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Benoît J.C. Duchemin, Roger Newman, Mark Staiger. Phase transformations in microcrystalline cellulose due to partial dissolution. *Cellulose*, Springer Verlag, 2007, 14 (4), pp.311-320. 10.1007/s10570-007-9121-4 . hal-02922530

**HAL Id: hal-02922530**

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Submitted on 3 Sep 2020

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## Phase transformations in microcrystalline cellulose due to partial dissolution

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*This is a Preprint version of: Duchemin, B.J.Z., Newman, R.H. & Staiger, M.P. Phase transformations in microcrystalline cellulose due to partial dissolution. Cellulose 14, 311–320 (2007). DOI: 10.1007/s10570-007-9121-4*

### Abstract

All-cellulose composites were prepared by partly dissolving microcrystalline cellulose (MCC) in an 8.0 wt.% LiCl/DMAc solution, then regenerating the dissolved portion. Wide-angle X-ray scattering (WAXS) and solid-state <sup>13</sup>C NMR spectra were used to characterize molecular packing. The MCC was transformed to relatively slender crystallites of cellulose I in a matrix of paracrystalline and amorphous cellulose. Paracrystalline cellulose was distinguished from amorphous cellulose by a displaced and relatively narrow WAXS peak, by a 4 ppm displacement of the C-4 <sup>13</sup>C NMR peak, and by values of T<sub>2</sub>(H) closer to those for crystalline cellulose than disordered polysaccharides. Cellulose II was not formed in any of the composites studied. The ratio of cellulose to solvent was varied, with greatest consequent transformation observed for  $c < 15\%$ , where  $c$  is the weight of cellulose expressed as % of the total weight of cellulose, LiCl and DMAc. The dissolution time was varied between 1 and 48 h, with only small additional changes achieved by extension beyond 4 h.

Keywords: All-cellulose composite; Cellulose I; Cellulose II; Cellulose IV; LiCl/DMAc; Microcrystalline cellulose; Solid-state  $^{13}\text{C}$  NMR; X-ray diffraction.

Abbreviations: Microcrystalline cellulose (MCC), *N,N*-dimethylacetamide (DMAc), nuclear magnetic resonance (NMR), Wide-angle X-ray scattering (WAXS)

## Introduction

Crystalline cellulose I has a tensile modulus of 138 GPa (Nishino et al. 1995) and an ultimate tensile strength of at least 2 GPa (Kroon-Batenburg et al. 1990; Yano et al. 2005), based on experimental data. If values as high as these could be achieved in reinforcement for composite materials, cellulose I could compete with steel or high-performance synthetic fibres (Nishino et al. 2004; Yano et al. 2005). Failure to achieve such high performance has been attributed to poor bonding between polar cellulosic fibres and less-polar polymer matrices (Bledzki and Gassan 1999; Lu and Wu 2000). Fibre-matrix compatibility can be improved by using cellulose itself as the matrix. Nishino et al. (2004) were the first to take this approach, introducing a new class of high strength, biodegradable materials known as all-cellulose composites.

While the mechanical properties of all-cellulose composites are known, there are very few references to the nature of the molecular packing in the matrix (Gindl and Keckes 2005). We sought insights from studies based on X-ray diffraction and solid-state  $^{13}\text{C}$  NMR spectroscopy.

Two distinct strategies have been used in preparation of all-cellulose composites.

(1) *Regeneration*. Nishino et al. (2004) dissolved kraft fibre and regenerated the cellulose in the presence of ramie fibres.

(2) *Partial dissolution.* Gindl and Keckes (2005) and Gindl et al. (2006a, b) partly dissolved cellulose I and precipitated the dissolved portion to form a matrix around the undissolved portion.

Similar composites have also been prepared by using esters such as cellulose acetate butyrate (CAB) as the matrix (Glasser et al. 1999; Gindl and Keckes 2004). While those composites were based primarily on cellulose, esterification altered the polarity of the matrix relative to the fibres and mechanical performance was not as good as for true all-cellulose composites. Gindl and Keckes (2004) reported a tensile strength of 129 MPa for CAB reinforced with bacterial cellulose, compared with 480 MPa for a true all-cellulose composite prepared by regeneration (Nishino et al. 2004).

We chose to follow Nishino et al. (2004), Gindl and Keckes (2005) and Gindl et al. (2006a, b) in preparing all-cellulose composites by partial dissolution in lithium chloride/N,N-dimethylacetamide (LiCl/DMAc).

## **Experimental**

### *Preparation of composites*

Cellulose dissolution using DMAc initially involves an activation step in which the cellulose structure is first swollen via solvent exchange (Striegel 2002; Dupont 2003). The increased molecular mobility of cellulose allows the LiCl/DMAc solvent to penetrate the cellulose structure more easily (McCormick et al. 1985; Ishii et al. 2003). In the present work, microcrystalline cellulose (MCC) powder (Avicel, Merck, particle size between 20 and 160  $\mu\text{m}$ ) was immersed in distilled water at 20°C for 48 hrs and vacuum-filtered through Whatman No. 1

filter paper, twice immersed in acetone (Biolab, laboratory grade) at 20°C for 24 hrs and filtered through Whatman No. 1 filter paper to remove the acetone each time, twice immersed in DMAc (Merck, synthesis grade) at 20°C for 24 hrs and each time filtered through Whatman No. 1 filter paper afterward, vacuum-dried for 48 hrs at 60°C and then sieved (90 µm). The activated MCC was vacuum-dried for a further 48 hrs at 60°C and finally sealed in a container for storage.

### *Partial dissolution*

A solution of 8.0% (by total weight) LiCl in DMAc was prepared by mixing LiCl (Unilab, 99 % purity) and DMAc in a 2 L Schott bottle. The bottle was immediately sealed to prevent moisture absorption. The mixture was mechanically stirred for 24 h until the salt appeared to be completely dissolved.

A portion of 1 g activated MCC was immersed in a Petri dish containing sufficient LiCl/DMAc to achieve cellulose concentrations of  $c = 5\%$ , 10%, 15% or 20%, where  $c$  is expressed as % of the total weight of cellulose, LiCl and DMAc. The solution was placed under vacuum and stirred for 1 h, 4 h, 8 h or 48 h at 20 °C. The regeneration of the dissolved cellulose began initially with light spraying of water onto the surface of the gel in order to fix the shape of the final sample. The partially regenerated gel was then carefully transferred to a beaker and immersed in water for 48 hrs at 20 °C. The water was changed at least every 24 h. Residual LiCl or DMAc was removed by further thorough rinsing of the specimen with water. The specimens were then dried 48 h in a vacuum oven at 60°C to ensure complete solidification.

### *Wide Angle X-ray Scattering (WAXS)*

WAXS was performed on as-received MCC, activated MCC and on the final composites. X-ray patterns were obtained with a Philips PW1729 diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.1540$  nm), voltage of 50 kV and current of 40 mA with  $2\theta$  increased in steps of  $0.02^\circ$ . The X-ray data was smoothed over 30 adjacent points using the adjacent averaging smoothing function in Origin $^{\text{©}}$  Pro 7.5 and plots were then area-normalized. Peaks were assigned according to the monoclinic unit cell described by Sugiyama et al. (1991). Peak positions and widths were measured from plots by using the method described by Gjønnes and Norman (1958). We did not use curve fitting software because of the complexity of the diffractograms, with peak positions and widths expected to be related to crystallite dimensions as well as crystalline forms of cellulose, as discussed below. Instead, we confined precise measurements to samples that had not been in contact with LiCl/DMAc.

