Distinguishing liquid ammonia from sodium hydroxide mercerization in cotton textiles

Avinash P. Manian · Doris E. Braun · Barbora Široká · Thomas Bechtold

Received: 16 October 2021 / Accepted: 10 March 2022 / Published online: 25 March 2022

© The Author(s) 2022

Abstract The question addressed in this paper is whether cotton textiles mercerized with liquid ammonia (L-NH₃) can be distinguished from NaOH mercerized cotton textiles with FTIR-ATR spectroscopy. In collaboration with a process-house, cotton textiles were treated with L-NH₃, NaOH, neither or both. The treatment conditions were set to mimic commercial-scale operations. The samples were then analyzed with FTIR-ATR spectroscopy, and for comparison, also with powder X-ray diffraction. The analyses were aimed at detecting changes in the cellulose crystal lattice structure that result from the two mercerization processes. The measured spectra and diffractograms were evaluated both visually and with Principal Component Analysis (PCA), and the results show that with FTIR-ATR spectroscopy it was possible to differentiate between the untreated, L-NH₃ mercerized and NaOH mercerized textiles, whereas with X-ray diffraction it was difficult to detect differences between the untreated and treated samples. The better performance of FTIR-ATR spectroscopy is attributed to the method being more sensitive to changes on sample surfaces, whereas X-ray diffraction results are more representative of the sample bulk. The samples were treated under conditions mimicking commercial-scale operations, which are optimized to maximize treatment speed. Hence, the mercerization induced changes are likely to be limited to sample surfaces. The samples were treated under conditions mimicking commercial-scale operations, which are optimized to maximize treatment speed. Hence, the mercerization induced changes are likely to be limited to sample surfaces.

Keywords Cellulose III · Cotton textile · Liquid ammonia treatments · FTIR-ATR spectroscopy · FTIR transmission spectroscopy · X-ray diffraction · Principal Component Analysis
Introduction

After weaving, cotton textiles undergo a series of treatment processes to improve their aesthetic qualities. Some key elements that define textile aesthetics are surface texture, drape, resilience and color (Brand 1964; Kar et al. 2006; Kanai et al. 2011); and swelling treatments are an integral part of the processing operations undertaken to improve them. The swelling agents generally employed are aqueous solutions of NaOH and liquefied anhydrous ammonia (L-NH$_3$), with the former representing the majority case.

The NaOH treatments are of two types, ‘causticization’ and ‘mercerization’ (Tomasino 1992; Wagaw and Chavan 2013). The former is performed primarily with a view to improving the dye uptake, and is conducted with NaOH concentrations in the range of ca. 10–16% w/w with no tension applied across the fill (or weft) direction. In mercerization, the NaOH concentration ranges between ca. 20–30% w/w, fabrics are held to length along the fill direction, and the treatment is performed to improve luster and mechanical properties along with the dye uptake.

In L-NH$_3$ treatments, NH$_3$ gas is liquefied at atmospheric pressure by cooling down to ca. -33 °C (i.e. below the boiling point), and fabrics are transported through the fluid with no tension applied across the fill direction (Hazard 1994). One of two modes is employed to remove the NH$_3$ from fabrics as they emerge from the treatment bath (Greenwood 1987; Bredereck and Commarmot 1998; Commarmot and Bredereck 1998),

- **Evaporation**: over 90% of the NH$_3$ is vaporized by passing fabrics over drying cylinders heated to 130–145 °C, and the remainder is removed by washing in demineralized water at about 80 °C.
- **Washing**: the fabrics are directly washed in demineralized water at about 80 °C to remove the NH$_3$.

The two removal modes yield different results. The evaporation mode improves surface texture, resilience, and softness, whereas the washing mode improves gloss, dyeability, and evenness of dyeing (Jung et al. 1975; Ladisch and Cheek 1984; Bertoniere et al. 1986; Bredereck and Commarmot 1998; Lee et al. 2015). The term **mercerization**, coined for NaOH treatments as described above, has come to be used for L-NH$_3$ treatments as well since they yield similar effects.

NaOH treatments are found more effective for improving dyeability, and L-NH$_3$ treatments more effective in improving fabric texture and mechanical properties (Rowland et al. 1984; Bertoniere et al. 1986; Wakida et al. 1995, 2000; Commarmot and Bredereck 1998). Thus, NaOH + L-NH$_3$ (i.e. NaOH followed by L-NH$_3$) treatments are also awarded to cotton textiles.

There are occasions when it becomes of interest to obtain unequivocal confirmation if a cotton textile claimed to be L-NH$_3$ treated is indeed so, for example in public tendering contracts. As described above, both NaOH and L-NH$_3$ treatments exert similar influence but to differing degrees and it is difficult to delineate a boundary between them. The two treatments also change porosity (pore sizes and their distribution), degree of crystallinity, and sorption properties (Bredereck and Saafan 1982; Rowland et al. 1984; Bertoniere et al. 1986; Bredereck and Commarmot 1998); but again, it is difficult to arrive at categorical distinctions between the changes observed with one vs. the other treatment.

A potential method of incontrovertibly distinguishing L-NH$_3$ treated from untreated and NaOH treated cotton, is through determinations of the crystal lattice structure. Celluloses are semi-crystalline polymers, and different lattice structures (i.e. allomorphs) have been identified in their crystalline domains – labeled I, II and III. In brief, native celluloses (such as cotton) exhibit the lattice structure type I, which on mercerization with NaOH transforms to type II. On ammonia mercerization, the I and II type lattice structures transform to types III$_I$ and III$_II$ respectively. The ‘causticization’ with NaOH causes no change in the crystal lattice structure of native celluloses. For more information on cellulose lattice structures and their characteristics, the reader is referred to the following sources in literature (O’Sullivan 1997; Pérez and Mazeau 2005; French 2014).

A variety of techniques have been employed to characterize lattice structures in cellulose crystalline domains, including Fourier Transform Infra-red (FTIR) spectroscopy, Raman spectroscopy, CP/
MAS $^{13}$C-NMR spectroscopy, X-ray diffraction (XRD), electron diffraction, and neutron diffraction (O’Sullivan 1997; Pérez and Mazeau 2005). Of these, FTIR spectroscopy is perhaps the most easily accessible, as the equipment is not very expensive, and the devices are easy to operate without need for extensive training.

Thus, in cooperation with a process-house specializing in commercial L-NH$_3$ treatments, Veramtex s.a.2 (Brussels, Belgium), we performed a series of standard treatments on woven cotton fabrics:

• NaOH treatments (causticization, mercerization),
• L-NH$_3$ treatments (both modes of ammonia removal), and
• Combinations, i.e. NaOH treatments (causticization, mercerization) followed by L-NH$_3$ treatments (both modes of ammonia removal).

The treated substrates were analyzed for transformations in their crystal lattice structure with FTIR spectroscopy and X-ray diffraction. The analyses were performed directly on the treated fabric pieces (or on small discs punched out of them to fit in measurement devices), on fibers extracted from the pieces (from both the warp and fill directions), and on powders obtained from the fibers by cutting and ball milling. A summary of the analyses is presented in Table 1.

The FTIR spectra and X-ray diffractograms were visually analyzed for assessments of differences, as well as with Principal Component Analysis (PCA) to determine effectiveness of the measurement methods in discriminating between the different treatment types. A sample of regenerated cellulose (a generic viscose) was included in each analytical method, as a reference for the Cellulose II allomorph. The methodologies and results are presented below.

