

FTIR Spectroscopic Analysis of Structural Changes of Cellulosic Fibres During Papermaking Process^{*1}

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ABSTRACT

Structural changes of cellulosic fibres during the papermaking process were studied by analysis of FTIR spectra collected by the transmission method. The spectra were obtained from a carefully prepared handsheet, using a special infra-red (IR) cell suitable for evacuating the sample. The deconvolution technique was also applied for sharpening the FTIR spectra in the frequency range of the OH and CH stretching bands, which gave detailed information on the structural changes of cellulose. The intensity of some bands was decreased by predrying the sample as a result of the removal of adsorbed moisture. An increase in intensity of some bands in the frequency range of 3700 to 3200cm⁻¹ was shown at a higher beating level. This increase in intensity was caused by changes in the crystal domain of cellulose resulting from the exposure of the crystalline area on the fibre surface.

Keywords : FTIR, spectrum, cellulosic fibre, beating, hydrogen bond, deconvolution, papermaking, fine structure, accessibility

1. INTRODUCTION

Cellulosic fibres are subject to various structural changes caused by the actions of chemicals, temperature, and mechanical forces during pulping, beating, pressing, drying, and converting processes. In papermaking, these processes are considered fundamental factors that determine paper properties. Although these changes are mostly detrimental, they do resist in a few positive effects on the structure of the fibre.

Macroscopic changes of cellulosic fibres have been evaluated with the aid of spectroscopic analysis. Li *et al.* (1993) used ¹H- and ²H-nuclear magnetic resonance (NMR) in investigating the

change of fibre cell wall structure. They studied the variations in pore size in the walls of beaten fibres using the NMR relaxation method and reported the increase in pore size as being related to an increase in fibre surface area. Carbon-13-cross polarization magic angle spinning (13CCP/MAS)-NMR spectroscopy has been tried for monitoring the conversion of cellulose I_α to cellulose I_β during the beating of cellulose, and this technique has been applied to the study of crystalline structure of cellulosic fibres (Atalla, 1980; Li, 1991). Raman spectroscopy has also been used to measure the enhanced mobility of cellulose and the proportion of cellulose II by beating treatment (Woitkovich *et al.*, 1985).

In this paper, the structural changes of cellulosic

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fibres were characterised by FTIR spectroscopy. In particular, modern FTIR spectroscopy has a powerful performance with a good signal-to-noise ratio, a wider range of linearity, and high wavenumber accuracy, compared to other techniques (Ludwig & Fengel, 1992; Fengel, 1992; Fengel *et al.*, 1992). For the analysis of the fine structure of cellulosic fibres, a deconvolution technique was suggested in the spectral range of OH and CH stretching band regions, which contain much information on the molecular and supramolecular structure of cellulose and its changes induced by thermal and mechanical influences.

2. MATERIALS & METHODS

2.1 Pulp

Unbleached kraft pulp was used in all experiments. Kraft pulping was carried out in a Hatto laboratory forced-circulation digester. The composition of kraft cooking liquor and the cooking conditions were as follows: charge, 1200g/o.d. wood; sulfidity (as Na₂O), 25%; liquor-to-wood ratio, 6 : 1; maximum cooking temperature, 170 °C; time to maximum temperature, 1.5 hour; and time at maximum temperature, 2 hours. After pulps were discharged, washed, and screened for removal of rejects, they were stored under refrigeration at 4 °C without drying for further analysis of pulp properties and making handsheets.

2.2 Beating

Beating of fibres was conducted in an PFI mill in order to modify fibre structural properties. A 30-g pulp mat (10% consistency) was torn into small pieces of flakes and was charged as evenly as possible into the internal wall of the beater housing. The fibre samples were subjected to three beating levels-0, 500, and 3,000 revolutions-in a PFI mill. The wetness levels were 18, 30.5, and 82° SR, respectively. After the required number of roll revolutions, all pulps were discharged to a beaker and were diluted with 2,000ml of deionised water and

then disintegrated for 10,000 revolutions to get uniform defibration.

