FTIR Spectroscopic Study of the Effect of Microwave Heating on the Transformation of Cellulose I into Cellulose II during Mercerization

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ABSTRACT: Fourier transform infrared (FTIR) spectroscopy techniques were used in the study of the effect of microwave (MW) heating on the structural properties of cotton fibers and on the mercerization mechanism of these fibers. Samples of the fibers were microwave heated for different times and different microwave powers. Also, mixtures of cotton fibers and aqueous solution of NaOH with different concentrations were exposed to microwave radiation for different times and different powers. It was found that microwave heating of cotton fibers under these experimental conditions causes no observable changes in their spectral features apart from slight changes in the intensities of the absorption bands. The determined values of the absorbances ratio A1375 cm^{-1}/A2900 cm^{-1} revealed that microwave heating for short periods and at low powers decreases the crystallinity of cotton as the result of the drying effect of microwave heating, while microwave heating for longer periods and at higher power results in recrystal-

lyzation of the fibers. The analysis of the experimentally obtained data revealed that microwave heating that causes molecular motions by migration of ions and rotations of the dipoles produces no considerable effects on the mechanism of mercerization but only reduces the concentration of NaOH in the solution and the time of treatment which are needed for the complete transformation of cellulose lattice type I into cellulose lattice type II without any heating. Also it was found that the magnitude of reductions depends on the applied power. Moreover the results proved that the deconvolution and the second derivatives of the FTIR spectra of cotton fibers can be used as a useful tool for distinguishing cellulose lattice type II from cellulose lattice type I. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 30–36, 2008

Key words: FTIR spectroscopy; microwave heating; cellulose I & II; mercerization

INTRODUCTION

A lot of attention has been devoted in recent years to the application of micro wave heating in polymer and textile fibers processing.[1–7] The microwave heating is more effective than the conventional heating because it has specific property that is the equilibrium heating inside the matter. Typically, the microwave energy is lost to the sample by two mechanisms, ionic conduction and dipole rotation. In many practical applications of microwave, ionic conduction and dipole rotation take place simultaneously. In conventional heating, heat can be transferred to the material by radiation, conduction, and convection. Therefore, in case of textile processing as in dye fixation, heating setting, or drying the product, the conventional heating means a slow process involving a number of stages in the transfer of the energy before the material to be heated reaches a uniform state of molecular activity and temperature. The property of

microwaves, which makes them attractive for dye fixations and other uses is their ability and suitable conductions to produce rapid and uniform heating throughout the material exposed to them. The use of FTIR and XRD (X-ray diffraction) methods in the study of structure or properties of cotton cellulose has been a subject of interest for a number of researchers.[8–13] However, till the present time the effect of microwave heating on the structural properties of cotton fibers and on the mercerization mechanism has not yet been fully investigated. The main purpose of the present study is to apply FTIR spectroscopy to investigate the microwave heating induced changes in the structural properties of cotton fibers and also the effect of microwave irradiation on the mercerization mechanism of cotton fibers.

EXPERIMENTAL

Cotton fibers of Giza 75 were used in the preparation of the samples investigated in the present study. The cellulose lattice type II was prepared by immersing cotton powders of particle size (180–125 μm in diameter) in 18% concentration (w/w) of NaOH

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solution at room temperature (25°C) for 8 min. The material liquor ratio was 1 : 50 (w/w). The fibers were washed with 1% acetic acid solution for 5 min. The fibers were again washed with distilled water and dried at 50°C. Samples (2 g/each) of cotton fibers of the same particle size were heated in microwave oven operating at the frequency 2450 MHz for an input power 900 W under different times namely (10, 20, 30, and 40 min) at different powers of microwave heating energy, 270, 450, 630, and 900 W in closed glass tubes.

All FTIR spectra were recorded by using the single beam Fourier Transform Infrared Spectrometer Nexus 670 FTIR spectrometer, Nicolet, USA. This instrument has a ceramic IR source, KBr beam splitter, and DTGS IR detector. The FTIR spectra of the samples were obtained in the spectral range 4000–400 cm^{-1} with a scanning speed of 2 mm/s and resolution 4 cm^{-1}. The number of scans was set to 32 scans. The KBr technique was used to prepare the samples for IR measurements.