The Scherrer equation was used to calculate the crystal thickness by using the half-width at half-height of the peak assigned to (200) planes:

$$D = K\lambda/(B\cos\theta) \quad (1)$$

where  $D$  is the crystal thickness,  $\lambda$  the radiation wavelength,  $\theta$  the diffraction angle and  $B$  the full width of the diffraction peak measured at half maximum height prior to smoothing. The correction factor,  $K$ , was set to 0.9 (Murdock 1930). A crystallinity index  $CrI$  was used as defined by Segal et al. (1959):

$$CrI = 100(I-I')/I \quad (2)$$

Here  $I$  is the height of the peak assigned to (200) planes, typically located in the range  $2\theta = 21^\circ$  to  $22^\circ$ , and  $I'$  is the height measured at  $2\theta = 18^\circ$ , which is where the maximum appears in a diffractogram of amorphous cellulose.

*Solid state  $^{13}\text{C}$  nuclear magnetic resonance (NMR)*

Each composite was crushed to particle dimensions of ~0.5 mm, combined with a similar or larger weight of water, and packed into a zirconium oxide rotor. Excess water was expelled during packing to prepare samples with a typical solids content of 55% by dry weight. The rotor was sealed with a Kel-F® cap.

Solid state CP-MAS  $^{13}\text{C}$  NMR spectra were obtained on a Bruker Avance DRX200 FT-NMR spectrometer at a frequency of 50.3 MHz and at a magic-angle spinning frequency of 5 kHz. Each  $90^\circ$  proton preparation pulse of 5  $\mu\text{s}$  was followed by a delay  $\tau$ , a contact time of 1 ms, acquisition time of 20 ms, and a recycle delay of 1 s. Two spectra were acquired for each sample and labelled **S** ( $\tau = 1 \mu\text{s}$ ) and **S'** ( $\tau = 15 \mu\text{s}$ ). Bold type is used for these symbols since they represent vectors, i.e., lists of the signal heights measured across a range of chemical shifts. Transients from a minimum of 10,000 pulses were averaged in both cases.

Signals from crystalline cellulose were partly suppressed in **S'**, through relatively rapid  $T_2(\text{H})$  decay during the delay  $\tau$ . The discrimination was enhanced by proton spin relaxation editing (PSRE). This method is more commonly used to process spectra modified by rotating-frame relaxation (Newman 1999) but has been used to process spectra modified by  $T_2(\text{H})$  (Newman et al. 1996). PSRE involves computing linear combinations:

$$\mathbf{A} = k\mathbf{S} + k'\mathbf{S}' \quad (3a)$$

$$\mathbf{B} = (1 - k)\mathbf{S} - k'\mathbf{S}' \quad (3b)$$

The values of  $k$  and  $k'$  are adjusted until signals assigned to poorly-ordered matter are excluded from **A** and signals well-ordered matter are excluded from **B**. In this case, signals at 80 ppm and 89 ppm were assigned to C-4 in poorly-ordered and crystallite-interior cellulose, respectively (Newman 1999). Details concerning the adjustment of  $k$  and  $k'$  can be found elsewhere (Newman and Hemmingson 1995). The fraction  $F$  of crystalline cellulose in each composite was estimated by dividing the area of **A** by area of **S**.

The subspectra labeled A showed two partly-resolved C-4 signals, assigned to crystallite-interior and crystallite-surface glucosyl residues, at 89 ppm and 84 ppm respectively. Signal areas were delimited by the baseline and a vertical line drawn at 86.4 ppm. Relative areas were used to estimate the percentage  $X$  of cellulose chains contained in crystallite interiors (Newman 1999). Assuming a simplified model of a square cellulose crystallite with cross-sectional dimensions  $L \times L$  and only a monolayer of cellulose chains exposed to the surface, an estimate of the apparent average crystallite size can be given by the expression (Newman 1999):

$$L = 1.14 / (1 - X^{1/2}) \quad (4)$$

## Results and Discussion

### *WAXS diffractograms*

Activation showed only a minor effect on the WAXS diffractogram (Fig. 1). The peak assigned to (200) planes appeared at  $2\theta = 22.6^\circ$  and  $22.8^\circ$  in as-received MCC and activated MCC, respectively, as in published WAXS diffractograms for cellulose I (Isogai 1989; Ishii et al. 2003). The full widths  $B$  at half maximum height were  $1.75^\circ$  and  $1.68^\circ$ , giving crystal thicknesses of 4.5 and 4.9 nm, respectively, according to Eq. (1).

Peaks at  $2\theta = 15.1^\circ$ ,  $16.8^\circ$  and  $34.8^\circ$  in the diffractogram for activated cellulose were also consistent with peaks in published WAXS diffractograms for cellulose I (Isogai 1989; Ishii et al. 2003). The crystallinity index  $CrI$  calculated from Eq. (2) decreased from 87% for MCC to 80% after activation (Table 1).

The WAXS diffractograms for all-cellulose composites showed a small shoulder at  $2\theta = 20.8^\circ$  that progressively developed into a distinct diffraction peak with decreasing cellulose concentration in the solvent (Figs. 2, 3). The peak was more distinct in composites prepared with



a dissolution time of 8 h (Fig. 3), relative to 1 h (Fig. 2). Plots for other dissolution times indicated that equilibrium was reached after approximately 4 h, with little further change to 48 h. Gindl and Keckes (2005) observed this peak in WAXS diffractograms of all-cellulose composites, and assigned it to regenerated cellulose. They observed a similar peak in a WAXS diffractogram of cellulose produced by dissolving cellulose II in LiCl/DMAc and regenerating it.

The peak at  $2\theta = 20.8^\circ$  was  $5.0^\circ$  wide at half maximum height, and this width was too small for the peak to be assigned to amorphous cellulose. Ball-milled cellulose is commonly used as a reference standard for amorphous cellulose. The peak position has been reported as  $2\theta = 18^\circ$  (Segal et al. 1959; Mann 1962) or  $2\theta = 20^\circ$  (Schroeder et al. 1986), but it is generally agreed that the width is approximately  $10^\circ$ . The width of  $5.0^\circ$ , observed in Fig. 3, corresponds to a crystallite thickness of  $D = 1.6$  nm according to Eq. (1). For (200) planes separated by 0.4 nm (Sugiyama et al. 1991) that corresponds to crystallites containing just 4 planes.

A commonly-used crystallinity index  $CrI$ , expressed in Eq. (2), exploits the fact that the maximum for amorphous cellulose falls between peaks in the diffractogram for cellulose I. The diffractograms in Figs. 2 and 3 showed increasing height at  $2\theta = 18^\circ$ , for increasing degrees of transformation, but the value of  $CrI$  never dropped below 39% (Table 1).

