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THE TEMPERATURE DEPENDENCE OF ELECTRICAL CONDUCTIVITY OF COTTON CELLULOSES IN CORRELATION WITH THEIR CRYSTALLINE STRUCTURE

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ABSTRACT

In the present study, the electrical conductivity of ball-milled and NaOH-treated cotton cellulose was measured in vacuum as a function of temperature. The activation energies, ΔE, of the samples were calculated. It was found that σ increases while ΔE decreases linearly with increase of the amorphous content of the mechanically decrystallized samples. It was noted that treatment of cotton fibres with 10% NaOH solution for 12 min at 27°C reduces the value of σ and produces no appreciable changes in the ΔE value. Continued increase in NaOH concentration to 14, 18, 22, 26 and 30% resulted in a progressive increase in σ values and decrease in ΔE values. These results were compared with the resolutions of the peaks of the X-ray diffraction patterns and the crystallinity index determined from infrared measurements. It was concluded that the electrical conductivity measurements could be considered as a precise and rapid method of following small changes in crystalline structure resulting from mechanical or chemical treatments.

INTRODUCTION

It is well known that static charges built up on textile materials cause a variety of problems in the textile industry [1–3]. The limiting conditions for high static charges and, hence, the susceptibility to problems in use has been shown to depend on the resistance of the material; the number of problems increase with increasing resistance with the very high-resistance synthetic fibres giving most problems.

Actually, moisture content, moisture distribution, ion concentration, chain length, ash, density and species are the most important factors influencing the d.c. resistance of textile fibres. It was found that the resistance of fibres

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is extremely sensitive to the amount of moisture which they contain [1–7]. Thus, one way of avoiding static charges is to operate in a damp atmosphere. But the humidities which would be needed for work with high resistance fibres are not practical because they would be unpleasant to operatives, damaging to machinery and expensive or difficult to maintain. Other methods of dissipating charges can be used.

However, the textile industry still needs cotton fibres. In recent years, physical and/or chemical modifications of the native fibre to impart new or improved properties have become a major factor in cotton utilization. Mercerization is a well-known technique for enhancing certain physical properties of cotton fibres [8–12]. In this technique, which involves the swelling of cotton in caustic soda, varying degrees of structural change take place with regard to transformation of cellulose I to cellulose II, molecular orientation and crystallinity. A high degree of lustre, high strength and better dyeability are also achieved. In fact, a quite detailed study of the effect of structural and physical modifications of cotton fibres brought about by mercerization or mechanical treatments on the electrical resistance or conductivity has not yet been fully explored. Therefore, the present work was undertaken to study quantitatively the effect of crystalline structure on the electrical conductivity of cotton celluloses.

EXPERIMENTAL

Fibres of Giza 66 were first washed with hot ethanol, then boiled with a solution of 1% NaOH for 25 h, washed with bidistilled water and dilute acetic acid, neutralized with dilute NH_4OH and finally washed several times with twice-distilled water.

The dried fibres were cut into small pieces and then ground in a hardened stainless steel vial containing two hardened stainless steel balls. This vial was especially manufactured by Spex for this purpose. The vial was fitted to a Spex mixer mill which was rotated several times for short periods. The powder obtained was then sieved to particle size fractions of different particle sizes.

The powder was immersed in NaOH solution of various concentrations at room temperature (27°C) for 12 min. The material: liquor ratio was 1 : 50. The powder was then washed with distilled water and then treated with 1% acetic acid solution for 5 min.

The conductivity measurements were carried out on the investigated samples using a d.c. electrometer of type TR-150 I (Orion-K.T.V., Budapest). A sample holder or conductivity cell, made from pyrex tube was used. The pyrex tube was provided with a ground joint to be connected to a detachable head through which one electrical lead passed by way of a tungsten rod to the glass seals. In a diametrically opposite side of the tube, the second lead was spot welded and sealed in glass via a tungsten rod. The two electrodes were made of platinum. The conductivity cell with the specimen inside could be evacuated well by means of an upper tube leading from the ground joint.

The samples used in the measurements were pressed into cylindrical pellets at a pressure of about 200 kg cm^{-2}. This pressure was chosen as it was found that below it, the electrical conductivity depends on pressure.

