

Enhancing the Reactivity and Strength of Cotton Fibers

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SYNOPSIS

Both sodium hydroxide solution of mercerizing strength and anhydrous methylamine are suitable pretreatments for enhancing the reactivity of cotton cellulose. Favorable results are achieved by maintaining the fiber material in the never-dried state after the swelling treatment. Extraction by organic solvents is to be preferred over water-washing in order to remove the swelling agent. When cotton is swollen with either aqueous sodium hydroxide or anhydrous methylamine and then washed and dried, its crystallinity, as determined by X-ray diffraction is not lowered as much as it is if it is acetylated to an acetyl content of about 9% before drying. The greatest modifications of the crystal structure of cotton were found on methylamine treatment followed by chloroform and pyridine washing and acetylation in the never-dried state (MeCP product), as well as by alcoholic mercerization followed by ethanol and pyridine washing and acetylation in the never-dried state (AMEP). As determined by moisture regains, no significant differences are apparent between the accessibility of samples of low acetyl content (ca. 9%) prepared by either the AMEP or by the MeCP treatment. The DTA curves of methylamine-treated cotton with an acetyl content close to that of commercial diacetate and the commercial product are dissimilar. It can be concluded from the DTA curve of the deacetylated product prepared from this MeCP sample that it has a highly disordered structure. The tensile properties of the acetylated products of low acetyl content are considerably improved if acetylation is preceded by mercerization with subsequent solvent exchange, and less so if it is preceded by methylamine followed by solvent exchange. Incorporation of acetyl groups significantly enhances the breaking strength and extensibility of mercerized solvent-washed materials.

INTRODUCTION

The improvement of reactivity and accessibility of cellulosic fibers has been the purpose of numerous investigations.^{1,2} Swelling treatments in aqueous alkali metal hydroxides or in amines represent one possibility of attaining this aim. It is well known^{1,2} that the accessibility of cellulose fibers is increased by treatment with a large number of reagents. However, this does not necessarily mean that the overall reactivity is improved as well.^{3,4} For example, when cotton is mercerized with a strong aqueous solution of sodium hydroxide and then dried its reactivity towards acetylation deteriorates. Several attempts have been made to maintain the increased reactivity of the fibers by using organic solvents instead of

water to wash out the sodium hydroxide, or by varying the mercerizing conditions.^{5,6}

Anhydrous ethylamine has been used to reduce the crystallinity and increase the reactivity of cotton cellulose.^{7,8,9} However, according to Klenkova et al.¹⁰ the decrystallizing effect of dry methylamine is greater than that of anhydrous ethylamine.

The strength of some types or strains of cotton increases on slack mercerization. It has been speculated that the extensibility, as well as other physical properties, of the fibers may be enhanced by the formation of a derivative with a low degree of substitution before fibers swollen with an intracrystalline swelling agent are dried for the first time.¹¹

The objectives of the present paper were first to determine whether methylamine decrystallized cotton cellulose and increased its reactivity to acetylation more than mercerization; second, to establish whether the decrystallizing effects of mercerization and methylamine treatment were improved when

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the swelling agents were extracted with organic solvents instead of water; and third, to ascertain whether a lower crystallinity could be maintained and the tensile properties of the fibers improved by introducing a few acetyl groups after an appropriate swelling treatment. Finally, we wished to examine the effect of the treatments on the thermal properties of the products.

EXPERIMENTAL

Materials

An American Upland cotton was used. The cotton, in loose form, was scoured with 4% aqueous sodium hydroxide (w/w) at 100°C for 90 min. The sample was then washed thoroughly with distilled water and dried in an air oven at 50°C for 4 h. Methylamine was supplied in a cylinder (Matheson Gases). All other chemicals were of reagent grade.

Swelling Treatments

Alkali Treatment (Mercerization)

Cotton was mercerized in 20% aqueous sodium hydroxide solution (1 : 50, material-to-liquor ratio) at 0°C for 1 h under slack conditions. The reagent was removed by one of the following methods:

1. The alkali-swollen material was washed with cold distilled water followed by 10% acetic acid and then again washed with distilled water until a neutral extract was obtained. The mercerized, water-washed, product (MWD) was air dried.
2. After the same washing treatment as above and, without intermediate drying, the water was exchanged with pyridine. The mercerized, water-washed, pyridine-treated fiber (MWP) was kept in pyridine for acetylation.
3. Absolute ethanol was substituted for distilled water in the washing treatment. Thus the alkali-swollen sample was steeped in ethanol, followed by 10% acetic acid in absolute ethanol, and then again with ethanol. Finally, the ethanol was exchanged for pyridine and the mercerized, ethanol-washed, pyridine-treated material (MEP) was retained in pyridine for acetylation.

One sample was treated with a 20% solution of sodium hydroxide, the solvent consisting of a 20 : 80 mixture of ethanol and water. Other conditions were

similar to those for the treatment with pure aqueous sodium hydroxide. The product [mercerized with an alcoholic solution, ethanol-washed, pyridine-treated (AMEP)] was washed in the same manner as the MEP fiber.

Methylamine Treatment

Scoured cotton was treated with anhydrous methylamine at -20°C for 15 min. in a closed system. The methylamine had been dried over potassium hydroxide. In one set of samples (MeCD), the amine was then exchanged with chloroform and the fibers were air dried. In a second set of experiments the chloroform was exchanged with pyridine and the samples (MeCP) were retained in pyridine for acetylation.

Acetylation

The acetylation reaction was carried out with acetic anhydride and pyridine (50 : 50, w/w) at 30°C in a thermostated bath. To terminate the reaction, the samples were washed with distilled water and then air dried.

Deacetylation

Samples of high acetyl content were deacetylated using 1% sodium hydroxide in ethanol.¹²

Product Characterization

Acetyl Content

The method has been described previously.⁸

X-Ray Diffractograms

Air-dried fibers (0.25 g) were ground in a Wiley mill so as to pass through a 20-mesh screen and were then pressed into pellets. The diffraction spectra were measured with a Diano-XRD 8000 X-ray machine, using CuK_α radiation.