### Table 1 Methods employed for analysis of crystal lattice transformations

| Substrate form | Analytical method(s) |
|----------------|----------------------|
| Fabric         | FTIR spectroscopy in Attenuated Total Reflection mode (FTIR-ATR) | X-ray Diffraction (XRD) |
| Fiber          | XRD                  |
| Powder         | FTIR-ATR             |
|                | FTIR spectroscopy in transmission mode (KBr pellet method) | XRD |

#### Experimental

**Materials**

The substrate was a scoured and bleached, 1×1 plain-woven cotton textile, of 127 g/m$^2$ basis weight, with 46 warp threads and 31 fill threads per cm. For the treatments with NaOH, technical grade NaOH (50% w/w) and CH$_3$COOH (80% w/w) were purchased from Deuring GmbH & Co KG (Hörbranz, Austria), and the wetting agent Lyogen MC was obtained from Clariant AG (Basel, Switzerland).

**NaOH treatments**

The treatments were performed with NaOH at concentrations of 16 Bé°, 28 Bé° and 36 Bé°, (equivalent to ca. 11% w/w, 22% w/w and 30% w/w respectively). About 10 L volumes of each concentration were required, and that was infeasible to formulate with analytical grade reagents and deionized water. Therefore, technical grade reagents and soft water were employed. The achieved concentrations were confirmed with a hydrometer, and finally, the alkali-stable wetting agent Lyogen MC was mixed in to a concentration of 0.5 g/l.

The fabric was cut into pieces of dimensions 43 cm × 34.5 cm along warp and fill directions respectively for the treatments. In mercerization treatments (i.e. with 22% w/w and 30% w/w NaOH), the pieces were pinned taut along all four sides on a stainless steel stenter pin-frame, with the distance between pins of 40.5 cm × 25 cm along the warp and fill directions respectively. In the causticization treatment (i.e. with 11% w/w NaOH), the pieces were pinned taut only along the warp direction, with the distance between pins of 40.5 cm. The pieces so pinned were immersed for 1 min in 10 L of alkali liquor in a plastic trough at room temperature (ca. 25 °C), then rinsed under running hot water (at 60–70 °C) for 5 min. Next, the

2 [http://www.veramtex.com/index_en.html](http://www.veramtex.com/index_en.html)
pieces were taken off the frame and immersed for 45–60 min at room temperature in a 10 L neutralization bath containing 5 ml/L of the technical grade CH₃COOH (80% w/w). After that, they were awarded a final rinse for 2–3 min under running cold water, and line dried overnight. Five fabric pieces were treated per concentration of NaOH in this manner. An immersion time in alkali of only 1 min was chosen to mimic the usual residence time of fabrics in alkali during commercial-scale operations.

L-NH₃ treatments

Four fabric pieces per NaOH concentration from the treatments described above, together with untreated pieces, were sent to the process house Veramtex s.a. for L-NH₃ treatments. The treatments were performed as described in the Introduction section, on pilot-scale equipment, with a fabric residence time in L-NH₃ of about 12 s, chosen to mimic commercial-scale operations. Both the evaporation and washing modes of ammonia removal were used, labeled L-NH₃ A and L-NH₃ S respectively in this paper. The treatments performed in this work and the labels employed to designate them are listed in Table 2.

Sample preparation for analyses

The measurements on fabrics were performed directly on the pieces from treatments or on discs of 20 mm diameter punched out from the approximate center of pieces. To extract fibers, yarns from both the warp and fill directions were pulled out, untwisted by hand, and pulled through metal combs. For obtaining powders, the fibers were first cut into ca. 2 mm length with sharp scissors, then ground into ca. 2 mm in an agate container with yttria-stabilized zirconia balls (5 mm diameter, Inframat® Advanced Materials, USA) on a ball mill (Specamill, Graseby-Specac, England). The particles in the resulting powders had long dimensions on average of 0.31 ± 0.03 mm.

To prepare KBr pellets for FTIR transmission spectroscopy, the powdered substrates were dried at 110 °C for 3 h in a laboratory oven. IR Spectroscopy grade KBr (Carl Roth®, Austria) was ground in an agate mortar and pestle to a fine consistency and dried at 110 °C for 3 h in the oven. Then ca. 3 mg powder was mixed with ca. 300 mg KBr, ground in the ball mill for 3 min, and dried again at 110 °C for 1 h. The mixtures were then transferred into a pellet die of 13 mm diameter (Specac, England), and subjected to 10-ton load for 10 min, under evacuation, in a hydraulic press (Specac, England). The pellets so formed were immediately utilized for spectroscopy.

FTIR spectroscopy

The FTIR-ATR spectra on fabrics and powders were recorded independently on two devices to assess inter-machine variability:

- Invenio S spectrometer (Bruker Optik GmbH, Germany), equipped with a MIRacle™ Horizontal ATR accessory fitted with a diamond crystal double reflection universal plate from PIKE Technologies (USA). The absorbance spectra were recorded from an aggregate of 128 scans in the wavenumber range of 4000–500 cm⁻¹ at a resolution of 2 cm⁻¹.
- Vertex 70 spectrometer (Bruker Analytische Messtechnik GmbH, Germany), equipped with a GladiATR™ accessory fitted with a diamond crystal from PIKE Technologies (USA). The absorbance spectra were recorded from an aggregate of 64 scans in the wavenumber range of 4000–400 cm⁻¹ at a resolution of 2 cm⁻¹.

Table 2 The treatments performed in this work and the labels used to designate them

| Treatments | Labels |
|------------|--------|
| Untreated  | Unt    |
| L-NH₃ alone (both modes of ammonia removal) | L-NH₃ A (evaporation), L-NH₃ S (washing) |
| 11% (w/w) NaOH, alone and followed by L-NH₃ treatments | NaOH 11, NaOH 11 L-NH₃ A, NaOH 11 L-NH₃ S |
| 22% (w/w) NaOH, alone and followed by L-NH₃ treatments | NaOH 22, NaOH 22 L-NH₃ A, NaOH 22 L-NH₃ S |
| 30% (w/w) NaOH, alone and followed by L-NH₃ treatments | NaOH 30, NaOH 30 L-NH₃ A, NaOH 30 L-NH₃ S |
Invenio S spectrometer, where absorbance spectra were recorded from an aggregate of 128 scans in the wavenumber range of 4000–500 cm\(^{-1}\) at a resolution of 2 cm\(^{-1}\).

Background corrections were performed automatically by the onboard software from measurements in air (FTIR-ATR) and measurements on KBr pellets without sample (FTIR transmission). Multiple spectra were recorded per sample in each instance, and all spectra smoothed and min–max normalized with the onboard software (OPUS versions 8.2.28 and 7.8). The resulting data is available in Online Resource 1.

**X-ray diffraction**

The X-ray diffraction patterns (XRD) from fabric, fiber and powder samples were recorded in transmission mode (at 25 °C) on a powder diffractometer (X’Pert PRO, PANalytical Inc., The Netherlands). It was equipped with a \(\theta/\theta\) coupled goniometer in transmission geometry, programmable XYZ stage with well plate holder, and Cu-K\(_a\) radiation source with a focusing mirror. The incident beam side featured a 0.5° divergence slit, a 0.02° Soller slit collimator and a 1° anti-scattering slit; and the diffracted beam side featured a 2 mm anti-scattering slit, a 0.04° Soller slit collimator, a Ni-filter, and a solid state PIXcel detector. The patterns were recorded at a tube voltage of 40 kV, tube current of 40 mA, with a step-size of 0.013° 2\(\theta\) in the angular range of 2°–40° 2\(\theta\) at 400 s per step. Multiple diffractograms were recorded per sample. All samples were oscillated in one direction (1 mm) during measurements to increase the sampling area.

The sample holder was an aluminum block with depressed cavities, each with a hole punched out of the bottom. The samples for measurement were held in place across these holes with appropriate clamps. The fabric samples could be directly loaded whereas the fiber and powder samples were first sandwiched between two 6 µm Mylar® foils before loading. The sample loading is illustrated with representative photographs in Online Resource 2.

