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**Morphological and Wettability Properties of Thin Coating Films Produced from Technical Lignins**

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INTRODUCTION

Lignin is the second most abundant biopolymer on Earth and, together with cellulose and hemicelluloses, one of the three main components of the plant cell wall. Lignin is synthesized from three monolignol precursors (sinapyl, coniferyl, and p-coumaryl alcohols) that produce syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) units. These phenylpropane units form a highly cross-linked and amorphous macromolecule whose composition largely depends on the botanical origin of the plant. For instance, lignin in softwoods contains more than 95% G units with minor amounts of H units, hardwoods contain mainly S and G units (often close to 50–50% ratio), and grasses contain all three (S, G, and H) units in varying ratios. The $\beta-O-4$ bond is generally accepted to be the main linkage between the lignin units, but several other bonds (e.g., $4-O-S$, $\beta-S$, $\beta-1$, $\beta-\beta$, and $S-S$) also exist. The exact structure of lignin is not known because it is not possible to isolate native lignin without causing changes in its chemical structure. Therefore, the term "technical lignin" is commonly used to refer to lignin extracted from biomass by pulping and other extraction methods.

Wood pulping and other biorefinery industries extract more than 50 million tonnes of lignin annually, but only 2% of these are recovered for utilization in material and chemical applications. The major contributor to the extraction of lignin is the kraft pulping process, which is by far the dominant chemical pulping process for the production of paper-grade pulps. Kraft lignin is mostly burned in the pulp mill recovery boiler to produce energy, but it is estimated that about 30% of the lignin could be separated from the black pulping liquor without significantly altering the chemical and energy balances of the mill. Until recently, the only industrial kraft lignin that was commercially available was Indulin AT ($\sim$60 kilotonnes/year), produced by MeadWestvaco (now WestRock, USA). Currently, industrial kraft lignin is also commercialized by Stora Enso (Finland) under the name Lineo ($\sim$50 kilotonnes/year) and by Domtar (USA) under the name BioChoice ($\sim$27 kilotonnes/year). Both of these lignins are obtained through the LignoBoost process. Another kraft lignin available in quantities around 10 kilotonnes per year is produced by West Fraser (Canada), using their proprietary LignoForce method.

The second major wood pulping process is sulfite pulping, which is mainly used for the production of dissolving and
specialty cellulose pulps. In the last decade, sulfite pulps have lost part of their market share to the competing prehydrolysis kraft pulps. In spite of this, sulfite lignin (or lignosulphonate) remains as the main technical lignin commercially available, in amounts slightly above 1 million tonnes.\(^\text{7}\) Lignosulphonates are soluble in water because of the presence of sulfonic acid groups, and thus, they often find application as dispersants, binding agents, or animal feed.\(^\text{3}\) The largest producers of lignosulphonates are Borregaard (Norway) and Domsjö (Sweden). A third type of technical lignin that is commercially available is soda lignin, typically obtained by pulping of grasses or their processing residues (e.g. wheat straw and sugarcane bagasse) with sodium hydroxide (NaOH). The company GreenValue SA (Switzerland) was the main producer of soda lignin worldwide with an annual production of about 5–10 kilotonnes.\(^\text{3,4}\) Their soda lignin was commercialized under the name ProtoBind.

Other important technical lignins, although not available from commercial scale operations, are organosolv and hydrolysis lignins. Organosolv lignins are extracted from biomass using a variety of organic solvents such as methanol, ethanol, formic acid, acetic acid, and so forth.\(^\text{8}\) The Alcell process is possibly the most notable example of organosolv (ethanol-based) process for wood pulping that reached a precommercial scale at the end of last century.\(^\text{10}\) Lignol Biorefinery Technology, largely based on the Alcell process, was later implemented in pilot scale as a pre-treatment of wood for the production of biofuels.\(^\text{11}\) Since 2012, organosolv lignin from an ethanol-based pulping process has been produced by the Fraunhofer Institute (Germany) in their pilot plant, designed to extract up to 4 kilotonnes of lignin per year.\(^\text{12}\) Hydrolysis lignins, on the other hand, are the solid residues left after enzymatic saccharification of the polymeric sugars (cellulose and hemicelluloses) in lignocellulosic biomass for their conversion to ethanol and other bio-based fuels.\(^\text{13}\) Companies like St1 (Finland) can generate 30 kilotonnes of softwood hydrolysis lignin per year (at full capacity) in their bioethanol plant.

