

SOLUBILITY OF LIGNOCELLULOSE IN N,N-DIMETHYLACETAMIDE/
LITHIUM CHLORIDE. WAXS, ^{13}C CP/MAS NMR, FTIR AND SEM STUDIES
OF SAMPLES REGENERATED FROM THE SOLUTIONS

NINA KOTELNIKOVA, YULIA BYKHOVTSOVA*, ALEXANDRA MIKHAILIDI**, MAXIM
MOKEEV, NATALIA SAPRYKINA, VIKTOR LAVRENT'EV and ELENA VLASOVA

Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia
**Institute of Chemistry, Komi Scientific Center, Russian Academy of Sciences, Ural Branch, Syktyvkar, Komi
Republic, Russia*

***Saint-Petersburg State University of Technology and Design, St. Petersburg, Russia*
✉ *Corresponding author: Nina Kotelnikova, nkotel@mail.ru*

Received August 17, 2013

The solubility of powder lignocelluloses from flax wastes and wood pulps in the N,N-dimethylacetamide/lithium chloride (DMAc/LiCl) system was studied. The chemical “purity” and the degree of polymerization of the lignocelluloses mainly affected their dissolving capacity. Regenerated cellulose samples prepared by precipitating cellulose solutions with water were studied with wide angle X-ray diffraction (WAXS), high-resolution ^{13}C CP/MAS nuclear magnetic resonance in a solid state (^{13}C CP/MAS NMR), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). WAXS study revealed that the cellulose I supramolecular structure of the powder samples regenerated from solutions underwent a mixture of polymorph modifications. As revealed with FTIR, C₁-C₄ conformational transitions of the anhydroglucose units did not occur. However, changes in the H-bond system in the lignocellulose chains for the regenerated samples were registered. The powder samples degraded at the fibrillar level in the solutions.

Keywords: lignocellulose, waste flax, wood pulp, DMAc/LiCl, WAXS, ^{13}C CP/MAS NMR spectroscopy, IR-Fourier spectroscopy, SEM

INTRODUCTION

Direct dissolution of cellulose in the N,N-dimethylacetamide/lithium chloride system has been studied since the 60s of last century. The search for new systems capable to dissolve cellulose became particularly significant for Russia in the 90s because of the loss of cotton cellulose sources from the former Soviet Union Republics of Central Asia. The manufacture of cellulose from wood, flax and straw by their dissolution opened prospects to make new fibres and film materials.

The dissolution of cellulose samples of various natural origins [cotton, softwood kraft pulps (pine and spruce), hardwood pulps (birch, beech, eucalypt)] in DMAc/LiCl was extensively studied.¹⁻¹² However, some questions concerning the dissolution of the cellulose samples in this solvent remained to be answered. For example, no specific explanations were given for the fact that

the cellulose samples of different origins and with different degrees of chemical “purity” under similar processing conditions dissolved to a different extent in this solvent. There were virtually no data on the influence of the lignin content in the samples on their solubility. The supramolecular structure and chemical properties of the samples regenerated from the solutions were also studied. However, the properties of cellulose materials prepared after regeneration from DMAc/LiCl solutions were not enough described.^{1,13} The properties of the solutions obtained by dissolving cellulose samples and those of the final products regenerated from the solutions appreciably differed depending on the dissolution procedure. The variety of treatments of cellulose samples prior to dissolution and of the dissolution methods indicated that the search for the best dissolving conditions ensuring the

formation of final products with specified functional properties was being continued.

The objectives of the current study were to explain how the degree of polymerization of lignocellulose of various origins and the lignin content affected the dissolution of the samples in DMAc/LiCl. Another significant goal was to determine the regeneration of the samples from solutions and monitoring the physicochemical properties of the final products.

EXPERIMENTAL

Materials and procedures

The samples isolated from short flax fibres (FF) and bleached softwood kraft pulp and bleached sulphite hardwood pulp were subjected to dissolution. The flax fibres were linseed waste. The wood pulps were purchased from Syktyvkar Timber Plant ("Mondi", Syktyvkar, Russia).¹⁴ The flax lignocellulose used for comparison was prepared from the flax fibers by alkali cooking and bleached with hydrogen peroxide.

The wood pulps and the flax fibres were subjected to hydrolytic degradation with 10 wt% aqueous solutions of nitric acid, sulfuric acid, hydrochloric acid or peroxyacetic acid at 100 °C and at a solid-to-liquid ratio of 1:10 for 2 h. Rinsing of the hydrolyzed samples, drying, measuring of the intrinsic viscosity and calculation of the average degree of polymerization DP_v were performed by standard methods. The α -cellulose content was determined by dissolving the samples in 17.5 wt% aqueous solution of NaOH, and the lignin content was determined with the sulfuric acid method, according to Komarov's modification.¹⁵ The hydrolysis yielded lignocellulose samples in a powder form.

