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Probing the macromolecular structure of wood and pulps with proton spin-lattice relaxation time measurements in the solid state

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Summary By measuring the proton spin-lattice relaxation times (T_1) in the solid state, for a series of progressively sulphonated and methylated black spruce pulps, the molecular mobilities of carbohydrates and lignin have been evaluated as a function of chemical treatment. These measurements were made possible only after the paramagnetic metal ion impurities were removed from the samples. For untreated wood the proton T_1 values of carbohydrates and lignin were virtually undistinguishable, irrespective of the applied magnetic field strength. The introduction of sodium salts of carboxylic and sulphonic acid groups in softwood pulps and the introduction of methoxyl groups, seem to very significantly increase the molecular mobilities of carbohydrates and lignin. The opposite was true when calcium were the counterions of the acidic groups. These observations have been attributed to the disruption of associative lignin-carbohydrate hydrogen bonding interactions otherwise operating within untreated wood.

Introduction

Wood may be considered a composite material comprised of cellulose linear chains embedded in a matrix of hemicelluloses and lignin (Fengel and Wegener 1984; Harada and Cote 1985). Cellulose is the beta-(1-4) linked polymer of anhydroglucose units, known to exist in at least four polymorphs (Fyfe et al. 1983). Hemicelluloses, are branched

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polysaccharides composed of a variety of different sugar residues. Lignin is a complex aromatic network polymer comprised of substituted phenyl-propane units linked together mainly by ether bonds. Accumulating evidence points to the likelihood that lignin is not simply deposited on the cell wall of polysaccharides, but it is linked and associated in a certain architecture with the cellulose (Merewhether 1957; Koshijima et al. 1989) and the hemicelluloses (Eriksson and Lindgren 1977). At present, the nature of lignin-carbohydrate interactions in plant tissues is a subject of substantial scientific and industrial interest.

Advances in the technology of nuclear magnetic resonance spectroscopy, namely, the introduction of cross-polarization and magic angle spinning (CP/MAS) (Schaefer and Stejskal 1976; Fyfe 1983) have allowed high resolution spectra to be obtained for solid wood samples, with well resolved signals for cellulose (Atalla et al. 1980; Fyfe et al. 1983; Newman and Leary 1991), hemicellulose and lignin (Hatfield et al. 1987; Manders 1987, Newman and Leary 1991), different wood species resulted in characteristic spectra (Hatfield et al. 1987; Manders 1987). In addition, our understanding of the nuclear spin relaxation mechanisms has provided a powerful tool for probing molecular motions (Schaefer et al. 1977; McBrierty and Douglass 1981; Cory and Ritchey 1989) and miscibility (McBrierty et al. 1978; Grobelny et al. 1990) in polymeric materials. The determination of the relaxation time profiles for individual polymers present in composites and blends has become an indispensable tool toward elucidating microstructural details of such systems, with wood representing no exemption.

During the past several years a number of accounts have appeared in the literature addressing specific questions in relation to wood microstructure, by determining proton and carbon spin-lattice (T_{1H}, T_{1C}), spin-spin (T_2) and spin-lattice in the rotating frame $T_{1\rho}$, relaxation times for the principal polymeric components of wood (Teeäär et al. 1985; 1986a,b; Newman 1987; Tekely and Vignon 1987a,b; Gravitis et al. 1991) in the solid state.

The changes induced on the carbohydrates and lignin during the process of steam explosion of wood have been elucidated by determining these parameters. Teeäär et al. 1985; 1986a,b) in their efforts to determine the proton T_1 values for lignin and carbohydrates for two wood species (poplar and birch), before the steam-explosion treatment, found them to be nearly identical. Their findings, however, were contrary to those of Tekely and Vignon (1987a,b), who reported a difference in the proton T_1, before the treatment, at the same magnetic field strength (i.e. 240 ms for lignin, and 410 ms for carbohydrates). Both groups report significant differences in the proton T_1 and $T_{1\rho}$ (Tekely and Vignon 1987b) after the wood was steam exploded. This was interpreted in terms of the "successful destruction" of the polymeric "supramolecular network" present in wood. Steam explosion caused the separation of the lignin from the carbohydrates in such a manner that spin diffusion can no longer average out the measured relaxation parameters.

The structural alterations that are taking place within carbohydrates and lignin when wood was subjected to high shear and pressure was studied by Gravitis et al. (1991) by measuring, amongst other parameters, the proton T_1 values of these biopolymers before and after the treatment employing a 200 MHz instrument. The reported proton T_1 values in untreated wood were in the region of 650–670 ms for carbohydrates and lignin. These values were found to decrease after the action of shear and pressure on the sample.

It is likely that the apparent discrepancies in the literature for the reported proton T_1 values are due to a paramagnetic relaxation mechanism operating on the protons of carbohydrates and lignin, when they interact with the unpaired spins of paramagnetic metal ions present as impurities within the samples. The effect of such ions on the measurement of proton T_1 values was not discussed in the above studies.

