Performance of Lignin as a Sustainable Anticorrosion Coating

Arman Dastpak
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Abstract

Synthetic polymers play a pivotal role in many industrial applications that includes their utilization as barrier coatings for corrosion protection of metal surfaces. However, use of such non-renewable coatings results in environmental pollution both during production and use. As such, there is a global effort to find/produce more sustainable metal coatings from renewable resources including biomass-based polymers. Consequently, this thesis investigates the performance of technical lignin—a primary waste from biomass processing industries—as an organic binder in anticorrosion coatings, with a focus on the industrial applicability of these materials and associated deposition techniques.

Electrochemical properties of stainless steel spin-coated with two different organosolv lignin (dissolved in 1,4-Dioxane) were investigated. Results showed that the coatings enhanced the resistance of surfaces against corrosion with a lignin source-dependent variation of the barrier properties. In order to address the limited lignin solubility in many organic solvents, the screening of a series of industrially-applicable organic solvents was undertaken. Findings indicated that two solvents—diethylene glycol monobutyl ether (DEGBE) and propylene glycol monomethyl ether (PGME)—act as strong solvents for a kraft and an organosolv lignin, and that DEGBE also has a plasticizing effect on lignin. However, electrochemical analysis of lignin-coated steel prepared from PGME following prolonged immersion (24 hours) in 5 wt.% NaCl, showed that these coatings offer limited protection. Furthermore, cracking of lignin-PGME coatings was observed, which was found to be mitigated by addition of triethyl citrate (TEC) as a plasticizer.

An alternative and more environmentally benign route for the preparation of lignin-based coatings was further achieved by the preparation of aqueous dispersions of colloidal lignin particles (CLPs) using DEGBE as the starting solvent in a solvent-exchange procedure. Consequently, it was possible to prepare combined lignin-cellulose composite coatings using electrophoretic deposition (EPD) from aqueous dispersions at low deposition potentials, and resulted in coatings with enhanced durability during long term immersion (15 days) in 3.5 wt.% NaCl electrolyte. An important outcome of this process was the coalescence of CLPs during drying—as a result of the DEGBE—that enabled the formation of compact coatings. Such techniques and coalescing characteristics could be exploited in the preparation of water-borne lignin layers with enhanced corrosion protection capabilities as part of a future fully sustainable coating formulation.

Keywords Lignin; Organic coating; Steel; Corrosion protection
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Espoo, November 2021
Arman Dastpak
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<tbody>
<tr>
<td>$^{13}$C NMR</td>
<td>Carbon-13 nuclear magnetic resonance</td>
</tr>
<tr>
<td>$^{31}$P NMR</td>
<td>Phosphorus-31 nuclear magnetic resonance</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated total reflectance Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>BP</td>
<td>Boiling point</td>
</tr>
<tr>
<td>CCD</td>
<td>Corrosion current density (mA·cm$^{-2}$)</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td><em>cf.</em></td>
<td>Conferatur (as compared)</td>
</tr>
<tr>
<td>CLPs</td>
<td>Colloidal lignin particles</td>
</tr>
<tr>
<td>COO$^-$</td>
<td>Carboxylate anion</td>
</tr>
<tr>
<td>COOH</td>
<td>Carboxyl functional group</td>
</tr>
<tr>
<td>D [4,3]</td>
<td>Volume mean diameter</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DEGBE</td>
<td>Diethylene glycol monobutyl ether</td>
</tr>
<tr>
<td>DI</td>
<td>De-ionized</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>DoC</td>
<td>Degree of condensation</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td><em>e.g.</em></td>
<td>Exempli gratia (for example)</td>
</tr>
<tr>
<td>EC</td>
<td>Equivalent circuit</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EPD</td>
<td>Electrophoretic deposition</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>f</td>
<td>Frequency (Hz)</td>
</tr>
<tr>
<td>GDP</td>
<td>Gross domestic product</td>
</tr>
<tr>
<td>H</td>
<td>ρ-hydroxyphenyl (monolignol)</td>
</tr>
<tr>
<td>HDG</td>
<td>Hot-dip galvanized (steel)</td>
</tr>
<tr>
<td>HOL</td>
<td>Hardwood organosolv lignin</td>
</tr>
<tr>
<td>HPLC</td>
<td>High-performance liquid chromatography</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>i.e.</td>
<td>Id est (that is)</td>
</tr>
<tr>
<td>ISO</td>
<td>International organization for standardization</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
</tr>
<tr>
<td>M</td>
<td>Molarity (mol·L$^{-1}$)</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number average molecular weight</td>
</tr>
<tr>
<td>MPa</td>
<td>Megapascal</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight average molecular weight</td>
</tr>
<tr>
<td>$N_2$</td>
<td>Nitrogen gas</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium chloride</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>OH</td>
<td>Hydroxyl functional group</td>
</tr>
<tr>
<td>OM</td>
<td>Optical microscopy</td>
</tr>
<tr>
<td>OMe</td>
<td>Methoxyl functional group</td>
</tr>
<tr>
<td>PBS</td>
<td>Phosphate buffered saline</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity index</td>
</tr>
<tr>
<td>PGME</td>
<td>Propylene glycol monomethyl ether</td>
</tr>
<tr>
<td>pH</td>
<td>Power of hydrogen</td>
</tr>
<tr>
<td>PhOH</td>
<td>Phenolic hydroxyl group</td>
</tr>
<tr>
<td>$R_c$</td>
<td>Coating resistance [Ω·cm$^2$]</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>charge transfer resistance [Ω·cm$^2$]</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>RMB</td>
<td>Renminbi (Chinese Yuan currency)</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>S</td>
<td>Syringyl (monolignol)</td>
</tr>
</tbody>
</table>
SEM  Scanning electron microscopy
SiC  Silicon carbide
SKL  Softwood kraft lignin
SOL  Softwood organosolv lignin
SS 316L  Stainless steel AISI 316L alloy
TEC  Triethyl citrate
T\textsubscript{g}  Glass transition temperature (°C)
THF  Tetrahydrofuran
TOCN  TEMPO-Oxidized cellulose nanofibrils
VOC  Volatile organic compound
vs.  Versus
WE  Working electrode
Wt.%  Weight percentage
Z  Impedance modulus (Ω)
Zn\textsuperscript{2+}  Divalent zinc cation
ZnO  Zinc oxide
δ\textsubscript{h}  Hansen’s hydrogen bonding interaction parameter (MPa\textsuperscript{1/2})
δ\textsubscript{p}  Hansen’s polar interaction parameter (MPa\textsuperscript{1/2})
ζ  Zeta (potential)
Ω  Ohm
This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their Roman numerals

I. Dastpak, Arman; Yliniemi, Kirsi; Monteiro, Mariana Cecilio de Oliveira; Höhn, Sarah; Virtanen, Sannakaisa; Lundström, Mari; Wilson, Benjamin, P. *From Waste to Valuable Resource: Lignin as a Sustainable Anti-Corrosion Coating*. Coatings, 2018, 8 (12), 454. DOI: 10.3390/coatings8120454.


IV. Dastpak, Arman; Ansell, Philip; Searle, Justin, R; Lundström, Mari; Wilson, Benjamin, P. *Biopolymeric Anticorrosion Coatings from Cellulose Nanofibrils and Colloidal Lignin Particles*. Applied Materials & Interfaces, 2021, 13 (34), DOI: 10.1021/acsami.1c08274.
Author’s Contribution

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

B.P.W. conceived and designed the experiments and A.D. alongside with K.Y., M.C.d.O.M., S.H. and B.P.W. conducted the experimental work. The formal analysis of data was achieved by A.D., K.Y., S.H., S.V., and B.P.W. The writing of original draft was done by A.D., K.Y., and B.P.W. and all others took part in the reviewing, editing, and approving the final manuscript. Funding acquisition and supervision was provided by B.P.W. and M.L.

Publication II) Solubility study of lignin in industrial organic solvents and investigation of electrochemical properties of spray-coated solutions

A.D. and B.P.W. conceived and designed the experiments and A.D. conducted the experimental work, except NMR spectroscopy studies that was conducted by T.V.L and M.B., and GPC analysis by SF.H. The formal analysis of data was achieved by A.D., T.V.L., M.B., and SF.H. The writing of original draft was done by A.D. with the assistance of T.V.L. and M.B. All authors took part in the reviewing, editing, and approving the final manuscript. The conceptualization, funding acquisition and supervision was provided by B.P.W. and M.L.

Publication III) A sustainable two-layer lignin-anodized composite coating for the corrosion protection of high-strength low-alloy steel

A.D. and P.H. conceived and designed the experiments and conducted the experimental work, analysis of data and the writing of original draft. All authors took part in reviewing, editing, and approving the final manuscript. The conceptualization, funding acquisition and supervision was provided by B.P.W. and M.L.

Publication IV) Biopolymeric Anticorrosion Coatings from Cellulose Nanofibrils and Colloidal Lignin Particles

A.D. conceived and designed the experiments and conducted the experimental work, except SVET analysis that was conducted by P.A. and J.R.S. The formal analysis of data was conducted by A.D. with the assistance of P.A., J.R.S., and B.P.W. The writing of original draft was undertaken by A.D. with the assistance of P.A. All authors took part in reviewing, editing, and approving the final manuscript. Funding acquisition and supervision was provided by B.P.W. and M.L.
1. Introduction

1.1 Background

Corrosion is an inevitable phenomenon that occurs unceasingly for (almost) all metals and alloys. If not mitigated, it affects the functionality and performance of metals used in engineering applications or infrastructure present in our everyday lives. Its occurrence, not only induces damage to society and the environment, but is also an economically costly phenomenon [1]. The direct cost of corrosion in the United States (in 2013) was estimated to be 2.7% of the total gross domestic product (GDP, equivalent to 451.3 billion US dollars) [2], and about 3.3% of GDP for China (in 2014, about 2128 billion RMB) [3]. Considering that 15–35% of these values could be reduced by proper mitigation strategies [3], it is clear that corrosion protection is a significantly important topic for both industry and academia.

Organic coatings are the most common used method for the protection of metallic surfaces. By forming a homogenous and adhesive layer on the metal surface, organic coatings perform as a barrier that minimizes the substrate’s contact with the surrounding environment [4]. Furthermore, owing to their diverse chemistry, organic coatings potentially provide a matrix for the introduction of additional functionalities (organic or inorganic additives such as pigments, corrosion inhibitors, hardening and drying agents, surface activating compounds, to name but a few [5]), further enhancing their performance and popularity. Nevertheless, the production and utilization of organic coatings are associated with various adverse effects on the environment. For example, production of many traditional organic coatings depends on finite petro-chemical resources [6], they generally contain organic solvents and monomers that contribute to emission of volatile organic compounds (VOCs) [7], and their wear (e.g., through exposure to the elements like rain and sun) contributes to the accumulation of microplastics in terrestrial and aquatic environments with the associated issues for planetary life [8, 9]. Such adverse effects are the ultimate driving force for the development of biomass-based products to simultaneously minimize the pollutive characteristics and the overall carbon footprint of organic coatings.

