Structural Changes of Cellulose, Wood, and Paper under Shear Deformation and High Pressure

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SYNOPSIS

Structural changes of wood and its components have been studied after shear deformation under high pressure (SDHP) at up to 6 GPa. Cellulose amorphization and chain depolymerization was observed. Approximately 30% of microcrystalline cellulose was soluble in water after a 360-degree twist of the Bridgman anvils. The water-insoluble part was recrystallized into cellulose II lattice. Repeated treatment applied to the nondissolved part of the sample, the so-called cascade experiment, permits the dissolving of about 30% of the residual nondissolved material once again. Extraction with water, followed by 10% sodium hydroxide, allows almost complete dissolving of microcrystalline cellulose (98%). Water-soluble saccharides were studied by HPLC and ^{13}C NMR. It was found that destruction of the wood lignin network needs more severe treatment conditions than cellulose destruction does. Lignin domains in wood act as "grinding stones" during cellulose destruction. Long-living lignin free radicals have been detected with EPR after SDHP. ^{13}C NMR CP/MAS spin diffusion studies showed that SDHP leads to separation of wood components into different biopolymer domains, which turns the system toward thermodynamic equilibrium. SDHP does not permit achievement of initial compulsary compatibility of components in native wood. SDHP technique appears as a promising method for wood delignification and carbohydrate saccharification in the solid state without using harmful chemical reagents or solvents, which is important for technological safety and ecology.

INTRODUCTION

Simultaneous action of shear deformation and high pressure (SDHP) applied to solid objects, as well as original equipment for its realization, were introduced by P. Bridgman.[1,2] According to him, in a highly compressed state an equilibrium is formed in the substance between friction resistance, occurring between the anvil and sample surfaces, and intrinsic flow stress. This is why plastic flow is created in the substance.

Many physical and chemical processes proceed very efficiently during this plastic flow. SDHP method has several specific features, making it principally distinguishable from any other method used in solid state chemistry and physics.[3,4] Reactions proceed only during shear deformation (SD); their extent depends on the amount of deformation (twist angle, in our case). The latter is a parameter analogous to reaction time in ordinary chemical reactions. Reaction rates can increase by about 3 to 8 orders of magnitude in comparison with similar reactions in solutions, depending on pressure and slightly on temperature (the activation energy ΔE decreases by about one order of magnitude). The applied pressure plays a rather critical threshold role, determining whether the process proceeds or does not proceed. SDHP provides extremely effective mass transfer on the near-to-molecular structural level. Its formal estimation via "diffusion coefficient" gives a value about 10 to 15 orders of magnitude higher than the values in the solid state without SD, and 3 to 5 orders higher than that in solution.

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Different chemical reactions (polymerization, depolymerization, crosslinking, and substitution) and physical phenomena (modification of crystal lattice, its amorphization and formation of compatibile polymer mixtures) in polymers have been observed as a result of SDHP.[3-5]

Wood biopolymers form a sophisticated native blend of these components. The aim of current research was to study structural changes occurring in the wood during SDHP, and to establish possibilities of wood delignification with this method. The latter is rather important, because traditional delignification procedures need large amounts of energy and harmful chemicals, and create large amounts of waste. SDHP also seems to permit separation of the carbohydrates into monomers and oligomers. In this manner the traditional hydrolysis technique can be avoided. Shear deformation and high pressure (SDHP) have been realized in some pilot devices (extruders with conical ferrule, extruders with twin screws) for production of synthetic fibers, disintegration of elastomers, wood delignification, and production of cellulose derivatives.[6] Although the pressure in these works was moderate, the effects are worthy. One of the current authors has developed an extruder with a rotating core, capable of creating 3 GPa pressure.[7] It must be pointed out that severe structural changes in wood occur under these conditions. They will be discussed in further detail. Considering that SDHP does not need additional chemical reagents and proceeds very quickly, its chances to become a new technology in wood chemistry should not be ignored. Some preliminary results have been reported in earlier publications.[8-10]

EXPERIMENTAL

Bridgman anvils[3] were used to perform shear deformation under high pressure. The device (Fig. 1) consists of a pair of metal anvils, having the form of a truncated cone and made of a special alloy. The bottom anvil is supported by a ball bearing, permitting rotation of this anvil relative to the top anvil. The sample was placed between polished working surfaces of the anvils. The device was placed in a hydraulic press to apply high pressure to the sample. Shear deformation was created by rotation of the bottom anvil. Its magnitude was characterized by the rotation angle of the bottom angle in degrees. The amount of sample which could be handled in one experiment was about 3 to 10 mg.

Birch wood (*Betula pubescens*) powder (< 0.2 mm) with a 6% to 8% moisture content (MC) was

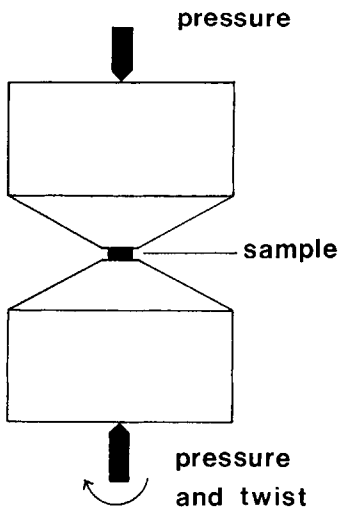

Figure 1 Schematic picture of the Bridgman anvils.

subjected to the SDHP treatment. Samples were extracted in a boiling benzene/ethanol mixture (2 : 1 by volume) for 10 h in a Soxlete type aparatus and subsequently with boiling water for 10 h to remove extractives. (Application of SDHP treatment to so-called steam explosion-treated wood are discussed in the "Results and Discussion" section.) For these specific experiments, a steam-exploded birch wood pulp sample was obtained by treating chips with 4.05 MPa pressure steam for 60 s, followed by explosive release of the pressure. The water-soluble sugars were removed by water extraction (24 hours, 20°C). A powder sample (< 0.2 mm; MC 3.4%) was used in SDHP experiments. A more detailed description of the steam explosion treatment is given in Gravitis et al.[10]

Finely powdered microcrystalline cellulose LT from "Lachema," Czechoslovakia (MC 4.6%); PH-101 "Avicel," from the USA (MC 4.4%); and laboratory filter paper sheets (MC 5.1%) were used in SDHP experiments. The lignin sample was spruce wood Björkman lignin powder (MC 3.5%), separated after 500 hours of ball milling. Sugars used for calibration in HPLC experiments were β-D(+)-glucose (SIGMA), D(+)-cellobiose (FLUKA), and D(+)-raffinose (FLUKA). All samples used in the SDHP experiments were air-dry.