Furthermore, Newman (1987; 1992) and Willis and Herring (1987) have noted that this spin relaxation parameter may also be affected by the amount of water present on a wood sample. This may be another reason for the differences in the reported T_1 values.

The paramagnetic-induced relaxation effects on *Piceae glauca* pulp have been systematically studied by Gerasimowitz et al. (1984). Ferric ions when used as a probe together with proton T_1 and $T_{1\rho}$ measurements gave information on the structural connectivity of carbohydrates and lignin present in wood pulps. Similar linkages were also invoked by Kolodziejski et al. (1982) who studied the ^{13}C CP/MAS NMR spectra of lodgepole pine wood.

In this paper an attempt is made to determine the structural changes induced on the carbohydrates and lignin of the fibre wall when wood is sulphonated under conditions used in commercial practice for the production of high yield chemithermomechanical (CTMP) and chemimechanical (CMP) pulps. For this purpose high resolution ^{13}C CP/MAS NMR spectroscopy was employed. The concentration of paramagnetic metal ions present in the samples was also monitored in order to document and eliminate these salient sources of error for the proper execution of such measurements, aimed at resolving the controversy that exist as to the exact magnitude of the proton T_1 values of carbohydrates and lignin is untreated wood samples.

Experimental

Preparation of wood and pulp samples of varying ionic content

A series of ultra-high yield pulp samples were prepared at the Andritz Sprout-Bauer pilot plant located in Springfield Ohio, utilizing semi-commercial pilot plant equipment. Black spruce (*Picea mariana*) chips were pre-steamed for 30 minutes prior to impregnation with sodium sulphite solutions, using a 560 GS Impressafiner at a 4:1 compression ratio. The impregnated chips were then subjected to a vapour phase thermal treatment, pressed, and refined. Six series of samples were produced using an impress-cook-press sequence. The parameters varied were: concentration of sodium sulphite in the impregnation stage, thermal treatment time and temperature. The concentrations of chemicals applied in these experiments expressed in percent of oven dried (od) wood are shown in Table 1. The acid group profiles for the produced samples were determined by using the conductometric titration procedure of Katz et al. (1984) and are given in Table 2.

Table 1. Operating conditions used for the production of the series of sulphonated pulps studied

Sample number	Concentration of Na_2SO_3 (g/L)	(% on wood)	pH after impregnation	Thermal treatment Temp. (°C)	Time (min.)
1	15.9	2.28	7.0	135	5
2	32.8	4.60	7.2	135	10
3	49.1	6.30	7.3	135	20
4	62.4	7.00	7.3	150	30
5	97.7	9.50	7.4	150	45
6	129.8	13.70	7.7	150	55
7 [(1)]	126.0	75.60	—	160	75

[(1)] This sample was produced at a yield of 83%, from a black spruce thermomechanical pulp with the thermal treatment described above, at 6:1 liquor to wood ratio

Table 2. Carboxylate and sulphonate group contents for the studied wood and pulp samples, determined by conductometric titration

Sample	Acid group content (mmol/kg)		Total ionic content (mmol/kg)
	–COOH	$-SO_3H$	
Original wood	90.8	0.0	90.8
1	93.0	30.2	123.3
2	105.6	33.6	139.3
3	107.9	98.9	206.8
4	116.0	86.5	202.5
5	130.2	107.7	238.0
6	135.5	170.9	306.4
7[1]	169.0	518.0	687.0

[1] Triplicate determination

Exchanging the acid groups of wood and pulps to specific ionic forms

To convert the pulps to their sodium or calcium forms, the metal free pulp (2.0 g), with their acidic groups in their proton forms, were dispersed in 400 mL of a solution of either (a) 0.1 N NaCl or (b) 0.1 N $CaCl_2$. The pH of the solution was adjusted to 8.0–8.5 using a solution of either (a) 0.1 N NaOH or (b) saturated $Ca(OH)_2$, respectively. The pulp dispersions were gently stirred at these conditions for 30 minutes. The samples were drained on a wire mesh-covered Buchner funnel. The fine, non-fibrous material, was recycled and washed on the buchner with 100 mL of deionized water. The wet pad of pulp was finally dispersed in 400 mL of deionized water, stirred, drained and briefly washed with deionized water. In the text unless otherwise stated, the acidic groups of the samples are in the sodium form.

Carboxymethylation of fully bleached kraft pulp

A mixture of 25 g of bleached kraft pulp and 75 mL of a methanol solution containing 0.25 mol each of NaOH and chloroacetic acid was heated and slightly agitated for variable periods of time to give samples of variable degree of carboxymethylation. The carboxymethylated pulp samples were then thoroughly washed with deionized water.

