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FTIR analysis of cellulose treated with sodium hydroxide and carbon dioxide

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Abstract—Cellulose samples treated with sodium hydroxide (NaOH) and carbon dioxide in dimethylacetamide (DMAc) were analyzed by FTIR spectroscopy. Absorbance of hydrogen-bonded OH stretching was considerably decreased by the treatment of NaOH and carbon dioxide. The relative absorbance ratio ($A_{4000–2995}/A_{993}$) represented the decrease of absorbance as a criterion of hydrogen-bond intensity (HBI). The absorbance of the band at 1430 cm^{-1} due to a crystalline absorption was also decreased by NaOH treatment. The absorbance ratio of the bands at 1430 and 987–893 cm^{-1} (A_{1430}/A_{900}), adopted as crystallinity index (CI), was closely related to the portion of cellulose I structure. With the help of FTIR equipped with an on-line evacuation apparatus, broad OH bending due to bound water could be eliminated. FTIR spectra of the carbon dioxide-treated cellulose samples at 1700–1525 cm^{-1} were divided into some bands including 1663, 1635, 1616, and 1593 cm^{-1}. The broad OH bending due to bound water at 1641–1645 cm^{-1} was resolved to two bands at 1663 and 1635 cm^{-1}. As a trace of DMAc, the band at 1616 cm^{-1} is disappeared by washing for the cellulose treated with carbon dioxide (Cell 1-C and Cell 2/60-C). The decrease of HBI, the easy removal of DMAc, and the band at 1593 cm^{-1} supported the introduction of new chemical structure in cellulose. The bands shown at 1593 and 1470 cm^{-1} was assigned as hydrogen-bonded carbonyl stretching and O–C–O stretching of the carbonate ion.

Keywords: Cellulose; Sodium cellulose; Carbon dioxide; FTIR; Hydrogen-bond intensity (HBI); Crystallinity index (CI); Carbonate ion

1. Introduction

Cellulose, a β-(1→4)-linked polymer of D-glucopyranosyl units and the most abundant renewable resource on the earth, does not melt before thermal degradation because of strong intra- and intermolecular hydrogen bonding. In order to fulfill the various demands for its industrial use, it is often modified by physical, chemical, enzymic, or genetic means. Modification leads to changes in the solubility, properties and behavior of the polymer, and, consequently, improvement of the positive attributes and/or reduction of the negative characteristics can be achieved.[1] Chemical modification is based on reactions of the free hydroxyl groups in the glucopyranose units, resulting in the formation of cellulose derivatives.

As a typical industrial application of indirect dissolution, the viscose process produces regenerated cellulose fiber called viscose rayon. The conventional viscose process involves the treatment of pulp with sodium hydroxide (NaOH) and an ageing step to reduce the degree of polymerization and to enhance the reaction with carbon disulfide. The use of carbon disulfide causes harmful effects such as occupational disease and environmental loads.[2,3] For decades, researchers have focused on the manufacture of regenerated cellulose fiber in an eco-friendly manner via two routes, that is, enhancement of viscose process or development of direct dissolution processes. Cellulose is transformed to sodium cellulose by treatment with concentrated NaOH solution, and then reverts to cellulose by washing. During this process, smaller hydrates of the sodium hydroxide dipole

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penetrate into the cellulose crystalline regions and destroy the strong intermolecular hydrogen bonding to form sodium cellulose.[4]

We have reported on the treatment of sodium cellulose with carbon dioxide and have successfully dissolved the reaction product in NaOH solution.[5] This study focuses on analyzing the physical and chemical transformations of the reaction using FTIR spectroscopy. The treatment of cellulose with carbon dioxide was also attempted for comparison. An FTIR spectrometer equipped with an on-line evacuation apparatus was applied to elucidate the introduction of the carbonate ion band in cellulose.

2. Experimental

2.1. Materials

Cellulose pulp sheet (Cellunier-F®, Rayonier Fernandina Mill, USA, DP 850, 92% α-cellulose) was shredded to the form of a powder (∅ 1 mm). All samples were oven dried at 60 °C in air. Commercially available compressed carbon dioxide gas (>98%) for the reaction with cellulose and all the other chemicals of first grade were used as received.

2.2. Reaction of cellulose with NaOH and carbon dioxide

Approximately 15 g of controlled cellulose (Cell 1) was treated with 500 mL of NaOH solution at 25 or 60 °C for 2 h and then filtered to obtain NaOH-treated cellulose (NC). The concentrations of NaOH solution were chosen as 5, 10, 15, and 20 wt %. NC was washed with excess water up to pH 7 for filtrates to obtain Cell 2 sample. Approximately 15 g of shredded Cell 1 (or NC) in 300 mL of DMAc (*N*,*N*-dimethylacetamide) was treated with CO_2 at 40–50 bar in a high-pressure reactor at −5–0 °C with stirring for 2 h. The mixture was then filtered. All the cellulose samples treated were washed with excess water 3–4 times and then oven dried at 60 °C (Table 1).

2.3. FTIR analysis

Pellets of ca. 2 mg of cellulosic samples were prepared by mixing with 200 mg of spectroscopic grade KBr. IR spectra (4000–400 cm^{-1}) were recorded using a Nicolet 520P spectrometer with a resolution of 4 cm^{-1} and 64 scans per sample. To elucidate some bands shielded by the broad OH bending mode of bound water, a FTIR spectrometer (BIO-RAD 175C) equipped with evacuation line was used. For this analysis, the pellets were prepared without KBr. Approximately 4 mg of the cellulose samples were pressed in a standard device using a pressure of 98 kN/cm^2 to produce 13-mm diameter pellets. These were then analyzed by on-line evacuation at 50 °C and 1.3×10^{-1} Pa up to 90 min, or at some temperature (50, 100, 150 °C) for 30 min.[6] A total of 64 scans were taken per sample with a resolution of 4 cm^{-1} (4000–500 cm^{-1}).

Table 1. Treatment processes of the samples used in this study

Sample code	NaOH treatment		CO_2 treatment/ DMAc	Washing/ drying
	25 °C	60 °C		
Cell 1	×	×	×	○
Cell 2/25	○	×	×	○
Cell 2/60	×	○	×	○
Cell 1-C	×	×	○	○
Cell 2/25-C	○	×	○	○
Cell 2/60-C	×	○	○	○

○: treated, ×: not treated.

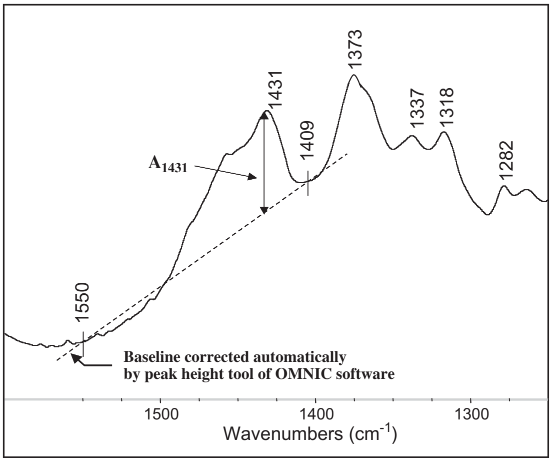


Figure 1. Baseline correction of the band at 1431 cm^{-1} in peak height tool of OMNIC software used in this study.

