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Investigation of the anticorrosion performance of lignin coatings after crosslinking with triethyl phosphate and their adhesion to a polyurethane topcoat

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Abstract. This study investigates the anticorrosion properties of sustainable organic coatings, which were prepared by dissolution of two different types of technical lignins - organosolv lignin (OL) and kraft lignin (KL) - in an organic solvent and applied onto iron-phosphated steel by air-assisted spray coating. Influence of triethyl phosphate (TEP) as a crosslinking agent for lignin and its effect on the anticorrosion properties of coatings during 24 h of immersion in 3.5% NaCl were investigated. Results obtained from electrochemical impedance spectroscopy (EIS) of coated steels suggest that the initial protection performance (1 h immersion) of non-crosslinked OL is higher than that of KL. Nevertheless, KL coatings that contained TEP and were heat-treated at elevated temperature (180 °C) demonstrated the best overall anticorrosion performance. In contrast, a similar trend was not observed for OL coatings, which indicates that the structural properties of lignin may be a crucial factor in applicability of TEP as a crosslinking agent. In addition, a layer of polyurethane was applied on all the different types of lignin coatings prepared and their adhesion characteristics were studied by crosscut adhesion measurements (ISO 2409). These adhesion results revealed that neither KL-TEP nor OL-TEP coatings demonstrate proper adhesive characteristics with a polyurethane (PU) topcoat and consequently these coatings are not suitable for utilization as a primer coating for the PU topcoat studied.

Key words: corrosion protection, kraft lignin, organosolv lignin, triethyl phosphate crosslinker, sustainable coatings.

INTRODUCTION

Organic coatings are one of the most common methods for the protection of metallic surfaces against corrosion (Lyon et al., 2017). Generally, most organic coating systems contain multiple layers for enhanced functionalities, for example, a layer adjacent to the surface of metal – also known as primer – is usually utilized to not only protect the surface of metal from oxidation, but also to enhance the adhesion of the subsequent layers (Hinder et al., 2005). Nevertheless, as the production of most organic coatings is dependent on finite and depleting petroleum resources, there is an increasing shift in industrial and scientific communities to replace petroleum-based materials with alternatives sourced from sustainable and renewable feedstocks (Deka & Karak, 2009).

Amongst these materials, lignin – the second most abundant biopolymer on earth – is a promising candidate, due to its chemically-rich structure, low price and high production rate as a by-product of pulp, paper and biorefinery industries (Holladay et al., 2007; Upton & Kasko, 2016; Brzonova et al., 2017).

Lignin is one of the main constituents of wood biomass (Kriauciuniene et al., 2008; Vitázek et al., 2019), and is hydrophobic in nature (Kunecová & Hlaváč, 2019). The potential of lignin as the main ingredient of anticorrosion coatings has been recently recognized (Dastpak et al., 2018; Haro et al., 2019), although the corrosion inhibition capability of lignin is well-understood (Ren et al., 2008; Hazwan Hussin et al., 2015). In a recent work (Dastpak et al., submitted), it was demonstrated that coatings prepared from kraft lignin have a high degree of protection in the early stages of immersion within an aggressive electrolyte, but prolonged exposure negatively affects the protection performance of the coating. In a study by Basso et al. (2017), the authors have demonstrated an easy route for enhancing the functionality of lignin coatings (resistance to water uptake and adhesion) by crosslinking the materials with triethyl phosphate (TEP). However, the anticorrosion properties of TEP-crosslinked lignin for metallic surfaces was not addressed in that study. Consequently, this study aims to investigate the anticorrosion properties of lignin coatings that are crosslinked with TEP, using electrochemical impedance spectroscopy (EIS). Furthermore, this study investigates the adhesion of the TEP-crosslinked coatings to a commonly used topcoat chemistry (polyurethane) to determine the applicability of crosslinked lignin as a primer coating.

