

Infrared Spectroscopical Investigation of Cotton Subjected to Swelling and Deswelling Treatments*

HARALD ÅSNES and BENGT O. WICKMAN, *Swedish Institute for Textile Research (TEFO), Gothenburg, Sweden*

Synopsis

The setting of textiles made from cellulosic materials can be done with swelling and deswelling processes. Standard cotton fibers, purified by extraction, have been set in sodium hydroxide solutions with and without additions of thiocyanate salts. Treatments have also been done in zinc chloride and calcium thiocyanate and in a solution of potassium hydroxide in a mixture of butanol and kerosene. After rinsing and drying of the cotton samples, KBr pellets for infrared investigations were produced. Deuteration of the fiber sample for investigation was made in a special apparatus. Single and differential infrared diagrams have been run with and without previous deuteration of the set cotton samples. The infrared maximum of absorption of the OH band changes as a result of the setting treatment. The infrared diagrams show that the setting treatment in alkaline solution gives a broadening of the OH band towards higher and lower wavelengths, which indicates a transfer of the hydrogen bonding energy both to higher and lower energies. The diagrams from the deuterated samples indicate that the strong hydrogen bonds resulting from the setting treatment are partly resistant to deuteration. The results are discussed on the basis of setting and setting reactions.

INTRODUCTION

Setting has become very important in the production of wash-and-wear textiles in order to stabilize the fabric geometry and release internal tensions. For textiles from cellulosic material, this can be done with a swelling and deswelling process.¹

In the cellulose fiber material both morphological and molecular structures are changed as a result of the swelling and deswelling treatment, and on the macroscopic level, this can be noticed in the setting effect, e.g., form stabilization of fiber, yarns, and fabrics.

The wash-and-wear properties of cellulose fabrics are considered to be mainly an effect of crosslinking between cellulose molecules. Many efforts have been made to find out if crosslinking really takes place and what amorphous, crystalline, and morphological units are involved.² Therefore the effects of different crosslinking reactions are of great importance.

SCOPE OF THE INVESTIGATION

The scope of this limited investigation was to find what differences brought about by the swelling and deswelling treatments on cotton that

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would be shown in the infrared spectra. It was hoped that this would give us more information and lead to a better understanding of the setting process.

Although the swelling treatment does not introduce covalent crosslinks in the cellulose material, there are effects on the treated textile which, to some degree, resemble a treatment with covalent crosslinkers, but without the loss in strength properties usually accompanied with the covalent crosslinking reaction.¹ The swelling and deswelling treatment would, however, break and rebuild hydrogen bonds and also affect the crystalline order of the cellulose material.

Previous infrared investigations on cellulose materials mainly concern regenerated cellulose films, bacterial cellulose, and wood pulp.³⁻⁸ According to these earlier works, differences should be expected in the OH-stretching region at wavenumbers of ca. 3600-3000 cm.^{-1} and in the region of ca. 1500-900 cm.^{-1} . The changes in hydrogen bonding could possibly give an indication of what happens in the setting process. Intermolecular hydrogen bonding should be especially involved in the setting reaction.

A more detailed study of the OH-stretching region is possible after deuteration of the accessible OH groups in the vapor phase.^{4,9} In order to study the differences between set and unset material and also between the different setting treatments, the technique of differential spectra was used. This technique was previously used by Kyrklund and Sihtola,¹⁰ on hydrocellulose from mercerized and nonmercerized pulp. A study of deuterated samples was, however, not reported.

EXPERIMENTAL

Material

The investigation was mainly done on standard cotton samples which had been purified by extraction. Some parallel investigations were also made on yarns and fabrics.

Preparation of KBr Pellets

The cotton fibers were cut on a microtome to a length of about 0.06 mm. A 3-mg. portion of the dried sample was weighed on a micro balance to get an accurate concentration and mixed thoroughly with 500 mg. of dried, ground KBr. The pellets were pressed in the usual way.

Treatment

The different setting treatments to which the cotton samples were subjected are listed in Table I. After the treatments in the setting solutions, the samples were rinsed in 3% acetic acid and tap water before drying at 70°C. for 1 hr.