^{13}C CP/MAS NMR and proton T_1 measurements

All samples were conditioned at $45 \pm 5\%$ relative humidity prior to these measurements, thus, the moisture content varied from 6.25–8.2% (on oven dried wood basis). ^{13}C solid state NMR spectra and proton spin-lattice relaxation time measurements were obtained on Chemagnetics M-100 and CMX-300 spectrometers operating at ^{13}C frequencies of 25.12 and 75.4 MHz respectively. All CP/MAS experiments were performed with a spinning rate of 3.5–4.0 kHz (M-100) and 4.9–5.1 kHz (CMX-300), a contact time of 1 ms and proton $\pi/2$ pulses of 4.5–5.0 μs duration. The proton spin-lattice relaxation times were measured from the ^{13}C cross polarized spectra immediately after the application of a $\pi - \tau - \pi/2$ inversion recovery pulse sequence to the proton spins. Then the T_1 data was fitted to the following three parameter expression 1:

$$M_\tau = M_{\tau=\infty}[1 - (1+\alpha)\exp(-\tau/T_{1H})] \quad (1)$$

where T_{1H} is the proton spin-lattice relaxation time, M is the equilibrium magnetization and α is the inversion efficiency of the proton π pulse. For perfect inversion ($\alpha = 1.0$); the values of τ ranged between 0.80 and 0.90 s i.e. approximately five times the T_1. In all

relaxation experiments, recycle times of 2–3 s (M-100) and 6 s (CMX-300) were used. The number of acquired transients varied depending on the field strength i.e. 4000–8000 transients were accumulated when the M-100 instrument was used while 1000–2000 for the CMX-300. Spectra were obtained on 9 different τ values prior to the application of Eq. 1. The proton T_1 values for carbohydrates and lignin were derived by measuring the intensity of the signals at 73.8 ppm and at 148.9 ppm respectively. These values did not appreciably change when other weaker signals were examined. Attempts to selectively probe the proton T_1 values of the hemicelluloses were unsuccessful due to the small amounts of hemicelluloses present in softwoods. This subjected the T_1 values for this component to considerable errors. This is the reason why no distinction is made in this paper between the relaxation profiles of cellulose and hemicelluloses.

Results and discussion

Effect of metal ions on the proton T_1

Two series of measurements were conducted in order to evaluate the effect of paramagnetic metal ions on the proton T_1 values of carbohydrates and lignin present in wood and pulps. Initially, the proton T_1 values of carbohydrates and lignin were determined in wood and a series of unwashed, sulphonated pulps which contained the metal ion profiles shown in Table 3. These measurements were then repeated for the same samples after their metal ions had been removed by thorough chelation followed by an acid wash. This procedure was most effective in removing most of the paramagnetic metal ion impurities present in the original samples (Table 3).

The proton T_1 values for carbohydrates and lignin as a function of total ionic group content (i.e. total acid groups) in wood and a series of unwashed sulphonated pulp samples are shown in Fig. 2. The proton T_1 values are nearly independent of total ionic content, within experimental error ($\pm 5\%$). The original unsulphonated wood sample whose ionic content was 90.8 mmol/kg, mainly due to carboxylate ions (Table 2), resulted in slighlty lower T_1 values. The feature of this graph is the fact that for unsulphonated wood the proton T_1 values of carbohydrates and lignin are very similar, possibly indicating close interaction between these two components. These interactions seem to be somewhat reduced after sulphonation. In general, the data of Fig. 1 indicate that for the sulphonated samples the proton T_1 values were around 67 ms for lignin and 78 ms for carbohydrates, irrespective of sulphonation conditions. These values are of the same order of magnitude to those obtained by Gerasimowicz et al. (1984), measured at 60 MHz. They report proton T_1 values of 79 ms for carbohydrates and 37 ms for lignin.

Table 3. Metal ion profiles (in ppm) for unwashed and washed pulp samples, as determined by atomic absorption

Sample	Before washing			After washing		
	Fe	Mn	Cu	Fe	Mn	Cu
Original wood	80.3	133.1	1.5	18.2	0.4	1.1
1	47.6	76.6	1.3	37.0	0.3	0.6
2	36.3	65.6	1.4	21.1	0.2	0.6
3	28.4	65.9	1.2	11.2	0.2	0.9
4	40.8	66.3	1.7	23.9	0.3	0.7
5	36.3	64.1	1.6	28.2	0.4	0.6
6	22.1	64.3	1.5	12.5	0.5	0.7