Analytical grade anhydrous LiCl, purum p.a., was purchased from Fluka. LiCl was annealed at 200 °C for 4 h, then stored in a desiccator over P₂O₅ before use and employed without further purification. Analytical grade N,N-dimethylacetamide was purchased from Sigma-Aldrich and used as received. All other chemicals were of analytical grade and used without further purification.

Dissolution of powder samples

The lignocellulose samples from the flax fibres (FLC) and from the softwood and hardwood pulps (SLC and HLC, respectively) were submitted to dissolution in DMAc/LiCl. For each sample, not less than three sub-samples were studied. The dissolution was performed by a procedure described elsewhere^{4,16} and adapted to the above samples. The solutions were prepared in several steps.

Pretreatment of the sample

The air-dried sub-sample of lignocellulose (1 g) was suspended in 200 ml of deionised water with

continuous stirring for 2 h. Excess water was removed by suction filtration, the sample was washed twice with DMAc, placed in 10 ml of DMAc and left overnight at room temperature. Then excess DMAc was removed by suction filtration and the sample was ready for dissolution.

Procedure

100 cm³ of DMAc was poured into a three-neck flask and the flask was heated to 165 °C. A portion of the lignocellulose sample was added to DMAc to prepare a solution with the concentration of 1 wt% and was stirred continuously for 2 h. The resulting suspension was refluxed for 30 min, then LiCl was added to obtain a 9.0 wt% solution. The mixture was kept under stirring for 4 h. The solution was cooled to room temperature and filtered by suction filtration (the pore size of the Schott filter was 10 μ m) in order to separate the insoluble solids. The resulting solution was optically clear.

The evaluation of the dissolving capacity was done for every sample. The change in the weight of the lignocellulose powder sample and the weight of the rinsed and dried residue on the filter after filtration was monitored gravimetrically. The dissolving capacity (DC, %) was calculated from the equation: $DC = [(W_p - W_r)/W_p] \cdot 100$, where W_p is the weight of the powder sample and W_r is the weight of the insoluble residue. The DC values were expressed as an average of 3 measurements.

Regeneration of samples from the solutions

A special procedure was developed for the regeneration of the samples from the solutions. We prepared regenerated samples in the form of spherical particles and films. To obtain spherical particles, a solution was poured into a separating funnel placed over a precipitation bath with distilled water and arranged on a magnetic stirrer. The regeneration was performed by the drop procedure. The drops from the funnel were regulated with an appropriate rate ensuring the formation of the spherical particles in the precipitation bath. While preparing films, the solutions were cast on glass plates and slightly air-dried, then the plates were placed in a precipitation bath with distilled water. The cast solutions were coagulated and regenerated. The regenerated samples were separated from the solutions, rinsed thoroughly consequentially with cold, hot and again with cold distilled water, and finally left in cold water for 24 h. Then the samples were air-dried at room temperature or in a vacuum oven at 40 °C.

Methods

The structure and properties of the powder and the regenerated samples were studied with wide-angle X-ray scattering (WAXS), high-resolution ¹³C CP/MAS NMR spectroscopy in a solid state, and Fourier transform IR spectroscopy (FTIR).

X-ray scattering intensity curves (XSICs) were measured with an X-ray DRON-2.0 diffractometer using monochromated CuK_α radiation in a 2θ range between 4° and 40° at an angle step of $2\theta/\text{min}$ and constant time (3 s). The powder samples were used without additional treatments. The spherical particles and films were sealed with an X-ray neutral film.

^{13}C CP/MAS NMR spectra were recorded with a Bruker AVANCE-II-500WB spectrometer at a frequency of 125 MHz. The samples were packed into zirconium rotors with a diameter of 4 mm. The spectra were taken at 20°C with magic angle spinning at a frequency of 5-8 kHz, using the cross-polarization technique. The chemical shifts were given in ppm, relative to the signal of tetramethylsilane.

FTIR spectra were recorded with a Bruker IFS 88 FTIR spectrometer. The spectra of the fibres and powder samples were taken in the reflection mode. Dried samples were embedded into KBr pellets (5-6 mg sample/100 mg KBr). The spectra resulting from measurements included 64 scans at a spectral resolution of 8 cm^{-1} between 600 and 4000 cm^{-1} . The spectra of the spherical particles or films preliminary dried at room temperature were recorded using a MiracleTM ATR for FTIR spectrometer.

The sample surface morphology was examined with scanning electron microscopy (SEM). The electron micrographs were taken with a Jeol JSM-35CF scanning electron microscope at a voltage of 15-30 kV. The samples were sputtered in argon using a gold target.