Lignin valorization is one of the cornerstones for the economic viability of lignocellulosic biorefineries. Technical lignins can be potentially used in the production of fuels, chemicals, and materials.\(^\text{14}\) The transformation of lignin into fuels and chemicals requires the application of conversion technologies (i.e. pyrolysis, hydrogenolysis, and hydrolysis) to depolymerize the lignin into monomers,\(^\text{15,16}\) which adds costs to the lignin valorization path. Moreover, lignin depolymerization typically results in a complex and heterogeneous mixture of monomers together with other degradation products. Therefore, the use of technical lignins as polymers in material applications might be a more direct and attractive route for valorization.\(^\text{17}\) One area of active research is the use of lignin in composite films and coatings.\(^\text{18–21}\) Such research is strongly driven by the interest of the packaging industry to replace traditional fossil-based films with renewable and bio-based materials. Owing to its aromatic structure, lignin possesses antioxidant and UV-blocking properties and can also provide other functionalities (e.g. antimicrobial) that are highly desirable in the formulation of packaging films.\(^\text{12–24}\) The incorporation of lignin coatings into (multilayered) films requires an understanding of the surface properties of lignin to elucidate its interaction with the substrate as well as with other elements, most notably water. The surface properties (including wettability) of lignin have been previously investigated by preparation of thin films by spin-coating or other techniques (e.g. Langmuir–Blodgett).\(^\text{25–30}\) However, the overall number of studies is rather limited, and they have focused on kraft and milled wood lignins (MWLs). Because technical lignins exhibit distinct chemical and structural properties based on their botanical source and isolation method,\(^\text{3,31–33}\) their performance as coatings could be expected to differ accordingly.

In this study, we have used six different technical lignins for the preparation of thin films by spin-coating. In addition to technical lignins from traditional pulping processes (kraft, acid sulphite, soda, and organosolv), two other lignin materials were obtained by novel modification methods (LigniOx and Ecohelix) on their way toward commercialization. LigniOx is a lignin oxidation process conducted with molecular oxygen (O₂) in alkali, according to the process patented by VTT.\(^\text{34}\) On the other hand, the Ecohelix lignin is a lignin–carbohydrate polymer obtained in the early stages of sulfite pulping and further cross-linked by oxidation with laccase.\(^\text{35,36}\) Here, we have first characterized the chemical, molecular, and structural properties of the technical lignins. Then, we have investigated their film forming ability as well as the morphology, surface energy, and wettability of the spin-coated films. Finally, the surface properties of the thin films are discussed in relation to the properties of the starting technical lignins.

### MATERIALS AND METHODS

#### Lignin Samples

The technical lignins used in this study are listed in Table 1. Softwood Kraft lignin isolated through the LignoBoost process was obtained from UPM Biochemicals (Finland). Organosolv lignin from ethanol–water pulping of beech wood in pilot scale was provided by Fraunhofer CBP (Germany). Soda lignin (Proto-Bind1000) from wheat straw was purchased from GreenValue SA (Switzerland). Oxidation of soda lignin was performed with O₂ in an aqueous alkaline (NaOH) solution, according to the patented LigniOx process.\(^\text{34}\) The oxidized soda lignin was concentrated by membrane filtration and finally recovered by spray drying. Softwood lignosulfonate was obtained from Domsjö Fabriker (Sweden), and Ecohelix lignin (27% w/w in water) was provided by Ecohelix (Sweden). The Ecohelix lignin sample originated from the same batch as the sample used by Abbadessa et al.\(^\text{35}\)

From the six technical lignins listed in Table 1, three (K, OS, and S) were insoluble in water while the other three (SOX, LS, and ECO) were water-soluble. The concept of water-insoluble lignin is here used...

<table>
<thead>
<tr>
<th>Lignin sample</th>
<th>Abbreviation</th>
<th>Plant Source</th>
<th>Production Process</th>
<th>Producer/Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kraft lignin</td>
<td>K</td>
<td>Softwood</td>
<td>Kraft pulping</td>
<td>UPM Biochemicals</td>
</tr>
<tr>
<td>Organosolv lignin</td>
<td>OS</td>
<td>Beech wood</td>
<td>Organosolv pulping</td>
<td>Fraunhofer CBP</td>
</tr>
<tr>
<td>Soda lignin</td>
<td>S</td>
<td>Wheat straw</td>
<td>Soda pulping</td>
<td>GreenValue SA</td>
</tr>
<tr>
<td>Soda oxidized lignin</td>
<td>SOX</td>
<td>Wheat straw</td>
<td>Soda pulping followed by alkali-O₂ oxidation</td>
<td>VTT</td>
</tr>
<tr>
<td>Lignosulfonate lignin</td>
<td>LS</td>
<td>Softwood</td>
<td>Acid sulphite pulping</td>
<td>Domsjö Fabriker</td>
</tr>
<tr>
<td>Ecohelix</td>
<td>ECO</td>
<td>Softwood</td>
<td>Acid sulphite pulping and laccase-mediated oxidation</td>
<td>Ecohelix</td>
</tr>
</tbody>
</table>
to refer to those technical lignins that could not be fully dissolved in water at neutral or near-neutral pH.

**Characterization of the Technical Lignins. Chemical and Elemental Composition.** The carbohydrate and lignin contents in the samples were determined after a two-stage acid hydrolysis. Neutral monosaccharides in the acidic hydrolysate were quantified by high-performance anion exchange chromatography with pulse amperometric detection in a Dionex ICS-3000 (Thermo Fisher Scientific, Waltham, MA, USA) instrument equipped with a CarboPac PA1 column. The amount of Klason lignin was quantified gravimetrically, and the amount of acid soluble lignin was determined by UV-spectrometry at 215 and 280 nm, using the Goldschmidt equation.37 The ash content was determined gravimetrically after combustion of the lignin samples at 550 °C for 23 h (including heating time). The elemental composition (C, H, N, O, and S) was determined using a FLASH 2000 series organic elemental analyzer (Thermo Fisher Scientific, Waltham, MA, USA). All samples were analyzed in duplicates.