KBr disks were prepared from the treated samples. The infrared spectra were recorded on a Beckman spectrophotometer. The X-ray diffraction patterns were obtained on a Siemons U500 diffractometer. The powder was filled in the specimen holder and all the samples were subjected to the same pressure.

RESULTS AND DISCUSSION

Measurements of electrical conductivity, σ, were carried out on samples of cotton powder of particle-size diameter ranging from 0.07 to 0.46 mm in the form of compressed disks. Values of σ were measured at different temperatures from 476 to 333 K and in vacuum. The variation of log σ for the various samples with the reciprocal of absolute temperature ($1000/T$) is shown in Fig. 1.

As can be seen from Fig. 1, the conductivity increases with decreasing particle size. The conductivity of the sample of largest particle size, for example, assumes a value of the order $-11.5\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 375 K, whereas, that of the smallest particle size is of the order $-10.7\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at the same temperature.

Since there is a positive temperature coefficient of electrical conductivity ($\mathrm{d}\sigma/\mathrm{d}T$) for all curves, all the investigated specimens have a semiconducting character in the temperature range investigated. The conductivity varies exponentially with absolute temperature according to the well-known relation [13]

$$\sigma = \sigma_0\ \mathrm{e}^{-\Delta E/2kT}$$

where σ is the electrical conductivity at a given temperature T, σ_0 is the initial conductivity, ΔE is the activation energy for conduction and k is the Boltzmann constant. From this linear relationship, the activation energy, ΔE, was calculated. The relatively slight response of σ with temperature involves ΔE values which can be interpreted by a simple single-band model. The variation of log σ (measured at 100°C) and ΔE with the particle size is represented graphically in Figs. 2 and 3, respectively. It is evident from Figs. 2 and 3 that log σ decreases while ΔE increases linearly with the increase of particle size. This will be discussed later using the results from IR measurements.

The electrical conductivity was compared with the degree of crystallinity

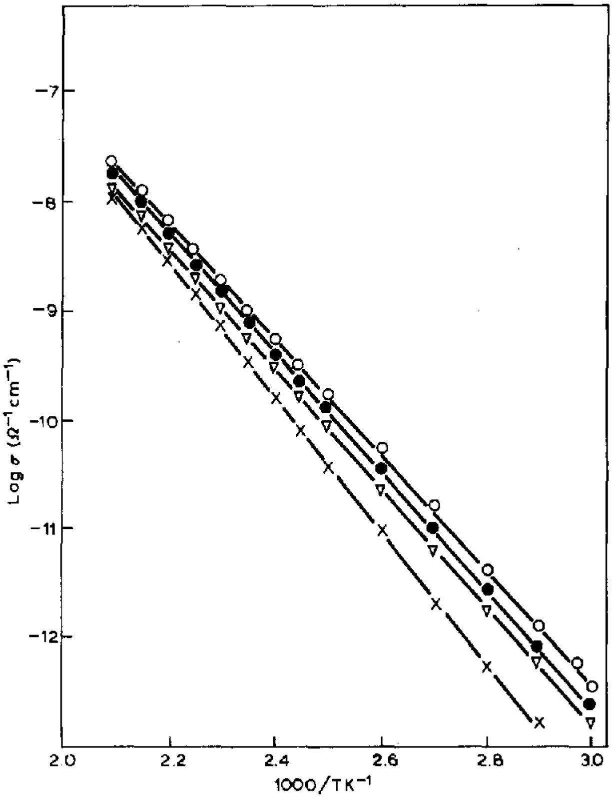

Fig. 1. Variation of the electrical conductivity of the ball-milled cotton fibres with temperature. ⊙, 0.461 mm; Δ, 0.252 mm; ●, 0.167 mm; O, 0.070 mm.

as measured by IR methods. The IR method of the determination of the degree of crystallinity is based on the interpretation that the crystalline regions in a cellulosic material give rise to specific absorption bands, while the non-crystalline regions give rise to characteristic absorption bands. However, the infrared ratio *a* 1375 cm^{-1}/*a* 2900 cm^{-1} proposed by Nelson [14] for measuring crystallinity (*Cr*) in cellulosic materials was measured for the samples analyzed. The variation of ΔE and log σ_{100} with particle size and *Cr* is shown in Table 1. Relationships between *Cr* and log σ_{100} and ΔE are represented graphically in Figs. 3(a) and 3(b) respectively. It appears from Figs. 3(a) and 3(b) that log σ increases linearly while ΔE decreases linearly as *Cr* increases.