Most of the spectra subtracted the spectrum of carbon dioxide and are shown without the absorbance scale. With the same absorbance scale, they are shifted parallel to the wavenumber axis. Absorbance of the band obtained from a local baseline between adjacent valleys was automatically calculated at the maximum absorbance found by a sensitivity of 100 using the OMNIC 4.0 software as shown in Figure 1. A deconvolution technique was applied to the smoothened spectra at 1750–1525 cm^{-1} using the Gaussian distribution and Microcal™ Origin™ program. The spectra obtained by the BIO-RAD 175C FTIR spectrometer were resolved into four bands of fixed full width half maximum and wavenumber (1663, 1637, 1616, and 1593 cm^{-1}), which were determined previously by the difference spectra.

3. Results and discussion

3.1. Sodium hydroxide and carbon dioxide treatment and FTIR analysis

In our previous research, all the factors affecting the solubility of cellulose samples by carbon dioxide treatment, that is, organic medium, pressure, reaction temperature, and time, were examined to get a better dissolution state.[5] At the higher pressure and the lower temperature of carbon dioxide within the ranges of 0–50 bar and −5–25 °C, we got better solubility in aqueous NaOH. Generally, interfibrillar swelling takes place in water and in dilute NaOH concentration of less than 10–15 wt %. In more concentrated solutions, the swelling becomes intrafibrillar with the participation of higher lateral order. Mercerization, that is, the transformation from cellulose I to Na-cellulose I and finally to cellulose II, is completed at higher than 15 wt %.[7] Drawing from the previous works, reaction conditions such as 5, 10, 15, and 20 wt % of NaOH and temperatures of 25 and 60 °C were chosen. To confirm that alkali treatment of cellulose is essential to get better solubility, untreated cellulose was also used for the carbon dioxide treatment.

Recent developments of high-resolution instruments and analyzing software render FTIR spectroscopy as a powerful technique for the characterization of cellulose.[8,9] We applied this technique for analyzing the cellulose samples treated with NaOH and/or carbon dioxide. Figure 2a shows the FTIR spectra of cellulose (Cell 1) and cellulose treated with carbon dioxide (without alkali treatment, Cell 1-C). Some characteristic bands related to the physical and chemical changes are the hydrogen-bonded OH stretching at ca. 4000–2995 cm^{-1}, the OH bending of adsorbed water at 1635 or 1638 cm^{-1}, the CH stretching at 2900 cm^{-1}, the HCH and OCH in-plane bending vibrations at 1430 cm^{-1}, the CH deformation vibration at 1375 cm^{-1}, the COC, CCO, and CCH deformation modes and stretching vibrations in which the motions of the C-5 and C-6 atoms are at 900 cm^{-1},[10] and the C–OH out-of-plane bending mode at 668 cm^{-1}.[8] Bands at 4000–2995 cm^{-1}, 2900 cm^{-1}, 1430 cm^{-1}, 1375 cm^{-1}, and 900 cm^{-1} are especially sensitive to the state of the crystalline and amorphous regions.

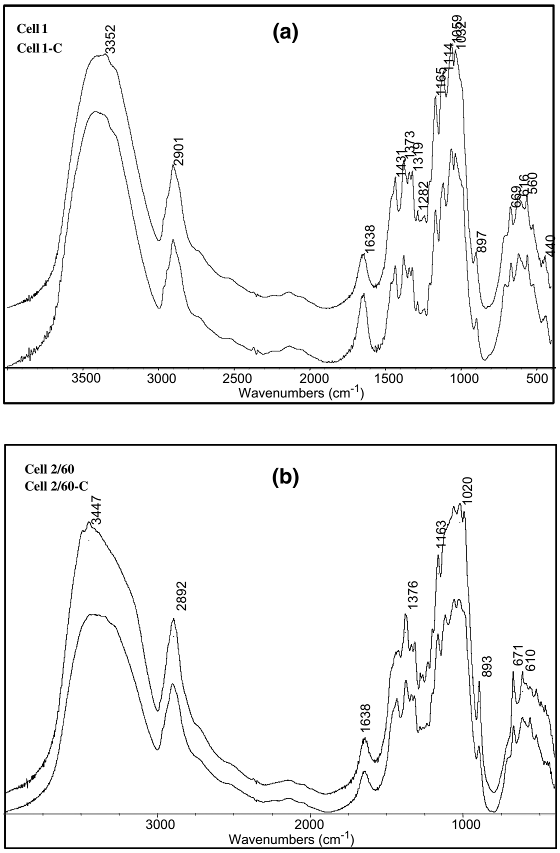
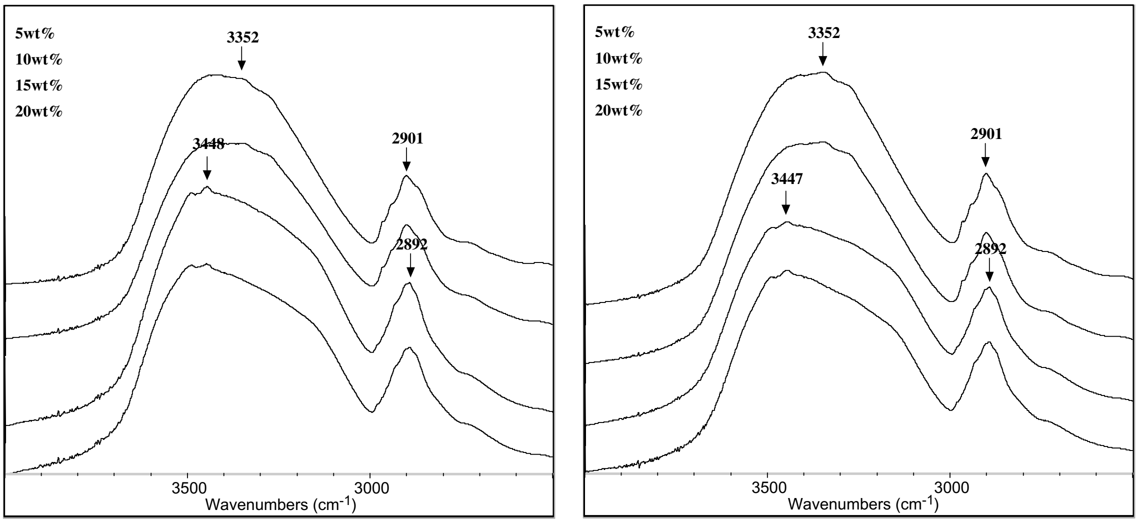


Figure 2. FTIR spectra of (a) Cell 1 (and Cell 1-C) and (b) Cell 2/60 (and Cell 2/60-C) prepared at 20 wt % of NaOH.

3.2. Physical changes of cellulose by NaOH and carbon dioxide treatment

Compared with the spectra of Cell 1 and Cell 1-C (Fig. 2a), most of the characteristic bands are changed in absorbance and/or wavenumber as shown in the spectra of Cell 2 and Cell 2-C (Fig. 2b). Strong hydrogen-bonded OH stretching at around 4000–2995 cm^{-1} is commonly observed for all the spectra. For the Cell 2 samples prepared at different NaOH concentrations and temperatures, the maximum absorbance of hydrogen-bonded OH stretching is shifted to higher wavenumber (from 3352 to 3447 cm^{-1}) at higher NaOH concentration as shown in Figure 3. The CH stretching mode at 2901 cm^{-1} is also shifted to lower wavenumber at ~2892 cm^{-1} at higher NaOH concentration. The intramolecular hydrogen bonding of O(2)H···O(6) and O(3)H···O(5), and the intermolecular hydrogen bonding of O(6)H···O(3) in cellulose are generally shown at 3455–3410, 3375–3340, and 3310–3230 cm^{-1}, respectively.[8,11] For both treatment temperatures, the maximum absorbance of the OH stretching vibration is shifted to 3447 cm^{-1} showing the intramolecular hydrogen bonding of O(2)H···O(6) for Cell 2 treated under the mercerization conditions (15–20 wt %). The crystal system of cellulose is changed from cellulose I to cellulose II by mercerization.[7] Following treatment with of carbon dioxide, the absorbance of the OH stretching vibration in the overall range is decreased considerably for Cell 2/25 and Cell 2/60 (20 wt % NaOH) as well as Cell 2/60 (5 wt % NaOH) (Figs. 4 and 5a). In addition, the OH stretching mainly due to intramolecular hydrogen bonding is decreased by mercerization and even more by subsequent carbon dioxide treatment.