The original data from all measurements, including those of the backgrounds without sample (for fabric) and with mylar foils (for fiber and powder) are available in Online Resource 3. The file also lists the d-spacing values corresponding to the diffraction angles.

It was determined that background corrections were not required, as no significant difference was observed between diffractograms with background correction and without. The diffractograms were also not baseline corrected to avoid the risk of amorphous halos, but only min–max normalized. The results, between 2theta 5°–50° are available in Online Resource 4.

**Crystallite size estimation**

Crystallite sizes in the cellulose samples was estimated from the X-ray diffractograms with Scherrer’s Eq. (1) (Scherrer 1918; Langford and Wilson 1978):

\[
\tau = \frac{K\lambda}{(\beta\cos\theta)}
\]

where, \(\tau\) is thickness of the crystal perpendicular to the lattice plane represented by the peak; \(K\), a constant that depends on the crystal shape (0.89); \(\lambda\) wavelength of the incident beam in the diffraction experiment; \(\beta\), full width at half maximum (FWHM) in radians of the corrected and deconvoluted peaks corresponding to the (1–10), (110) and (200) lattice planes (Le Bail et al. 1988); and \(\theta\), the Bragg angle.

**Principal Component Analysis (PCA)**

The analysis was performed with Simca-P software (Version 11.0, Umetrics AB, Umeå, Sweden). The number of principal components (PCs) were selected by the PRESS function (predicted residual error sum-of-squares), and a leave-one-out cross-validation was performed on the models. The data preparation for PCA was as follows:

| XRD | The PCA results presented in the main section of the manuscript were performed over the 2theta range of 10°–30° after only min–max normalization of the measured diffractograms, i.e. no background correction (see Online Resource 4 for the PCA input data) |
| FTIR (ATR and transmission) | The PCA was performed after calculating quadratic five-point first derivatives of the min–max normalized spectra (see PCA input data in Online Resource 5) |
Results and discussion

X-ray diffraction – Visual analysis of results

Model diffractograms of the different cellulose allomorphs, plotted with data from French (2014), are available in Supplementary Fig. 1, and their characteristic diffraction peaks, also highlighted in the figure, are listed in Table 3. The diffractograms measured on fabric, fiber and powder specimens from untreated samples are available in Supplementary Fig. 2, and all show characteristic peaks of the Cellulose Iβ allomorph, but with slight shifts in peak positions – at 2theta ca. 14.7°–14.9°, 16.3°–16.4°, 20.4°–20.5° and 22.7°–22.9° as compared to the model values in Table 3. Such differences may arise from factors in experimental substrates such as ordered aggregations of polymer chains in non-crystalline domains, variations in crystallite sizes, and presence of moisture (Nishiyama et al. 2012).

It is hard to detect any evidence of the Cellulose II allomorph in diffractograms of the NaOH 22 and NaOH 30 samples from measurements on fabric, fiber or powder specimens (see Supplementary Fig. 3). There is no peak at 2theta ca. 12.2°, and the two peaks in the 2theta region 20°–23° look very similar to patterns from the NaOH 11 and untreated samples. In contrast, the pattern from the viscose reference shows a clear peak at 2theta ca. 12.2°, and the two peaks in the 20°–23° 2theta region are very similar to the model Cellulose II pattern. Thus, it appears the immersion of fabric pieces in NaOH liquors for only 1 min, in imitation of commercial-scale treatments, was insufficient to cause significant changes to the crystal lattice. That it is often difficult to detect the presence of Cellulose II allomorphs with X-ray diffraction, in materials that are NaOH-mercerized in commercial-scale operations, is also reported by other authors (Bredereck 1981; Kafle et al. 2014; Saafan and Habib 1989).

Representative X-ray diffractograms from measurements on fabric specimens of samples treated with L-NH₃ and NaOH + L-NH₃ combinations are shown in Fig. 1. The presence of peaks at 2theta ca. 14.9° and 16.6° in all patterns indicates that all treated samples retained a significant proportion of the original Cellulose Iβ allomorph. The L-NH₃ A samples (see part a) show, additionally, low intensity reflections at 2theta ca. 11.7° and 17.2°, which suggests presence of a measurable proportion of the Cellulose III_I allomorph. The NaOH 11 samples (see part b) show the signs of decrystallization described above. The NaOH + L-NH₃ A combinations also show signs of decrystallization. A slight deviation from the baseline at 2theta ca. 11.7° may indicate minor amounts of the Cellulose III allomorph being present, but if true, the proportions will be far lower than in the L-NH3 A treated samples. It is interesting to note that samples from the combination NaOH + L-NH₃ treatments show stronger signs of decrystallization than the NaOH treatments alone. The estimated crystallite sizes (see Online Resource 8) are consonant with the indications of decrystallization observed in diffractograms. In comparison to the untreated, the average crystallite sizes are smaller in the samples treated with L-NH₃, NaOH 22 and NaOH 30, and the average

3 All supplementary figures are available in Online Resource 7.
crystallite sizes after NaOH + L-NH₃ are smaller than after NaOH alone.

Diffractograms measured on the fiber and powder specimens are shown in Supplementary Figs. 4 and 5, and the observations described above for the fabric specimens and model diffractograms of the Cellulose Iβ, II, IIII and IIIII allomorphs (calculated with 1.5° peak widths and for random orientation of crystallites) are included for comparison.

**Table 3** Positions of characteristic diffraction peaks (scattering angle, 2θ (°)) in model diffractograms of cellulose allomorphs, and Miller indices (in parentheses) of the contributing reflecting planes (French 2014)

| Cellulose Iβ | Cellulose II | Cellulose IIII | Cellulose IIIII |
|--------------|--------------|----------------|----------------|
| 14.9° / (1–10) | 12.2° / (1–10) | 11.7° / (010) | 12.1° / (010) |
| 16.6° / (110) | 20.0° / (110) | 17.2° / (002) | 20.9° / (1–10), (100) |
| 20.6° / (012), (102) | 22.0° / (020) | 20.8° / (100), (012), (1–10) | |
| 23.0° / (200) | | | |
results also apply to the results from the fiber and powder measurements. The estimated crystallite sizes also exhibit the same trends.

**X-ray diffraction – visual analysis summary**

In summary, X-ray diffraction of the samples reveals evidence only of the Cellulose III’allomorph apart from the original Cellulose I, and of a reduced crystallinity in the samples. No clear evidence of other cellulose allomorphs is available. However, a complete absence of Cellulose II cannot be surmised since minor proportions of the allomorph (e.g. <5%) are difficult to detect against a background of Cellulose I with X-ray diffraction (Chidambareswaran et al. 1976; Ghosh and Dilanni 1994; Kolpak et al. 1978; Niaz and Tahir 1989).