Lignin—identified alongside cellulose as a separate structural component of wood in 1838 [10]—is the second largest naturally occurring polymer on earth [11]. Unlike cellulose that is a long-established substance for use in industrial products [12], lignin has typically been considered as a cheap waste, yet to find its value as a source material in industrial production processes. As the main
by-product of pulp and paper industries and cellulosic biorefineries, lignin is conventionally incinerated as a source of energy and generally has a low economic value [13–15]. Nevertheless, with the increasing availability of technical lignin on one hand, as well as the economic and environmental credentials of lignin-based products on the other [14, 16], it is necessary to evaluate the lignins’ functionality in a host of different plausible applications. It is within this context that this compendium aims to provide information on the application and performance of technical lignin as a surface coating for corrosion protection of steel.

1.2 Objectives and scope

The utilization of lignin as a raw material for the preparation of anticorrosion coatings has not been widely investigated, although the core of this research is inspired by previous studies that have demonstrated the performance of lignin as a corrosion inhibitor [17–20]. Considering the potential value of lignin as a cheap, readily available, and renewable resource, the primary objective of this thesis was to evaluate the applicability of technical lignin as a generic coating in corrosion protection applications, with a focus on utilization of raw materials and deposition techniques that are applicable to current industrial processes. It is clear that the economic advantage of lignin as a cheap and sustainable resource could be only realized if valorization is not based on extensive chemical modification, as this could dramatically alter the economic feasibility of a (hypothetical) lignin-based product [21]. In this context, the chemical modification of lignin was outside the scope of this research.

The main objectives of this work can be defined as follow:

1. To determine the anticorrosive properties of spin-coated lignin coatings in physiological solutions as a plausible coating for protection of a metallic implant. (Publication I)

2. To investigate the dissolution of a softwood kraft lignin (SKL) and a hardwood organosolv lignin (HOL) in industrial organic solvents, and to evaluate the effect of solvents on the properties of spray-coated lignin layers. (Publication II)

3. To evaluate the applicability of triethyl citrate (TEC) as an environmentally benign plasticizer in high-solid SKL coatings. (Publication III)

4. To develop aqueous-based coatings by preparation of colloidal lignin particles (CLPs) and its simultaneous electrophoretic deposition with TEMPO-Oxidized cellulose nanofibrils (TOCN) onto hot-dip

---

1 Current production of lignin is about 100 million tonnes/year and is estimated to rise by 225 million tonnes/year in 2030 [14].

2 Technical lignin refers to the final form of lignin, obtained after a series of biomass processing steps. Depending on the isolation process, these lignin are classified into various types including lignosulfonates, Kraft and Organosolv lignin [13].
Introduction

Figure 1 outlines the relationship between the different areas explored in this compendium. In publication I–III, the focus was on the preparation of lignin coatings from organic solutions, while publication IV investigated an alternative route for the preparation of lignin-cellulose composite coatings from an aqueous dispersion. To further maximise the environmental benefits of lignin use, the amounts of organic-based solvent utilized to produce the coatings was decreased by either increasing the solid-content of lignin (Publications I–III), or by preparation of aqueous dispersions with minimized VOC content (Publication IV). Furthermore, the applicability of deposition method and the utilized materials for up-scaled processes were also considered. It is worth mentioning that except in publication I, which investigated the coatings’ performance for protection of a metallic implant in a physiological buffer solution, the coatings’ application area (e.g., as a direct-to-metal or a primer) were not explicitly considered in publication II–IV.

Figure 1. Relationship between the stated objectives and the publications presented in the thesis.

1.3 New scientific contribution and applications

This compendium, for the first time, investigates the valorization of technical lignin as the basis of an anticorrosive system for steel substrates, and explores various aspects relevant to the performance of lignin as a coating. The following research outcomes are believed to comprise the original findings present within this thesis:

1. The corrosion protection capability of lignin as a surface coating for stainless steel and its functionality in enhancing the corrosion resistance of immersed substrates was demonstrated for the first time. Furthermore, it was shown that the protection performance of coatings is affected by selection of the source material (Publication I, relating to Objective 1).

2. Solubility of lignin in several industrial organic solvents was investigated and two types of solvents—propylene glycol monomethyl ether (PGME) and diethylene glycol monobutyl ether (DEGME)—were discovered to be
excellent lignin solvents with strong solvating power. Moreover, the influence of the utilized solvents on the properties of spray-coated lignin coatings were demonstrated for the first time (Publication II, relating to Objective 2).

3. Performance of triethyl citrate (TEC) as a plasticizer for a high-solid content lignin coating was determined (Publication III, relating to Objective 3).

4. An aqueous dispersion of colloidal lignin particles (CLPs) was prepared from DEGBE solvent and was co-deposited with TEMPO-Oxidized cellulose nanofibrils (TOCN) using electrophoretic deposition (EPD). It was shown that a fully biopolymeric coating demonstrates prolonged protection performance against the corrosion of hot-dip galvanized (HDG) steel in 3.5 wt.% NaCl. The three novel findings from this study were the utilization of DEGBE for preparation of CLPs, co-deposition of CLPs and TOCN using the EPD method and demonstration of the anti-corrosive functionality of cellulose-lignin composite coatings. None of these findings have been reported previously in the literature (Publication IV, relating to Objective 4).

1.4 Structure of thesis

This thesis consists of four scientific peer-reviewed journal publications (I–IV) alongside the present compendium, and the publications are attached in the Appendices. Chapter 2 briefly presents the theoretical background on fundamental aspects of corrosion protection by organic coatings, on aspects relevant to lignin’s interaction with organic solvent, on lignin’s utilization as a polymer and its applicability in corrosion protection. The experimental methods and procedures used in publications I–IV are described in chapter 3. In chapter 4, the main findings are divided into three sections, the initial section provides the proof of concept for the anticorrosive performance of lignin coatings (Publication I), the second covers different aspects of lignin coatings prepared from organic solutions (Publications II–III) and the third section covers lignin-cellulose composites prepared from aqueous dispersions (Publication IV). Chapter 5 outlines the recommendations for future work and open research questions relevant to the utilization of lignin as anticorrosive coatings, and chapter 6 outlines the main conclusions of this thesis.
2. Fundamentals

It is essential to begin this chapter with a brief outline of the principal reactions that occur during the corrosion of a ferrous metal. Consider a scenario where iron is immersed in a neutral aqueous solution that contains oxygen; On immersion an electrochemical cell forms at the water/metal interface, which is constituted of anodic and cathodic reactions, as respectively described in Equations (1) and (2) [22]:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2 \, \text{e}^{-} \quad (1)
\]

\[
\text{O}_2 + 2 \, \text{H}_2\text{O} + 4 \, \text{e}^{-} \rightarrow 4 \, \text{OH}^{-} \quad (2)
\]

The ions liberated from these reactions (\(\text{Fe}^{2+}\) and \(\text{OH}^{-}\)) react to form a ferrous hydroxide, according to Equation (3):

\[
\text{Fe}^{2+} + 2 \, \text{OH}^{-} \rightarrow \text{Fe} (\text{OH})_2 \quad (3)
\]

Given sufficient time and oxygen, ferrous hydroxide converts to \(\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}\), forming the “red rust” layer, typically observed on the surface of corroded iron. The overall reaction for this transformation is described in Equation (4):

\[
4 \, \text{Fe} (\text{OH})_2 + \text{O}_2 \rightarrow 2 \, \text{Fe}_2\text{O}_3 + 4 \, \text{H}_2\text{O} \quad (4)
\]

Note that, this is a simplified scheme for the corrosion and the nature of oxide layer generally depends on the oxidation state of iron, amongst other parameters like surface composition/alloying elements, electrolyte nature and concentration, as well as temperature [22].

Nevertheless, the above equations highlight that these reactions cannot initiate without the presence of water and the oxidant (\(\text{O}_2\) in this case) and does not proceed without the transfer of ions between the anodic and cathodic reaction sites (\(i.e.,\) ionic charge flow). Additionally, the rate of corrosion is always determined by the kinetics of the slowest reaction (either anodic or cathodic). Consequently, the suppression of either the anodic or cathodic reaction, alongside the limitation of ion transfer, are amongst the fundamental steps available to corrosion engineers to minimise metals degradation [22–24].
2.1 Corrosion protection mechanisms of organic coatings

Traditionally, the protection capability of organic coatings was believed to originate from the physical barrier properties, which mitigated the permeation of water and oxygen to the coating-metal interface, thereby inhibiting the cathodic oxygen reduction reaction (Equation 2). In a study by Mayne [25], it was demonstrated that the permeation of both O₂ and H₂O in common organic coatings is sufficiently high, thus their ability to resist permeation is not a determining factor in corrosion rate of the underlying substrate surface. It was, subsequently, suggested that the ionic resistance in organic coatings is responsible for limiting the corrosion reactions by restricting the ionic charge flow between the local reaction sites that occurs through the solution [24, 26]. Figure 2 illustrates the general scheme for this protection mechanism, when a corrosion cell forms in a coated metallic surface, and how the resistance of the coating in anodic/cathodic regions limit the charge transfer. Naturally, this is only the case when the anodic and the cathodic regions are not formed in the same proximity.

Another protection mechanism in organic coatings originates from their ability to incorporate “inhibitive pigments”, which can be of importance for extending the long-term protection performance of a coating (e.g., due to aging/in-service coating damage). When an active corrosion cell forms at the covered surface, the function of the inhibitor is to limit the rate of electrochemical reactions [4]. This is generally achieved by manipulation of the affected interface (in some cases the electrolyte) to subsequently suppress the anodic and/or cathodic reaction sites, and through several different mechanisms. The most common example for this class (e.g., inorganic pigments) was chromate-based corrosion inhibitors [28], which were capable to passivate metal surfaces through forming adherent oxide/hydroxides that resisted the further dissolution of the corroding surface [29].

Coating homogeneity is also a vital characteristic for a reliable protection performance. In addition to the role of structural discontinuities (e.g., pores or “holidays”) in coating networks [30], it is accepted that the variations in the degree of cross-linking provide loci for the initiation of corrosion and enhance the ionic ingress through the network [4, 31, 32].
Fundamentals

Coatings’ wet adhesion (i.e., the adhesion after permeation of water to the coating-metal interface) could also be mentioned as an important property of an organic coating [33], although its importance in protection performance of coatings is widely debated [4, 31, 34]. Whereas Funke [33] emphasizes that the wet adhesion is a key factor that determines the long-term protective performance of coatings, Mayne and others believe that the importance of wet adhesion is inferior to that of coating resistance against ionic charge transfer and ionic pathways evolution [4]. Nevertheless, the water-uptake in a coating also enhances the ionic diffusion through the coating network and thus, is generally considered to be an undesirable phenomenon [35, 36].