To estimate the state of order in the cellulose samples, the crystallinity ratio (Cr.R.) was calculated using the formula¹³:

$$\text{Cr.R.} = 1 - \frac{I_1}{I_2}$$

where I_1 is the intensity at the minimum (between $2\theta = 18^\circ$ and 19° for cellulose I and between $2\theta = 13^\circ$ and 15° for cellulose II), and I_2 is the intensity of the crystalline peak at the maximum (between $2\theta = 22^\circ$ and 23° for cellulose I and between $2\theta = 18^\circ$

and 22° for cellulose II). The same formulae were used for acetylated samples, except that in this instance the ratio is termed the molecular order index (MOI).

The definition of Cr.R. excludes the cellulose III lattice as well as mixed lattices. Therefore, the Cr.R. and MOIs of the methylamine-treated samples could not be calculated.

Moisture Sorption

Samples of approximately the same acetyl content were dried over phosphorous pentoxide until constant weight was recorded. They were conditioned at constant temperature and humidity [21°C, 65% relative humidity (R.H.)] for at least 7 days in a vacuum desiccator over a saturated solution of sodium nitrite, and were then reweighed on consecutive days until weights were constant. Then the moisture regain and the sorption ratio (S.R.) or acetylated sorption ratio (A.S.R.) were calculated where:

$$\text{S.R.} = \frac{\text{moisture regain of cellulosic sample}}{\text{moisture regain of cotton}} \\ \text{at the same R.H. and temp.}$$

A.S.R.

$$= \frac{\text{moisture regain of acetylated product}}{\text{moisture regain of acetylated scoured cotton of comparable acetyl content}} \\ \text{at the same R.H. and temp.}$$

Differential Thermal Analysis

Differential thermal analysis (DTA) was carried out on 5 mg samples in nitrogen atmosphere on a Mettler thermal analyzer. To ensure uniform packing the samples were cut in a Wiley mill so as to pass through a 20-mesh screen. The DTA curves, using aluminium oxide as reference, were obtained for a temperature range of 30 to 400°C at a heating rate of 5°C/min. Peak temperature and onset temperature were calculated as described previously.¹⁴

Tensile Tests

The tensile strength and elongation at break of single fibers were determined with an Instron tensile tester at 65% R.H. and 21°C using a 12.5 mm gage length. The rate of extension was 10 mm/min. Fifty fibers were tested per sample.

RESULTS AND DISCUSSION

Reactivity to Acetylation

In agreement with earlier publications,^{3,5,9} the reactivity of mercerized cotton towards acetylation was very poor when the fiber material was washed out with water and dried (Table I). Only 5% acetyl content was obtained after 264 h reaction time compared to 13.8% for the scoured cotton. However, considerable improvement was achieved by retaining the fibers in the wet state by exchanging the water for pyridine followed by immediate acetylation. Using ethanol instead of water as the washing medium proved to result in a further increase of the reactivity (Fig. 1). The acetylation of this material proceeded at a high initial rate. The rate of acetylation fell after 24 h and then became roughly similar to that of the other celluloses. The presence of ethanol in the mercerization solution appeared to reduce the initial reaction rate relative to treatments made with pure aqueous sodium hydroxide (cf. AMEP and MEP, Table I).

The highest attainable acetyl contents were found for samples where methylamine treatment was followed by amine exchange (first with chloroform, then with pyridine), before acetylation without drying of the material (MeCP, Table I). In this case after 240 h the acetyl content of the product was 38.8%, which equals a degree of substitution (D.S.) of 2.33 and is very close to the D.S. of commercial diacetate which is 2.4. Drying of the material after the swelling treatment in methylamine had an unfavorable impact on the reactivity of the product, even though the washing medium was chloroform instead of water (Fig. 2). However, the product still maintained a higher reactivity than mercerized cotton which had been dried.

It can be observed by comparing the data in Table I that, in terms of its ability to maintain the reactivity of the cellulose, water is the least suitable solvent for extracting the swelling agents, while ethanol and chloroform seem to be alike in effectiveness. Ethanol has a lower hydrogen bonding capacity than water. Thus, ethanol unlike water, does not form multiple hydrogen bonds with the free hydroxyl groups and hinders the cellulose molecules from coming close enough to form interchain hydrogen bonds before solvent exchange with pyridine.⁵ Presumably chloroform, which is polar, behaves in a similar manner. Reactivity increases may have been induced by changes in the porosity of the fibers after swelling. Nelson and Oliver¹⁵ have demonstrated a relation between reactivity to acetylation and the microporosity of acetic acid swollen pulp fibers.

Table I Rate of Acetylation at 30°C After Various Swelling Treatments^a

Acetylation Time	Acetyl Content [%]						
	Scoured Control	Sodium Hydroxide Treatments				Methylamine Treatments	
		MWD	MWP	MEP	AMEP	MeCD	MeCP
10 min	—	—	—	8.6	—	—	—
15 min	—	—	—	9.2	—	—	9.5
30 min	—	—	—	11.1	9.7	—	11.5
1 h	8.4	1.8	11.5	12.8	11.0	2.8	13.5
24 h	8.8	1.9	20.0	27.6	18.0	2.2	26.4
72 h	—	—	—	—	—	5.8	35.0
98 h	11.6	4.2	—	—	—	—	—
100 h	—	—	26.0	—	27.5	—	—
120 h	—	—	26.2	31.0	—	—	—
144 h	—	—	—	—	—	9.6	35.0
192 h	—	—	26.3	32.6	—	—	—
240 h	—	—	—	—	—	13.9	38.8
264 h	13.8	5.0	29.8	34.1	—	—	—

^a MWD = mercerized, water washed, dried; MWP = mercerized, water washed, pyridine exchanged; MEP = mercerized, ethanol washed, pyridine exchanged; AMEP = alcoholic mercerization, ethanol washed, pyridine exchanged; MeCD = methylamine treated, chloroform washed, dried; MeCP = methylamine treated, chloroform washed, pyridine exchanged.

Crystallinity of the Samples

In order to determine whether there is a direct correlation between high reactivity and the amount of fiber decrystallization, X-ray diffractograms were obtained on dried samples.

The mercerization of the scoured cotton sample led to a lattice conversion from cellulose I to cellulose

II, with small traces of the cellulose I lattice still present (cf. diffractometer tracings in Figs. 3 and 4). In the case of the methylamine treatment the cellulose I pattern was found, with only small evidence of cellulose III, when the amine was evaporated or removed by chloroform washing and the product was air dried (cf. Figs. 3 and 5).