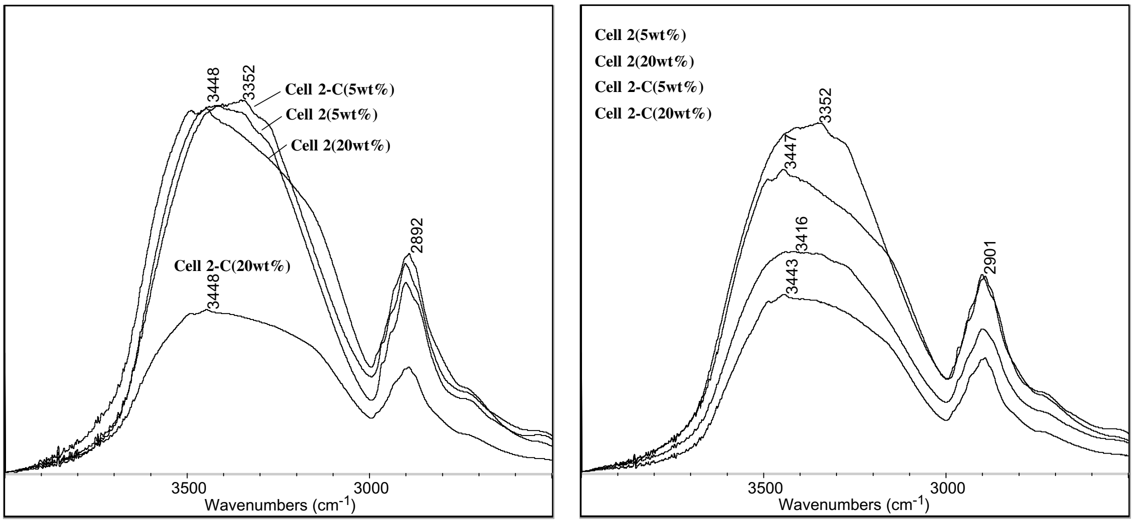
Considering the chain mobility and bond distance, the hydrogen-bond intensity (HBI) of cellulose is closely related to the crystal system and the degree of intermolecular regularity, that is, crystallinity, as well as the amount of bound water. Previously, the ratio of the absorbance at 4000–2995 cm^{-1} to those that at ~1337 cm^{-1} due to C–OH in-plane stretching[12] was introduced as an empirical HBI.[13] Both of the bands at 4000–2995 and 1337 cm^{-1} are decreased in absorbance,



(a) Cell 2/25

(b) Cell 2/60

Figure 3. FTIR spectra (4000–2500 cm^{-1}) of Cell 2 samples prepared at different NaOH concentration and the temperature of (a) 25 °C and (b) 60 °C.



(a) Cell 2/25 and Cell 2/25-C

(b) Cell 2/60 and Cell 2/60-C

Figure 4. FTIR spectra (4000–2500 cm^{-1}) of Cell 2 and Cell 2-C samples prepared at 5 and 20 wt % of NaOH concentration and a temperature of (a) 25 °C and (b) 60 °C.

but the ratio ($A_{4000–2995}/A_{1337}$) of mercerized cellulose is increased by mercerization and carbon dioxide treatment. This is contrary to the absorbance change of hydrogen-bonded OH stretching ($A_{4000–2995}$) as shown in Figure 5a. Some other bands of constant or increased absorbance are applied to substitute the band at 1337 cm^{-1}. Among the bands applied, the band at 993 cm^{-1} (CO stretching, Fig. 6) is chosen for the internal standard of HBI. The absorbance ratio ($A_{4000–2995}/A_{993}$) shows the decrease with the treatment of NaOH and carbon dioxide as shown in Figure 5b. The decrease in absorbance for hydrogen-bonded OH stretching observed in this study is better explained by this ratio than $A_{4000–2995}/A_{1337}$.

The band at 1430 cm^{-1} decreases and eventually disappears by grinding, whereas the band at 897 cm^{-1} showed a remarkable increase.[14] The first band is designated as a ‘crystalline’ and the second one as an ‘amorphous’ absorption band. The absorbance ratio was defined as an empirical ‘crystallinity index’ (CI). The absorbance intensities at ~900 and 1430 cm^{-1} are also very sensitive to the amount of crystalline versus amor-

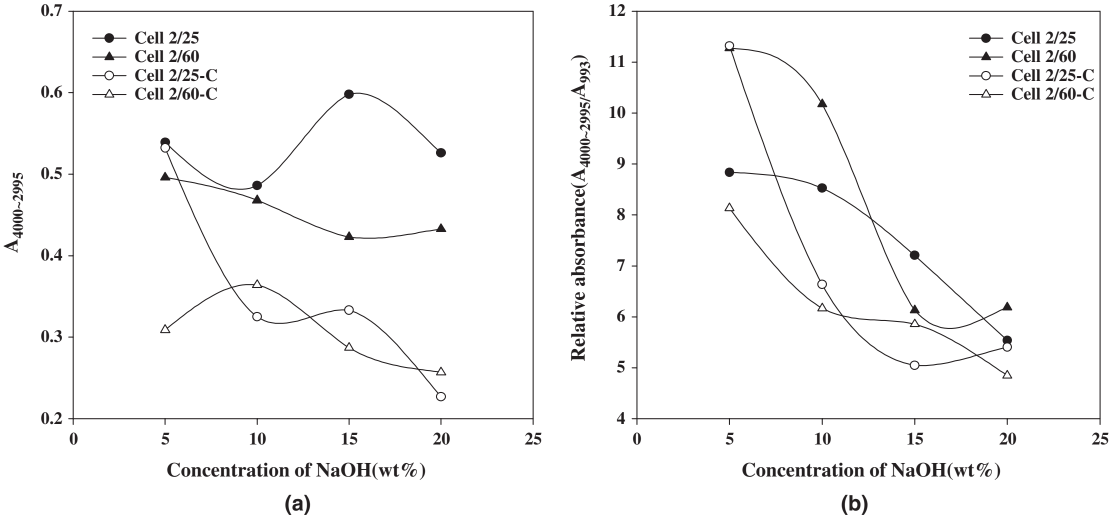
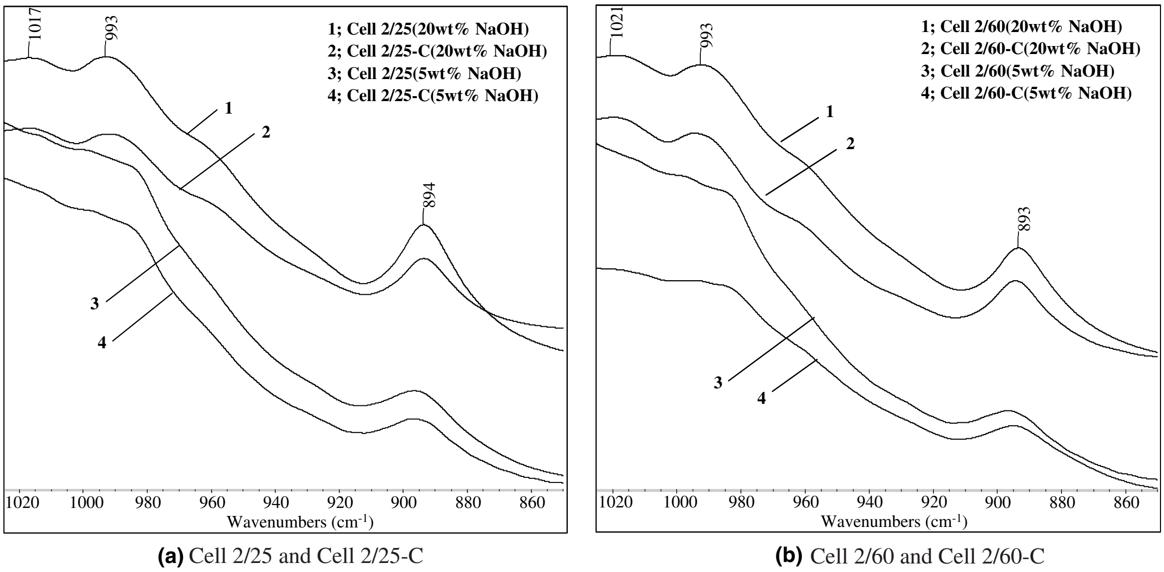