2.2 Lignin as a biopolymer

Lignin is the most abundant aromatic polymer that is biosynthesized in vascular plants and typically constitutes 15–30% of the dry weight in lignocellulosic biomass [11]. As one of the three main components in a cell wall, lignin provides a water barrier to polysaccharide components and its phenolic structure enhances the cell wall rigidity [37, 38]. Structurally, lignin has a three-dimensional heterogeneous network of phenylpropane units (monolignols), mainly p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units that are linked together through various C–C and C–O bonds, as illustrated in Figure 3 [39]. The relative ratio of these units is predominantly a function of plant species, although the composition and quantity of lignin in an individual species can vary as a function of age or the location of the tissue [39, 40]. For example, hardwood lignin is generally composed of S and G units (SG type), while softwood is mainly composed of G units [41]. These variations in the content of monolignols influence the structure of lignin, for example, the extent of the inter- and intramolecular condensation reactions [42].
In addition to the source-dependent structural difference of various lignins, the isolation of lignin from a woody biomass alters—to a different extent depending on the process and its severity [43]—the nature of the linkages and abundance/presence of functional groups (thus inducing additional heterogeneity within the resultant lignin), which further complicates the up-scaled valorization possibilities for technical lignin [44, 45]. For example, kraft lignins are obtained through a relatively severe isolation process and usually contain sulfur-based impurities, while ethanol-based organosolv lignins usually contain EtO-groups and have high purities [39, 43].

2.3 Lignin interaction with organic solvents

One of the very first systematic (and recorded) study of lignin-organic solvents interaction goes back to 1952 [46]. This research clarified that solvents with a Hildebrand solubility parameter around 22.5 MPa$^{1/2}$ demonstrate a good performance for dissolving lignin, and that the lower molecular weight fractions of lignin are soluble in solvents with a wider range of solubility parameters. Furthermore, a direct relationship was established for enhancement of solvents’ power (with comparable solubility parameters) as a function of hydrogen bonding capability [46]. Later on, Hansen solubility parameters were considered for lignin dissolution and it was demonstrated that solvents’ polarity and hydrogen bonding capability are indeed important characteristics for lignin solvation [47–52]. Nevertheless, lignins’ structural characteristics such as the monolignols’ ratio and the content of functional groups, alongside the molecular weights
and polydispersity index (PDI) also affect the lignins’ solubility in organic solvents [53, 54].

Lignin-solvent interactions are also important in solvent fractionation procedures, in which lignin is separated into fractions with more homogenous molecular weights [55]. This process is based on the partial solubility of lignin in different organic solvents with varying solubility parameters [47]. For example, in sequential fractionation procedures, lignin is first dissolved in a weak lignin solvent that separates the low molecular fraction of the starting sample and consequently the residue (i.e., the insoluble fraction) is dissolved in a stronger lignin solvent [56–58]. As such, increasing the solvent’s power (i.e., a result of solvent’s polarity and hydrogen bonding capability) results in dissolution of lignin fractions with higher molecular weights and often a higher polydispersity index [52, 57–59]. Furthermore, the higher molecular weight fractions are generally associated with a higher glass transition temperatures (T_g), and the content of functional groups also differs in the resultant fractions [52, 57, 60, 61]. However, due to the inherent differences in various lignins—in addition to the effect of solvent on the functional groups present in different fractions [52, 60]—it is not possible here to provide a general trend as to the content of functional groups in different fractions.

Lignin-solvents interactions are also pertinent to the solvent-shifting (or nanoprecipitation) procedures utilized in formation of colloidal lignin particles (CLPs) [62]. This method is based on the self-assembly of colloidal lignin particles upon the addition of a lignin-containing solution (i.e., a water-miscible organic solvent)—or that of a binary solvent-water mixture—to an anti-solvent phase (commonly water) [63]. This method is particularly appealing for the preparation of spherical micro-/nanoparticles from technical lignin, as such particles generally demonstrate a hydrophilic characteristic. Such hydrophilicity originates from the formation mechanism of particles where the large molecular weight fractions (most hydrophobic and less polar molecules) participate in the nucleate formation, and the growth of particles is through the adsorption of low molecular weight fraction (i.e., enriched with hydrophilic moieties such as carboxyl and hydroxyl functional groups [64, 65]). A thorough explanation of CLPs nucleation and growth obtained from different solutions is explained in a recent work, highlighting the contribution of the solvent on the characteristics of the prepared particles [62]. Nevertheless, the presence of a hydrophilic shell not only provide an available site for the physical/chemical modification of CLPs [63], but also could be exploited in a (hypothetical) latex coating (i.e., from a water-borne dispersion of particles with a coalescing characteristic) where the presence of a particle shell with a lower T_g could facilitate the film-formation at lower temperatures [66, 67].

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3 As the low molecular fractions are more soluble in organic solvents with a wider range of solubility parameters [46].
2.4 Lignin-based polymers

As mentioned earlier, a typical coating is constituted of various components including binder, pigment and additives [66]. In the context of this compendium, lignin was investigated solely as a binder, which is responsible for film-formation and the adhesion to a substrate and components of a coating [66], although its functionality as a barrier nanofiller [68] or as spherical particles with self-healing characteristics [69]—incorporated in an epoxy matrix—has been demonstrated. Nevertheless, to realize lignin as an organic coating’s binder it is necessary to provide a baseline for comparison with synthetic counterparts.

A traditional way to categorize synthetic polymers is through their classification as a thermoplastic or a thermoset. In thermoplastics, the polymer molecules (or individual chains) do not form strong chemical bonds (i.e., often irreversible) and thus when heated individual molecules could flow, which results in the softening of the bulk thermoplastic material. Conversely, when the individual molecules are capable to form a chemical bond (often by addition of a second component), the bulk material hardens to form a three-dimensional network. This group are categorized as a thermoset and cannot be re-processed after the hardening stage [70]. Applying this to organic coatings, the film-formation in a thermoplastic coating occurs (after the evaporation of the solvent) through arrangement of molecules/chains on the surface. This differs from that of a thermoset coating that occurs in a comparable manner, although proceeds with the formation of chemical bonds between the molecules. An exception to this classification is latex coatings, where the coalescence of individual insoluble particles on the applied surface prompts the formation of a continuous film, which may or may not involve the formation of chemical bonds [66, 71].

Concerning a lignin-based polymeric network, thermoset or thermoplastic categories do not strictly apply. This is due to the formation of irreversible cross-links in a heat-treated network of lignin [72, 73], and the simultaneous presence of non-covalent intermolecular interaction (such as hydrogen bonding and aromatic interactions) between lignin molecules [74]. The extent of these interactions are generally dictated by the chemistry of the starting material and the solvent system that is used for the preparation of lignin network [75, 76]. Consequently, both lignin-based thermosets and thermoplastics have been reported in the literature [77–79], although generally after a fractionation/chemical modification stage. In thermoplastic blends, chemical modification of lignin is undertaken to achieve an enhanced miscibility with other components and to improve the thermal processibility [80–82], and in thermosetting networks to improve the reactivity of lignin for cross-linking reactions with the synthetic components and to enhance network homogeneity [83–85]. Moreover, solvent fractionation has recently demonstrated great potential for tailoring the properties of lignin-based polymers, which could have relevance for thermosetting networks [86–88].

It should be also noted that the strong interactions of hydroxyl groups of lignin [89], combined with the rigid polyaromatic structure [79], result in a high $T_g$ and brittle characteristic of lignin-based networks. As such, the utilization of
plasticizers (i.e., small molecular weight substances) could decrease $T_g$ and increase the molecular mobility by interfering with interactions between lignin molecules [81].

2.5 Lignin in corrosion protection applications

To date, the application of lignin (as the main component/additive) in anticorrosion coatings, has been the subject of only a handful of studies in the literature. Silanization of THF-soluble fractions of kraft lignin has been conducted for preparation of anticorrosion coatings for aluminium alloys [90]. As an additive, benzotriazole-loaded lignin microspheres were prepared via solvent-exchange before being utilized in an epoxy matrix, which provided a pH-responsive and self-healing coating for the protection of carbon steel [69]. Organosolv lignin was incorporated (up to 1 wt.%) into siloxane-poly(methyl methacrylate) and enhanced multiple functionalities in the subsequent matrix coating [91]. In addition, epoxidized lignin has been synthesized and utilized as a filler (up to 10 wt.%) in an epoxy matrix and enhanced the corrosion protection capability of a coating for carbon steel [92]. Other studies have been based on the addition of Lignosulfonate-modified ZnO in water-based polyurethane coatings [93], lignosulfonate doped polyaniline for epoxy coatings [94], lignosulfonate-based tripolymer in combination with graphene as an additive in a commercial lacquer [95], acid-precipitated lignin nanoparticles as additive (up to 1.5 wt.%) for an epoxy coating [68], and kraft lignin-oleic acid esters as aqueous dispersions that were utilized for the protection of aluminum surface [96]. The best corrosion protection performance reported in the literature was related to a water-borne thermosetting polyurethane coating from an enzymatic hydrolysed lignin (35–53 wt.% of lignin), synthesized via thiol–ene chemistry, which demonstrated exceptional anticorrosion capabilities for carbon steel [97].

Conversely, studies on the utilization of lignin-based corrosion inhibitor are relatively abundant [19, 20, 106, 98–105]. In general, the inhibitive action of organic inhibitors is based on adsorption (physisorption, chemisorption, or mixed-type adsorption) on the metallic surfaces, which usually occurs via the heteroatoms of N, S, P and/or O that are present within the inhibitor molecule [107]. This is similar for lignin, in which the presence of various functional groups (e.g., hydroxyl, carboxyl and methoxyl groups [108]) enables its adsorption on metallic surfaces [107]. It can be generally understood from the available literature that the adsorption of lignin molecules on the surface of metal is predominantly a physical adsorption (i.e., physisorption through electrostatic interactions) and follows the Langmuir adsorption isotherm. Nevertheless, the charge transfer between π-electrons of lignin and the metallic surface has also been claimed to enhance the adsorption characteristics of lignin molecules in some cases [102–104, 106].
3. Experimental methods

This section summarizes the materials, equipment, and methodologies utilized in the preparation and characterization procedures of Publication I–IV, relevant to the dissertation compendium. Extensive details on experimental procedures are to be found in respective publications. The presented procedures cover the methods used in preparation and deposition of lignin from an organic (Publications I–III) or aqueous medium (Publication IV), for the characterization of lignin as a raw material (Publication II), and those that were conducted on the different coating surfaces (Publications I–IV).

