Fibers from DMAc-LiCl Solutions of Steam Exploded Wood

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SYNOPSIS

Poplar wood was steam exploded under various experimental conditions (230°C, 120–360 sec) and was then dissolved in dimethylacetamide-lithium chloride (DMAc-LiCl). Solutions of different concentrations (c_p 4–10%) were obtained without any activation. Mesophases were not formed in any of the conditions tested. The good spinnability of the solutions led to wood fibers that were evaluated in terms of physico-mechanical properties and morphological and supramolecular characteristics. The tensile strength and the modulus of the wood fibers, improved through delignification treatments, were comparable to those of conventional rayons. After annealing treatments at 260°C in protic solvent, X-ray and CP MAS ^{13}C–NMR experiments revealed evidence of a marked modification of the fiber supramolecular structure. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The viscose process for producing regenerated cellulose fibers is being discarded, due to its high cost, energy consumption, and adverse environmental impact. However, the attractive properties of such regenerated cellulosic fibers, as well as interest in high modulus/high strength fibers, has focused studies on the preparation of anisotropic solutions that can be used as dope in spinning processes.[1,2]

Cellulose, and its derivatives, exhibit anisotropic solutions in various kinds of solvents[3-8] when the polymer concentration exceeds a critical value (c_p'). If solubility problems do not interfere, the amount of the anisotropic phase can be increased by increasing the polymer concentration (c_p). Correspondingly, the isotropic phase is reduced and becomes zero at a value c_p''. The c_p' and c_p'' are characteristic of the polymer–solvent pair. A pure anisotropic phase of cellulose in DMAc–7% LiCl was never observed, due to crystallization phenomena which occur at concentrations almost equal to c_p''. On the contrary, no formation of crystalline phase was observed at $c_p' < c_p < c_p''$, even after a long period, during which the solutions were left standing.[9] Therefore, the polymer concentration in the spinning dope should be within the biphasic region.

The direct spinning of lignocellulosic materials, without having to delignify them, would be a technological breakthrough, but there are some drawbacks, such as the dissolution of the cellulose itself and mesophase formation, which have to be taken into account.

A new process, called the steam explosion process (SEP), was introduced to defibrate wood into fiber fragments and to fractionate lignocellulosics into their individual components.[10-13] The process results in a remarkable increase of the extractable lignin and the almost complete elimination of hemicelluloses, without markedly changing the molecular characteristics of the cellulose. It was found that, after the process, the cellulose showed a higher reactivity towards chemical and biochemical reagents.[14,15]

The aim of the present work is to determine whether poplar wood, exploded under suitable experimental conditions, could be dissolved in the DMAc-LiCl solvent system, resulting in new fibers with structural and physicomechanical properties comparable to those of conventionally regenerated celluloses.

EXPERIMENTAL

Materials

Mixed poplar hardwoods in the form of chips were used. The explosion runs of wood were performed in a Deltalab EC 300 (Cermav Patent) flash hydrolysis apparatus, equipped with a 1 L vessel. Usually, consecutive runs were made so as to obtain enough of the product for spinning.

Samples of the poplar wood were heated with saturated steam at 230°C (28 kgf/cm²) for different lengths of time: 120 sec for sample SEWA, 240 sec for sample SEWB, and 360 sec for sample SEWC. They were then rapidly (1–2 sec) discharged at atmospheric pressure, bringing about an adiabatic expansion of the water present in the wood tissues. The wet steam exploded wood samples (SEW), after washing with water, were extracted at first with ethanol (EtOH) and then with acetone, at room temperature under mechanical stirring (450 rpm), and then were dried at 40°C in vacuo.

A fourth sample, SEWB-B, was prepared by delignifying SEWB with 0.1 M sodium chlorite in a 0.05 M sodium acetate buffer solution (pH 4.0) at room temperature for one week. Under these mild conditions, as verified with simulated experiments, no degradation of cellulose chains occurred.

