Macromolecules 1987, 20, 1554-1556

(8) Hahn, E. L. *Phys. Rev.* **1950**, *80*, 850.
(9) Zimmerman, J. R.; Brittin, W. E. *J. Phys. Chem.* **1957**, *61*, 1328.
(10) Andrew, E. R.; Bryant, D. J.; Cashell, E. M. *Chem. Phys. Lett.* **1980**, *69*, 551.
(11) Kalk, A.; Berendsen, H. J. C. *J. Magn. Reson.* **1976**, *24*, 343.
(12) Shirley, W. M.; Bryant, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 2910.
(13) Solomon, I. *Phys. Rev.* **1955**, *99*, 559.
(14) Bloembergen, N.; Purcell, E. M.; Pound, R. V. *Phys. Rev.* **1948**, *73*, 679.
(15) Bone, S.; Pethig, R. *J. Mol. Biol.* **1985**, *181*, 323.
(16) Ramachandran, G. N.; Chandrasekharan, R. *Biopolymers* **1968**, *6*, 1639.
(17) Cook, W. J.; Einspahr, H.; Trapane, T. L.; Urry, D. W.; Bugg, C. E. *J. Am. Chem. Soc.* **1980**, *102*, 5502.

Effect of Water in the ^{13}C CP/MAS NMR Spectrum of White Spruce Wood

J. M. Willis† and F. G. Herring*

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6. *Received September 22, 1986*

ABSTRACT: Improved resolution and signal-to-noise ratio were observed for the ^{13}C CP/MAS NMR spectra measured for white spruce wood saturated with water, in comparison to that measured for dry wood. Variable contact time experiments illustrated that the cross-polarization step of the CP/MAS NMR technique was more efficient for the wet sample and that the presence of water had a larger effect on the carbohydrate component than the lignin component of the wood.

Introduction

Extensive studies have been performed on the analysis of cellulose macromolecules of varying crystallinity and conformation by using the ^{13}C CP/MAS (cross-polarization/magic angle spinning) NMR technique.[1-9] In some cases,[10-12] it was noted that the hydration of cellulosic materials resulted in line narrowing of the NMR spectra. The recent study by Horii et al.[10] illustrated how the presence of excess water in samples of cotton increased the resolution of some of the lines in the ^{13}C CP/MAS NMR spectrum. The decrease in the line widths was attributed to relaxation effects where a more ordered structure was possible due to the presence of water. Similar hydration effects were noted in the ^{13}C CP/MAS NMR spectra of 1,3-β-D-glucans[11] and various native cellulosic materials.[12]

There were two objectives for the present study. Firstly, the effect of hydration on the ^{13}C CP/MAS NMR spectrum of a sample of white spruce wood was investigated to determine if the lignin component would undergo the same line narrowing as that observed for cellulose. Secondly, a variable contact time analysis of wet and dry white spruce was performed to give further insight to the observed hydration effects.

Experimental Section

Sample Preparation. In preparation for the NMR measurements, air-dried white spruce (Picea Glauca) chips were ground to pass 40 mesh in a Wiley mill. Samples saturated with water were prepared by introducing approximately 0.5 mL of distilled water to 250 mg of ground wood. The effect of the extent of hydration was not investigated in the present study. Such a study was performed by Horii et al.,[10] who had observed a maximum effect of hydration using saturated samples. As a result, only saturated samples were used in the present investigation.

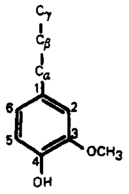
NMR Measurements. The ^{13}C CP/MAS NMR spectra were obtained by using a Bruker CXP 200 NMR spectrometer, operating at resonance frequencies of 200 and 50.3 MHz for protons and carbon-13 nuclei, respectively. Spin-locked cross-polarization was used to establish the single contact Hartmann-Hahn condition.[13] A delay time of 1 s was used between successive sampling pulses. For a 20-kHz spectrum, between 8000 and 10 000 scans were accumulated for each experiment. Phase alternation was used throughout the signal acquisition to minimize base-line and intensity artifacts.

The magic angle setting was adjusted by monitoring the ^{79}Br spectrum of potassium bromide.[14] This was facilitated by adding 20–50 mg of KBr to each sample before packing the Kel-F rotor. A spinning rate of 2.5 ± 0.5 kHz was used in all NMR measurements. The chemical shifts were measured relative to tetramethylsilane (Me_4Si) using benzene as an internal reference.

