of wet spinning parameters on the properties of novel cellulosic fibres. Cellulose 15:671–680. https://doi.org/10.1007/s10570-008-9219-3

Vehviläinen M, Kamppuri T, Grönqvist S, Rissanen M, Maloney T, Honkanen M, Nousiainen P (2015) Dissolution of enzyme-treated cellulose using freezing-thawing method and the properties of fibres regenerated from the solution. Cellulose 22:1653–1674

Yang Q, Qi H, Lue A, Hu K, Cheng G, Zhang L (2011) Role of sodium zincate on cellulose dissolution in NaOH/urea aqueous solution at low temperature. Carbohydr Polym 83:1185–1191