Macroscopic images of the samples were obtained with digital cameras Canon Power Shot A3400 IS and Canon Power Shot SX20 IS (both made in Japan).

RESULTS AND DISCUSSION

Solubility of lignocelluloses in DMAc/LiCl

Some characteristics of the flax fibres, pulps and powder lignocelluloses and the data on their solubility in DMAc/LiCl are listed in Table 1.

The flax fibres had $\text{DP}_v = 2130$ and contained 10.0 wt% lignin. For the flax lignocellulose, DP_v was considerably lower (530) and the lignin content was also low (0.3 wt%). These two samples appreciably differed in solubility. The flax fibres did not noticeably dissolve in DMAc/LiCl. Isolation of flax lignocellulose from FF by alkali cooking led to the removal of resins and fat impurities and resulted in an almost complete delignification and a decrease in DP_v (almost 4 times lower). This increased the dissolution of the sample to 54 wt%. Hydrolytic degradation of FF decreased the DP_v of the powder samples 5.6-8.9 times. DP_v values ranged between 240 and 380 for FLC powder samples, depending on the acid used. The depolymerisation of FF was not accompanied by delignification, when it was hydrolysed with hydrochloric acid, and the delignification occurred to a small extent when it was hydrolysed with sulfuric acid. The treatments with nitric or peroxyacetic acids resulted in a decrease in the lignin content of the powder samples (3 and 6 times, respectively). FLC samples obtained after hydrolysis with HCl and H_2SO_4 dissolved to 80 wt%, and they dissolved completely after hydrolysis with HNO_3 and CH_3COOOH .

Table 1
Some characteristics of initial samples and powder lignocelluloses and their solubility in DMAc/LiCl

Sample/acid used for hydrolysis	Content, %		DP_v	DC, %
	lignin	α -cellulose		
Flax fibre (FF)*	10.0	67.0	2130	Does not dissolve, swells**
Flax cellulose	0.3	94.8	530	54
Powder FLC/ HNO_3	3.4	88.4	270	100
Powder FLC/ H_2SO_4	8.8	88.5	270	80
Powder FLC/HCl	10.0	88.2	240	80
Powder FLC/ CH_3COOOH	1.6	52.0	380	100
Hardwood pulp	9.3	73.1	650	80
Powder HLC/ HNO_3	4.0	79.5	240	98
Softwood pulp	8.7	87.5	1200	Swells**
Powder SLC/ HNO_3	7.5	82.2	220	100

Note: Concentration of lignocellulose 1 wt%, concentration of LiCl 9.0 wt%

* Powder samples were prepared from flax fibre

** Solubility could not be determined because of strong swelling



Figure 1: Digital images of regenerated samples of HLC precipitated with distilled water; (1) spherical particles and (2) a film

The hardwood and softwood pulps had DP_v of 650 and 1200, respectively, and contained 9.3 and 8.7 wt% lignin, respectively. The dissolution of the hardwood pulp in DMAc/LiCl was 80 wt%. Taking into account that the lignin content in this pulp was only slightly lower than the lignin content in FF, it can be concluded that the major factor affecting the dissolution of the sample was the DP_v value. For the hardwood pulp DP_v was more than 3 times lower than for FF. The decrease of DP_v to 240 after hydrolysis with HNO_3 (preparation of HLC) and a simultaneous decrease in the lignin content (more than 2 times lower) increased the dissolution to 98 wt%.

The softwood pulp strongly swelled in DMAc/LiCl. After hydrolysis with HNO_3 , the DP_v of this sample decreased to 220 with a simultaneous slight decrease in the lignin content, and its dissolution increased to 100 wt%.

Thus, the DP_v of the lignocelluloses and lignin and the impurity contents strongly affected their dissolution in the DMAc/LiCl solvent system.

After the dissolution of the powder lignocelluloses and subsequent regeneration, we obtained samples in the form of spherical particles and films. Digital images of the samples precipitated from 1 wt% HLC solutions to water are shown in Figure 1.

Comparison of supramolecular structure, functional composition and morphological structure of the powder lignocelluloses and of the samples regenerated from solutions