The X-ray diffraction pattern of the acetylated

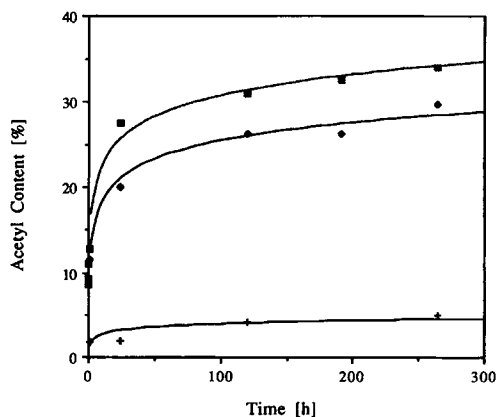


Figure 1 Rate of acetylation of cotton cellulose after mercerization: MWD = mercerized, water-washed, dried; MWP = mercerized, water-washed, pyridine-exchanged, never-dried; MEP = mercerized, ethanol-washed, pyridine-exchanged, never-dried.

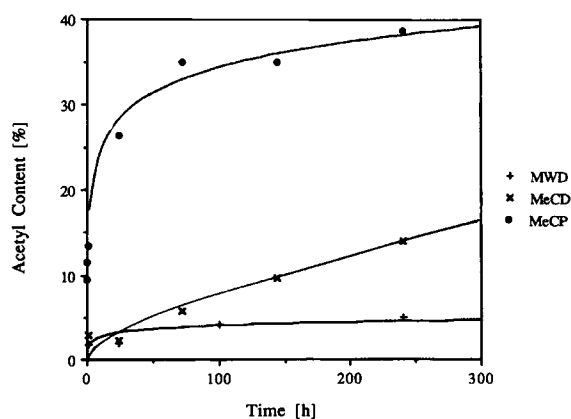


Figure 2 Rate of acetylation of cotton cellulose after methylamine treatment: MWD = mercerized, water-washed, dried (control); MeCD = methylamine-treated, chloroform-washed, dried; MeCP = methylamine-treated, chloroform-washed, pyridine-exchanged, never-dried.

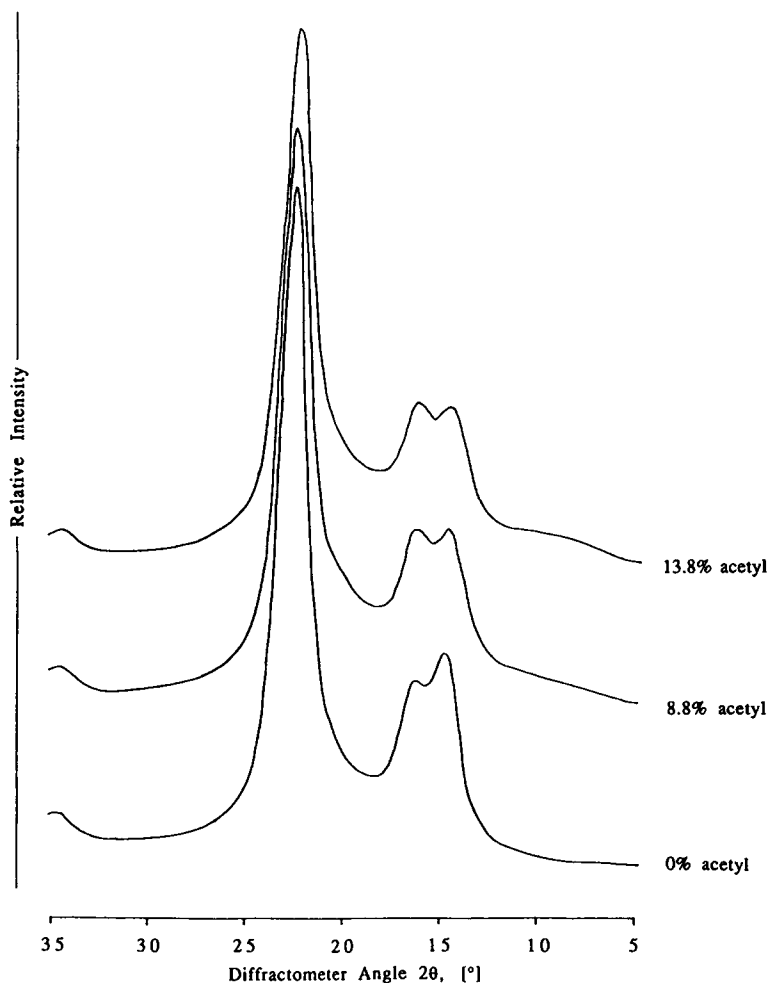


Figure 3 X-ray diffraction patterns of scoured cotton cellulose with gradually increased acetyl content.

scoured cotton (Fig. 3) remained little affected even after prolonged acetylation times. Thus it seems that at low acetyl contents the acetylation reaction itself does not have any significant impact on the crystallinity of the samples. The same observation was made with the mercerized, water-washed, and dried (MWD) sample (cf. Cr.R. of nonacetylated samples and MOI of acetylated samples of low acetyl content in Table II), and the methylamine treated, chloroform washed, and dried (MeCD) sample. Since diffraction patterns had not changed, none are presented in this paper.

In the case of the acetylated MWP samples with acetyl contents less than 20%, the original cellulose-II lattice showed small changes. The (002) and (10 $\bar{1}$) peaks were slightly less distinct and the amorphous scattering barely increased. For example the MOI value of acetylated MWP with 9.5% acetyl content was 0.73.

If the mercerization solution was removed by absolute ethanol, instead of water, and the ethanol solvent was exchanged with pyridine, slightly higher decrystallization was observed at low acetyl contents (Fig. 4 and cf. MOIs of MWP and MEP samples of approximately 9% acetyl content in Table II). The X-ray diffractogram had an almost symmetrical peak with an indistinct maximum in the region of $2\theta = 20$ to 21° while the (101) peak of the cellulose-II lattice seemed unaffected. According to the high acetylation rate one might have expected a more decrystallized acetylated product.

