



From Waste to Valuable Resource: Lignin as a Sustainable Anti-Corrosion Coating

Arman Dastpak ¹, Kirsi Yliniemi ², Mariana Cecilio de Oliveira Monteiro ^{3,4}, Sarah Höhn ³, Sannakaisa Virtanen ³, Mari Lundström ¹ and Benjamin P. Wilson ^{1,*}

- ¹ Hydrometallurgy and Corrosion, Department of Chemical and Metallurgical Engineering (CMET), School of Chemical Technology, Aalto University, P.O. Box 16200, FI-00076 Aalto, Finland; arman.dastpak@aalto.fi (A.D.); mari.lundstrom@aalto.fi (M.L.)
- ² Department of Chemistry and Materials Science (CMAT), School of Chemical Technology, Aalto University, P.O. Box 16200, FI-00076 Aalto, Finland; kirsi.yliniemi@aalto.fi
- ³ Institute for Surface Science and Corrosion (LKO), Department of Materials Science and Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany; m.monteiro@lic.leidenuniv.nl (M.C.d.O.M.); hoehn.sarah@web.de (S.H.); virtanen@ww.uni-erlangen.de (S.V.)
- ⁴ Catalysis and Surface Chemistry, Leiden Institute of Chemistry, Leiden University, Gorlaeus Laboratories, Einsteinweg 55, 2333 CC Leiden, The Netherlands
- * Correspondence: ben.wilson@aalto.fi; Tel.: +358-50-308-7810

Received: 18 October 2018; Accepted: 3 December 2018; Published: 8 December 2018



Abstract: In this study, a waste of biorefinery—lignin—is investigated as an anticorrosion coating on stainless steel. Corrosion behavior of two lignin types (hardwood beech and softwood spruce) was studied by electrochemical measurements (linear sweep voltammetry, open circuit potential, potentiostatic polarization, cyclic potentiodynamic polarization, and electrochemical impedance measurements) during exposure to simulated body fluid (SBF) or phosphate buffer (PBS). Results from linear sweep voltammetry of lignin-coated samples, in particular, demonstrated a reduction in corrosion current density between 1 and 3 orders of magnitude cf. blank stainless steel. Furthermore, results from cross cut adhesion tests on lignin-coated samples demonstrated that the best possible adhesion (grade 0) of ISO 2409 standard was achieved for the investigated novel coatings. Such findings suggest that lignin materials could transform the field of organic coatings towards more sustainable alternatives by replacing non-renewable polymer coatings.

Keywords: stainless steel; polymer coatings; anodic/cathodic protection; cyclic voltammetry; infrared (IR) spectroscopy

1. Introduction

A shift from primary to secondary resources in the large-scale processes used in the metals or pulp and paper industries is essential in order to combat the declining availability of raw materials. Consequently, it is necessary to follow the principles of circular economy in the development of sustainable industrial ecosystems, and, from this perspective, it is surprising how underutilized some of the side-streams of the biorefinery (pulp and paper) industries are. In particular lignin, which is a very abundant natural polymer that provides the structural strength of plants [1,2] and has an annual production of approximately 100 million tons globally. Nevertheless, despite this high level of output, currently only 2% is utilized in value-added products, and the rest is predominantly burnt as a heat source in the integral processes of pulp/papermaking [3]. The primary applications of isolated lignin are surfactants, adhesives, and dispersants [3], although fundamental research on possible applications of lignin is ongoing, including green replacements for plastics and packaging applications [4–6].



This study demonstrates a proof-of-concept application of pure lignin as a corrosion protection coating for metal surfaces. The main idea is that lignin alone can be utilized as the main material for creating superior protection for metal surfaces, rather than considering lignin as a low profit margin waste material. As far as the authors are aware, despite lignin's well-known properties such as water impermeability [7], hydrophobicity [2], and film-forming ability [8], as well as low cost and abundance, pure lignin has not been suggested as a polymeric corrosion protection coating for metal surfaces. So far, lignin has only been studied as a minor additive to barrier coatings from the perspective of structural, mechanical [2,9], and corrosion inhibition [10–14]. Furthermore, the antimicrobial properties [9] and biocompatibility [15] of this material could widen the application range to include functional coatings, used for example in biomedical applications.

In general, lignin is classified into three categories—softwood, hardwood, and annual plant—and all three types comprise, in varying amounts, three propane units: guaiacyl (G), syringyl (S), and 4-hydroxylphenyl (H), which are linked with carbon–carbon and ether bonds [7]. The amount and ratio of propane units within a particular lignin depends on the plant origin and, as a result, different lignins can have different properties, potentially providing an additional route to control the resulting film properties [16]. Hence, this study uses lignin from two different sources, beech (hardwood) and spruce (softwood).

In order to exploit the significant quantities of lignin available, any intended application should ideally be equivalently large scale and high volume. The corrosion of metals has a huge impact on global economics, and it has been estimated that the cost of corrosion is approximately 3%–4% of the gross national product, regardless of the country [17]. In addition to the economic impact of corrosion, this phenomenon can also potentially pose a risk to health, with related failures ranging from large-scale infrastructure like buildings and bridges, to highly specialized products like metal-based medical implants. For example, even if stainless steel 316L is considered to be corrosion resistant and is thus widely used in architectural [18,19], marine [18,20], and biomedical applications (like intravascular stents [21], joint replacement prostheses [22], dental implants [23]), corrosion can take place when it is exposed to chloride containing solutions [24]. As an example, it has been estimated that 90% of 316L alloy implant failures are as a result of localized corrosion [22], therefore the exposure to physiological environments can result in the release of allergens and/or potentially carcinogenic ions like Cr and Ni into human body [21,22]. In order to tackle these problems, one method is to cover the surface of the implant with a biocompatible coating to enhance the corrosion resistance, and to control the dissolution of metal ions [22].

Although many different biopolymer hybrid coatings have been developed for functionalities like increased mechanical, anti-bacterial, and corrosion protection [25–31], less research has been dedicated to coating systems based solely on sustainable, bio-sourced, polymeric material combinations like lignin, cellulose, and alginate [32,33]. In this research, the corrosion behavior of lignin coatings from two different sources (hardwood and softwood) on stainless steel 316L in physiological solutions was studied. Results clearly demonstrate that properties vary depending on wood source, and that the strongly adhered lignin coatings show significant barrier properties against corrosion.