3.1 Materials

Studied lignins comprised of a softwood organosolv (SOL) and a hardwood organosolv lignin (HOL) [109], provided by the Fraunhofer Center for Chemical-Biotechnological Processes (CBP, Germany) (Publication I). The latter sample (HOL), alongside a softwood kraft lignin (SKL, BioPiva™ 190, UPM-Kymmene, Finland) were utilized and studied in Publication II. SKL was also the basis of the studies detailed in Publications III and IV. Triethyl citrate (TEC, ≥ 98 %, Sigma-Aldrich, Finland) was used as a plasticizer for lignin (Publication III), and commercial TEMPO-Oxidized cellulose nanofibrils (TOCN gel, 1 wt.% solid concentration, 1.4 mmol COONa·g⁻¹, Cellulose Lab, Canada) were used in the preparation of cellulose-lignin composite coatings (Publication IV).

Metallic substrates used for the deposition of lignin were stainless steel 316L (SS 316L, Publication I), iron-phosphated steel (Q-Lab, USA, Publication II), high-strength low-alloy S355 steel (SSAB, Finland, Publication III) and hot-dip galvanized steel (SSAB, Finland, Publication IV). The preparation of steel surfaces was undertaken by a sequential grinding with SiC paper (grits #80 to #800 in Publication I and #80 to #500 in Publication III, Struers, Denmark). Surfaces relevant to Publications II and IV were not ground/polished. The cleaning of substrates involved sonication in a mixture of ethanol (Etax B ~94 % purity, Altia, Finland) and deionized (DI) water (1:1 ethanol:water, Publication I), or wipe-cleaning with low lint tissues (Light-duty, VWR, Germany) and ethanol (Publication II), or by sonication in pure ethanol and a subsequent rinsing step with DI water (Publications III–IV). The resistance of DI water in all experiments was ~15 MΩ·cm.
3.1.1 Solvent-based media

The organic solvent initially investigated was 1,4-Dioxane (99.8 %, Sigma-Aldrich, Germany) at a lignin concentration of 60 g·L\(^{-1}\) (Publication I). Two glycol ether solvents of diethylene glycol monobutyl ether (DEGBE, ≥ 98 %, Sigma-Aldrich, Germany) and propylene glycol monomethyl ether (PGME, ≥ 99.5 %, Sigma-Aldrich, Germany) constituted the media for lignin dissolutions (Publications II–III). In Publication II, the lignin concentration in each solvent was 20 g·L\(^{-1}\) for the study of solubility, and 100 g·L\(^{-1}\) (in both solvents) for the preparation of coatings. In Publication III, a volumetric ratio of 3:1 PGME:DEGBE were mixed before preparation of 400 g·L\(^{-1}\) lignin dissolutions and additionally contained 5 wt.% TEC (vs. the initial weight of lignin) for plasticized samples. In Publication IV, the initial solution of lignin (prior to solvent exchange and formation of CLPs) was obtained in DEGBE at a 150 g·L\(^{-1}\) concentration. Mixing of all organic solutions (Publication I–IV), was achieved by stirring with a fixed rotational speed and duration (300 rpm, 24 hours in Publication I–III and 48 hours in Publication IV).

3.1.2 Aqueous media

Colloidal lignin particles (CLPs) were prepared by solvent exchange through the addition of 5 mL lignin solution (150 g·L\(^{-1}\)) to 50 mL deionized water (Publication IV). The medium for deposition of cellulose-lignin coating consisted of 50 mL CLPs dispersion and 50 mL TOCN suspension with 0.1 wt.% and 0.2 wt.% solid concentrations (a dilution factor of 10 and 5, respectively). The higher concentration of TOCN suspension (0.2 wt.%) was also used in the preparation of reference TOCN coatings/free-standing films (Publication IV).

3.2 Equipment

3.2.1 Preparation of solutions/dispersions and application of coatings

Preparation of lignin solutions was the primary step in all studies. Glass beakers (25 mL to 100 mL) were used in the preparation of organic solutions (Publications I–IV), volumetric flasks (100 mL to 1000 mL) for preparation of aqueous suspensions and dispersions (Publication IV). The mixing of organic solutions (Publications I–IV) and aqueous dispersions (Publication IV) was achieved using a magnetic stirrer (VMS-A, VWR, Germany), while an overhead mixer (with a 4-bladed propeller, IKA R 1345, Germany) was utilized in the preparation of diluted TOCN suspensions (Publication IV). Centrifugation of organic solutions (Publications II–IV) and CLPs dispersions (Publication IV) was done by Heraeus Megafuge (ThermoFisher Scientific, Germany). The deposition of coatings was achieved by a spin-coater (Laurell Technologies, USA, Publications I & III), by an air-assisted spray gun (Satajet 20 B, Germany, Publication II) or by a potentiostat (IviumStat.XRe, the Netherlands) for electrophoretic deposition (Publication IV). A universal drier (UN30, Memmert, Germany) was used for the drying/curing of coatings (Publications I–IV).
3.2.2 Characterization of lignin

Characterization of chemical compositions (Publication II) utilized a furnace (Nabertherm, Germany), an autoclave (Systec D-23, Finland), filtering crucibles (1G3, PYREX™), and a spectrophotometer (Shimadzu UV-2550, Japan). For the molecular weight measurements (Publication II), a high-performance liquid chromatography instrument (HPLC, 1100 series, Agilent, Sweden) with polymer standards service (PSS, Germany) columns (pore sizes of 100 Å, 500 Å, and 1000 Å) were used, and the values calculated were obtained using Agilent OpenLab Software. For the nuclear magnetic resonance (NMR) analysis (³¹P NMR and ¹³C NMR, Publication II) a spectrometer (Avance 400 MHz, Bruker, USA) was used. Determination of glass transition temperatures (Tₘ, Publications II–III) was conducted by differential scanning calorimetry (DSC Q2000, TA Instruments, USA). The size measurements of colloidal lignin particles (CLPs, Publication IV) were undertaken by a laser diffraction analyser with a Hydro LV dispersion unit (Mastersizer 3000, Malvern, UK). Morphology of dried CLPs was studied by scanning electron microscopy (SEM, Zeiss Sigma VP, Germany), following SEM surface preparation by a sputter coating instrument (EM ACE600, Leica Microsystems, Germany). The surface charge of biopolymers (Publication IV) in aqueous suspensions/dispersions was characterized by zeta (ζ) potential measurements (Zetasizer Nano ZS90, Malvern, UK). All procedures for the characterization of lignin—except molecular weight measurements and NMR studies—were conducted in triplicate.

3.2.3 Characterization of coating

Electrochemical characterizations on coated surfaces (Publications I, III–IV) were conducted by a potentiostat (IviumStat.XRe, the Netherlands). The wet thickness of coatings was determined using a wet film wheel (Elcometer 3230, UK, Publication II). All surface images (Publications II–IV) were obtained by optical microscopy (OM, Motic BA310Met-t, China), while scanning electron microscopy (SEM, Zeiss Sigma VP, Germany) was used to obtain micrographs from coating surfaces for morphological analysis (Publication IV). For thickness measurements, coating cross-sections were studied by SEM (LEO 1450 VP, Carl Zeiss in Publication I, and Zeiss Sigma VP in Publication IV). Cross-cut adhesion measurements on the coated steel (Publication II & IV) were conducted by a crosshatch cutter (Paint Test Equipment, UK) and an adhesive tape (XA001, Paint Test Equipment, UK). Deposition mass (Publication IV) was determined by gravimetric measurements of the coated and dried surfaces by a high precision balance (XSE202, Metler Toledo, USA). The chemical characteristics of coatings (Publications III–IV) was studied by attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR, Platinum-ATR, Bruker, USA) using a reflection diamond ATR-D cell. All characterization methods used for the different coatings were conducted in triplicate, except for the deposition mass, which was an average value obtained from 10 depositions/sample (Publication IV).
3.3 Methods and procedures

3.3.1 Preparation of coating’s medium and deposition of coatings

Centrifugation was used in the separation of insoluble lignin from organic solution (5000 rpm/4612 g force, 600 seconds) in Publications II–IV, and for the separation of non-stable colloidal particles from CLPs dispersions (2500 rpm/1153 g force, 300 seconds) in Publication IV. Information relevant to the deposition of coatings (Publications I–IV) is summarized in Table 1.

Table 1. Information relevant to deposition parameters used in Publications I–IV.

<table>
<thead>
<tr>
<th>Application method</th>
<th>Publication</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin coating</td>
<td>I</td>
<td>Static dispense, 200 rpm, 300 seconds. Drying at 120 °C for 30 minutes</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>Static dispense, 2000 rpm, 300 seconds. Drying at 50 °C for 48 hours</td>
</tr>
<tr>
<td>Spray coating</td>
<td>II</td>
<td>106 Pa air pressure, 25 cm distance and 90° relative angle. 72 hours ambient drying, followed by drying at 130 °C for 30 minutes</td>
</tr>
<tr>
<td>Electrophoretic deposition</td>
<td>IV</td>
<td>2-electrode setup, potentiostatic deposition at 0.5 V or 3 V. 12 hours ambient drying, followed by drying at 105 °C for 60 minutes</td>
</tr>
</tbody>
</table>

3.3.2 Characterization of lignin

Ash content of lignins were determined by pyrolyzing experiments at 525 °C for 4 hours (Publication II). The acid-soluble, acid-insoluble and carbohydrate content were ascertained following the standard protocol of NREL/TP-510-42618 [110] (Publication II). Molecular weight measurements were carried out using a UV detector at 280 nm (Publication II), with NaOH (0.1 M concentration, 0.7 mL·min⁻¹ flow rate) used as an eluent and a fixed sample volume (50 μL). Calibration curves were obtained with polystyrene sulfonate standards (400 g·mol⁻¹ to 100 g·mol⁻¹) and syringol (154 g·mol⁻¹). NMR characterization of lignin was conducted following previously optimized protocols that are described in the literature for ³¹P NMR [111] and ¹³C NMR [43] (Publication II). The glass transition temperatures (Tgs, Publications II–III) were obtained from ~7 mg of dried samples (72 °C for 48 hours in Publication II, 50 °C for 48 hours in Publication III). Measurements were conducted in a nitrogen (N₂) atmosphere, following a cycle of heating (20 °C to either 190 °C or 200 °C, rate of 10 °C·min⁻¹), hold (200 °C for 5-10 minutes), cooling (0 °C or 10 °C, rate of 10 °C·min⁻¹), and a final heating (190 °C or 200 °C, rate of 10 °C·min⁻¹). Tgs was obtained from the last heating cycle and was defined as the midpoint of the temperature range where changes in the heat capacity occurred [112].