Gjønnnes and Norman (1958) and Ioelovich and Larina (1999) reported lattice expansion in thin crystallites of cellulose I, so that an increase in peak width was associated with a displacement to low values of  $2\theta$ . A curve published by Gjønnnes and Norman (1958) indicated that an increase in peak width to  $7^\circ$  was sufficient to displace the peak to  $2\theta = 21^\circ$ . The peak at  $2\theta = 20.8^\circ$  in Figs. 2 and 3 is therefore consistent with cellulose I crystallites split to fine dimensions.

When regenerated cellulose crystallizes to the cellulose II allomorph it shows WAXS peaks at  $2\theta = 12.1^\circ$ ,  $19.8^\circ$  and  $22.0^\circ$  (Isogai et al. 1989). Changes in lattice dimensions influence the positions of WAXS peaks for cellulose II, but the pattern of displacements is different from

that for cellulose I. Gjønnnes and Norman (1960) showed that the peak at  $2\theta = 19.8^\circ$  is displaced to higher values, and the peak at  $2\theta = 22.0^\circ$  to lower values, as the peaks broaden. Extrapolation from their data suggested that the two peaks might form a single peak, with a width of approximately  $7^\circ$ , at a value of  $2\theta$  somewhere between  $20^\circ$  and  $21^\circ$ . Yamashiki et al. (1992) confirmed movement towards an intermediate value of  $2\theta$  by published WAXS diffractograms for cellulose II as viscose and cuprammonium rayons, showing a broad peak at  $2\theta = 20.0^\circ$  with a shoulder at  $2\theta = 21.6^\circ$ . The peak at  $2\theta = 20.8^\circ$  in Fig. 3 is therefore indistinguishable from the pattern predicted for very narrow crystallites of cellulose II.

Cellulose III, when prepared from cellulose I, shows a strong WAXS peak  $2\theta = 20.7^\circ$  and a weaker peak  $2\theta = 11.7^\circ$  (Isogai et al. 1989). The former peak matched the broad peak in WAXS diffractograms of the most severely treated specimens (Figs. 2 and 3), but the latter was not observed.

The peak assigned to (200) planes of cellulose I remained visible as a shoulder at  $2\theta = 22.3^\circ$  in WAXS diffractograms of specimens with the greatest degrees of transformation, i.e., the lower two traces in Figs. 2 and 3. The shoulder was too weak for measurement of the peak width, but the curve published by Gjønnnes and Norman (1958) indicated that displacement to  $2\theta = 22.3^\circ$  corresponded to a peak width of  $3^\circ$ , for which Eq. (1) indicated a crystallite thickness of approximately 3 nm. The diffractogram of MCC (Fig. 1) showed a peak assigned to (004) planes. This peak was weak or absent in diffractograms of all-cellulose composites prepared with the greatest degrees of transformation, e.g., the lowest diffractogram in Fig. 3. The disappearance of this peak suggests longitudinal disorder, consistent with a paracrystalline matrix.

*Solid-state  $^{13}\text{C}$  NMR*

The  $^{13}\text{C}$  NMR spectrum of activated MCC (Fig. 4) resembled a published spectrum of Avicel MCC (Newman and Hemmingson 1995), confirming WAXS indications of little change in molecular packing associated with activation. Minor changes were revealed by PSRE (Fig. 4). In the published PSRE results (Newman and Hemmingson 1995) subspectrum **A** accounted for 84% of the area of the total spectrum **S**. This proportion decreased to 73% after activation (Fig. 4), indicating transformation of some of the cellulose I to a less ordered form of cellulose. A published  $^{13}\text{C}$  NMR study of Avicel MCC indicated a crystallite width of  $L = 5.9$  nm (Newman 1999). Peak areas in subspectrum **A** of Fig. 4, interpreted according to the same procedure, indicated a crystallite width of  $L = 6.3$  nm for activated MCC (Table 1).

Fig. 5 shows  $^{13}\text{C}$  NMR spectra of the composites regenerated after a dissolution time of 8 h. Peaks are assigned to cellulose I, as in Fig. 4. Cellulose II would have contributed a peak at 108 ppm, assigned to C-1 in crystallite-interior chains (Hemmingson and Newman 1995; Newman and Hemmingson 1995). No such peak was detected in Fig. 5, so there was no evidence for regeneration to cellulose II in crystallites of sufficient size for chains to be enclosed.

A peak at 89 ppm was assigned to C-4 peak of crystallite-interior chains of cellulose I. This peak was observed in all of the spectra in Fig. 5, but decreased with decreasing values of  $c$ . PSRE was used to split the NMR spectra into subspectra labeled **A** (Fig. 6), assigned to crystalline cellulose, and subspectra labeled **B** (Fig. 7), assigned to cellulose that was less well ordered.

The fraction  $F$  of cellulose associated with subspectrum **A** dropped steadily from 0.84 for MCC to  $F = 0.24$  for the composite treated for 8 h at  $c = 10\%$ , then rose to  $F = 0.37$  for  $c = 5\%$  (Table 1). The last of these values might have been distorted by the difficulty in separating subspectra **A** and **B**.

Relative peak areas within subspectrum **A** were used to calculate  $X$ , i.e., the crystallite-interior cellulose expressed as % of crystalline cellulose contributing to subspectrum **A**. The

values (Table 1) confirmed the visual impression (Figs. 5, 6) of a steady decline in  $X$  as the value of  $c$  was decreased. The values of  $X$  were used to calculate crystallite widths  $L$ , according to Eq. (5). Values (Table 1) indicated a decrease to  $L = 2.3$  nm for the most severe treatment.

The chemical shift for C-4 is particularly sensitive to the conformation of a cellulose chain (Horii et al. 1987). Chemical shifts in the range 79 to 81 ppm are characteristic of the random-coil conformation of cellulose dissolved in trifluoroacetic acid (Bock et al. 1991) or regenerated as amorphous cellulose (Hirai et al. 1990; Newman and Hemmingson 1995). Chemical shifts in the range 84 to 90 ppm are characteristic of the linear conformations of chains in crystalline cellulose (Horii et al. 1987). El-Kafrawy (1982) dissolved cellulose in LiCl/DMAc and observed a C-4 peak at 79 ppm, confirming a true solution of random-coil cellulose. All of the traces in Fig. 7 showed a dip at 80 ppm, labeled C-4a, but the fact that the dip did not extend to the baseline suggested a contribution from amorphous cellulose. Most of the C-4 signal area was found in a peak at 84 ppm, i.e., the same chemical shift as reported for C-4 in cellulose chains in linear molecular conformations exposed on the surfaces of cellulose I, with hydroxymethyl groups in the *gauche-gauche* conformation (Newman and Davidson 2004). The C-6 signal area was found in a peak at 62 ppm, also consistent with chains exposed on surfaces of cellulose I (Newman and Davidson 2004). It is possible to construct models for crystallites of cellulose I in which all chains are exposed on surfaces, but the widths must be no more than 2 nm. Such crystallites might be described as ‘paracrystalline’, so we have used the label C-4p in Fig. 7.