2. Materials and Methods

Stainless steel 316L was used as the substrate for the coating deposition, and the composition is outlined in Table A1 [34,35]. The substrates were cut into 20 mm \times 20 mm \times 5 mm pieces and were polished with 800-grit (~25 µm) grinding paper. Afterwards, substrates were sonicated for 5 min in a 1:1 ethanol:water solution to ensure a clean surface, before being dried with compressed air.

The two different lignin samples used in this study were prepared by organosolv-pulping processes of beech (hardwood) and spruce (softwood) [Fraunhofer Center for Chemical-Biotechnological Processes (CBP) [36], Germany, see Table 1] [37,38]. Both samples were dissolved in 1,4-Dioxane solvent (Sigma-Aldrich, Steinheim, Germany, 99.8%) to produce two comparable solutions with a lignin concentration of 60 mg·mL⁻¹. Lignin coated surfaces were prepared by pipetting a lignin solution

(0.5 mL) onto the 316L stainless steel substrate and spin-coating at 200 rpm for 300 s. Following spin-coating, samples were annealed in a preheated oven at 120 $^{\circ}$ C (Memert, UN30) for 30 min.

Table 1. Plant source and G:S:H ratio of selected organosolv lignin [37,38]. G—guaiacyl, S—syringyl, H—4-hydroxylphenyl groups found in different lignin types.

Plant Source	G	S	Н
spruce (softwood)	94	1	5
beech (hardwood)	43.2	55.4	1.4

Contact angle measurements were performed using a CAM200 goniometer (KSV, Helsinki, Finland). For each spin-coated sample, the average contact angle value was determined from five measurements of (5 μ L) distilled water (repeated for two separate samples from both lignin sources). The thickness of lignin coating was measured by cross-sectional scanning electron microscopy (SEM, LEO 1450 VP, Zeiss, Jena, Germany). Prior to imaging, samples were cut across the center, polished, and sonicated for 2 min in a 1:1 ethanol:water solution, before being dried with compressed air. In addition, the coated samples were characterized by fourier transform infrared spectroscopy (FTIR) (Nicolet 6700, Thermo Scientific, Waltham, MA, USA) with an ATR-D cell—32 scans over a spectral range of 500 to 4000 cm⁻¹—in order to study the effect of annealing and influence of exposure to the physiological solution, after linear sweep voltammetry (LSV) measurements.

The surface morphology of the lignin coatings on stainless steel 316L for both non-annealed and annealed samples was investigated by atomic force microscopy (AFM, Bruker AXS Inc., Madison, WI, USA). Stainless steel samples of 10 mm \times 10 mm were prepared in the same manner outlined above—polished with diamond paste (down to 0.25 µm), sonicated in 1:1 ethanol:water solution for 5 min, and dried with compressed air—before being spin-coated with the lignin solutions and annealed as appropriate. Images of 4 µm² were obtained with a MultiMode 8 scanning probe microscope, and with a silicon cantilever (NSC15/AIBS from Ultrasharp MikroMasch, Tallinn, Estonia). Imaging was conducted in tapping mode, and the typical resonance frequency of cantilever was 325 kHz. Images were obtained from two different regions of each sample, and from two replica samples of each lignin coating.

For all electrochemical measurements-except cyclic potentiodynamic polarization and electrochemical impedance spectroscopy (EIS)-samples were exposed to simulated body fluid (SBF) solution (pH = 7.4). The nominal ion concentration of the SBF used is presented in Table A2, and it was prepared by following the procedure outlined in Kokubo and Takadama [39]. For cyclic potentiodynamic polarization (CPP) and electrochemical impedance spectroscopy (EIS) measurements, samples were immersed in phosphate buffered saline (PBS) solution (pH = 7.4), which was prepared by dissolving a PBS tablet (Sigma-Aldrich) in distilled water (200 mL) (Table A2). All electrochemical measurements were conducted at room temperature using a three-electrode setup, with Ag/AgCl (saturated KCl) as the reference electrode (RE), platinum (Pt) as the counter electrode (CE), and the spin-coated samples as the working electrode (WE) (Figure A1). For polarization and linear sweep voltammetry (LSV) measurements, a PGSTAT 302N electrochemical workstation (Autolab, Utrecht, The Netherlands) was used, whereas open circuit potential value (OCP), EIS, and CPP measurements were carried out with an Iviumstat XRe (Ivium Technologies, Eindhoven, The Netherlands). The potential range of LSV was -0.8 to 0.4 V vs. Ag/AgCl (sweep rate = 25 mV·s⁻¹), and exposed WE area was 0.95 cm². The polarization was performed at +50 mV vs. OCP-OCP determined after 30 min of stabilization-and the polarization time was 90 min. All the measurements were performed with both non-annealed and annealed coatings, always using new samples. Corrosion current density was determined from the linear region of the Tafel diagrams in the range of 100 to 200 mV, from corrosion potential.

For CPP measurements, the experimental setup consisted of a working electrode (1.9 cm²) covered with an O-ring (diameter of 1.7 cm) and a regular hexagon shaped plastic sheet (transparent laser sheet with a diagonal 1.7 cm, Epson, Nagano, Japan), in order to provide crevices, as shown in Figure A2. The reference electrode was Ag/AgCl, and the counter electrode Pt sheet. The CPP procedure was based on a modified ASTM G61 standard (scan rate = $0.167 \text{ mV} \cdot \text{s}^{-1}$) [40]: forward scans were started at 100 mV below a sample's corrosion potential and continued until current density was equal to 1 mA·cm⁻², and the subsequent reverse scan was recorded until the forward scan was intercepted. All the electrochemical measurements were undertaken in triplicate using fresh solutions.

The electrochemical impedance spectroscopy measurements were performed with a similar three-electrode configuration during a 24 h immersion in PBS solution (200 mL), with the lignin-coated or blank samples as the working electrode (surface area = 0.785 cm²). The frequency range of 100 kHz–0.01 Hz was utilized, in which frequency values were spaced logarithmically (10 steps per decade) and with an amplitude of sinusoidal voltage signal of 10 mV rms (root-mean-square). All the measurements were carried out after 60 min stabilization of individual samples, and at open circuit potential (OCP).