Deuteration

Deuteration was carried out in the vapor phase on the cut and weighed samples in the apparatus shown in Figure 1. This apparatus has been described earlier by Mann and Marrinan.⁴

TABLE I
Setting Treatment of Standard Cotton and Absorption Maximum of the OH Band in the Infrared Diagram

Treatment no.	Setting treatment	Absorption maximum, cm. ⁻¹
0	Untreated standard cotton	3355
1	20% NaOH, 1/2 min., 20°C.	3370
2	6% KOH in 1:1 butanol-kerosene 1 hr., 92°C.	3390
3	63.5% ZnCl ₂ , 17 hr., 20°C.	3405
4	63.5% ZnCl ₂ , 1 hr., 92°C.	3370
5	60% Ca(SCN) ₂ , 1 hr., 92°C.	3370
6	20% NaOH + 4.2% LiSCN, 1 hr., 92°C.	3440
7	20% NaOH + 10% NH ₄ SCN, 17 hr., 20°C.	3405
8	20% NaOH + 10% NH ₄ SCN, 1 hr., 92°C.	3390
9	98% ethylenediamine, 17 hr., 20°C.	3380
10	20% NaOH, 1 hr., 92°C.	3405
11	30% NaOH + 5% NaSCN, 17 hr., 20°C.	3440
12	" 5 min., 20°C.	3430
13	" 1/2 min., 20°C.	3415
14	" 1 hr., 92°C.	3450
15	" 5 min., 92°C.	3430
16	" 1/2 min., 92°C.	3430
17	30% NaOH, 1/2 min., 20°C.	3410
18	" 5 min., 20°C.	3410
19	" 1 hr., 20°C.	3415
20	" 1/2 min., 92°C.	3430
21	" 5 min., 92°C.	3430
22	" 1 hr., 92°C.	3430
23	" 17 hr. 20°C.	3430

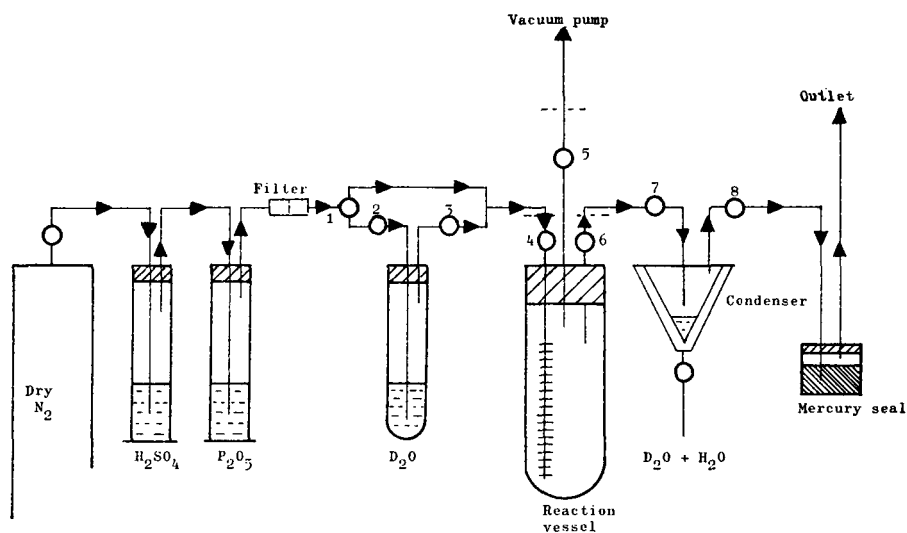


Fig. 1. Apparatus for deuteration.

Experiments showed that, after 4 hr., the deuteration reaction had come to an equilibrium (no change in the OH and OD intensities).

To avoid rehydrogenation of the sample through atmospheric moisture, the samples, deuterated and dried under nitrogen atmosphere, were also handled under dry nitrogen atmosphere during the mixing with KBr and pressing into pellets. The deuterated pellet samples were stored in a desiccator over P_2O_5 . These pellet samples could be run in the infrared instrument under ambient atmospheric conditions and stored in the described manner for at least 1 month before any changes in the OH and OD intensities could be observed.

The homogeneity of the pellet samples proved to be good if the KBr was thoroughly ground and mixed with the cut cotton sample before pressing the pellet.