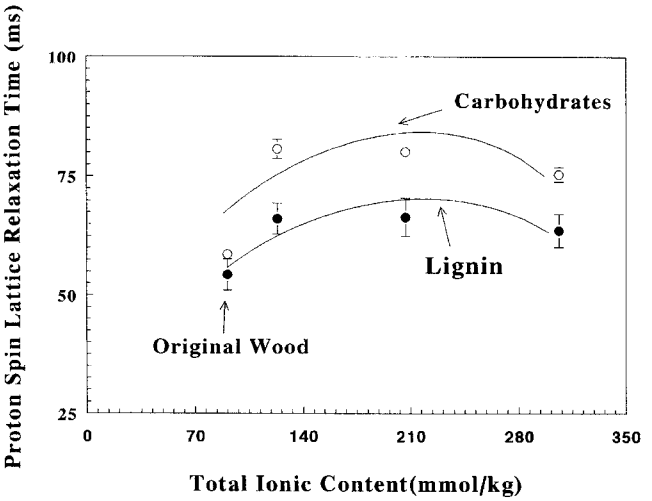

Fig. 1. The dependence of proton spin-lattice relaxation times for lignin and carbohydrates as a function of total ionic content, for a series of sulphonated pulps, whose metal ions have not been removed, measured at 100 MHz

The concentration of ferric ions in "zero-doped" pulp reported by Gerasimowich et al. (1984), was 153 ppm, while the amount of such ions in our samples varied between 22–47 ppm (Table 3). It is likely that the differences in the lignin proton T_1 values obtained between the two laboratories can be correlated with the difference in the concentration of ferric and manganese ions present in the samples. This is because the magnetic moment of an unpaired electron, present in manganese and ferric ions, is over two orders of magnitude greater than the proton nuclear magnetic moment. As such, the dipole–dipole interactions between proton nuclei and unpaired spins are more effective than proton–proton dipolar interactions. The presence of such metal ions in a sample results in a very efficient transfer of magnetization from the nuclear spins to the surrounding lattice which is reflected in significant lowering of the proton T_1 values.

In the absence of paramagnetic ionic impurities a different set of proton T_1 values was obtained for the same samples (Fig. 2). The overall magnitude of the proton T_1 values was considerably increased when the metal ions were removed. Since no relaxation mechanism other than dipole–dipole relaxation was operational on these samples the molecular motions of carbohydrates and lignin and the way they are affected by the total ionic content can be deduced from the data of Fig. 2. This is a clear illustration of the necessity of removing metal ions from wood samples prior to measuring its spin relaxation parameters. Atack and Heitner (1979), have examined the dynamic mechanical properties of black spruce wood for a variety of sulphonate contents. Their method of introducing ionic groups to wood pulps was similar to ours. Progressive reductions of the softening temperatures and the elastic shear moduli were apparent when the total ionic content was increased, while, only marginal increases in the energy dissipation factors ($\tan \delta$) were observed. Furthermore, the work of Ludwig et al. (1964) documents the presence of extensive interchain hydrogen bonds within lignin. In actual fact, all hydroxyl groups in lignin were found to be hydrogen bonded (Ludwig et al. 1964). Since it was suggested by Mark and Atlas (1977) that "the extent of hydrogen bonding in polymers is major factor which determines its softening temperature and elastic modulus", Atack

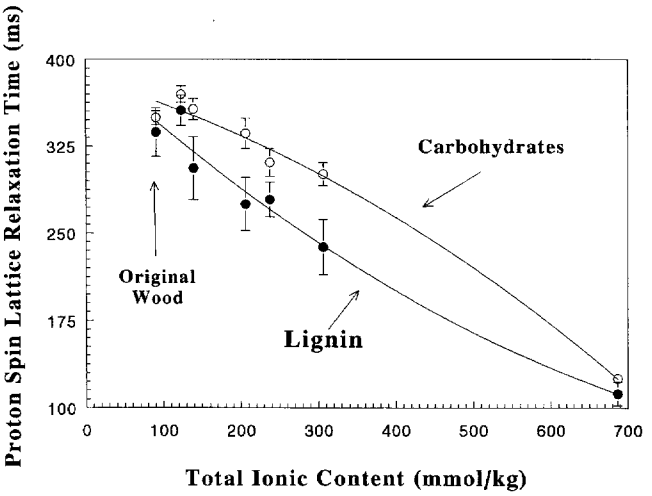

Fig. 2. The dependence of proton spin-lattice relaxation time of lignin and carbohydrates as a function of total ionic content, for wood and pulp samples after the removal of paramagnetic metal ion impurities, measured at 100 WHz. The decrease of the proton T_1 values demonstrates an increase in the molecular mobility of carbohydrates and lignin as a function of sulphonation