Adhesion measurements were conducted on annealed coated surfaces using a crosshatch cutter, (Paint Test Equipment, Congleton, UK) and were based on the ISO 2409 [41]. A multiple blade cutter was applied normal to the surface plane; this was followed by the attachment of an adhesion test tape that was then removed after 5 min at an angle of ~60°. Results were assessed using a 0 to 5 scale, where zero is equivalent to perfect adhesion, i.e., the edges of cuts are smooth and none of the lattice squares are detached from the substrate.

3. Results and Discussion

In order to determine the surface characteristics and applicability of lignin coatings, atomic force microscopy (AFM), FTIR (before and after exposure to the solutions), goniometry, and standard adhesions tests were carried out. The morphology of annealed and non-annealed lignin coatings from hardwood (beech) and softwood (spruce) was studied by AFM (Figure 1). Both the beech and spruce lignins displayed a globular surface typical of lignin [42] and a porous surface prior to annealing, whereas after 30 min treatment at 120 °C these layers transformed to a smoother, more uniform layer, possibly as a result of lignin softening during the heating process [43]. The roughness parameters of the measured samples can be seen in Table A3.

The coatings were also investigated with FTIR, in order to determine if any changes to the coating chemistry occurred either during the annealing or due to immersion in the simulated body fluid (SBF) solution. The characteristic fingerprint FTIR regions ($800-1800 \text{ cm}^{-1}$) for both lignin types investigated are shown in Figure 2, and their associated band assignments are listed in Table 2 [44–46]. The full spectrum (500 to 4000 cm⁻¹) of coatings is demonstrated in Figure A3. For both beech and spruce coatings, the characteristic bands related to lignin remained after both annealing and SBF exposure, which demonstrates the persistence of lignin adhesion on the stainless steel surface. In contrast, two bands at 889 and 1253 cm⁻¹—related to the vibration and stretching of the dioxane solvent hydrogen rings—were observed to disappear after annealing due to solvent evaporation [47].

Contact angle measurements were also conducted, in order to evaluate the wettability of spin-coated surfaces. In general, such behavior has an effect on corrosion susceptibility, as more hydrophobic surfaces (contact angles $\geq 90^{\circ}$) tend to favor enhanced resistance against wet corrosion. When compared to bare steel ($62^{\circ} \pm 2^{\circ}$), both beech ($90^{\circ} \pm 3^{\circ}$) and spruce ($84^{\circ} \pm 2^{\circ}$) lignin coatings showed enhanced surface hydrophobicity. Typically, lignin contains both hydrophilic phenolic/aliphatic hydroxyl groups [48], and therefore the contact angle values can differ from source to source. In the literature, the reported water contact angle values are in the range of 45° – 102° [49–52]. However, the results of this study are not comparable with those of studies in which the reported values are primarily for bulk and cast lignin, rather than the spin-coated surfaces of this study, which would naturally affect the wetting behavior of a surface.



Figure 1. Atomic force microscopy (AFM) topographical images of spin-coated lignin samples on polished stainless steel 316L. Beech before (**a**) and after (**b**) annealing, and spruce before (**c**) and after (**d**) annealing.

No.	Spruce	Beech	Assignment
	Band Position (cm ⁻¹)	Band Position (cm^{-1})	
1	1599	1590	Aromatic ring vibration [44,45] C=C stretch of aromatic ring [46]
2	1501–1512	1500-1510	Aromatic ring vibration [44,45]
3	1467	1467	C–OH deformation [44] C–H asymmetric deformation [45] C–H bend methyl/methylene [46]
4	1420	1420	C–OH in-plane deformation (aromatic stretch) [44] C–H deformation [46]
5	1322	1324	C=O stretch syringyl units [44–46]
6	1263	-	C–O stretch of guaiacyl units [44–46]
7	1205	1211	C-C/C-O/C=O stretch guaiacyl units [46]
8	1114	-	Aromatic C–H or guaiacyl unit [46]
9	_	1115	C–H deformation syringyl units [46]
10	1079	1079	C–O stretch of secondary alcohol [46]
11	1027	1027	C–O stretch of primary alcohol [46]
12	-	913	C-H bending syringyl units, aromatic ring [46]
13	869	869	C–H out of plane [44]
14	_	825	C–H bending of syringyl units [46]

Table 2. Summary of infrared (IR) bands and assignments for spruce and beech coatings in fourier transform infrared spectroscopy (FTIR) fingerprint region ($800-1800 \text{ cm}^{-1}$).



Figure 2. FTIR transmittance spectra of beech (**a**) and spruce (**b**) lignin samples in the characteristic fingerprint region.

As adhesion is also a key property of organic coatings [53], crosshatch tests of dry coated surfaces were performed in line with the ISO 2409 [41]. Figure 3 illustrates optical microscope images from crosscut area. As can be observed, both coatings demonstrated smooth edges proximal to the crosscuts—equivalent to an ISO = 0/5 classification, i.e., the highest possible adhesion—which clearly demonstrates the ability of lignin to form strong polymeric films. A digital photograph of surfaces for adhesion tests for both annealed beech and spruce coatings is presented in Figure A4. As can be observed, no coating detachment from the steel's surface is evident for either hardwood beech or softwood spruce lignin coatings.



Figure 3. Optical microscopy (OM) images of beech coating (**a**) and spruce coating (**b**) after cross cut test. Smooth edges of cuts can be seen for both coatings (scale bar: 100μ m).

