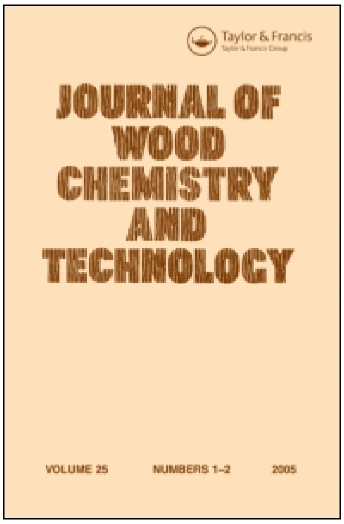

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Dissolution of Ethylenediamine Pretreated Pulp with High Lignin Content in LiCl/DMSO without Milling

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Abstract: Various hardwood and softwood chemical pulps, including those with relatively high lignin content (up to *ca.* 10.5%), were completely dissolved without milling in lithium chloride/dimethyl sulfoxide (LiCl/DMSO) after a pretreatment with ethylenediamine (EDA). Because milling of the sample is not required, degradation of the cell wall components caused by milling does not take place. After the EDA pretreatment, the crystallinity of the pulps remained as high as the original pulps, although the crystal structure changed. This is the first time that transparent solutions of underivatized pulps with high lignin content were obtained in a simple organic solvent system. Interestingly, even in the case of coarse wood meal (40–80 mesh) about 70% could be dissolved after repeating the dissolving procedure two times. The formation of a pulp–EDA or wood–EDA complex seems to be critical for the dissolution in LiCl/DMSO. The nuclear magnetic resonance (NMR) spectrum of the EDA treated pulp solution had good resolution even though the degree of polymerization (DP) of the cellulose in the pulp is very high.

Keywords: Cellulose–EDA complex, cellulose solvent, dissolution of pulp, high kappa pulp, lithium chloride/dimethyl sulfoxide (LiCl/DMSO)

INTRODUCTION

Wood is an important regenerative natural composite consisting of different polymers, mainly cellulose, hemicellulose, and lignin. Evaluation of the interactions between these polymers has been one of the key subjects in the field of

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wood and pulping chemistry. It is important to clarify whether or not chemical bonds exist between these polymers in the native wood and corresponding pulp, because the difficulties encountered in the latter stages of delignification are usually attributed to such chemical bonds between lignin and carbohydrates. Although a lot of indirect observations have been reported examining these interactions, so far it has not been clarified as to whether these interactions are due to chemical linkages or physical adsorption. One promising method to examine these interactions is through pulp dissolution. However, there are no reported solvent systems for dissolving underivatized pulp with relatively high lignin content.

In recent decades, many solvent systems have been reported to dissolve cellulose, which is the major component of chemical pulp.[1] Lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) was presented as a good solvent system for dissolving cellulose.[2] However, several problems were reported when this solvent system is applied to pulp dissolution. When applied to softwood bleached kraft pulp, the dissolution is incomplete.[3,4] As well, the cellulose is degraded detrimentally by heating the system to facilitate dissolution.[5,6] LiCl/1,3-dimethyl-2-imidazolidinone (LiCl/DMI) is another solvent system known for dissolving cellulose. A transparent and colorless solution is obtained when unmodified cellulose is dissolved in this system.[7] However, more than 2 weeks are required to dissolve softwood kraft pulp, even with relatively low, about 2% lignin content.[8] Similarly, Berthold et al. reported that derivatization of unbleached softwood kraft pulp with ethyl isocyanate could be dissolved in 8% LiCl/DMAc.[9] Thus, there is no good solvent system for dissolving pulp with high lignin content without derivatization. The development of a solvent system for pulps with high lignin content is required not only to examine interactions between pulp components, but also to utilize such pulps as a new source of fibrous materials.

Petrus et al. reported that LiCl/dimethyl sulfoxide (LiCl/DMSO) can dissolve regenerated cellulose that is prepared from cellulose acetate.[10] Recently, we found that LiCl/DMSO can dissolve wood meal finely ground by planetary ball mill for 2 h, but the cellulose crystallinity of the ground wood meal is dramatically decreased even by 1 h of milling.[11] Thus, a pretreatment method other than milling nor regeneration is a prerequisite to dissolve highly crystalline cellulose or pulp for analyzing entire plant cell wall components, including cellulose.