Chemical and Physicochemical Analysis

The Klason lignin content was determined, according to the Tappi UM 250 method, as being the sum of the insoluble and soluble lignin, the latter being determined spectrophotometrically at 205 nm. Hemicelluloses were evaluated as pentosans (Tappi T-223 hm-84), while cellulose was evaluated by subtracting hemicellulose from the total reducing sugar content.[16]

The degree of polymerization of cellulose in cupriethylenediamine (CED) was determined by the UNI 8282 method, after delignification of the material, with sodium chlorite in the same conditions as mentioned above, which were used to prepare sample SEWB-B. In order to extract hemicelluloses, after treatment with chlorite, the untreated wood was treated with 5 M NaOH solution, under a nitrogen stream, at room temperature for 24 h.

Gel Permeation of the Cellulose Carbanilates

The carbanilation reaction of the delignified wood was carried out in DMAc–5% LiCl solution, under milder conditions than those reported in the literature.[17] A catalytic quantity of pyridine and phenylisocyanate (0.4 mL, 3.7 mmol) was added to a solution of delignified wood (0.2 g, 1.2 mmol) in DMAc–5% LiCl (10 mL). The derivatization reaction was carried out at 80°C for 3 h. After cooling, methanol (2 mL) was added to eliminate any excess phenylisocyanate and the mixture precipitated in H_2O–MeOH (30 : 70). The cellulose carbanilates were subsequently washed with H_2O–MeOH and water, and were dried under vacuum. The yield was quantitative and the complete substitution was verified by elemental analysis. GPC measurements were carried out using a Knauer pump, type 6400, a Rheodyne injector, an RI detector, Erma CR Inch model ERC-7512 (Japan), and a linear column Phenogel (Phenomenex, USA), size 7.8 × 600 mm. Freshly purified and stabilized THF was used at a flow rate of 1 mL/min at room temperature. Solvent and solution were filtered using 0.45 Mm filters. Polymer concentration was 1 mg/mL; injected volume was 100 μL. Universal calibration with polystyrene standard and the Mark–Houwink coefficients, reported by Wood et al.[18] were used.

Dissolution and Spinning of SEW Samples

Weighed amounts of polymer and solvent were used to prepare 4–10% wood solutions in DMAc–7% LiCl. No activation was needed to dissolve the samples. Only in the more concentrated solutions was a certain amount of insoluble material observed (5–10%), which was removed by centrifugation.

The solutions were extruded with a wet spinning line (described in a earlier work[19]), using an 100 μm spinnerette die with a length/diameter ratio of 1. The piston diameter was 12.7 mm for extrusion rates V_0 4.5–12.9 m/min. Corresponding to this V_0 range, the shear rate (V) at the spinnerette was 600–17,200 sec⁻¹. The monofilament, extruded in H_2O at 20°C, and collected after the coagulation bath by a set of rollers (take up rate V_1), passed into a water bath and then through a second set of rollers, having a take-up rate of V_2; finally the filament was wound up by a bobbin, operated at take-up rate of V_r.

The V_1/V_2 and V_1/V_r ratios were invariably kept equal to 1. Different V_1/V_f ratios were used, V_f being the velocity of the freely extruded filament. The bobbins were washed in running water for 24 h, were dried under vacuum at 40°C for 40 h, and were stored over $CaCl_2$.

Some fibers from the SEWB sample were annealed in ethyleneglycol at 250–260°C for 30 min.

Fiber Characterization

Water Retention Values (WRV)

The WRV values were determined by submerging the samples in an excess of distilled water. After 20 h, the excess water was removed by filtration through a glass filter (G4) and then was centrifuged for 10 min at 4000 rpm. The amount of water absorbed by the sample was calculated from the equation:

$$WRV(\%) = \frac{W1-W0}{W0} \times 100$$

where W1 and W0 are the weights of the samples after centrifugation and drying to constant weight at 105°C.

Mechanical Properties

The tensile strength and the elongation at the breaking point, as well as the Young's modulus, were measured with an Instron model 1122 tensile machine, 10–30 runs were made for each measurement. Prior to testing, the fibers were conditioned for 24 h at 20°C and 65% relative humidity. The measurements were performed using a 50 mm gauge distance and a 0.1 min^{-1} deformation rate.

Birefringence Measurements

The birefringence values were determined to be the difference between two refractive indices, measured under an Ortolux Leitz optical polarizing microscope, using the method of the compensator of Berek,[20,21] that is, the measurement of the difference in velocity of the two beams, into which the incident light was resolved as it passed through the fiber.