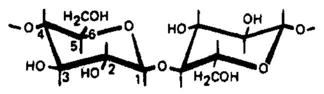
Variable contact time experiments were performed by using an automation program available on CXP NMR software. The contact times ranged from 0.01 to 6 ms.

Results

Figure 1 illustrates the ^{13}C CP/MAS NMR spectra obtained for dry and wet white spruce at a contact time of 1 ms. The peaks at 150 and 56 ppm correspond to the C_3, C_4 aromatic carbons and methoxyl groups of lignin (**1**), respectively. The peak at 105 ppm corresponds to the C_1 anomeric carbon of cellulose (**2**). For both cellulose and hemicellulose, the C_4 carbons appear at 85 and 89 ppm, the C_6 carbons at 62 and 66 ppm, and the C_2, C_3, C_5 carbons at 74 and 77 ppm. The acetyl methyl carbon of hemicellulose appears at 22 ppm.



1



2

By comparing the two spectra in Figure 1, it can be seen that the resolution of the peaks is far better for the wet sample than the dry one. This is particularly true for the carbohydrate peaks. Due to the convolution of these peaks, it is not possible to accurately measure the line widths. As a result, an assessment of the resolution enhancement can only be made qualitatively.

---

† Present address: Industrial Materials Research Institute, National Research Council of Canada, Boucherville, Quebec, Canada J4B 6Y4.

0024-9297/87/2220-1554$01.50/0

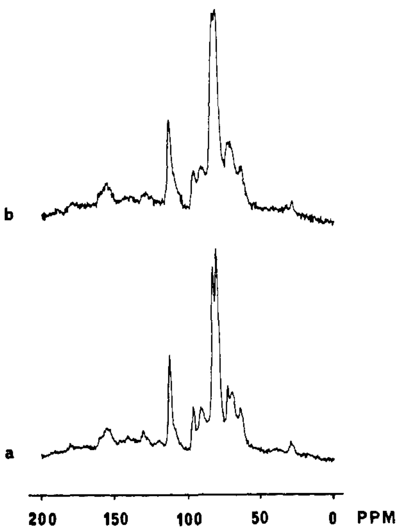


Figure 1. ^{13}C CP/MAS NMR spectra obtained for (a) wet and (b) dry white spruce wood.

Table I
Improvement in the Signal-to-Noise Ratio of the Peaks in the ^{13}C CP/MAS NMR Spectra of Dry and Wet White Spruce Wood

	signal-to-noise ratio		
peak, ppm	dry wood	wet wood	% improvement in signal-to-noise ratio
150	1.8	2.8	1.6
105	8.2	23.7	2.9
89	3.5	10.7	3.1
85	4.1	10.6	2.6
77	17.8	46.1	2.6
74	18.3	51.2	2.8
66	6.2	16.3	2.6
62	6.3	14.8	2.3
56	4.0	10.7	2.7
22	1.3	3.7	2.8

The signal-to-noise ratio of the spectrum measured for the wet wood improved by as much as 3 times, in comparison to that of the dry wood. Values of the signal-to-noise ratio determined for the spectra shown in Figure 1 are given in Table I. For the carbohydrate peaks, the average signal-to-noise improvement was found to be 2.7. The peak corresponding to lignin at 56 ppm also had an increase in signal-to-noise ratio of 2.7, while that of the aromatic carbon peak at 150 ppm was only 1.6.

To determine the optimum contact time corresponding to each peak in the CP/MAS spectrum, the absolute intensity (measured as peak height) of each peak is plotted as a function of contact time. The optimum contact time is thus the maximum point of the curve. This is illustrated in Figure 2, for the peaks at 105 and 150 ppm. In this manner the optimum values of the contact time were determined for each peak and are given in Table II.

It is interesting to note that the contact times obtained for the wet sample are shorter than those of the dry wood. It is also apparent that the carbohydrate components of wood are influenced to a larger extent than the lignin fraction. On the average, the difference between the dry and wet contact time was 12% for the peaks corresponding to lignin, and 32% for those corresponding to the carbohydrates.

Discussion

From the results presented, it is clear that hydration has an effect on both the carbohydrate and lignin components of wood. The improvement in signal-to-noise ratio, as well as the difference in the optimum contact time, was greater for those peaks in the ^{13}C CP/MAS NMR spectra which correspond to aliphatic carbons (cellulose, hemicellulose, and lignin from 105 to 22 ppm), in comparison to aromatic carbons (lignin, 150 ppm).