Infrared Spectra

Most differential infrared diagrams were run with the unset cotton sample in the reference beam. Many pellets contained slightly varying amounts of unset material (2.75–3.00 mg.) so that possible variation in concentration of the set samples could be matched. As a criterion for equal sample concentration in the reference and sample beam, no absorption difference should be found in the CH-absorption band at 2900 cm.^{-1} .

The infrared spectra were obtained on Perkin-Elmer infrared spectrophotometers, Nos. 137, 237, and 337.

RESULTS AND CONCLUSIONS

From Table I the wavenumber corresponding to the absorption maximum in the OH-stretching region can be seen. This maximum of absorption is, however, not very well defined, because the band is unsymmetric and broad. The maximum of absorption is usually shifted to higher wavenumbers by setting with swelling and deswelling treatment.

In Figure 2, the single and differential spectra of standard cotton with

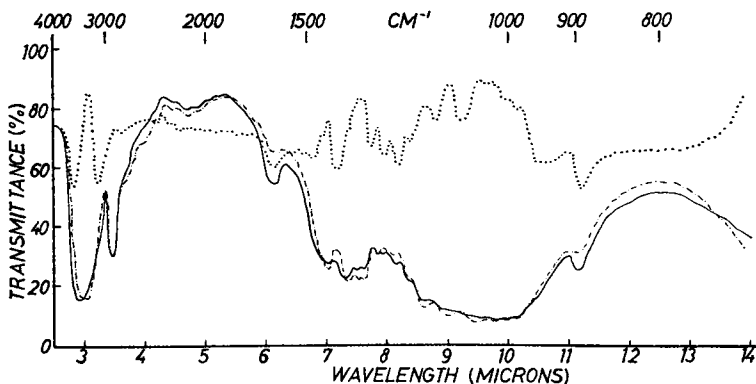


Fig. 2. Infrared spectra of standard cotton: (---) untreated standard cotton (1); (—) cotton treated with 30% (w/w) NaOH for 17 hr. at 20°C . (2); (···) differential spectrum of (2) against (1) as reference.

and without a setting treatment in sodium hydroxide solution are shown. The differential spectrum clearly shows that a broadening of the hydroxyl-stretching region results from the treatment in sodium hydroxide. This means that hydrogen bonds with higher and lower energies are formed compared with the untreated sample. The energy E of the hydrogen bond (in kilocalories/mole) can be calculated from eq. (1):

$$E = (1/K)[(\nu_0 - \nu)/\nu_0] = (1/K)(\Delta\nu/\nu_0) \quad (1)$$

where ν is the wavenumbers, $K = 1.6 \times 10^{-2}$ kcal. $^{-1}$, and $\nu_0 = 3650$ cm. $^{-1}$.

In the region of wavenumbers about 900–1500 cm. $^{-1}$, marked differences can be found between the treated and untreated sample. Two bands of great interest are at 1425 and 893 cm. $^{-1}$. The former has been called a crystalline band, because it increases with increasing crystallinity, and the second, an amorphous band because it increases with increasing amorphous fraction of the sample. The infrared ratio between the absorption intensities at these two bands ($a_{1425 \text{ cm.}^{-1}}/a_{893 \text{ cm.}^{-1}}$) has sometimes also been taken as a measure of crystallinity and called the crystallinity index. Both bands are, however, influenced in a similar way by transformation of cellulose I to cellulose II and could therefore not be used as a measurement of crystallinity in connection with alkali treatments. This infrared ratio could, however, probably be applicable as a measure of the degree of mercerization, which for practical reasons would be very interesting with this special kind of treatment. Table II shows this infrared ratio calculated for some of the set cotton samples. The ratio decreases with increasing time of treatment. Cotton samples of different origin gave different infrared ratios, as expected.

TABLE II
Infrared Ratio ($a_{1425 \text{ cm.}^{-1}}/a_{893 \text{ cm.}^{-1}}$) after Different Setting Treatments on Different Cotton Materials