For the size distribution measurements on CLPs (Publication IV), either centrifuged or non-centrifuged dispersions were added to the dispersion unit (agitation rate of 1800 rpm) until a comparable laser obscuration level (~4 %) was reached. The morphology of CLPs was studied by SEM (Publication IV), after placing multiple drops of diluted dispersions (dilution factor of 200) on a clean silicon wafer, followed by immediate drying in a pre-heated oven (180 °C for 30 minutes). Furthermore, a similar procedure for SEM sample preparation was
used for non-diluted CLPs, which were dried at ambient temperature (~21 °C, 30 days). Surface conductivity of SEM samples was achieved by sputtering an iridium layer (~3 nm) on surfaces, and SEM micrographs were obtained using an in-lens detector with an acceleration voltage of 1 kV. Zeta potential measurements (Publication IV) were conducted on ~2 mL diluted dispersions (dilution factor of 50) and the calculation of results was automatically performed by the instrument and based on Smoluchowski theory.

3.3.3 Characterization of coating

Electrochemical characterizations of coated substrates (Publications I–II & IV) were conducted using a three-electrode setup. The counter electrode (CE) was a platinum sheet (Kultakeskus Oy, Finland), and the reference electrode (RE) was an Ag/AgCl-saturated KCl (Publications I–II), which was combined with a platinum wire (Kultakeskus, Finland) in a parallel arrangement (using a 100 nF capacitor) to form a dual-reference electrode (Publication IV). The working electrode (WE) comprised of lignin-coated steel (Publications I–II) or lignin-cellulose composite-coated steel (Publication IV), and blank steel surfaces (Publications I–II and IV). The area of the WE that was exposed to the electrolyte was 0.785 cm² for electrochemical impedance spectroscopy (EIS) measurements (Publications I–II and IV). For EIS measurements (Publications I–II & IV), the electrolyte was either a phosphate buffered saline (PBS, Publication I) or NaCl at a concentration of either 5 wt.% (Publication II) or 3.5 wt.% (Publication IV). PBS electrolyte was prepared by dissolving a pre-formulated tablet (Sigma-Aldrich, Germany) in 200 mL of DI-water. All EIS measurements were conducted over the frequency range of 100 KHz-0.01 Hz, with a signal amplitude of 10 mV_{rms}, and logarithmically spaced frequency points of 10 steps/decade (Publications I–II) or 12 steps/decade (Publication IV). The first data set from the EIS measurements were obtained after 1-hour stabilization of coatings exposed to the electrolyte. Total duration of exposure used in the EIS measurements was either 0–24 hours (Publications I–II) or 0–360 hours (Publication IV). The EIS measurements were conducted either in duplicate (Publication I) or triplicate (Publication I & IV). Quantification of EIS data (Publications IV) was done by equivalent circuit (EC) fitting, using ZView® analysis software (Scribner Associates, USA).

The wet thickness of coatings (Publication II) was obtained by following the ISO 2808-1B standard [113]. Dry thickness of coatings (Publication IV) was determined by cross-sectional SEM micrographs and samples for this analysis were prepared by vertical mounting of coated substrates in an epoxy resin, which after hardening, were cut proximal to the centre of coatings before being sequentially polished with SiC papers (#320 to #1200 grit, Struers, Denmark) and polycrystalline diamond (3 μm and 1 μm, Struers, Denmark). Prior to SEM imaging, samples were cleaned by sonication in ethanol and sputter-coated with either a gold layer (~10 nm, Publication I) or an iridium layer (~3 nm, publication IV) to achieve electrical conductivity. Coating thicknesses from cross-sectional micrographs were determined using an open-source software (ImageJ, National Institutes of Health, USA). The SEM micrographs from differently
EPD treated surfaces (Publication IV) were obtained on dried coatings (Table 1) after sputter coating with an iridium layer (~3 nm).

Adhesion measurements (Publications II & IV) were based on the ISO 2409 standard [114]. Briefly, the crosshatch cutter (6 parallel blades with 1 mm spacing) was applied normal to the surface of coatings, the surface was gently dusted with a brush, and adhesive tape was applied on the coating surfaces. After 5 minutes, the tape was removed at a specific angle (~60°) and the cut area was investigated by optical microscopy. Adhesion values were determined from a coating’s condition proximal to the cut area and was quantified on the scale of 0 (no flaking of coating) to 5 (> 65% flaking of coating).

ATR-FTIR measurements were conducted on the surface of lignin and TEC-plasticized coatings (Publication III), as well as that of TOCN coatings and free-standing films (Publication IV). Surface measurements were performed on surfaces using 24 scans over a spectral range of 4000 cm⁻¹ to 750 cm⁻¹.
4. Results and discussion

Sections 4.1–4.2 highlight the results linked with Objective 1–3 and relate to the lignin coatings that were deposited from lignin-organic solvent solutions. Section 4.1 demonstrates the capability of lignin to act as a corrosion resistant coating in physiological solutions and highlights the effect of lignin source on the corrosion protection of a stainless steel (Objective 1). Section 4.2 details the chemical and structural characteristics of the studied lignins and illustrates the applicability of two organic solvents for the dissolution of lignins and their subsequent effect on the properties of deposited coatings (Objective 2). Additionally, the performance of a plasticizer (triethyl citrate) is illustrated as a part of Section 4.2 (Objective 3). Section 4.3 outlines a process for the preparation of coatings from an aqueous dispersion of lignin—in this case colloidal lignin particles—and its co-deposition with TEMPO-Oxidized cellulose nanofibrils, thus providing an additional route to enhance the protective performance of lignin-based biopolymeric coatings (Objective 4).

4.1 Corrosion protection performance of lignin coatings

Electrochemical impedance spectroscopy (EIS) was used to investigate the protection performance of the coatings during extended immersion (up to 24 hours) in phosphate buffered saline (PBS), and the Bode representation of EIS data is illustrated in Figure 4. At the initial stage of immersion (1 hour), both SOL and HOL (with comparable coating thickness of 1.35 ± 0.16 μm and 1.34 ± 0.17 μm, respectively) demonstrated comparable protection capabilities and had relatively high values for their respective impedance modulus (|Z|) at low frequencies (10⁻¹ to 10⁻² Hz, Figure 4a) that were 1–2 orders of magnitude higher than that of the bare steel. With an extension of immersion to 24 hours, SOL coatings maintained their performance while the corresponding plots of HOL coatings demonstrated a decay in impedance values, indicating the degradation of coating [115]. This observation might suggest that the source of lignin plays a crucial role in the anticorrosive capability of coatings, especially during long-term immersion to an electrolyte.
The exact mechanism behind the superiority of SOL (cf. HOL) in long-term protection performance could not be clearly determined as the number of lignin sources under study was limited, and an examination of the chemical/structural characteristics was not undertaken. (Publication I)
4.2 Applicability of Industrial organic solvents for development of solvent-based lignin coatings

One of the key challenges in the valorization of lignin is the initial conversion of the material into a more useful and processible form (e.g., by dissolution) [49]. Although a variety of organic solvents have been previously screened for the solvation of lignin [46, 49], the development of a lignin-based coating technology necessitates the screening of organic solvents that are relevant to coating and paint industries—like glycol ethers—is required [116].

4.2.1 Solubility of lignin in organic solvents

Figure 5 outlines the solubility values of a softwood kraft lignin (SKL) and the hardwood organosolv lignin (HOL) in two selected organic solvents⁴, which demonstrated a high solvating power at the examined concentration (20 g·L⁻¹). Both solvents, diethylene glycol monobutyl ether (DEGBE) and propylene glycol monomethyl ether (PGME), belonged to the same group of solvents (glycol ethers) [116]. A near-complete solvation of lignins was achieved in DEGBE with performances comparable with that of dimethyl sulfoxide (DMSO), which is generally considered as a good solvent for lignin [47]. PGME also demonstrated a high solvating power (≥ 98 %), although its solubility performance was marginally less than that of DEGBE. Recent studies have highlighted that a higher polarity for an organic solvent alongside hydrogen bonding capability is generally favorable for lignin solution [51, 52], which further explains the better performance of DEGBE (Hansen solubility parameters of δ_p = 7 and δ_h = 10.6 MPa¹/²) when compared to PGME (δ_p = 4.7 and δ_h = 11.6 MPa¹/²). Furthermore, although one of the very first published studies on lignin solubility [46], indicated glycol ethers were potentially good solvents for lignin, a more detailed examination of the performance or utilization of this class of solvents for the dissolution of lignin have still remained relatively unexplored. Nevertheless, in an earlier study, PGME was used as a solvent in the aqueous solvent fractionation of kraft lignin [117]. (Publication II)

⁴ Out of 6 organic solvents that were investigated in Publication II, only two solvents demonstrated acceptable performance, therefore these are the sole focus of the discussion provided here.
Figure 5. Solubility (%) of softwood kraft lignin (SKL) and hardwood organosolv lignin (HOL) in propylene glycol monomethyl ether (PGME), diethylene glycol monobutyl ether (DEGBE) and dimethyl sulfoxide (DMSO).

Figure 5 further illustrates a difference in the solubility percentage of the two lignin, which can be explained by the variance in the chemical compositions of SKL and HOL (Table 2). The higher purity in HOL was apparent with a total lignin content of 95 % (~87 % for SKL) and smaller contents of carbohydrates and ash. These observed differences are believed originate from the isolation process of lignin, as the organosolv process is known to result in lignins with high purities [42]. Consequently, the higher purity of HOL gave rise to the higher solubility values—compared to SKL—observed in the selected organic solvents. (Publication II)

Table 2. Chemical composition of softwood kraft lignin (SKL) and hardwood organosolv lignin (HOL). (in wt.% of lignin dry weight, Publication II).

<table>
<thead>
<tr>
<th>Constituent</th>
<th>SKL</th>
<th>HOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Klason lignin</td>
<td>82.52 (± 0.29)</td>
<td>93.73 (± 0.22)</td>
</tr>
<tr>
<td>Acid-soluble lignin</td>
<td>4.46 (± 0.07)</td>
<td>1.72 (± 0.08)</td>
</tr>
<tr>
<td>Lignin (total)</td>
<td>86.98 (± 0.36)</td>
<td>95.45 (± 0.30)</td>
</tr>
<tr>
<td>Ash</td>
<td>0.92 (± 0.03)</td>
<td>0.13 (± 0.01)</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>6.23 (± 0.02)</td>
<td>0.90 (± 0.05)</td>
</tr>
</tbody>
</table>

Another noticeable difference between SKL and HOL was the molecular weight and the polydispersity index (PDI) of the two lignins, as shown in Figure 6. Compared to HOL, SKL contained a higher weight average molecular weight ($M_w$), which resulted from the denser softwood structure (G-type lignin). While the formation of C–C interunit linkages in softwood lignin is feasible via the
electron-rich C5 positions, the presence of methoxyl groups at C5 in the lignin syringyl groups (for hardwood lignin or GS-type) lowers the overall condensation in the hardwood lignin structures [118]. Consequently, softwood lignin generally contains higher molecular weights than hardwood lignin [119, 120]. Furthermore, a high PDI was also evident for SKL (6.3 cf. 2.1 for HOL) as the kraft pulping process, generally yields more heterogenous lignin when compared to the ethanol-based organosolv process [42, 121]. In the main, a higher PDI and a higher molecular weight lignin are known to result in decreased solubilities in organic solvents [46, 53], which further explains the lower solubility values obtained for SKL (cf. HOL).

