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# Smooth Model Surfaces from Lignin Derivatives. I. Preparation and Characterization

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Lignin model surfaces were prepared from aqueous alkaline solutions by spin-coating on silica wafers. Films of thicknesses between 20 and 140 nm were easily made by variations in the spinning rate or in the lignin concentration. The roughnesses of the lignin surfaces were relatively low, approximately 1.1 nm (rms) on an area of 25 $\mu m^2$, as determined by atomic force microscopy imaging. The stability of the lignin films in aqueous solutions was found to be excellent. No changes in the thickness of model surfaces immersed in slightly alkaline solutions (pH 9.2) could be detected even after 5 h soaking. A 10 percent reduction in the thickness of the lignin film was observed after 5 h of exposure to a solution containing 0.1 M NaCl. This novel preparation method opens great possibilities for further fundamental studies, where interactions between lignin and other substances are of interest to investigate.

## Introduction

In nature, lignins provide mechanical strength and water resistive functionality to woody species such as trees, straws, and grass.[1,2] The lignins are the second most abundant group of biopolymers and thus have a great potential for exploitation. However, in comparison to many other natural polymers, the use and benefits from lignins as such are relatively low. This is due to lignins' complicated chemical structure as well as their chemical and physical heterogeneity. Moreover, harsh conditions are often needed to isolate the lignins, leading to depolymerization of the macromolecules and often destroying their native chemical structure.[3,4] Thus, technical lignins are usually regarded only as byproducts from more important processes such as the production of chemical pulps. Many times, the calorific value of the lignin byproduct is the only interest.

The general picture of native softwood lignin resembles either highly concentrated amounts of lignin in the middle lamella or patches of lignin randomly distributed in the cell wall layers. In the latter case, the lignin is surrounded by a matrix of hemicelluloses and situated between bundles of cellulose fibrils.[5−7] Under kraft pulping, the lignin is made soluble by bond cleavage followed by ionization of the formed phenolic and carboxylic groups in a highly alkaline cooking liquor.[4] Delignification mainly involves depolymerization of the lignin structure, but to some extent, it is also due to lignin−hemicellulose bond breakage.[8,9] In sulfite pulping, cleavage of various intra and intermolecular bonds are accompanied by sulfonation of the lignin structure.[4] This increases the hydrophilicity of the lignin derivative and thus the solubility in the cooking liquor. As the majority of the lignin is removed in order to liberate the fibers during chemical pulping, the mechanical characteristics of lignin are of minor importance to the final chemical pulp fiber quality. Interfacial properties related to the surface chemistry will of course be affected by lignin partially covering external and internal fiber surfaces, especially in unbleached chemical pulp grades.[10,11] In high-yield pulps of various kinds, for example groundwood, refiner and thermomechanical pulps as well as chemithermomechanical pulp, the lignin is not removed from the fibers. Instead, the physical properties of the lignin macromolecules in wood are manipulated by various pretreatments before refining, e.g., high-temperature impregnation and sulfonation. The specific contribution to the fiber surface properties by lignin is of course more pronounced here than in the case of chemical pulps.[12,13]

The picture for technical lignins emerging from solution studies resembles almost spherical or disklike macromolecules.[14,15] Self-association between lignin macromolecules into colloids might occur under certain circumstances.[16] The colloidal stability of dilute solutions of technical lignins is found mainly to be controlled by three parameters, alkalinity, ionic strength, and temperature.[16−18] Regarding lignin self-aggregation and precipitation, specific sensitivity toward ions in the Hofmeister series has been identified.[19] The changes in the chemical structure and the physical properties of lignin during pulping are relatively

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**Table 1. Earlier Published Preparation Methods of Lignin Model Surfaces on Various Substrates**

| film preparation method | lignin source(s) | substrate | refs |
|---|---|---|---|
| evaporation, heat molding | softwood (Indulin AT, dioxane lignin, periodate lignin), hardwood (REAX 31) | glass | 22 |
| evaporation, spin-coating | ZL-DHP (synthesized) | glass | 23−26 |
| Langmuir−Blodgett | sugar cane bagasse (acetosolv lignin), Pinus caribaea hondurensis (organosolv lignin) | glass, calcium fluoride | 27−29 |
| Langmuir−Blodgett, evaporation | sugar cane bagasse (saccharification lignin, ethanol lignin, acetone-oxygene lignin, soda lignin) | mica | 30,31 |
| adsorption | lignosulfonate (commercial) | glass, quartz | 32 |
| adsorption | softwood (CURAN 100) | mica | 33 |

well understood; however, physical interactions involving lignin have received little attention. In the manufacturing of various paper grades from lignin-containing pulp fibers, the molecular interactions occurring in the contact zone between the fibers are difficult to study in situ. Here for instance, the lignin−lignin interactions, not to mention the interactions between the lignin and cellulose,[20,21] hemicelluloses, or various paper chemicals, are of greatest interest to investigate. However, to study this seriously, well-defined systems including stable lignin model surfaces are required.