**Molar Mass Distribution.** The molar mass distribution was determined by size exclusion chromatography in PSS (Polymer Standards Service GmbH, Mainz, Germany) MCX columns (1000 and 100,000 Å) with a precolumn, using 0.1 M NaOH as an eluent (pH 13, 0.5 mL/min, temperature 25 °C). The molar mass distribution, weight average molar mass ($M_w$), and number average molar mass ($M_n$) were calculated against polystyrene standards ($8 \times PSS,$ 3420–148,500 g/mol) using Waters Empower 3 software. Polydispersity (PD) was calculated as the ratio of $M_w$ to $M_n$. All samples were analyzed in duplicates.

**Functional Groups.** Phenolic hydroxyls, aliphatic hydroxyls, and carbonylic acids in the lignin materials were determined by $^1$H nuclear magnetic resonance (NMR) in a Bruker 500 MHz (Billerica, MA, USA) spectrometer, according to the method developed by Granata and Argyropoulos.38 The methoxyl group content was determined by headspace gas chromatography equipped with an electron capture detector (Agilent, Santa Clara, CA, USA), following the method by Baker39 with some modifications. All samples were analyzed in duplicates.

**Spin-Coating of Lignin Thin Films.** Lignin solutions (4 g/L) were prepared by adding measured amounts of technical lignin in 1 M aqueous ammonia (NH$_3$·aq), which was prepared by diluting a stock solution of 25% NH$_3$ in water (JT Baker, Phillipsburg, NJ, USA). The lignin solutions were stirred with a magnet for over 16 h, and the solubility of the lignins was confirmed by filtering small volumes of solution through cellulose acetate filters (0.2 μm). In all cases, less than 2% of the lignin material was retained in the filters.

Prior to spin-coating, silica wafers (1 cm$^2$; Compugraphic, Jena, Germany) were immersed in 2.5 M NaOH for 15 min, washed with tap water and rinsed with Milli-Q water, dried with nitrogen gas (∼0.2 bars pressure), and placed in a UV-ozonizer (UV/Ozone ProCleaner, Bioforce Nanosciences, Ames, IA, USA) for 15 min. Next, polystyrene ($M_w \sim 192,000$; Merck KGaA, Darmstadt, Germany) was dissolved in toluene (purity ≥99.9%; Merck KGaA, Darmstadt, Germany) in a 0.5 wt % concentration. The silica wafers were then wetted with pure toluene, followed by spin-coating the polystyrene/toluene solution and finally the lignin solution. The spin-coating was performed in a WS-400 BZ-6NPP-LITE device (Laurell Technologies Corporation, North Wales, PA, USA) at 2000 rpm for 2 min and 2014 rpm/s acceleration.

Preliminary trials to elucidate the number of lignin layers needed to produce smooth and continuous films that fully covered the solid substrate were first conducted by spin-coating 1, 2, or 8 layers of K lignin. Based on the morphology and wettability of the films containing different layers of K lignin, subsequent thin films were prepared by spin-coating a single layer of lignin. Spin-coating of the SOX and ECO lignin solutions on polystyrene did not result in uniform films, probably because of incompatibility between the hydrophobic polystyrene and the water-soluble lignins. Therefore, the three water-soluble lignins used in this study (SOX, LS, and ECO) were spin-coated directly on silica substrates, without polystyrene.

The SOX lignin solution was also filtered through a 0.22 μm filter prior to spin-coating.

**Morphology of Thin Films.** The morphological features of the thin films were investigated by atomic force microscopy (AFM) using a NanoTAM AFM+ instrument (Anasys Instruments, Bruker, Billerica, MA, USA) with a mounted standard silicon tapping mode probe (tip radius <8 nm) with an Al reflex coating (Applied NanoStructures Inc, Mountain View, CA, USA). AFM images were recorded in the tapping mode in air with scan rates of 0.4–0.6 Hz. The damping ratio was around 0.7–0.85. Images were flattened to remove possible tilts in the image data. The root mean square (RMS) roughness and 3D images of the films were obtained using instrument software Analysis Studio v3.11.

The thickness of the films was determined after making an incision to the films with a sharp blade until the underlying silica substrate was reached, and a wide area (80 × 80 μm$^2$) of the sample surface containing both the smooth bottom (i.e., pure silica substrate) and the untouched lignin surface nearby the incision was scanned. The thickness of the film, that is, the z directional distance between the two parallel lines representing the bottom of the incision and the untouched surface of the lignin film, was obtained from the height profile of the AFM image using the software Analysis Studio. The presented height values are the average of at least three different measurements per sample.