and Heitner (1979) attributed their findings to the elimination of hydrogen bonds from within lignin on progressive sulphonation of wood. In a manner similar to Atack and Heitner (1979), the results obtained during this work can be explained by invoking a model in which carbohydrates are closely associated with lignin, most probably through a system of intermolecular hydrogen bonds. Replacing ether and hydroxyl groups that are involved in hydrogen bonding between lignin and carbohydrates by the sodium salts of sulphonic acid groups, would decrease the extent of hydrogen bonding. Therefore, an increased mobility for lignin and perhaps carbohydrate macromolecules is to be expected if this concept is valid. In actual fact a progressive decrease of the proton spin-lattice relaxation times should be observed as a function of sulphonation. This is indeed the case for the data obtained at 100 MHz (Fig. 2), which is revealing in several ways. The divergence of the T_1 values of carbohydrates and lignin as a function of total ionic content, into two significantly different sets of values indicates that the sulphonation disrupts the macromolecular structure of pulp, possibly via the disruption of associative lignin-carbohydrate hydrogen bonding interactions. The fact that the proton T_1 values decrease as a function of sulphonation demonstrates an increase in the molecular mobility of both carbohydrates and lignin as a function of sulphonation. Both of these points are not surprising when one invokes the breaking of lignin-carbohydrate associative interactions when the degree of sulphonation increases.

Additional evidence, supporting the close association of carbohydrates and lignin within wood can be sought by the fact that sulphonation of wood is known to take place selectively on the lignin without affecting the chemistry of carbohydrates (Heitner et al. 1982). It is not surprising, therefore, that a reduction in the proton T_1 of lignin as a function of total ionic content was observed (Fig. 2). However, the data of Fig. 2 also indicates that the molecular motions of carbohydrates are increasing when the total ionic content of the sample increases, in a manner similar to that observed for lignin. The changes operating in the mobility of lignin as a function of sulphonation seem to be

transmitted to the mobility of the carbohydrates, even if no chemical transformation has taken place on the carbohydrates.

The rate of exchange of proton nuclear spin magnetization with the surrounding lattice for carbohydrates and lignin seems to be the same for unsulphonated wood, since both proton T_1 values were nearly identical (around 365 ms). Such a behaviour is indicative of a uniform spin temperature maintained throughout the sample by spin diffusion. This result is in qualitative agreement with the work of Teeäär et al. (1985; 1986a, b) who have reported the proton T_1 values for carbohydrates and lignin in untreated wood samples to be 670 and 650 ms respectively, at a static magnetic field of 200 MHz. The observed quantitative difference in the measured proton T_1 values may be partly due to the different static magnetic fields used by the two groups. Efforts to understand the effect of the static magnetic field, temperature and other variables on the magnitude of proton T_1 for the principal wood components will be published elsewhere.

The effect of calcium counterions on proton T_1

In accordance with the model discussed so far, it appears that the hydrogen bounded network structure of wood is disrupted when the hydroxyl groups, within lignin, and the carboxyl groups, within largely the hemicelluloses, are replaced by sulphonic and carboxyl groups bearing sodium counterions. In an effort to confirm that the observed changes in the proton spin-lattice relaxation times of sulphonated pulps were due to alterations in the overall hydrogen bounding crosslinking efficiency operating on the studied samples, the following experiments were carried out. The sodium counterions of the carboxylic and sulphonic acid groups present in the samples depicted in Fig. 3 were substituted with calcium ions and the proton spin-lattice relaxation times of the samples were reevaluated at 100 and 300 MHz. This was done in order to induce ionic crosslinking between the acid groups, in a manner similar to that observed for synthetic ionomers in the solid state (Eisenberg 1970). The measurements depicted in Fig. 3 confirmed that the reduction on the proton T_1 values, observed in Fig. 2, were indeed due to the disruption of a hydrogen bonded network structure. This is because the data of Fig. 3 clearly demonstrates increases in the proton T_1 values of carbohydrates and lignin when ionic crosslinking was induced within the wood pulps by calcium counterions.

A closer examination of the data of Fig. 3 reveals differences in the magnitude of the proton T_1 values when carried out at the two static magnetic fields. The proton T_1 values at 100 MHz are considerably lower to those carried out at 300 MHz. The reasoning for this will be discussed in subsequent publications. The range of proton T_1 values obtained by both sets of measurements in Fig. 3 are smaller to those obtained at 100 and at 300 MHz when sodium were the counterions of the acid groups (Fig. 2). The theoretical implications of this are not clear; it may be a result of a substantially lower degree of molecular mobility in these samples relative to their sodium counterparts, due to an ionic crosslinking effect. The practical implications, however, are that solid state spectra may be acquired approximately three to four times faster (depending on the magnetic field strength) since the T_1 values of carbohydrates and lignin are reduced three to four fold in the presence of calcium ions.