RESULTS AND DISCUSSION

Samples of cotton cellulose I of particle size (180–125 μm in diameter) were exposed to microwave radiation in a microwave oven of operating frequency 2450 MHz and of input power 900 W. The samples were microwave heated in closed glass tubes for various times namely 10, 20 30, and 40 min at different
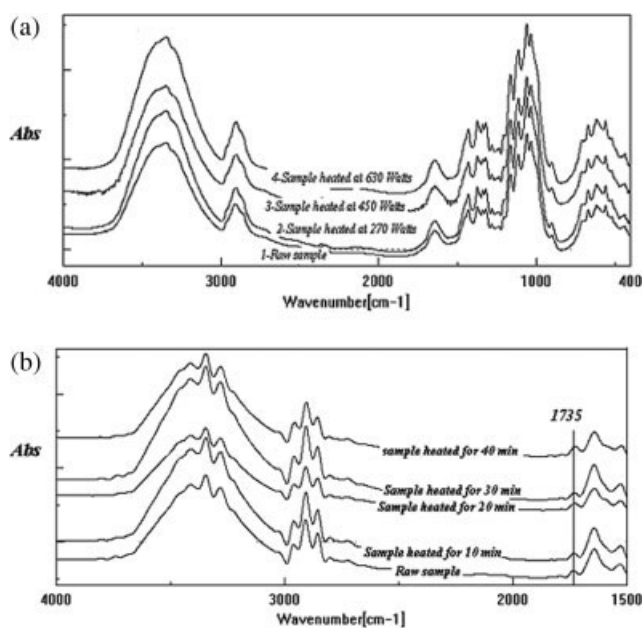
TABLE I
Contains the Percentage Rate of Change of Nelson Crystallinity Index of Cotton Fibers (Cellulose I) Heated in Closed Tubes

Time of heating	270 W	450 W	630 W	900 W
Raw sample	0.0	0.0	0.0	0.0
10 min heating	+9.8 %	−12.2 %	+3.9 %	+0.3 %
20 min heating	−13.2 %	−11.8 %	−3.7 %	+2.7 %
30 min heating	−8.7 %	+4.2 %	+5.5 %	+2.0 %
40 min heating	+7.9 %	+3.2 %	−2.1 %	−2.3 %

powers viz, 270, 450, 630, and 900 W. The ordinary and deconvoluted FTIR spectra of the irradiated samples were recorded and examples of these spectra are given in Figure 1(a,b). The visual examination of these spectra reveals that heating of celluloses I with microwave radiation for any given time or at any power causes no observable changes in their spectral features apart from slight changes in the absorbance of some absorption bands.

To evaluate the effects of microwave irradiation on the structure of cellulose I on quantitative basis, the absorbances ratio A1375 cm^{-1}/A2900 cm^{-1} [which is known as Nelson crystallinity index][14] was determined and its percentage rate of change is given in Table I. The relationship between the absorbances ratio and the time of heating at different powers is given in Figure 2.

The analysis of the obtained data indicates that microwave heating of cellulose I in closed tubes at 900 and 630 W for any given time causes no significant changes in the absorbances ratio A1375 cm^{-1}/A2900 cm^{-1} (where the band at 1375 cm^{-1} is assigned to CH_2 bending and the band at 2900 cm^{-1} is assigned to CH stretching). The slight changes are in the range of the experimental errors. The most evident decreases in this ratio occur when the samples are heated for 20 and 30 min at 270 W and for
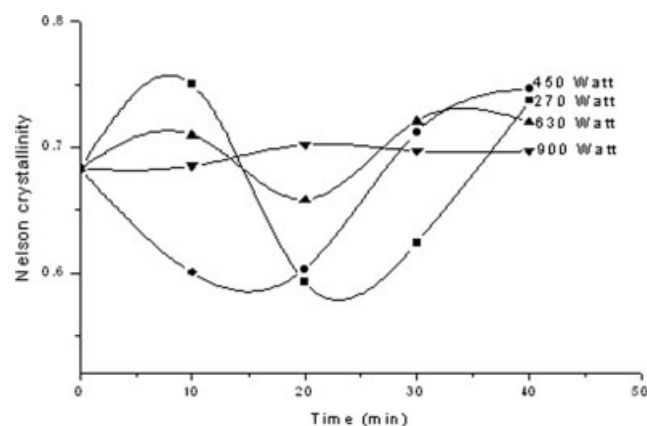

Figure 1 (a) FTIR spectra of cellulose I samples microwave heated at different powers for 20 min in closed tubes. (b) Deconvolution of the FTIR spectra of cellulose I samples microwave heated for different times at 900 W in closed tubes.