![Figure 6. Weight average (Mw) and number average (Mn) molecular weights and polydispersity index (PDI) of softwood kraft lignin (SKL) and hardwood organosolv lignin (HOL).](publication II)

The functional groups and structural characteristics of SKL and HOL were determined by 31P NMR and 13C NMR spectroscopy, respectively (Table 3). Results further confirmed the hardwood nature of HOL as demonstrated by the presence of higher quantities of 5-substituted PhOH (2.66 cf. 1.94 of SKL), a higher content of methoxyl groups (OMe) and a lower degree of condensation (DoC). Additionally, although subtle differences could be observed for the total OH and COOH content of SKL and HOL, nevertheless a clear correlation between the lignin content of functional groups and their solubility in organic solvents could not be readily established. (Publication II)
Table 3. Functional groups and structural characteristics of softwood kraft lignin (SKL) and hardwood organosolv lignin (HOL), as determined by $^{31}$P NMR and $^{13}$C NMR (mmol·g$^{-1}$ lignin, Publication II).

<table>
<thead>
<tr>
<th>Methodology</th>
<th>Moiety</th>
<th>SKL</th>
<th>HOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{31}$P NMR</td>
<td>S + Gnon-cond PhOH</td>
<td>1.94</td>
<td>2.66</td>
</tr>
<tr>
<td></td>
<td>Gnon-cond PhOH</td>
<td>2.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>H PhOH</td>
<td>0.32</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Total Phenolic</td>
<td>4.26</td>
<td>3.66</td>
</tr>
<tr>
<td></td>
<td>Aliphatic</td>
<td>2.27</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td>COOH</td>
<td>0.62</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>Total OH</td>
<td>7.15</td>
<td>6.56</td>
</tr>
<tr>
<td>$^{13}$C NMR</td>
<td>OMe</td>
<td>4.73</td>
<td>6.23</td>
</tr>
<tr>
<td></td>
<td>DoC, %</td>
<td>76</td>
<td>44</td>
</tr>
</tbody>
</table>

4.2.2 Effect of solvents on lignin’s glass transition temperature ($T_g$)

Figure 7 displays the thermograms obtained from technical SKL and HOL as supplied, and after drying following dissolution in the selected solvents (DEGBE and PGME). The $T_g$ obtained for the technical SKL (~151 °C) was lower that that of the technical HOL (~139 °C), which was in line with previously reported values for these types of lignin [122, 123]. $T_g$ values for post-dissolved samples in PGME were comparable with the $T_g$ of technical lignins (~149 °C for SKL and ~137 °C for HOL), although those obtained from DEGBE demonstrated much lower values (~76 °C for SKL and ~81 °C for HOL). This decrease in $T_g$ obtained for DEGBE following lignin dissolution and subsequent drying indicated that the solvent has a plasticizing effect on both SKL and HOL. Considering the high boiling point (BP) of DEGBE (~230 °C), it was speculated that DEGBE acts as an external plasticizer for lignin as the action of slow-evaporating organic solvents as external plasticizer for a polymer is a well-established concept [124].
Results and discussion

Figure 7. Differential scanning calorimetry thermographs obtained from (a) SKL and (b) HOL technical lignin, and after their dissolution and drying in the PGME and DEGBE solvents. (Publication II)

4.2.3 Effect of solvents on coating morphology and adhesion

Solutions of lignin-solvents with a higher concentration (100 g·L\(^{-1}\)) were prepared and applied to iron-phosphate steel using spray-coating (Figure 8). While solutions of PGME provided relatively homogenous surfaces, solutions of DEGBE demonstrated a flowing behaviour (i.e., sagging) during and after the
deposition process. The sagging of lignin-DEGBE solutions was due to the high boiling point of the solvent (~230 °C) and is an established phenomenon with slowly evaporating solvents [125]. Consequently, use of DEGBE as the main solvent of lignin for spray-coating applications is not recommended, at least at the solid contents (100 g·L⁻¹) investigated in this work.

**Figure 8.** Images of spray-coated lignin on iron-phosphate steel from solutions of (a) SKL-DEGBE, (b) SKL-PGME, (c) HOL-DEGBE and (d) HOL-PGME. The size of each steel panel is 10 x 15 cm. (Publication II)

The adhesion of these lignin coatings onto the steel surface were examined by the cross-cut adhesion method and optical microscopy (OM) images of the coatings obtained following examination are shown in Figure 9. As can be seen, the lignin-DEGBE coatings had well-defined edges around the cut area without any obvious coating detachment, whereas lignin-PGME coatings demonstrated a localized flaking of the coating adjacent to the cut area and showed a relatively
lower level of adhesion. The superiority of adhesion for lignin-DEGBE coatings was speculated to result from the plasticizing effect of the solvent, although the slower evaporation rate of DEGBE might have further contributed to the better substrate wetting capability of solutions when applied on the steel surface. (Publication II)

**Figure 9.** Optical microscopy (OM) images from the surface of lignin coatings after cross-cut adhesion measurement on (a) SKL-DEGBE, (b) SKL-PGME, (c) HOL-DEGBE and (d) HOL-PGME. (scale bar: 100 μm). (Publication II)

In addition to the inferior adhesion properties of lignin-PGME coatings (cf. lignin-DEGBE), it was also observed that a thickness-dependent cracking occurs for PGME-based coating systems after drying (Figure 10). For coatings with initial wet thickness values of 6–8 μm, a small degree of cracking was observed (especially for HOL-PGME), while coatings with a wet thickness of 30–32 μm from both HOL and SKL demonstrated a high degree of crack development. This behavior implied that the fast evaporation of the PGME solvent during drying of the coating could have resulted in accumulated stress within the dried coatings. Accumulation of this stress is thought to originate from the constrained shrinkage of the coatings during drying, which become more pronounced with increased levels of coating thickness [126]. A similar cracking phenomenon has been previously reported for non-modified SKL coatings at submicron thicknesses [127], further highlighting the susceptibility of lignin coatings to crack formation.
Figure 10. Optical microscopy (OM) images of lignin-PGME coatings with initial wet thickness of (a, c) 6–8 μm and (b, d) 30–32 μm for (a, b) SKL and (c, d) HOL. (scale bar: 100 μm).

4.2.4 Corrosion protection performance of solvent-based coatings in NaCl

The corrosion protection performance of SKL-PGME coatings with an initial wet thickness of 6–8 μm was evaluated by EIS and the Bode plots of the coating after 1 hour and 24 hours immersion in 5 wt.% NaCl are compared in Figure 11. The EIS measurements after 1-hour of immersion clearly demonstrate that the coated surface charge transfer resistance ($R_{ct}$, at $0.5 \times 10^{-1}$ Hz) is about 2 order of magnitude higher than that of iron-phosphated steel. However, a relatively fast degradation of the coating is evident after 24 hours immersion as shown by the decreased impedance modulus values over the scanned frequency range (Figure 11a). Therefore, it could be concluded that the longer-term surface protection performance of lignin coatings prepared in this way is somewhat limited.
Results and discussion

4.2.5 High-solid content SKL coatings and the applicability of triethyl citrate (TEC) as a plasticizer

The effect of solid concentration on the cracking of SKL coatings was further investigated by preparing solutions with solid concentrations of 400 g·L$^{-1}$ from a mixture of the two organic solvents (PGME:DEGBE, 3:1 volumetric ratio). Figure 12a shows the OM image obtained from the surface of SKL coatings (with a

**Figure 11.** EIS Bode plots obtained during immersion of SKL-PGME coatings to 5 wt.% NaCl solution for up to 24 hours. (a) impedance modulus and (b) phase angle. (Publication II)
final thickness of ~19 μm), illustrating the presence of surface cracks. These results suggest that the susceptibility to crack formation in SKL coatings increased as a function of lignin concentrations in the stock solution. Nevertheless, addition of 5 wt.% TEC (vs. initial weight of lignin) as a plasticizer to the initial SKL solution was found to decrease the extent of crack formation in dried coatings, as can be clearly seen in Figure 12b. (Publication III)

![Figure 12. Optical microscopy (OM) images obtained from the surface of (a) SKL coatings and (b) TEC-plasticized SKL coatings. (scale bar: 100 μm). (Publication III)](image)

The plasticizing effect of TEC on SKL was further investigated by ATR-FTIR measurements (Figure 13). In general, the spectral characteristics of both samples were similar except for the bands centered at ~3400 cm\(^{-1}\) and ~1700 cm\(^{-1}\) correlating to the O–H stretching of hydroxyl and C=O stretching of unconjugated lignin carbonyl groups, respectively [128, 129]. For plasticized SKL, both bands were shifted to higher wavenumbers (3396 cm\(^{-1}\) and 1724 cm\(^{-1}\)), implying a weaker hydrogen bond strength within the TEC-SKL network. This observed difference suggests that the TEC plasticizer increases the structural spacing through SKL network through insertion inbetween the polymeric lignin chains. (Publication III)
Development of aqueous coatings from colloidal lignin particles (CLPs) and TEMPO-Oxidized cellulose nanofibrils (TOCN)

The next section of the compendium highlights an alternative technique for the preparation of lignin-based coatings from aqueous dispersions (Publication IV). This approach initially involved the formation of CLPs through the solvent exchange method for the preparation of aqueous lignin dispersions. Subsequently, the addition of CLPs dispersion to TOCN suspensions provided an aqueous medium of negatively charged biopolymers that enabled their co-deposition by electrophoretic deposition (EPD). Not only does this technique minimize the content of organic solvents within the deposition medium—a critical concern for the paint industry—but also enabled a potentially scalable deposition procedure for the preparation of cellulose-lignin composite coatings.

4.3.1 Formation of colloidal lignin particles (CLPs) by solvent exchange method

Figure 14 illustrates the size and distribution of the SKL particles—determined by dynamic light scattering (DLS) measurements—that were produced by addition of 5 mL SKL-DEGBE solution (150 g·L⁻¹, 96.2 ± 0.1 % solubility) into 50 mL DI water. Initially, the dispersion contained colloidal particles with a bimodal size distribution and volume weighted mean of $D_{[4,3]} = 11.1 \, \mu m$. Centrifugation of dispersions resulted in the precipitation of the larger particulates, and analysis of the supernatants showed that they contained a wide distribution of submicron particles ($D_{[4,3]} = 146 \, nm$). Gravimetric measurements performed on the precipitated particles revealed a conversion efficiency of about
82 % of 0.75 g non-dried technical lignin into sub-micron colloidal particles. The presence of larger particulates originated from the concentration of the SKL-DEGBE solution (150 g·L\(^{-1}\)), which was significantly higher than typical concentrations (below 40 g·L\(^{-1}\)) used for solvent exchange processes [63]. In general, a higher solution concentration has been found to result in particle aggregation during the formation of CLPs, which leads to an increase in the average size of the formed particles [63].