The effect of methylation of wood components on their proton T_1

Since the working hypothesis of this paper has been that, substitution of the hydroxyl and ether groups present in lignin with the sodium salts of sulphonic acids results in the destruction of a hydrogen bonded crosslinked network operating within wood, an additional set of experiments were carried out to further confirm its validity. The free phenolic hydroxyl groups present in lignin as well as a significant number of carbohydrate

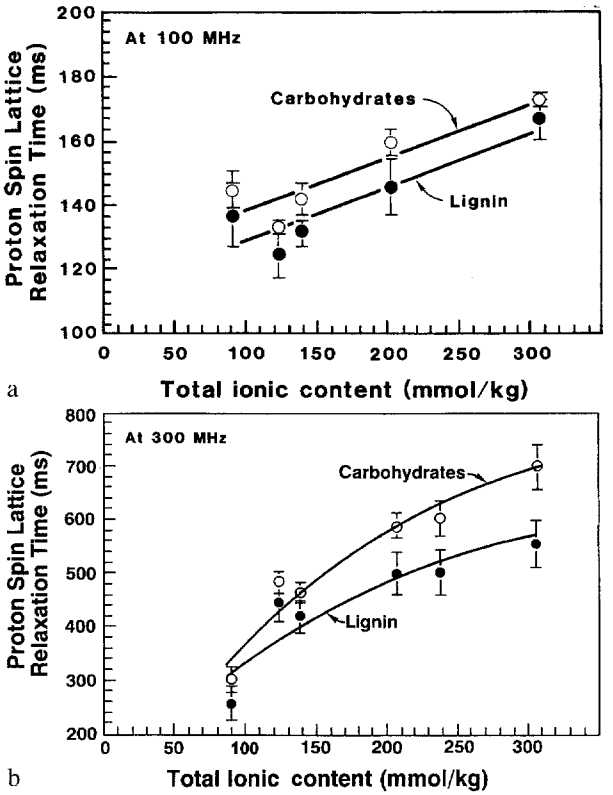

Fig. 3a and b. The dependence of proton spin-lattice relaxation time of lignin and carbohydrates as a function of total ionic content, measured at 100 MHz (a) and at 300 MHz (b). The counterions of the carboxylic and sulphonic acid groups present in these samples were calcium ions. An increase in the proton T_1 values of carbohydrates and lignin is observed when ionic crosslinking is induced by calcium counterions

hydroxyls were substituted with methoxyl groups by methylating pulp samples with dimethyl sulphate under controlled, strongly alkaline conditions. The phenolic hydroxyl content of these samples (expressed per 100 lignin phenyl propane units) when evaluated, were found to be 12.8% for untreated wood, progressively reducing to 3.9% after methylation The proton T_1 values of these samples when evaluated at 300 MHz resulted in the data of Fig. 4. Apparently, methylation of wood induces significant changes in its microstructure, since it has profound effects on the proton T_1 values of lignin and carbohydrates. The T_1 values progressively decrease with increasing methoxyl content as expected if the destruction of a hydrogen bonded crosslinked network is taking place. This is in complete agreement with the notion that substitution of potential hydrogen bonding sites within wood changes the overall rigidity of its constituent biopolymers. Our findings are also qualitatively supported by those of Hatfield et al. 1987, who measured the proton T_1 values of red oak and lodgpole pine acidolysis lignins before and after methylation, at a proton frequency of 100 MHz. For red oak lignin the proton T_1 was found to decrease from 0.86 s to 0.55 s after methylation, while for lodgpole pine lignin the proton T_1 was found to decrease from 0.97 s to 0.63 s.

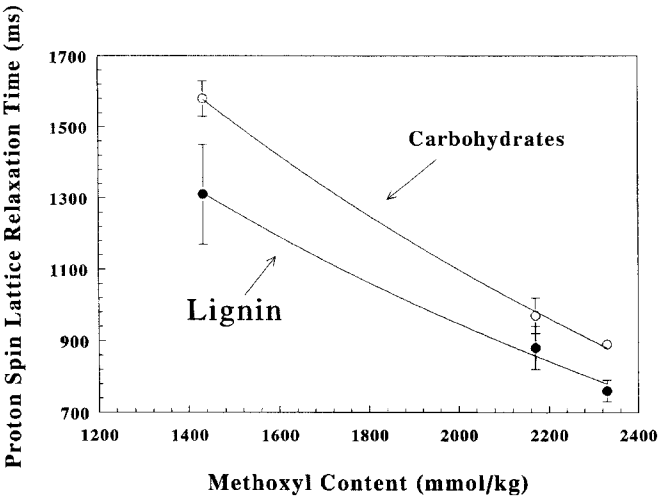

Fig. 4. The effect of methylation of black spruce pulps on the proton T_1 values of lignin and carbohydrates, measured at 300 MHz. Progressive methylation destroys the intermolecular hydrogen bonded network present in wood. This increases the molecular mobilities of carbohydrates and lignin, which consequently decrease the proton spin-lattice relaxation times