Figure 2 The relationship between Nelson crystallinity index of cellulose I and time of heating at different microwave heating powers.

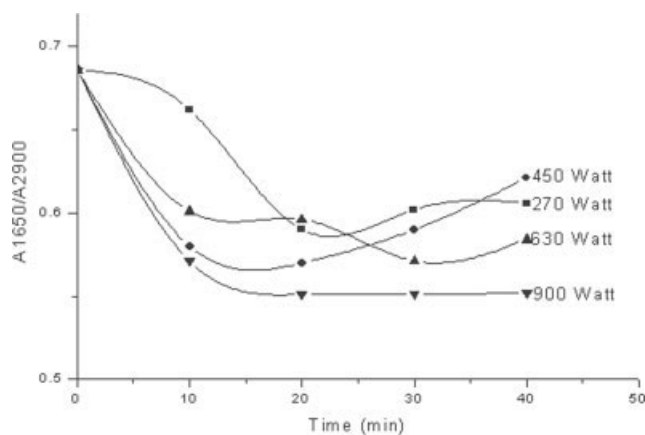**Figure 3** The relationship between the ratio A1650 cm^{-1}/A2900 cm^{-1} of cellulose I and time of heating at different microwave heating powers.

10 and 20 min at 450 W. The decrease of this ratio could be attributed to the decrease in the degree of crystallinity of cotton fibers resulted from the drying effect of microwave heating. The microwave heating for longer periods and at higher powers results in the recrystallization of the fibers. The obtained absorbances of the FTIR bands are the averages of three replicate runs. The accuracy of the measured values was found to be ±2.7%.

It has been accepted that the microwave heating depends on the water content of the sample. For this reason the ratio A1650 cm^{-1}/A 2900 cm^{-1} was calculated for the cotton samples under investigation, where the absorption band 1650 cm^{-1} is due to absorbed water. The determined values of this ratio revealed that microwave heating of cellulose I in closed tubes at any power for any given time causes substaintional decreases in the values of the ratio A1650 cm^{-1}/A2900 cm^{-1} and the lowest rate of change (−3.5%) occurs when the fibers are microwave heated at 270 W for 10 min and the highest rate of change (−19.7%) occurs when the fibers are microwave heated at 900 W for 30 and 40 min. The relationship between this ratio and the time of heating at different powers is given in Figure 3. The decreases in the values of this ratio may be attributed to the removal of absorbed water due to microwave heating.

Samples of cotton powder of cellulose I were immersed in aqueous solution of NaOH under various concentrations namely 6, 9, 12, 15, and 18% (w/w) for 8 min at two microwave heating powers 450 and 900 W.

Figures 4(a,b) give the deconvolutions and the second derivatives of the FTIR spectra of cellulose I samples (over the region 4000 to 2500 cm^{-1}) treated with 6, 9, 12, 15, and 18% aqueous solution of NaOH during microwave heating at 450 W for 8 min. These

figures indicate that the spectra of the samples treated with 6 and 9% aqueous solution of NaOH carry out the same spectral features as untreated sample, and the spectrum of sample treated with 12% aqueous solution of NaOH gives two peaks at 3495 cm^{-1} and 3443 cm^{-1} which are assigned to O—H stretching vibrations of cellulose II and another two peaks at 3345 cm^{-1} and 3278 cm^{-1} which are assigned to O—H stretching vibrations of cellulose I, while the spectra of the samples treated with 15% and 18% aqueous solution of NaOH show the same spectral features as those of cellulose II sample.