The variation of σ and ΔE with particle size could be attributed to a decrease in the degree of crystallinity or to the extension and formation of amorphous regions in crystalline cotton as a consequence of which there is an increased freedom of movement of the side groups and of portions of the cellulose molecules. This is in agreement with the fact that the current will be

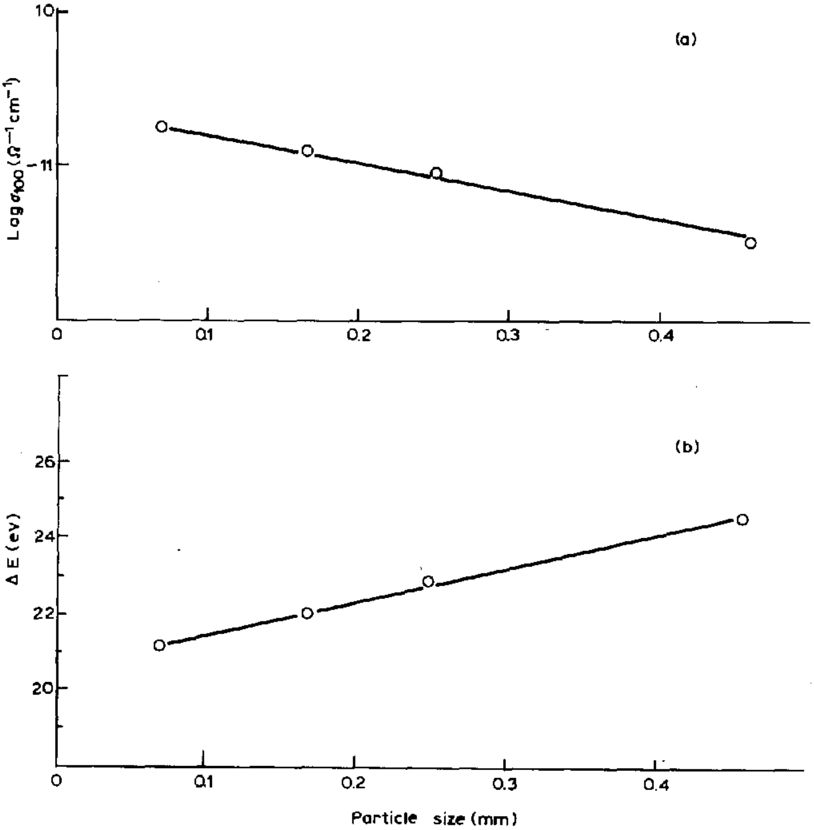

Fig. 2. (a) Variation of log σ_{100} with the particle size of cotton fibres. (b) Variation of the activation energy with the particle size of cotton fibres.

flowing in the non-crystalline regions of the fibres [1–3]. Indeed, the ordered arrangements of cellulose materials in crystalline regions would be expected to be highly insulating.

These considerations lead to the conclusion that conductivity measure-

TABLE 1

Variation of ΔE and log σ_{100} with particle size and IR crystallinity index (*Cr*) of cotton cellulose

ΔE(eV)	2.91	2.74	2.67	2.59
log σ_{100} (Ω^{-1} cm^{-1})	−11.5	−11.02	−10.9	−10.7
Particle size (mm)	0.46	0.252	0.167	0.07
Cr	1.66	1.60	1.50	1.30