2.3 Preparation of handsheets

Handsheets were formed according to the British standard method and prepared to a basis weight of 25g/m² for FTIR work. They were then wet-pressed under 50 lb/in². During the initial stage of wet pressing, wet handsheets were transferred to a standard polished steel plate, pressed second time, and then dried in a standard conditioning room for 24 hours.

2.4 FTIR measurements

The IR spectra were collected on a single-beam BioRad(FTS-7) Fourier transform infrared spectrometer controlled by commercial software (Win-IR). The optical bench of the spectrometer was totally sealed and equipped with potassium bromide windows; dry nitrogen gas was passed into the optical bench to remove moisture or CO₂ in the air. All spectra were obtained by the transmission method and were collected using 64 scans in the wave number range of 4000 to 900cm⁻¹, with a spectral resolution of 8cm⁻¹.

A special IR cell (Beta gas cell, BUCK Scientific) was used to reduce noise level over the whole spectrum; the cell was designed to be suitable for investigating evacuated samples. The length and outer diameter of the cell body were 5cm and

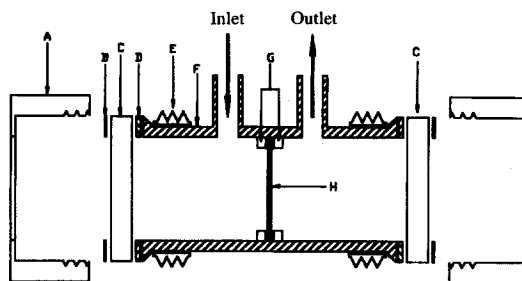


Fig. 1. Exploded view of IR cell.

Notes; A : Cell cover cap, B : Teflon gasket,
C : CaF₂ windows, D : O-ring, E : replaceable rubber septa, F : Cell body, G : Sample holder, H : Paper sample.

2.5cm, respectively. For the IR transmission measurements, the sample was placed in the center of cell, as shown in Fig. 1. Two calcium fluoride (CaF₂) windows (25- by 4-mm) were attached to the cell body by means of O-rings and cover caps. Before collecting the spectra, the cell with cell slide-holder was constructed in the sample chamber of the IR spectrometer.

2.5 Deconvolution

To improve band resolution, the spectra were deconvoluted, using the Win-IR software (Bio-Rad Laboratories, Inc.). Deconvolution is a mathematical processing techniques made possible by the computer software attached to the FTIR. This mathematical processing of FTIR spectra provides clear resolution in the overlapped OH absorption range. Optimum band resolution was obtained by applying a Bessel apodization function with a gamma factor 5 and a smoothing function of 80%.

3. RESULTS & DISCUSSION

3.1 Characteristic FTIR spectra 1 bands in cellulosic material

Fig. 2 shows typical FTIR spectra for cellulosic

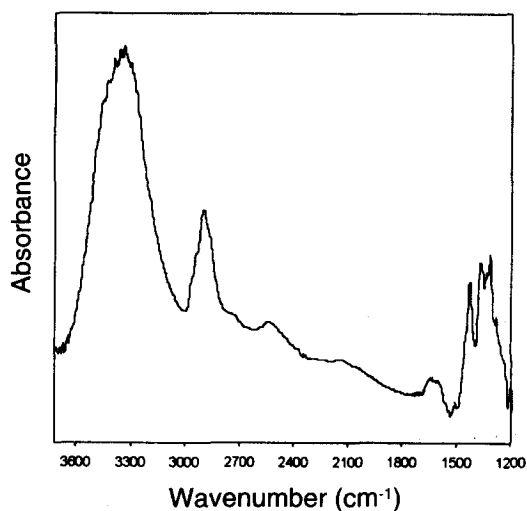


Fig. 2. Typical FTIR spectrum for cellulosic fibre.

fibres. The characteristic bands observed in the spectra of cellulose are O-H and C-H stretching vibrations. The band at 3700~3000cm⁻¹, where the broad absorption is characteristic of hydrogen bonding, is due to the OH stretching vibration. In the hydroxyl stretching band, the frequency range at 3700~3370cm⁻¹ is assigned to free OH. The differences of spectral shape in this region between cellulosic materials are closely related to this free OH (Fengel *et al.*, 1992; Fengel, 1993).