Figures 5(a,b) represent the deconvolutions and the second derivatives of the FTIR spectra of cellulose I samples treated with 6, 9, 12, 15, and 18% aqueous solution of NaOH during microwave heating at 900 W for 8 min. These figures indicate that the spectrum of the sample treated with 6% aqueous solution of NaOH carries out the same spectral features as those of the untreated sample, but the spectrum of the sample treated with 9% aqueous solution of NaOH gives two peaks at 3495 cm^{-1} and 3443 cm^{-1} which are assigned to O—H stretching vibrations of cellulose II and another two peaks at 3345 cm^{-1} and 3278 cm^{-1} which are assigned to O—H stretching vibrations of cellulose I, while the spectra of the samples treated with 12, 15, and 18% aqueous solution of NaOH show the same spectral features as those of cellulose II sample. The characteristic
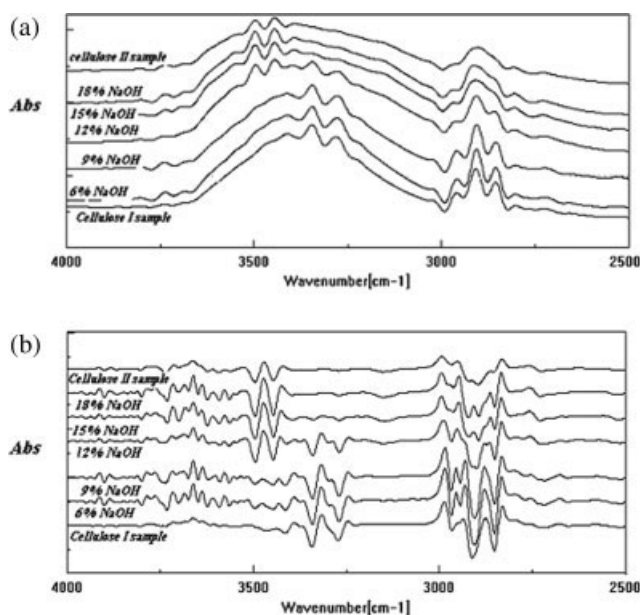

Figure 4 (a) Deconvolution of FTIR spectra of cellulose I samples treated with different concentrations of NaOH and microwave heated at 450 W. (b) Second derivatives of FTIR spectra of cellulose I samples treated with different concentrations of NaOH during microwave heating at 450 W.
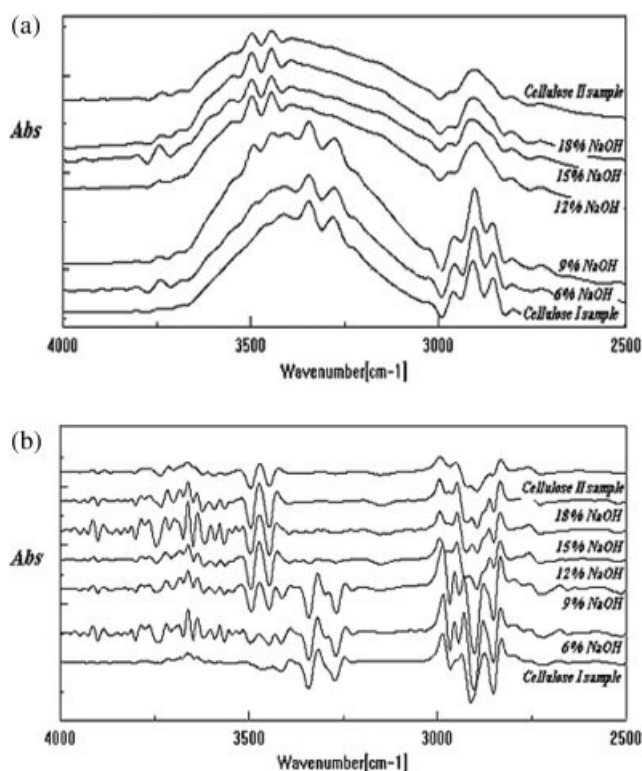
Figure 5 (a) Deconvolution of FTIR spectra of cellulose I samples treated with different concentrations of NaOH during microwave heating at 900 W. (b) Second derivatives of FTIR spectra of cellulose I samples treated with different concentrations of NaOH during microwave heating at 900 W.

bands of cellulose I and cellulose II over the O—H stretching region are shown in Figures 6(a,b) and 7(a,b).