The orientation factor, $\Delta n / \Delta n'$, has been defined by Hermans[22] as the ratio of the birefringence of the fiber to that of the mercerized ramie, considered an ideal fiber, in which the molecules are perfectly oriented parallel to the fiber axis. In our case, a sample of ramie, mercerized under free swelling conditions and then pulled to the original length, yielded a value of $\Delta n'$ of 0.090, not 0.050 as reported in the literature.[22] Thus, in the fiber orientation calculations, we used the 0.090 value.

Scanning Electron Microscopy

Electron microscopy observations, using a Philips 515 SEM operated at 9–12.5 KV, were performed on the lateral surface of the intact fiber and also on the fractured surface of the fibers.

X-Ray Diffractometry

X-Ray powder patterns were recorded using Ni-filtered Cu Kd radiation from a Siemens 500 D diffractometer, equipped with a scintillation counter and a linear amplifier.

CP MAS ^{13}C NMR Spectroscopy

CP MAS^{13}C NMR spectra were obtained with a Bruker CXP-300 (75 MHz) spectrometer. The cross polarization time was 1 msec, while the repetition time and the ^{1}H 90 pulse were 10 sec and 3.5 μsec, respectively. Full width at half-height of glycine was 27 MHz. Chemical shifts were measured with respect to trimethylpropionic acid sodium salt (TSP), 3000–5000 scans were taken, and the rotation speed was about 3.4 KHz.

RESULTS AND DISCUSSION

It is known[23-24] that SEP induces marked changes in the chemical composition, supramolecular structure, and morphology of wood. Owing to chemical autohydrolysis, most hemicelluloses and lignin become soluble in water and organic solvents, respectively.

Table I reports the changes in the SEW composition, related to the residence time in the SE vessel, after washing the samples with water and extraction with solvents.

It can be observed that in all cases, a number of unaccounted for substances were found. The composition of the spun fibers is also given in the Table I.

The relationship of the lignin/cellulose (L/C) and lignin/reducing sugar (L/RS) ratios, and residence time of the wood in the vessel, is reported in Figure 1. After washing with water, the decrease of the hemicellulose content induces an increase in the L/RS ratio (mainly in the case of short residence times). The L/C ratio hardly changes when the severity of SEP increases.

The treatment of SEW with organic solvents extracts the degraded lignin, hence both the L/RS and the L/C ratios markedly decrease as the steam explosion treatment becomes more drastic. Some of the degrated lignin is solubilized during the spinning dope preparation, but it does not precipitate in the coagulation bath, regardless of the SE conditions.

The morphological changes, induced by SEP, were evaluated by measuring the WRV value, which is related to the specific surface of the samples.[25]

Table I Compositional Analysis (%) of the Wood and Fiber Samples

Samples	Lignin		Cellulose	Hemicelluloses
	Soluble	Insoluble		
Poplar wood	3	24	37	24
Steam exploded wood				
A_{H_2O}	2	37	56	2
B_{H_2O}	3	36	54	1
C_{H_2O}	3	34	52	1
$A_{EtOH-Acetone}$	2	22	61	2
$B_{EtOH-Acetone}$	1	21	62	1
$C_{EtOH-Acetone}$	1	19	64	1
Fibers				
A	2	12	76	—
B	1	13	76	—
C	1	15	73	—

For the samples SEWA, SEWB, and SEWC, WRV was 65, 92, and 130%, respectively.