The films were also imaged by confocal laser scanning microscopy (CLSM) in a Zeiss LSM 10 (Zeiss, Jena, Germany) instrument attached to a Zeiss Axio Imager.Z1 microscope. Each film was imaged as such on a microscopy slide without a cover slip. A diode laser line of 405 nm was used for excitation of autofluorescence arising mainly from lignin, and emission was collected at 410–524 nm. The images present individual optical sections taken with a resolution of 1024 × 1024 and a 20× objective (Zeiss EC Epiplan-Neofluar, numerical aperture of 0.50) using ZEN software.

Additional images of the OS and SOX films were taken from Au–Pt sputtered (4 nm layer) surfaces in a Merlin Zeiss (Jena, Germany) field emission scanning electron microscope (SEM), using a secondary electron detector at an acceleration voltage of 2 kV.

**Wettability and Critical Surface Tension.** The wettability of the thin lignin films was determined by static water contact angle (WCA) measurements using the sessile drop method in a CAM 200 (KSV Instruments Ltd, Helsinki, Finland) goniometer equipped with video camera and placed in a room conditioned at 23 °C and 50% relative humidity. The WCA was measured from the droplet completely wetted the surface of the film, and emission was calculated as the average value of at least three different measurements per sample.

The CA of the K, OS, and S lignin films was also measured with three different concentrations (1.6, 3.2, and 5% mol) of acetic acid. The same procedure as described above for the determination of the WCA was applied with different acetic acid concentrations. The critical surface tension of the films was then determined by means of a Zisman plot, in which the CAs were plotted as a function of the surface tension values of the testing liquids published by Álvarez et al.41 The critical surface tension is defined as the liquid surface tension that completely wets the material (i.e., the CA is 0).

The water wettability of the technical lignin was also determined from lignin pellets. A manual hydraulic press for making pellets for Fourier transform infrared measurements was used here to produce 200 mg of lignin pellets, at an applied pressure of 8 tons for 2 min. The pellets (∼10 mm in diameter) were stored in a desiccator prior to the WCA measurements. The WCA for each technical lignin was...
calculated from at least three different droplets placed in different positions (randomly selected) of each pellet.

### RESULTS AND DISCUSSION

#### Characterization of Technical Lignins

The chemical, molecular, and structural properties of the technical lignins used in this study are summarized in Table 2. It is readily apparent that the lignin materials had widely varying composition and structure, as expected from their different botanical source and extraction (or modification) process. The actual lignin content of the water-soluble lignins (SOX, LS, and ECO) was rather low, which was mainly a consequence of their high ash content (20–40%). In the SOX lignin, the high ash content may be attributed to the presence of sodium salts (mainly sodium carbonate) that were not degraded during the ash determination at 550 °C. In the LS and ECO lignins, the high ash content may be explained by the combustion residues of sulfonic acid groups. The carbohydrate content of the ECO lignin was also exceptionally high (~18%) because this material is obtained from the initial stages of acid sulfate pulping, in which relatively large amounts of carbohydrate residues are still covalently bound to dissolved lignin fragments as lignin–carbohydrate complexes.

The molar mass ($M_w$) of the OS and S lignins was the lowest, while the molar mass of the LS and particularly of the ECO lignin was clearly the highest (Table 2). It should be noted that molar mass data for the LS and ECO lignins were obtained from Abbadessa et al., and thus, the results may not be directly comparable to those obtained in this study for the other lignins, even if alkali (NaOH) was the same eluent used. Indeed, the challenges in obtaining representative and comparable molar mass values for lignin in different laboratories are well-known, as the lack of established standards leads to use of different eluents, column systems, calibration standards, calculation methods, and so forth. The higher molar mass of the SOX lignin compared to the original SL lignin was due to the occurrence of repolymerization reactions during the oxidation and subsequent concentration of the oxidized lignin.

In terms of lignin functionalities, the phenolic –OH and methoxyl group (–OCH$_3$) content of the water-insoluble lignins (K, OS, and S) was considerably higher than that of the water-soluble lignins, and the aliphatic OH content was the highest in the LS and ECO lignins. The composition and structure of the technical lignins listed in Table 2 were generally in good agreement with previous reports on lignins from similar sources.

The elemental composition of the lignin materials indicated that the K, OS, and S lignins had a carbon content between 61 and 64%, much higher than 41–48% of the SOX, LS, and ECO lignins (Table 3). The hydrogen content of the water-insoluble lignins was also slightly higher, but their oxygen content was lower. As expected, the sulfur content of the LS and ECO lignins was relatively high because these lignins were obtained from an acid sulfate pulping process during which lignin is sulfonated. On the other hand, the sulfur content in the K lignin was only 2.1%, in line with previous studies. The small amounts of sulfur (<1%) found in the S and SOX lignins were probably traces of sulfuric acid, which is used to precipitate and recover the soda lignin from the alkaline liquor. According to Table 3, about 10% of the elemental composition of the SOX, LS, and ECO lignins was not identified, although one may expect that sodium accounted for a large share of the unidentified element(s). Sodium would have been incorporated to the structure of the SOX lignin during the oxidation process with O$_2$ in sodium hydroxide. Sodium is also the base counterion used in the acid sulfate pulping process of Domsjö Fabriker, from where the LS and ECO lignins were obtained. Calcium may also be present in the lignins from sulfate pulping.