The effect of lignin coatings on corrosion resistance of stainless steel was investigated electrochemically by linear sweep voltammetry (LSV), open circuit potential (OCP), polarization, cyclic potentiodynamic polarization (CPP), and electrochemical impedance spectroscopy (EIS). Figure 4 presents LSV diagrams of blank stainless steel samples and lignin coated samples, (a) immediately after exposure to SBF solution (pH = 7.4), and (b) after 90 min of exposure. As can be seen in Figure 4, both coatings increased the corrosion potential from 0.15 to 0.2 V vs. Ag/AgCl. Furthermore, both the cathodic and anodic current density values were between 1 and 3 orders of magnitude lower for the coated samples than for blank stainless steel, demonstrating the strong corrosion protection effect of coatings. Comparison between the two different lignin sources shows that beech provided marginally better protection against corrosion than spruce, with a current density value of beech being 1.1×10^{-9} mA·cm⁻² and for spruce being 7.3×10^{-9} mA·cm⁻², whereas the value was two orders of magnitude higher for the blank 316L sample (6.6×10^{-7} mA·cm⁻²) for short immersion times of 90 min or less in the LSVs. This result can be considered to be remarkable, not only as SS316L itself is sufficiently corrosion resistant that it is used for temporary implants in the human body [54], but also as the coating only comprises solvent extracted lignin that has not been modified in any way.



Figure 4. Linear sweep voltammograms of samples after $0 \min(\mathbf{a})$ and $90 \min(\mathbf{b})$ exposure to simulated body fluid (SBF) solution (sweep rate: $25 \text{ mV} \cdot \text{s}^{-1}$).

After 90 min exposure, both lignin coatings became less effective; the measured current density decreased to $1.4 \times 10^{-8} \text{ mA} \cdot \text{cm}^{-2}$ for beech and $6.6 \times 10^{-8} \text{ mA} \cdot \text{cm}^{-2}$ for spruce, most likely due to water uptake into the coating. Nevertheless, it is worth noting that these values are still one order of magnitude lower than that of bare stainless steel, which highlights the anti-corrosive nature of lignin coatings.

Moreover, these results demonstrate an improvement on previous investigations of bio-sourced hybrid systems such as cellulose nanocrystal–alginate and raw lacquer–lignin tripolymer coated steels [33,55]. These findings suggest that beech lignin initially forms a more stable film than spruce, which could be due to the different monolignol contents (Table 1); beech has more syringyl (S) units, and thus more methoxy groups (–OCH₃), than spruce. It is hypothesized that during annealing, chemical changes that depend on the methoxy content occur [56], and therefore beech lignin forms a more compact coating (thickness of 1.3 μ m, determined by cross- sectional SEM) than spruce lignin (1.6 μ m). This is confirmed by analysis of the IR spectrum band between 2800 and 2950 cm⁻¹, which contains CH stretching related to the presence of aromatic methoxyl groups and methyl/methylene side chains groups [57].

The IR results in Figure 5 clearly demonstrate that during annealing, the peaks related to lignin methoxy groups were reduced, suggesting the coatings became more compact when heated to 120 °C. This is consistent with the findings of Kim et al. [56], who postulated that the depolymerization of methoxy groups and condensation of lignin takes place at elevated temperatures (150–300 °C), although in this research the adsorption to stainless steel surface may also have an additional—as yet undetermined—effect due to better heat transfer.

The corrosion behavior of the samples was further investigated by measurement of OCP as a function of time during the 90 min exposure to the SBF solution (Figure A5). For bare stainless steel, the potential increased continuously with a declining rate, as a result of an increase in the thickness of oxide layer.

This steady increase in OCP indicates that the uncoated steel remained electrochemically active during the measurement, and that the continuous formation of surface metal oxides occurred. In contrast, both beech and spruce lignin coated samples showed an almost constant OCP, demonstrating a more stable behavior than the bare stainless steel sample.

In order to study the corrosion inhibition of the coatings under more aggressive conditions, samples were polarized at +50 mV with respect to the sample's OCP (as determined after 30 min from the OCP measurements shown in Figure A5). As can be seen in Figure 6, the current density for both beech and spruce coated samples remained at a low and constant value, showing that the underlying metal surface was protected from corrosion for the whole measurement duration. Conversely, the uncoated sample had a relatively high current density, signifying that the surface

was electrochemically active during the measurement. These results suggest that the presence of the lignin coating blocks the electrochemically active surface sites, and thus minimizes any electrochemical corrosion reactions.



Figure 5. FTIR transmittance spectra of the carboxymethyl bands in beech (**a**) and spruce (**b**) lignin coated samples before and after annealing at 120 °C.



Figure 6. Polarization diagram of samples to +50 mV vs. OCP (OCP_{beech/spruce} \approx 50 mV, OCP_{stainless} steel \approx -50 mV vs. Ag/AgCl) in SBF solution. Full duration (5400 s) (**a**) and first 1000 s of measurement (**b**).

A comparison of the LSV results for the lignin coatings with that of SS316L reveals that the rate of both the cathodic and anodic reactions was significantly reduced for coated samples. During corrosion of SS316L in neutral solutions (pH = 7.4), the main cathodic reaction is the reduction of oxygen, according to Equation (1) [58]:

$$O_2 + 2 H_2 O + 4e^- \to 4 O H^-$$
 (1)

The associated anodic reaction primarily involves the dissolution of the metallic elements present in SS316L, i.e., Fe, Ni, and Cr, via Equation (2) [58]:

$$M \to M^{n+} + ne^- \tag{2}$$

In addition, the LSV curves for coated and SS316L samples (Figure 4) show a similar profile which indicates that the anodic and cathodic reactions taking place on the different surfaces were identical. Nevertheless, it is clear from the data that the extent of these reactions was significantly reduced by the presence of the lignin coating.

In order to understand this phenomenon, the inherent ability of lignin to act as a mixed mode—cathodic and anodic—corrosion inhibitor must be taken into account [59]. Previous research has highlighted the mixed mode inhibition properties of lignin when used as a minor additive in the corrosion test solution [11,12,60,61]. For example, studies by Hussin et al. [14] demonstrated that concentrations of 500-ppm organosolv lignin resulted in inhibition efficiencies of up to 98%, depending on the type of lignin used. The inhibition was observed to be predominantly present in the anodic branch of the LSV diagrams, and was related to the antioxidant/inhibitor capability of lignin. Additionally, it was also found that protonated lignin molecules adsorbed electrostatically to the metal surface, resulting in a decreased rate of Cl⁻ adsorption to the surface. Similar investigations of mild steel corrosion in both near neutral 3.5% NaCl solution [10] and 0.5 M H_2SO_4 [13] have further demonstrated the ability of lignin to act as a corrosion inhibitor in both the anodic and cathodic branches of LSV diagrams. Therefore, it was concluded that lignin molecules adsorb to the mild steel surface-to form ferric-lignin compounds-via the functional hydroxyl groups (specifically phenolic -OH) present, resulting in an increase in charge transfer resistance that led to the observed corrosion inhibition. Results from the present investigations also display a similar mixed mode corrosion inhibition, as the electrochemical data show reductions in both the anodic and cathodic branches (Figure 4), and more stable behavior (Figures 6 and A5) with a lignin coating compared to the uncoated stainless steel.