When cellulose is treated with ethylenediamine (EDA) it forms a "cellulose–EDA complex." The structure and characteristics of cellulose–EDA complexes have been investigated by Loeb et al.,[12–15] Lee et al.,[16] and Wada et al.[17] Gagnaire et al. reported that bacterial cellulose treated with 75% EDA can be dissolved in N-methyl morpholine-N-oxide/DMSO (NMMO/DMSO),[18] but they did not refer to the dissolution of pulp containing lignin. It was found that EDA pretreated holocellulose, followed by a solvent exchange with DMI has improved solubility in LiCl/DMI, while maintaining the original crystal structure albeit with a lower crystallinity.[19] In this article, LiCl/DMSO was applied to the dissolution of EDA pretreated pulp with high lignin content, and the behavior during the pretreatment and dissolution processes was investigated.

MATERIALS AND METHODS

Materials

Unbleached and bleached kraft pulps with different kappa numbers were used as pulp samples. Pulp properties are shown in Table 1. Hardwood unbleached kraft pulps (HUKP) were produced from paulownia wood chips. Different cooking conditions were used to prepare the pulps with different lignin contents. Lignin contents of the prepared pulps were measured by Kappa number method (TAPPI test method, T 236 om-99). The obtained Kappa number of each pulp

Table 1. Various pulps for dissolution

				Pulp-EDA complex		
Samples[a]	Wood species	Kappa number	Lignin content (%)[b]	Name	Content of EDA (%)	Solubility[c]
$\mathrm{HBKP_{P0}}$	Paulownia	Bleached	/	$\mathrm{HBKP_{P0}}$-EDA	20.1	+
$\mathrm{HUKP_{P1}}$	Paulownia	12.1	1.8	$\mathrm{HUKP_{P0}}$-EDA	20.8	+
$\mathrm{HUKP_{P2}}$	Paulownia	17.6	2.6	$\mathrm{HUKP_{P1}}$-EDA	20.8	+
$\mathrm{HUKP_{P3}}$	Paulownia	22.6	3.4	$\mathrm{HUKP_{P3}}$-EDA	20.6	+
$\mathrm{HUKP_{P4}}$	Paulownia	37.3	5.6	$\mathrm{HUKP_{P4}}$-EDA	20.5	+
$\mathrm{HUKP_{P5}}$	Paulownia	69.7	10.5	$\mathrm{HUKP_{P5}}$-EDA	19.6	+
$\mathrm{HUKP_{P6}}$	Paulownia	97.0	14.6	$\mathrm{HUKP_{P6}}$-EDA	18.3	±
$\mathrm{SBKP_{M0}}$	Mixture of softwood	Bleached	/	$\mathrm{SBKP_{M0}}$-EDA	18.9	+
$\mathrm{SUKP_{M1}}$	Mixture of softwood	30	4.5	$\mathrm{SUKP_{M1}}$-EDA	19.5	+
$\mathrm{SUKP_{D1}}$	Douglas fir	20	3.0	$\mathrm{SUKP_{D1}}$-EDA	18.4	+
$\mathrm{SUKP_{D2}}$	Douglas fir	30	4.5	$\mathrm{SUKP_{De}}$-EDA	19.4	+
$\mathrm{SUKP_{D3}}$	Douglas fir	55	8.3	$\mathrm{SUKP_{D3}}$-EDA	19.8	+

[a] HBKP: Hardwood bleached kraft pulp; HUKP: hardwood uncleached kraft pulp; SBKP: softwood bleached kraft pulp; SUKP: softwood unbleached kraft pulp; subscripts $_{\mathrm{P0}\ldots\ldots\mathrm{D3}}$ represent pulps prepared from different wood species (paulownia wood chips . . . . . . douglas fir wood chips) with different kappa number (bleached . . . ..55).