**FTIR spectroscopy**

The detection of crystal lattice types and their transformations with FTIR spectroscopy is based on changes in the –OH stretch region of 3600–3200 cm\(^{-1}\) and the fingerprint region of 1500–850 cm\(^{-1}\), at the following approximate positions:

| Wavenumber (cm\(^{-1}\)) | Interpretation |
|--------------------------|----------------|
| 3300–3340 cm\(^{-1}\)    | Cellulose I exhibits a sharp peak here, not seen for other allomorphs, attributed to stretching vibrations of the hydrogen bonded 2OH•••6OH•••3OH•••5O groups (Kafle et al. 2014; Kim et al. 2013; Makarem et al. 2019; Široký et al. 2010) |
| 3270 cm\(^{-1}\)         | Cellulose I exhibits a weak peak here, not seen for other allomorphs, attributed to stretching vibrations of the intramolecular hydrogen bonded 2O[i•••5O][i•••3O groups (Kafle et al. 2014; Kim et al. 2013; Makarem et al. 2019) |
| 1429 cm\(^{-1}\)         | The peak is attributed to symmetric bending of CH\(_2\) groups (scissoring), and appears as a strong signal in Cellulose I. In Cellulose II, there is a shift of the peak to 1420 cm\(^{-1}\) accompanied by a drastic reduction in intensity. In Cellulose III, there is a shift of the peak to 1425 cm\(^{-1}\) accompanied by a moderate reduction in intensity (Nelson and O’Connor 1964; Široký et al. 2010) |
| 1163 cm\(^{-1}\)         | The peak is attributed to the antisymmetric stretching mode of the C–O–C group, C–O stretching, or O–H bending. The intensities are similar for Cellulose I, II and III, but a transformation from Cellulose I to II is accompanied by a shift of the peak to lower wavenumbers, while there is no shift with a transformation to Cellulose III (Nelson and O’Connor 1964; Široký et al. 2010) |
The peak is attributed to ring asymmetric valence vibration and is also thought analogous to a similar signal in primary and secondary alcohols attributed to the influence of hydrogen bonding on stretching vibration of the C–O bond. The peak intensity at this position is strong for Cellulose I, and there is a shift of the peak position to lower wavenumbers in Cellulose III. In Cellulose II, the peak at this position is transformed into a shoulder, due to the appearance of a strong, broader peak in the region of 1090 cm$^{-1}$ (Nelson and O’Connor 1964; Široký et al. 2010). 

893 cm$^{-1}$ The peak is attributed to valence vibration of the C–O–C group or vibrational modes of groups at the 1C position. It appears as a weak, broad peak in Cellulose I, but changes to a sharp and strong peak on transformation to Cellulose II. In Cellulose III, the peak exhibits an intermediate intensity (Colom and Carrillo 2002; Nelson and O’Connor 1964).

As is evident from the description above, it is difficult to differentiate between Cellulose III$_I$ and Cellulose III$_II$ allomorphs with FTIR spectroscopy and hence in the discussions to follow, reference will only be made to the Cellulose III allomorph. The key differences in FTIR spectra between the allomorphs are summarized in Table 4.

FTIR-ATR spectroscopy – Visual analysis of results

No significant differences were observed at the key wavenumber regions between results from the two devices used in FTIR-ATR spectroscopy (Invenio S and Vertex 70), and no differences between multiple measurements on the same sample. Hence, only a representative spectrum per treatment is plotted in figures.

Spectra measured on fabric and powder specimens from samples treated with NaOH alone, from an untreated sample, and from a sample of generic viscose, are shown in Supplementary Fig. 6. The key wavenumber regions are highlighted in the plots. The untreated sample shows typical characteristics of cellulose I, but not always at the exact positions reported in literature. The viscose sample shows typical characteristics of Cellulose II, except that only inflections are observed at 3484 cm$^{-1}$ and 3450 cm$^{-1}$, rather than any peaks. The spectra from the untreated sample and the viscose do not differ between measurements on the fabric and powder specimens.

The NaOH 11 spectra, from both fabric and powder measurements, do not differ from that of the untreated, which is to be expected, as the treatment does not result in crystal lattice transformations. The fabric spectra of NaOH 22 and NaOH 30 resemble that of the viscose in certain elements: inflections at 3484 cm$^{-1}$ and 3450 cm$^{-1}$, shoulder at 1107 cm$^{-1}$, and increase in peak acuity at 895 cm$^{-1}$. But unlike the viscose spectrum, the spectra from NaOH 22 and NaOH 30 fabrics show peaks at 3340 cm$^{-1}$ and 3270 cm$^{-1}$ only marginal changes at 1429 cm$^{-1}$, and no peak shift at 1160 cm$^{-1}$ — which are all signs of the original Cellulose I. The evidence for Cellulose II in NaOH 22 and NaOH 30 is weaker in results from the powder measurements, with only mild inflections being observed at 3484 cm$^{-1}$ and 3450 cm$^{-1}$. All other aspects are indicative of a Cellulose I allomorph. It points to an incomplete conversion of the crystal lattice structure, with stronger evidence for Cellulose II being observed in FTIR-ATR measurements on fabric, which is more representative of the sample surface, and the evidence becoming weaker when the same measurements are repeated on powders, where more of the bulk is exposed to measurements.

Representative spectra from measurements on fabric specimens of samples treated with L-NH$_3$ and NaOH+L-NH$_3$ are shown in Fig. 2. The results from L-NH$_3$ A and L-NH$_3$ S treated samples (part a) show some characteristics of a Cellulose III allomorph, namely a shift of the 1170 cm$^{-1}$ peak that is greater for L-NH$_3$ A than L-NH$_3$ S, and a rise in peak intensity at 895 cm$^{-1}$ that is more evident for L-NH$_3$ A than L-NH$_3$ S. Further, there is the appearance of an inflection rather than a strong peak at 3484 cm$^{-1}$, but only for L-NH$_3$ A and not L-NH$_3$ S. The peaks at 3340 cm$^{-1}$ and 3270 cm$^{-1}$, indicative of Cellulose I, persist in the spectra and the expected change to the
peak at 1429 cm\(^{-1}\), is not observed. The spectrum from NaOH 11 should not differ from the untreated and that is observed (see part b), while the spectra from NaOH 11 L-NH\(_3\) A and NaOH 11 L-NH\(_3\) S samples, expected to show all features of a Cellulose III allomorph, show only the peak shift at 1107 cm\(^{-1}\) and a rise in peak intensity at 893 cm\(^{-1}\). It may be noted that at 1107 cm\(^{-1}\), the spectrum appears more like a “step” than a peak.

The spectra from NaOH 22 and NaOH 30 (see parts c and d), as discussed above, show indications of both Cellulose I and Cellulose II. The spectra after combination treatments of NaOH 22 and NaOH 30 with L-NH\(_3\) show a strong shoulder at 1107 cm\(^{-1}\) that is evidence of Cellulose II, but the other typical characteristics, viz. peaks at 3484 cm\(^{-1}\) and 3450 cm\(^{-1}\) or peak shifts at 1429 cm\(^{-1}\) and 1160 cm\(^{-1}\), are not evident. The strong shoulder at 1107 cm\(^{-1}\) makes it difficult to confirm a peak shift, and as no other signs of Cellulose III are observed, it is difficult to confirm presence of the allomorph. Interestingly, the Cellulose I peaks at 3340 cm\(^{-1}\) and 3270 cm\(^{-1}\), which persist after either NaOH or L-NH\(_3\) alone, are found to reduce in distinction or disappear after the combination NaOH + L-NH\(_3\) treatments.

In the spectra from powders available in Supplementary Fig. 7, the L-NH\(_3\) A and L-NH\(_3\) S samples show features similar to those from fabric
measurements. There is a peak shift at 1107 cm\(^{-1}\) that is greater for the L-NH\(_3\) A, a mild inflection at 3484 cm\(^{-1}\) that is observed only for L-NH\(_3\) A, and a rise in peak acuity that is more evident for the L-NH\(_3\) A. The persistence of the Cellulose I peaks at 3340 cm\(^{-1}\) and 3270 cm\(^{-1}\) is also observed, and so is the lack of change at 1429 cm\(^{-1}\). The spectra of NaOH 11 + L-NH\(_3\) from powder measurements is also similar to results from the fabric measurements, with limited signs of the Cellulose III allomorph being observed, viz. the peak shift at 1107 cm\(^{-1}\) and rise in peak intensity at 895 cm\(^{-1}\). The difference in the spectra of NaOH 22 and NaOH 30 between the measurements on fabric and powder specimens has been described above. There are differences also between the fabric and powder results of samples treated with the combination of NaOH 22 and NaOH 30 followed by L-NH\(_3\). The strong shoulder at 1107 cm\(^{-1}\), indicative of the Cellulose II allomorph, seen in the fabric results is absent from the powder results. And the Cellulose I peaks at 3340 cm\(^{-1}\) and 3270 cm\(^{-1}\), which were diminished or absent from the fabric results, are evident in the powder results. In addition, perhaps due to the absence of a strong shoulder, a shift of the peak at 1107 cm\(^{-1}\) indicative of the Cellulose III allomorph, is observable.