Setting solution	Time	Temp., °C.	$a_{1425 \text{ cm.}^{-1}}/a_{893 \text{ cm.}^{-1}}$		
			Standard cotton	Cotton thread (mer- cerized)	Cotton weave
Untreated	—	—	2.77	1.90	2.90
30% NaOH	1/2 min.	20	1.04	1.16	1.30
“	17 hr.	20	0.79	0.77	1.16
“	1/2 min.	92	0.83	0.94	1.30
“	1 hr.	92	0.76	0.85	0.92
30% NaOH + 5% NaSCN	1/2 min.	20	0.89	1.17	1.30
“	17 hr.	20	0.67	0.78	1.15
“	1/2 min.	92	0.74	0.94	1.10
“	1 hr.	92	0.65	0.93	0.87
6% KOH in 1:1 butanol- kerosene	1 hr.	92	1.23	1.02	1.49
63.5% ZnCl ₂	17 hr.	20	1.18	1.81	2.54
“	1 hr.	92	2.61	1.93	2.87
60% Ca(SCN) ₂	1 hr.	92	2.91	1.94	3.08

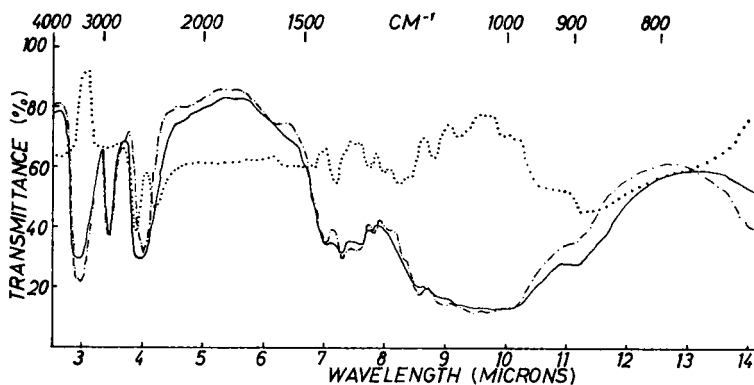


Fig. 3. Infrared spectra of deuterated standard cotton samples: (---) untreated standard cotton (1); (—) cotton treated with 30% (w/w) NaOH for 17 hr. at 20°C. (2); (· · ·) differential spectrum of (2) against (1) as reference.

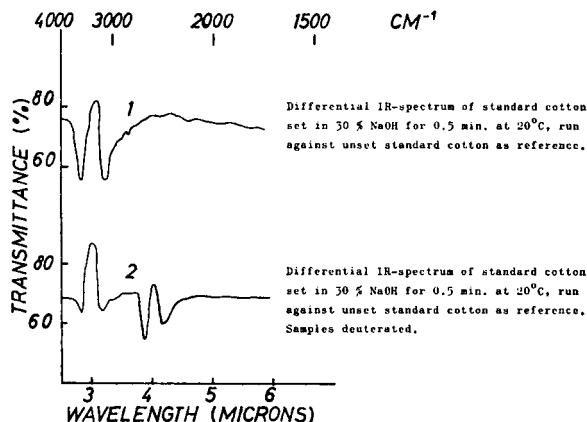


Fig. 4. Differential spectra with and without deuteration for comparison of the OH and OD absorption bands.

To indicate the degree of crystalline and amorphous fractions, Nelson and O'Connor¹¹ used the infrared ratio of the bands at the 1372 and 2900 cm.^{-1} ($a_{1372 \text{ cm.}^{-1}}/a_{2900 \text{ cm.}^{-1}}$). This infrared ratio ranked samples of cellulose I and cellulose II and those containing mixed lattices in the same order as did crystallinity parameters derived from x-ray diffraction, density measurement, and moisture sorption data. Our calculations of this ratio gave, however, great standard deviations, probably due to the instrument not being suitable for this purpose.

In the OH-stretching region, the accessible and nonaccessible OH could be studied separately after deuteration. Figure 3 shows the single and differential spectra of deuterated standard cotton with and without setting in sodium hydroxide solution.

As can be seen, the highest degree of deuteration is found in the alkali-treated sample, and the difference curve indicates that deuteration occurs mainly on the low energy side of the band. That means a shift to higher wavenumbers provided that the ratio of the optical densities for the K_{OD}/K_{OH} deuterium oxide and hydroxide band is constant over the whole band width. The value of this ratio is 1.11 according to Mann and Marrinan.⁴ In Figure 4 this is shown more clearly.

According to different authors, the intermolecular OH bonds should lie on the right-hand side of the OH band, that is, at low wavenumbers. Kyrklund and Sihtola⁹ believe that strong hydrogen bonds are formed as a result of the alkali treatment if the fiber is surrounded by an outer layer strong enough to exert a restrictive influence on the swelling of the fiber, and the cotton fiber has a comparatively strong outer layer.