Due to susceptibility of stainless steel to crevice corrosion, samples were also characterized by cyclic potentiodynamic polarization (CPP) based on the ASTM G61 standard, and the results are shown in Figure 7. Two critical potentials are used to evaluate a substrate's susceptibility to crevice corrosion: breakdown potential (E_b) , where the passive film breaks down—typically observed as a rapid increase in anodic current—and repassivation potential (E_{rp}) , where a passive film of corrosion products is formed, i.e., the potential at which the hysteresis loop is completed. In general, more positive potential values indicate that a sample is less susceptible to crevice corrosion [40]. A comparison of the breakdown potential of bare SS316L with that of the lignin-coated samples shows that SS316L has higher values of E_b , 500 mV cf. \approx 300 mV than the coated samples. The same trend was recorded for the repassivation potentials (E_{rp}): ≈ -130 mV vs. ≈ -170 mV for steel and coated substrates, respectively. This finding is similar to previous research undertaken by Bryant et al. [62], who discovered that the presence of poly(methyl methacrylate) PMMA bone cement layers on 316L stainless steel could actually accelerate crevice corrosion initiation and propagation. In addition, recent work on 316L has demonstrated that the material of the crevice former used to initiate corrosion can also affect markedly the subsequent behavior seen [63]. Subsequent observation of all three surfaces—SS316L, beech coatings, and spruce coatings—after the experiments clearly showed evidence of crevice formation (Figure A6). This suggests that, although lignin coatings do not provide any specific protection against crevice corrosion for stainless steel substrates, they also do not visually appear to enhance the susceptibility to crevice corrosion, even if the breakdown and repassivation potentials are more negative.

In order to study the stability of coatings during longer immersion times, electrochemical impedance spectroscopy (EIS) measurements were conducted for all samples during a 24 h immersion time. Figure 8 displays bode plots for the amplitude of impedance and phase angle as a function of frequency for both lignin-coated and bare stainless steel. As shown in Figure 8a, both lignin coatings demonstrated a capacitive behavior with higher impedance values over the whole frequency range of measurements than that of the bare SS316L. After 24 h of immersion, the bode plot of the spruce coating (Figure 8b) had a similar capacitive behavior as that of the freshly immersed coatings, which indicates the effective barrier performance of the coating. The similarity in behavior after both 1 and 24 h immersion is visible in the bode plots, which also possess a similar time constants—an indication of the barrier properties of an organic coating [64]. On the other hand, beech coatings displayed a completely different behavior after 24 h of immersion, with a dramatic drop in impedance values and appearance

of a second time constant, which indicates that the beech coating degraded with longer immersion times and was unable to provide prolonged protection for the steel substrate.



Figure 7. Cyclic potentiodynamic polarization curves of samples in phosphate buffered solution (PBS).



Figure 8. Bode plots of samples obtained from electrochemical impedance spectroscopy (EIS) measurements during 24 h immersion in PBS solution: (**a**) impedance modulus vs. frequency, (**b**) phase angle vs. frequency.

These results highlight lignin's potential for use as anti-corrosion coating material due to its unique combination of hydrophobicity, excellent adhesion, and corrosion inhibition properties, particularly when in contact with a physiological environment. The corrosion protection could be further enhanced by careful selection of the lignin source, as this seems to have an effect on the corrosion behavior of the coatings.

4. Conclusions

This study demonstrates that pure lignin creates a coating on stainless steel surfaces with excellent adhesion and corrosion properties. FTIR results show that the coating chemistry remains stable during exposure to physiological solutions, and LSV results show that the coatings have even 2 orders of magnitude lower current densities than bare stainless steel 316L, demonstrating the high level of performance possible with these coatings. Of the two different lignin sources investigated, spruce (softwood) coating provides a better corrosion protection when compared to beech (hardwood) for longer periods of exposure (24 h), which probably results from the differences in their monolignol content, particularly between the associated methoxy groups in the syringyl and guaiacyl components.

Overall, these results highlight the possibility for the large-scale application of residual lignin from biorefinery side-streams for a new generation of biosourced and sustainable anti-corrosion coatings.

Author Contributions: Conceptualization, B.P.W.; Formal Analysis, A.D., K.Y., S.H., S.V., M.L. and B.P.W.; Funding acquisition, S.V., M.L. and B.P.W.; Investigation, A.D., K.Y., M.C.d.O.M., S.H. and B.P.W.; Methodology, A.D., K.Y., M.C.d.O.M. and B.P.W.; Project Administration, M.L. and B.P.W.; Resources, K.Y., M.C.d.O.M., S.V., M.L. and B.P.W.; Supervision, S.V., M.L. and B.P.W.; Visualization, K.Y. and B.P.W.; Writing–Original Draft, A.D., K.Y. and B.P.W.; Writing–Review & Editing, A.D., K.Y., S.V, M.L. and B.P.W.

Funding: This research was funded by Technology Industries of Finland Centennial/Jane and Aatos Erkko Foundations "Future Makers: Biorefinery Side Stream Materials for Advanced Biopolymer Materials (BioPolyMet)" and Academy of Finland (NoWASTE, No. 297962).

Acknowledgments: This work made use of facilities provided by the RawMatTERS Finland Infrastructure (RAMI) at Aalto University, supported by the Academy of Finland. In addition, special thanks to Michael Hummel for providing the different lignin materials used as part of this work.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Element	wt %
С	< 0.03
Si	<1
Mn	<2
Ni	10
Cr	18
Мо	3
S	< 0.03
Р	< 0.045
Fe	Balance

Table A1. Composition of stainless steel 316L (wt %) [34,35].