All the SEP samples, after washing with water and extraction with organic solvents, were soluble in the DMAc–LiCl solvent system without any activation, the residue (5–10%) being mainly lignin. This indicates both the efficacy of the SEP to enhance the solubility of the lignocellulosics and its ability to induce their simultaneous fractionation.
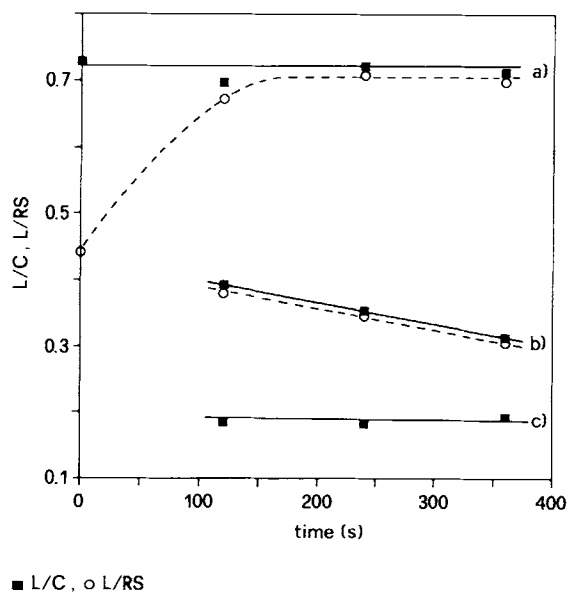
However, the highest c_p values attained were still not enough to give rise to mesophase formation and thus hindered the generation of high modulus fibers.

The GPC profiles of the delignified woods (Fig. 2), as well as the DP_w/DP_n polydispersity values
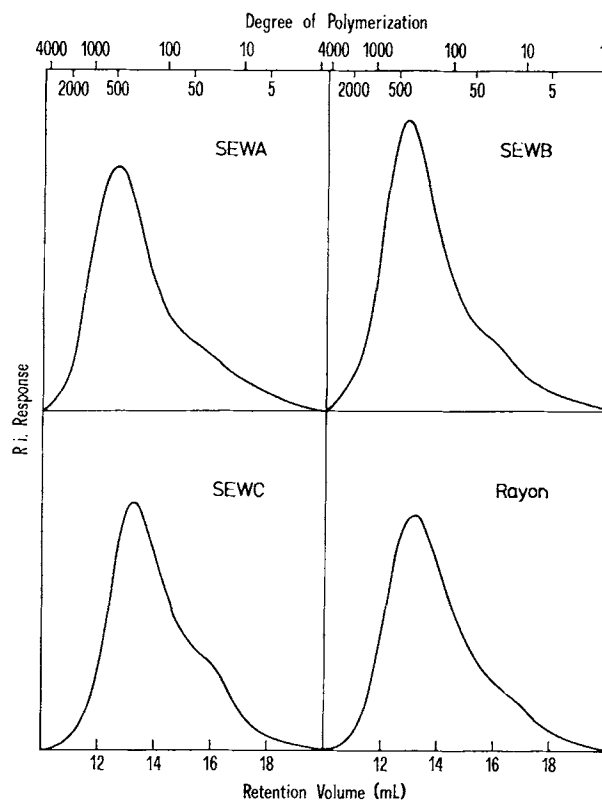

■ L/C , o L/RS

Figure 1 Lignin/cellulose (L/C) and Lignin/reducing sugars (LRS) content of SEWA, SEWB, and SEWC wood samples as a function of their residence time in the vessel. (a) SEW samples extracted with water, (b) SEW samples extracted with EtOH-acetone, and (c) wood fibers.

Figure 2 Gel permeation chromatograms of the cellulose tricarbanilates from delignified SEW samples.

Table II   Degree of Polymerization (DP) of the SE Wood Celluloses

Sample	Viscosity in CED DP_V	GPC of Tricarbanilated Derivatives		
		DP_w	DP_n	DP_w/DP_n
Untreated Wood	1.780	—	—	—
SEWA	480	455	45	10.1
SEWB	250	390	48	8.1
SEWC	210	257	43	5.9
Commercial Rayon	250	280	41	6.8

(Table II), show a decrease of polydispersity as the severity of the SEP increases. The polydispersity of the sample SEWC matches that of a commercial viscose. As can be seen in Table II, the DP_v values decrease on passing from the untreated to the SEWA, SEWB, and SEWC samples.

Physicomechanical Properties of the Fibers

In a previous work, one of the authors found that 100% cellulose fibers were obtained by spinning from isotropic and biphasic DMAc–LiCl solutions.[9] Improved mechanical properties of the fibers were obtained by using anisotropic solutions, rather than isotropic ones. This indicates that anisotropic dopes are a prerequisite for attaining high modulus fibers, even though mechanical orientation during spinning also plays an important role; this is mainly true in the case of polymers that are unable to form anisotropic solutions.