The band arising from the C-H stretching vibration occurs in the region of 3000~2800cm⁻¹. The positions of the C-H stretching vibrations are among the most stable in the spectrum. This band is therefore frequently used as a standard in quantitative analysis.

The next important band in the cellulose spectrum occurs around 1650cm⁻¹ and is thought to be due to adsorbed water. In the case of pure cellulose, this band disappears upon complete drying. The bands at 1600cm⁻¹ and 1500cm⁻¹ originate from aromatic ring vibration and are attributed to typical lignin bands. This band does not appear in the pure cellulose spectrum, like cotton linters.

The band at 1370cm⁻¹ in the cellulose spectrum is due to the CH₂ bending vibration. This band was used to evaluate the crystallinity index (Nelson & O'Connor, 1964a,b).

Additional bands in the cellulose spectrum include the C = O stretching band (1730cm⁻¹), CH₂ symmetric bending band (1430cm⁻¹), and CH₂ wagging band (1317cm⁻¹).

3.2 Drying effect of handsheet on FTIR spectra

Fig. 3 shows the transmission spectra for unbleached kraft pulp that had been dried by strong evacuation within the IR cell, according to the sequence of evacuation time. Results show that drying reduced the intensity of certain bands that are assigned to either adsorbed or free water, due to the removal of adsorbed moisture from the sheet. Fengel (1993) stated that water may be free or hydrogen-bonded with the C(2)OH groups in the cellulose structure and its vibration should appear

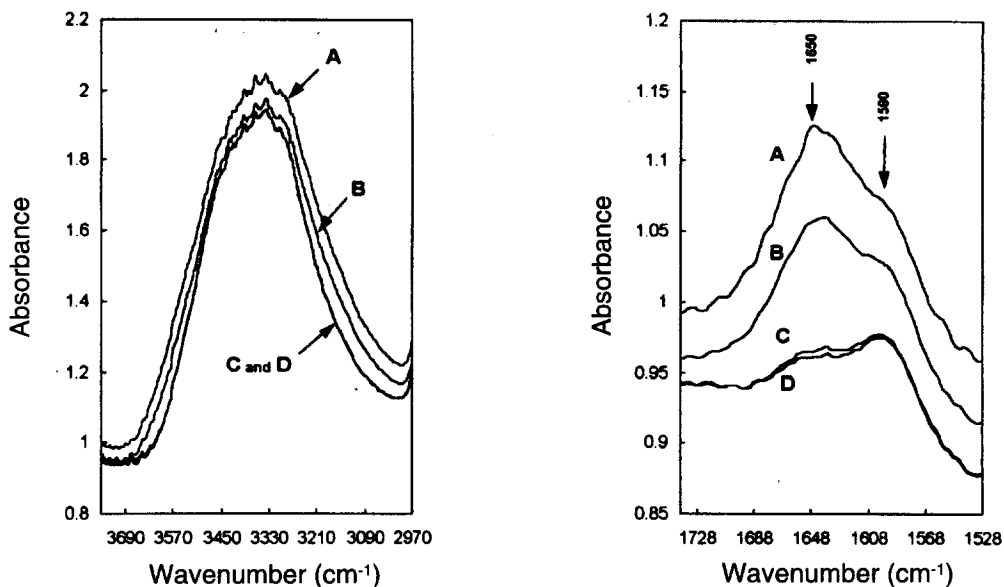


Fig. 3. Spectral changes caused by pre-drying in the frequency range of 3750~3000cm⁻¹ and 1750~1520cm⁻¹
 Notes; A : never-dried, B : pre-dried for 15min., C : pre-dried for 1 hr., D : pre-dried for 5 hr.