A general scheme for sample preparation by SDHP and the following extraction with water and NaOH appear in Figure 2. Solubility of the samples was determined by 24-h extraction of an absolutely dry sample with water (1 : 50 by weight) at room temperature. The precipitate was removed by centrifugation, washed with water, and centrifuged

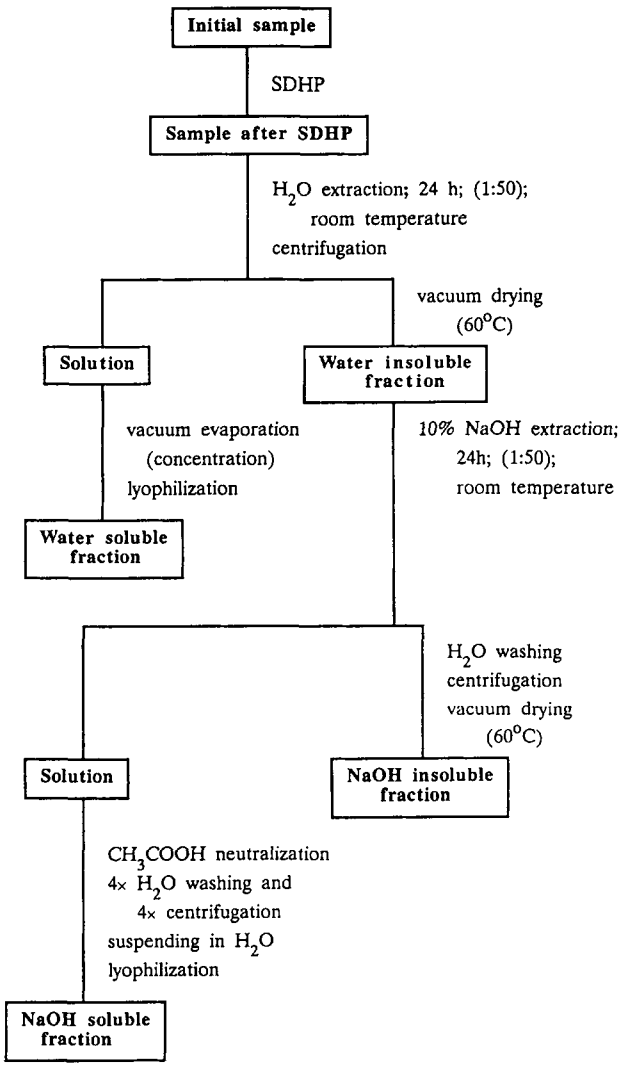

Figure 2 Fractionation of SDHP sample. Full scheme for microcrystalline cellulose. For birch wood, filter paper and cascade experiments only water extraction was carried out.

again. Nondissolved residue was dried in a vacuum at 60°C until constant mass was obtained. Solubility was calculated as relative mass difference between the two weights. The dissolved fraction was recovered by lyophilization of the solution. The so-called cascade experiment was also performed with microcrystalline cellulose (MCC). In this case the water-insoluble residue was subjected to SDHP treatment and to the following separation once again.

After SDHP, the water insoluble fraction of MCC was further treated with 10% NaOH for 24 h at room temperature. This resulted in partial dissolving of the sample. Nondissolved and dissolved fractions were recovered as shown in Figure 2.

Molecular weight distribution (MWD) of water-soluble saccharides after SDHP was determined using high-performance size exclusion chromatography. A Gilson liquid chromatograph with refractive index detector (RI 131) and a 30 × 0.75 cm TSK G2000 PW column were used. Injection volume was 20 μl and 10 mg/ml. 0.05M (pH 6.0) phosphate buffer eluent with 0.6 ml/min flow rate was used. β-D(+)-glucose (MW 180), D(+)-cellobiose (MW 342), and D(+)-raffinose (MW 504) served as molecular standards.

Fractions for ^{13}C NMR studies in solution were obtained by size exclusion chromatography using a 60 × 1.6 cm TOYOPEARL HW-40 (F) column and distilled water with 0.7 ml/min flow rate as an eluent. The above-mentioned molecular standards were used for calibration. Sample loading was 1.5 ml (5% solution). Six fractions were chosen for further analysis and lyophilized. For NMR measurements, the samples were dissolved in D_2O.

High-resolution NMR spectroscopy was used to characterize the samples in the solid state and as solutions, obtained by dissolving the SDHP-treated substances.

^{13}C NMR investigation of the solid samples was performed by using the cross polarization magic angle spinning (CP MAS) technique.[11] A home-built MAS probehead with double bearings was used as MAS accessory to a Bruker CXP 200 NMR spectrometer, operating at 50.3 MHz for ^{13}C. To average the chemical shift anisotropy, a 7 mm outer diameter rotor with about 0.4 cm^3 sample volume was rotated at 4 to 5 kHz at the "magic angle" of 54.7° with respect to the external magnetic field direction. Cross polarization and decoupling radio frequency field strengths were about 55 kHz. The number of accumulations before the Fourier transform varied from several thousand to several tens of thousands, depending on the sample. No further treatment of the samples was used before NMR measurements.

To investigate relaxation behaviour in native and treated wood cell walls, proton spin-lattice relaxation time measurements were carried out. To monitor relaxation selectively in different components after magnetization inversion and relaxation delay, polarization was transferred to carbons and carbon spectra were registered. Intensities of the signals in the spectra were used to characterize proton magnetization time dependence.