Fibers with mechanical properties, comparable to those of conventional rayons, have been obtained

by dissolving steam exploded wood pulps in N-methylmorpholineoxide (NMMO) solutions, and then by spinning the solute with the jet/wet spinning technique.[26] However, it has been pointed out that lignin has a negative influence on the orientation of cellulose chains. In fact in the cellulose–lignin solution, a rigid polymer, cellulose, is mixed with a random coil low molecular weight polymer, lignin. Thus, according to Flory's theory,[27] beyond a critical concentration ratio of the two polymers, and in the absence of strong intermolecular interactions, incompatibility can be expected, based on the interference of the random coil polymer with a mutual orientation of the molecules of the rod-like polymer molecules.

In the present work, phase separation was not evident in any SEW solution. As reported in Table III, the breaking strength of the wood fibers is similar to those obtained from the neat cellulose solution in various solvents, while the modulus values are slightly lower.

As suggested by Chanzy et al.,[26] this phenomenon

Table III   Physicomechanical and Birefringence Characteristics of the Wood Fibers[a]

Sample	C_p (%, w/w)	$V_1/V_F = 1$				$V_1/V_F = 3$			
		E (GPa)	σ_b (GPa)	ε_b (%)	$\dfrac{\Delta_n}{\Delta'_n}$[b]	E (GPa)	σ_b (GPa)	ε_b (%)	$\dfrac{\Delta_n}{\Delta'_n}$[b]
SEWA	4.1	11	0.20	11	0.52	14	0.20	5	—
	6.3	12	0.21	7	0.54	18	0.29	5	0.53
SEWB	4.5	9	0.16	10	0.31	12	0.17	7	0.33
	6.7	10	0.16	—	—	12	0.19	9	—
	9.7	11	0.15	10	0.54	13	0.19	4	0.53
SEWB-B	4.1	12	0.24	13	0.72	—	—	—	0.67
	7.5	12	0.22	18	—	17	0.25	8	—
SEWC	3.6	10	0.15	7	0.24	—	—	—	0.29
	6.6	10	0.16	13	—	12	0.20	9.0	—
	9.0	10	0.18	8	0.49	14	0.22	9.0	0.51