In general, for swollen mercerized samples which had not been dried before esterification the progress of the acetylation reaction was indicated by an increasingly steep rise in the region of the diffractogram where $2\theta = 5$ – 7° , and by the formation of two broad peaks with their maxima around $2\theta = 11.5^\circ$ and 20.5° (Fig. 4). Each peak contained a shoulder

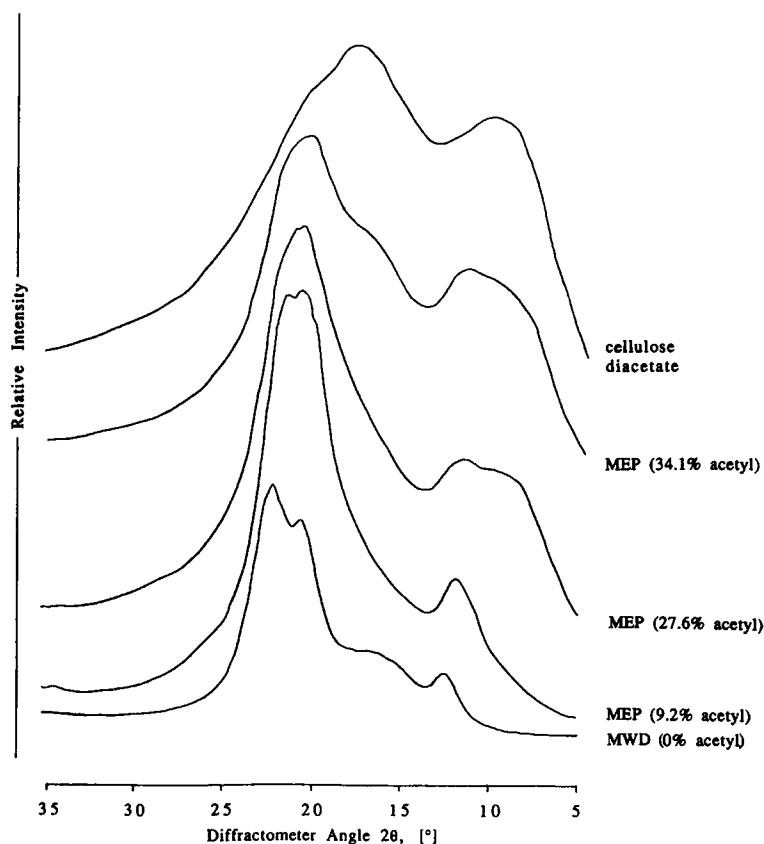


Figure 4 Changes in the X-ray diffractograms of increasingly acetylated mercerized cotton cellulose compared to the nonacetylated mercerized sample (MWD) and to commercial cellulose diacetate. Sodium hydroxide was washed out with ethanol and the ethanol was exchanged for pyridine (MEP).

and when the X-ray spectra are compared to those of commercial diacetate it will be observed that the shoulders are located at the positions of the peak maxima of cellulose diacetate. Thus there appear to be mixed crystals in the products.

In contrast to these results, the X-ray spectra of the acetylated methylamine-treated, solvent exchanged, and never-dried samples (MeCP, Fig. 5) indicate that there is already considerable decrystallization in the initial acetylation stage, even though from its X-ray diffractometer tracing, the crystallinity of the nonacetylated product did not appear to be very low. Broad (002), (10 $\bar{1}$), and (101) reflections were present in the nonacetylated methylamine-treated samples (cf. the tracing of scoured cotton in Fig. 3 with that of MeCD in Fig. 5). At low acetyl contents the never-dried product showed only a broad-based single peak at about $2\theta = 21.7^\circ$ with a shoulder in the region of 17° (see, for example, MeCP of 9.5% acetyl content in Fig. 5).

Compared to the samples which had been mercerized with aqueous sodium hydroxide, markedly different results were obtained for the acetylated materials which had been treated with a solution of sodium hydroxide containing 20% absolute ethanol. The X-ray spectra of these products resembled those of the acetylated amine-treated, never-dried samples (Fig. 6). Nevertheless, the reaction rate and the attainable acetyl content after alcoholic mercerization were less favorable compared to the MEP and MeCP treatments (cf. Table I). Ethanol obviously promotes the decrystallization and lattice distortion caused by the alkali hydroxide treatment, but after extraction by ethanol and pyridine, the never-dried product does not support the incorporation of acetyl groups at as high a rate as the MEP system.

In order to obtain an indication of the permanence of the decrystallizing effect of the pretreatments discussed, the samples with the highest achievable acetyl content under the given conditions

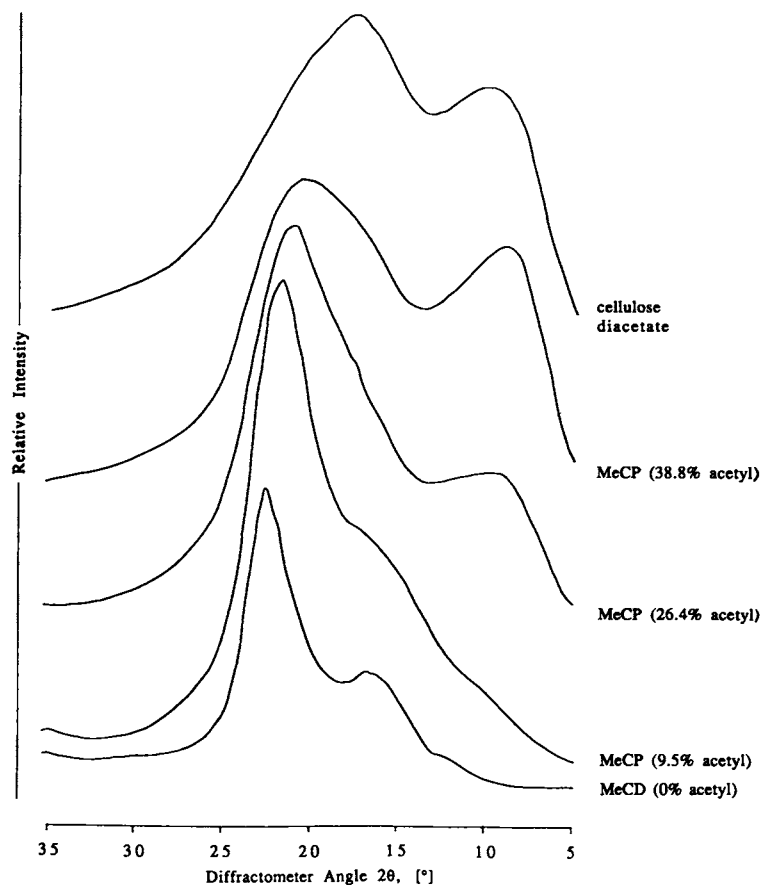


Figure 5 Changes in the X-ray diffractograms of increasingly acetylated methylamine-treated cotton cellulose compared to the nonacetylated methylamine-treated sample (MeCD) and to commercial cellulose diacetate. Methylamine was washed out with chloroform and the chloroform was exchanged for pyridine (MeCP).

were deacetylated and their X-ray diffraction patterns determined (cf. Fig. 7). The mercerized samples, whether water-washed, air-dried, or acetylated in the wet state, showed recrystallization and formation of cellulose II with only slightly decreased crystallinity after deacetylation, as can be inferred from the Cr.R. presented in Table II.