MATERIALS AND METHODS

Materials and sample preparations

Two different grades of lignin were used for coatings preparation, namely a commercial grade softwood kraft lignin (KL), BioPiva™ 190 (UPM, Finland) and a pilot-scale hardwood organosolv lignin (OL) (Fraunhofer Centre for Chemical-Biotechnological Processes (CBP), Germany). Two lignin dissolutions were prepared by mixing each type of lignin (9 g) with an organic solvent (30 mL), i.e. diethylene glycol monobutyl ether (Butyl Carbitol™, $\geq 98\%$; Sigma-Aldrich, Germany), in order to form dissolutions with comparable lignin concentrations of 300 g L^{-1} . Furthermore, in some samples Triethyl phosphate (TEP) ($\geq 99\%$, Merck, Germany) was added with a 1:1 weight ratio of TEP:lignin. Solutions were magnetically stirred for (24 h) at room temperature and were subsequently applied by spray coating using a conventional cup gun equipment (Satajet 20 B, Germany) onto commercial grade iron-phosphated steel panels (R-46-ICF, Q-lab, USA). The elemental composition of the utilized steel is outlined in Table 1.

Table 1. Elemental composition of the utilized iron-phosphated steel panel (Q-lab, <https://www.q-lab.com/q-panel-selector/>)

Element	C	P	S	Mn	Fe
Wt. %	< 0.15	< 0.03	< 0.035	< 0.6	balance

Prior to application of coatings, surfaces were cleaned with a low lint tissue paper (VWR, USA) and ethanol (94.2%, Altia Oyj, Finland). Following coating, panels were placed in a pre-heated oven and dried at different temperatures and durations (Table 2).

In the final stage, for specific samples (#3 and #6 in Table 2) a layer of a commercial grade polyurethane (PU) topcoat (TEKNODUR 0290, Teknos, Finland)

sprayed onto the lignin-coated samples, which were then left to cure at ambient temperature for 7 days. As a reference, a PU layer with the same thickness was applied directly on the iron-phosphated steel panel. Measurements of the dry thickness values for these coatings were conducted using a thickness gauge (Elcometer 456, UK) for sample #3 and #6 (Table 2) before and after application of the PU topcoat.

Table 2. The parameters used for preparation of samples. In the sample designations, OL stands for organosolv lignin, KL for kraft lignin, TEP for triethyl phosphate, and numbers for the heat-treatment temperatures

No.	Sample Designation	TEP:lignin weight ratio	Heat-treatment temperature (°C)	Heat-treatment duration (min)
#1	OL	-	90	60
#2	OL-TEP-90	1:1	90	60
#3	OL-TEP-180	1:1	180	20
#4	KL	-	90	60
#5	KL-TEP-90	1:1	90	60
#6	KL-TEP-180	1:1	180	20

Characterization of coated surfaces

The lignin coated surfaces were primarily characterized with electrochemical impedance spectroscopy (EIS) in order to evaluate their anticorrosion properties. Measurements were carried out using an Iviumstat XRe (Ivium Technologies, Netherlands) after exposure of a fixed surface area (0.785 cm^2) to 5 wt.% sodium chloride (NaCl) solution at room temperature. The set-up comprised of a conventional three-electrode cell with a Ag/AgCl (saturated KCl) as the reference electrode (RE), a platinum (Pt) wire as the counter electrode (CE) and the coated/uncoated steel surfaces as the working electrode (WE). Prior to commencement of measurements, coatings were immersed and left to stabilise in the electrolyte for 1 h. EIS measurements were performed at open circuit potential (OCP) and over a frequency range of 100 kHz to 0.01 Hz, with logarithmically spaced frequency values (10 steps per decade) and a voltage amplitude of 10 mV_{rms} (root mean square). The EIS data were obtained after 1 h and 24 h immersion in the NaCl electrolyte.

For adhesion studies, a crosshatch cutter (Paint Test Equipment, UK) was utilized and measurements were performed using the EN ISO 2409 (2013) standard procedure. Firstly, all lignin-coated surfaces were cut using a multiple blade cutter and an adhesive tape was applied to the incised area, which was subsequently removed after 5 minutes at a fixed angle ($\sim 60^\circ$). Result of these adhesion tests were evaluated by optical microscopy imaging (OM, Motic BA310Met-T, China). Similar measurements were also conducted for the double layer coating systems, which contained a lignin layer (sample #3 and #6 in Table 2) and an additional PU topcoat as well as the iron-phosphated steel-PU top-coated reference for comparison.