[a] Spinning conditions: $V_0 = 7.9$ m/min; $V_r/V_1 = 1$.
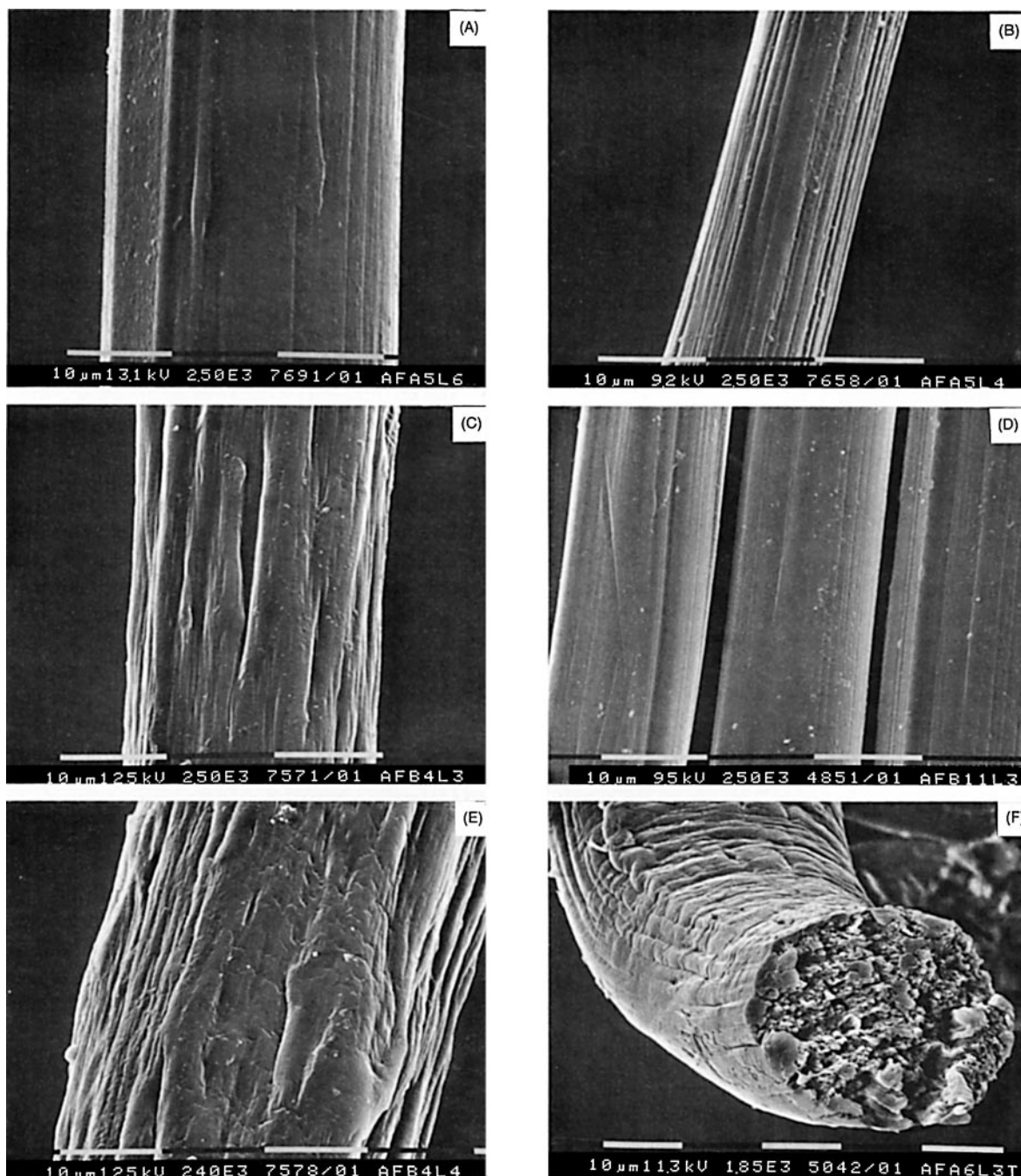[b] $\Delta'_n = 0.090$ birefringence value of mercerized ramie.

Figure 3 Scanning electron micrgraphs of wood fibers. (a) SEWA fibers: c_p = 4.8% (w/w); V_0 = 12.9 m/min; V_1/V_f = 1, (b) SEWA fibers: c_p = 4.8% (w/w); V_0 = 7.9 m/min; V_1/V_f = 4, (c) SEWB fibers: c_p = 10.0% (w/w); V_0 = 7.9 m/min; V_1/V_f = 2.4, (d) SEWB fibers: c_p = 4.1% (w/w); V_0 = 7.9 m/min; V_1/V_f = 4, (e) SEWB fibers: c_p = 10.0% (w/w); V_0 = 12.9 m/min; V_1/V_f = 1, and (f) fracture observation of (a) after annealing at 260°C for 30 min.

could be attributed to the presence of lignin that hinders the cellulose chain's orientation, both in solution and/or during spinning. In order to shed light on this hypothesis, a completely delignified sample (SEWB-B) was spun (Table III). A significant in-

crease in fiber modulus was observed, as well as an increase in breaking elongation. Furthermore, the orientation factor $\Delta n / \Delta n'$ (Table III), already high at the higher molecular weights of the cellulose component, as well as at higher c_p values of the wood

solution, increased even further after sample delignification, thus confirming the negative role of the lignin on the orientation of cellulose macromolecules during spinning. A high orientation factor value $(\Delta n / \Delta n' = 0.85)$ was obtained after the annealing of the SEWB sample at 260°C. As referred to later, high temperature treatment in a protic solvent induces marked modifications in the suprastructure of the wood fibers and, hence, also in its birefringence.

Scanning Electron Microscopy

Scanning electron microscopy was utilized to investigate the effect of SEP conditions and of the spinning parameters (extrusion velocity and draw ratio) on the morphology of the fibers produced. Microscopy observation showed that, unlike other solvent systems,[28] fibers with a dense, well-defined fibrillar structure can be obtained from DMAc–LiCl solutions (Fig. 3).