#### Morphological Features of Thin Lignin Films

Thin films were first prepared by spin-coating a given number of layers of K lignin over polystyrene, which had been precoated on silica wafers. The AFM images of the films showed that irrespective of the number of coated layers (1, 2 or 8), the lignin formed continuous and homogeneous films that fully covered the polystyrene (Figure 1). The surface RMS roughness of the lignin films was between 1 and 3 nm, clearly higher than 0.5 nm measured for the pure polystyrene film, which supported the observation that the lignin had successfully coated the polystyrene substrate. Further evidence was obtained from the WCA values (60–65°), as the lignin coating increased the wettability of the otherwise rather hydrophobic polystyrene (WCA ~ 85°). The WCA of polystyrene measured in this study was in agreement with values reported in the literature.

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Table 2. Summary of Chemical, Molecular, and Structural Composition of Technical Lignins

<table>
<thead>
<tr>
<th></th>
<th>K</th>
<th>OS</th>
<th>S</th>
<th>SOX</th>
<th>LS</th>
<th>ECO</th>
</tr>
</thead>
<tbody>
<tr>
<td>lignin (%)</td>
<td>96.4</td>
<td>98.0</td>
<td>98.2</td>
<td>63.5</td>
<td>80.5</td>
<td>72.8</td>
</tr>
<tr>
<td>sugars (%)</td>
<td>1.5</td>
<td>0.2</td>
<td>2.4</td>
<td>2.4</td>
<td>3.2</td>
<td>17.9</td>
</tr>
<tr>
<td>ash (%)</td>
<td>1.9</td>
<td>0.0</td>
<td>4.2</td>
<td>39.5</td>
<td>28.9</td>
<td>19.1</td>
</tr>
<tr>
<td>$M_w$ (kDa)</td>
<td>3.7</td>
<td>2.1</td>
<td>2.5</td>
<td>4.8</td>
<td>10.5</td>
<td>31.4</td>
</tr>
<tr>
<td>PD</td>
<td>2.9</td>
<td>1.9</td>
<td>2.2</td>
<td>2.3</td>
<td>5.2</td>
<td>4.9</td>
</tr>
<tr>
<td>aliphatic –OH (mmol/g)</td>
<td>1.95</td>
<td>1.77</td>
<td>1.43</td>
<td>1.06</td>
<td>3.27</td>
<td>5.44</td>
</tr>
<tr>
<td>phenolic –OH (mmol/g)</td>
<td>4.12</td>
<td>3.43</td>
<td>3.40</td>
<td>0.89</td>
<td>0.83</td>
<td>0.14</td>
</tr>
<tr>
<td>–COOH (mmol/g)</td>
<td>0.49</td>
<td>0.12</td>
<td>0.96</td>
<td>1.28</td>
<td>0.74</td>
<td>0.40</td>
</tr>
<tr>
<td>–OCH$_3$ (%)</td>
<td>12.48</td>
<td>19.60</td>
<td>14.27</td>
<td>12.8</td>
<td>4.23</td>
<td>5.56</td>
</tr>
</tbody>
</table>

Table 3. Elemental Composition of the Technical Lignins, Shown as % of the Dry Material

<table>
<thead>
<tr>
<th></th>
<th>K</th>
<th>OS</th>
<th>S</th>
<th>SOX</th>
<th>LS</th>
<th>ECO</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon (%)</td>
<td>64.2</td>
<td>63.4</td>
<td>61.0</td>
<td>48.1</td>
<td>41.2</td>
<td>43.6</td>
</tr>
<tr>
<td>hydrogen (%)</td>
<td>5.6</td>
<td>5.6</td>
<td>5.5</td>
<td>3.9</td>
<td>4.1</td>
<td>4.6</td>
</tr>
<tr>
<td>nitrogen (%)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.6</td>
<td>0.5</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>oxygen (%)</td>
<td>27.2</td>
<td>30.3</td>
<td>29.7</td>
<td>36.0</td>
<td>35.1</td>
<td>36.2</td>
</tr>
<tr>
<td>sulfur (%)</td>
<td>2.1</td>
<td>0.0</td>
<td>0.9</td>
<td>0.3</td>
<td>8.1</td>
<td>6.8</td>
</tr>
<tr>
<td>total (%)</td>
<td>99.1</td>
<td>99.5</td>
<td>97.7</td>
<td>88.8</td>
<td>89.0</td>
<td>91.5</td>
</tr>
</tbody>
</table>
bility limitations derived from single measurements of roughness and wettability, it was concluded that one single layer of lignin was sufficient to produce thin model films to study the surface properties of lignin coatings.