These strong hydrogen bonds should be mainly interfibrillar or intermolecular. Our investigation indicates that such strong hydrogen bonds are formed and that at least part of these bonds are resistant to deuteration. This could very well explain the macroscopic similarities between a setting with a swelling and deswelling treatment and setting with reagents producing covalent crosslinking.

As to the setting with other swelling agents, such as salt solutions, differences in the OH absorption band between treated and untreated samples could not always be found, even after deuteration. If we suppose that this kind of setting treatment breaks and rebuilds hydrogen bonds of the same energy and that these bonds are not broken either in the unset or in the set sample by the usual water treatment, detection in changes of the OH or OD bands would be impossible. The macroscopic setting effects would, of course, be observed.

This kind of information has the limitation that it only concerns the starting material and the material obtained after deswelling and drying. For the study of partially swollen structures other techniques would be necessary.

This investigation has given us some valuable information about the mechanism of setting of cotton by swelling and deswelling processes. More detailed information would be possible by similar infrared spectroscopic investigations in polarized light; these however, probably would have to be done on single fibers.

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Résumé

On peut conférer la stabilité dimensionnelle de textiles à base de matériaux cellulosiques par procédé de gonflement et de dégonflement successifs. Les fibres de coton étalon, purifiées par extraction, ont été ainsi traitées dans des solutions d'hydroxyde de sodium avec et sans addition de sulfocyanures. Les traitements ont également été effectués dans du chlorure de zinc et du sulfocyanure de calcium dans une solution d'hydroxyde de potassium dans un mélange de butanol et de kérosène. Après rinçage et séchage des échantillons de coton des pastilles de bromure de potassium ont été faites pour examen infrarouge. La deutération de l'échantillon de la fibre pour l'étude a été faite à l'aide d'un appareil spécial. Les diagrammes infrarouges simples et différentiels ont été effectués avec et sans deutération préalable de l'échantillon de coton. Le maximum d'absorption infrarouge de la bande OH change suivant les conditions de traitement. Les diagrammes infrarouges montrent que le traitement donne une solution alcaline, provoque un élargissement de la bande OH vers les longueurs d'onde plus grandes et plus basses, ce qui indique un transfert d'énergie de liaisons hydrogènes à la fois vers des énergies plus grandes et plus faibles. Les diagrammes au départ des échantillons deutérés indiquent que les liaisons hydrogènes fortes résultant du traitement sont en partie résistantes à la deutération. Les résultats sont discutés sur la base du procédé et des réactions qu'il comporte.

Zusammenfassung

Textilien aus Cellulosematerialien können einer Veredlung durch Quellungs- und Entquellungsprozesse unterzogen werden. Durch Extraktion gereinigte Standardbaumwollfasern wurden in Natriumhydroxydlösungen mit und ohne Zusatz von Rhodansalzen behandelt. Weitere Behandlungen wurden in Zinkchlorid und Calciumthiocyanat und in einer Lösung von Kaliumhydroxyd in einer Mischung von Butanol und Kerosin vorgenommen. Nach Spülung und Trocknung der Baumwollproben wurden KBr-Presslinge zur Infrarotuntersuchung hergestellt. Die Deuterierung der Faserprobe für weitere Untersuchungen wurde in einer Spezialapparatur durchgeführt. Einfache und Differential-Infrarotspektren wurden mit und ohne vorheriger Deuterierung der behandelten Baumwollproben aufgenommen. Das Infrarotabsorptionsmaximum der OH-Bande verschiebt sich als Folge der Behandlung. Das Infrarotspektrum zeigt, dass die Behandlung in alkalischer Lösung eine Verbreiterung der OH-Bande gegen höhere und niedrigere Wellenlängen liefert, was für eine Verschiebung der Energie der Wasserstoffbindung zu höheren und niedrigeren Werten spricht. Das Diagramm der deuterierten Proben zeigt, dass die durch die Behandlung gebildeten starken Wasserstoffbindungen zum Teil gegen Deuterierung resistent sind. Die Ergebnisse werden auf Grundlage der bei der Behandlung auftretenden Reaktionen diskutiert.

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