NMR measurements of the dissolved samples were performed on a Bruker AM 500 spectrometer operating at 125 MHz for ^{13}C using 10 mm sample tubes, broad band decoupling, and an internal D_2O lock.

EPR measurements were performed on a home-built 10 GHz spectrometer at 77 K. A ruby monocrystal used as an etalon was oriented in the magnetic field so that the ruby line did not overlap with the spectrum of the studied sample. A stable nitroxyl radical standard with 3.5×10^{17} spins/g was used. Concentration of radicals in the sample was determined by comparison of the sample signal area with that of the standard according to the formula:

$$[R] = \frac{3{,}5 \cdot 10^{17}}{750} \cdot \frac{S}{128 \cdot h} \cdot \frac{K}{m},$$

where [R] = concentration of radicals, S = sample signal area, h = etalon signal amplitude, K = spectrum expansion factor, and m = sample mass.

RESULTS AND DISCUSSION

CP MAS NMR

SDHP was applied to a sample of pure cellulose to characterize and study the changes taking place in this component of the cell wall. Cellulose Avicel PH 101 was chosen because it has been characterized earlier by X-ray diffraction and NMR spectroscopy.[12] The ^{13}C NMR spectrum of microcrystalline cellulose shown in Figure 3 allows investigation of the sample's crystallinity on the basis of different chemical shifts of the atoms, especially C4, in different phases of the sample. Numerous investigators have established that a sharp signal at about 89 ppm corresponds to anhydroglucose units situated inside the three-dimensional crystallites, while C4 atoms of noncrystalline regions contribute to a much broader signal centered at 83 to 84 ppm. This was first proposed by Atalla and VanderHart in 1980.[13] Such resolution has initiated a discussion as to whether it is possible to determine the degree of crystallinity directly from NMR spectra. According to Sterk,[14] there is no direct correlation between crystallinity (as determined from x-ray scattering measurements) and the areas of C4 signals centered around 89 and 84 ppm. Our experiments showed that areas of these signals depend significantly on the experimental conditions, especially upon cross-polarization time. Numerical results obtained in our experiments by X-ray analysis and NMR methods were fairly close to each other.[12] Without going into the details of the crystallinity measurements, it can be said that ^{13}C NMR gives plausible insight into structural changes of cellulose during SDHP.

Figure 3.1 gives the ^{13}C NMR spectrum of the

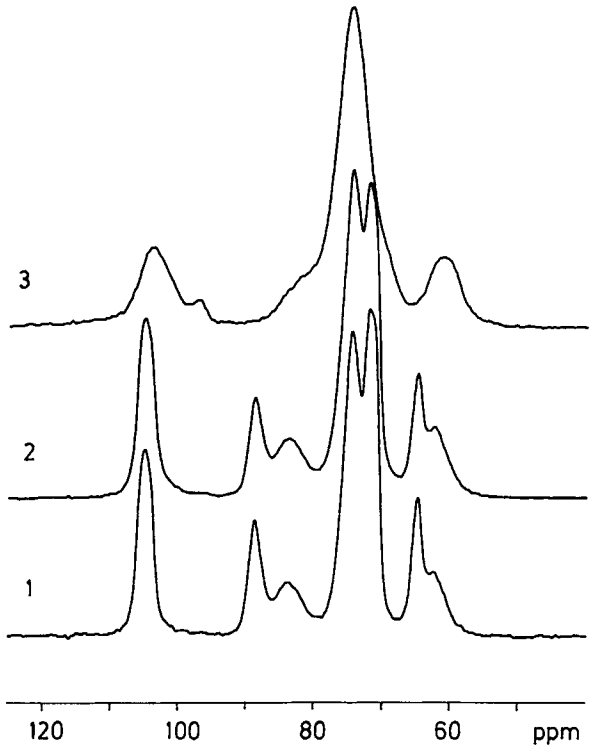

Figure 3 ^{13}C MAS NMR spectra of microcrystalline cellulose. (1) starting material, (2) after 6 GPa pressure, (3) after 6 GPa pressure and 360 deg twist.

starting material. Note that this spectrum displays a rather intense signal at 89 ppm and also at 84 ppm. According to our earlier measurements, this sample's degree of crystallinity was 0.56. Figure 3.2 presents a spectrum of the same substance after subjecting it to the pressure-only treatment. It can be said that 6 GPa pressure has no effect upon the sample structure on the molecular level—the spectrum remains practically unchanged. The situation is totally different after applying shear deformation simultaneously with pressure (see Fig. 3.3); here, it is noted that the 89 ppm and 65 ppm signals have disappeared. Overall resolution in the 72 to 75 ppm region has diminished—what was initially a doublet has become one broader line. According to the calculation method proposed earlier, the sample was amorphous. Similar zero crystallinity changes can be seen in the ^{13}C NMR spectrum after intensive ball-milling, which is used for cellulose amorphization. It is not difficult to conclude that shear deformation under high pressure destroys the crystalline structure and turns the material into a noncrystalline state. It is obvious that a small signal has appeared at about 97–98 ppm. The 97 ppm region is where the C1 atom of the chain-reducing (β) end

resonates; and the 98 ppm signal has been associated with cellulose depolymerization during intense ball milling.[15] Hence these small lines indicate severe depolymerization of the cellulose macromolecules in our treatment. Similar results were achieved when high pressure and shear deformation were applied to the microcrystalline cellulose of Lachema, as well as to a filter paper sample. In some experiments a very weak signal was registered at about 93 ppm. This is a region of chain-reducing (α) end resonances.