Thin films were subsequently produced by spin-coating one layer of the different technical lignins previously dissolved in aqueous ammonia. The water-soluble lignins (SOX, LS, and ECO) could have been simply dissolved in water but were nonetheless dissolved in NH₃ (aq) to avoid solvent-related effects on the formation and properties of the films. The AFM height images (5 × 5 μm) in Figure 2 showed that all the technical lignins formed continuous films that fully covered the surface of the substrate (see Figure S1 for the corresponding AFM phase images). The films were also seemingly smooth even though the presence of particles in the nanometer range could be observed, particularly in the S, SOX, and LS films. It is possible that colloidal inorganic particles such as silica (from wheat straw) in the S and SOX lignin solutions and calcium carbonate in the LS lignin solution were precipitated onto the films. Similar types of particles have also been shown in thin films of lignin from sugar cane bagasse produced by the Langmuir–Blodgett technique, and their formation appeared to be dependent on the lignin isolation method. The presence of particles and the overall morphology of the lignin films were further evident from the 3D profile images, which showed that the ECO lignin formed films with a remarkable smooth-looking surface (Figure 2). The seemingly superior film-forming properties of the ECO lignin may be related to their higher carbohydrate content. Otherwise, the molecular and structural features of the technical lignins did not seem to have a clear influence on the formation and morphology of thin films.

The surface RMS roughness of the K, OS, and S lignin films, measured from the 5 × 5 μm area, was between 1.2 and 1.6 nm, while the RMS values of the SOX, SL, and ECO lignins were between 0.5 and 0.9 nm (Table 4). The higher roughness of the films from water-insoluble lignins might be partly related to the slightly higher roughness of the substrate, as these lignins were spin-coated on polystyrene (RMS = 0.5 ± 0.3 nm) while the water-soluble lignins were spin-coated directly on...
silica (RMS $\sim 0.35$ nm). The RMS values also appeared to indicate that the presence of small precipitates was not a decisive factor for the surface roughness of the films because films with a widely varying number of particles had similar RMS values. The RMS values determined in this study were in agreement with 0.4–1.4 nm previously reported for spin-coated films from kraft and MWL. However, other studies have reported roughness values between 2 and 6 nm for thin films of acetone-extracted lignin and MWL from various lignocellulosic materials.

The thickness of the spin-coated films was, in average, between 5 and 11 nm (Table 4). For the films from water-insoluble lignins, the thickness of the actual lignin films was obtained after subtracting the thickness of the polystyrene layer (19.4 $\pm$ 0.1 nm) from the total thickness. In the case of the OS lignin film, a negative thickness value was obtained because the total thickness (18.5 $\pm$ 3.4 nm) was lower than the thickness measured for the polystyrene layer, and for this reason, the thickness of the OS film is not shown in Table 4. The discrepancy in the thickness of the OS lignin film might be due to measurement errors caused by the compression of the film edges during the incision with the blade or alternatively to the presence of thinner polystyrene layer below the OS lignin film. In any case, the AFM images and roughness data indicated that the OS lignin had formed a thin film, and harder evidence was further obtained from the confocal microscopy images and the wettability values (see Results and Discussion below). Other methods like ellipsometry have previously been used for measuring the thickness of spin-coated films, yielding values between 9 and 23 nm for single layer films from kraft and MWL. Altering the thickness of the lignin films should be possible by adjusting the number of coated lignin layers, the lignin concentration in the solution, and the speed and time of the spin-coating procedure.

The morphology of the films was further investigated by optical microscopy to better understand the appearance of the films at a larger scale, that is, in the micrometer range. The images in Figure 3 revealed that despite the uniform and smooth appearance of the films in the nanoscale, a large number of particles were scattered throughout the surface of the films from water-insoluble lignins. The presence of particles was particularly evident in the films from OS and S lignin. On the other hand, the films from water-soluble lignins were mostly clean, although some particles could also be observed in the films from SOX and LS lignin. According to SEM micrographs, some of the particles in the OS and SOX films were considerably larger than 1 μm (Figure S2). In films from water-insoluble lignins, these microparticles could have predominantly formed by aggregation of lignin during evaporation of the solvent, as the ammonia probably evaporated faster than the water and thus promoted the condensation or aggregation of water-insoluble lignin particles. Obviously, this phenomenon would not occur with water-soluble lignins, and thus, the presence of particles due to partial delamination of the lignin film or deposition of external contaminants should not be excluded. The autofluorescence of lignin shown in Figure 3b clearly confirmed that despite a large number of microparticles present on the surface, the OS lignin had formed a thin film on top of the polystyrene layer (as discussed above).

**Wettability of Thin Lignin Films.** The wettability in contact with liquid water is one of the most important properties of films and coatings, together with their mechanical performance and capability to act as a barrier to gases (most notably to oxygen and water vapor). Therefore, the wettability of the thin films was determined by the WCA method. The WCA of the films made from water-insoluble lignins was about 43–58°, with the S lignin film having the lowest WCA as well as the highest variability between individual measurements (Table 4). It is known that increasing roughness in surfaces with tendency to wetting leads to lower CAs to counteract the increase in interfacial energy at the solid surface. However, the roughness of the films from S lignin was similar to that of films from K and OS lignins, which suggests that other variables such as the higher content of polar carboxylic acid groups in the S lignin may explain the lower WCA of the S lignin film (see discussion in the next section). The WCA values determined here were nonetheless in line with 46–64° previously measured for kraft and MWLs.