RESULTS AND DISCUSSION

Electrochemical properties of the prepared surfaces were investigated by electrochemical impedance spectroscopy (EIS) and during 24 h immersion in 5% NaCl. Fig. 1 represents the Bode representations of EIS data, in the form of impedance modulus

vs. frequency, for coatings based on organosolv lignin (OL, Fig. 1, a) and kraft lignin (KL, Fig. 1, b). A straightforward method for evaluation of Bode impedance modulus plot, is the comparison of impedance values within the low frequency region, which for coated metals means that higher impedance values demonstrate a higher degree of a protection due to the coating (Kumar & Buchheit, 2006). By comparing the total impedance values of OL samples at low frequencies (Fig. 1, a) after 1 h immersion, it can be seen that OL coatings provide the highest impedance values when compared to either bare steel or TEP containing samples. Moreover, neither the addition of TEP nor the curing temperature appears to have an impact on the anticorrosion capability of the coatings. Consequently, among the three different OL samples investigated the non-treated sample (OL) demonstrates the best anticorrosion capabilities. Nevertheless after 24 h immersion, the total impedance of coatings (OL, OL-TEP-90 and OL-TEP-180) dropped dramatically, which suggests that the degree of protection against corrosion is severely decreased during the immersion period and the trend in the Bode impedance modulus (Fig. 1, a) of all three OL coatings are comparable with those of the bare steel. On the other hand, for coatings that were made from kraft lignin (Fig. 1, b), the best anticorrosion performance for both 1 h and 24 h immersion durations were obtained from the KL-TEP-180 coatings, followed by KL and KL-TEP-90, respectively. Furthermore, it can be noticed that KL-TEP-180 coatings that were immersed for 24 h outperformed the other two KL coatings (KL and KL-TEP-90) already after 1 h immersion, which suggests that the addition of TEP and subsequent heat-treatment at 180 °C enhanced the performance of kraft lignin coatings. Consequently, it is clear that the addition of TEP alone is not enough to enhance the anticorrosion capability of kraft lignin and heat-treatment is a necessary step in the coating preparation. Moreover, amongst the three different KL coatings tested, the KL-TEP-180 is least affected by the electrolyte (5% NaCl) over the 24 h immersion, which suggests the coating protection is maintained.

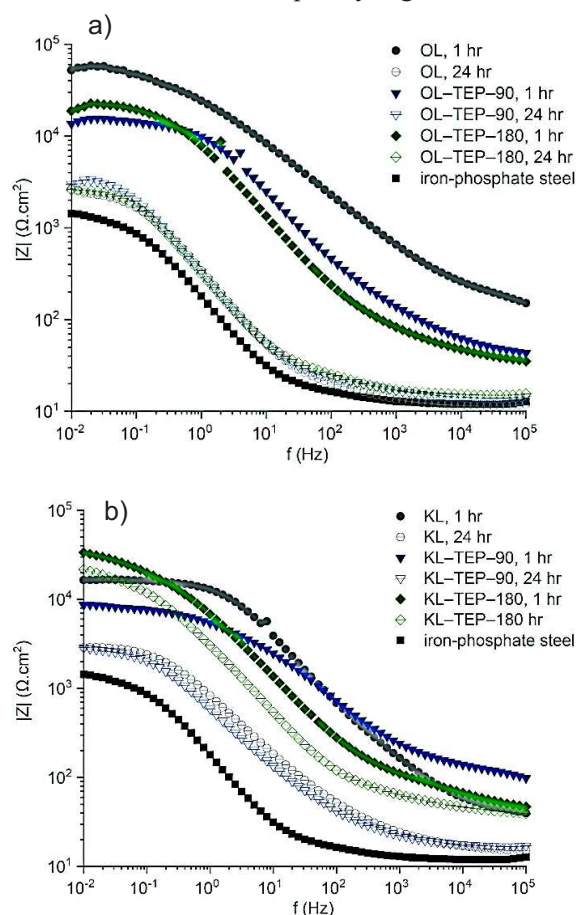


Figure 1. EIS Bode plots of impedance modulus vs. frequency for coatings prepared based on a) organosolv lignin (OL) and b) kraft lignin (KL).