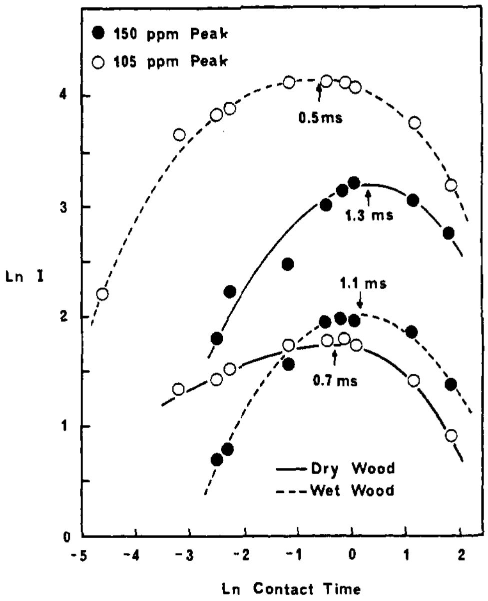


Figure 2. Natural logarithm of the absolute intensity (I) of peaks at 105 and 150 ppm as a function of contact time, for dry and wet white spruce wood.

Table II
Optimum Contact Time Values Obtained for Dry and Wet White Spruce Wood

	optimum contact time		
peak, pm	dry wood	wet wood	% difference
150	1.26	1.15	9.1
105	0.66	0.53	21.8
89	0.69	0.41	50.9
85	0.63	0.45	33.3
77	0.54	0.39	32.3
74	0.54	0.45	18.2
66	0.57	0.42	30.3
62	0.58	0.34	52.2
56	0.77	0.67	13.9
22	0.69	0.60	14.0

There are two mechanisms which may help to explain these results. The first mechanism is that suggested by Horii et al.[10] based on a CP/MAS study of cotton containing varying amounts of water. The presence of water apparently relaxed the noncrystalline regions to a more ordered state, thus resulting in narrower lines and enhanced resolution. A similar observation was made by Fyfe et al.[11] by comparing X-ray diffraction patterns of dry and hydrated curdlan and paramylon. In the case of white spruce wood, the reordering of the microstructure of the carbohydrates due to the hydration would give rise to an enhanced resolution of the corresponding peaks in the NMR spectrum. However, it is unlikely that the carbon nuclei of the lignin component of wood would benefit from relaxation to a more ordered state. This is due to the fact that the native lignin in wood is a three-dimensional network polymer.[15] The amorphous nature of lignin would prevent any relaxation to a more ordered conformation. As a result, it is not unexpected to find that the line width of the peak at 150 ppm, corresponding to the aromatic carbons of lignin, does not change upon hydration.

The fact that the peaks corresponding to lignin at 150 and 56 ppm have improved signal-to-noise ratios, as well as shorter optimum contact times, suggests that there is another mechanism to giving rise to the observed results. From the contact time data, it is evident that cross-polarization, where magnetization is transferred from the proton spin reservoir to that of the carbon nuclei, is more efficient for the wet sample. Thus, as a second mechanism, it is possible that the presence of water might assist the cross-polarization step through hydrogen bonding. In this case, carbon nuclei adjacent to hydrogen-bonded sites would experience a more efficient magnetization transfer. In other words, the aliphatic carbons of the carbohydrate and lignin would undergo larger hydration effects than the aromatic carbons of lignin. This was found to be the case, as can be seen from data given in Tables I and II. The improvement in signal-to-noise ratio upon hydration was more than 50% higher for the aliphatic carbons in comparison to the aromatic carbons. In addition, the difference in optimum contact times was more than 100% greater for the aliphatic carbons.

Concluding Remarks

It is evident from the results presented that the presence of excess water in the wood sample has a significant effect on the ^{13}C CP/MAS NMR spectra. Although the average optimum contact time for both dry and wet samples is roughly 1 ms, there is a considerable enhancement in resolution and signal-to-noise ratio for the wet sample in comparison to the dry sample. There is a tremendous advantage in using wet samples since much less time is required to obtain a spectrum with a good signal-to-noise ratio.

The results presented are important with respect to the semiquantitative analysis of ^{13}C CP/MAS NMR spectra of wood and pulp. When studying the effect of a particular process on the components of wood, it is common practice to compare the spectra measured for the different samples, as for example in chemical pulping,[16,17] thermomechanical pulping,[18] chemimechanical pulping,[19] biochemical degradation,[20] biomass transformation,[21] and steam explosion and hydrolysis processes.[22-24] The improved resolution obtained using wet samples presumably allows for a better comparison to be made between spectra. In addition, the increased signal-to-noise ratio allows more reliable information to be extracted from the spectra.