In the birch wood ^{13}C CP MAS spectrum, signals belonging to different components of the cell wall are well resolved (see Fig. 4.1). According to literature data[16] and our results, 172 and 21 ppm lines belong to the acetate groups of hemicelluloses; and 153 ppm signal to the C3, C4, and C5 carbons of syringyl units alkylated at C4; while nonsubstituted (protonated) aromatic carbons resonate at about 136 ppm. A rather broad signal centered at about 116 ppm belongs to the C1 carbons of phenylpropane syringyl-type units. Hemicellulose and cellulose signals overlap in the region of 60 to 110 ppm. Nevertheless, 105 ppm can be assigned to cellulose C1; 89 and 84 ppm to cellulose C4, according to the previous interpretation; and 65 and 62 ppm mainly to cellulose C6 in crystalline and noncrystalline regions. The 72 to 76 ppm region contains signals from C2, C3, and C5 atoms of (hemi)celluloses, and the 56 ppm signal belongs to the oxymethyl groups in lignin.

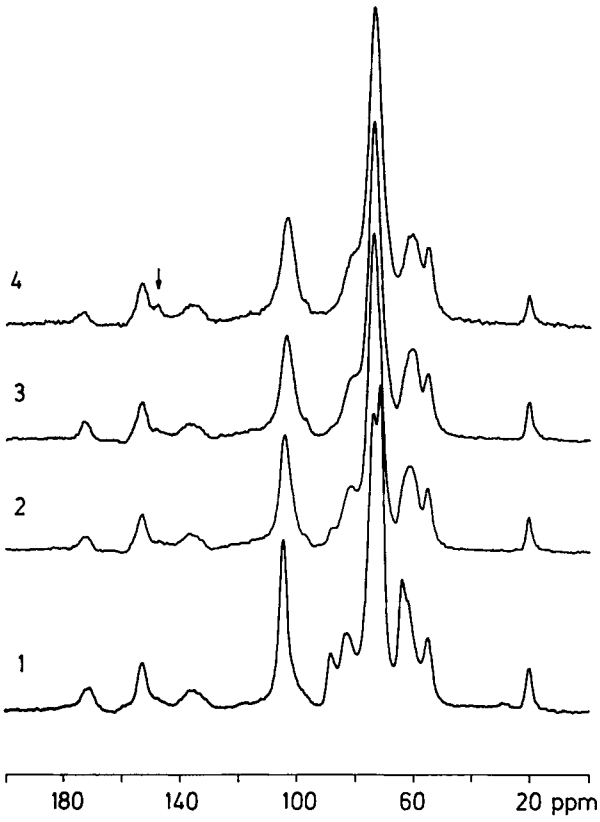

Figure 4 ^{13}C MAS NMR spectra of the birch wood samples. (1) initial, (2) 6 GPa, 10 deg, (3) 0.6 GPa, 180 deg, (4) 6 GPa, 360 deg. An arrow is indicating the 148 ppm signal.

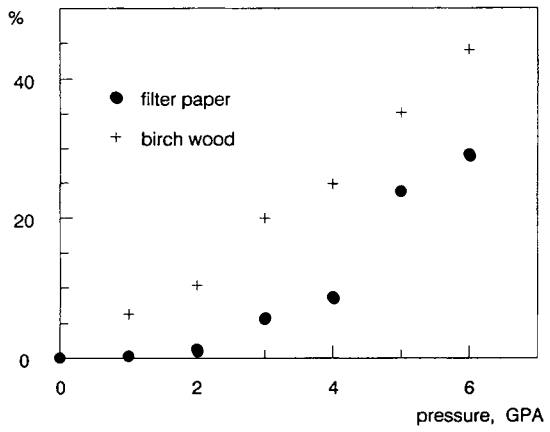

Figure 5 Solubility of birch wood (+) and filter paper (●) after SDHP depending on pressure. Shear deformation 360 deg.

The 89 and 84 ppm lines are well resolved and provide a good opportunity to monitor crystallinity of the cellulose fraction in the wood sample, depending upon the treatment parameters. Figure 4.2 presents a spectrum registered after only 10 degrees twist while 6 GPa pressure was applied. It can be seen that the 89 ppm "crystalline" line has decreased dramatically. Amorphization of the cellulose in a wood sample is even more complete even if only 10 to 12% of the maximum pressure was applied in connection with a 180-degree twist (Fig. 4.3).

Solubility

Cellulose amorphization and decomposition cause high solubility of wood and other cellulose-containing materials in water, as can be seen from the solubility graphs (Fig. 5 and Fig. 6). It must be noted that a solubility limit as a function of the applied pressure was not achieved (Fig. 5) because the experimental device did not permit operation above 6 GPa. At the same time, the limiting rotation angle is about 400° for 9.1 mm-diameter anvils. Subsequent increase of this rotation angle causes only a rather small increase of sample solubility (Fig. 6). About 30% of MCC was dissolved after the treat-

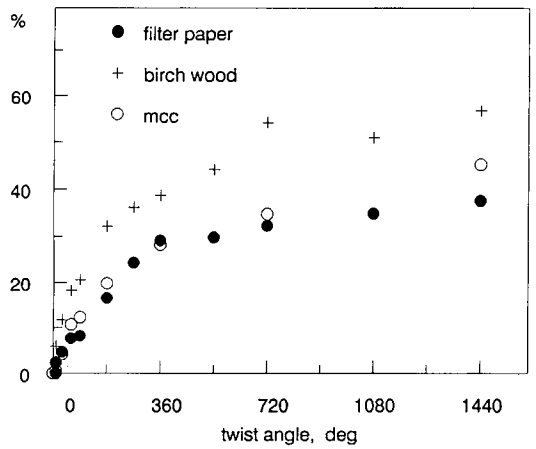

Figure 6 Solubility of birch wood (+), microcrystalline cellulose LT from Lachema (○) and filter paper (●) after SDHP at 6 GPa depending on extent of shear deformation.

ment. SDHP-subjected wood exhibits higher solubility, 39%, than fully cellulosic material, because of the contribution of wood hemicelluloses. A more detailed analysis remains a subject for further research. In the cascade experiment, 33% of the nondissolved residue (approximately the same relative amount of the sample) was dissolved in water after the second SDHP treatment (Table I).