[b] Lignin content was obtained from kappa number by multipying 0.15.

[c] +: complete soluble; ±: incomplete soluble.

was converted to lignin content by multiplying by 0.15. A hardwood bleached (delignified) kraft pulp (HBKP) sample was prepared by adding 1 g of $NaClO_2$ and 0.2 ml of acetic acid into 150 ml water contain 2.5 g of $HUKP_{P3}$ (Table 1). The mixture was kept in a water bath at 75°C for 1 h. The mixture was then cooled to room temperature, and the reagents were added again. The addition of these reagents was repeated for a total of three times. Softwood unbleached and bleached kraft pulps (SUKP and SBKP, respectively) were kindly provided by Oji Paper Industries Co., Ltd. (Tokyo, Japan). Hardwood (beech) coarse wood meal was prepared by Wiley milling, and a fraction (40–80 mesh) was used as a sample for dissolution.

Pretreatment of Pulp with EDA

Various pulps (0.5 g) were soaked in 30 ml of EDA, and stirred for 1 day at room temperature. The EDA treated pulps were then freeze-dried, and are referred to as "pulp–EDA complex." The EDA content of pulp–EDA complex was determined gravimetrically by the gain in weight.

Dissolution of Pulp–EDA Complex in LiCl/DMSO Solvent System

A pulp–EDA complex (20 mg) was suspended in 2 ml of 8% LiCl/DMSO. The mixture was kept with stirring at room temperature for 24 h. The mixture was heated up to 75°C, and kept with stirring at this temperature for 1 h, and which point a clear solution was obtained. Different concentrations of LiCl (2%, 4%, and 6%) in DMSO were applied to examine the solubility of the pulp–EDA complex obtained from $HUKP_{P1}$ by the aforementioned procedure under the same conditions.

X-Ray Diffraction Analysis

Original pulps and pulp–EDA complexes were converted into pellets using a disc apparatus for infra-red (IR) measurement, and subjected to X-ray diffraction analysis using the reflection method and diffraction angle 2θ from 4° to 30° on of a Rigaku RINT 2000 with a Ni-filtered Cu $K\alpha$ radiation (λ 0.15418 nm) at 40 kV and 40 mA.

Nuclear Magnetic Resonance (NMR) Measurement

The $HUKP_{P1}$–EDA complex (Table 1) was dissolved in 8% LiCl/DMSO-*d6*. The concentration of $HUKP_{P1}$–EDA complex was 2%. The analysis of ^{13}C-NMR was performed on a JEOL Alpha 500 spectrometer (JEOL, Japan).

Optical Transmittance

Each of the LiCl/DMSO pulp–EDA complexes (0.2% concentration based on the pulp weight) solutions was introduced into a cuvette (1 cm width), and the transmittance was measured from 400 to 700 nm using a Shimadzu UV-VIS spectrophotometer (UV-240). The 8% LiCl/DMSO was used as a reference sample for the measurement of transmittance of the solutions.

UV Absorbance

The UV absorbance at 280 nm of the LiCl/DMSO solutions of pulp–EDA complexes was determined using the above-described UV-240.

RESULTS AND DISCUSSION

Effect of EDA Treatment on the Characteristics of the Pulp Samples

In this study, various pulps with different kappa numbers, HBKP, HUKP, SBKP, and SUKP as shown in Table 1, were soaked in EDA with stirring for 1 day at room temperature followed by freeze drying. Because EDA is not removed completely by freeze drying, the EDA treated freeze dried pulps, referred to as "pulp–EDA complex," contained about 20% EDA (Table 1). This is in accordance with the result of Loeb et al.[12]

The crystal structure of $HUKP_{P1}$ and the corresponding pulp–EDA complex ($HUKP_{P1}$–EDA) was investigated by their X-ray diffraction patterns (Figure 1). The crystal structure of cellulose in $HUKP_{P1}$ changed with the EDA treatment, but the crystallinity of the $HUKP_{P1}$–EDA complex appears to be as high as $HUKP_{P1}$.