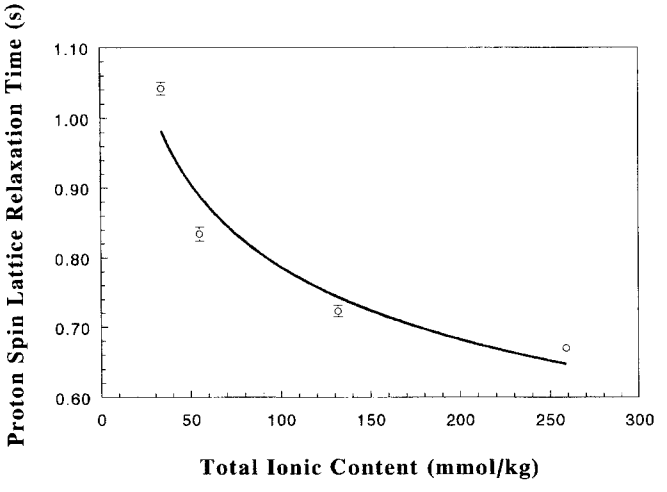

Fig. 5. The effect of carboxymethylation of cellulose on its proton T_1 values, measured at 300 MHz. Replacing hydroxyl groups involved in interchain hydrogen bonding within cellulose by the sodium salts of carboxymethyl acid groups, decreases the extent of hydrogen bonding

The effect of carboxymethylation of cellulose on its proton T_1

The role of acid groups on the mobility of cellulose alone was studied by introducing controlled amounts of carboxylic acids to cellulosic fibres by carboxymethylation ($-CH_2COOH$). The acidic groups were then transformed to sodium salts ($-CH_2COONa$) and the proton T_1 values of these samples were determined at (Fig. 5). The data of Fig. 5 is

in complete agreement with the model discussed so far. Replacing hydroxyl groups involved in interchain hydrogen bonding within cellulose by the sodium salts of carboxymethyl acid groups, would decrease the extent of hydrogen bonding. Therefore, an increased mobility of the cellulosic chains is apparent as evidenced by the dramatic decrease of the proton T_1 values for ionic contents varying between 40–250 mmol/kg.

Conclusions

Substantial information in relation to changes in the microstructure of wood and pulps as a function of sulphonation (or any other chemical treatment) can be obtained by measuring the proton spin-lattice relaxation times of its constituent biopolymers. In order for these measurements to adequately reflect the mobilities of cellulose and lignin, the paramagnetic metal ion impurities must thoroughly be removed. Sulphonation of wood pulps seems to destroy its macromolecular hydrogen bonded network structure. This most likely, takes place by replacing the hydrogen bonding sites within the carbohydrates and lignin with the sodium salts of sulphonic and carboxylate anions.

References

Atack, D.; Heitner, C. 1979: Dynamic mechanical properties of sulphonated eastern black spruce. Transactions, CPPA 5: TR99–TR108

Atalla, R. H.; Gast, J. C.; Sindorf, D. W.; Bartuska, V. J.; Maciel, G. E. 1980: ^{13}C NMR spectra of cellulose polymorphs. J. Am. Chem. Soc. 102: 3249–3251

Cory, D. G.; Ritchey, W. M. 1989: Inversion recovery cross-polarization NMR in solid semicrystalline polymers, Macromolecules 22: 1611–1615

Eisenberg, A. 1970: Clustering of ions in organic polymers. A theoretical approach. Macromolecules 3: 147–154

Eisenberg, A. 1967: Ionic forces in polymers. Adv. Polymer Sci. 5: 59–112

Eriksson, O.; Lindgren, B. O. 1977: About the linkage between lignin and hemicelluloses in wood, Svensk. Papperstidn. 80: 59–63

Fengel, D.; Wegener, G. 1984: Wood Chemistry, Ultrastructure and Reactions, Berlin: Walter de Gruyter & Co

Fyfe, C. A. 1983: Solid state NMR for chemists. Guelph: C.F.C. Press

Fyfe, C. A.; Dudley, R. L.; Stephenson, P. J.; Deslandes, Y.; Hamer, G. K.; Marchessault, R. H. 1983: Application of high-resolution solid-state NMR with cross-polarization magic angle spinning (CP/MAS) techniques to cellulose chemistry. J. Macromol. Chem. Phys., C23: 187–216

Gerasimowicz, W. V.; Hicks, K. B.; Pfeffer, P. E. 1984: Evidence for the existence of associated lignin-carbohydrate polymers as revealed by carbon-13 CP/MAS solid state NMR spectroscopy. Macromolecules 17: 2597–2603

Gravitis, J.; Kokorevics, A.; Teeäär, R.; Zharov, A.; Lippmaa, E. 1991: Structural changes of wood and its components initiated by the simultaneous action of shear deformation and high pressure. J. Pulp Paper Sci. 17: J119–J123

Grobelny, J.; Rice, D. M.; Karasz, F. E.; MacKnight, W. J. 1990: High-resolution solid state carbon-13 nuclear magnetic resonance study of polybenzimidazole/polyimide blends. Macromolecules 23: 2139–2144

Harada, H.; Côté, W. A. 1965: Structure of wood. In: Higuchi, T. (ed.) Biosynthesis and biodegradation of wood components, Orlando, San Diego: Academic Press, 1–42