**FTIR transmission spectroscopy**

The transmittance spectra from the untreated and NaOH treated samples, together with a sample of generic viscose, is shown in Supplementary Fig. 8. It may be noted that there are small differences in the wavenumbers of key peaks between the FTIR-ATR and FTIR transmittance spectra. Peak shifts between results from ATR and transmittance measurements are commonly observed, and attributed to the effects of sample thickness and refractive index in ATR measurements (Harrick and du Pré 1966; Nunn and Nishikida 2008).

It is difficult to detect differences between the generic viscose (Cellulose II) and untreated sample (Cellulose I) in the region of 3600–3200 cm\(^{-1}\), but the viscose spectrum exhibits all characteristic features of a Cellulose II in the 1500–850 cm\(^{-1}\) region. However, the spectra from all NaOH treated samples resemble that of the untreated, with no signs to indicate presence of a Cellulose II allomorph. The same is true for the spectra of samples treated with L-NH\(_3\) alone, or with the combination NaOH followed by L-NH\(_3\) (see Supplementary Fig. 9). They all resemble the spectrum of a Cellulose I, with no indications for the presence of the Cellulose II or Cellulose III allomorphs.

**FTIR spectroscopy – visual analysis summary**

In summary, the FTIR-ATR spectra measured on fabric specimens consistently yielded signals of the Cellulose II allomorph in the NaOH 22 and NaOH 30 samples, and of the Cellulose III allomorph in the L-NH\(_3\) A and L-NH\(_3\) samples, although signals of the Cellulose I allomorph persisted in all spectra. The spectra from NaOH 11 samples, as expected, did not differ from the untreated, but signals of Cellulose III are observed in the spectra of NaOH 11 + L-NH\(_3\). The samples from the combination treatment of NaOH 22 and NaOH 30 followed by L-NH\(_3\), all showed evidence only of Cellulose II, but the signals for Cellulose I either were diminished or absent.

The FTIR-ATR spectra measured on powder specimens yielded signals only for the presence of Cellulose III. The diminishing of Cellulose I signals observed in the fabric spectra did not occur in the powder results, and evidence of the allomorph persisted in the results from all samples. No signals of Cellulose II could be detected in the spectra, and perhaps as a result, evidence of Cellulose III was detected in the spectra from the samples treated with NaOH 22 and NaOH 30 followed by L-NH\(_3\). The FTIR transmittance spectra yielded no signs apart from that of Cellulose I.

**Principal Component Analysis (PCA)**

A good description of the principle and advantages of PCA is provided by (Beattie and Esmonde-White 2021). In brief, it is a multivariate statistical analysis technique, which allows for the capture of all differences in measured data between test substrates into a few “principal components (PCs)”. Each PC is a unique combination of observed differences, with the first, PC1, capturing the maximum fraction of the total difference between substrates, and subsequent components (PC2, PC3 …) capturing progressively lower fractions. Scatter plots of PC scores (commonly of the first two PCs, since they capture the most differences) can lead to identification of groups
or clusters among test substrates, where those that cluster together exhibit similar results. We performed PCA on the measured x-ray diffractograms and FTIR spectra to determine if the differences identified in the visual analyses are reflected in the clustering of treatment groups in PC-score scatter plots.

**PCA of X-ray diffractograms**

We began with a combined analysis of all measured diffractograms (i.e. all results from fabric, fiber and powder specimens) together with that of the generic viscose (as Cellulose II reference). A score-score scatter plot of the first two PCs from that is shown in Supplementary Fig. 10. It is seen that the diffractograms cluster around specimen type, i.e. there are larger differences between the fabric, fiber and powder results than between the treatments. In addition, the viscose result is positioned distinctly separate from the treated sample results. The plot is consistent with observations in the visual analysis that no evidence of Cellulose II could be detected in the diffractograms from any sample, and that it was difficult to detect differences between most treatment types.

The score-score plot of the first two PCs from analysis of only the fabric diffractograms is shown in Fig. 3. A level of clustering around treatment types is observed, e.g. the NaOH + L-NH₃ cluster separately from the corresponding NaOH alone results. That is supported to a degree with respect to L-NH₃ A by suggestions of a peak presence at 2theta ca. 11.7° in diffractograms. However, with respect to L-NH₃ S, no evidence suggestive of the treatment could be detected in the sample diffractograms except perhaps of decrystallization. The results from different NaOH concentrations are separated from each other as well as from the untreated, but again there are no indications in their diffractograms that could be used as a basis for that differentiation. Thus, it appears there are patterns of differences between diffractograms from different treatment types, but in most cases, they are too subtle to be detected in a visual analysis.

Score-score plots from PCA of the fiber and powder results are shown in Supplementary Fig. 11. As compared to the fabric plot, a far greater level of scattering between diffractograms from the same treatment type is observed in the fiber plot; and in the powder plot, there is greater degree of clustering among all diffractograms i.e. the separation between treatment types is far lower. Thus, it appears the greatest degree of treatment type differentiation is available from fabric diffractograms, but as mentioned above, the differences between treatment types (apart from that of L-NH₃ A) appear too subtle to be evident in a visual analysis.

On recommendation of a reviewer, the following treatments of the XRD data were separately attempted prior to the PCA: (a) truncation to the 2theta range of 10°–25°, (b) correction for measured background, (c) Multiplicative Scatter Correction (MSC) (Geladi et al. 1985). The score-score plots from the different attempts are available in Online Resource 9, where it may be observed that the results do not differ from the plots presented in the main section of the manuscript.

**PCA of FTIR-ATR spectra measured on fabrics**

The following analyses were performed: a combined analysis of the spectral range 3675–2600 cm⁻¹ and 1500–400 cm⁻¹; of only the spectral range 3675–2600 cm⁻¹ and of only the spectral range 1500–400 cm⁻¹. The latter two were performed to assess if spectral differences were more distinct in the –OH stretch region or fingerprint region. The score-score plots of the first two PCs from these analyses are shown in Fig. 4, and the clustering patterns observed are schematically illustrated in Table 5.
In general, the spectra from untreated, NaOH 11 and L-NH₃ S alone samples clustered separately from the spectra of all other treated samples. The L-NH₃ S spectra clustered separately from the untreated and NaOH 11, which is in line with spectral differences being observed at the key wavenumbers of interest in the L-NH₃ S spectra. The spectra of untreated and NaOH 11 samples either clustered together or were in close proximity, in agreement with the observation that no differences could be detected between them in the visual analysis.

In contrast, the L-NH₃ A spectra, which always clustered separately from the L-NH₃ S, are found to cluster together with spectra from NaOH 11 L-NH₃ S, NaOH 22, NaOH 30, NaOH 30 L-NH₃ A, NaOH 30 L-NH₃ S, or to be located separately from other treatment types in the different plots. Although the spectra from both L-NH₃ A and L-NH₃ S evince signs of Cellulose III, it is true there are differences between them, namely the appearance of an inflection in the –OH region only for the former and a lower intensity of changes in the fingerprint region for the latter. It is also possible to understand the clustering together of the L-NH₃ A with NaOH 11 + L-NH₃, as the latter exhibited signs of Cellulose III. However, it is difficult to account for the clustering together of L-NH₃ A with spectra from the NaOH 22 and NaOH 30 and NaOH 30 + L-NH₃ samples as differences between them could be detected at the key wavenumbers in both the –OH stretch and fingerprint regions.