Figure 5. The maximum band height at (a) 4000–2995 cm^{-1} and relative absorbance ($A_{4000-2995}/A_{993}$) (b) of Cell 2 and Cell 2-C samples prepared at different NaOH concentration.



(a) Cell 2/25 and Cell 2/25-C

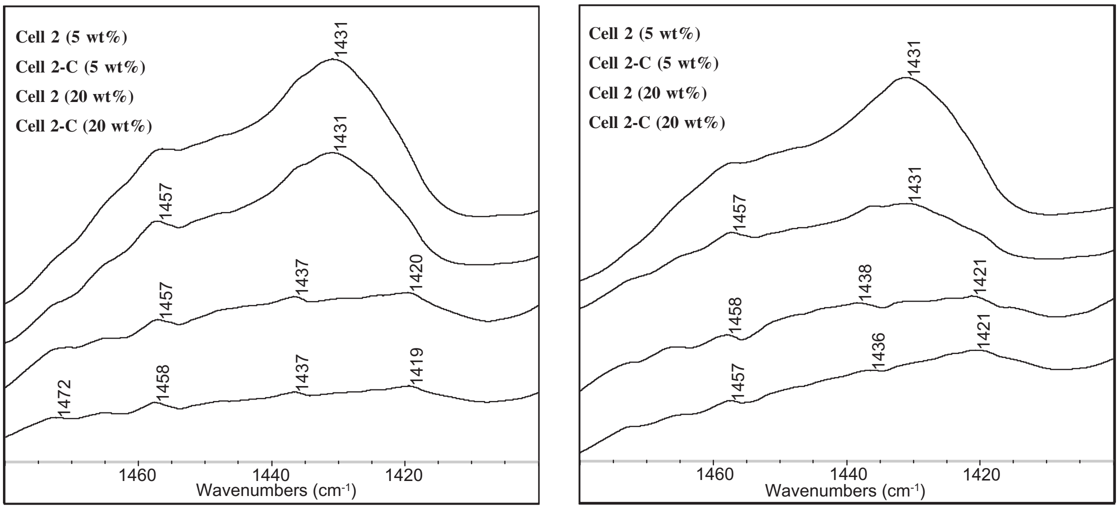
(b) Cell 2/60 and Cell 2/60-C

Figure 6. FTIR spectra (1025–850 cm^{-1}) of Cell 2 and Cell 2-C samples prepared at 5 and 20 wt % of NaOH concentration and the temperature of (a) 25 °C and (b) 60 °C.

phous structure of cellulose, that is, broadening of these bands reflects higher amount of disordered structure. As shown in Figure 6, C–H bending mode at 897 cm^{-1} is shifted to lower wavenumber about 3–4 cm^{-1} and increased its absorbance by the treatment of 20 wt % NaOH. Contrary to C–H bending at ~900 cm^{-1}, the 1431 cm^{-1} band disappears upon mercerization (Fig. 7).

As the absorbance at ~900 cm^{-1} is increased with the transformation from cellulose I to cellulose II by mercerization, the absorbance ratio of the bands at ~1430 and 900 cm^{-1} (A_{1430}/A_{900}) was previously adopted as the CI.[15] The CI of Cell 2 and Cell 2-C decreases at higher concentration of NaOH treatment as shown in Figure 8. Cellulose treated with sodium hydroxide and carbon dioxide has a lower CI than that treated with 5–10 wt % NaOH, only. It decreases to a minimum at higher concentration than 15 wt % NaOH for both of Cell 2/25-C and Cell 2/60-C. As cellulose I is transformed to cellulose II during mercerization, the ratio (A_{1430}/A_{900}) is closely related to the cellulose I system.

The band of 1375 cm^{-1} was also reported to give the same information as the band at 1431–1430 cm^{-1}.[14] As shown in Figure 9, the band at 1375–1373 cm^{-1} is decreased in absorbance by mercerization as well as the



(a) Cell 2/25 and Cell 2/25-C

(b) Cell 2/60 and Cell 2/60-C

Figure 7. FTIR spectra (1480–1400 cm^{-1}) of Cell 2 and Cell 2-C samples prepared at 5 and 20 wt % of NaOH concentration and the temperature of (a) 25 °C and (b) 60 °C.