Unlike mercerization, the swelling in methylamine appears to have the more lasting effect on the crystalline structure of cotton cellulose (Fig. 7). While the deacetylated MeCD sample indicates a poorly defined cellulose I lattice with high amorphous scatter, the deacetylated MeCP sample yields a highly decrystallized structure with a broad peak centered at $2\theta = 20^\circ$. It will be noted that Klenkova et al.¹⁰ claimed they had obtained an amorphous cellulose by methylamine swelling. In our case we were only able to achieve essentially complete amorphousness after deacetylation of acetylated methylamine-treated products.

Influence of the Pretreatment on Hygroscopicity

Water sorption determinations were made to obtain additional information about the amount of disorder in cellulose, since water molecules can only penetrate the non-crystalline regions of the fiber. Under defined conditions moisture adsorption can be used as a measure of accessibility.² Without any swelling treatment the acetylation reaction is limited to the disordered regions of the cotton fiber. Since acetyl groups have less affinity for water than hydroxyl groups, it is not surprising that the water sorption of acetylated scoured cotton was considerably lower than that of the nonacetylated control (Table III).

As expected the moisture regain of cotton increased by approximately 50% on mercerization.^{1,2} The increase on methylamine treatment was 33% which is similar to the increase on ethylamine treatment.⁹ Thus methylamine did not appear to improve the accessibility of cotton any more than ethylamine.

Table II Influence of the Swelling Treatment on the X-Ray Crystallinity Ratios (Cr.R.)¹³ and the Molecular Order Index (MOI), of Acetylated Cotton Cellulose

Treatment ^a	Acetyl Content (%)	Cr.R.	MOI
Scoured Control	0.0	0.87	
	8.8		0.82
	13.8		0.81
MWD	0.0	0.82	
	1.9		0.79
	5.0		0.79
MWP	9.5		0.73
	20.0		0.71
	29.8		0.56
MEP	0.0	0.75	
	9.2		0.70
	27.6		0.55
	34.1		0.23
Deacetylated Samples ^b			
MWP (29.8)	0.0	0.74	
MEP (34.1)	0.0	0.77	

^a Treatment codes are given in Table I.

^b Samples with the highest achievable acetyl content under the reaction conditions were deacetylated. The acetyl content is given in parentheses.

When the moisture regain of acetylated products of similar acetyl contents are compared, it will be observed that all samples when first pretreated with either a mercerizing solution or methylamine had higher moisture uptakes than acetylated scoured cotton.

In the case of the sodium hydroxide treatment the effect of water as the washing medium becomes quite obvious when the moisture regains of the different treatment types are compared. If the swollen material is extracted with water, recrystallization and collapse of part of the disordered fiber regions occurs, leading to a decline in the accessibility for water vapor. By extraction of alkali with ethanol instead of water, greater accessibility after swelling is retained since the ethanol washing does not appear to promote crystallization. It will be noted that the acetylated sorption ratio of either MEP or AMEP is higher than the sorption ratio of the nonacetylated mercerized cotton. Also, even though some of the hydroxyl groups present in the cotton cellulose have been acetylated, the moisture regain of MEP or AMEP with acetyl contents of 11% are higher than that of the unacetylated mercerized product. Thus,

it appears that acetylation has enabled the product to retain at least part of the high accessibility which it had in the swollen state. We have made similar observations before on the retention of high accessibility when samples are acetylated in the swollen state.^{5,8,9}

The acetylated MeCP sample had a moisture regain comparable to those of the acetylated MWP, MEP, or AMEP samples. As expected, reduction of accessibility was caused by drying the methylamine-treated material before acetylation. As in the case of the acetylated scoured cotton, the acetylation of the MeCD samples entailed a decrease in the accessibility for water vapor. Nevertheless, the regain of the acetylated MeCD sample is higher than that of the scoured cotton cellulose with an almost equivalent acetyl content. Although the reactivity to acetylation of MeCD was less than that of the starting cotton, the swelling in the amine had disrupted the structure of the fiber considerably and the disruption was maintained in the final product.

Thermal Analysis of the Acetylated Samples

Previous studies have shown that the thermal properties of cotton fibers depend on crystallinity and lattice type of the sample.^{14,16} Usually, after moisture has been desorbed, one major endotherm between 330 and 360°C is observed, which results from the decomposition of the cellulose. Its peak shifts towards lower temperatures upon transformation of cellulose I to cellulose II or III, as well as when the crystallinity of the sample is lowered. If a certain level of disorder is exceeded, a drastic change in the DTA curve will occur: the endotherm is replaced by a series of small exotherms due to a different decomposition mechanism.¹⁴

In agreement with previous work the peak temperature of the nonacetylated samples decreased from 345°C for the scoured control to 322°C and 326°C for the dried mercerized and the dried methylamine-treated samples (MWD, MeCD), respectively (Table IV).

Irrespective of the type of pretreatment, the decomposition temperature shifted to higher values upon acetylation. While the increase was insignificant when intermediate drying of the samples was involved (cf. MWD, MeCD samples, Table IV), it was considerably higher in the case of the material which had not been dried before acetylation, namely the MEP and MeCP samples.