WAXS study

Figure 2 shows the X-ray scattering intensity curves (XSIC) of HLC and FLC samples (1, 3) and of the same samples regenerated from the solutions with the shape of spherical particles (2, 4). The positions of the main reflections at $2\theta=14^\circ-16^\circ$, $22^\circ30'$, and $34^\circ-35^\circ$ corresponded to

those from the $1\bar{1}0$, 110, 200, and 040 planes of the cellulose cell, respectively,¹⁷ for HLC and FLC, and were also consistent with peaks for cellulose I.¹² For the regenerated samples, the positions of the reflections appreciably differed. Thus, the reflections at $2\theta=14^\circ-16^\circ$ were virtually absent, the intensity of the reflection at $22^\circ30'$ decreased, and new reflections at $2\theta=10^\circ-12^\circ$ ($1\bar{1}0$) and 20° (200, strong) appeared. The intensity of the reflection at $2\theta=34^\circ-35^\circ$ (040) for the regenerated HLC sample was very low, and this reflection was absent in the XSIC of the regenerated FLC sample. The XSICs of the regenerated samples could not be characterized as a definite structural modification; they contained reflections distinctive to celluloses II and III.¹⁸⁻²⁰ The reflections at $2\theta=10^\circ-12^\circ$ and 20° were typical for cellulose II, but the decreased intensity of the 200 reflection and the low intensity or absence of 040 reflection were characteristic of the structural modification III to a greater extent.^{19,20}

The structural transformation of natural cellulose I into modification III generally occurred by treatment of cellulose I with ammonia or with aliphatic mono- and diamines,^{21,22} but the dissolution of the cellulose and the preparation of the fibres, films and other cellulose materials regenerated from the solutions usually transformed cellulose I into polymorph II.¹² In our case, the dissolution of the samples in DMAc/LiCl and the subsequent regeneration were accompanied by the transformation of the crystallographic cell of cellulose I and by the formation of mixed polymorph structures. According to S.-L. Maunu *et al.*,²² the transformation of cellulose I into another structural modification, in particular, into polymorph II, involves changes in the conformation of the cellulose chains. They

become asymmetric, compared to the symmetric structure in cellulose I, and thus become more accessible to chemical reagents. A comparison of the crystallinity of the regenerated samples with those of the powder FLC and HLC samples, whose relative crystallinity before dissolution was 64 wt%,¹⁷ showed that the crystallinity of the regenerated samples was considerably lower.

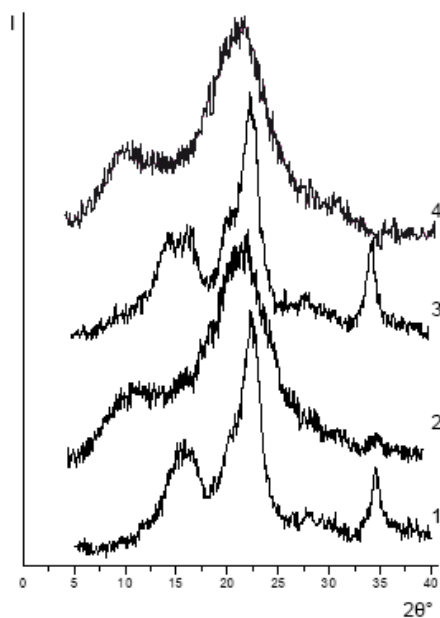


Figure 2: WAXS intensity curves of (1) HLC, (2) regenerated HLC, (3) FLC and (4) regenerated FLC. HLC and FLC samples were prepared by the hydrolysis of the pulp and the flax fibre with a H_2SO_4 solution; the regenerated samples had the shape of spherical particles. (I) Intensity and (2θ) Bragg angle

¹³C CP/MAS NMR study

¹³C CP/MAS NMR spectra of HLC (1) and SLC (3) samples and of the same samples regenerated from the solutions (2, 4) are displayed in Figure 3. The chemical shifts in the spectra of HLC and SLC samples ranged between: 104-105 ppm for C_1 , 84-89 for C_4 (doublet), 71-75 for $C_{2,3,5}$ (triplet and doublet for HLC and SLC, respectively), and 62-65 for C_6 (doublet) (Table 2).^{23,24}

¹³C CP/MAS NMR spectra of the regenerated samples appreciably differed from those for HLC and SLC and these differences appeared for all chemical shifts in the spectra.

The chemical shifts of the C_4 and C_6 atoms are the most sensitive to structural changes.²⁴ The C_4 shifts at 88-89 ppm (strong and symmetric) were

Nevertheless, it can be noted that the regenerated lignocelluloses were poor crystalline. Similar results were obtained for the sample regenerated from a solution of powder SLC. These data differ from those for the regenerated samples of the lignocelluloses obtained from other solvents, which are basically amorphous.