Several investigations have been published where films have been prepared on various substrates from different lignins and by various methods (see Table 1).[22−33] Despite that, the use of lignin model surfaces in further fundamental experiments has been limited.[32] This could partly be due to some standard problems related to the quality of model surfaces in general, e.g., high roughness, nonuniformity, or instability. As for the Langmuir−Blodgett technique (LB) utilized by some researchers, the tedious preparation method could also provide limitations.

The aim of this study has been to find a simple method for preparing well-defined lignin model surfaces, suitable for use in fundamental studies of various phenomena occurring in nature, in pulp and papermaking, and as part of model systems in the development of new materials.

## Experimental Section

**Materials.** All chemicals used, except the lignin, were supplied by Sigma-Aldrich and were of analytical quality. Milli-Q water was used throughout the investigation.

Silica wafers were supplied by Peregrine Semiconductor Australia (Homebush Bay, Australia). The thickness of the $SiO_2$ layer was 3 nm as determined by ellipsometry. To increase hydroxylation of the silica wafers before use, the wafers were immersed in 10% NaOH solution for 20 s and subsequently rigorously rinsed with milli-Q

water and finally nitrogen-dried. This cleaning procedure did not appreciably increase surface roughness as determined by AFM imaging. The entire cutting, cleaning, and handling procedure of the silica wafers was performed in a laminar flow cabinet.

*Isolation and Purification of Kraft Lignin.* To 100 mL of kraft cooking liquor (softwood pulp of kappa number 24.7) was added EDTA-disodium (1 g in 80 mL water) to chelate any present metal ions. Then the liquor was neutralized with sulfuric acid to pH = 5.05 (0.5 M $H_2SO_4$) while gaseous nitrogen was bubbling through the liquor in order to remove the malodorous gases. The combined precipitate and solution was frozen overnight. After towing to 0 °C, the lignin precipitate was collected on a glass filter, G4, and washed with small amount of icy water. The lignin was suspended in water and freeze-dried. Subsequently, the lignin was extracted with pentane for 8 h to remove extractives. To remove carbohydrates, the lignin was suspended in dioxane:water (9:1) at room temperature and stirred for 2 h. After that the solution was centrifuged and the residue was repetitively treated with dioxane:water until the solution remained colorless. After evaporation of the dioxane, the suspension of lignin was freeze-dried. To remove the low molecular weight fraction from the lignin, the isolated lignin was stirred in dichloromethane for 2 h at room temperature (approximately 1 g of lignin per 100 mL of $CH_2Cl_2$). The lignin was filtered through a glass filter and washed with $CH_2Cl_2$ until the filtrate remained colorless. The insoluble lignin was collected and dried.

**Methods.** *Determination of the Molecular Mass Distribution of Kraft Lignin.* [1]H Pulsed field-gradient (PFG) nuclear magnetic resonance (NMR) self-diffusion measurements were performed on a Bruker Avance DPX 250 MHz spectrometer (Bruker BioSpin, Germany). ^{1}H PFG NMR self-diffusion measurements provide the possibility to determine several differently diffusing components in a multicomponent sample at the same time. This is obtained by incrementing the field-gradient's magnetic strength, $g$, which successively decreases the signals attributed by the protons of the molecules in the sample. Thus, in a dilute multicomponent sample, the faster the signal (intensity or area) decay, $I(k)$, the higher the self-diffusion coefficient and the smaller the molecule. Here, $k$ is related to the magnetic field strength by $k = g^2\gamma^2\delta^2(\Delta-\delta/3)$, where $\gamma$ is the nuclear magnetogyric ratio, $\delta$ is the length of the magnetic pulse, and $\Delta$ is the time of diffusion. The parameters in the evaluation model applied are then numerically fitted to eq 1, and determinations of complete distributions, $P(D)$, of self-diffusion coefficients for polydisperse samples are then obtainable

$$I = \int P(D) \exp(-kD) \, dD \qquad (1)$$

From the measurements of the isolated kraft lignin derivative, a log-normal distribution function (eq 2), often applied in evaluations of polymer samples,[34] was found matching the obtained echo decays very well

$$P(D) = \frac{1}{D\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln(D) - \ln(D_m))^2}{2\sigma^2}\right) \qquad (2)$$