Fractionation

Figure 7 shows an elution profile of water solution of SDHP-treated Avicel PH101 cellulose. Chromatograms of the dissolved model compounds glucose, cellobiose, and raffinose clearly show that a remarkable part of the dissolved substances were monomers (maximum retention of time 15.3 s; see Fig. 7), dimers (14.2 s), trimers (13.3 s) and some other higher oligomers (unresolved peak at 11.7 s). Maximum retention times of the sample chromatogram closely matched those of the calibration curve. According to the normalized peak areas, the solution contained 2.6% glucose, 9.6% cellobiose, and 16.6% cellotriose. As mentioned in the experimental section, the dissolved substances were chromatographically separated into six fractions for further analysis by ^{13}C NMR.

NMR of Chromatographically Separated Fractions

Fraction 1

Interpretation of the NMR spectrum (Fig. 8.1) is based on comparison with the data reported by Pfeffer et al,[17] and shown in Table II.

Experimental lines fit with literature data within ±0.08 ppm. The spectrum contains very weak lines characteristic for cellobiose, indicating traces of cellobiose in Fraction 1.

The spectra contain some additional lines which do not fit the glucose signals: 102.29, 78.50, 76.37, 74.85, 73.86, 70.57, 66.12, and 65.95. These lines are weaker than those of glucose. The origin of these signals is not yet clear. The spectrum shows α- and β- configuration glucose signals, which are connected with mutarization in water. Weak cellobiose signals at 103.46, 96.66, 92.74, and 79.55 have also been identified.

Fraction 2

The spectrum of Fraction 2 (shown in Fig. 8.2) displays mainly the ^{13}C signals characteristic for cellobiose and glucose.

The 96.82 and 93.00 ppm lines can easily be assigned to C1 carbons of glucose β and α anomers, correspondingly. Several glucose signals overlap with those of cellobiose but some can be resolved and assigned: 76.65 to C3β, 75.06 to C2β, 73.65 to C3α, and 70.48 and 70.54 to C4α and C4β atoms. Double intensity signals in the spectrum of this fraction can easily be assigned to cellobiose nonreducing end residues (Table III).

The assignment of reducing end residues, more complicated because of smaller intensity and overlapping of the lines, is proposed in Table IV.

Table I Solubility of Samples after SDHP Treatment (360 deg, 6 GPa)

Sample	H_2O Extraction	H_2O and 10% NaOH Extraction
MCC "Avicel"	26%	
MCC "Lachema"	31%	98%
Filter paper	29%	
Birch wood	39%	
MCC "Lachema", 2 times SDHP (cascade experiment)	54%	

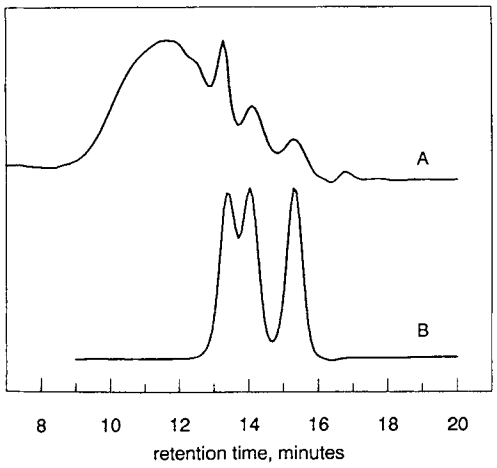

Figure 7 SEC elution profile of water-dissolved SHDP-treated Avicel PH101 cellulose (A) and SEC elution profiles of glucose, cellobiose and raffinose (B).

Fractions 3 to 6

Analysis of Fractions 3 to 6 was performed by comparing these spectra (Fig. 8.3 to 8.6) with the results published by Dudley et al.[18]

A spectrum of Fraction 3 exhibits a 103.4/103.2 ppm doublet, characteristic of cellotriose and higher oligomers. In this doublet the 103.2 ppm line belongs to the internal residues and the 103.4 ppm line to the nonreducing end units. As cellotriose has only one internal residue as well as one nonreducing end unit, the intensity ratio of these lines should be 1 : 1. Cellotetraose and higher oligomers should show the 103.2 ppm line stronger than the 103.4 ppm line. The intensity ratio increases with increasing DP, as seen on the spectra published by Dudley et al.[18] The intensity ratio in our Fraction 3 spectrum is somewhere between that for triose and tetraose, probably due to incomplete separation during SEC. NMR spectra of the samples taken as slices from the chromatography curve tend to change continuously towards the final spectrum, e.g., spectrum with greater MW. This can be assumed from studying Fractions 3 to 6. Positions of the spectral lines are mainly unchanged while some change in multiplicities and significant change in some signal intensities are seen.

According to our interpretation, nonreducing end unit signals should be assigned as follows: C2 to 74.03, C3 to 76.39, C4 to 70.35, and C6 to 61.49 ppm. The intensities of these lines are close to intensities of the remaining signals, thus indicating that DP is still rather low in Fraction 3. The spectrum is very similar to that of pure cellotriose reported by Dudley et al.[18] A small amount of cellotetraose is included in this sample. It should be mentioned that a weak signal at 75.1 ppm corresponds to the reducing end unit C2 atom in β anomers of glucose oligomers. Further resolution of Fractions 4 to 6, corresponding to the samples with higher MW, was not possible.

On the spectra of Fractions 4, 5, and 6 we note changes only in the relative intensities of the NMR lines. Thus the line intensity for 103.4 ppm decreases in comparison with that of 103.2 ppm.

The signals for 76.85, 76.38, 74.03, and 61.48 ppm decrease simultaneously. This should be interpreted as a result of differences in DP of these fractions: end units contain relatively fewer atoms.