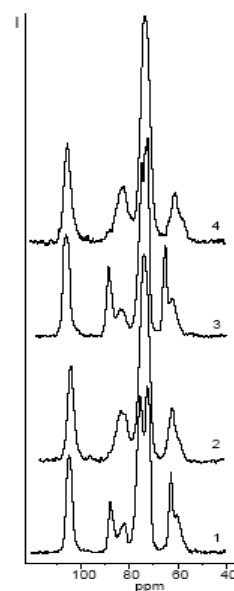


Figure 3: High-resolution solid-state ¹³C CP/MAS NMR spectra of (1) HLC, (2) regenerated HLC, (3) SLC and (4) regenerated SLC. HLC and SLC samples were prepared by the hydrolysis of the pulps with a H_2SO_4 solution; the regenerated samples had the shape of spherical particles. (I) Intensity and (δ) chemical shift, ppm

assigned to the ordered domains of the cellulose structure polymorph I,²⁴ and those at 83-84 ppm, to the disordered domains.^{25,26} The shifts corresponding to the crystalline region were not found, due to the decrease of cellulose crystallinity in the dissolution process. The fuzzy shape of the monosignals at 83-84 ppm and the positions of the shift in the spectra of the regenerated samples were typical of the spectra of celluloses II and/or III, as well as of less-ordered celluloses. The C_6 shifts at 60-66 ppm are usually interpreted on the basis of cellulose polymorphism²⁷ and/or amorphisation.²² Changes in the position of the C_6 shift were attributed to the changes in the rotational isomeric composition of the hydroxymethyl groups in the cellulose unit. In the spectrum of cellulose II, there is a doublet

at 62.9 and 61.4 ppm or a single at 62 ppm²⁸ and a doublet at 62.0 and 65.2 ppm in the spectrum of cellulose III. The amorphous phase gives a broad shift at 60-62 ppm. In the spectra of HLC and SLC powder samples (polymorph I), the dominant isomer gives the shifts at a higher

position (65.48 and 65.79 ppm, respectively), and in the spectra of the regenerated samples C₆ atoms give the broad shifts at a lower position (59.8 and 63.04 ppm).

Table 2
Chemical shifts of signals in the high-resolution solid-state ¹³C CP/MAS NMR spectra of powder lignocelluloses and regenerated samples

Sample	Chemical shift, ppm			
	C ₁	C ₄	C _{2,3,5}	C ₆
SLC	105.40	84.00	72.18	63.24
	105.05	89.43	73.29	65.79
	—	—	75.38	—
Regenerated SLC	104.43	82.80	74.19	59.80
	—	83.10	—	62.72
HLC	105.72	84.00	72.82	63.24
	105.40	89.43	75.38	65.48
Regenerated HLC	105.40	81.40	74.51	60.05
	—	83.74	—	63.04
Hydrate cellulose film*	104.70	87.00	73.80	62.40

*The chemical shifts in the high-resolution solid-state ¹³C NMR spectrum of the hydrated cellulose film are given for comparison

This fact suggests a change in the rotational isomeric composition of the hydroxymethyl groups in the cellulose unit. In addition, the shifts with the maxima at 74.19 and 74.51 ppm (C_{2,3,5}) in the spectra of the powder lignocelluloses were double and triple (SLC and HLC, correspondingly) (Table 2) and these shifts in the spectra of the regenerated SLC and HLC were single and almost symmetric. This indicates that the chain conformation and molecular surrounding of C_{2,3,5} carbon atoms in the regenerated samples differ from those in cellulose I.²⁵

We compared the ¹³C CP/MAS NMR spectra of the regenerated samples with that of cellulose II prepared by mercerization of cotton cellulose and with that of a hydrate cellulose film (the chemical shifts in the ¹³C CP/MAS NMR spectrum of the hydrated cellulose film taken from an earlier work²⁹ are shown in Table 2). The shift positions of C_{2,3,5}, C₄, and C₆ atoms in the spectra of the regenerated samples are close to the shift positions of the same atoms in the spectrum of the hydrate cellulose film. These results correspond to the data obtained with WAXS and confirm that the regenerated samples are poor crystalline and consist of cellulose polymorphs II and III. Probably, the transformation of the cellulose I structure into other polymorph forms

occurred due to a change in the rotational isomeric composition of the hydroxymethyl groups of cellulose I, which leads to the changes in the conformation of the cellulose chains.

FTIR study

The FTIR-Fourier transform spectra of the samples regenerated from the solutions of powder FLC and HLC in DMAc/LiCl differed from the spectra of the corresponding powder lignocelluloses (Figure 4). However, there are no visible changes in some absorption ranges. For instance, the absorption range at 850-900 cm⁻¹ being a superposition of deformation of the anomeric CH, C-O stretching and C₁-O-C₄ ring stretching asymmetric out-of plane vibrations³⁰ indicates C₁-C₄ conformational transitions of the anhydroglucose units. Thus, the dissolution and regeneration from solutions were not accompanied by C₁-C₄ conformational transitions of the anhydroglucose units, and altered forms of units did not appear.³¹ The changes in the conformation of the cellulose chains confirmed by the results of WAXS and NMR studies were not accompanied by the changes in the conformation of cellulose units in the chains. The intensity of the bands at 1630 cm⁻¹ attributed to the bending mode of the adsorbed water was not also essentially changed in the spectra of the

regenerated samples, compared to the powder samples.