Generally, the concentration of the SEW solutions, rather than the fibers' chemical composition, and physicochemical parameters, such as the DP_v and the molecular polydispersity of the cellulosic component, seem to play an important role in the fiber structuration. When considering the spinning parameters, the extrusion velocity was more effective than the draw ratio on the surface structurating. According to the birefringence values and the physicomechanical properties, a comparison of the wood fibers, before and after delignification (not shown), evidenced a slightly more oriented surface structure of the delignified fibers. The annealing treatment of the fibers, from the sample SEWB, did not show a significant effect on the sample morphology.

Fiber Structure Characterization

Gilbert[29] pointed out the important role of the cellulose polymorph structure on the physicomechanical properties of the regenerated fibers, and suggested that high strength/high modulus fibers can be realized only in the presence of either cellulose I or IV polymorphs.

Powder X-ray diffractograms of the wood fibers (Fig. 4) show the presence of lightly packed structures, constituted by crystals of small dimension.

The position of the 020 reflection rules out the presence of the cellulose I and II, but matches that of cellulose III, while the 101 reflection, though partly superimposed, is close to that of cellulose I.[30] This seems to indicate the occurrence of a mixed
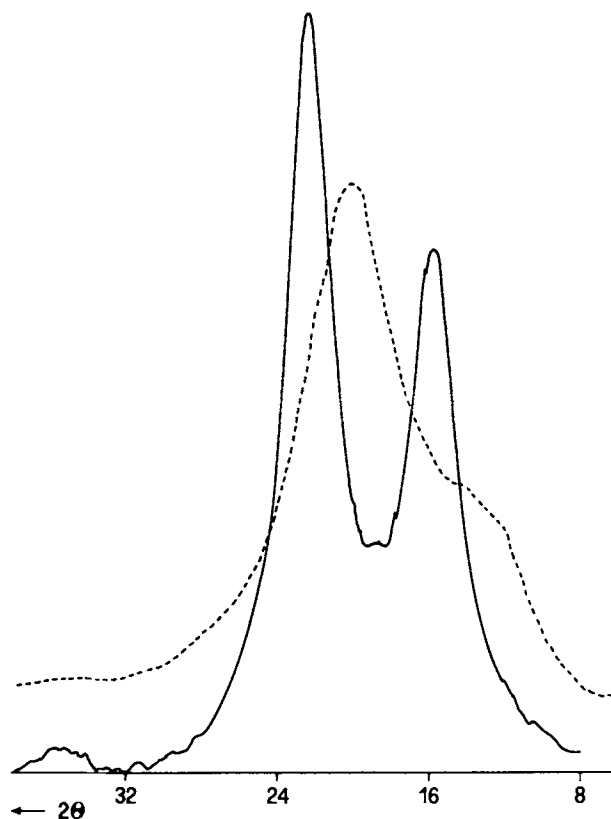

Figure 4 X-Ray diffractograms of fibers from SEWB sample. (– – –) untreated fibers, and (———) annealed fibers.

lattice, in which cellulose I and III could coexist. After the annealing (Fig. 4), X-ray diffractograms show a more compact structure, in which the reflections are sharper and are not superimposed. On the base of the position of the reflections of the 020 and 101 and 10$\bar{1}$ crystallographic planes, a cellulose IV can be envisaged, but it is not possible to identify its true polymorphic structure (IV_I or IV_{II}).[30]

Before sample annealing, the NMR spectrum [Fig. 5(a)] shows signals that, in terms of both chemical shifts and half-height width, seem to belong to the polymorphs of the phase III_{II}.[31]