Focusing on the MEP products, the amount of acetyl groups in the fibers obviously does not have any impact on the decomposition temperature. Even

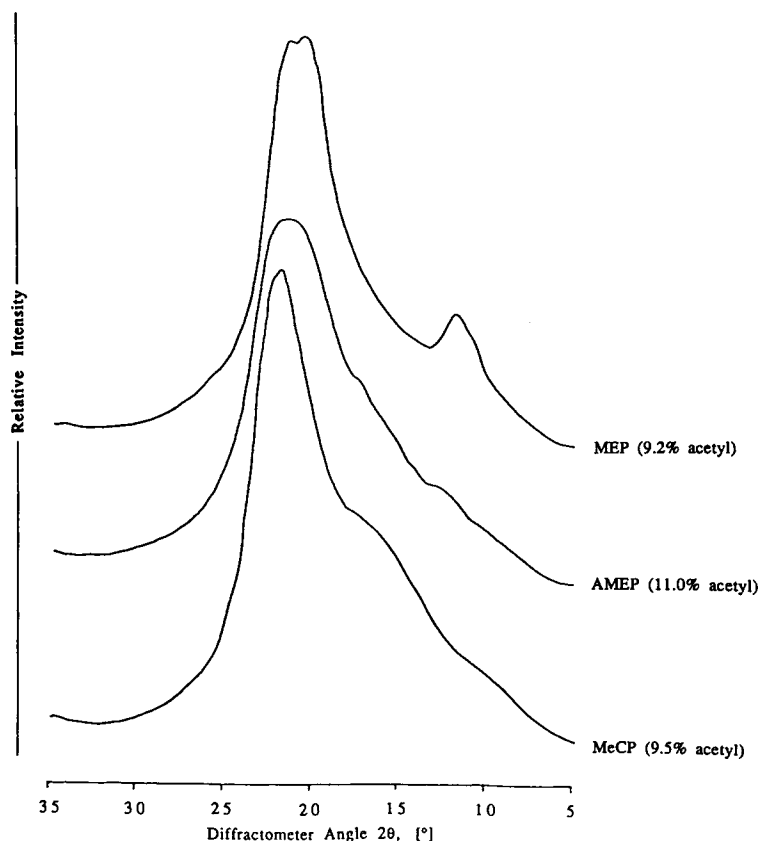


Figure 6 X-ray diffractogram of an acetylated mercerized sample, where the mercerizing solution contained 20% absolute ethanol (AMEP), compared to an acetylated mercerized and an acetylated methylamine-treated sample. (MEP = mercerized, ethanol-washed, pyridine-treated; MeCP = methylamine-treated, chloroform-washed, pyridine-treated).

at 34.1% acetyl content, the peak temperature of the decomposition endotherm had not changed within the margins of error although the onset temperature was lower. In addition, for the thermal properties of the samples, it does not seem to make any difference if the mercerizing solution contained any ethanol (cf. AMEP and MEP samples in Table IV).

The most interesting results were obtained from the MeCP sample with 38.8% acetyl content. In Figure 8 the DTA curves of this sample, as well as of the deacetylated material, are set against those of the scoured control and of commercial diacetate. If compared to the scoured control the major endothermic decomposition peak of the MeCP sample is reduced in height, while weak and very broad exothermic peaks are observed at lower temperatures. The DTA curve of the MeCP sample did not show any similarity to commercial diacetate (cf. Fig. 8) even though the acetyl contents were comparable. This may be due to differences in the method of

forming these products. In the case of the commercial sample a highly acetylated cellulose is deacetylated in solution to the appropriate acetyl content whereas in the case of the MeCP fiber the acetylation was performed on a swollen sample of cellulose. Thus it is likely that the acetyl groups are more uniformly located throughout the commercial sample. It is also likely that the distribution of acetyl groups on the C-2, C-3, and C-6 hydroxyl groups of the cellulose differ in the two cases. The highly disordered structure of this MeCP sample, as indicated by X-ray diffraction, became visible after deacetylation and it will be observed that the DTA curve of this product consists of a series of exothermic peaks. As stated above such peaks are typically found when cellulose of low crystallinity is pyrolyzed.¹⁴

Tensile Properties

From the macroscopic point of view, a loss in crystallinity of cotton by swelling treatments may be

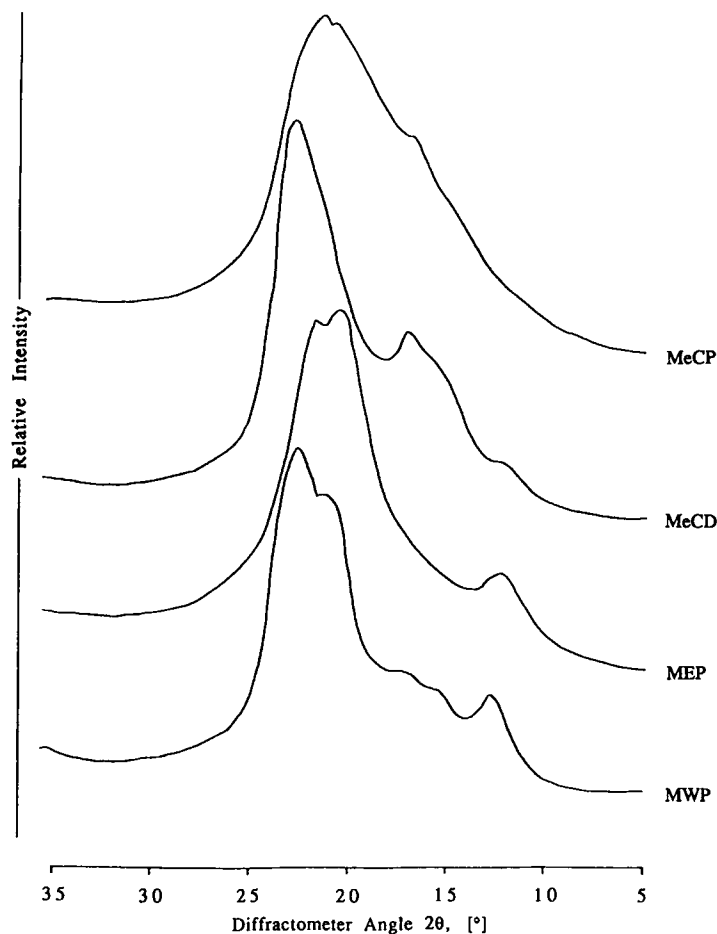


Figure 7 X-ray diffraction patterns after deacetylation of the never-dried samples with the highest attainable acetyl content under the applied reaction conditions (MWP = mercerized, water-washed, pyridine-treated; MEP = mercerized, ethanol-washed, pyridine-treated; MeCD = methylamine-treated, chloroform-washed, dried; MeCP = methylamine-treated, chloroform-washed, pyridine-treated).

indicated by an increase in the breaking strength and extensibility of the products, because the increased disorder permits greater flexibility of the chain molecules. Also the treatment allows some alleviation of the internal stresses present in the fibers.¹¹ If this hypothesis is correct then it is possible that the effect of the pretreatment will be reflected in the tensile properties of the acetylated fibers. The test results of single fiber breaking load and elongation at break for samples of low acetyl content and with different pretreatment history are summarized in Table V.