Table A2. Nominal ion concentrations of simulated body fluid (SBF) [39] and phosphate buffered saline (PBS) used in corrosion studies.

Ion	Solution Concentrations (mM)		
1011	SBF	PBS	
Na ⁺	142	137	
K^+	5	4.2	
Mg ²⁺	1.5	-	
Ca ² +	2.5	-	
Cl-	147.8	139.6	
HCO ₃ -	4.2	-	
$H_2PO_4^{3-}$	-	1.5	
HPO_4^{2-}	1	8.1	
SO_4^{2-}	0.5	_	
pH (25 °C)	7.4	7.4	

Table A3. Roughness parameters obtained from AFM measurements for studied samples.

No.		Sample	R _Q (nm)	R _A (nm)	R _{Max} (nm)
1		SS 316L	2.99	2.28	22.46
2	Beech	Non-Annealed	2.54	1.79	21.8
3	Spruce	Non-Annealed	6.62	4.97	46.1
4	Beech	Annealed	0.349	0.273	4.8
5	Spruce	Annealed	0.5	0.397	7.05



Figure A1. Experimental setup for electrochemical measurements. The distance between reference electrode (Ag/AgCl) tip and the surface of sample was constant for all the measurements.



Figure A2. Top to bottom view of surfaces for cyclic potentiodynamic polarization (CPP) measurements, after addition of experimental crevice former (black). The circular area demonstrates the total exposure provided by an o-ring on the surface, and gray area represents the surfaces with direct contact to phosphate buffered saline (PBS) solution.



Figure A3. The full FTIR spectra for beech coatings (a) and spruce coatings (b).



Figure A4. Surface of annealed spruce coating (**a**) and beech coating (**b**) after conducting crosscut test, according to ISO 2409. No sign of coating's detachment from the square lattices was observed.



Figure A5. Open circuit potential (OCP) of samples as a function of time after immersion in SBF solution.



Figure A6. Digital photographs ($\mathbf{a}, \mathbf{c}, \mathbf{e}$) and optical microscopy images ($\mathbf{b}, \mathbf{d}, \mathbf{f}$) of crevices formed during CPP measurements on the surface of SS316L (\mathbf{a}), spruce-coated (\mathbf{b}), and beech-coated (\mathbf{c}) lignin. Optical microscopy images were obtained from the spots marked with an arrow (scale bar: 100 µm).

References

- 1. Gargulak, J.D.; Lebo, S.E.; McNall, T.J. *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons Inc.: New York, NY, USA, 2015. [CrossRef]
- Harb, S.V.; Cerrutti, B.M.; Pulcinelli, S.H.; Santilli, C.V.; Hammer, P. Siloxane–PMMA hybrid anti-corrosion coatings reinforced by lignin. *Surf. Coat. Technol.* 2015, 275, 9–16. [CrossRef]
- 3. Global Lignin Products Market—Segmented by Product Type, Source, Application, and Geography—Trends and Forcasts (2015–2020)—Reportlinker Review. Cision PR Newswire Website. Available online: https://www.prnewswire.com/news-releases/global-lignin-products-market---segmented-by-product-type-source-application-and-geography---trends-and-forecasts-2015-2020---reportlinker-review-300145371.html (accessed on 18 October 2018).
- 4. Ragauskas, A.J.; Beckham, G.T.; Biddy, M.J.; Chandra, R.; Chen, F.; Davis, M.F.; Davison, B.H.; Dixon, R.A.; Gilna, P.; Keller, M.; et al. Lignin valorization: Improving lignin processing in the biorefinery. *Science* **2014**, *344*, 1246843. [CrossRef]
- 5. Hult, E.; Ropponen, J.; Poppius-Levlin, K.; Ohra-Aho, T.; Tamminen, T. Enhancing the barrier properties of paper board by a novel lignin coating. *Ind. Crops Prod.* **2013**, *50*, 694–700. [CrossRef]
- 6. Nair, S.S.; Zhu, J.Y.; Deng, Y.; Ragauskas, A.J. High performance green barriers based on nanocellulose. *Sustain. Chem. Process.* **2014**, *2*, 23. [CrossRef]
- 7. Bajpai, P. Carbon Fiber from Lignin; Springer: Singapore, 2017; p. 11.
- 8. Hakala, T.; Kruus, K. *The Making of Bioeconomy and Transformation*; VTT: Helsinki, Finland, 2017.
- Eraković, S.; Janković, A.; Veljović, D.; Palcevskis, E.; Mitrić, M.; Stevanović, T.; Janaćković, D.; Mišković-Stanković, V. Corrosion stability and bioactivity in simulated body fluid of silver/hydroxyapatite and silver/hydroxyapatite/lignin coatings on titanium obtained by electrophoretic deposition. *J. Phys. Chem. B* 2013, *117*, 1633–1643. [CrossRef]
- 10. Akbarzadeh, E.; Ibrahim, M.N.M.; Rahim, A.A. Corrosion inhibition of mild steel in near neutral solution by kraft and soda lignins extracted from oil palm empty fruit bunch. *Int. J. Electrochem. Sci.* **2011**, *6*, 5396–5416.
- 11. Hussin, M.H.; Rahim, A.A.; Mohamad Ibrahim, M.N.; Brosse, N. Improved corrosion inhibition of mild steel by chemically modified lignin polymers from *Elaeis guineensis* agricultural waste. *Mater. Chem. Phys.* **2015**, 163, 201–212. [CrossRef]
- 12. Ren, Y.; Luo, Y.; Zhang, K.; Zhu, G.; Tan, X. Lignin terpolymer for corrosion inhibition of mild steel in 10% hydrochloric acid medium. *Corros. Sci.* **2008**, *50*, 3147–3153. [CrossRef]
- Shivakumar, M.; Dharmaprakash, M.S.; Manjappa, S.; Nagashree, K.L. Corrosion inhibition performance of lignin extracted from black liquor on mild steel in 0.5 M H₂SO₄ acidic media. *Port. Electrochim. Acta* 2017, 35, 351–359. [CrossRef]
- 14. Hussin, M.H.; Mohd Shah, A.; Rahim, A.; Ibrahim, M.; Perrin, D.; Brosse, N. Antioxidant and anti corrosive properties of oil palm frond lignins extracted with different techniques. *Ann. For. Sci.* **2014**, *72*, 17–26. [CrossRef]
- 15. Raschip, I.E.; Vasile, C.; Ciolacu, D.; Cazacu, G. Semi-interpenetrating polymer networks containing polysaccharides. I xanthan/lignin networks. *High Perform. Polym.* **2007**, *19*, 603–620. [CrossRef]
- 16. Derkacheva, O.; Sukhov, D. Investigation of lignins by FTIR spectroscopy. *Macromol. Symp.* **2008**, 265, 61–68. [CrossRef]
- 17. Revie, R.W.; Uhlig, H.H. Corrosion and Corrosion Control, 3rd ed.; John Wiley & Sons Inc.: New York, NY, USA, 1985.
- Lo, K.H.; Shek, C.H.; Lai, J.K.L. Recent developments in stainless steels. *Mater. Sci. Eng.* 2009, 65, 39–104. [CrossRef]
- 19. Houska, C. *Stainless Steel in Architecture, Building and Construction;* Reference Book Series No. 11024; Nickel Institute: Toronto, ON, Canada, 2014.
- 20. *Guidelines for Nickel Stainless Steels for Marine Environments Natural Waters and Brines;* Reference Book Series No. 11003; Nickel Institute: Toronto, ON, Canada, 1987.
- Shih, C.C.; Shih, C.M.; Chen, Y.; Su, Y.Y.; Shih, J.S.; Kwok, C.F.; Lin, S.J. Growth inhibition of cultured smooth muscle cells by corrosion products of 316 L stainless steel wire. *J. Biomed. Mater. Res.* 2001, 57, 200–207. [CrossRef]