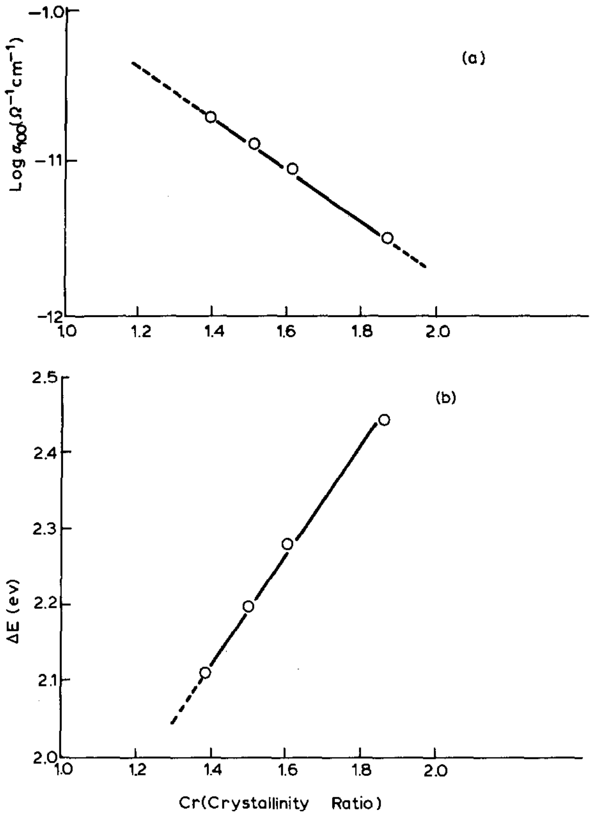

Fig. 3. (a) Relationship between the crystallinity ratio, *Cr*, and the electrical conductivity of the ball-milled cotton samples. (b) Relationship between the crystallinity ratio, *Cr*, and the activation energy of the ball-milled cotton fibres.

ments may be used to follow small and rapid changes in crystalline content arising from mechanical treatments.

Samples of cotton powder of the same particle size (0.167 mm in diameter) were immersed in aqueous NaOH solutions of various concentrations, namely, 10, 14, 18, 22, 26 and 30% (w/w) for 12 min at room temperature (27°C). The electrical conductivity was then measured at different temperatures. The results are shown in Fig. 4.

Log σ_{100} values were calculated and are given in Table 2. The variation of log σ_{100} values with NaOH concentration is represented graphically in Fig. 5(a). It appears from this relation that log σ_{100} initially decreases after treating with 10% NaOH solution and then increases as the concentration of NaOH is increased to 14%, but its value is still lower than that for native celluloses. Increasing the NaOH concentration up to 18, 22, 26 and 30% results in a progressive increase of log σ.