As found for the family II polymorphs of cellulose fibers,[32] C-1, C-4, and C-6 signals of the wood fibers occurred at 105.6, 85.6, 84.1, 83.3, and 63.5 ppm, respectively, while C-2,3,5 signals matched a single peak at 76.0 ppm. After annealing [Fig. 5(b)], a more detailed structure of C-2,3,5 was observed, the components occurring at 76.1, 75.3, and 74.0 ppm, while the signal of C-4 was split only into two signals at 84.5 and 83.4 ppm, respectively. This seems to indicate the occurrence of a phase IV_{II}, as is expected when heating a polymorph of the family II. Further investigations are in progress.
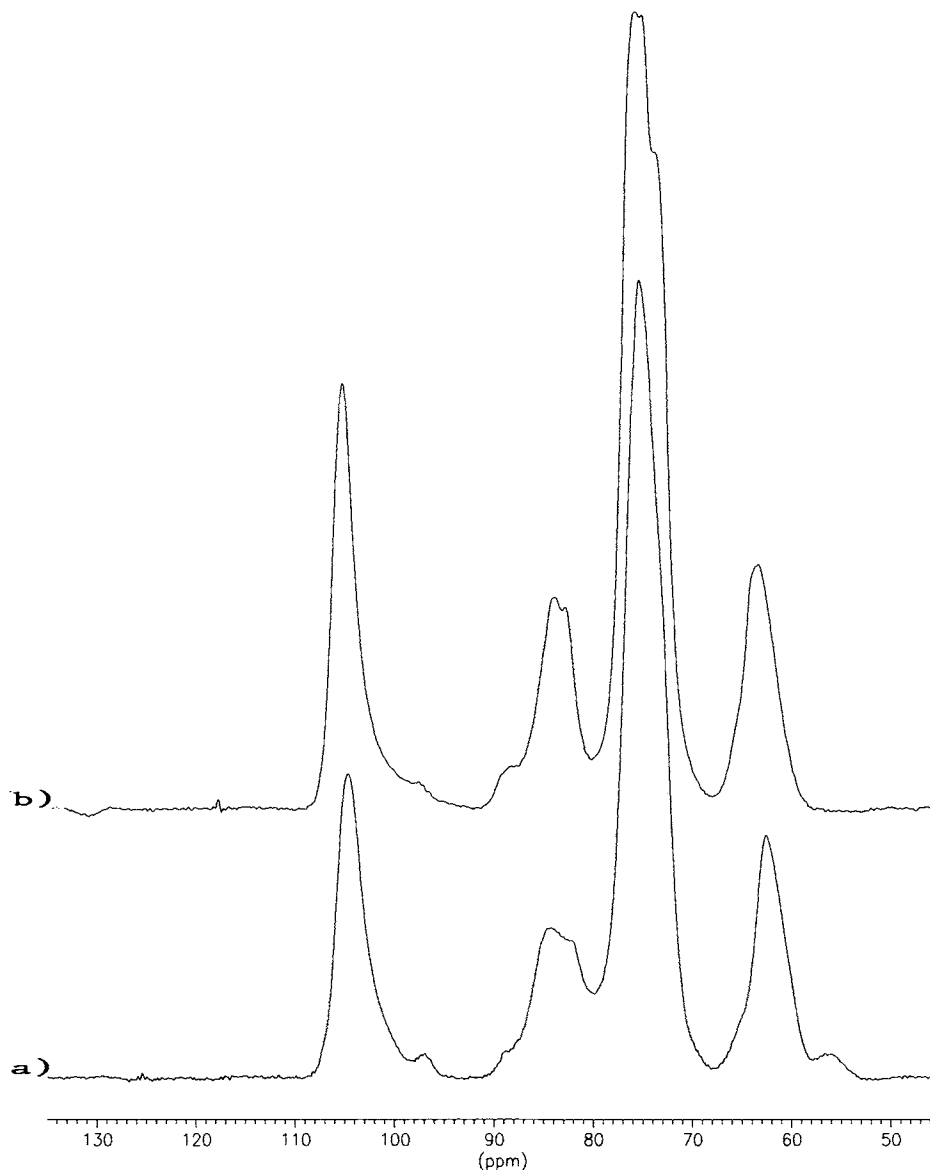
Figure 5 CP–MAS ^{13}C–NMR of fibers from SEWB sample. (a) untreated fibers, and (b) annealed fibers.

CONCLUSIONS

The SEP of wood chips is a powerful pretreatment for obtaining pulps, which can be dissolved into a DMAc–LiCl system without any activation. The optimization of the steam explosion conditions is a prerequisite for elimination of most noncellulosic components, preserving the characteristics of the cellulose component. As shown by the birefringence and physicomechanical measurements, the orientation of the cellulose chains, during both the dissolution and spinning process, is hindered by the presence of lignin. A further refining of SEP is needed to reduce the pulps' lignin content; this would open new horizons for an effective alternative to the conventional viscose process.

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