The Fraction 6 spectrum is qualitatively rather similar to the spectrum of cellohexaose reported by Dudley.[18]

One interesting area of the spectrum is the region between 79 and 80 ppm, where C4 atoms of the internal residues and reducing end units resonate. Chemical shifts for some oligomers are reported in Table V, based on the literature data.[17,18]

According to Table IV, higher oligomers have their spectral lines in a higher field. Figure 9 presents a simulation of the 79 to 80 ppm region for cellobiose, -triose, -tetraose, and pentaose assuming an α : β anomers ratio of 2 : 3 in each of these oligomers. Simulated spectra provide some additional information about our chromatographically separated samples:

- Fraction 1 contains a small amount of cellobiose, as indicated by the weak doublet at 79.6/79.5 ppm. Cellobiose concentration is about one order of magnitude less than that of glucose.
- Besides cellobiose as a main component, Fraction 2 contains a small amount of cellotriose, which is verified by the 79.3 ppm peak.
- The fraction 2 spectrum consists of five well-resolved, lines, indicating that this sample is a superposition of several subspectra, mainly those corresponding to cellotriose and -tetraose.
- The 79 to 80 ppm region Fractions 4 to 6 have multiplets with the most intense line in the higher field, resembling the spectra of pentaose and higher oligomers reported by Dudley et al.[18]

NMR Spectrum of Cellulose Oligomers Dissolved in D_2O

Figure 10 displays a spectrum of the Avicel PH 101 sample subjected to SDHP and dissolved in D_2O after that. Almost all the signals are multiplets, in-

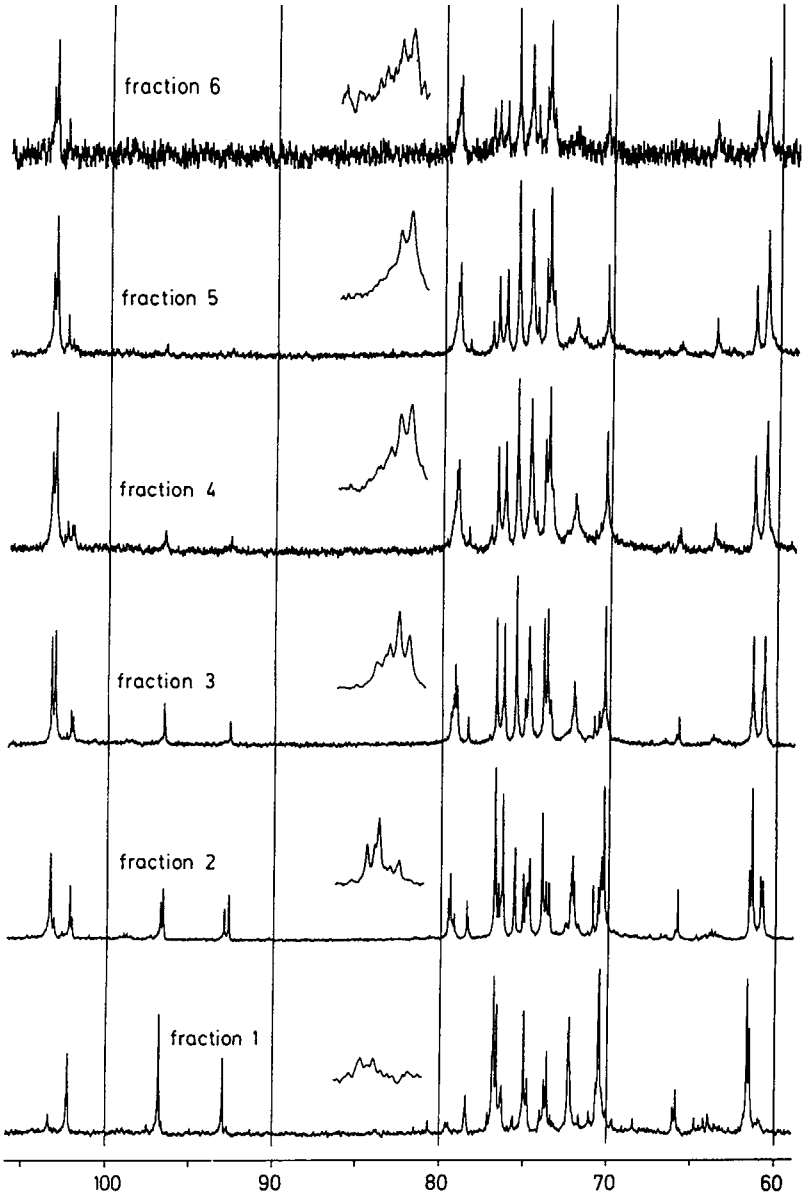

Figure 8 ^{13}C NMR spectra of chromatographically separated fractions 1 to 6, 79–80 ppm region expanded.

dicating that the solution contains several different components. It is certainly not difficult to imagine that solutions may contain glucose monomers, dimers, trimers, and other higher oligomers. Several signals on this spectrum can be assigned to glucose molecules and to the corresponding oligomers on

Table II ^{13}C Chemical Shifts for Fraction 1

	C1	C2	C3	C4	C5	C6	Ref.
Experiment	93.00	72.40	73.68	70.53	72.34	61.52	
α-D-glucose	92.94	72.47	73.75	70.56	72.28	61.59	17
Experiment	96.82	75.06	76.68	70.57	76.84	61.67	
β-D-glucose	96.74	75.14	76.71	70.60	76.78	61.74	17

Table III ^{13}C Chemical Shifts for Fraction 2, Internal Residues

	C1	C2	C3	C4	C5	C6	Ref.
Experiment	103.43	74.05	76.40	70.35	76.86	61.47	
	103.27	74.12	76.52	70.44	76.83	61.59	17

the basis of comparison with literature data and spectra of the SEC separated samples. The 103.4/103.2 ppm doublet corresponds to oligomers with DP $\geq$ 2. As described earlier,[18] if DP $\geq$ 4, the intensity of the 103.2 ppm line is considerably higher than the line for 103.4 ppm. We can conclude that average DP in the sample is rather low.

The 96.8 and 93.0 ppm signals belong to the β- and α-glucose correspondingly while the 96.6 and 92.7 ppm lines correspond to cellobiose and to higher oligomers.

At about 79 ppm it has been possible to resolve signals at 79.5, 79.4, 79.3, 79.2, and 79.1 ppm. This multiplet is caused by superposition of C4 signals of different oligomers with DP $\geq$ 2. Higher oligomers contribute mainly to the higher field part of this complicated region.