- 22. Hansen, D.C. Metal corrosion in the human body: The ultimate bio-corrosion scenario. *Electrochem. Soc. Interface* **2008**, *17*, 31–34.
- 23. Chew, K.; Zein, S.; Ahmad, A. The corrosion scenario in human body: Stainless steel 316L orthopaedic implants. *Nat. Sci.* **2012**, *4*, 144–148. [CrossRef]
- 24. Malik, A.U.; Mayan Kutty, P.C.; Siddiqi, N.A.; Andijani, I.N.; Ahmed, S. The influence of pH and chloride concentration on the corrosion behaviour of AISI 316L steel in aqueous solutions. *Corros. Sci.* **1992**, *33*, 1809–1827. [CrossRef]
- 25. Heise, S.; Wirth, T.; Höhlinger, M.; Hernández, Y.T.; Ortiz, J.A.R.; Wagener, V.; Virtanen, S.; Boccaccini, A.R. Electrophoretic deposition of chitosan/bioactive glass/silica coatings on stainless steel and WE43 mg alloy substrates. *Surf. Coat. Technol.* **2018**, *344*, 553–563. [CrossRef]
- 26. Zhitomirsky, I.; Pang, X. Fabrication of chitosan-hydroxyapatite coatings for biomedical applications. *ECS Trans.* **2007**, *3*, 15–22. [CrossRef]
- 27. Huang, J.; Lyu, S.; Fu, F.; Wu, Y.; Wang, S. Green preparation of a cellulose nanocrystals/polyvinyl alcohol composite superhydrophobic coating. *RSC Adv.* **2017**, *7*, 20152–20159. [CrossRef]
- 28. Rahman, O.U.; Shi, S.; Ding, J.; Wang, D.; Ahmad, S.; Yu, H. Lignin nanoparticles: Synthesis, characterization and corrosion protection performance. *New J. Chem.* **2018**, *42*, 3415–3425. [CrossRef]
- 29. Naseem, A.; Tabasum, S.; Zia, K.M.; Zuber, M.; Ali, M.; Noreen, A. Lignin-derivatives based polymers, blends and composites: A review. *Int. J. Biol. Macromol.* **2016**, *93*, 296–313. [CrossRef]
- Seyed Shahabadi, S.I.; Kong, J.; Lu, X. Aqueous-only, green route to self-healable, UV-resistant, and electrically conductive polyurethane/graphene/lignin nanocomposite coatings. *ACS Sustain. Chem. Eng.* 2017, *5*, 3148–3157. [CrossRef]
- Erakovic, S.; Jankovic, A.; Tsui, C.G.; Tang, C.; Miskovic-Stankovic, V.; Stevanovic, T. Novel bioactive antimicrobial lignin containing coatings on titanium obtained by electrophoretic deposition. *Int. J. Mol. Sci.* 2014, 15, 12294–12322. [CrossRef]
- 32. Vagin, M.Y.; Trashin, S.A.; Karyakin, A.A. Corrosion protection of steel by electropolymerized lignins. *Electrochem. Commun.* **2006**, *8*, 60–64. [CrossRef]
- 33. Chen, Q.; de Larraya, U.P.; Garmendia, N.; Lasheras-Zubiate, M.; Cordero-Arias, L.; Virtanen, S.; Boccaccini, A.R. Electrophoretic deposition of cellulose nanocrystals (CNs) and CNs/alginate nanocomposite coatings and free standing membranes. *Colloids Surf. B* **2014**, *118*, 41–48. [CrossRef]
- 34. 316/316L Stainless Steel; Product Data Bulletin; AK Steel Corporation: West Chester, OH, USA, 2016.
- Alonso Frank, M.; Meltzer, C.; Braunschweig, B.; Peukert, W.; Boccaccini, A.R.; Virtanen, S. Functionalization of steel surfaces with organic acids: Influence on wetting and corrosion behavior. *Appl. Surf. Sci.* 2017, 404, 326–333. [CrossRef]
- 36. Rossberg, C.; Janzon, R.; Saake, B.; Leschinsky, M. Effect of process parameters in pilot scale operation on properties of organosolv lignin. *BioResources* **2018**, submitted.
- 37. Ragauskas, A. Typical H:G:S Ratio for Lignin from Biomass. Available online: http://biorefinery.utk.edu/ technical_reviews/lignin%20HGS.pdf (accessed on 18 October 2018).
- Lê, H.Q.; Zaitseva, A.; Pokki, J.; Ståhl, M.; Alopaeus, V.; Sixta, H. Solubility of organosolv lignin in γ-valerolactone/water binary mixtures. *ChemSusChem* 2016, *9*, 2939–2947. [CrossRef]
- 39. Kokubo, T.; Takadama, H. How useful is SBF in predicting in vivo bone bioactivity? *Biomaterials* **2006**, 27, 2907–2915. [CrossRef]
- 40. *Annual Book of ASTM Standards, Wear and Erosion, Metal Corrosion (03.02);* ASTM International: West Conshohocken, PA, USA, 1993.
- 41. EN ISO 2409:2013 Paints and Varnishes—Cross-cut Test; ISO: Geneva, Switzerland, 2013.
- 42. Hansen, A.T.M.; Hidayat, J.B.; Mogensen, K.K.; Jeppesen, D.M.; Jorgensen., B.; Johansen, S.K.; Thygesen, G.L. Enzyme affinity to cell types in wheat straw (*Triticum aestivum* L.) before and after hydrothermal pretreatment. *Biotechnol. Biofuels* **2013**, *6*, 54. [CrossRef]
- Brodin, I. Chemical Properties and Thermal Behaviour of Kraft Lignins. Licentiate Thesis, KTH, Stockholm, Sweden, 2009.
- 44. Pandey, K.K. A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy. *J. Appl. Polym. Sci.* **1999**, *71*, 1969–1975. [CrossRef]
- 45. Fengel, D.; Wegener, G. Wood: Chemistry, Ultrastructure, Reactions; Walter de Gruyter & Co.: Berlin, Germany, 1989.