The ΔE values of the treated samples are given in Table 2 and their

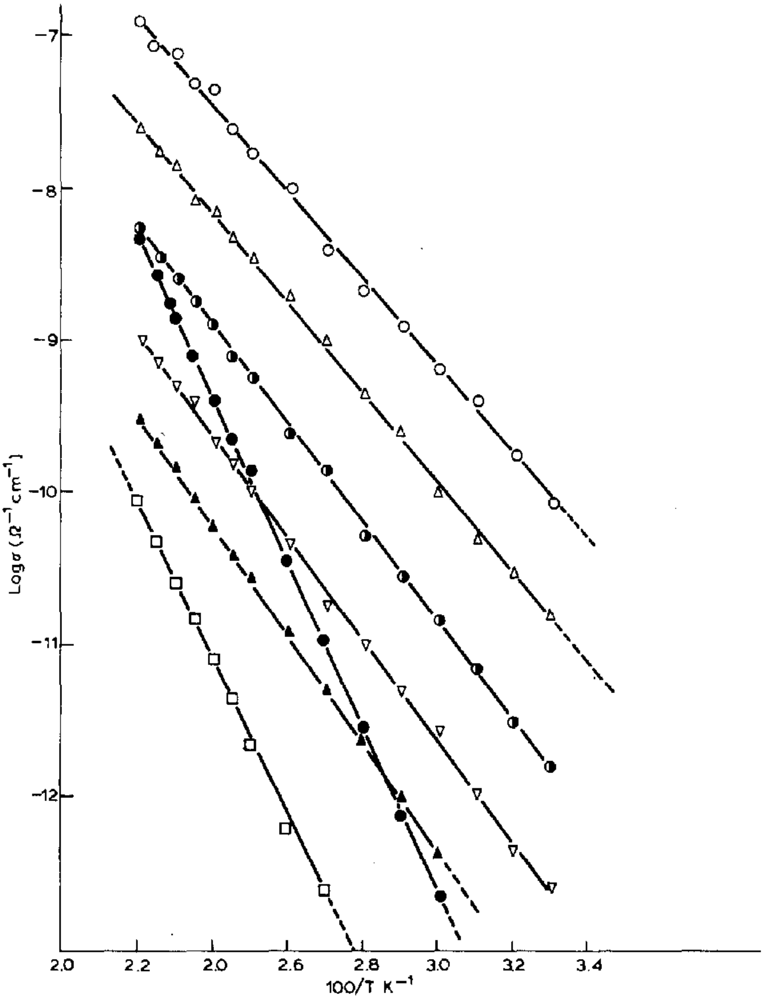

Fig. 4. Relationship between the electrical conductivity of the mercerized cotton fibres and temperature. ●, Purified cotton; □, 10% NaOH; ▲, 14% NaOH; ⊿, 18% NaOH; ⊙, 22% NaOH; △, 26% NaOH; ○, 30% NaOH.

TABLE 2

Variation of ΔE and log σ_{100} with the resolution (R) of XRD peaks and the infrared crystallinity index, *Cr*, of native and mercerized cotton cellulose

	Concentration of NaOH(%)						
	Native	10	14	18	22	26	30
ΔE(eV)	2.67	2.69	1.775	1.64	1.54	1.72	1.78
Log σ_{100} (Ω^{-1} cm^{-1})	−10.9	−11.65	−11.2	−10.65	−9.73	−8.15	−8.97
R	2.40	2.80	2.81	2.64	2.52	2.73	2.79
Cr	1.69	1.42	1.42	0.73	0.69	0.81	1.10

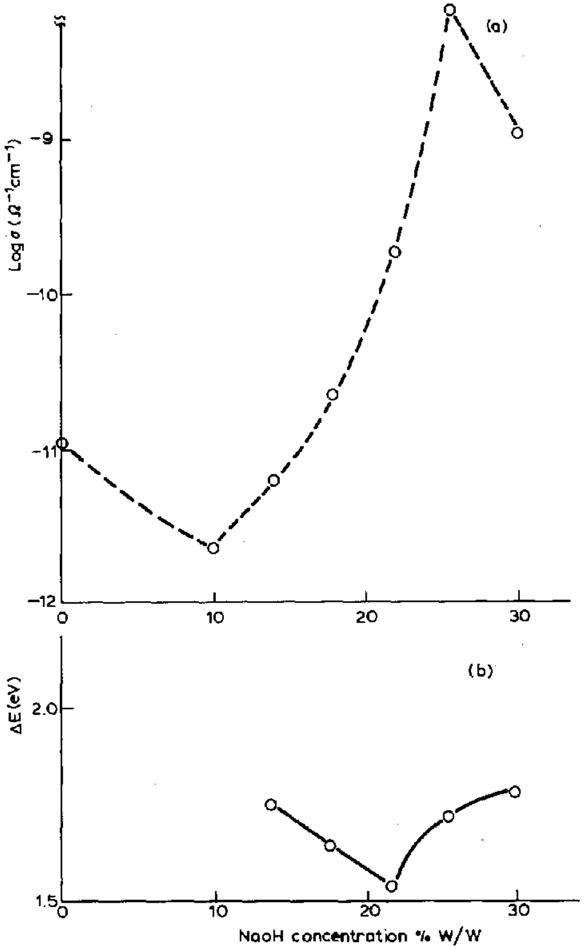

Fig. 5. (a) The variation of log σ_{100} as a function of NaOH concentration. (b) The variation of ΔE values as a function of NaOH concentration.

variation with the NaOH concentration is illustrated in Fig. 5(b). It can be easily seen from Table 2 and Fig. 5(b) that treatment of cotton cellulose with 10% NaOH solution produces no changes in activation energy while treatment with 14% NaOH solution causes a considerable decreases in ΔE values. Continued increases of NaOH solution to 18, 22, 26 and 30% further decreases the ΔE values.