Here, $D_m$ is the mass-weighted median self-diffusion coefficient and $\sigma$ is a measure of the log-normal distribution width. By combining

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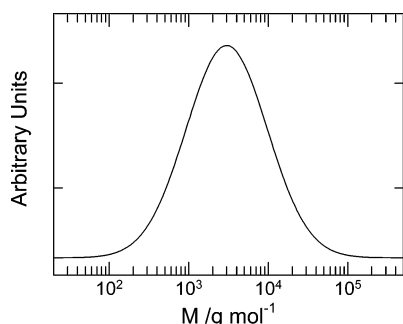
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**Figure 1.** Mass-weighted log-normal molecular mass distribution of the isolated kraft lignin derivative used for the preparation of lignin model surfaces as determined from $^1$H PFG NMR self-diffusion measurements.

eq 2 with the Mark−Houwink equation, $D = KM^{\alpha}$, it is possible to outline the complete molecular mass distribution if the scaling parameters $K$ and $\alpha$ are known. In this study, scaling parameters obtained from measurements of lignosulfonate samples were used to give the molecular mass distribution for the kraft lignin used.

*Dynamic Light-Scattering Measurements.* A Brookhaven 90 Plus particle size analyzer (Brookhaven Instruments Corp., USA) equipped with a 15 mW solid-state laser, was used to investigate the lignin solvency prior to spin-coating.

*Spin-Coating.* A Laurell Technologies Corporation WS-400B-6NPP/LITE spin-coater (Laurell Technologies Corp., U.S.A.) was used. Speed, time, and lignin solution concentration were all varied throughout the procedure in order to prepare films of different thicknesses. The preparation of the lignin model films was performed in a laminar flow cabinet.

*Ellipsometry.* A high-resolution phase modulated ellipsometer (Beaglehole Instruments, New Zealand) with coincident He−Ne laser and capable of spatial mapping of dielectric properties of thin or thick films, on solid or liquid interfaces was used to determine the thicknesses of prepared lignin model surfaces. This ellipsometer has an imaging capability with a ccd camera as detector. This allows a determination of the optical properties of a thin film with excellent spatial resolution (on the order of 10 microns). Furthermore, the variation in optical properties over a much larger area can be determined statistically and the influence of any defects in the film can be quantified. Thus, a distribution of the $x$ and $y$ ellipsometric parameters was measured over an area of approximately 2 mm. Comparison of the mean values using the imaging technique to standard ellipsomteric measurements with an incident He−Ne laser and photomultiplier tube as detector showed agreement to within 5%. The thickness of the lignin film was determined from the measurement of the $x$ and $y$ parameters as the angle of incidence was varied between 65° and 80°. The model was air/lignin/silica/silicon and all materials were assumed to be optically isotropic. The refractive indices of the materials were 3.8 (silicon) and 1.48 (silica). The calculations employed a least squares iterative fitting procedure using both thickness and refractive index of the lignin layer as fitting parameters. The measurements were performed under ambient air and relative humidity conditions. The measurements were repeated several times at different positions on the surface measurements and with different surfaces prepared under the same conditions.

*Surface Analysis by TOF−SIMS.* A Kratos PRISM ToF−SIMS (Kratos Analytical, U.K.) was used. Positive spectra were obtained using a 25 keV primary beam $^{69}$Ga liquid metal ion source. The area of analysis was approximately 0.15 mm × 0.15 mm. The analysis was performed under static SIMS conditions.