in the frequency range of 3800 to 3000cm⁻¹ and 1700 to 1500cm⁻¹. While the handsheets were being dried, the peaks appearing at 3700 to 3000cm⁻¹, attributed to hydroxyl stretching vibrations, and at 1700 to 1550cm⁻¹, attributed to adsorbed water, were decreased. Reduction in band intensity was rapid at initial drying. After drying for 1 hour, no further reduction was observed in the hydroxyl stretching band, and the band at 1650cm⁻¹ had almost disappeared. Therefore, prior to collecting the spectrum, the handsheet sample must be dried for at least 1 hour in order to reduce experimental errors that can be caused by contribution of adsorbed water to the OH stretching band.

3.3 Advantage of deconvolution of FTIR spectrum

In spite of the usefulness of infrared spectroscopy for analysing the fine structure of cellulose fibres, some limitations have been reported in resolving the overlapping bands arising from large numbers of OH and CH groups with similar absorption frequencies (Fengel, 1993; Michell, 1991; Nelson & O'Connor, 1964a,b; Pandey,

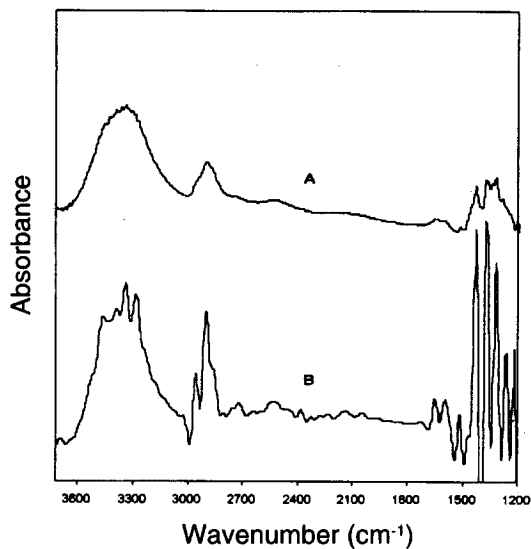


Fig. 4. FTIR spectrum (A) and its deconvoluted FTIR spectrum (B) of kraft pulp.

1987). New applications of FTIR spectroscopy, such as deconvolution (Fengel, 1992-1993; Fengel *et al.*, 1992) and derivatives (Pandey, 1987; Michell, 1991), have been introduced to assist in

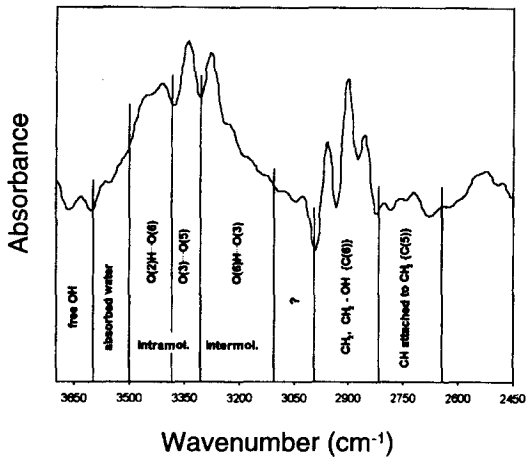


Fig. 5. Characteristic band attributions of deconvoluted FTIR spectrum of cotton linter.

sharpening and resolving these bands in the cellulose spectrum.

Fig. 4 shows typical FTIR spectrum (A) and deconvoluted FTIR spectrum (B) for unbleached kraft fibres. In particular, this figure shows that the ranges for OH stretching and CH/CH₂ stretching vibrations (generally shown in the frequency range between 3800 and 2400cm⁻¹) (Fengel, 1993) and absorbed water (between 1670 and 1480cm⁻¹) are well-defined when applying the deconvolution technique. These ranges are important for monitoring the proportions of ordered and disordered regions in relation to IR accessibility (Mann & Marrinan, 1956b).