Dissolution of Pulp–EDA Complex in LiCl/DMSO

It was examined whether or not various pulp–EDA complexes could be dissolved in LiCl/DMSO solvent system (Table 1). All the pulp–EDA complexes were dissolved completely under the conditions described earlier (Figure 2), except the pulp–EDA complex of $HUKP_{P6}$. It is quite significant that transparent solutions were obtained. Even the pulp–EDA complex prepared from $HUKP_{P5}$ with high lignin content (10.5%), was completely dissolved in this solvent system. Based on the data shown in Figure 1, it is presumed that the crystallinities of the pulp–EDA complexes are maintained at the same levels as those of the corresponding original pulps. Consequently, the LiCl/DMSO solvent system is quite effective at dissolving pulps with high lignin content

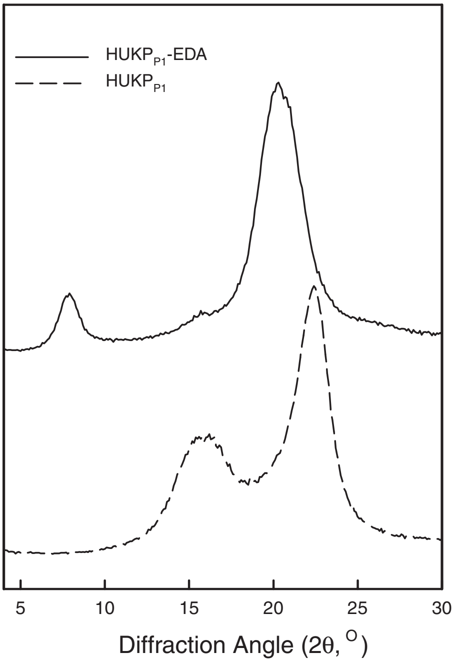

Figure 1. X-ray diffraction patterns of the original HUKP$_{P1}$ and corresponding HUKP$_{P1}$–EDA complex.

after EDA pretreatment. Other cellulosic materials were also dissolved by this solvent system. Cellulose–EDA complexes, such as EDA treated microcrystalline cellulose (Whatman CF11), cotton, cellulose I, cellulose II, cellulose III, and holocellulose were found to be completely dissolved in the LiCl/DMSO system. Interestingly, about 70% of the coarse wood meal (40–80 mesh) sample could also be dissolved in LiCl/DMSO. In this case, however, EDA pretreatment and dissolution in LiCl/DMSO had to be repeated two times. Namely, the residue from the first dissolution (about 60%) was again treated with EDA and subjected to the dissolution in LiCl/DMSO. The second dissolution process left only about 30% of the original wood weight as a residue. The EDA untreated wood meals or pulps could not be dissolved in LiCl/DMSO unless they were finely ground as reported in our previous paper.[11] Similarly, pulps with fairly high lignin content, such as HUKP$_{P6}$ cannot be dissolved by a single EDA treatment. In these cases, only suspensions were obtained with low transparencies. Therefore, both the lignin content and the formation of the EDA complex seem to be important for the dissolution in LiCl/DMSO. As well, different concentrations of LiCl (2%, 4%, 6%, and 8%) in DMSO were also tried to dissolve the HUKP$_{P1}$–EDA complex using the aforementioned procedure under the same

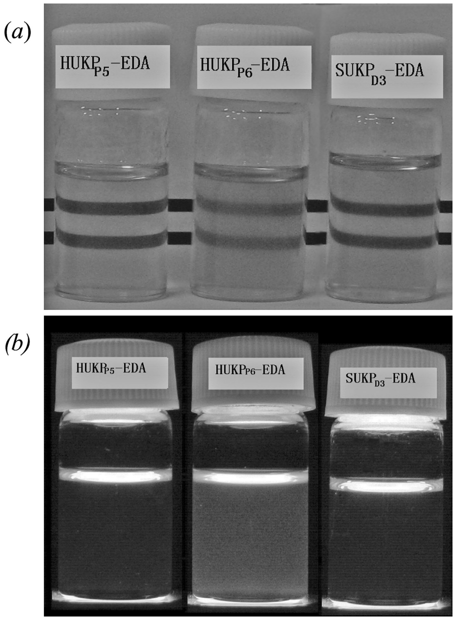

Figure 2. Photographs of solutions or suspensions for the pulp–EDA complex in 8% LiCl/DMSO with 0.5% concentration [(*a*) was taken by using white paper marked with two black lines as background in a bright room, (*b*) was taken in a dark room with a white light comes from bottom of the bottles].

conditions. When the concentration of LiCl was less than 6%, the systems were unble to dissolve the HUKP$_{P1}$–EDA complex.