The changes in tensile strength and extensibility of the scoured cotton were insignificant after acetylation to 8.8% acetyl content, indicating that the acetylation had not affected the tensile properties of the product.

As expected, the strength and extensibility of the scoured cotton were increased markedly by mercerization.¹¹ The MWP sample of 11.5% acetyl content maintained its breaking load and extensibility when compared to the nonacetylated mercerized product. Thus once again, acetylation did not appear to have a detrimental effect on tensile properties. A significant improvement in strength and extensibility was obtained when ethanol was used instead of water as the washing medium. Comparing the properties of samples with progressively increasing acetyl content in the MEP series (Table V) it can be observed that strength and extensibility pass through a maximum. At the peak the acetylated products have markedly increased strength and extensibility. Relative to nonacetylated mercerized cotton the strength and extensibility are higher by 20% and 28%, respec-

Table III Influence of the Pretreatment on the Hygroscopicity at 65% R.H. and 21°C of Cotton Cellulose with Comparable Acetyl Content

Treatment ^a	Acetyl Content (%)	Moisture Regain (%)	S.R. ^b	A.S.R. ^c
Scoured Control	0.0	7.13	1	—
MWD	0.0	10.88	1.52	—
MeCD	0.0	9.45	1.33	—
Scoured	11.6	5.32	—	1
MWP	11.5	10.43	—	1.96
MEP	11.1	11.64	—	2.19
AMEP	11.0	12.75	—	2.40
MeCD	13.9	8.24	—	1.55
MeCP	11.5	11.87	—	2.23

^a Treatment codes are given in Table I.

^b S.R. = sorption ratio where

$$\text{S.R.} = \frac{\text{moisture regain of cellulosic sample}}{\text{moisture regain of cotton at the same R.H. and temp.}}$$

^c A.S.R. = sorption ratio of the acetylated products where

$$\text{A.S.R.} = \frac{\text{moisture regain of acetylated product}}{\text{moisture regain of acetylated scoured cotton of comparable acetyl content at the same R.H. and temp.}}$$

tively, and relative to the starting cotton an increase of 68% and 126%, respectively, is obtained. The number of cellulosic hydroxyl groups that are blocked with acetyl groups seems to be the factor deciding the tensile properties for fibers which had initially received a mercerization treatment. At low acetyl contents the ester groups maintain a low degree of crystallinity in the samples which is favorable in terms of the tensile properties. At higher acetyl contents it appears that interchain hydrogen bonding, which, it is proposed is contributing to fiber strength, has been reduced to such an extent that the tensile strength decreases.

Surprisingly the presence of ethanol in the mercerization solution, which was beneficial to the decrystallization of the products as shown by X-ray diffraction, does not improve the tensile properties of the acetylated fibers in the same way. While the elongation at break was maintained, the breaking strength of AMEP of 11% acetyl content decreased slightly compared to the nonacetylated MWD fibers, and an overall drop in strength and extensibility is observed when compared to the acetylated MEP samples.

Table IV Differential Thermal Analysis Data of Acetylated Cotton Cellulose

Treatment ^a	Acetyl Content (%)	Endothermic Peaks		Exothermic Peak Temp. (°C)
		Peak Temp. (°C)	Onset-Temp. (°C)	
Scoured	0.0	345	329	
	8.8	349	338	
MWD	0.0	322	301	
	5.0	326	305	
MWP	11.5	355	334	
MEP	9.2	338	314	
	11.1	342	322	
AMEP	12.8	341	320	
	27.6	340	320	
	34.1	337	299	
	11.0	336	309	
MeCD	0.0	326	304	
	13.9	333	310	
MeCP	9.5	339	316	
	13.5	330	318	
	38.8	359	348	
Deacetylated MeCP	0.0			216
				242
				305
Diacetate	40.0	204		360
		231		

^a Treatment codes are given in Table I.

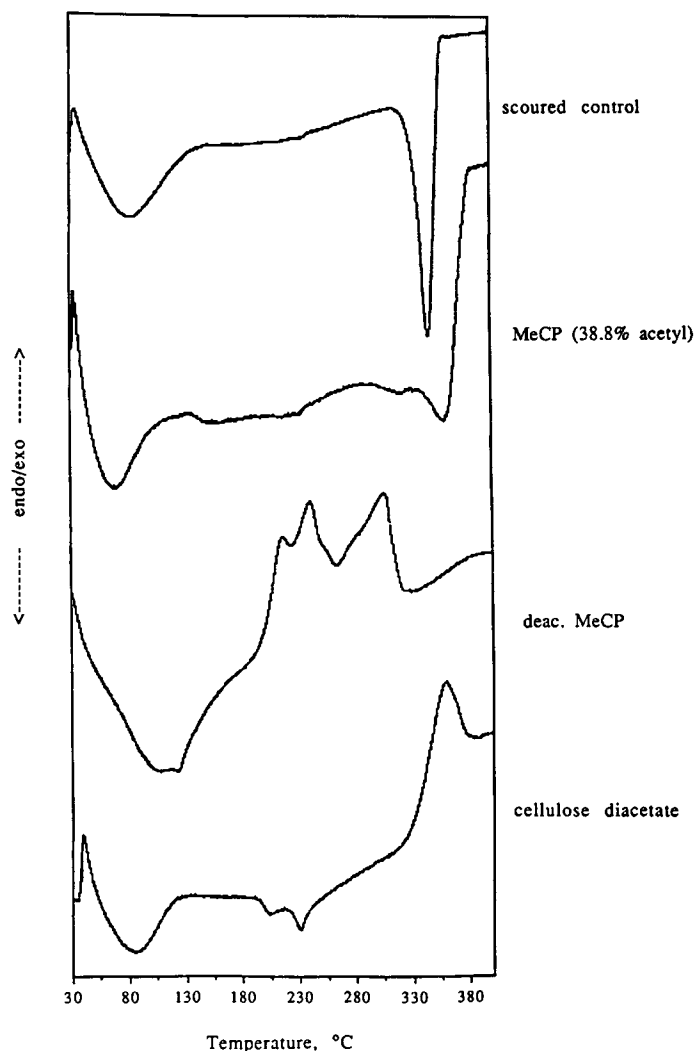


Figure 8 DTA curves of the scoured control, the methylamine-treated, chloroform washed and pyridine exchanged sample, acetylated (MeCP) and deacetylated (deac. MeCP), and the commercial diacetate.