The X-ray diffraction patterns (XRD) of these samples are given in Fig. 6. As can be clearly seen from this figure, the diffractogram of purified cotton displays the (101), $(10\bar{1})$ and (002) diffraction peaks at 2θ values of 14.80, 16.5 and 22.6°, respectively, which are characteristic of the cellulose I lattice [4,10]. On the other hand, the X-ray diffractograms of each sample pretreated with 14, 22, 26 and 30% NaOH solutions show these peaks at 2θ

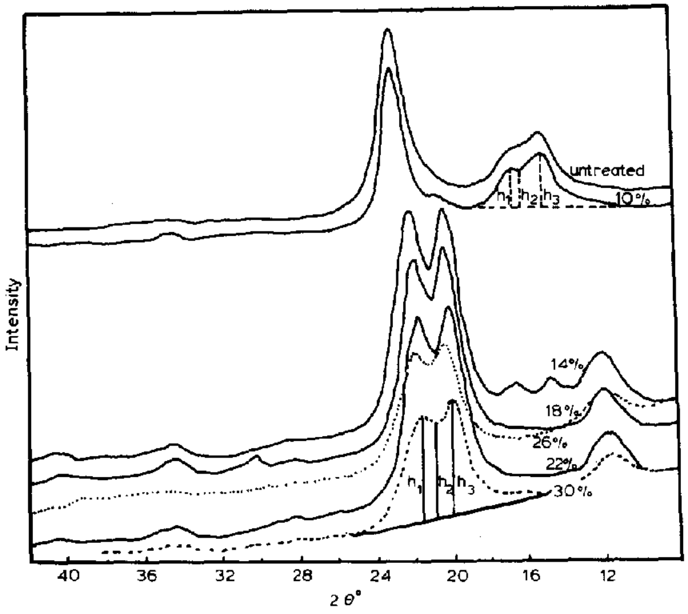

Fig. 6. The X-ray diffraction (XRD) patterns of NaOH-treated cotton fibres.

values of 12, 20.2 and 21.8° which are characteristics of the cellulose II lattice [4,10]. It can be seen from Fig. 6 that the sample treated with 10% NaOH solution indicates the presence of cellulose I in addition to a small fraction of cellulose II. The peaks in the X-ray diffraction patterns of the sample treated with 14% NaOH solution indicate that this sample is a mixture of cellulose lattice types I and II.

The resolution (R) of the (101) and $(1\bar{0}1)$ peaks of the XRD scan of cellulose I and that of (101) and (002) peaks of cellulose II were determined for the samples under investigation by using the relation [15]

$$R = \frac{h_1 + h_3}{h_2}$$

where, for cellulose I, h_1, h_2 and h_3 are the peak heights at 2θ values of 16.5, 15.8 and 14.8°, respectively, in the scan above a background line drawn connecting the points at 2θ values of 10 and 18° (Fig. 6). For cellulose II, h_1, h_2 and h_3 are the peak heights at 2θ values of 21.8, 20.9 and 20.2°, respectively, in the scan above a background line drawn connecting the points at 2θ values of 8 and 28° (Fig. 6). The R values determined are given in Table 2.

As established graphically, it is evident that ΔE increases linearly as R values increase and this means that ΔE correlates well with R.

The infrared absorption spectra of the mercerized samples are illustrated in Fig. 7. The infrared spectrum of cellulose I shows three absorption bands

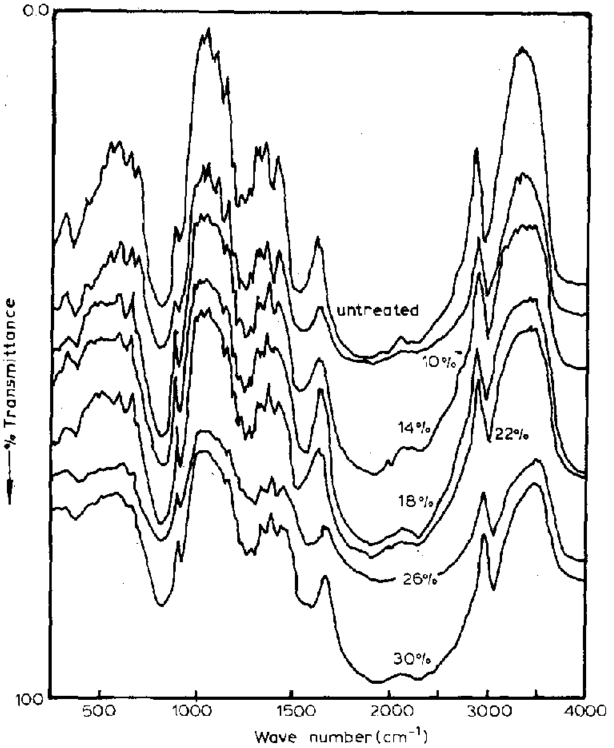

Fig. 7. The infrared (IR) absorption spectra of untreated (native) and NaOH-treated cotton samples.