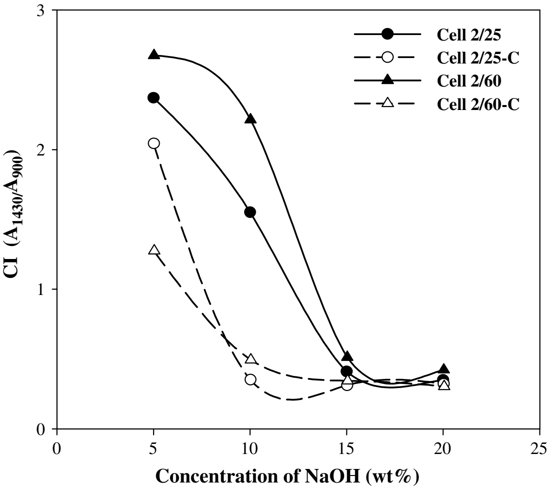


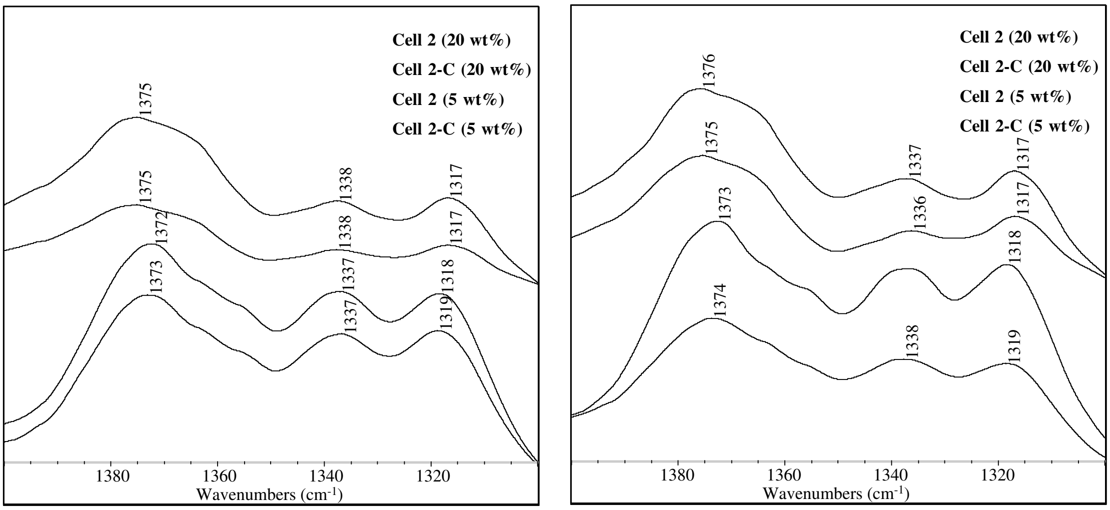
Figure 8. CI of Cell 2 and Cell 2-C prepared at different NaOH concentrations and temperatures.

bands at 1337 and 1319–1317 cm^{-1}. Compared with the band at 1431–1430 cm^{-1}, a small absorbance change of the band at 1375–1373 cm^{-1} indicates that this is not linearly proportional to cellulose I. Some other absorbance ratios such as A_{1376}/A_{2902} and A_{1278}/A_{1263}[12,16] are suggested as the criteria for CI. The band at 1282–1278 cm^{-1} is slightly decreased by mercerization like the band at 1375 cm^{-1}. It is confirmed that both the ratios, A_{1376}/A_{2902} and A_{1278}/A_{1263}, do not show good correlation with A_{1430}/A_{900}.

3.3. Chemical changes of cellulose by carbon dioxide treatment

Considering the chemistry of the xanthation reaction, sodium cellulose and carbon dioxide may react to form a sodium cellulose carbonate. The carbonation reaction is not so favorable because carbon dioxide is gaseous and chemically stable. Moreover, the identification of the carbonate ion band that appears around 1700–1600 cm^{-1} by FTIR is quite difficult because the OH bending mode due to bound water is also observed in this region. Taking this into consideration, we analyzed all the treated cellulose samples by using an FTIR instrument equipped with an on-line evacuation apparatus (Fig. 10). As KBr is hygroscopic and impossible to dehydrate during on-line evacuation, we prepared the pellets of the cellulose samples, only. Figure 10 shows the IR spectra of Cell 1 and Cell 1 treated with DMAc at −5–0 °C for 2 h and then neutralized by washing and drying. Absorbance of the broad band at ~1700–1560 cm^{-1} decreases with increasing evacuating time at 50 °C. The characteristic band at 1616 cm^{-1} is also shown in Cell 1 treated by DMAc and then washed (Fig. 10b). By on-line evacuation, the band decreased at 1700–1560 cm^{-1} can be assigned as OH bending due to absorbed water. Smoothening all the spectra at ~1700–1560 cm^{-1} are required because the OH bending mode is strongly perturbed by bound water.

Figure 11 shows the IR spectra (1800–1500 cm^{-1}) of Cell 1 and Cell 1-C samples at 50 °C with evacuation time. The absorbance of the band at 1700–1560 cm^{-1} decreases with increasing temperature for both of Cell 1 and Cell 1-C. With the adsorptions of bound water in cellulose sample, the absorbance related to OH-bending decreases with increasing temperature. The bands at 1663 and 1637 cm^{-1} are decreased and divided into some very small bands at 50 °C with evacuation time. Compared with the difference between Cell 1 and Cell 1-C, Cell 2/60-C is clearly different from Cell 2/60 as



(a) Cell 2/25 and Cell 2/25-C

(b) Cell 2/60 and Cell 2/60-C

Figure 9. FTIR spectra (1400–1300 cm^{-1}) of Cell 2 and Cell 2-C samples prepared at 5 and 20 wt % of NaOH concentration and the temperature of (a) 25 °C and (b) 60 °C.

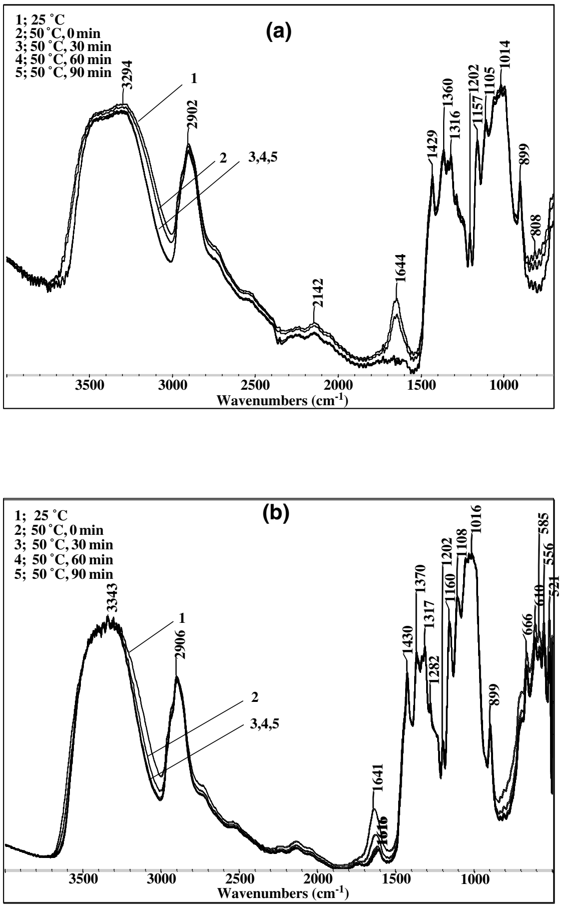


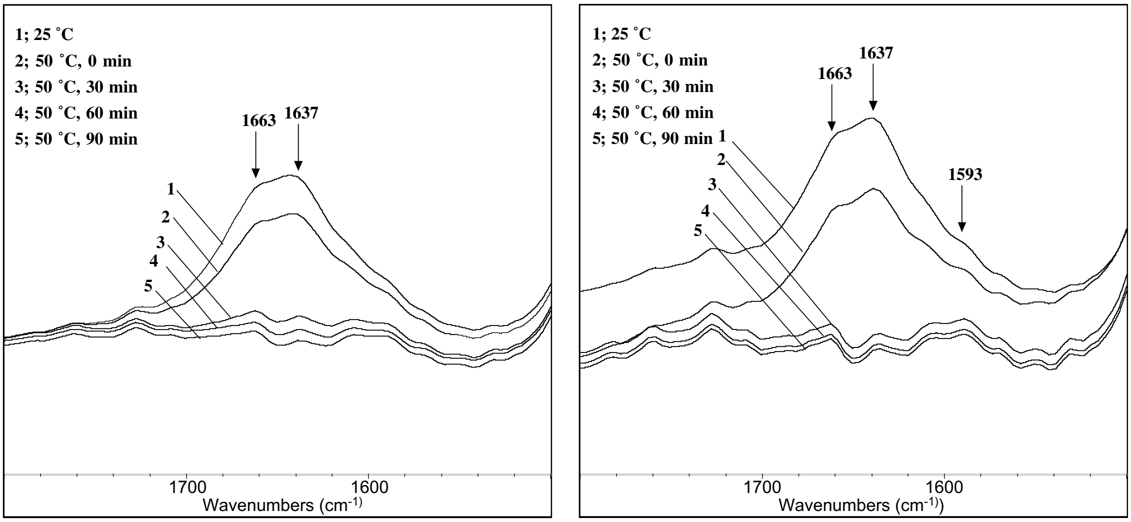
Figure 10. FTIR spectra (a) of Cell 1 and (b) of Cell 1 treated with DMAc analyzed after maintaining at 50 °C in vacuo.

shown in the spectra of Figure 12. The spectra obtained by evacuation at higher temperature for 30 min also shows the more pronounced band at around 1593 cm^{-1} (Fig. 13).