The breaking strength of the nonacetylated methylamine-treated samples (MeCD), compared to the scoured control, remained unchanged, but extensibility increased by 62%. While an elongation at break of about 11% was maintained, the breaking load of MeCD improved considerably upon acetylation. However, the strength level of the nonacetylated MWD sample was not achieved.

The effect of solvent exchange and acetylation compared to drying of the material followed by acetylation becomes quite obvious when the acetylated MeCD and MeCP samples are compared. The MeCP treatment yielded higher breaking loads than attained with the MeCD process. However, the extensibility of these samples was slightly lower (Table V). It will be recalled that relative to nonacetylated

MeCD the crystallinity of acetylated MeCD remained unchanged while that of acetylated MeCP was lower. Compared to the nonacetylated MWD fibers, low acetyl content MeCP samples had similar strength but the extensibilities were slightly less. However at low acetyl contents, the strengths and extensibilities obtained with acetylated MEP products were superior to those obtained by acetylation after the MeCP process, even though the diffractometer tracings of the latter products indicated lower crystallinity.

It appears therefore that the relation between crystallinity and tensile properties is complex. One possible explanation for the higher strength of acetylated MEP samples when compared to MeCP samples of similar low acetyl contents is that the mer-

Table V Tensile Properties of the Acetylated Samples

Treatment ^a	Acetyl Content (%)	Breaking Load (mN) ^b	Elongation at Break ^b (%)
Scoured	0.0	41.3 (2.1)	6.8 (0.4)
Scoured	8.8	44.6 (2.8)	6.0 (0.4)
MWD	0.0	58.1 (2.6)	12.0 (0.6)
MWP	11.5	58.6 (2.7)	13.1 (0.6)
MEP	6.8	62.6 (2.1)	14.4 (0.6)
	8.6	68.7 (2.4)	14.6 (0.6)
	9.2	69.7 (2.9)	15.4 (0.8)
	34.1	44.7 (1.5)	13.8 (0.7)
AMEP	11.0	54.4 (2.7)	12.8 (0.6)
MeCD	0.0	41.5 (2.4)	11.0 (0.5)
	9.6	47.9 (2.7)	10.3 (0.5)
	13.9	52.3 (2.9)	11.0 (0.5)
MeCP	9.5	57.8 (3.2)	9.1 (0.5)
	11.5	55.5 (3.3)	10.5 (0.6)
	38.8	62.6 (3.2)	10.1 (0.6)

^a Treatment codes are given in Table I.

^b Standard errors in brackets.

cerization treatment swells the fibers more than methylamine and thus disorients the low order regions more. The subsequent higher extensibilities of the acetylated MEP products on application of a tensile force permits increased orientation of the crystalline regions of the fibers before fracture occurs and consequently higher strength.

It is interesting to note also that the breaking load of the MeCP sample with 38.8% acetyl content was distinctly superior to the MEP sample with 34.1% acetyl. The reason for this is not known at this time.

CONCLUSION

Both sodium hydroxide solution of mercerizing strength and anhydrous methylamine are suitable pretreatments for enhancing the reactivity of cotton cellulose if the fiber is maintained in the never-dried state after the swelling treatment. Extraction by organic solvents is to be preferred over water-washing when removing the swelling agent.

The crystallinity of cotton is further lowered and its accessibility is further increased if, after a swelling treatment to raise its reactivity, it is acetylated a small amount (ca. 9 to 11% acetyl content) before it is dried.

The tensile properties of acetylated cotton with acetyl contents of approximately 9 to 11% are considerably improved if acetylation is preceded by mercerization with subsequent solvent exchange and less so if it is preceded by methylamine swelling followed by solvent exchange.

REFERENCES

1. J. O. Warwicker, R. Jeffries, R. L. Colbran, and R. N. Robinson, *A Review of the Literature on the Effect of Caustic Soda and other Swelling Agents on the Fine Structure of Cotton*, Shirley Institute Pamphlet No. 93, Shirley Institute, Manchester, England, 1966.
2. S. H. Zeronian, in *Cellulose Chemistry and Its Applications*, T. P. Nevell and S. H. Zeronian, Eds., John Wiley & Sons, New York, 1985, p. 159.
3. L. Loeb and L. Segal, *Text. Res. J.*, **24**, 654 (1954).
4. N. I. Klenkova, O. M. Kulakova, and L. A. Volkova, *J. Appl. Chem. USSR*, **36**, 155 (1963).
5. S. H. Zeronian, *J. Appl. Polym. Sci.*, **14**, 365 (1970).
6. A. K. Kulshreshtha and N. E. Dweltz, *J. Appl. Polym. Sci.*, **21**, 2085 (1977).
7. L. Segal, *Decrystallized Cotton*, Merrow Monographs, Merrow Publishing Co., Watford, U.K., 1971.
8. T. P. Nevell and S. H. Zeronian, *Polymer*, **3**, 187 (1962).
9. S. H. Zeronian, *J. Appl. Polym. Sci.*, **9**, 313 (1965).
10. N. I. Klenkova, O. M. Kulakova, N. A. Matveeva, and L. A. Volkova, *J. Appl. Chem. USSR*, **38**, 906 (1965).
11. S. H. Zeronian, *J. Appl. Polym. Sci. Appl. Polym. Symp.* **47**, 445 (1991).
12. R. Jeffries, *J. Appl. Polym. Sci.*, **12**, 425 (1968).
13. O. Ant-Wuorinen and O. A. Visapaa, *Norelco Repr.*, **9**, 48 (1962).
14. K. E. Cabradilla and S. H. Zeronian, in *Thermal Uses and Properties of Carbohydrates and Lignins*, F. Shafizadeh, K. V. Sarkanen, and D. A. Tillman, Eds., Academic Press, New York, 1976, p. 73.
15. R. Nelson and D. W. Oliver, *J. Polym. Sci., C*, **36**, 305 (1971).
16. K. E. Cabradilla and S. H. Zeronian, in *Modified Cellulosics*, R. M. Rowell, and R. A. Young, Eds., Academic Press, New York, 1978, p. 321.

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