The absorption bands in the range of 3700~3650 cm⁻¹ are due to free water present in the mat of the sheet sample. Mann & Marrinan (1956a) reported that the unbonded or free hydroxyl group of alcohols and phenols absorbs in the 3625 ± 10 to 3605 ± 10cm⁻¹ range. The band near 3623cm⁻¹ results from a monomer structure, whereas the broad absorption near 3333cm⁻¹ arises from the polymeric structure. The O-H stretching regions are closely related to intra- and inter-molecular hydrogen bonding (Fengel, 1992). The band near 3100~3300 cm⁻¹ is assigned to the intermolecular hydrogen bond, and the band near 3300~3500cm⁻¹ results from the

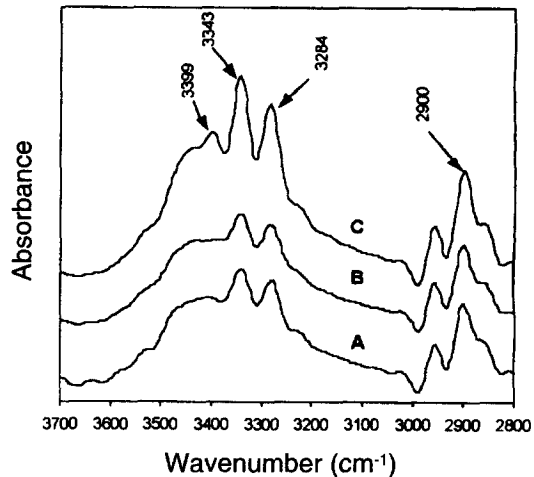


Fig. 6. Deconvoluted spectra of unbleached kraft fibres after beating.

Notes; A: never-beaten fibres, B: beaten fibres to 500 PFI-rev., C: beaten fibres to 3000 PFI-rev.

intramolecular hydrogen bond. With the aid of the deconvolution technique, Fengel (1992) reported that the study of cellulose OH groups can be improved by deconvoluting the spectrum in the range of 3700~2500cm⁻¹ and indicated the characteristic band attribution of groups and linkages as shown in Fig.5.

3. 4 Changes in fine structure of cellulosic fibres by beating

Changes in the fine structure of unbleached kraft pulp during beating treatment as shown by deconvoluted FTIR spectra are shown in Fig. 6. As described in the experimental section, never-dried kraft pulps were beaten in a PFI mill at 10% consistency. Handsheets were prepared with three levels of beaten pulps and dried in an air-conditioned room before being measured by FTIR. A strong vacuum was applied to remove excess moisture within the specific IR cell before the IR spectra were collected.

Results indicate that the bands around 3400, 3340, and 3280cm⁻¹ increased with higher degrees of beating. Increases in bands at 3340 and 3280cm⁻¹

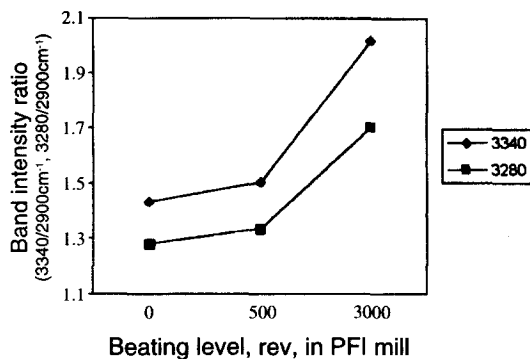


Fig. 7. Variation in relative band intensity ratio at 3420/2900cm⁻¹ during beating.

were particularly dramatic with the increased beating levels. These two bands also showed a greater increase at a beating level of 3000 PFI revolutions than at 500 PFI revolutions. Fengel (1997) pointed out that these bands are attributed to the inter- and intra-molecular hydrogen bond. It has also been suggested that the increases in band intensity at 3340 and 3280cm⁻¹ imply an increase in crystallinity (Nelson & O'Connor, 1964a,b; Kim, 1997). These relationships are redrawn in Fig. 7 in order to compare the relative proportions of the crystalline domain at different beating levels. This figure also confirms that the increase in these two bands at higher levels of beating is due to an increase in crystallinity.