*Surface Imaging and Roughness Determination.* The prepared lignin surfaces were imaged with Tapping Mode atomic force microscopy (Nanoscope III, Multimode SPM, Veeco Inc., U.S.A.) to determine the surface roughness and morphology. These images were recorded in ambient air conditions (25 °C and 50% relative humidity) with a TESP, rectangular silica cantilever (Veeco, Inc. U.S.A.). Roughness values were determined from the height images over a 1 $\mu$m$^2$ and 25 $\mu$m$^2$ image and are presented as root-mean-

**Table 2. Lignin Solvents Investigated in This Study**

| solvent | lignin solubility[a] | surface properties[b] |
|---|---|---|
| ethanol:water (9:1) | poor | poor, rough |
| acetone:water (9:1) | good | intermediate, rough |
| *N,N*-dimethylformamide | good | poor, rough |
| dimethyl sulfoxide) | good | poor, rough |
| tetrahydrofurane | poor | poor, rough |
| 2,4-dioxane:water (9:1) | good | intermediate, rough |
| NH$_4$OH (0.75 M) | good | excellent |

[a] Naked eye inspection/dynamic light-scattering   [b] Naked eye inspection/atomic force microscopy.

square (RMS) values. A minimum of 4 images was taken for each sample and the RMS roughness values presented here are an average.

*Contact Angle Measurements.* The contact angle of water on the lignin surfaces was measured using a video controlled KSV CAM 200 contact angle goniometer (KSV Instruments Ltd., Finland). The contact angles were determined by curve fitting of the drop shape. All measurements were undertaken with controlled humidity.

## Results and Discussion

**Preparation of Lignin Model Surfaces.** Spin-coating is a useful method for application of thin, uniform films to flat substrates. An excess amount of polymer solution is placed on the substrate. The substrate is then rotated at high speed in order to spread the fluid by centrifugal force. Rotation is continued for some time, with fluid being spun off the edges of the substrate, until the desired film thickness is achieved. The solvent used is usually volatile, providing for its simultaneous evaporation. The viscosity of the polymer solution, the wetting and spreading characteristics of the chosen solvent, as well as the evaporation rate are some important factors that need to be considered for a successful result. Another crucial parameter for preparation of smooth surfaces is the quality of the solvent. Polymer self-aggregates or incompletely dispersed polymer particles will implacably cause increased film roughness on a nanoscale.

Kraft lignin was dispersed in a series of different solvents that are regularly used in the preparation of lignin solutions (Table 2).

Except for the ethanol:water mixture and tetrahydrofurane sample, the lignin seemed properly dissolved from inspections by the naked eye. However, when more thoroughly examined by dynamic light-scattering, undissolved submicron particles or self-aggregates were detected in most of the samples. In aqueous ammonium hydroxide solution, no scattering due to undissolved particles or lignin self-aggregates could be observed.

In Figure 2a−d, lignin model films spin-coated from some of the solvents presented in Table 2 are shown.

Depending on a number of parameters such as the solvent-lignin interactions, the wetting/spreading behavior on the substrate and evaporation rate of the solvent, the lignin model surfaces shown in Figure 2a−d look very different on a macroscopic scale. Figure 2a,b shows comparably uniform lignin films spin-coated from 0.75 M NH$_4$OH, which vary in colors due to light interference created from the differences in film thickness. In Figure 2c,d, poor wetting and too fast evaporation, respectively, give rise to a much worse film uniformity. The latter picture is also true for all of the other solvents presented in Table 2. Due to the obvious macroscopic inhomogenities that are experienced with most of the solvents tested, in this investigation, films spun from aqueous NH$_4$OH solutions were chosen for further characterization.

The p$K_a$ value of ammonia is 9.25, and according to this, the pH value in a 0.75 M NH$_4$OH solution is 11.6. When 0.5−3.0% of kraft lignin is added, the pH value decreases slightly. Compared
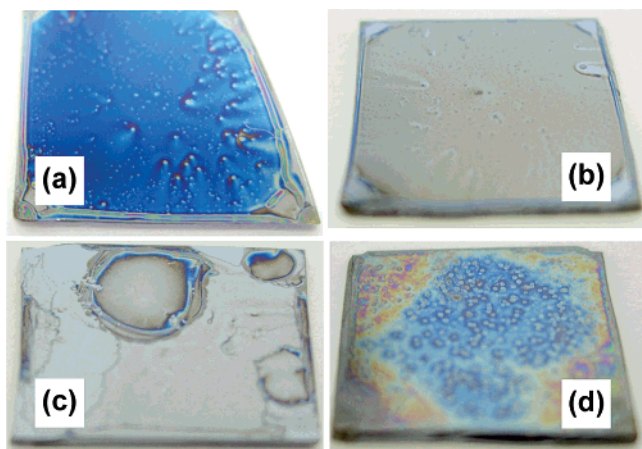
**Figure 2.** Some examples of the macroscopic appearance of lignin model surfaces spin-coated from various solvent systems. (a) and (b) 0.75 M NH₄OH, film thicknesses about 100 and 50 nm, respectively. (c) DMSO or DMF. (d) acetone:water (9:1).