Figure 14 is the difference spectra (1700–1560 cm^{-1}) of Cell 1 (or Cell 1-C) samples with increasing evacuation time at 50 °C. The difference spectra are obtained between the spectra at 25 °C and those at 50 °C with changing evacuation times. Both of the maximum difference spectra are due to the band of total absorbed water in the cellulose sample. Cell 2 and Cell 2-C samples also show similar tendency under the treatment conditions, such as 20 wt % NaOH and 60 °C (Fig. 15). From the difference spectra of Figures 14 and 15, it is clear that the broad band at 1641–1645 cm^{-1} is due to the OH bending of bound water.

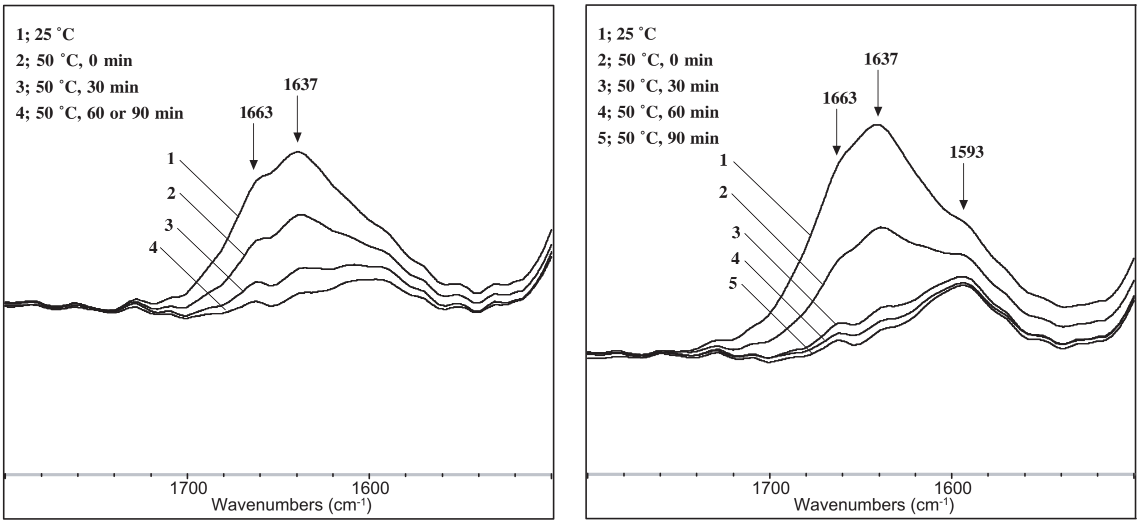
By applying deconvolution techniques, the IR bands of cellulose samples at 1750–1525 cm^{-1} are resolved to two (Figs. 16a and 17a) and four bands (Figs. 16b and 17b) at 1663, 1637, 1616, and 1593 cm^{-1}. In Cell 1-C and Cell 2/60-C, the bands are resolved to four bands, that is, two bands due to OH bending of bound water, one band due to DMAc, and one band due to the reaction with carbon dioxide. The band at 1593 cm^{-1} is not shifted with increasing evacuation temperature and time for the cellulose treated with carbon dioxide (Cell 1-C and Cell 2/60-C, Figs. 11–13). The 1593 cm^{-1} band is clearly shown for all the cellulose samples treated with carbon dioxide.

Two bands due to OH bending of bound water are expected for Cell 1 and Cell 2/60 because they are not treated with carbon dioxide in DMAc. The dotted lines of Figures 16 and 17 are the accumulated spectra of the bands resolved. As shown in both figures, the dotted lines are in good correspondence with the original spectra. Two bands at 1616 and 1593 cm^{-1} are clearly



(a) Cell 1 **(b)** Cell 1-C

Figure 11. FTIR spectra (1800–1500 cm^{-1}) of (a) Cell 1 and (b) Cell 1-C samples analyzed after maintaining at 50 °C in vacuo.

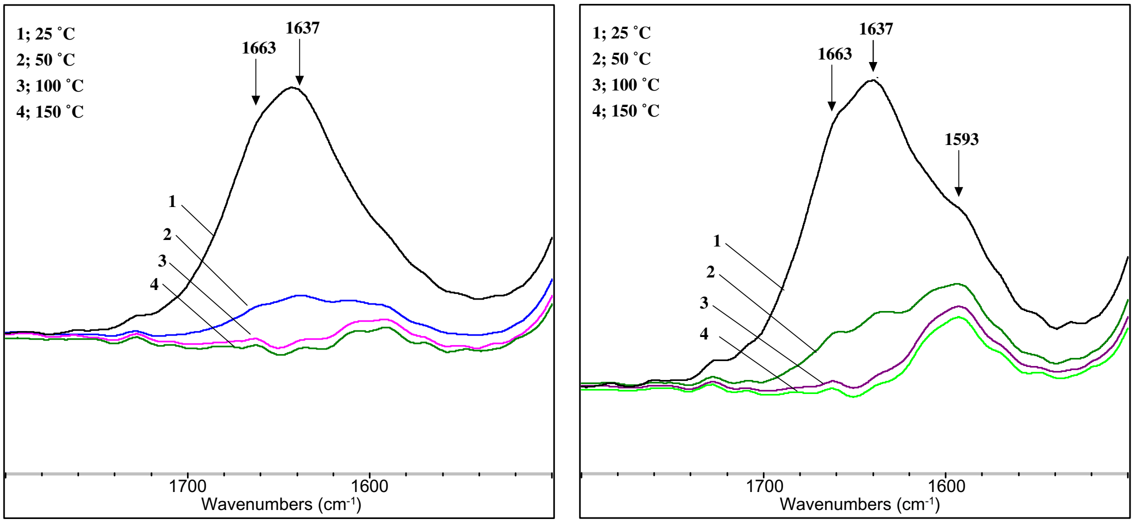


(a) Cell 2/60 (20 wt% NaOH) **(b)** Cell 2/60-C (20 wt% NaOH)

Figure 12. FTIR spectra (1800–1500 cm^{-1}) of (a) Cell 2/60 and (b) Cell 2/60-C samples analyzed after maintaining at 50 °C in vacuo.

resolved, and the band at 1616 cm^{-1} shows the cellulose treated with carbon dioxide (Cell 1-C and Cell 2/60-C). DMAc is easily removed by washing the cellulose samples treated with carbon dioxide. In addition to the huge decrease of HBI and the band appearing at 1593 cm^{-1}, the easy removal of DMAc also supports the introduction of a new chemical structure.