NMR Analysis of the Pulp Solutions

NMR spectra of cellulose dissolved in various solvent systems have been reported by many researchers. According to the results of Yanagisawa et al.[20] no clear signal was observed in the ^{13}C-NMR spectrum of microcrystalline cellulose (MCC) with degree of polymerization (DP) 200–300 when it was dissolved in 8% LiCl/DMAc or 8% LiCl/DMI. They consequently used cellulose with a DP 15 to observe a clear NMR spectrum. In the present study, the solution containing HUKP was subjected to NMR analysis. The ^{13}C-NMR spectrum of the HUKP$_{P1}$–EDA complex dissolved in 8% LiCl/DMSO-*d6* is shown in Figure 3. The spectrum is well resolved and shows clear signals at around 101 ppm (C-1), 80 ppm (C-4), 74–75 ppm (C-5, C-3), 73 ppm (C-2), and 60 ppm (C-6). The peak of EDA appears at around 44 ppm. No clear peak

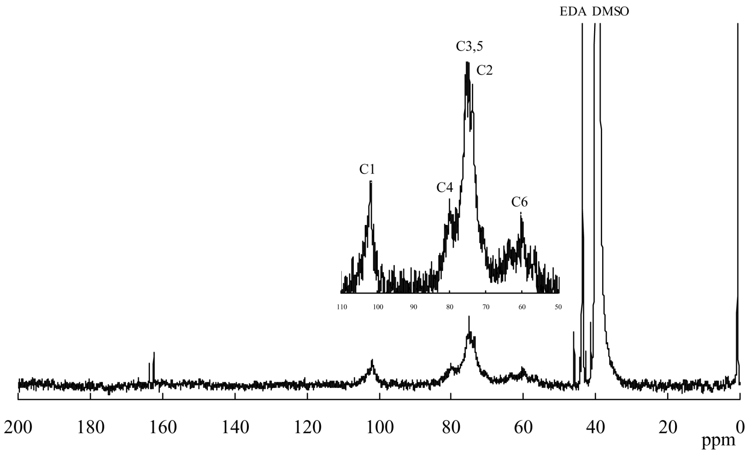

Figure 3. Solution-state ^{13}C-NMR spectra of HUKP$_{P1}$–EDA in LiCl/DMSO-*d6*.

of lignin is observed, because the amount of lignin in HUKP$_{P1}$ is only about 1.8%.

Light-Transmittance of the Pulp Solutions

The visible light transmittance of the pulp–EDA complex solutions were measured at 0.2% concentrations. As shown in Figure 4, if the pulp–EDA complex was soluble, the transmittance of the solution at the region of visible light was relatively high. The transmittance of HBKP$_{P0}$ and SBKP$_{P0}$ solutions were over 92.4% and 93% in the visible region, respectively. The transmittance of the incompletely soluble solution was fairly low over the whole range. It can be seen that all the transmittances are relatively low in the short wavelength range, and the higher the lignin content of the original pulp, the lower the transmittance. It is known that new structures such as quinone structures are introduced in lignin during the pulping reactions. These structures, as well as the complexation of lignin with metals strongly affects the color of pulp, even though the native lignin itself does not absorb light in the visible region.[21,22] Therefore, the observed phenomena can be attributed to the presence of lignin in the pulp.