The wettability of the water-insoluble lignins was also determined using flat pellets, and the obtained WCA values for the K and OS lignins were similar to those obtained from their
thin films (Table 4). The WCA of the S lignin was somewhat higher than the WCA measured from the corresponding film but more in line with the values obtained for the other lignins. The preparation of pellets to assess the wettability of lignins may be a preferred method over the formation of thin films because possible variabilities in WCA measurements due to the formation of aggregates during the spin-coating procedure are eliminated. Moreover, the preparation of pellets is a more direct and rapid method than the dissolution of lignin and subsequent formation of thin films. In any case, surface roughness and other morphological features of the pellets would be necessary to compare the pros and cons of each methodology, which could be the subject of future studies.

According to the WCA values in Table 4, the films from water-insoluble lignins were rather hydrophilic (hydrophobic materials have WCAs above 90°). Despite their hydrophilicity, lignin coatings may still decrease the wettability of cellulose-based films, with typical WCA values between 25° and 35°.51,52 while providing relevant functions like antioxidant activity and UV-protection. Moreover, recent studies have shown that lignin enhances the strength, ductility, and hydrophobicity of nanocellulose/lignin composite films.53,54 On the other hand, films made from water-soluble lignins might find application in packaging if they were incorporated in inner layers of multilayered systems. Alternatively, these films may be used in applications where high wettability and solubility in water is required (e.g. encapsulation). The practical utilization of lignins in packaging and other applications may require further chemical modifications, which should be selected according to their compatibility with the other polymers in the composite system as well as on the desired properties to be enhanced in the final end product.

Finally, the CA of the films produced from the water-insoluble lignins (K, OS, and S) was determined not only with water but also with acetic acid solutions of varying concentrations (1.6, 3.2 and 5% mol). This allowed the construction of a Zisman plot, in which the CA of the film for a particular liquid is plotted as a function of the surface tension of that liquid, and the critical surface tension is determined by extrapolating a linear fit up to the intersect with the x-axis (cos θ = 1). As shown in Figure 4, the critical surface tension was roughly within the range of 42–48 mN/m. Poorer linear fits for the S and OS lignins (r² = 0.89–0.94), compared to the K lignin (r² = 0.99), may be related to the larger number of microparticles observed in the films (see Figure 3), which enhanced the inhomogeneity of the surface and increased the variability of the wettability measurements. This variability was particularly evident in the water WCA measurements for the S lignin films.

The critical surface tension determined through Zisman plots is only an approximation of the surface free energy and typically gives values which can be 10–15% lower than surface free energy values determined by other methods.55,56 Notley and Norgren57 determined the surface energy of kraft and MWL to be 53–59 mJ/m², and dispersive interactions were prevalent over polar interactions, particularly in MWL with both hardwoods and softwoods for which the dispersive component was about 43–47 mJ/m². Similarly, the dispersive component of the surface energy in organosolv, kraft, and steam exploded lignin was measured to be 45–49 mJ/m² by Belgacem et al.58 using a series of alkanes as probe liquids, and thus, there were not polar interactions. Although details on the polar and dispersive components of the surface energy would be needed to further discuss the differences between the lignins, the results from Figure 4 appear to support the fact that surface energy values for different lignin materials may be in fact very similar, regardless of their chemical and structural differences.

Correlations between Lignin Structure and Film Properties. Some of the features observed in the thin lignin films appeared to be related to the composition of the starting lignins. As discussed above, the nanometer-sized particles observed on the surface of the S, SOX, and LS lignin films were likely formed by precipitation of inorganic compounds such as silica and carbonates. On the other hand, the general lack of microparticulate features in films from water-soluble lignins was probably due to the presence of charged groups in those lignins, which rendered them soluble in water and prevented aggregation phenomena during evaporation of ammonia. In order to elucidate any other possible relations between the compositional or structural parameters of lignin and the properties of the resulting spin-coated films, a simple correlation analysis was performed. The following discussion should be interpreted with caution, based on the small number of samples and limited data available (particularly on wetting) for statistical analyses.

The correlation coefficients in Table 5 show that the roughness of the films was strongly dependent on the actual lignin content in the sample, as well as on lignin-specific features such as phenolic hydroxyl and methoxyl group contents. The lignin content was obviously dependent on the ash content, and consequently, the roughness of the films was also correlated with the ash content. The positive dependence between the methoxyl group content and roughness suggests that hardwood lignins, with higher degree of methoxylation than lignins from softwoods and grasses, would produce rougher thin films. Contrary to the roughness, the thickness did not show any strong correlation with any of the lignin properties, which supports the understanding that film thickness is mainly dependent on the parameters of the spin-coating procedure (i.e. lignin concentration and spinning rate).29 Both the roughness and the thickness showed a moderate but negative dependence on the molar mass of the lignins.

The WCA of the films correlated well with the ash and sugar content, as well as with the aliphatic hydroxyl and carboxylic acid group contents in the lignins (Table 5). Cellulose and other sugar-based films typically show rather high wettability, owing to the high number of available hydroxyl groups.