The combination of C-4 and C-6 peaks at 84 and 62 ppm, respectively, has also been reported for the NMR spectrum of cellulose IV (Isogai et al. 1989). This is consistent with a suggestion that cellulose IV is simply a poorly-crystalline form of cellulose I (Tsuda and Mukoyama 1957; Wada et al. 2004). Cellulose IV has been identified as a product of the viscose process for regenerating cellulose (Tsuda and Mukoyama 1957).

Chemical shifts for crystallite-surface chains in cellulose II have been reported as 88.0 and 86.5 ppm (C-4s) and 63.2 and 62.9 ppm (C-6s) (Newman and Davidson 2004). Those chemical shifts differ from the values observed in Fig. 7. Hong (1998) reported evidence for cellulose III in cellulose fibre regenerated from LiCl/DMAc. The chemical shifts for crystallite-interior cellulose III are similar to those for cellulose II (Isogai et al. 1989), but crystallite-surface signals have not been reported.

The relevant proton spin relaxation time constants provide clues to the nature of the matrix. The experiments described in this paper were based on differences in  $T_2(H)$  between crystallites and the matrix. Subspectra were separated from spectra of the primary walls of *Arabidopsis thaliana* by Newman et al. (1996), and the values of  $k$  and  $k'$  in Eq. (3) indicated  $T_2(H) = 8.5 \mu\text{s}$  and  $19 \mu\text{s}$  for crystalline cellulose and amorphous matrix polysaccharides, respectively. Using the same expressions for  $k$  and  $k'$  in the present work indicated  $T_2(H) = 8.6 \mu\text{s}$  and  $11 \mu\text{s}$  for crystallites and matrix, respectively. The value of  $T_2(H)$  for the cellulosic matrix was not greatly increased over the value for the crystallites, suggesting paracrystallinity rather than amorphicity.

The subspectra stacked in Fig. 7 could not be used to determine the relative proportions of paracrystalline and amorphous cellulose, since the C-4 peaks were not resolved. Overlap between the C-4 and C-2,3,5 bands might even account for much of the signal strength in the dip at 80 ppm.

Kondo et al. (2001) introduced the concept of 'nematic ordered cellulose' to cover intermediate states of molecular ordering such as those described in this work, i.e., states that display some of the features of each of the crystalline allomorphs of cellulose, yet no perfect match to any one of those allomorphs.

*Comparisons between WAXS and NMR*

The WAXS index  $CrI$  showed strong correlations with both of the NMR indices tabulated in Table 1. Linear least-squares fits gave correlation coefficients  $R^2 = 0.92$  and  $0.94$  for  $CrI$  against  $F$  and  $X$  respectively. The correlation coefficient rose to  $R^2 = 0.99$  for  $CrI$  against the product  $FX$ , i.e., crystallite-interior cellulose expressed as % of total cellulose.

The crystallite dimensions  $D$  and  $L$  showed similar trends, i.e., decreasing cross-sectional dimensions as a result of partial dissolution. A perfect match was not expected for these parameters, since they represent cross-sectional measurements in orthogonal directions:  $D$  perpendicular to the (200) planes,  $L$  across those planes (Newman 1999).

### *Transformation mechanisms*

When considered together, the WAXS and NMR results suggest the following mechanism.

Exposure to LiCl/DMAc peels layers of cellulose from crystallites. The residual core of the crystallite becomes thinner as successive layers are removed. The peeled layers might retain some of the molecular ordering of the cellulose I structure from which they were removed, but are too thin to contain crystallite-interior chains. When the LiCl and DMAc are washed away, the peeled layers of cellulose are regenerated into a paracrystalline matrix. The paracrystalline structures are sufficiently disordered to show  $T_2(H)$  values slightly longer than those characteristic of crystalline cellulose. On the other hand, they are sufficiently distinct from amorphous cellulose to show a WAXS peak just half as broad. They are also sufficiently distinct to show a 4 ppm displacement of the C-4  $^{13}C$  NMR peak, from 80 ppm for amorphous cellulose to 84 ppm for the matrix of the composites.

The partly-ordered nature of the matrix helps account for the superior mechanical properties observed for all-cellulose composites.

Using relatively high concentrations of cellulose in LiCl/DMAc has several advantages. Above all else, it minimizes the shrinkage undergone by the material during the precipitation and drying stage. This minimizes many manufacturing constraints like large mould opening, shape loss or amount of residual water in the material before drying. There are also financial, environmental and health interests in minimizing the amount of solvent used for a given amount of polymer. Conio et al. (1984) suggested that a concentration  $c < 15\%$  was necessary for partial dissolution in 8% LiCl/DMAc, and a concentration  $c < 11\%$  was necessary for complete dissolution. Our results show that partial dissolution could be observed at  $c = 20\%$ . More work is required to test whether the degree of transformation was sufficient to provide satisfactory mechanical properties. Transformation was nearly complete for  $c = 10\%$ , but we detected a trace of residual crystalline cellulose.

## **Conclusions**

Partial dissolution and regeneration of cellulose, using LiCl/DMAc, yields all-cellulose composites with a matrix comprising a mixture of paracrystalline and amorphous cellulose. Both WAXS and NMR results point to distinct differences from a fully amorphous matrix. More work is needed to test the consequences of paracrystallinity on the mechanical properties of all-cellulose composites.

## **Acknowledgements**

The authors would like to thank the Biopolymer Network Limited (New Zealand) for financial assistance and technical support provided to this project. One of the authors (MPS) would like to thank the Brian Mason Scientific and Technical Trust for financial assistance. The authors thank Mr. S. Hill (Scion Limited, Rotorua, New Zealand) for assistance with solid-state NMR and Mr. S. Brown for acquisition of the WAXS patterns.

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Table 1. Data for starting materials and all-cellulose composites prepared by partial dissolution for 8 h at cellulose concentrations  $c$  expressed as % of the total weight of cellulose, LiCl and DMAc.

Sample	$CrI$ (%)	$D$ (nm)	$F$	$X$ (%)	$L$ (nm)
MCC	87	4.5	(0.84) <sup>a</sup>	(65) <sup>a</sup>	(5.9) <sup>a</sup>
Activated	80	4.8	0.73	67	6.3
$c = 20\%$	71	- <sup>b</sup>	0.56	61	5.2
$c = 15\%$	59	- <sup>b</sup>	0.52	49	3.8
$c = 10\%$	39	- <sup>b</sup>	0.24	32	2.6
$c = 5\%$	39	- <sup>b</sup>	0.37	24	2.3

<sup>a</sup> literature values (Newman and Hemmingson 1995)

<sup>b</sup> not done because of peak overlap

## FIGURE CAPTIONS

Figure 1 WAXS diffractograms of MCC before and after activation. Peaks assignments use the monoclinic cellulose I unit cell of Sugiyama et al. (1991).

Figure 2 WAXS diffractograms of all-cellulose composites prepared from activated cellulose by partial dissolution for 1 h with values of  $c$  shown above each trace.

Figure 3 WAXS diffractograms of all-cellulose composites prepared from activated cellulose by partial dissolution for 8 h with values of  $c$  shown above each trace.