UV Absorbance of Pulp Solution

The UV absorbance of the HUKP–EDA complex solutions, which contain certain amounts of lignin, were analyzed at 280 nm (Figure 5). A significantly high correlation was observed between the UV absorbance of the solutions and the

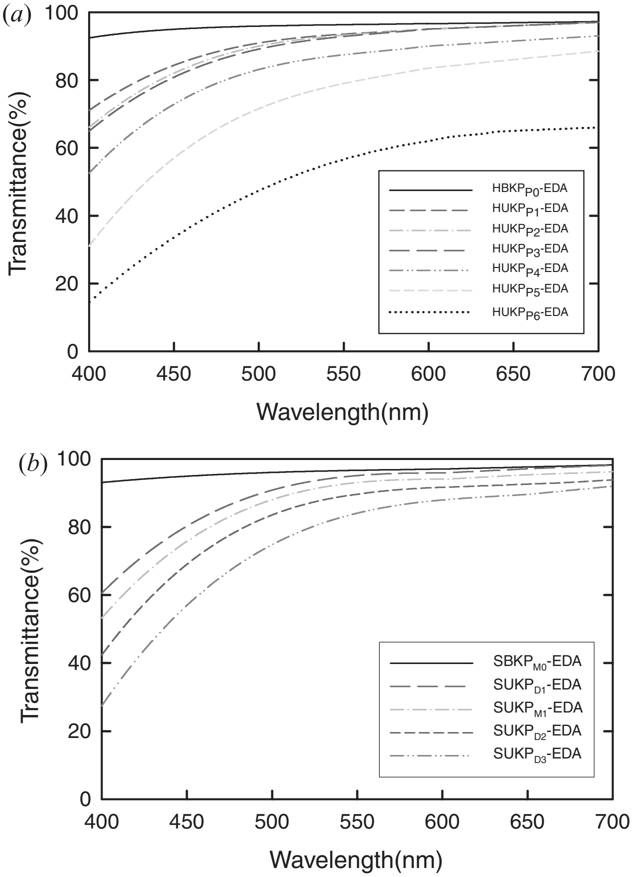

Figure 4. Visible light-transmittance of solutions or suspensions of (a) HKP–EDA complex and (b) SKP–EDA complex in 8% LiCl/DMSO.

lignin content expressed as kappa numbers of the corresponding HUKPs. This result was an unexpected result, as the structure of residual lignin in pulp differs depending on the stage of delignification. Thus, the absorption coefficient of lignin must be different in pulps with different amount of lignin. In addition, kappa number method detects not only lignin, but also other conjugated structures including non-lignin compounds such as hexenuronic acid, which does not show an absorbance maximum at 280 nm. Nevertheless, the absorbance of the pulp solutions at 280 nm correlated very well to the kappa number of the corresponding pulp. At this moment, this result cannot be interpreted, but is important information to understand the structure of permanganate consuming substances, which are expressed as kappa number.

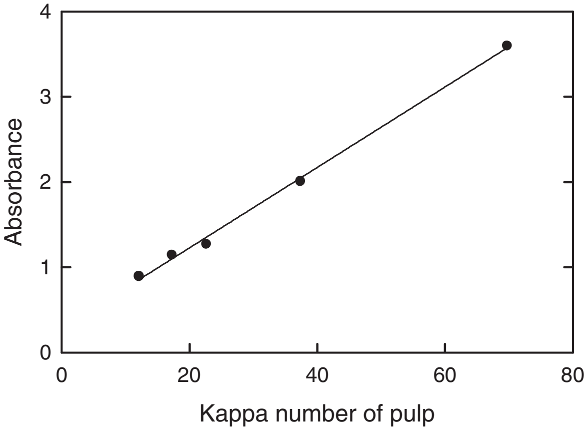

Figure 5. Relationship between UV absorbance of lignin at 280 nm in 0.2% HUKP solution in 8% LiCl/DMSO and kappa number of HUKP.

CONCLUSIONS

An excellent solvent system, lithium chloride/dimethyl sulfoxide (LiCl/DMSO), was established for dissolving lignocellulosic materials after a pretreatment with ethylenediamine (EDA). Various EDA pretreated chemical pulps, including pulps with high lignin content, could be completely dissolved in LiCl/DMSO. This is the first report of successfully dissolving an underivatized pulp with high lignin content in any solvent system.

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