The spectra from NaOH 11 are always positioned separately from those of NaOH 22 and NaOH 30, and that is supported by the differences observed in their spectra. The NaOH 22 and NaOH 30 appear in the same cluster in most plots, which is also supported by the lack of discernible differences in their spectra. The one exception is part (b) in Fig. 4, but in general, the cluster predictability overall was lower in analysis of the –OH stretch and fingerprint regions combined, and of each region individually:

- The spectra of untreated samples differ distinctly from those of the treated samples, and this is observed both in the PCA and visual analysis. The exception is that of the NaOH 11 treatment, where the PCA suggests differences may exist, but none is evident at key wavenumbers in the visual analysis, and none is expected.
- Differences between the spectra from L-NH₃ A, L-NH₃ S, NaOH 11 L-NH₃ A and NaOH 11 L-NH₃ S are frequently suggested in the PCA, but the visual analysis shows that apart from differences of magnitude (i.e. spectral changes of greater intensity are observed after L-NH₃ A as compared to L-NH₃ S), there are no qualitative differences between the spectra. In other words, all spectra show the same changes at the key wavenumbers of interest, but the magnitude of observed changes may differ between L-NH₃ A and L-NH₃ S.
- The spectra from NaOH 22 and NaOH 30 are similar to each other, but different from that of the untreated, NaOH 11, L-NH₃ A and L-NH₃ S – and this is suggested in the PCA results as well as observed in the visual analyses.
- The spectra from combination treatments of NaOH 22 and NaOH 30 with L-NH₃ A and L-NH₃ S are very similar to those from NaOH 22 and NaOH 30 alone. It is observed in the
Signals for changes of crystal lattice structure were most consistently observed in the region of 1107 cm\(^{-1}\), and hence a PCA was conducted of fabric FTIR-ATR spectra limited to that wavenumber region, the score-score plots from which are shown in Fig. 5. The clustering patterns from analyses of the data from both spectrometers are very similar, and also fit the consensus points derived from analyses of the \(-\text{OH} \) stretch and fingerprint regions.

PCA of FTIR-ATR spectra measured on powders

The score-score plots from PCA of the FTIR-ATR spectra measured on powder specimens are shown in Supplementary Fig. 12. Only results from the fingerprint region are shown, as most differences between treatment types were observed there in the visual analysis. The \(-\text{OH} \) region served only to confirm presence of the original Cellulose I allomorph. Again, the clustering patterns in results from the two spectrometers are similar to each other. The untreated and NaOH 11 spectra cluster separately from the rest of the treatment types, but among the rest, there is a large degree of scatter among spectra from the same treatment type. A broad clustering of spectra from all L-NH\(_3\) treated samples is observed, regardless of individual or combination treatments, and the spectra of samples treated with NaOH 22 and NaOH 30 alone appear indiscriminately distributed through the plots. That supports the visual analysis observation that although presence of the Cellulose III allomorph could be detected, there was no evidence of Cellulose II.

PCA of FTIR transmission spectra

The score-score plots from individual analysis of the \(-\text{OH} \) stretch and fingerprint regions from transmission spectra are shown in Supplementary Fig. 13. No evidence of allomorph changes could be detected in visual analysis of the spectra, and that is supported by the lack of distinct separation between untreated and treated samples in the score-score plots. The spectra from untreated samples closely cluster with NaOH 22 and NaOH 30 in the plot from the \(-\text{OH} \) stretch region, and is located amidst all spectra from treated samples in the plot from the fingerprint region.

In Online Resource 6, it is interesting to note that the R\(^2\)X (cum) of the first two principal components, which represent the total fraction of data variability captured, are very high in analyses of the PXRD (between 85\%–94\%); whereas those from analysis of the \(-\text{OH} \) stretch and fingerprint regions with fabric FTIR-ATR spectroscopy are relatively lower (between 36\%–66\%). However, the level of discrimination between the treatment groups is greater with fabric FTIR-ATR spectroscopy. The best combination of explained variance (R\(^2\)X (cum) of 82\%–85\%) and discrimination between treatment groups is observed in analysis of the 1138–1042 cm\(^{-1}\) region from fabric FTIR-ATR spectroscopy, suggesting this region is critical in the identification of treatment type. Similar to PXRD, the analysis of FTIR transmission spectra also yield high R\(^2\)X (cum) (of about 78\%) but poor discrimination between treatment groups.

Summary and conclusions

All X-ray diffractograms showed presence of the Cellulose I allomorph, and there was no clear evidence of any other allomorph being present, apart from that of Cellulose III in L-NH\(_3\) A treated samples. The only other information that could be derived is that the treated samples show evidence of decrystalization. The FTIR-ATR spectra of fabrics signaled the presence of Cellulose II and Cellulose III allomorphs as appropriate, but there persisted traces of Cellulose I in most cases. The FTIR-ATR spectra measured on powders yielded signs of only the Cellulose I allomorph, apart from Cellulose III being observed for samples treated with L-NH\(_3\) A. All FTIR
transmittance spectra, without exception, showed only signs of Cellulose I.

A major difference between the measurements techniques is that FTIR-ATR spectroscopy is a surface limited technique, with the depth of IR beam penetration into substrates limited typically to between 0.5–5 µm (Anon 2018), whereas X-ray diffraction and FTIR transmission spectroscopy are more representative of the sample bulk. The grinding of fabrics into powders exposes more of the bulk and thus the FTIR-ATR results from powders will be more representative of the bulk than the results from fabrics.

The results lend support to the notion that the short treatment durations applied in this work, to mimic commercial-scale treatments, are insufficient to allow for a thorough diffusion of the NaOH through substrates at mercerization concentrations. There appears to have been a comparatively greater depth of penetration of the L-NH$_3$ in treatments, and that may be attributed to the greater fluidity and

Table 4 Summary of key differences between cellulose allomorphs in their FTIR spectra from the descriptions above

| Wavenumber region (cm$^{-1}$) | Cellulose allomorph | Cellulose II | Cellulose III |
|-------------------------------|---------------------|--------------|---------------|
| 3484–3488                     | No peak             | Weak peak    | Strong peak   |
| 3410–3450                     | No peak             | Weak peak    | No peak       |
| 3300–3340                     | Strong peak         | No peak      | No peak       |
| 3270                          | Weak peak           | No peak      | No peak       |
| 1429                          | Strong peak         | Peak shifts to lower wavenumber with drastic reduction in intensity | Peak shifts to lower wavenumber with moderate reduction in intensity |
| 1163                          | Strong peak         | Peak shifts to lower wavenumber | No change |
| 1111                          | Strong peak         | Peak transforms into shoulder | Peak shifts to lower wavenumber |
| 893                           | Weak peak           | Strong, sharp peak | Peak of intermediate intensity |

All changes described are with reference to the spectrum of Cellulose I.
lower surface tension of L-NH₃ as compared to concentrated NaOH solutions (Hazard 1994).

The clearest evidence of treatment type is obtained from FTIR-ATR spectroscopy of fabrics. Distinctions can be made between the untreated sample, those treated only with L-NH₃ (both evaporation and washing modes of ammonia removal), and those treated only with NaOH at concentrations of 22% w/w and higher. The treatment with 11% w/w NaOH leaves no trace in the spectra, as the concentration is not sufficient to cause a change in the crystal lattice structure. Evidence of L-NH₃ treatment can be detected in the spectra of samples treated with 11% NaOH followed by the L-NH₃, but not in samples treated with 22% w/w and 30% w/w of NaOH followed by L-NH₃, as the spectra from combined treatments cannot be distinguished from the NaOH alone.