![Figure 4. Zisman plot for K, OS, and S lignin thin films, using water and acetic acid solutions as probe liquids. Surface tension of reference liquids from Álvarez et al.97](https://dx.doi.org/10.1021/acs.langmuir.0c00826)

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The wettability of the films was mostly dependent on the sugar, ash, aliphatic hydroxyl, and carboxylic acid contents of the lignins. To summarize, several lignin properties were found to correlate with the roughness and wettability of the corresponding thin films. The presence of inorganic compounds and charged groups in the lignins also presumably explained the formation of nano- and microparticles on the surface of the films. Interestingly, most of the lignin properties which had an effect on the morphological and wettability features of the films were actually dependent on whether the lignin was soluble or insoluble in water. Therefore, the dependence of wettability on the sugar content was somewhat expected and in line with the dependence on the aliphatic hydroxyl content. Interestingly, however, the amount of total hydroxyl groups only showed a weak correlation with wettability, contrary to previous suggestions. A possible explanation might be that phenolic hydroxyl groups present in the starting lignin material were involved in intermolecular hydrogen bonding on the film surface. The wettability of the films did not show any dependence on the molar mass of the lignin, although we recently reported that the wettability of acetone-extracted lignin from hydrothermally pretreated birch wood increased with decreasing molar mass. It is possible that molar mass may only correlate to wettability for lignins of same origin and similar extraction conditions, compared to the diverse plant origin and extraction process of the lignins used in the present study. Similar to water wettability, the critical surface tension of the films was mostly dependent on the sugar, ash, aliphatic hydroxyl, and carboxylic acid contents of the lignins.

To summarize, several lignin properties were found to correlate with the roughness and wettability of the corresponding thin films. The presence of inorganic compounds and charged groups in the lignins also presumably explained the formation of nano- and microparticles on the surface of the films. Interestingly, most of the lignin properties which had an effect on the morphological and wettability features of the films were actually dependent on whether the lignin was soluble or insoluble in water. More insight into the effects of lignin composition and structure on the properties of thin lignin films may be gained by selectively modifying specific parameters on lignins from the same botanical source and isolation method.

## CONCLUSIONS

Six technical lignins differing in their botanical source and isolation/modification method were first thoroughly characterized and then used to prepare thin films via spin-coating. Based on AFM images, all the lignins formed continuous and smooth films that covered the entire surface of the substrate, although some precipitates in the nanometer range could be observed. Confocal microscopy images also revealed that the films from water-insoluble lignins presented a large number of particles in the micrometer range, which may have formed by aggregation of lignin during drying of the film. Therefore, the use of microscopic techniques additional to AFM provides relevant and complementary data on the morphological features and overall appearance of thin lignin films. The films from water-insoluble lignins were rather hydrophilic (contact angle between 40 and 60°) and had similar surface energy. The water wettability was also measured after compressing the lignins into flat pellets. This simple method was proven to reproduce the contact angles obtained from thin films, which may be subjected to variations in structure and conformation associated with the dissolution of the lignin and subsequent drying into a film. Despite the widely diverse chemical, molecular, and structural properties of the studied technical lignins, the solubility in water was found to be the dominant parameter that determined the properties of the respective thin films.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c00826.

AFM phase images of thin lignin films and SEM micrographs of aggregate particles in thin lignin films (PDF)

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Table 5. Correlation Coefficients between the Lignin and Film Properties*1

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<th>sugars</th>
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<th>Mw</th>
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<th>PhOH</th>
<th>totOH</th>
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<th>OCH3</th>
<th>RMS</th>
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<th>CA</th>
<th>σc</th>
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<td>0.59</td>
<td>1.00</td>
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*1Lignin = lignin content (%); sugars = sugar content (%); ash = ash content (%); Mw = average weight molar mass (g/mol); alipOH = aliphatic hydroxyl content (mmol/g); PhOH = phenolic hydroxyl content (mmol/g); totOH = total hydroxyl content (mmol/g); COOH = carboxylic acid content (mmol/g); OCH3 = methoxyl content (%); RMS = root mean square roughness (nm); thick = film thickness (nm); CA = WCA (°); σc = critical surface tension (mN/m).

with affinity to water. Therefore, the dependence of wettability on the sugar content was somewhat expected and in line with the dependence on the aliphatic hydroxyl content. Interestingly, however, the amount of total hydroxyl groups only showed a weak correlation with wettability, contrary to previous suggestions. A possible explanation might be that phenolic hydroxyl groups present in the starting lignin material were involved in intermolecular hydrogen bonding on the film surface. The wettability of the films did not show any dependence on the molar mass of the lignin, although we recently reported that the wettability of acetone-extracted lignin from hydrothermally pretreated birch wood increased with decreasing molar mass. It is possible that molar mass may only correlate to wettability for lignins of same origin and similar extraction conditions, compared to the diverse plant origin and extraction process of the lignins used in the present study. Similar to water wettability, the critical surface tension of the films was mostly dependent on the sugar, ash, aliphatic hydroxyl, and carboxylic acid contents of the lignins.
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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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