to moderate alkaline solutions based on sodium hydroxide, ammonium hydroxide has a huge advantage. NH₄OH is formed when gaseous ammonia is dissolved in water, $NH_3$ (g) ↔ $NH_3$ (l), $NH_3$ (l) + $H_2O$ (l) ↔ $NH_4OH$ (aq). At equilibrium, these reactions are however strongly shifted to the left. Ammonia has a relatively low vapor pressure, which is often noticed as "refreshing" when opening a bottle of $NH_3$ (l). Due to this, the ammonium hydroxide electrolyte disappears quite rapidly from an open vessel as well as from the surface of any substrate when used as a solvent in spin-coating. Simultaneously, the pH value in the solution or at the surface decreases and the dissolved, anionic lignin slowly exchanges its counterions from $NH_4^+$ back to $H^+$. This is the opposite of what happens with a sodium hydroxide solution stored without sealing, where the pH value increases as the water evaporates. Moreover, use of NaOH as a solvent for lignin in spin-coating leads to an excess of sodium ions (and NaOH) at the surface and consequently a permanent ion-exchange from $H^+$ to $Na^+$. The salt excess has to be removed from the film by rinsing with water in order to gain the properties of lignin. Kraft lignin in its sodium form is however much easier to dissolve in water than its protonized analogue. This implies that in aqueous environments the stability of a lignin model film based on kraft lignin with sodium as counterions could be expected to be lower than the stability of a fully protonized lignin film. Hydrogen bonds are also more easily formed by the hydroxyl groups on the silica substrate when the lignin is protonized.

AFM tapping mode height images of a 55 nm thick lignin surface spin-coated from 0.75 M NH₄OH are shown in Figure 3a,b. Figure 3a shows a 25 $\mu m^2$ image and Figure 3b shows a 1 $\mu m^2$ image within the area of the former image. An almost uniform coverage of somewhat spherical aggregates is observed in these images, typically with a diameter of 10−20 nm. The morphology of the surfaces in these images shown in Figure 3a,b is characteristic for all of the prepared lignin surfaces using this spin-coating technique. Small-scale images of different areas on the same lignin film up to 500 $\mu$m apart showed that the film was continuous over a much larger area.

Analysis of the kraft lignin model surfaces by ToF−SIMS revealed typical peaks at $m/z$ = 137 and 151, corresponding to various guaiacyl residues.[35] Only very small traces of the solvent, water ($H_2O^+$, $H(H_2O)^+$) or $NH_4^+$, could be detected at $m/z$ = 18 and 19 (see Figure 4).[36]

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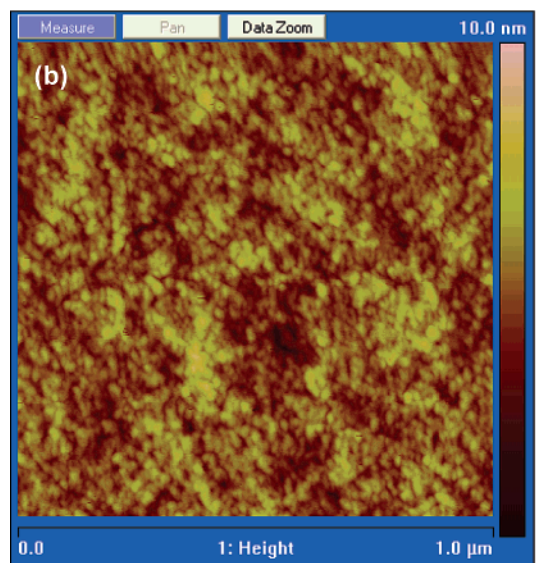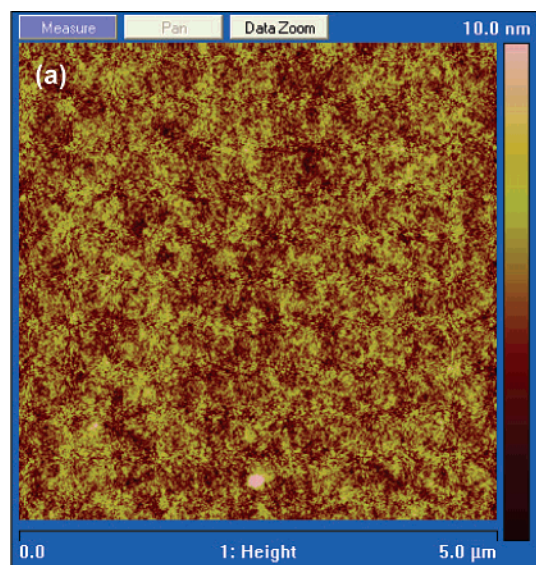