in the 3μ region corresponding to H-bonded hydroxyl groups, while that of cellulose II shows another three bands in the same region. The spectrum of the mixed-lattice structures exhibits five bands in the same region. Further marked differences can be found between the spectra of the treated samples in the region between 900 and 1500 cm^{-1}. However, when the infrared ratio a 1435 cm^{-1}/a 900 cm^{-1} taken by O'Connor et al. [15] as a measure of the degree of crystallinity (Cr) of cotton was applied, the variation of ΔE with Cr (as established graphically) was found to deviate slightly from linearity.

It is generally accepted that mercerization causes varying degrees of structural change in the phase transformation of cellulose I to cellulose II, molecular orientation and degree of crystallinity. Pandy and Lyengar [8] stated that cellulose crystallinity was reduced to a certain extent by treatment with NaOH solution. Patil et al. [9] pointed out that NaOH in aqueous solution acts as a decrystallizing agent at all concentrations in excess of 20%. Shenouda and Happy [10] observed that treatment of cotton fibres with 10% NaOH solution brings about a small increase in the amorphous fraction in the sample without formation of cellulose II. Furthermore, they pointed out that the decrease by 13.4% of the cellulose I fraction on treating the control with 11% NaOH solution is made up of an increase of 7.9% of the amorphous materials and an increase of only 5.5% of the cellulose II fraction, indicating that the conversion of the cellulose I fraction into amorphous regions predominates over the transformation to cellulose II fraction. They further stated that this order is reversed for higher concentrations. Besides these considerations different authors have shown that strong hydrogen bonds are formed as a result of alkali treatment if the fibre is surrounded by an outer layer strong enough to exert a restrictive influence on the swelling of the fibre and the cotton fibre has a comparative strong outer-layer. These strong hydrogen bonds should be mainly interfibrullar or intermolecular.

CONCLUSION

From the data obtained, it could be concluded that the measurement of the electrical properties of cotton celluloses could be considered as a precise and rapid method of following small changes in crystalline structure resulting from mechanical or chemical treatments. Moreover, conductivity, X-ray and IR studies could be successfully used to differentiate cellulose I from cellulose II and to evaluate the optimum conditions for cotton in industry.

REFERENCES

1 J.W.S. Hearle, J. Text. Inst., 48 (1957) 40.
2 W.E. Morton and J.W.S. Hearle, Physical Properties of Textile Fibres, Wiley, New York, 1975.
3 J.W.S. Hearle, J. Text. Inst., 44 (1953) 117.
4 J.E. Algie and I.C. Watt, Text. Res. J., 35 (1965) 922.
5 M. Hartel, G. Kassmell, G. Maneche, W. Willie, D. Wahrle and D. Zerpner, Angew. Makromol. Chem., 29/30 (1973) 307.
6 E.P. Goodings, Q. Rev., 95 (1976) 95.
7 H.F. Vermeas, Halgforschung, 29 (1975) 4.
8 S.N. Pandey and R.L.N. Iyengar, Text. Res. J., 39 (1969) 15, 23.
9 N.B. Patil, N.F. Dweltz and T. Radhaknishnan, Text. Res. J., 35 (1965) 517.
10 G.S. Shenouda and J. Happy, Appl. Polym. Sci., 20 (1976) 2069.
11 B. Kyrklund and H. Sihtola, Pap. Timber, 49 (1963) 275.
12 E.K. Baylstin and J.J. Helert, Text. Res. J., 49 (1979) 317.
13 K.A. Alzewel, M.M. Abou Sekkina and Z.M. Hanafi, Z. Phys. Chem. N.F., 94 (1975) 235.
14 M.L. Nelson, J. Appl. Polym. Sci., 8 (1964) 1311.
15 R.T. O'Connor, R.F. Dupre and D. Mitchun, Text. Res. J., 28 (1958) 382.