The broad absorption band of OH groups at 3000-3600 cm^{-1} (OH bending intra- and intermolecular vibrations), free and involved in hydrogen bonds in the cellulose chains^{32,33} in the spectra of regenerated samples had a more uniform shape than that in the spectra of FLC and

HLC. Probably, the number of intra-[O(3)H...O(6) and O(2)H...O(6)] and intermolecular [O(6)H...O(3)] hydrogen bonds in recovered samples was similar. However, the redistribution of intensities of OH-bands and the "smoothing" of the general shape of the band do not exclude the transformation related to the change of intra- and intermolecular bonds.

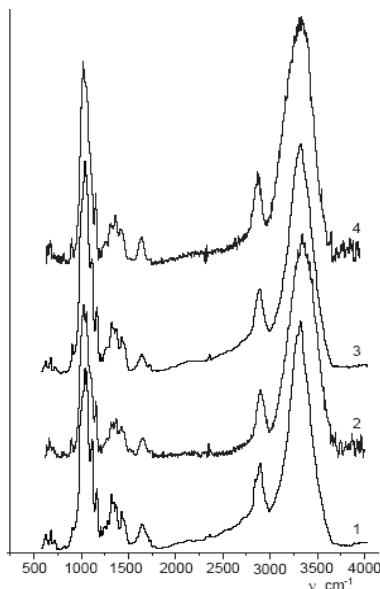


Figure 4: FTIR-Fourier spectra of (1) FLC and (2) regenerated FLC, (3) HLC and (4) regenerated HLC. The FLC sample was prepared by hydrolysis of the flax fibres with a H_2SO_4 solution, the HLC sample was prepared by hydrolysis of the pulp with a HNO_3 solution; the regenerated FLC sample had the shape of spherical particles, the regenerated HLC sample was prepared as a film. (I) Intensity and (v) wavenumbers, cm^{-1}

Some changes were noted in the absorption range 1250-1500 cm^{-1} . There was a group of at least 4 bands at 1280 cm^{-1} (CH deformation stretching vibrations), 1318 cm^{-1} (CH wagging vibrations at C_6), 1370 cm^{-1} (CH bending vibrations) and 1430 cm^{-1} (CH_2 symmetric bending mode at C_6).^{30,34,35} The changes in the intensities and/or positions of the bands at 1318 and 1430 cm^{-1} revealed variations in the environment/conformation of C_6 in CH_2OH groups.^{35,36} In the spectra of powder lignocelluloses the intensity of the band at 1318 cm^{-1} was the highest and it decreased to some extent in the spectra of the samples regenerated from the solutions. The band at 1430 cm^{-1} shifted to a higher wavenumber at 1440 cm^{-1} . Both changes indicated mostly variations in the conformation of hydroxymethyl groups, due to the changes in rotation of C_6 in CH_2OH groups. Those alterations could lead to conformation changes in the OH-bond system.

Generally, the FTIR spectra of the regenerated samples, as compared to the corresponding powder samples, were "smoothed" owing to the redistribution of the intensity of the components of the absorption bands. They were similar to the spectra of either hydrate cellulose film²⁹ or ramie cellulose,²⁸ which are characteristic of amorphous cellulose polymorph II. The chemical composition of the samples after recovering did not change.

SEM study

The morphological structure of the powder lignocelluloses essentially changed after the dissolution and regeneration of the samples from the solutions. In powder lignocelluloses, the fibres had mainly a rod-like shape (Figure 5, images 1, 4, 6). The particles of FLC fibres with a transverse size varying in a wide range (from 20 to 120 μm) consisted of fine rigid fibres with a size of 8-15 μm , arranged parallel to each other.

The surface structure of the fibres was not strictly ordered. On the surface, there were deep cracks¹⁷ and inclusions of fine inorganic particles (probably salts). HLC fibres (Figure 5, image 4) were considerably shorter than those of FLC fibres, their transverse size did not exceed 25 μm , and a number of the fibres had a tubular shape. Regularly arranged fibrils on the fibre surface occurred rarely, and the internal surface of the fibres seen in the voids of the fibres was also smoothed. SLC fibres (Figure 5, image 6) were still more broken than HLC fibres, they were shorter, but the transverse sizes of the fibres were similar.