Figure 4 Solid-state  $^{13}\text{C}$  NMR spectra of activated cellulose. Experimental results are labeled **S** and **S'**. PSRE subspectra **A** and **B** are assigned to crystalline and less-ordered cellulose, respectively.

Figure 5 Solid-state  $^{13}\text{C}$  NMR spectra of all-cellulose composites prepared from activated cellulose mixed with solvent at the weight % values shown above each trace and left for 8 h of dissolution.

Figure 6 Subspectra **A** separated from solid-state  $^{13}\text{C}$  NMR spectra of all-cellulose composites prepared from activated cellulose mixed with solvent at the weight % values shown above each trace and left for 8 h of dissolution. Labels C-4i and C-4s indicate chemical shifts for chains in the interior and on surfaces, respectively, of cellulose I crystallites.

Figure 7 Subspectra **B** separated from solid-state  $^{13}\text{C}$  NMR spectra of all-cellulose composites prepared from activated cellulose mixed with solvent at the weight % values shown above each trace and left for 8 h of dissolution. Labels C-4a and C-4p indicate chemical shifts for amorphous and paracrystalline cellulose, respectively.

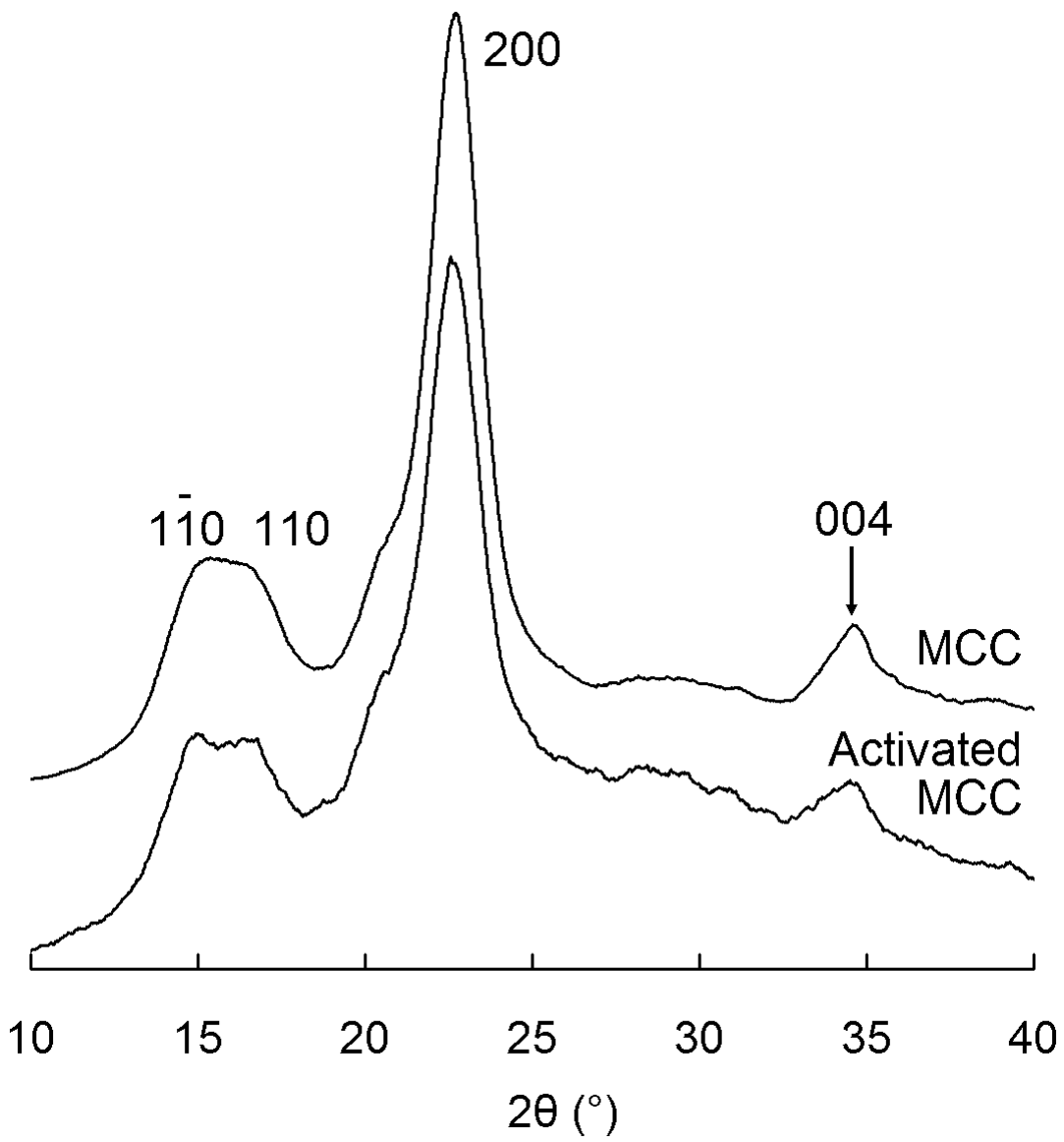


Fig. 1

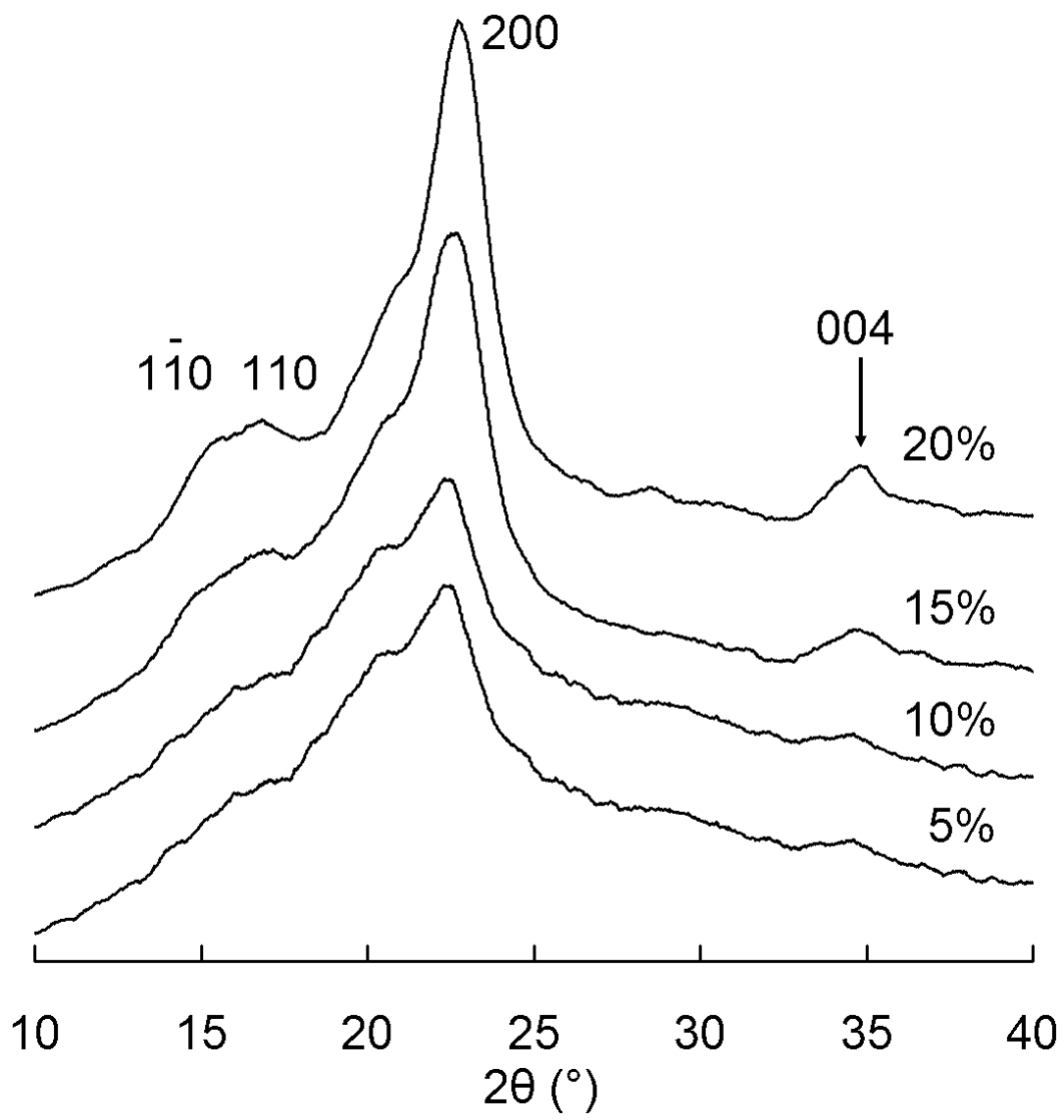


Fig. 2

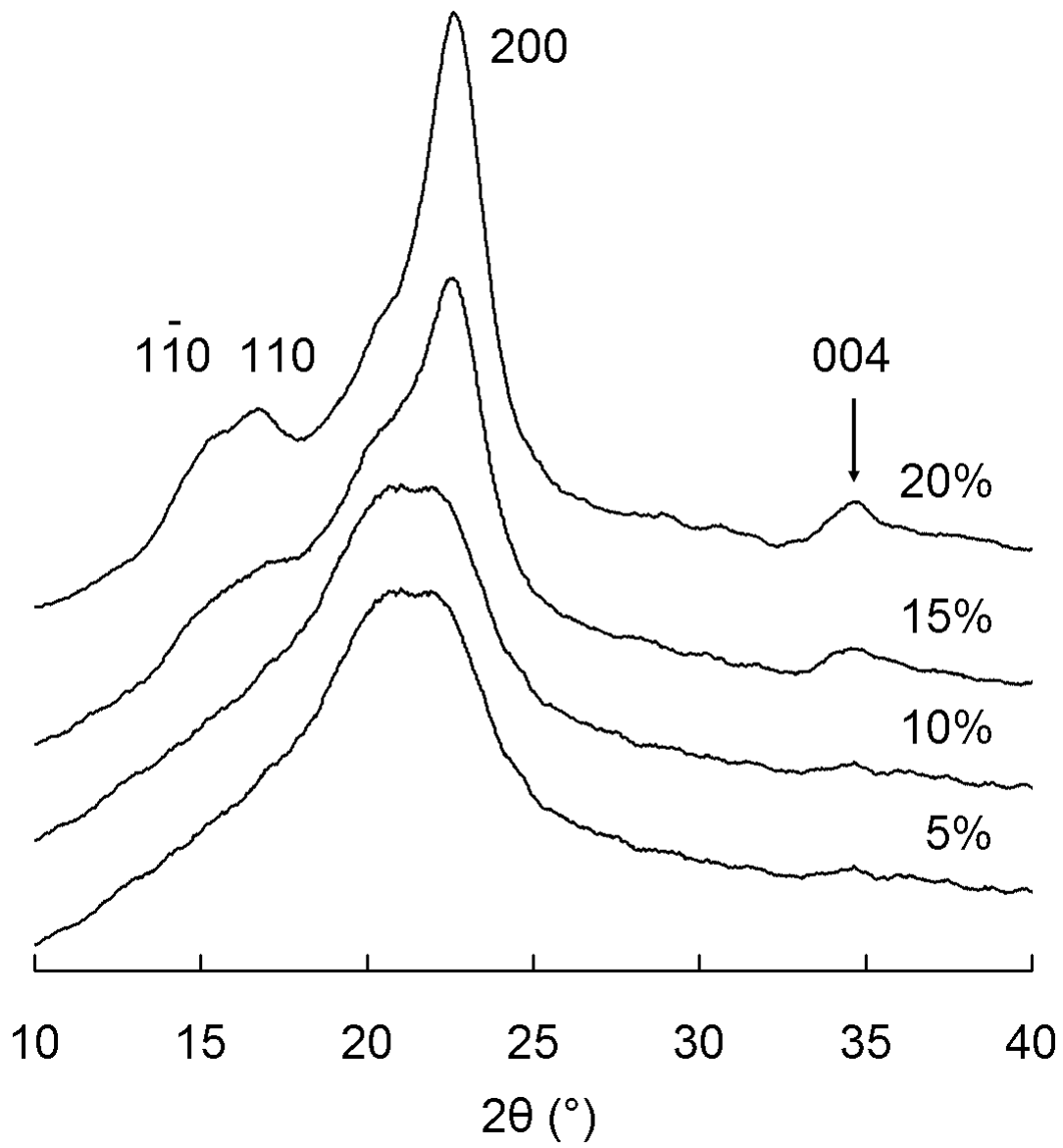


Fig. 3



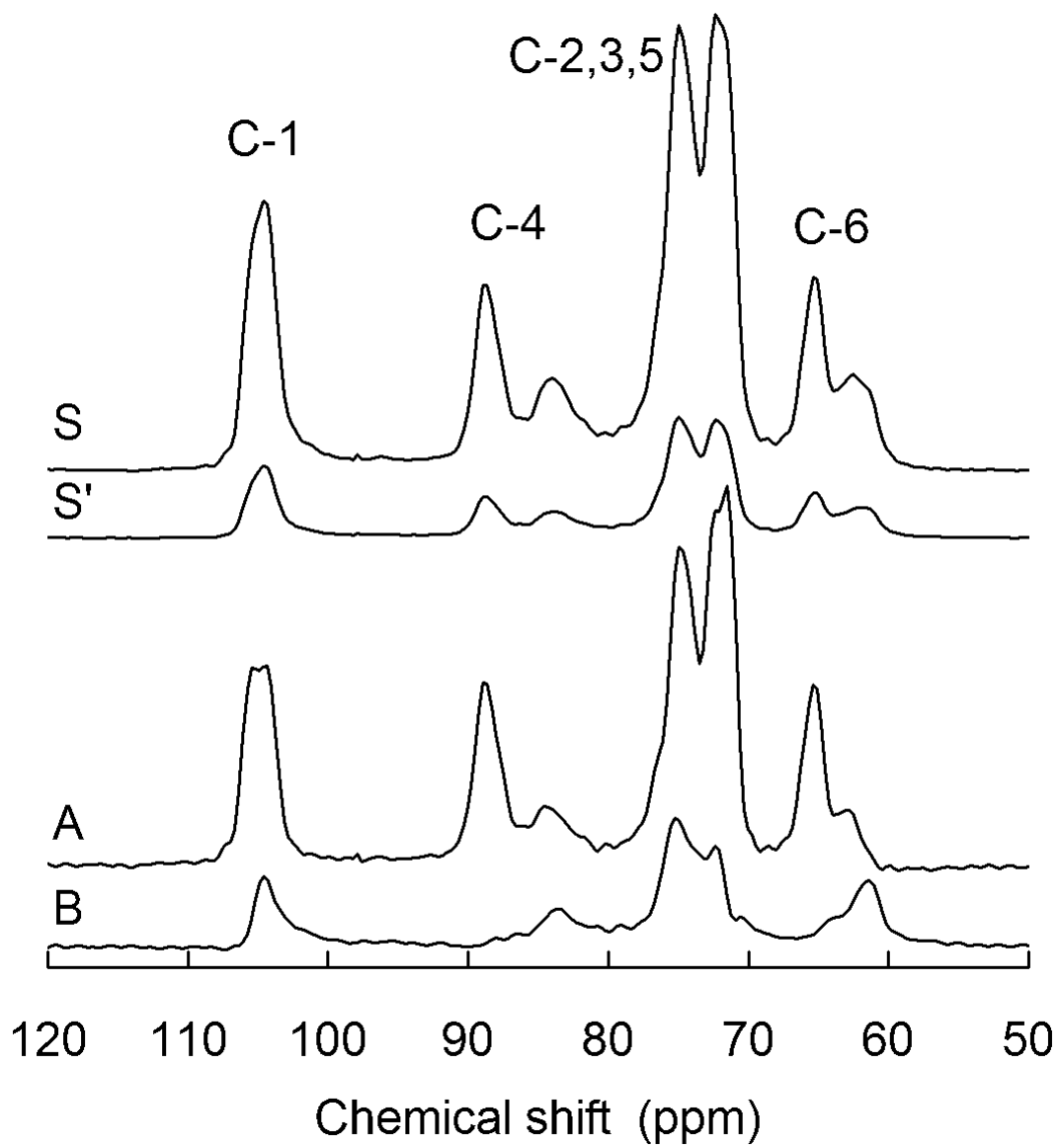


Fig. 4

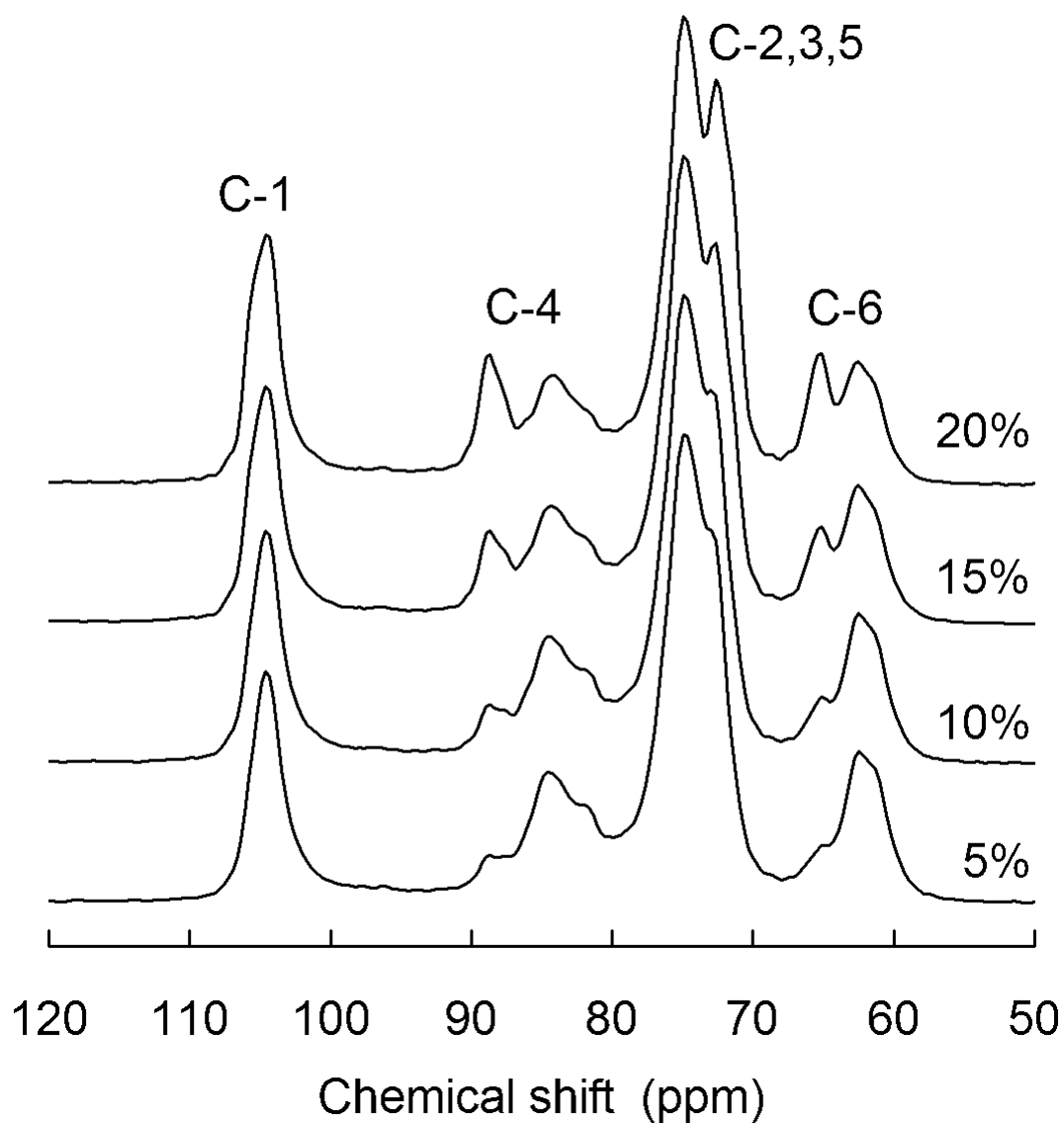


Fig. 5

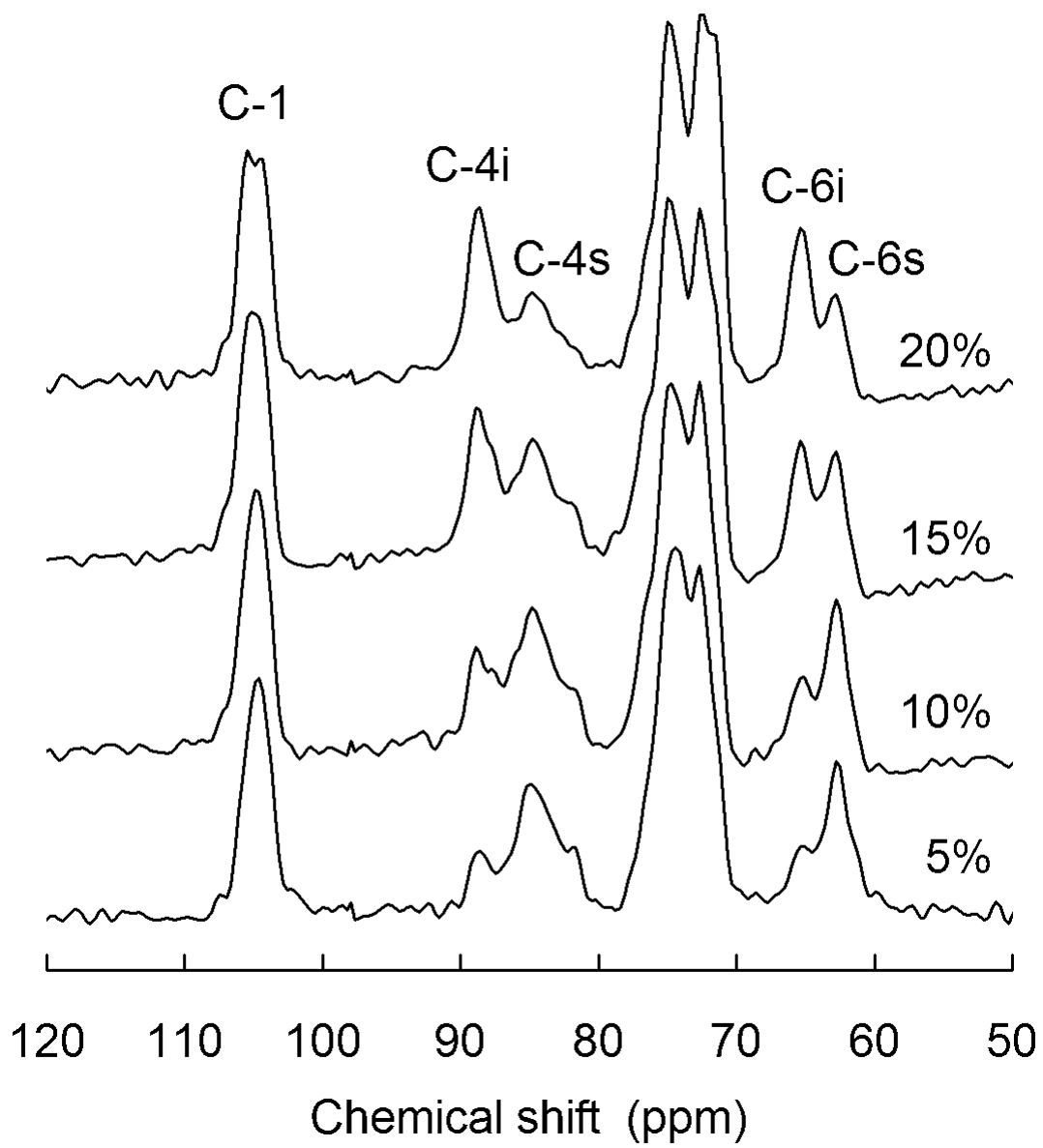


Fig. 6

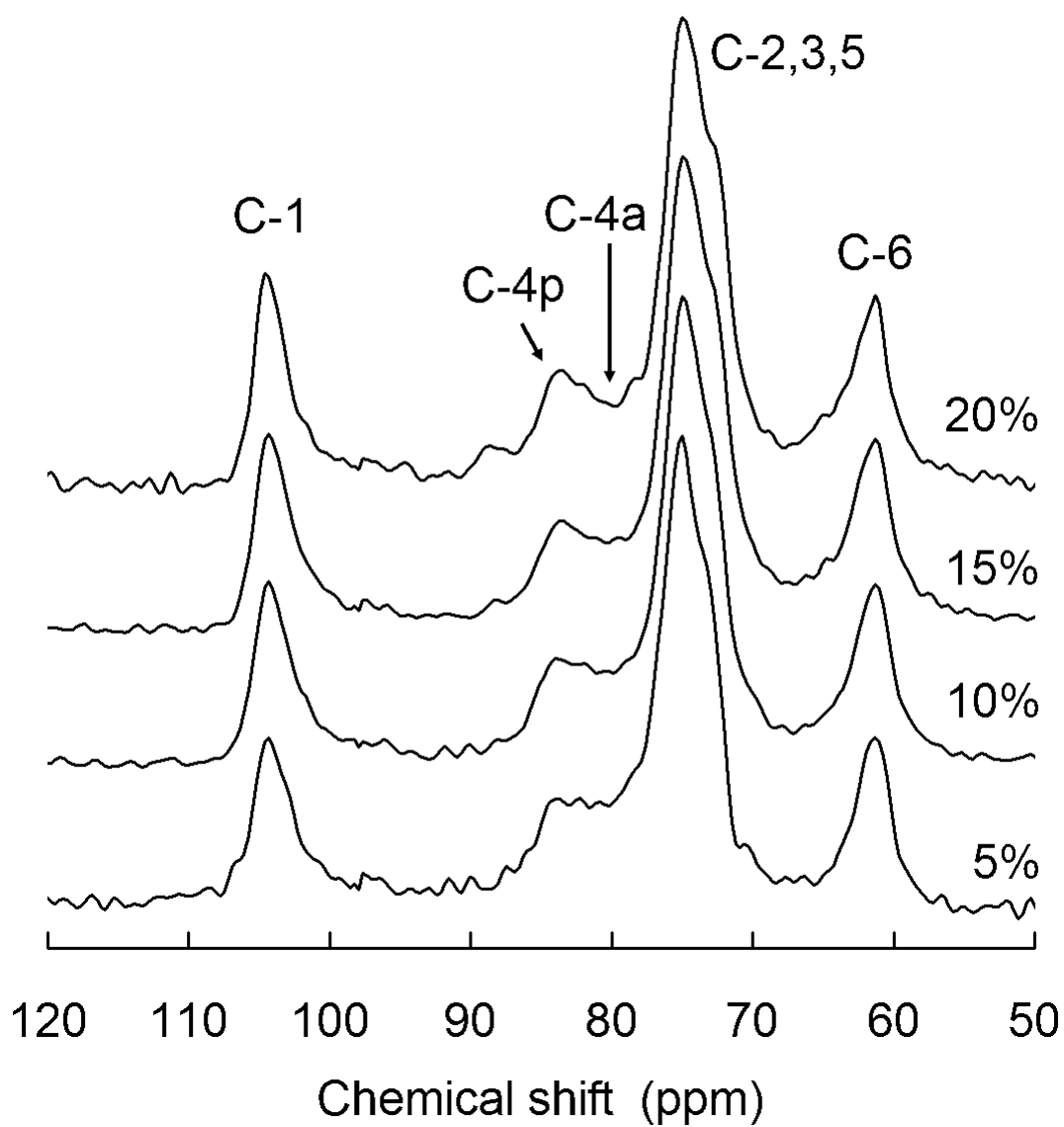


Fig. 7