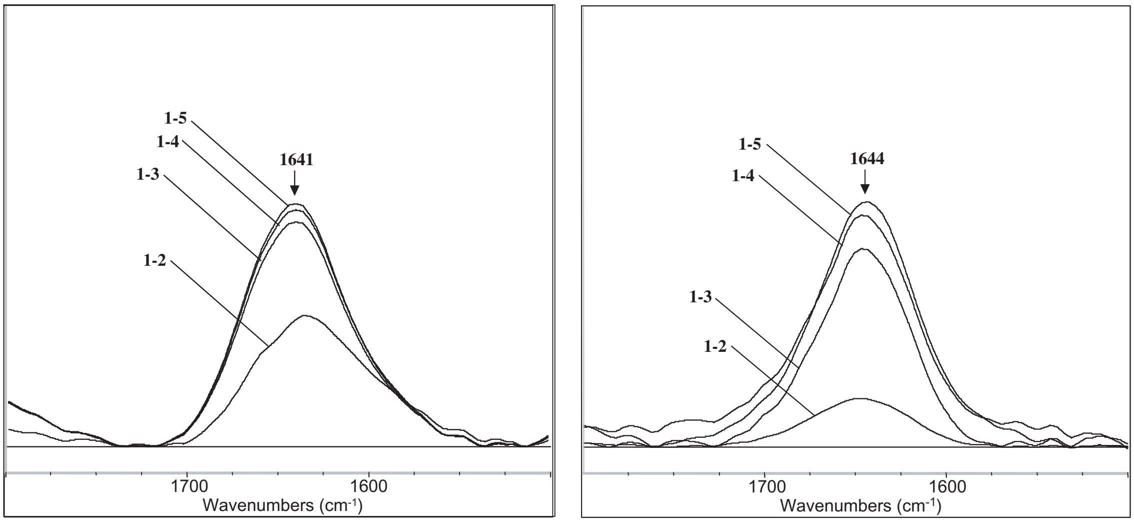
The band at 1593 cm^{-1} is not typical of any functional groups related to the reaction materials, that is, cellulose, carbon dioxide, or DMAc. Though there is no previous research available for reference, carbonation is most probable when sodium cellulose is treated with carbon dioxide. The carboxylation reaction by oxygen is disregarded for some reasons: (1) low reaction temperature (−5–0 °C) in the absence of air (oxygen), (2) no color change due to oxidation, (3) absence of characteristic asymmetric and symmetric carbonyl stretching bands (both strong at 1600 and 1430 cm^{-1}, respectively).[17] As for carbonation, some FTIR analyses have been reported related to the characteristic peaks of the carbonate ion. The characteristic peaks at 1673, 1350, and 1305 cm^{-1} are reported for sodium hydrogencarbonate ion.[18] Poly(ethylene carbonate) is degraded to form new bands at about 1650 and 1540 cm^{-1}.[19] And the peaks at 1450 and 1410 cm^{-1} are also shown for carbonate apatite.[20] The morphological and chemical nature of



(a) Cell 2/60 (20 wt% NaOH)

(b) Cell 2/60-C (20 wt% NaOH)

Figure 13. FTIR spectra (1800–1500 cm^{-1}) of (a) Cell 2/60 and (b) Cell 2/60-C samples analyzed after maintaining at some temperatures for 30 min in vacuo.



(a) Cell 1

(b) Cell 1-C

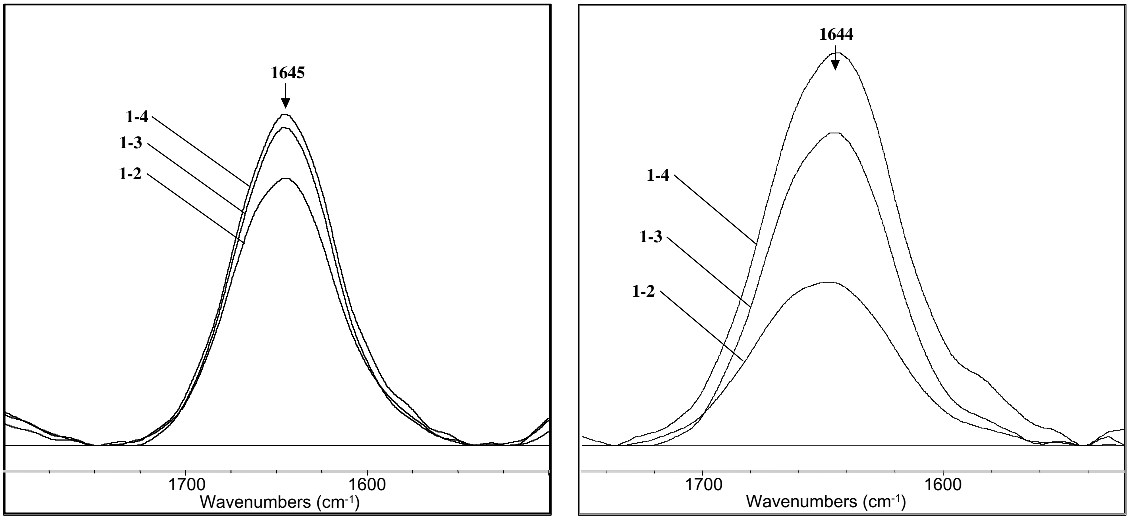
Figure 14. Difference spectra (1800–1500 cm^{-1}) subtracted between Cell 1 (or Cell 1-C) samples of different drying time at 50 °C in vacuo (Fig. 11).

adjacent groups may influence the shift of characteristic bands related to carbonate ions. The resolved peak at 1593 cm^{-1} is assigned as the asymmetric stretching of sodium cellulose carbonate ion. Compared with the peak at 1650 cm^{-1} of an alkyl carbonate ion, the shift up to lower frequency at ~60 cm^{-1} is possibly due to intra- and intermolecular hydrogen bonding between the carbonate ion and the adjacent hydroxyl group. Carbon dioxide treatment, only, of cellulose also shows a weak band at 1593 cm^{-1} in Figure 16b.

Figure 18 shows the O–C–O stretching vibration band at 1470 cm^{-1}. As expected, this broad band is much weaker than the asymmetric stretching band at 1593 cm^{-1} and is shifted to lower frequency at ~70 cm^{-1} compared with that of the alkyl carbonate ion.

4. Conclusions

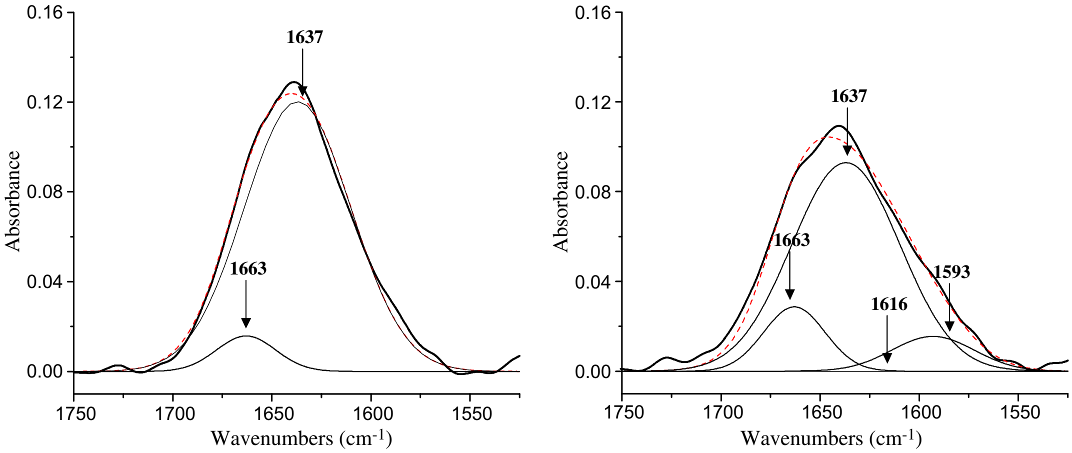
Physical and chemical changes of the modified cellulose obtained from the reaction of alkali cellulose (NC) and carbon dioxide in *N*,*N*-dimethylacetamide (DMAc) were analyzed by FTIR spectroscopy. The reaction of cellulose and carbon dioxide was also introduced for comparison.