**Figure 14.** Particle size distribution of CLPs before and after centrifugation of dispersions. (Publication IV)

Figure 15 displays SEM micrographs obtained from CLPs that were dried on a silicon wafer surface (from a diluted dispersion with a dilution factor 200) and these clearly demonstrate the wide distribution of submicron particles. Furthermore, it can be observed that CLPs appear to form a continuous film during the drying due to lignin particle coalescence, which was believed to be the result of DEGBE acting as a coalescing agent [130]. This further demonstrates DEGBE suitability as a solvent for the development of lignin-based coating systems as it offers multiple functionalities for lignin: as a solvent (section 4.1.), plasticizer (section 4.2.), and a coalescence promotion additive.
Figure 15. SEM micrograph of dried CLPs on a silicon surface, demonstrating the morphology and the coalescence of lignin particulates. (Publication IV)

Figure 16 shows an SEM micrograph of CLPs that were applied on silicon wafer surface from a non-diluted (centrifuged) CLPs dispersion and dried at ambient temperature (~21 °C). As can be observed, the surface comprises of a coalesced lignin layer that is disrupted by local crack propagation. Presence of a lignin layer confirmed that the coalescence occurs during the drying of CLPs at ambient temperature, although the exact origin of crack formation in the dried lignin layer remains undetermined. Various parameters can potentially play a role in crack formation including the size and size distribution of CLPs (like packing of particles and its effects on the extent of capillary forces and resultant irregularities in stress development) [131, 132], the content of coalescing additive (in this case DEGBE), the drying condition, and naturally the T_g of CLPs at different stages of the drying process [133].
4.3.2 Electrophoretic deposition (EPD) from aqueous dispersions and formation of lignin-cellulose composite coatings

A general scheme for the simultaneous electrophoretic deposition of CLPs and TOCN is illustrated in Figure 17a. As a result of the negative charge of both biopolymers when present in an aqueous dispersion—measured ζ-potentials = −40.5 ± 2.4 mV (CLPs) and −45.4 ± 1.2 mV (TOCN)—application of an external direct current (DC) resulted in the movement of biopolymers towards a positively charged HDG substrate. This accumulation of material proximal to the substrate surface is followed by charge neutralization that results in the subsequent deposition of biopolymers on the surface of HDG anode. Interestingly, additional experiments with the separate components showed that although the deposition of TOCN from CLPs-free suspensions was obtainable (Figure 17b), coating of the anode surface by CLPs alone could not be achieved in the absence of TOCN from the dispersion (Figure 17c). Furthermore, it was also evident that the presence of both biopolymers in solution yielded higher levels of wet thickness for the deposited coatings (Figure 17d).
The difference in deposit formation in the presence/absence of TOCN indicated that the formation of coatings resulted from an inherent interaction between TOCN and the HDG substrate. Based on this idea, a mechanism for deposit formation can be proposed in which the application of an external DC results in dissolution of the anode and release of metallic cations (in this case Zn²⁺) proximal to the electrode, which induces the formation of TOCN hydrogel at the anode surface. This surface hydrogel formation probably results from the cross-linking of carboxylate anions within the TOCN by the released cations. A similar trend for cation-induced hydrogel formation has been previously reported for cellulose nanofibrils [134, 135].

FTIR characterization of the electrophoretically deposited TOCN coatings (cf. TOCN free-standing films) showed a distinct change in the band position of the carboxylate anions present in TOCN coatings (Figure 18). The position of the asymmetric vibration band of carboxylate anions (~1600 cm⁻¹) was comparable between the deposited coatings and that of the free standing TOCN film, whereas the symmetric vibration band (~1419 cm⁻¹) undergoes a shift to higher wavenumbers when compared to that of the free-standing film (~1409 cm⁻¹), thereby implying the formation of a new complex between zinc cations from HDG and carboxylate anions from the deposited TOCN [134]. Consequently, when deposition was conducted from the co-dispersion of CLPs and TOCN, the formation of TOCN hydrogel onto the HDG surface assisted the immobilization of CLPs into the hydrogel network, resulting in the observed formation of the TOCN-CLPs composite coatings [136].
4.3.3 Physical properties and morphological features of lignin-cellulose coatings

Figure 19 displays the deposited mass and coating thicknesses achieved with different deposition parameters. Both coating thickness and mass were found to be proportional to the deposition potential, and application of a potential of 3 V resulted in the formation of relatively thicker coatings (~5 μm cf. ~1 μm of 0.5 V depositions) with 3–4 times higher mass deposits. An increase in the TOCN concentration within the deposition medium (from 0.1 wt.% to 0.2 wt.%) also enhanced both the thickness and mass of the coatings, although the effect was less discernible with deposition at 0.5 V. Both the deposition potential and dispersion concentration are fundamental parameters that allow coating thickness and mass of the deposit to be controlled in the EPD processes [137].
Results and discussion

Figure 19. Coating thicknesses and the deposited mass obtained from dispersions with varying TOCN concentration (0.1 wt.% and 0.2 wt.%) and deposition potentials (0.5 V and 3 V). (Publication IV)

Figure 20 presents the SEM micrographs obtained from the different coating surfaces produced by EPD. All four coatings demonstrate a comparable morphology, constituted of an entangled network of TOCN covered by coalesced CLPs. It is evident from these micrographs that coatings deposited from the medium with higher TOCN concentration (0.2 wt.%) has a higher apparent concentration of TOCN at the surface (Figure 20b and 20d).

Figure 20. SEM micrographs obtained from the surface of coatings: (a) 0.1 T–0.5 V, (b) 0.2 T–0.5 V, (c) 0.1 T–3 V and (d) 0.2 T–3 V. (Publication IV)
Figure 21 displays the optical microscopy (OM) images obtained from the surface of TOCN-CLPs coatings that had been characterized by cross-cut adhesion measurements. Coatings that were deposited at a lower deposition potential (0.5 V) demonstrated a high adhesion to HDG surfaces (0/5, according to ISO 2409), and the initial TOCN concentration in the deposition medium did not appear to affect the adhesion properties determined for 0.5 V deposited samples. Conversely, coatings deposited at 3 V demonstrated a lower level of adhesion to the substrate (1–2/5), and an increase in TOCN concentration had a detrimental impact on the adhesion of the coatings. This observed difference in adhesion properties could originate from the higher levels of stress accumulation in coatings, especially for those deposited at 3 V. Considering the high boiling point of DEGBE (BP ~230 °C), it can be postulated that the evaporation of water occurs during the initial stages of drying, resulting in the solidification of a TOCN network, which inhibits the evaporation of solvent from the coating network. Consequently, increasing the thickness of coating (through higher deposition potential and increased TOCN concentration) results in a higher barrier to solvent evaporation, which subsequently leads to a higher level of residual stress in the dried coatings [138]. Nevertheless, a higher deposited mass (specifically that of CLPs with a wide size distribution) in 3 V coatings might also contribute to enhanced stress generation through an increase in the capillary pressure during the drying, and resistance to the stress relaxation results from CLPs coalescence [131].

![Figure 21. Optical microscopy (OM) images of coatings’ surfaces after cross-cut adhesion measurements: (a) 0.1 T–0.5 V, (b) 0.2 T–0.5 V, (c) 0.1 T–3 V and (d) 0.2 T–3 V. (Scale bar: 1 mm). (Publication IV)](image-url)
4.3.4 Corrosion protection performance of aqueous composite coatings in NaCl

Electrochemical characterization of HDG substrate and deposited surfaces were undertaken with EIS after 1- and 15-days immersion in 3.5 wt.% NaCl, and the Bode plots obtained are displayed in Figure 22. At the initial measurement interval (1-day immersion, Figure 22a), the impedance modulus of coatings in the low frequency region (10^{-1} to 10^{-2} Hz) demonstrated more than one order of magnitude higher values compared to the uncoated HDG, highlighting the higher charge transfer resistance (R_{ct}) provided by coatings on HDG surfaces. Results obtained from the fitting procedure revealed R_{ct} values within the range of 21–34 × 10^3 Ω·cm² for the coatings, which was significantly higher than that of the bare HDG (0.9× 10^3 Ω·cm²) and confirmed the protection capability of coatings. Although the highest R_{ct} values at 1-day interval was obtained for coatings deposited at 3 V and 0.2 wt.% TOCN concentration, any clear correlation between the deposition parameters and the value of R_{ct} for the other coating parameters could not be easily established. Results from the 15-day measurement interval (Figure 22b), however, revealed that the best performance was maintained by the 0.2 T–3 V coating (R_{ct} = 13.7 × 10^3 Ω·cm²) and this was followed by 0.1 T–3 V (R_{ct} = 12.0 × 10^3 Ω·cm²), 0.2 T–0.5 V (R_{ct} = 7.1 × 10^3 Ω·cm²) and 0.1 T–0.5 V (R_{ct} = 6.0 × 10^3 Ω·cm²) coatings. From these results it could be concluded that from a corrosion protection perspective, an increased deposition potential—therefore the final thickness of the coating (Figure 19)—and TOCN concentration in dispersions, both have a positive impact on the level of protection provided by the TOCN-CLPs coatings during long-term immersion in a corrosive electrolyte.

---

5 The presented results were obtained by the fitting of EIS data, and the fitting accuracy (X²) for 1-day immersion samples were 2.9 × 10^{-3} (HDG), 3.5 × 10^{-3} (0.1 T–0.5 V), 0.1 × 10^{-3} (0.2 T–0.5 V), 0.4 × 10^{-3} (0.1 T–3 V), and 1.1 × 10^{-3} (0.2 T–3 V). The corresponding values for 15-day immersion samples were 0.2 × 10^{-3} (HDG), 0.2 × 10^{-3} (0.1 T–0.5 V), 0.3 × 10^{-3} (0.2 T–0.5 V), 3.9 × 10^{-3} (0.1 T–3 V), and 0.6 × 10^{-3} (0.2 T–3 V).
Table 4 compares the $R_{ct}$ values of lignin-cellulose composite coatings (Publication IV) with the reported values from several studies, selected from the literature. The collation was based on organic coatings prepared either partially or completely from biopolymeric feedstocks, although many of these studies are based on either chemically modified materials or include additional components for the enhancement of protection capabilities. Nevertheless, this table does not provide a quantitative comparison of results with other studies due to
the inherent differences (i.e., coating chemistries/thicknesses/substrates and test media) but serves to provide a general comparative overview for these types of coatings.