**Figure 3.** AFM Tapping mode height images of a 55 nm thick lignin surface. (a) 5.0 × 5.0 $\mu m^2$, RMS roughness 1.01 nm. (b) 1.0 × 1.0 $\mu m^2$ RMS roughness 0.59 nm.
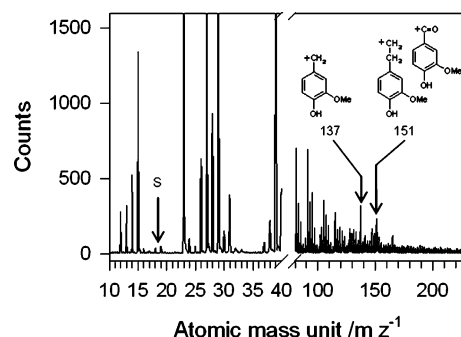


**Figure 4.** ToF−SIMS spectra of kraft lignin film spin-coated on silica wafer. The tiny peaks at S denote possible traces of solvent ($H_2O/NH_3$).

**Determination of Lignin Film Thickness.** The thickness of the prepared lignin thin films was determined using ellipsometry. The film thicknesses, as shown in Figure 5, were easily varied between 20 and 140 nm simply by choosing appropriate conditions such as solution concentration and spinning rate.

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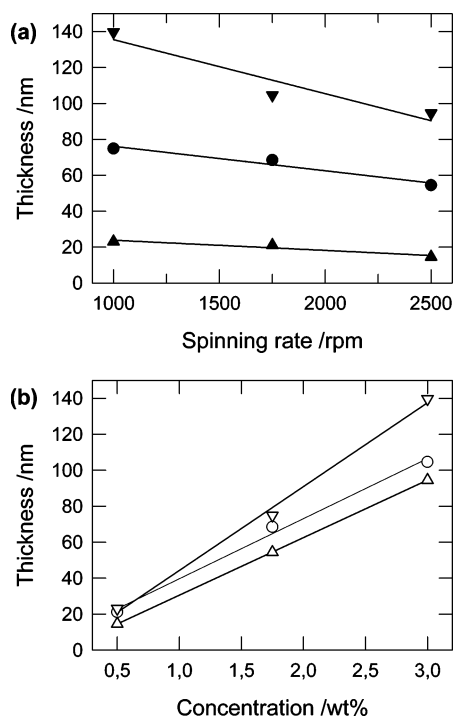
**Figure 5.** (a) Thickness of the lignin model film at various concentrations of the lignin solution as function of the spinning rate; ▼ 3.0 wt %, ● 1.75 wt %, ▲ 0.5 wt %. (b) Thickness of the lignin film versus lignin concentration of the spun solution at various spinning rates; ▽ 1000 rpm, ○ 1750 rpm, △ 2500 rpm.

**Table 3. Typical Thickness and RMS Roughness Data of Spin-Coated Lignin Model Surfaces**

| conc. (wt %) | spinning rate (rpm) | thickness (nm) | RMS $1 \mu^2$ (nm) | RMS $25 \mu^2$ (nm) |
|---|---|---|---|---|
| 0.5 | 1750 | $23.1 \pm 2.1$ | 1.13 | 1.28 |
| 1.75 | 1000 | $74.9 \pm 0.6$ | 1.04 | 1.17 |
| 1.75 | 1750 | $68.4 \pm 0.3$ | 1.08 | 1.39 |
| 1.75 | 2500 | $54.4 \pm 0.5$ | 0.59 | 1.01 |
| 3.0 | 1750 | $104.6 \pm 1.4$ | 1.02 | 1.32 |

Based on fitted data from more than 50 measurements, the refractive index was determined to be $n_D = 1.61 \pm 0.04$ for the kraft lignin derivative. This is a much higher value of the refractive index than was reported earlier for sugar cane bagasse lignin (acetosolv extracted) and lignin from *Pinus caribaea hondurensis* (organosolv extracted) by Constantino et al., which were found to be in the range of $1.04-1.30$ for wavelengths in the range of $350-800$ nm.[27] The comparably higher values obtained for kraft lignin in the present investigation indicate that compact films with very low porosity are formed.