The morphological elements of the samples regenerated from the solutions had the shape of agglomerated spherical particles rolled into clews. Their sizes were 1000-1200 μm in diameter. At a low magnification, the slightly ripply fibrillar

fragments on the surface of the clews could be observed (Figure 5, images 2, 5, 7). However, at a higher magnification, it could be seen (Figure 5, image 3) that the particles were formed by fibrillar elements twisted in spirals on the surface, which was loose and highly porous. The thickness of the fibrillar filaments that formed the clews was different. Thus, the thinnest fibrils (mean thickness about 2 μm) were observed in the SLC sample; the fibril thickness in the FLC sample was about 4 μm and that in the HLC sample was about 8 μm . Apparently, the rod-like particles of the powder samples after dissolution in DMAc/LiCl and subsequent regeneration fractured further on the fibrillar level in the longitudinal direction, and the fibril thickness became several times smaller than in the powder samples.

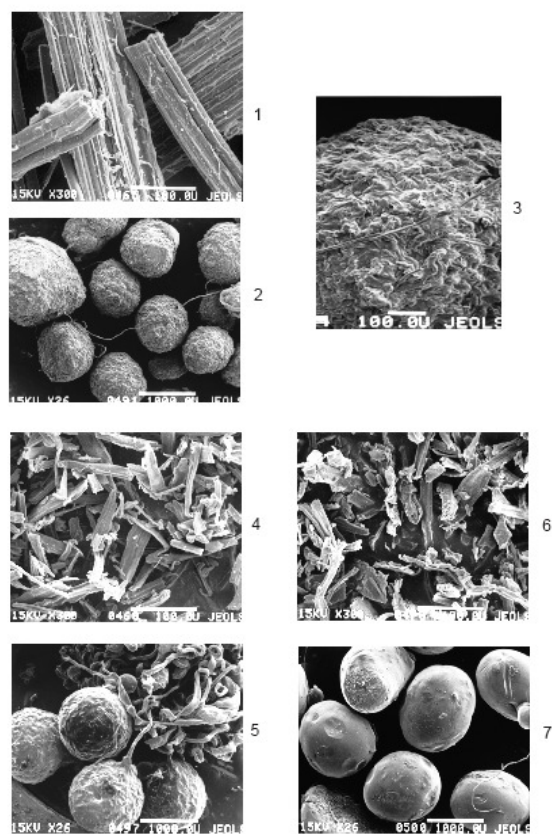


Figure 5: Scanning electron micrographs of the surface of (1) powder FLC prepared by hydrolysis with a HNO_3 solution, (2) spherical particles regenerated from the FLC solution, (3) segment of one of the particles at fourfold magnification, (4) powder HLC prepared by hydrolysis with a H_2SO_4 solution, (5) spherical particles regenerated from HLC solution, (6) powder SLC prepared by hydrolysis with a H_2SO_4 solution and (7) spherical particles regenerated from SLC solution

CONCLUSION

1. To attain the complete solubility of the powder lignocelluloses in the DMAc/LiCl system, a decrease of the DP_v values of the samples and of the lignin contents was necessary. Both parameters strongly affected the dissolving capacity.
2. The results obtained with WAXS and ¹³C CP/MAS NMR spectroscopy showed that the regenerated samples were poor crystalline. Their supramolecular structure corresponded to the cellulose polymorphs II and/or III.
3. The dissolution and regeneration of the lignocelluloses from the solutions were not accompanied by C₁-C₄ conformational transitions of the anhydroglucose units, as revealed by FTIR spectroscopy. Changes in the H-bond system in the lignocellulose chains were registered, due to the alterations either in the intensity or in the position of the bands in the range 1280-1500 cm⁻¹.
4. The fibres of the powder samples fractured in the longitudinal direction at the fibrillar level as a result of dissolution. The samples regenerated from the solutions with the shape of spherical particles were highly porous.

ACKNOWLEDGMENTS: The authors are grateful to Dr. Anje Potthast (BOKU, Vienna) for useful advice.

REFERENCES

- ¹ C. L. McCormick, P. A. Callais and B. H. Hutchinson, *Macromolecules*, **18**, 2394 (1985).
- ² T. R. Dawsey and C. L. McCormick, *JMS-Rev. Macromol. Chem. Phys.*, **C30**, 405 (1990).
- ³ S. L. Williamson, R. S. Armentrout, R. S. Porter and C. L. McCormick, *Macromolecules*, **31**, 8134 (1998).
- ⁴ A. Potthast, Th. Rosenau, H. Sixta and P. Kosma, *Tetrahedron Lett.*, **43**, 7757 (2002).
- ⁵ U. Henniges, S. Schiehser, Th. Rosenau and A. Potthast, *ACS Symp. Ser.*, **1033**, 165 (2010).
- ⁶ A. Potthast, Th. Rosenau, R. Buchner, Th. Roeder, G. Ebner *et al.*, *Cellulose*, **9**, 41 (2002).
- ⁷ U. Henniges, M. Kostic, A. Borgards, Th. Rosenau and A. Potthast, *Biomacromolecules*, **12**, 871 (2011).
- ⁸ A.-L. Dupont, *Polymer*, **44**, 4117 (2003).
- ⁹ S. Fernandez, PhD Dissertation, Regensburg University, Germany, 2003.
- ¹⁰ Devi Kongala Sirisha, V. K. Mathur, S. K. Nayak, S. Mohanty and M. Kumar, *Pharma Chem.*, **1**, 296 (2009)
- ¹¹ G. T. Ciacco, D. L. Morgado, E. Frollini, S. Possidonio and O. A. El Seoud, *J. Braz. Chem. Soc.*, **21**, 71 (2010).
- ¹² D. Ishii, D. Tatsumi and T. Matsumoto, *Biomacromolecules*, **4**, 1238 (2003).