**Table 4.** Comparison of charge transfer resistance ($R_{ct}$) or coating resistance ($R_c$) from this compendium and that of other studies from coatings with partial/complete incorporation of renewable feedstock.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Substrate &amp; test medium</th>
<th>$R_c/R_{ct}$ (Ω·cm$^2$) coated vs. bare substrate at initial immersion interval</th>
<th>$R_c/R_{ct}$ (Ω·cm$^2$) at prolonged immersion interval (hr)</th>
<th>Notes</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOCN-CLPs (0.2 T–3 V)</td>
<td>Hot-dip galvanized steel, 3.5 wt.% NaCl</td>
<td>$3.4 \times 10^4$ vs. $8.8 \times 10^3$</td>
<td>$1.4 \times 10^4$ (360)</td>
<td>Water-borne, swelling of coatings during immersion. Average coating thickness of ~5 μm</td>
<td>Publication IV [97]</td>
</tr>
<tr>
<td>Thermosetting polyurethane from lignin-based polyols with 38.6 wt.% of lignin</td>
<td>Q235 steel, 3.5 wt.% NaCl</td>
<td>$8.3 \times 10^{10}$ vs. $1 \times 10^3$</td>
<td>$3.9 \times 10^{10}$ (960)</td>
<td>Resistance values were estimated from Bode plots at 0.01 Hz. Coating thickness in the range of 50 ± 5 μm</td>
<td></td>
</tr>
<tr>
<td>Amoxicillin-doped cellulose acetate</td>
<td>Aluminum alloy, 0.05 M NaCl</td>
<td>$2.57 \times 10^5$</td>
<td>$1.14 \times 10^5$ (72)</td>
<td>Coatings cured in acetic acid</td>
<td>[139]</td>
</tr>
<tr>
<td>Hydroxypropyl methyl cellulose succinate</td>
<td>Steel alloy, mixture of 0.5 M NaCl and 1 M HCl (pH=3)</td>
<td>$1.07 \times 10^3$ (coating resistance) vs. NR</td>
<td>$3.11 \times 10^3$ (24)</td>
<td>Coating thickness in the range of 600 ± 20 μm</td>
<td>[140]</td>
</tr>
<tr>
<td>Water-borne epoxy incorporated with graphene and cellulose nanowiskers</td>
<td>Q235 steel, 3.5 wt.% NaCl</td>
<td>$3.19 \times 10^6$ vs. NR</td>
<td>NR</td>
<td>Impedance values (at 0.1 Hz) decreased during 240 h immersion</td>
<td>[141]</td>
</tr>
<tr>
<td>Water-borne epoxy coating incorporated with biomass porous carbon and chelating agents</td>
<td>Q235 steel, 3.5 wt.% NaCl</td>
<td>$2.1 \times 10^4$ vs NR</td>
<td>$1.0 \times 10^4$ (672)</td>
<td>Coating thickness of 100 μm before solidification, self-healing ability was reported</td>
<td>[142]</td>
</tr>
<tr>
<td>Self-healing epoxy incorporated with multicomponent nanocomposites of SiO$_2$/chi-</td>
<td>Q235 steel, 3.5 wt.% NaCl</td>
<td>$7.2 \times 10^3$ vs. NR</td>
<td>$1.6 \times 10^4$ (192)</td>
<td>Coating thickness 50 ± 5 μm, measurements conducted on scribed coatings,</td>
<td>[143]</td>
</tr>
</tbody>
</table>
It is highlighted here that coatings based on technical lignin, with the molecular and chemical heterogeneities, provide performances that fit well within the protection ranges offered by other researched biopolymers. These findings will hopefully motivate other researchers to take part in/accelerate the research on utilization of technical lignin as anticorrosion coatings. Nonetheless, the enhancement of coating performances will be necessary to fully enable the production of reliable and industrially applicable lignin-based coatings. As such, some relevant aspects on the enhancement of coating properties, alongside the personal suggestions of the author on the future direction of research are shortly discussed in the following chapter.

<table>
<thead>
<tr>
<th>Coating System</th>
<th>Corrosive Medium</th>
<th>Barrier Performance</th>
<th>Self-healing Capability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber incorporated with carbon nanotube modified Fe3O4</td>
<td>Iron, 0.1 M NaCl</td>
<td>12.7 × 10³ vs. 24</td>
<td>demonstrated self-healing</td>
</tr>
<tr>
<td>Oleic acid-grafted chitosan/graphene oxide</td>
<td>Carbon steel, 3.5 wt.% NaCl</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>Various types of epoxized vegetable oils</td>
<td>Low-carbon steel, aerated 0.1 M NaCl</td>
<td>2.07 × 10⁷ – 4.68 × 10⁶ vs. NR</td>
<td>UV-curable coatings</td>
</tr>
<tr>
<td>Poly(itaconic acid)-modified chitosan</td>
<td>Aluminum alloy (6061-T6), 0.5 M NaCl</td>
<td>1.2 × 10⁶ vs. 5.0 × 10⁵</td>
<td>higher than 1 × 10⁵ (1920)</td>
</tr>
<tr>
<td>Stearic acid grafted chitosan/epoxy blend</td>
<td>Mild steel, 3.5 wt.% NaCl</td>
<td>3.4 × 10⁷ vs. 1.85 × 10⁵</td>
<td>NR</td>
</tr>
<tr>
<td>Fluorinated chitosan doped with cerium nitrate</td>
<td>Aluminum alloy (2024-T3), 0.05 M NaCl</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>Bilayer coatings of cerium containing chitosan and a sol-gel based onorganosiloxane alcohol and titania nanoparticles</td>
<td>Aluminum alloy AA2024, 0.05 M NaCl</td>
<td>NR</td>
<td>NR</td>
</tr>
</tbody>
</table>

* Not reported
5. Challenges and prospects

The investigations undertaken in this thesis were to clarify the potential of technical lignins and to emphasize their relevance as a raw material for anticorrosion coatings. It is natural that investigating such a novel and unexplored topic ultimately results in more questions than definitive answers to the initial research questions. It is the purpose of this section to provide a discussion on shortcomings of this work, clarifying the research gaps, and to share a personal perspective on future research directions for enhancing the applicability of lignin to the field of anticorrosion coatings.

A primary question, for example, is that how coatings of comparable thicknesses that are prepared from different fractions of a technical lignin differ in terms of charge transfer resistances. The answer to this question could further clarify the contribution of the starting lignin and assist the selection of the proper fraction for plausible modifications. A research gap, when it comes to SKL-DEGBE, would be the content of functional groups within the soluble fractions or that are present in the colloidal lignin particles. Further research in lignin-DEGBE could elucidate the potential of DEGBE as a solvent in preparation of colloidal particles, and provide a baseline for the comparison of solvent behavior with the previously researched solvents [62]. The determination of the related mechanical properties of such coatings would also provide valuable information towards the goal of feasible lignin-based coatings.

Considering the rigid aromatic backbone of lignin, as well as the presence of active sites that are suitable for chemical modification, the thermosetting networks from lignin could be advantageous for the future direction of research [151]. This might also apply to water-borne anticorrosion coatings, when considering that a thermosetting network could provide a higher barrier against the ion transport through the coating network, when compared to that of a thermoplastic [152]. This aspect also suggests that investigation of water-borne lignin-based coatings is potentially cleaner and a more potent direction of research as opposed to that of the solvent-borne counterparts, further highlighting the potential benefits of colloidal lignin particles.

Considering the findings of this work on water-borne coatings with coalescing properties of CLPs, and (as an excellent example) the recent findings on water-borne thermosetting CLPs-epoxies [153], future research efforts should aim to investigate the potential of a combined cross-linking and coalescing coating from CLPs, although with a careful system design that takes into account the
competition between the coalescence (i.e., film-formation) and the cross-linking reactions [71].

Last but not least is the consideration of lignin’s degradability within a plausible coating system [154], and its prospects at the post-service/end-of-life stage. It is important to be mindful that using lignin as the raw material for a coating is not only to produce “wealth from waste”, but to also tackle the pollution associated with the synthetic polymers used in paints and coatings [155]. This further highlights the key importance of life-cycle analysis related to this area in the future related research.
6. Conclusions

In the quest for the development of sustainable coating solutions, this thesis investigated the application of technical lignin as the main component of anticorrosion coatings for the protection of steel (metal) surfaces. The chemical modification/fractionation of the technical lignin or composite preparation with synthetic (organic) additives were avoided in this work, firstly to obtain an understanding on the fundamental relevance of technical lignin as a raw material in anticorrosion coatings, and secondly to maintain the inherent economic and environmental characteristics of technical lignin. As such, this work focused on the direct dissolution of the raw material in organic solvents, followed by the deposition of solutions on metal surfaces using scalable deposition techniques. In doing so, a selection of industrial organic solvents was considered for the dissolution of lignin and their influence on the properties of the prepared coatings were investigated. Furthermore, the effect of triethyl citrate (TEC)—as a green plasticizer of lignin coatings—was also part of these investigations. To further enable a cleaner production route, the content of organic solvents was further decreased through preparation of aqueous dispersions from lignin, which were combined with cellulose nanofibrils for the preparation of full-biopolymeric coatings. Based on the results obtained through this work, the following conclusions can be drawn:

- Technical lignin as a surface coating provided protection against the corrosion of electrolyte-immersed steel, and the protection capability was speculated to be affected by the source of the utilized lignin. The protective characteristic of coatings after prolonged immersion in electrolyte were, however, limited.
- Propylene glycol monomethyl ether (PGME) and diethylene glycol monobutyl ether (DEGBE) were strong solvents for solution of tested lignins. The latter demonstrated plasticizing effect on solvent-based lignin coatings and when utilized in aqueous environment, induce coalescence on colloidal lignin particles. The coalescence was observed for both ambiently-dried and heat-treated surfaces.
- Solvent-based lignin coatings demonstrated a thickness-dependent cracking. Through the introduction of triethyl citrate (TEC), it was possible to control the cracking due to a plasticizing effect of this environmentally friendly additive.
Colloidal lignin particles (CLPs) prepared from solution in DEGBE and a subsequent solvent exchange in water, act as a binder in a TEMPO-Oxidized cellulose nanofibrils (TOCN) network (i.e., a hydrophilic matrix). Furthermore, the corrosion protection capability of CLPs-TOCN during prolonged immersion in 3.5 wt.% NaCl was drastically improved when compared to lignin-alone solvent-based coatings.

Electrophoretic deposition (EPD) from aqueous dispersion of biopolymers was achieved on hot-dip galvanized steel, highlighting the relevance of this deposition technique for preparation of biopolymeric coatings on conductive substrates and the possibilities for future industrial scale-up.
References


[17] Srivastava, K.; Srivastava, P. Studies-on Plant Materials as Corrosion Inhibitors,


[36] Swartz, N.A.; Clare, T.L. Understanding the Differences in Film Formation


Sameni, J.; Krigstin, S.; Sain, M. Solubility of Lignin and Acetylated Lignin in


References