These results show good agreement with the decreases in IR accessibility described in section 3.5. The increases in crystallinity at higher beating levels could be the result of exposure of areas of crystalline (ordered) structure on the surface of cellulosic fibres, due to the removal or leaching out of amorphous materials, such as fine, hemicelluloses and colloidal materials during fibrillation (Kim, 1997).

3.5 Variations in accessibility for beaten fibres

The variation of accessibility for beaten fibres was characterised from the band intensity of the FTIR spectra. Cellulosic fibres were deuterated by

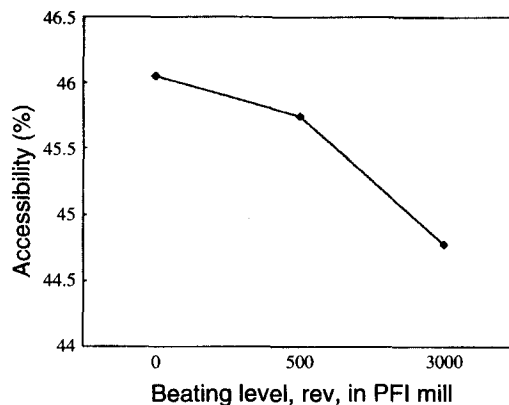


Fig. 8. Reduction rates in accessibility due to beating levels.

bubbling dry nitrogen gas through heavy water (D₂O) and then passing the saturated nitrogen gas over the sample in the IR gas cell. Accessibility was calculated from the ratio of the band intensity of the OD stretching vibration at 2530cm⁻¹ to that of the OH stretching vibration at 3360cm⁻¹, as described previously (Kim, 1997; Mann & Marrinan, 1954 · 1956a,b), by applying the Beer-Lambert law as follows.

Before applying this law, all bands in the spectra at 3800~900cm⁻¹ were baseline corrected to zero:

$$Ac = \frac{100 \times c_{OD}}{c_{OD} + c_{OH}} = \frac{100}{1 + \frac{K \cdot A_{OH}}{A_{OD}}}$$

where

Ac is accessibility expressed as a percentage
and $K = k_{OD} / k_{OH} = 1.11$.

Changes in accessibility obtained from spectra for unbleached kraft fibres beaten to 0, 500, and 3,000 PFI-revolutions are shown in Fig. 8. Results showed that the accessibility values decreased as beating levels increased. This would suggest that the fine structure of cellulosic fibres is changed by the action of beating. In particular, the accessibility values for unbleached kraft pulp beaten to 3000 PFI-revolutions were lower than those for the fibres beaten to 500 PFI-revolutions. As described above,

IR accessibility values were obtained from the relative proportions of the ordered and disordered fractions by calculating the ratio of OD and OH band intensity. During beating, some of the crystalline regions, which are strongly hydrogen-bonded, may become exposed through fibrillation. As beating increases, the exposure of strongly hydrogen-bonded areas may also increase. Hence, the intensity of the OH band increases compared to that of the OD band at higher beating levels. This theory is supported by the results obtained from the deconvoluted spectra in the range of 3700~2400cm⁻¹, as discussed in section 3.4.

4. CONCLUSION

The structural changes of cellulosic fibres were characterized by the investigation of some bands. Variation of cellulosic fibre structure was influenced by several factors that occurred during the papermaking process, as summarized below:

1. Drying of the handsheet decreased the band around 3340 and 1650cm⁻¹ due to the removal of adsorbed water and improved the resolution of the OH stretching band. Therefore, prior to collecting the spectrum, the sheet sample should be dried for at least 1 hour.
2. Band intensity at 3340 and 3280cm⁻¹ was increased with increased beating level. These results suggest an increase in the crystalline domain of cellulose, which could be the result of exposure of areas of crystalline structure on the fibre surface due to fibrillation. Such a change in the crystalline area of the fiber surface is also consistent with the decrease in the IR accessibility number.

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