The above mentioned data indicate that the transformation of cellulose I to cellulose II brought about by treatment with aqueous solution of NaOH depends on the concentration of NaOH and the power of microwave heating. Increasing the power from 450 W to 900 W decreases the concentration of NaOH in the solution during microwave heating which is needed for the complete transformation from cellulose I to cellulose II from 15 to 12%.

The absorbances ratio A1375 cm^{-1}/A2900 cm^{-1} of cellulose I samples treated with different concentrations of NaOH at different microwave powers (450 and 900 W) was determined. The percentage rate of change of the absorbances ratios A1375 cm^{-1}/A2900 cm^{-1} is listed in Table II.

It is obvious from the table that microwave heating of cotton fibers at 450 W during mercerization processing with 6, 9, and 12% aqueous solution of NaOH increases the ratio A1375 cm^{-1}/A2900 cm^{-1} by about 6, 8, and 8%, respectively, from its value for the untreated samples. Microwave heating of the samples treated with 15 and 18% NaOH solution at

the same power decrease this ratio by about 2 and 7%, respectively, from the original values of the untreated samples. Increasing the microwave power to 900 W results in increases of the ratio A1375 cm^{-1}/A2900 cm^{-1} by about 8, 11, 5, 3 for the samples treated with 6, 9, 12, and 15%, respectively, whereas in case of the sample treated with 18% NaOH solution this ratio suggests a decrease of about 3%. On the basis of these data one can come to the conclusion that the absorbances ratio A1375 cm^{-1}/A2900 cm^{-1} depends on the concentration of NaOH in the solution and the microwave heating power. But, since the two bands at 2900 cm^{-1} and 1375 cm^{-1} are common in both spectra of celluloses I and II, I it becomes very difficult to draw definite conclusion about the relation between the value of the absorbances of these two bands and the concentration of NaOH and the power of the microwave.

The samples of cotton powder of the same particle size were immersed in aqueous solution of NaOH with various concentrations viz; (9, 12, 15, and 18% w/w) for various times of heating namely 2, 4, and 6 min at 900 W.

Figures 8(a–c) and 9(a–c) represent the deconvolutions and the second derivatives of the FTIR spectra of cotton fibers treated with 9, 12, 15, and 18% solution of NaOH during microwave heating at 900 W
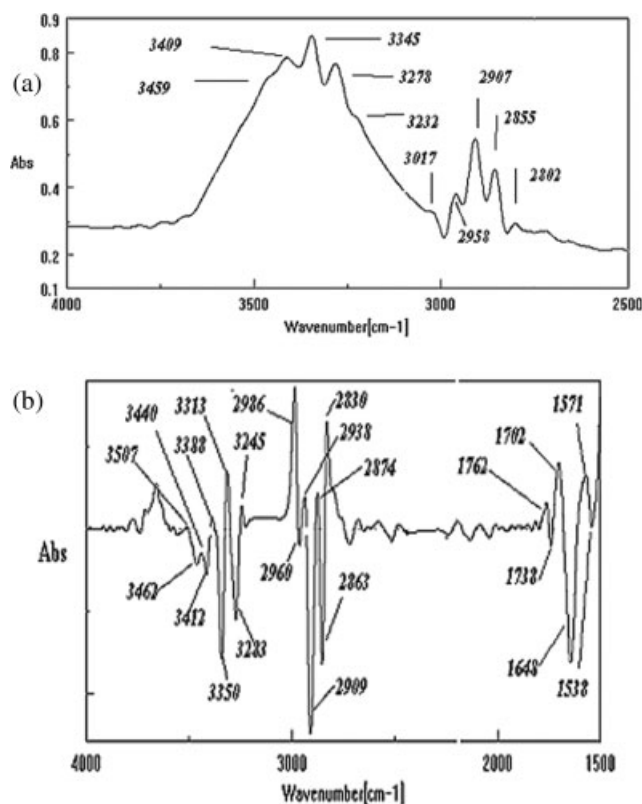