- 46. Kline, L.M.; Hayes, D.G.; Womac, A.R.; Labbe, N. Simplified determination of lignin content in hard and soft woods via uv-spectrophotometric analysis of biomass dissolved in ionic liquids. *BioResources* **2010**, *5*, 1366–1383.
- 47. Malherbe, F.E.; Bernstein, H.J. The infrared and Raman spectra of p-dioxane. *J. Am. Chem. Soc.* **1952**, *74*, 4408–4410. [CrossRef]
- 48. Zhang, Z. Lignin Modification and Degradation for Advanced Composites and Chemicals. Ph.D. Thesis, Georgia Institute of Technology, Atlanta, GA, USA, 2017.
- 49. Notley, M.S.; Norgen, M. Surface energy and wettability of spin-coated thin films of lignin isolated from wood. *Langmuir* **2010**, *26*, 5484–5490. [CrossRef]
- 50. Liukkonen, A. Contact angle of water on paper components: Sessile drops versus environmental scanning electron microscope measurements. *Scanning* **1997**, *19*, 411–415. [CrossRef]
- 51. Young, R.A. Wettability of wood pulp fibers applicability of methodology. Wood Fibers Sci. 1976, 8, 120–128.
- 52. Yang, Q.; Pan, X. Correlation between lignin physicochemical properties and inhibition to enzymatic hydrolysis of cellulose. *Biotechnol. Bioeng.* **2016**, *113*, 1213–1224. [CrossRef]
- 53. Deflorian, F.; Fedrizzi, L. Adhesion characterization of protective organic coatings by electrochemical impedance spectroscopy. *J. Adhes. Sci. Technol.* **1999**, *13*, 629–645. [CrossRef]
- 54. Metallic Materials. *Handbook of Materials for Medical Devices;* Davis, J.R., Ed.; ASM International: Materials Park, OH, USA, 2003; p. 21.
- 55. Deng, Y.; Bai, W.; Chen, J.; Zhang, X.; Wang, S.; Lin, J.; Xu, Y. Bio-inspired electrochemical corrosion coatings derived from graphene/natural lacquer composites. *RSC Adv.* **2017**, *7*, 45034–45044. [CrossRef]
- 56. Kim, J.Y.; Hwang, H.; Oh, S.; Kim, Y.S.; Kim, U.J.; Choi, J.W. Investigation of structural modification and thermal characteristics of lignin after heat treatment. *Int. J. Biol. Macromol.* **2014**, *66*, 57–65. [CrossRef]
- 57. Boeriu, C.G.; Bravo, D.; Gosselink, R.J.A.; Van Dam, J.E.G. Characterization of structure-dependent functional properties of lignin with infrared spectroscopy. *Ind. Crops Prod.* **2004**, *20*, 205–218. [CrossRef]
- 58. Anaee, R. Corrosion Behavior of Some Implant Alloys in Simulated Human Body Environment. Master's Thesis, Iraq University of Technology, Baghdad, Iraq, 2010.
- 59. Dariva, C.G.; Galio, A.F. Corrosion inhibitors-principles, mechanisms and applications. In *Developments in Corrosion Protection;* Aliofkhazraei, M., Ed.; InTech: Vienna, Austria, 2014; p. 365.
- 60. Altweiq, A.M.; Khouri, S.J.; Al-luaibi, S.; Lehmann, R.; Drucker, H.; Vogt, C. The role of extracted alkali lignin as corrosion inhibitor. *J. Mater. Environ. Sci.* **2011**, *2*, 259–270.
- 61. Yahya, S.; Othman, N.K.; Daüd, A.R.; Jalar, A. Surface morphology studies of low carbon steel treated in aqueous lignin. *Sains Malays.* **2013**, *42*, 1793–1798.
- 62. Bryant, M.; Hu, X.; Farrar, R.; Brummitt, K.; Freeman, R.; Neville, A. Crevice corrosion of biomedical alloys: A novel method of assessing the effects of bone cement and its chemistry. *J. Biomed. Mater. Res.* **2013**, 101, 792–803. [CrossRef]
- 63. Kim, S.; Lee, J.; Kim, J.; Kim, W. Effect of the crevice former on the corrosion behavior of 316L stainless steel in chloride-containing synthetic tap water. *Met. Mater. Int.* **2018**, *24*, 516–524. [CrossRef]
- 64. Gonzalez-Garcia, Y.; Gonzalez, S.; Souto, R.M. Electrochemical and structural properties of polyurethane coating on steel substrates for corrosion protection. *Corros. Sci.* **2007**, *49*, 3514–3526. [CrossRef]



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).