**Lignin Film Roughness Evaluation by AFM.** The root-mean-square (RMS) roughness was determined for the images in Figure 3 and was 1.01 and 0.59 nm for the 25 and 1 $\mu m^2$ images, respectively. The RMS roughness values for some prepared surfaces of various thickness (see Figure 5) are summarized in Table 3. Interestingly, the roughness remains relatively low independent of the film thickness. It is also important to note that the lignin films prepared using this spin-coating technique are continuous over a millimeter scale.

Recently, Pasquini et al. observed that the RMS roughness of prepared lignin LB films varies considerably depending on the extraction method used when isolating the lignin.[30,31] RMS roughness between 0.24 and 3.80 nm on 25 $\mu m^2$ were reported for five-layer LB films from sugar cane bagasse lignin. The ethanol−water and acetone−oxygen extraction procedures were shown to give LB films with the lowest RMS roughness. This
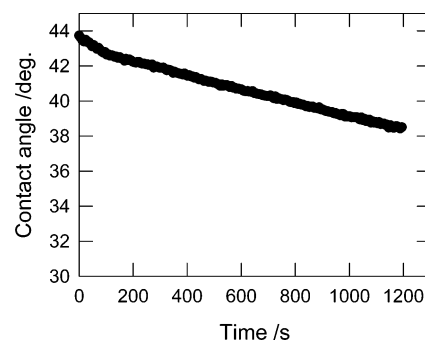


**Figure 6.** Variation of the sessile drop average contact angle of water on the lignin films over time.

was suggested to be due to a higher amount of polar groups, such as carbonyl and especially carboxylic, in the structure of the ethanol−water and acetone−oxygen lignins.[30,31] In the case of the present investigation where softwood lignin isolated from the kraft process is spun-coated from aqueous $NH_4OH$ solutions, isotropic films consisting of spherical lignin nanoparticles packed densely but, stochastically, were observed at all thicknesses in the range of 20 to 140 nm. A lignin derivative created under the conditions of kraft pulping is very rich in polar phenolic groups due to depolymerization reactions where aryl−ether bonds are cleaved by hydrogen sulfide via nucleophilic attack.[4] Furthermore, the amount of carboxylic acid groups is also increased. The current film preparation method differs very much from what is applied in the LB technique used by Pasquini et al. In the latter method either tetrahydrofurane[30] or a 1:9, v/v, mixture of *N,N*-dimethylacetamide and chloroform[31] are used as spreading solutions at the air−water interface. First, when going from a highly polar solvent such as the alkaline aqueous solution used in the current study, the phenolic and carboxylic groups in the kraft lignin macromolecules are more or less fully dissociated and well dispersed. Throughout spin-coating, the pH value rapidly decreases due to evaporation of ammonia, and protonization of the weakly acidic groups takes place. Accordingly, at least at the air−lignin interface, the drying process creates self-associates of spherical nanosized kraft lignin particles that are most probably held together intra and inter-particularly by hydrogen bonds and van der Waals attraction forces. Thus, the kraft lignin films formed under the present spin-coating conditions are not influenced by external compression forces, which on the other hand are necessarily present under the formation of films when applying the LB technique. The structural features of the kraft lignin model surface created by spin-coating resemble the structures that have been shown earlier for dehydrogenate polymers (DHP).[23−26] Furthermore, similarities to structures formed during the modes of aggregation of kraft lignin in aqueous solutions can also be observed.[16]

**Contact Angle of Kraft Lignin Surfaces with Water.** The contact angle that water makes with the lignin surfaces was measured as a function of time (see Figure 6). The initial equilibrium contact angle was 46 degrees. The contact angle was relatively stable; however, it did decrease slightly to 38 degrees during the next 20 min. This implies that the film is relatively nonswelling and nonporous. As the water evaporates, the contact angle decreases due to pinning of the drop at the three-phase line. It is also possible that some minor swelling of the film is contributing to this observed decrease. The observed contact angle is somewhat lower than the initial estimate of approximately 60° determined for softwood (Indulin AT, dioxane lignin, periodate lignin), hardwood (REAX 31) lignins by Lee and Luner.[22] However, in their measurements, the contact angle decreased rapidly with time to 0° due to the highly porous nature

of the lignin films prepared. It is reasonable to assume that these kraft lignin surfaces have a higher prevalence of polar groups, particularly hydroxyl groups, due to the present method of isolation/extraction, than the films prepared by Lee and Luner, or to native lignin, leading to a slightly lower contact angle with water. No effect of the measured contact angle was observed as a function of film thickness. The effect of lignin extraction and tree species on the contact angle of water on lignin thin films is currently under investigation.