Figure 6 (a) The deconvolution of FTIR spectrum of cellulose I. (b) Second derivatives of FTIR spectra of cellulose I.
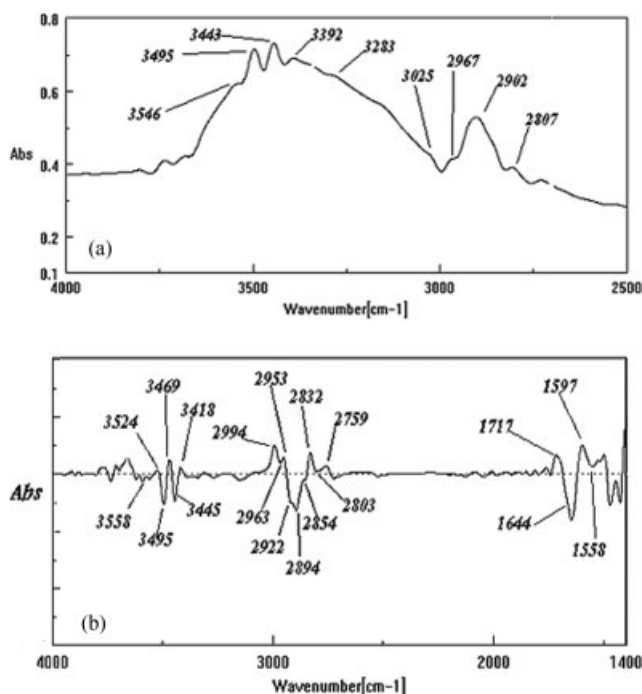
Figure 7 (a) The deconvolution of FTIR spectrum of cellulose II. (b) Second derivatives of FTIR spectrum of cellulose II.

for 2, 4, and 6 min. These figures indicate that the spectra of the samples treated with 15 and 18% NaOH solution during any given time of microwave heating (2, 4, or 6 min) exhibit only the characteristic absorption bands of cellulose II over the region of O—H stretching vibration. On the other hand the spectra of the sample treated with 12% NaOH solution for any of the above mentioned times give the characteristic bands of both celluloses I and II. The treatment of cotton fibers with 9% NaOH solution during microwave heating for 2, 4, or 6 min causes no significant changes in their spectral features.

TABLE II
Contains the Percentage Rate of Changes of the Ratio A1375 cm^{-1}/A2900 cm^{-1} of Cellulose I Samples Treated With Different Concentrations of NaOH at Different Microwave Powers (450 and 900 W)

Concentration of NaOH	A1375/A2900%
Untreated sample 450 W	0.0
6% NaOH	+6.0%
9% NaOH	+8.0%
12% NaOH	+8.2%
15% NaOH	−2.0%
18% NaOH	−7.5%
Untreated sample 900 Watt	0.0
6% NaOH	+8.0%
9% NaOH	+11.3%
12% NaOH	+5.1%
15% NaOH	+3.0%
18% NaOH	−3.0%

The above mentioned data indicate that the transformation of cellulose I to cellulose II brought about by treatment with aqueous solution of NaOH depends on the time of treatment during microwave heating.

The absorbance ratio A1375 cm^{-1}/A2900 cm^{-1}, in the spectra of cotton fibers treated with 9, 12, 15, and 18% solution of NaOH for different periods of time namely 2, 4, 6, and 8 min was determined. These ratios are given in Table III.