Table 5  Schematic illustration of clustering patterns observed in the score-score plots of Fig. 4. Treatment groups listed in the same box cluster together, and those listed in separate boxes cluster apart from each other

| Results from Invenio S spectrometer | Results from Vertex 70 spectrometer |
|-------------------------------------|-------------------------------------|
| **3675–2600 cm⁻¹ and 1500–400 cm⁻¹ combined** |
| Unt      | NaOH 11 | L-NH₃ S | Unt      | NaOH 11 | L-NH₃ S |
| L-NH₃ A  | NaOH 11 L-NH₃ S | NaOH 22 | NaOH 30 |
| NaOH 22  | NaOH 30 |
| NaOH 11 L-LNH₃ A | NaOH 22 L-NH₃ A | NaOH 30 L-NH₃ S |
| NaOH 22 L-NH₃ S | NaOH 30 L-NH₃ S |
| **3675–2600 cm⁻¹ alone** |
| Unt      | NaOH 11 | L-NH₃ S | Unt      | NaOH 11 | L-NH₃ S |
| L-NH₃ A  | NaOH 30 | NaOH 30 L-NH₃ A |
| NaOH 22  | NaOH 22 L-NH₃ A | NaOH 30 L-NH₃ S |
| NaOH 30 L-NH₃ A | NaOH 30 L-NH₃ S |
| **1500–400 cm⁻¹ alone** |
| Unt      | NaOH 11 | L-NH₃ S | Unt      | NaOH 11 | L-NH₃ S |
| L-NH₃ A  | NaOH 22 | NaOH 30 |
| NaOH 11 L-NH₃ S | NaOH 11 L-NH₃ S |
| NaOH 22 L-NH₃ A | NaOH 22 L-NH₃ A |
| NaOH 30 L-NH₃ S | NaOH 30 L-NH₃ S |
Signals of crystal lattice transformations are observable both in the –OH stretch region and fingerprint region of spectra, but the signals are weaker in the –OH stretch region, possibly due to interference from moisture/water (Makarem et al. 2019). In the fingerprint region, the changes at ca. 1107 cm\(^{-1}\) proved a most consistent indicator of treatment type.

In conclusion, FTIR-ATR spectroscopy may be employed to detect and confirm L-NH\(_3\) treatment on treatment type. 1107 cm\(^{-1}\) proved a most consistent indicator of 2019). In the fingerprint region, the changes at ca. weaker in the –OH stretch region, possibly due to interference from moisture/water (Makarem et al. 2014), Sum Frequency Generation (SFG) vibrational spectroscopy, also a surface-limited technique, may be employed for the same purpose as well. However, they report similar difficulties in detecting ammonia mercerization on samples that have previously been mercerized with NaOH. For that reason, the detection of ammonia mercerization on regenerated cellulosics will also be difficult with this method. As reported by (Kafle et al. 2014), Sum Frequency Generation (SFG) vibrational spectroscopy, also a surface-limited technique, may be employed for the same purpose as well. However, they report similar difficulties in detecting ammonia mercerization on samples that have previously been mercerized with NaOH. Thus, FTIR-ATR spectroscopy may be advantageous due to the ease of device operation and because the spectrometers are less expensive.

The textile materials in this work were treated in the laboratory in imitation of commercial-scale operations. Investigations have also been performed on textile materials from commercial-scale treatments, and the results will be reported in a follow-up publication.

Acknowledgments The authors gratefully acknowledge the cooperation of Mr. Marc Vanhoomissen and Mr. Daniel Hazard of Veramtex s.a. (Brussels, Belgium) in performing the liquid ammonia treatments.

Authors’ contributions Avinash P. Manian conceptualized the experimental plan, performed the alkali treatments and FTIR spectroscopy, and drafted the manuscript. Doris Braun performed FTIR spectroscopy and X-ray diffraction measurements, principal component analyses, and contributed to and reviewed manuscript drafts. Barbora Široká assisted with FTIR spectroscopy and reviewed manuscript drafts. Thomas Bech told contributed with experimental suggestions and reviewed manuscript drafts.

Funding Open access funding provided by University of Innsbruck and Medical University of Innsbruck. The experimental work was partly funded by the company Veramtex s.a. (Brussels, Belgium). The research leading to these results was performed in the frame of the project “Textile Competence Center Vorarlberg 2 (Project No. 882502)” funded under the COMET program – Competence Centers for Excellent Technologies – by the Federal Ministry for Climate Protection, Environment, Energy, Mobility, Innovation and Technology (BMK) and the Federal Ministry for Digitization and Business Location (BMDW), with co-financing from the federal province of Vorarlberg. The COMET program is administered by the Austrian Research Promotion Agency (FFG).

Data availability Online Resource 1.xlsx: FTIR data – background corrected, smoothed and min-max normalized.

Online Resource 2.pdf: Details on sample loading in X-ray diffraction measurements.

Online Resource 3.xlsx: Original data from X-ray diffraction measurements, with measured background values for fabric measurements (no sample) and fiber and powder measurements (mylar foils).

Online Resource 4.xlsx: X-ray diffraction data min-max normalized without background correction. This dataset was used in the principal component analysis (PCA) in the main section of the manuscript.

Online Resource 5.xlsx: The first derivatives (quadratic, five-point) calculated from FTIR spectra for use in PCA.

Online Resource 6.pdf: Tables of principle components and their explained variance from analyses discussed in the main section of the manuscript.

Online Resource 7.pdf: Supplementary figures that support discussions in the manuscript.

Online Resource 8.pdf: Crystallite sizes estimated from the measured x-ray diffractograms.

Online Resource 9.pdf: Score-score plots of first two principal components from analysis of x-ray diffraction after: (a) truncation to the 2theta range of 10°–25°, (b) correction for measured background, (c) Multiplicative Scatter Correction (MSC).

Declarations

Conflict of interest None to declare.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.
References

Anon (2018) ATR – Theory and Applications. PIKE Technologies, Inc. https://www.pikeotech.com/files/pdfs/PIKE_ATR_Theory-Applications.pdf. Accessed 6 Sept 2019

Beattie JR, Esmonde-White FWL (2021) Exploration of Principal Component Analysis: Deriving Principal Component Analysis Visually Using Spectra. Appl Spectrosc 75(4):361–375. https://doi.org/10.1177/0003702820987847

Bertoniere NR, King WD, Rowland SP (1986) Effect of mode of agent removal on pore structure of liquid ammonia treated cotton cellulose. J Appl Polym Sci 31(8):2769–2777. https://doi.org/10.1002/app.1986.070310830

Brand RH (1964) Measurement of Fabric Aesthetics: Analysis of Aesthetic Components. Text Res J 34(9):791–804. https://doi.org/10.1177/000370286403400909

Bredereck K (1981) Grundlagen und praktische Aspekte der Behandlung von Baumwollgeweben mit flüssigem Ammoniak. 9. Mitteilung: Behandlung von Baumwolle mit flüssigem Ammoniak und Natronlauge. Text-Prax Intl 36(9):1010–1015

Bredereck K, Commarmot A (1998) Ammonia treatment of cellulose fibers. Melland Textilber 79(12):64–68,E19-E22

Bredereck K, Saafan A (1982) Treatment of cotton with liquid ammonia. 10. Structural changes of cotton caused by practical treatment of cotton cloth with liquid ammonia. Melland Textilber 63(7):510–514

Chidambareswaran PK, Patil NB, Sundaram V (1976) Order in cellulose fibers. J Appl Polym Sci 20(8):2297–2298. https://doi.org/10.1002/app.1976.070200825

Colom X, Carrillo F (2002) Crystallinity changes in lyocell and viscose-type fibres by caustic treatment. Eur Polym J 38(11):2225–2230. https://doi.org/10.1016/S0014-8898(02)00132-5

Commarmot A, Bredereck K (1998) Practical aspects of the ammonia treatment of natural cellulose textiles. Int Text Bull 44(3):72–78

French AD (2014) Idealized powder diffraction patterns for cellulose polymorphs. Cellulose 21(2):885–896. https://doi.org/10.1007/s10570-013-0030-4