Hatfield, G. R.; Maciel, G. E.; Erbatur, O.; Erbatur, G. 1987: Qualitative and quantitative analysis of solid lignin samples by carbon-13 nuclear magnetic resonance spectrometry. Anal. Chem. 59: 172–179

Havens, J.; Koenig, J. 1983: Appl. Spectrosc., 37: 226–249

Heitner, C.; Beatson, R. P.; Atack, D. 1982: J. Wood Chem. Technol., 2:169–185

Katz, S.; Betason, R. P.; Scallan, A. H. 1984: The determination of strong and weak acidic groups in sulphite pulps. Svensk Paperstidn. 87: R48-R53

Kolodziejski, W.; Frye, J. S.; Maciel, G. E. 1982: Carbon-13 nuclear magnetic resonance spectrometry with cross polarization and magic angle spinning for the analysis of lodgepole pine wood. Anal. Chem. 54: 1419–1424

Koshijima, R.; Watanabe, T.; Yaku, F. 1989: Structure and properties of the lignin-carbohydrate complex polymer as an amphipathic substance. In: Lignin, properties and materials, Glasser, W.; Sarkanen, S. (eds.), Washington: ACS series, Ch 1, 11–28
Leary, G. J.; Newman, R. H. 1992: Cross polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectroscopy. In: Lin, S.Y.; Dence, C. W. (eds.) Methods in lignin chemistry. Heidelberg: Springer, 146–161
Lindberg, J. J. 1961: IR-spectroscopy of lignin and lignin models. Paperi Puu, 43: 672
Ludwig, C. H.; Niest, B. J.; McCarthy, J. L. 1964: The high resolution nuclear magnetic resonance spectroscopy of protons in compounds related to lignin. J. Am. Chem. Soc. 86: 1186–1196
Manders, W. 1987: Solid state ^{13}C NMR determination of the syringyl/guaiacyl ratio in hardwoods. Holzforschung. 41: 13–18
Mark, H.; Atlas, S. 1977: Introduction to polymer science. In: Introduction to polymer science and technology, Kaufman, H. S. and Falcetta J. L. (eds). New York, Wiley-Interscience:, ch. 1, 1–23
McBrierty, V. J.; Douglass, D. C. 1981: Macromol. Rev. 16: 295-366
McBriety, V. J.; Douglass, D. C.; Kwei, T. K. 1978: Compatibility in blends of poly(methyl methacrylate) and poly(styrene-co-acrylonitrile) 2. An NMR study. Macromolecules. 11: 1265–1267
Merewhether, W. T. 1957: A lignin-carbohydrate complex in wood, A review of the literature. Holzforschung. 11: 65–80
Newman, R. H. 1992: Nuclear magnetic resonance study of spatial relationships between chemical components in wood cell walls. Holzforschung. 46: 205–210
Newman, R. H. 1987: Carbon-13 nuclear magnetic resonance studies of molecular motion in wood and paper, Fourth Int. Symp. Wood and Pulping Chem. Paris: 195–199
Schaefer, J.; Stejskal, E. O. 1976: Carbon-13 nuclear magnetic resonance of polymers spinning at the magic angle. J. Am. Chem. Soc. 98: 1031-1032
Schaefer, J.; Stejskal, E. O.; Buchdahl, R. 1977: Magic-angle ^{13}C NMR analysis of motion in solid glassy polymers. Macromolecules. 10: 384–405
Teeäär, R.; Gravitis, J.; Andersons, B.; Lippmaa, E. 1986a: CP/MAS NMR of steam explosion-treated wood and its major constituents, Teubner-Texte zur Physik. 9: 240–249
Teeäär, R.; Gravitis, J.; Erins, P.; Pugulis, J.; Kulkevics, A.; Gromov, V. S.; Lippmaa, E. 1986b: Changes in the phase structure and conformation state of wood components during explosive autohydrolysis. Dokl. Akad. Nauk SSSR, 288: 932–935
Teeäär, R.; Lippmaa, E.; Gravitis, J.; Andersons, B.; Erins, P. 1985: Relaxation study of the native and steam-exploded wood supernetwork structure by solid-state high-resolution carbon-13 NMR spectroscopy. Khim. Drev. No 6, C.: 106–107
Tekely, P.; Vignon, M. R. 1987a: Cross polarization/magic angle spinning ^{13}C NMR characterization of steam exploded poplar wood. J. Wood Chem. Techol. 7: 215–228
Tekely, P.; Vignon, M. R. 1987b: Proton T_1 and T_2 relaxation times of wood components using ^{13}C CP/MAS NMR. J. Polym. Sci., Part C: Polym. Lett. 25: 257–261
Willis, J. M.; Herring, F. G. 1987: Effect of water in the ^{13}C CP/MAS NMR spectrum of white spruce wood. Macromolecules. 20: 1554–1556