**Stability of Lignin Model Surfaces.** A high stability threshold against deterioration in air as well as in aqueous environments is necessary if the model surfaces are going to be used in further experiments, e.g., adhesion, adsorption, and surface force measurements. To test how well the lignin films adhere to the substrate, the classical tape test was performed on a 68.2 nm thick film. The tape was put on the lignin film and gently rubbed to get in good contact. A slight pressure was applied for 1 min; hereafter, the tape was ripped off. Detectable damage to the lignin model surface could be observed neither by the naked eye nor by ellipsometry. In other words, the adhesion between the silica substrate and the kraft lignin film as well as between the intermediate lignin layers formed by the present preparation technique is very strong. The origin of the intermolecular forces acting between the protonized kraft lignin and the silica is probably due to hydrogen bonding between the various types of hydroxyl and carbonyl groups on the lignin macromolecules and silanol. This is found to be the major source of interactions in other systems where silica surfaces are exposed to hydroxyl group containing molecules.[37] To investigate the stability of the spin-coated lignin model films in aqueous solutions, the model surfaces were immersed in milli-Q water, $10^{-1}$ M NaCl, and $10^{-5}$ M NaOH (pH 9.2) under magnetic stirring for various periods of time. After each soaking, the surfaces were blow-dried by nitrogen and stored in air before the thickness was determined by ellipsometry. Table 4 shows the measured variations in thickness of the surfaces after exposure to various aqueous solutions and during different times of soaking. The stability of the lignin model surfaces in pure milli-Q water was found to be very good, which is probably due to hydrogen bonding between hydroxyl groups of the lignin film and the silica layer on the substrate. Lignin model surfaces were also immersed in aqueous alkaline solutions. As being a weak polyelectrolyte with an apparent average $pK_a$ value around 10.6,[38] it could be expected that the prepared kraft lignin model surfaces would be sensitive to

**Table 4. Thickness of Lignin Model Surface after Exposure to Various Solutions**

| solution | exposure time (h) | thickness (nm) |
|---|---|---|
| water | 0 | $54.1 \pm 1.4$ |
| | 5 | $56.1 \pm 3.0$ |
| | 50 | $56.7 \pm 1.7$ |
| $10^{-1}$ M NaCl | 0 | $89.6 \pm 4.3$ |
| | 5 | $78.3 \pm 2.2$ |
| $10^{-5}$ M NaOH | 0 | $91.6 \pm 3.1$ |
| | 5 | $91.2 \pm 0.6$ |

redissolution in alkaline environments if the pH value was sufficiently increased.

When one of the lignin surfaces was exposed to an aqueous solution of pH = 11, where about 50% of the phenolic groups in the lignin structure are dissociated,[38] the film deteriorated within 5 h. However, at a slightly lower alkalinity, pH = 9, where only about 10% of the phenolic groups are dissociated, the films were found stable and no redissolution of lignin could be observed (see Table 4). To test the lignin model film's response to neutral electrolytes, a lignin model surface was soaked in $10^{-1}$ M NaCl for 5 h. An approximately 10% reduction of lignin film thickness was observed. To some extent, this could depend on a compression/deswelling of the film due to electrostatic screening of charges on the lignin macromolecules. It is however most probably due to an ion-exchange process gradually taking part at the outermost layer of the film. Here, some of the hydrogen ions are exchanged to sodium ions, which decrease the hydrogen bonding capacity and the lignin in the film is slowly dissolved.

## Conclusions

A novel method for preparing smooth lignin films in the thickness range of 20−140 nm from kraft lignin by spin-coating is presented. The films are very simple to prepare, moreover, stable in air as well as in aqueous solutions and therefore very suitable for use in experiments where lignin interactions are of interest to investigate. Several studies, where the prepared lignin films are utilized in force measurements and as substrates for polymer adsorption, are currently under investigation.

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