The 76.8 and 76.4 ppm signals correspond to C5 and C3 atoms of the nonreducing end units of glucose oligomers. Intensity of these signals is related to DP because in higher oligomers the relative ratio of the nonreducing end units decreases rapidly, and intensity of those lines should decrease correspondingly. In our spectrum of the SDHP-treated PH 101 cellulose sample, the 76.8 and 76.4 ppm signals are rather strong, indicating that the average DP in the solution is low.

Many lines in the spectra actually contain contributions from different glucose oligomers but cannot be used for analysis because the spectral lines of different oligomers have the same chemical shifts. So the 75.6 ppm signal should be assigned to C5 atoms of internal and nonreducing β residues of different oligomers. The 74.7 to 75.0 ppm region contains similar contributions from different oligomers (C5 atoms) as well as from the 73.8 and 74.0 ppm signals (C2 atoms).

The 70.5 ppm signal is assigned to glucose C4 (α and β), while the 70.3 ppm signal corresponds to C4 of the nonreducing end units of cellobiose and higher oligomers. As this line has a strong intensity, it indicates once again the sample's low average DP.

The overlapping of the C6 resonances in different oligomers does not allow separation of the different oligomers, with the exception of glucose at 61.7 ppm (C6β).

Besides the described signals, the spectrum contains some lines which cannot be identified as arising from glucose oligomers. These signals are located at 102.5, 102.2, 70.0, 65.9, 65.2, 63.8, and 62.9 ppm. The origin of these lines remains a subject for further study.

^{13}C CP MAS NMR Spectra of Water-Insoluble Part

Figure 11 presents the ^{13}C CP MAS NMR spectra of nondissolved fractions of Avicel and filter paper after filtration and drying. As described earlier, it was not possible to totally dissolve in water cellulose, subjected to SDHP. These spectra differ significantly from the spectra of the starting material—cellulose I—as well as from the spectra registered after the SDHP treatment was applied. The spectra in Figure 11 are not well resolved, because of the significant contribution from amorphous (noncrystalline) regions of the sample. Comparing the broad

Table IV ^{13}C Chemical Shifts for Fraction 2, End Residues

	C1′	C2′	C3′	C4′	C5′	C6′	Ref.
Experiment	92.71	72.31	72.22	79.64		60.95*	
α-residue	92.69	72.25	72.30	79.60	79.96	61.09	17
Experiment	96.64	74.79	75.18	79.51	75.67	60.91*	
β-residue	96.61	74.92	75.25	79.48	75.59	61.09	17

* Assignment may be reversed.
Spectrum contains additional nonidentified lines at 102.25, 78.51, and 65.91 ppm.

Table V ^{13}C Chemical Shifts for Fractions 3 to 6

	-biose	-triose	-tetraose	-pentaose	-hexaose
Reducing end α	79.6	79.5	79.5	79.3	
Reducing end β	79.5	79.3	79.4	79.2	79.3
Internal residues		79.3	79.3	79.1	79.0

amorphous signal at about 84 ppm with "crystalline" C4 lines at 88–89 ppm, it is possible to estimate the amorphous/crystalline ratio. The typical amorphous spectrum is superimposed by much narrower lines, leading to the conclusion that the structure of this sample's crystalline regions corresponds to cellulose II reported elsewhere.[13,18,19] Characteristic for that spectrum are a sharp C6 line at 62.5 ppm; a triplet structure in the central region of the spectrum corresponding to the C2, C3 and C5 atoms; a very broad C4 signal from noncrystalline regions; a doublet structure of the C4 signal from crystalline regions at about 88 and 89 ppm; and a characteristic pattern of the C1 signal at 104 to 107 ppm, with a strong component of at 105 ppm and a much weaker one at about 107 ppm.

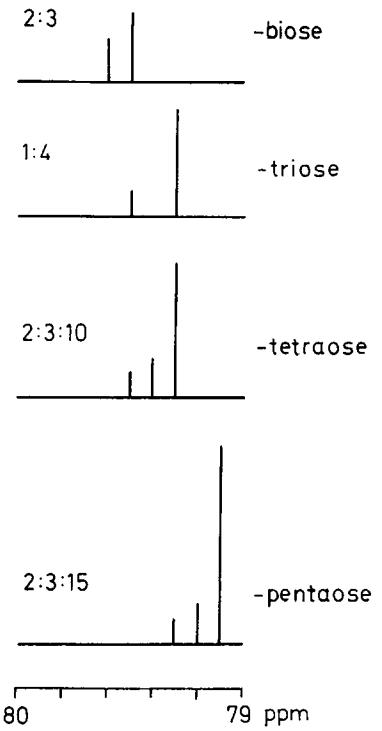

Figure 9 Simulated ^{13}C NMR spectra of 79 to 80 ppm region for glucose, cellobiose, -triose, -tetraose and -pentaose.

It can be concluded that phase transition from cellulose I to cellulose II has occurred. This can be explained by the destruction of the cellulose I crystal lattice by SDHP and the crystallization of cellulose in the presence of water into the cellulose II modification. Thus recrystallization turns the system into a thermodynamically more favorable state.[18] The reactivity of the cellulose sample after water treatment needs further study.

CONCLUSIONS

Native birch wood and microcrystalline cellulose do not exhibit EPR signals. After SDHP treatment the samples were frozen in liquid nitrogen and studied with EPR. Lignin and wood showed a typical long-lived lignin free radicals signal. After treatment, Bjorkman lignin radical concentration increased from $3.5 \cdot 10^{17}$ spins/g to $2.2 \cdot 10^{18}$ spins/g. Wood radical concentration was $3.6 \cdot 10^{17}$ spins/g. Free radical signals were not detected in pure cellulose, but this is not evidence that carbohydrate chains destruct through heterolytic mechanism. Carbohydrate radicals could be short-lived. Further study is needed to clarify the problem. The SDHP treatment must be performed directly at low temperature (in liquid nitrogen).