It appears from Table III that microwave heating of cotton fibers at 900 W during mercerization processing
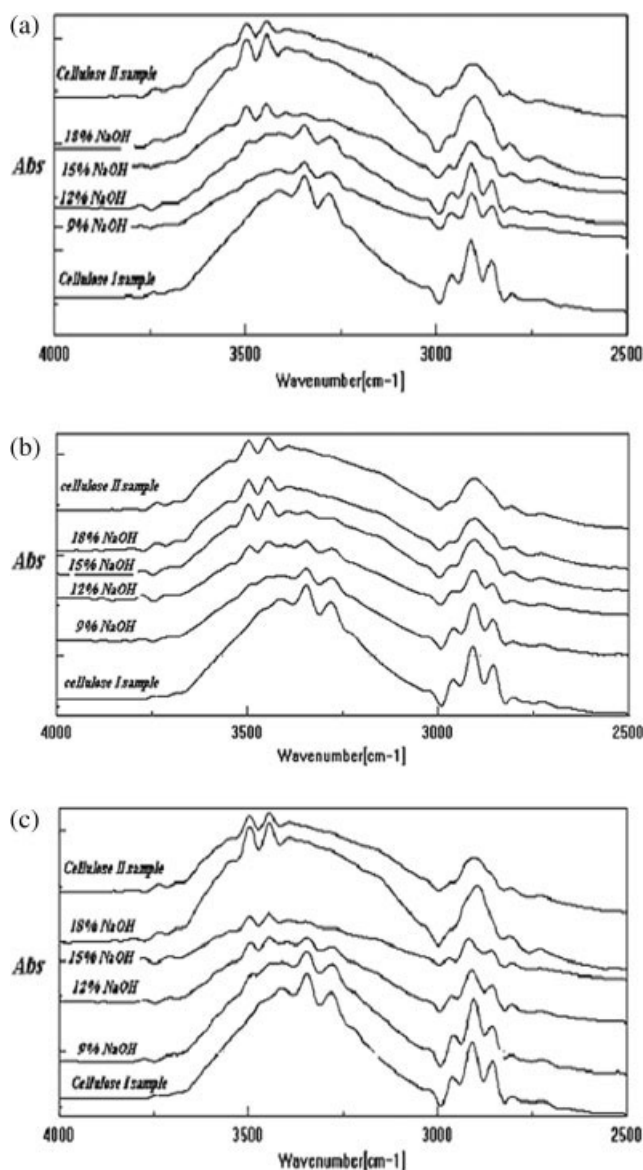

Figure 8 (a) Deconvolution of FTIR spectra of cellulose I samples treated with different concentrations of NaOH for 2 min at 900 W. (b) Deconvolution of FTIR spectra of cellulose I samples treated with different concentrations of NaOH for 4 min at 900 W. (c) Deconvolution of FTIR spectra of cellulose I samples treated with different concentrations of NaOH for 6 min at 900 W.
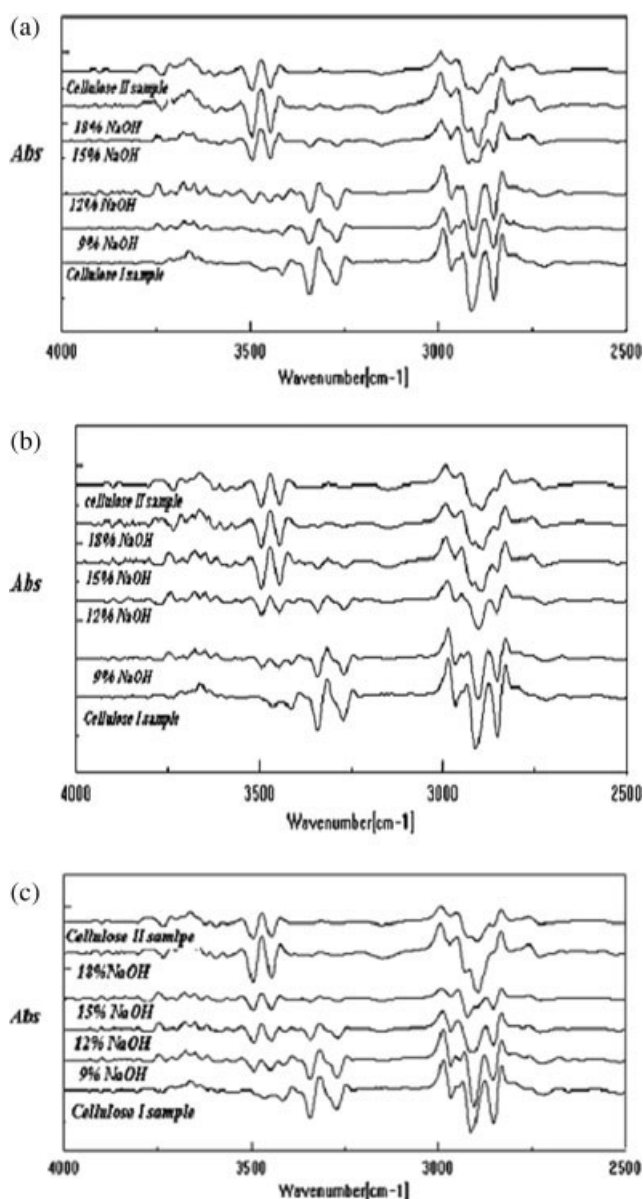
Figure 9 (a) Second derivatives of FTIR spectra of cellulose I samples treated with different concentrations of NaOH for 2 min at 900 W. (b) Second derivatives of FTIR spectra of cellulose I samples treated with different concentrations of NaOH for 4 min at 900 W. (c) Second derivatives of FTIR spectra of cellulose I samples treated with different concentrations of NaOH for 4 min at 900 W.