It is known that the cross-polarization efficiency is dependent on the proton rotating frame relaxation time. Therefore, shorter relaxation times would also give rise to a shorter optimum contact time. A detailed study of the effect of hydration on relaxation times is the subject of future work, in order to support the second mechanism proposed in this paper. If hydrogen bonding is indeed the predominant factor, giving rise to the signal-to-noise ratio enhancement and thus much shorter acquisition times, then it is conceivable that this concept may have general applicability to other polymer systems.

Acknowledgment. We are indebted to W. Y. Gee and Dr. J. V. Hatton of PAPRICAN, Vancouver, B.C., for generously supplying the wood sample. Financial support from NSERC, in the form of a Postdoctoral Fellowship (J.M.W.) and operating grants (F.G.H.), is gratefully acknowledged.

References and Notes

(1) Earl, L. W.; VanderHart, D. L. *J. Am. Chem. Soc.* **1980**, *102*, 3251.
(2) Atalla, R. H.; Gast, J. C.; Sindorf, D. W.; Bartuska, V. J.; Maciel, G. E. *J. Am. Chem. Soc.* **1980**, *102*, 3249.
(3) Atalla, R. H.; VanderHart, D. L. *Science (Washington, D.C.)* **1984**, *223*, 283.
(4) Maciel, G. E.; Kolodziejski, W. L.; Bertran, M. S.; Dale, B. E. *Macromolecules* **1982**, *15*, 686.
(5) Dudley, R. L.; Fyfe, C. A.; Stephenson, P. J.; Deslandes, Y.; Hamer, G. K.; Marchessault, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 2469.
(6) Earl, W. L.; VanderHart, D. L. *Macromolecules* **1981**, *14*, 570.
(7) Gast, J. C.; Atalla, R. H.; McKelvey, R. D. *Carbohydr. Res.* **1980**, *84*, 137.
(8) Horii, F.; Hirai, A.; Kitamaru, R. *Polym. Bull.* **1982**, *8*, 163.
(9) Cael, J. J.; Kwoh, D. L. W.; Bhattacharjee, S. S.; Pratt, S. L. *Macromolecules* **1985**, *18*, 821.
(10) Horii, F.; Hirai, A.; Kitamaru, R.; Sakurada, I. *Cell. Chem. Technol.* **1985**, *19*, 513.
(11) Fyfe, C. A.; Stephenson, P. J.; Taylor, M. G.; Bluhm, T. L.; Deslandes, Y.; Marchessault, R. H. *Macromolecules* **1984**, *17*, 501.
(12) VanderHart, D. L.; Atalla, R. H. *Macromolecules* **1984**, *17*, 1465.
(13) Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042.
(14) Frye, J. S.; Maciel, G. E. *J. Magn. Reson.* **1982**, *48*, 125.
(15) Goring, D. A. I. In *Lignins: Occurence, Formation, Structure and Reactions*; Sarkanen, K. V., Ludwig, C. H., Eds.; Wiley-Interscience: New York, 1986; pp 695–768.
(16) Haw, J. F.; Maciel, G. E.; Schroeder, H. A. *Anal. Chem.* **1984**, *56*, 1323.
(17) Willis, J. M.; Jagannathan, N. R.; Herring, F. G. *J. Wood Chem. Technol.* **1986**, *6*, 249.
(18) Willis, J. M.; Herring, F. G., submitted for publication in *Holzforschung.*
(19) Willis, J. M.; Herring, F. G., submitted for publication in *Wood Sci. Technol.*
(20) Barron, P. F.; Frost, R. L.; Doimo, L.; Kennedy, M. J. *J. Macromol. Sci. (Chem.)* **1985**, *A22*, 303.
(21) Haw, J. F.; Maciel, G. E.; Linden, J. C.; Murphy, V. G. *Holzforschung* **1985**, *39*, 99.
(22) Taylor, M. G.; Deslandes, Y.; Bluhm, T.; Marchessault, R. H.; Vincendon, M.; Saint-Germain, J. *Tappi* **1983**, *66*(6), 92.
(23) Hemmingson, J. A.; Newman, R. H. *J. Wood Chem. Technol.* **1985**, *5*, 159.
(24) Haw, J. F.; Maciel, G. E.; Biermann, C. J. *Holzforschung* **1984**, *38*, 327.