(a) Cell 2/60 (20 wt% NaOH)

(b) Cell 2/60-C (20 wt% NaOH)

Figure 15. Difference spectra (1800–1500 cm^{-1}) subtracted between Cell 2/60 (or Cell 2/60-C) samples of different drying temperature in vacuo (Fig. 12).



(a) Cell 1

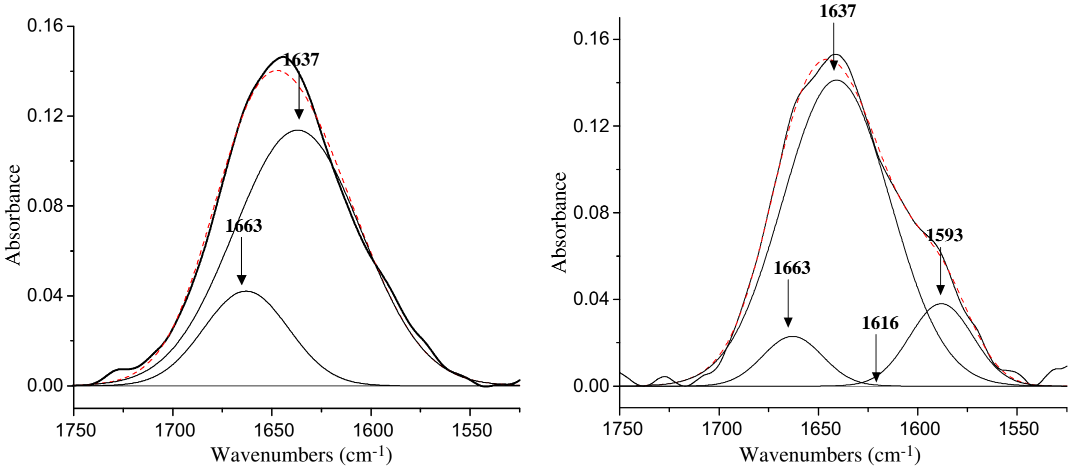
(b) Cell 1-C

Figure 16. Results of the band resolution of the FTIR spectra (1750–1525 cm^{-1}) of Cell 1 and Cell 1-C samples analyzed at 25 °C, 30 min in vacuo. Dotted line is the sum of (a) 1663 and 1637 cm^{-1} bands and (b) 1663, 1637, 1616, and 1593 cm^{-1} bands.

The relative absorbance ratio ($A_{4000-2995}/A_{993}$) is applied as a criterion of hydrogen-bond intensity (HBI). It was decreased by mercerization and even more by carbon dioxide treatment. The decrease of OH stretching mainly due to intramolecular hydrogen bonding is better explained by this ratio than $A_{4000-2995}/A_{1337}$.

The absorbance ratio of the bands at ~1430 and 900 cm^{-1} (A_{1430}/A_{900}), regarded as the crystallinity index (CI), is decreased with increasing NaOH concentration. By carbon dioxide treatment, the CI of the celluloses is decreased to a minimum at the concentration of 15–20 wt % NaOH. As cellulose I is transformed to cellulose II by mercerization, the ratio (A_{1430}/A_{900}) is closely related to the cellulose I portion.

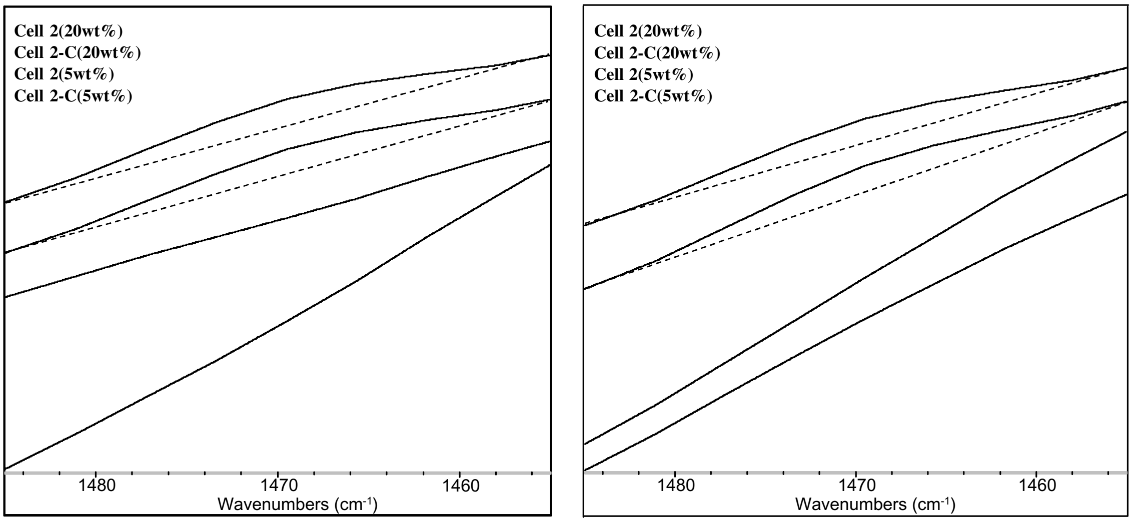
With the help of an FTIR instrument equipped with an on-line evacuation apparatus, the OH bending mode due to bound water is analyzed. FTIR spectra of the carbon dioxide-treated cellulose samples at 1700–1525 cm^{-1} are resolved into two or four bands at 1663, 1637, 1616, and 1593 cm^{-1}. The broad OH bending due to bound water at 1641–1645 cm^{-1} is also resolved into two bands at 1663 and 1635 cm^{-1}. As a trace of DMAc, the band at 1616 cm^{-1} disappears by washing of the carbonated cellulose (Cell 1-C and Cell 2/60-C). With the decrease of HBI and the appearance of the band at 1593 cm^{-1}, the easy removal of DMAc also supports the introduction of a new chemical structure. The bands at 1593 and 1470 cm^{-1} are assigned as



(a) Cell 2/60 (20 wt% NaOH)

(b) Cell 2/60-C (20 wt% NaOH)

Figure 17. Results of the band resolution of the FTIR spectra (1750–1525 cm^{-1}) of Cell 2/60 and Cell 2/60-C samples analyzed at 25 °C, 30 min in vacuo. Dotted line is the sum of (a) 1663 and 1637 cm^{-1} bands and (b) 1663, 1637, 1616, and 1593 cm^{-1} bands.



(a) Cell 2/25 and Cell 2/25-C

(b) Cell 2/60 and Cell 2/60-C

Figure 18. FTIR spectra (1485–1455 cm^{-1}) of Cell 2 and Cell 2-C samples prepared at (a) 25 °C and (b) 60 °C and analyzed after maintaining at 25 °C, 30 min in vacuo.

the hydrogen-bonded asymmetric carbonyl stretching and O–C–O stretching of the carbonate ion.

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