Geladi P, MacDougall D, Martens H (1985) Linearization and Scatter-Correction for Near-Infrared Reflectance Spectra of Meat. Appl Spectrosc 39(3):491–500

Ghosh S, Dilanni D (1994) Estimating the Degree of Mercerization using Near-Infrared Spectroscopy. J Text Inst 85(3):308–315. https://doi.org/10.1080/00405009408631276

Greenwood PF (1987) Mercerisation and liquid ammonia treatment of cotton. J Soc Dyers Colour 103(10):342–349. https://doi.org/10.1111/j.1478-4408.1987.tb01085.x

Harrick NJ, du Pré FK (1966) Effective Thickness of Bulk Materials and of Thin Films for Internal Reflection Spectroscopy. Appl Opt 5(11):1739–1743. https://doi.org/10.1364/AO.5.001739

Hazard D (1994) Mercerizing with ammonia. Int Text Bull Dyeing Print Finish 3:50–56

Jung HZ, Berni RJ, Benerito RR, Carra JH (1975) Liquid Ammonia vs. NaOH Mercerization as Pretreatment for the Cotton-Butadienedioxide Reaction. Spectral and Microscopical Studies. Text Res J 45(9):681–691. https://doi.org/10.1177/004051757504500906

Kafke K, Greenson K, Lee C, Kim SH (2014) Cellulose polymorphs and physical properties of cotton fabrics processed with commercial textile mills for mercerization and liquid ammonia treatments. Text Res J 84(16):1692–1699,1698. https://doi.org/10.1177/0040517514527379

Kanai H, Morishima M, Nasu K, Nishimatsu T, Shibata K, Matsuoka T (2011) Identification of principal factors of fabric aesthetics by the evaluation from experts on textiles and from untrained consumers. Text Res J 81(12):1216–1225. https://doi.org/10.1177/0040517511399960

Kar J, Fan J, Yu W (2006) 9 - performance evaluation of knitted underwear. In: Yu W, Fan J, Harlock SC, Ng SP (eds) Innovation and Technology of Women’s Intimate Apparel. Woodhead Publishing, pp 196–222. https://doi.org/10.1016/B978-1-84569-046-5.50009-4

Kim SH, Lee CM, Kafke K (2013) Characterization of crystalline cellulose in biomass: Basic principles, applications, and limitations of XRD, NMR, IR, Raman, and SFG. Korean J Chem Eng 30(12):2127–2141. https://doi.org/10.1007/s11814-013-0162-0

Kolpak FJ, Weihl M, Blackwell J (1978) Mercerization of cellulose: 1. Determination of the structure of Mercerized cotton. Polymer 19(2):123–131. https://doi.org/10.1016/0032-3861(78)90027-7

Ladisch CM, Cheek L (1984) Liquid ammonia pretreatment of cellulosic fabrics Part II. Effect on performance properties of hwm rayon, viscose and cotton. Cellul Chem Technol 18:535–544

Langford JI, Wilson AJC (1978) Scherrer after sixty years: A survey and some new results in the determination of crystallite size. J Appl Cryst 11:102–113. https://doi.org/10.1107/S00218898780012844

Le Bail A, Duroy H, Fourquet JL (1988) Ab-initio structure determination of Li5SbWO6 by X-ray powder diffraction. Mater Res Bull 23(3):447–452. https://doi.org/10.1016/0021-8898(88)90019-0

Lee IY, Jeong GE, Kim SR, Bengelsdorff C, Kim SD (2015) Effects of biowashing and liquid ammonia treatment on the physical characteristics and hand of denim fabric. Color Technol 131(3):192–199. https://doi.org/10.1111/cote.12142

Makarem M, Lee CM, Kafke K, Huang S, Chae I, Yang H, Kang J, Fan J, Harlock SC, Ng SP (eds) Innovation and Technology of Women’s Intimate Apparel. Woodhead Publishing, pp 196–222. https://doi.org/10.1016/B978-1-84569-046-5.50009-4

Matsuoka T (2011) Identification of principal factors of fabric aesthetics by the evaluation from experts on textiles and from untrained consumers. Text Res J 81(12):1216–1225. https://doi.org/10.1177/0040517511399960

Nelson ML, O’Connor RT (1964) Relation of certain infrared bands to cellulose crystallinity and crystal lattice type. Part I. Spectra of lattice types I, II, III and of amorphous cellulose. J Appl Polym Sci 8(3):1311–1324. https://doi.org/10.1002/app.1964.070083022

Niaz A, Tahir K-U-D (1989) Effect of Temperature of Alkali Solution on Mercerization. Text Res J 59(12):772–774. https://doi.org/10.1177/000370282005901214

Kubicki JD, Kim SH (2019) Probing cellulose structures and from untrained consumers. Text Res J 81(12):1216–1225. https://doi.org/10.1177/0040517511399960
Nishiyama Y, Johnson GP, French AD (2012) Diffraction from nonperiodic models of cellulose crystals. Cellulose 19(2):319–336. https://doi.org/10.1007/s10570-012-9652-1

Nunn S, Nishikida K (2008) Advanced ATR Correction Algorithm. ThermoFisher Application Note AN50581_E 05/08M. Thermo Electron Scientific Instruments LLC, Madison, WI (USA). https://assets.thermo Fisher.com/TFS-Assets/CAD/Application-Notes/D10241-.pdf. Accessed 21 Aug 2019

O’Sullivan AC (1997) Cellulose: the structure slowly unravels. Cellulose 4(3):173–207. https://doi.org/10.1023/a:1018431705579

Pérez S, Mazeau K (2005) Conformations, Structures, and Morphologies of Celluloses. In: Dimitriu S (ed) Polysaccharides: Structural Diversity and Functional Versatility. Marcel Dekker Inc, New York, pp 41–68

Rowland SP, Wade CP, Bertoniere NR (1984) Pore structure analysis of purified, sodium hydroxide-treated and liquid ammonia-treated cotton cellulos. J Appl Polym Sci 29(11):3349–3357. https://doi.org/10.1002/app.1984.070291112

Saafan AA, Habib A (1989) Strukturänderungen der Cellulose durch Flüssigammoniak-Behandlung von mercerisiertem Baumwollgewebe. Das Pap 43(1):8–11

Scherrer P (1918) Estimation of the Size and Internal Structure of Colloidal Particles by Means of Röntgen. Nachr Ges Wiss Göttingen 2:96–100

Široký J, Blackburn RS, Bechtold T, Taylor J, White P (2010) Attenuated total reflectance Fourier-transform Infrared spectroscopy analysis of crystallinity changes in lyocell following continuous treatment with sodium hydroxide. Cellulose 17(1):103–115. https://doi.org/10.1007/s10570-009-9378-x

Tomasino C (1992) Mercerizing. Chemistry & Technology of Fabric Preparation & Finishing. NCSU, Raleigh, pp 72–77

Wagaw T, Chavan RB (2013) Causticization followed by combined desizing, scouring and bleaching of cotton fabric. Colour 60(3):43–47

Wakida T, Lee M, Niu S, Yanai Y, Yoshioka H, Kobayashi S, Bae S, Kim K (1995) Dyeing properties of cotton fibres treated with liquid ammonia. J Soc Dyers Colour 111(5):154–158. https://doi.org/10.1111/j.1478-4408.1995.tb01714.x

Wakida T, Kida K, Lee M, Bae S, Yoshioka H, Yanai Y (2000) Dyeing and Mechanical Properties of Cotton Fabrics Treated with Sodium Hydroxide/Liquid Ammonia and Liquid Ammonia/Sodium Hydroxide. Text Res J 70(4):328–332. https://doi.org/10.1177/004051750007000408

Yao W, Weng Y, Catchmark JM (2020) Improved cellulose X-ray diffraction analysis using Fourier series modeling. Cellulose 27(10):5563–5579. https://doi.org/10.1007/s10570-020-03177-8

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.