It is interesting to note that to achieve changes in the lignin "domain" of wood, it was necessary to use extreme conditions: 6 GPa pressure and 360° twist. Under these circumstances a signal has appeared at 148 ppm (Fig. 4.4), which can be explained by lignin network depolymerization, especially the breaking of the β-O-4 aryl ether bonds connecting the syringyl units.[19] The same spectrum also indicates depolymerization of cellulose (appearance of the 97 ppm signal) similar to that described earlier concerning SDHP treatment of the Avicel sample. It has been shown that in a mixture of synthetic polymers with different shear strength values, deformation concentrates upon the component having the lowest shear strength. According to our measurements, cellulose and wood have equal shear

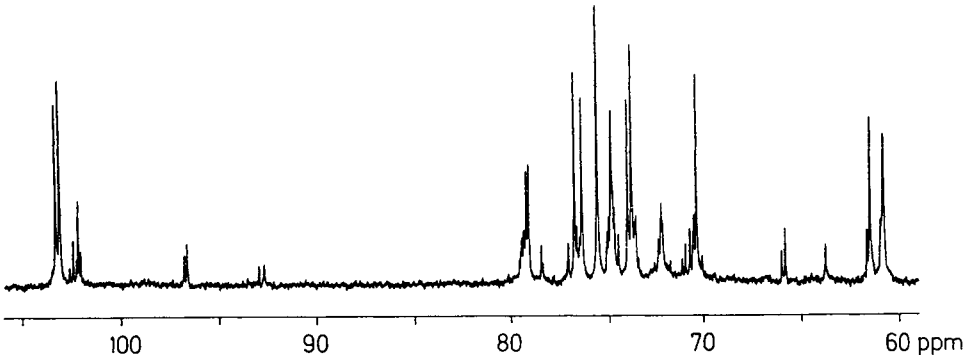

Figure 10 ^{13}C NMR spectrum of Avicel PH 101 sample dissolved in D_2O after SDHP (6 GPa, 360 deg).

strength values and shear deformation occurs first in the cellulose domain of wood. It can be proposed that lignin domains act as "grinding stones" for cellulose.

Earlier we investigated the so-called "steam explosion" treatment as applied to a native wood sample.[20] This process includes impregnation of wood chips with steam in the digester at a moderate temperature and pressure (about 250°C, 4.0 MPa) for a desired period of time (from some seconds to some minutes), after which the reactor is rapidly decompressed. As a result of the treatment, similar change occurred in the lignin domain of the ^{13}C NMR spectrum: the 148 ppm line appeared, indicating decomposition of lignin network. In contrast to SDHP, during steam explosion the crystallinity of cellulose increased, which was established by NMR as well as by X-ray analysis.[21] On the basis of proton spin-lattice relaxation measurements, it was established that in the native wood all major constituents had a common proton spin lattice relaxation time, while after the treatment lignin protons relaxed significantly faster than those of cellulose. The interpretation was that components in the native wood are closely associated by chemical, hydrogen bond, and physical linkages (chain entanglements), thus forming a compulsory compatible state. There is intensive spin diffusion between components in native wood. After the steam explosion treatment components separate from each other and aggregate into larger clusters. The efficiency of spin diffusion between them decreases and relaxation becomes heterogeneous. Selective investigation of the proton spin lattice relaxation permits the determination of the sample's morphology. When the same method was applied to the samples after performing SDHP, T_1 values of lignin signals varied between 319 and 330 ms while those of cellulose varied from 358 to 368 ms (see Table VI). According to these results, SDHP causes a significant change of the supermolecular structure and molecular mobility.

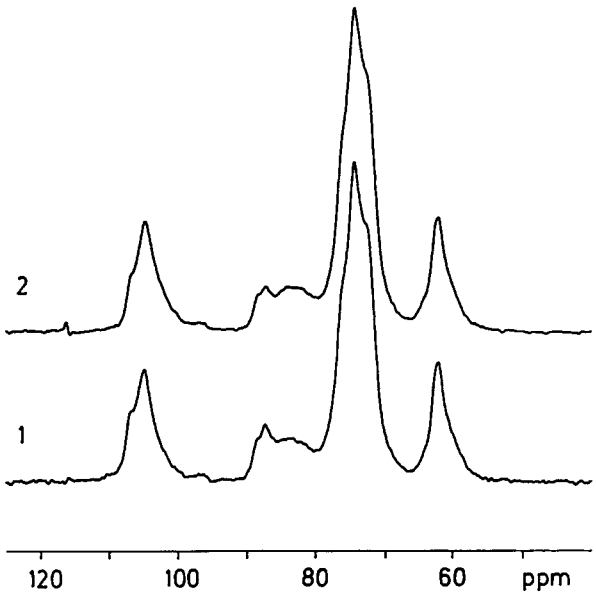

Figure 11 ^{13}C MAS NMR spectra of nondissolved residues. (1) Avicel, (2) filter paper.

In addition to the quantitative differences, a small but reproducible difference in relaxation times exists between the components, indicating that spin diffusion is not any more capable of average proton relaxation in lignin and cellulose. We interpret this fact as separation of the components. Thereby we can conclude that the initial compulsory compatibility of wood is not retained after SDHP, although it has been verified that mixtures of thermodynamically incompatible synthetic polymers become compulsarily compatible after SDHP treatment.[5]

It is significant that after SDHP is applied to

Table VI Proton Spin Lattice Relaxation Times of Variously Treated Wood Samples (ms)

	Lignin Signals at ppm				Cellulose Signals at ppm		
Sample	152	148	132	56	105	74/72	65/62
Native wood	648		653	653	630	662	661
SDHP treated wood	319	217	321	330	368	366	358
SEXT wood	276	260			385	386	
SEXT & SDHP		170	188	189	222	242	

MCC samples, extraction with water and the following extraction with 10% NaOH permits the sample to dissolve almost completely (98%), which seems to be rather important from an ecological point of view. It is also interesting to note that the cascade experiment allows the doubling of the amount of substance dissolved in water. As each twist can be performed in only seconds, SDHP can be very promising for wood chemistry and technology.

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