- ¹³ J. Kim, *Final Report AOARD-07-4073* (2007).
- ¹⁴ T. P. Shcherbakova, N. E. Kotelnikova and Yu. V. Bykhovtsova, *Khim. Rast. Syr'ya*, **3**, 33 (2011).
- ¹⁵ A. V. Obolenskaya, Z. P. El'nitskaya and A. A. Leonovich, *Laboratornye raboty po khimii drevesiny i tsellyulozy* (Laboratory Works on Wood and Cellulose Chemistry), Moscow, Ekologiya, 1991.
- ¹⁶ D. D. Grinshpan, *Nevodnye rastvoriteli tsellyulozy* (Nonaqueous Solvents for Cellulose), Minsk, Universitetskoe, 1991.
- ¹⁷ K. Leppanen, S. Andersson, M. Torkkeli, M. Knaapila, N. Kotelnikova *et al.*, *Cellulose*, **16**, 999 (2009).
- ¹⁸ L. M. Kroon-Batenburg and J. Kroon, *J. Glycoconjugate*, **14**, 677 (1997).
- ¹⁹ G. A. Petropavlovskii, N. E. Kotelnikova and L. A. Volkova, *Cellulose Chem. Technol.*, **16**, 247 (1982).
- ²⁰ H. Chanzy, K. Imada, A. Mollard, R. Vuong and F. Barnoud, *Protoplasma*, **100**, 303 (1979).
- ²¹ J. Hayashi, H. Kon, M. Takai, M. Hatano and T. Nozawa, *ACS Symp. Ser.*, **340**, 134 (1987).
- ²² S.-L. Maunu, T. Liitia, S. Kauliomaki, B. Hortling and J. Sundquist, *Cellulose*, **7**, 147 (2000).
- ²³ J. He, Yu. Tang, and Sh.-Yu. Wang, *J. Iranian Polym.*, **16**, 12, 807 (2007).
- ²⁴ N. E. Kotelnikova, A. Yu. Elkin, A. I. Kol'tsov, G. A. Petropavlovskii and Yu. N. Sazanov, in *Metody issledovaniya tsellyulozy* (Methods for Studying Cellulose), Riga, Zinatne, 1988, pp. 61-65.
- ²⁵ Y. Sun, L. Lin, H. Deng, J. Li, B. He *et al.*, *BioResources*, **3**, 297 (2008).
- ²⁶ A. Thygesen, J. Oddershede, H. Lilholt, A.B. Thomsen and K. Stahl, *Cellulose*, **12**, 563 (2005).
- ²⁷ J. C. Gast, R. H. Atalla, and R. D. McKelvey, *Carbohydr. Res.*, **84**, 137 (1980).
- ²⁸ M. Wada, L. Heux and J. Sugiyama, *Biomacromolecules*, **5**, 1385 (2004).
- ²⁹ N. Kotelnikova and A. Mikhailidi, *Cellulose Chem. Technol.*, **45**, 585 (2011).
- ³⁰ T. Baldinger, J. Moosbauer and H. Sixta, *Lenzinger Ber.*, **79**, 15 (2000).
- ³¹ G. A. Petropavlovskii and N. E. Kotelnikova, *Cellulose Chem. Technol.*, **19**, 591 (1985).
- ³² T. Kondo, *Cellulose*, **4**, 281 (1997).
- ³³ K. K. Pandey, *Polym. Degrad. Stabil.*, **90**, 9 (2005).
- ³⁴ R. H. Marchessault, *Pure Appl. Chem.*, **5**, 107 (1962).
- ³⁵ S. Y. Oh, D. I. Yoo, Y. Shin, H. C. Kim, H. Y. Kim *et al.*, *Carbohydr. Res.*, **340**, 2376 (2005).
- ³⁶ M. Frey, J. A. Cuculo, J. Hinestroza and R. Kotek, *NTC Project M05-CR02* (2006).