with 9% NaOH solution for 2 min increases the absorbances ratio by about 5% from its value of the untreated samples. The microwave heating at the same power during mercerization processing with 12, 15, and 18% for 2 min decreases this ratio by about 5%, 21%, and 17%, respectively.

Increasing the time of heating to 4 min during the mercerization processing with 9, 12, 15, and 18% decreases the ratio by about 1.5%, 5.3%, 17%, and 14%, respectively. The absorbances ratio A1375 cm^{-1}/A2900 cm^{-1} assumes decreases by about 1.1%,

12.2%, 18.4%, and 19.1% when the fibers are microwave heated for 6 min at the same power 900 W during mercerization processing with 9, 12, 15, and 18% NaOH solution, respectively. Microwave heating of cotton fibers at 900 W for 8 min during mercerization processing with NaOH solution of the concentration 9, 12, and 15% increases the ratio by about 11%, 5%, and 3%, respectively, while in case of the concentration 18% the ratio decreases by about 3%.

It is apparent from Table III that the absorbances ratio A1375 cm^{-1}/A2900 cm^{-1} is influenced by the time and power of microwave heating as well as the concentration of the NaOH solution. The relation between the percentage rate of change of this ratio and these factors is not clear because the two bands at 1375 cm^{-1} and 2900 cm^{-1} are common in both spectra of celluloses I and II.

The obtained experimental results proved that the deconvolution and the second derivatives of the FTIR spectra of cotton fibers can be used as a useful tool for distinguishing cellulose lattice Type II from cellulose lattice Type I. The transformation of cellulose lattice Type I into lattice Type II depends on the concentration of NaOH in the aqueous solution and on the time and power of microwave heating.

It seems very important to mention here that XRD methods were used in a previous study,[15] in the study of the effect of microwave heating on the transformation of cellulose I into cellulose II during mercerization. It was found that the results obtained by using FTIR methods are in good agreement with those obtained by using XRD methods.

TABLE III
Contains the Percentage Rate of Change in the Absorbances Ratio A1375 cm^{-1}/A2900 cm^{-1} of Cellulose I Samples Treated with Different Concentrations of NaOH for Different Times

Concentration of NaOH	A1375 cm^{-1}/A2900 cm^{-1} %
Untreated sample (9% NaOH)	0.0
2 min	+5.0%
4 min	−1.5%
6 min	−1.1%
8 min	+11.2%
Untreated sample (12% NaOH)	0.0
2 min	−5.5%
4 min	−5.3%
6 min	−12.2%
8 min	+5.1%
Untreated sample (15% NaOH)	0.0
2 min	−21.0%
4 min	−17.9%
6 min	−18.4%
8 min	+3.0%
Untreated sample (18% NaOH)	0.0
2 min	−17.9%
4 min	−14.3%
6 min	−19.1%
8 min	−3.0%

CONCLUSION

It is well known that mercerization is the swelling of cotton fibers in aqueous solution of sodium hydroxide. This swelling results in reorganization of the cellulose fiber, which becomes cellulose II when the swelling agent is removed. The swelling in sodium hydroxide breaks hydrogen bonds and weak van der Waal's forces between the cellulose chain molecules. Once the forces are broken between chains during swelling, the chains are freed to rearrange, expand, and reorient. When the sodium hydroxide is removed, these chains will form new bonds in this reorganized state.

Based on the foregoing data it could be concluded that microwave heating that causes molecular motions by migration of ions and rotations of the dipoles produces no considerable effects on the mechanism of mercerization but only reduces the concentration of NaOH in the solution and the time of treatment which are needed for the complete transformation of cellulose lattice Type I into cellulose lattice Type II without any heating. Moreover it was found that the magnitude of reductions depends on the applied power.

Also the obtained data lead to the conclusion that drying of cellulose causes slight changes in its crystallinity.

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