Basso et al. (2017), have previously obtained a TEP-crosslinked kraft lignin and their results highlighted that there is a temperature-dependent reaction of TEP with both the phenolic and aliphatic hydroxyl groups within lignin. In relation to the EIS studies detailed here, it can be hypothesised that the crosslinking reactions were successful with KL, but was essentially absent with OL coatings as the anticorrosion performance of the TEP-free sample (OL) was better than the TEP containing coatings (OL-TEP-90 and OL-TEP-180). In our recent work (Dastpak et al., submitted), the ^{31}P NMR studies of OL and KL lignin samples demonstrated that the content of both phenolic and aliphatic hydroxyl groups in KL was higher than OL, highlighting the idea that a higher number of reaction sites between KL and TEP facilitated a greater extent of crosslinking, which resulted in the better anticorrosion capabilities of KL-TEP-180 coatings.

In order to study the adhesion performance of lignin coatings to iron-phosphated steel surfaces, crosscut measurements were conducted. As illustrated in Fig. 2, the adhesion of the organosolv lignin coating (OL, Fig. 2, a) is slightly weaker than that of the kraft lignin (KL, Fig. 2, b) and addition of TEP to both coatings results in a decrease of the coating adhesion strengths (Fig. 2, c–f). However, the difference between detached area from the non-crosslinked samples and TEP containing samples is negligible (especially for coatings based on OL) and all samples can be similarly categorized according to the ISO 2409 standard as shown in Table 3.

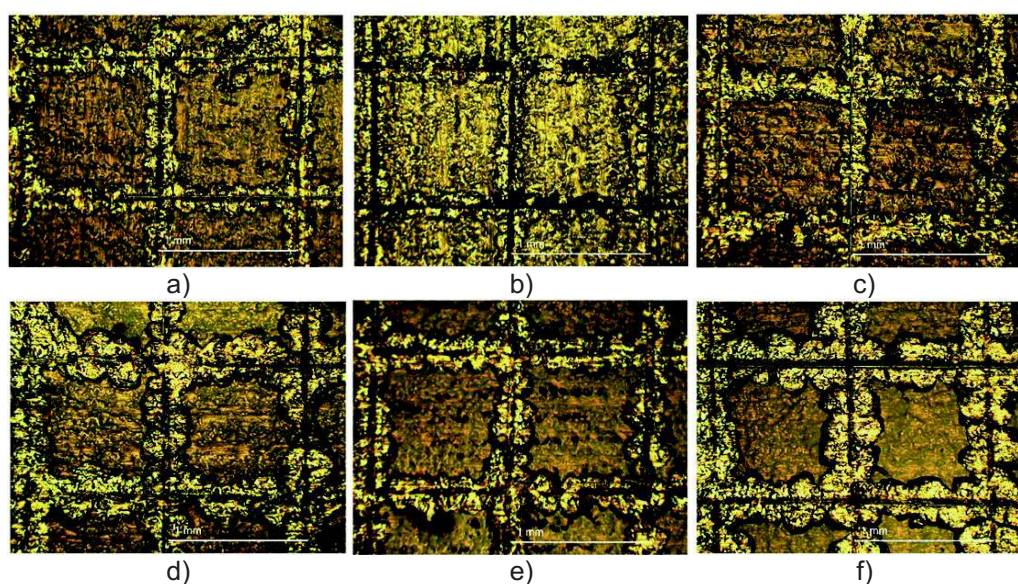


Figure 2. Optical microscopy (OM) images of lignin coatings after crosscut adhesion measurements, for a) OL, b) KL, c) OL-TEP-90, d) KL-TEP-90, e) OL-TEP-180 and f) KL-TEP-180. (scale bar: 1 mm).

In order to study the adhesion of a polyurethane topcoat with lignin coatings of OL-TEP-180 and KL-TEP-180, the crosscut adhesion measurements were also conducted on the lignin coatings that also contained a layer of PU coating with comparable thicknesses of 30 μm . Furthermore, a PU coating that was directly applied onto iron-phosphated steel surface with a similar thickness value was used as reference.

Digital images of the surfaces after the measurements are displayed in Fig. 3. As can be observed, the PU sample that was directly applied to surface demonstrates the best adhesion, unlike samples that contain lignin coatings of OL-TEP-180 (Fig. 3, a) and KL-TEP-180 (Fig. 3, b) that completely peel-off from the surface, to leave behind two different regions that either contain a layer of lignin coating (red circles, Fig. 3) or regions where the lignin coating is partially detached from the surface along with the PU top-coat (black circles, Fig. 3). Magnified OM images of these regions can be seen in Fig. 4 and the related adhesion results are detailed in Table 4.

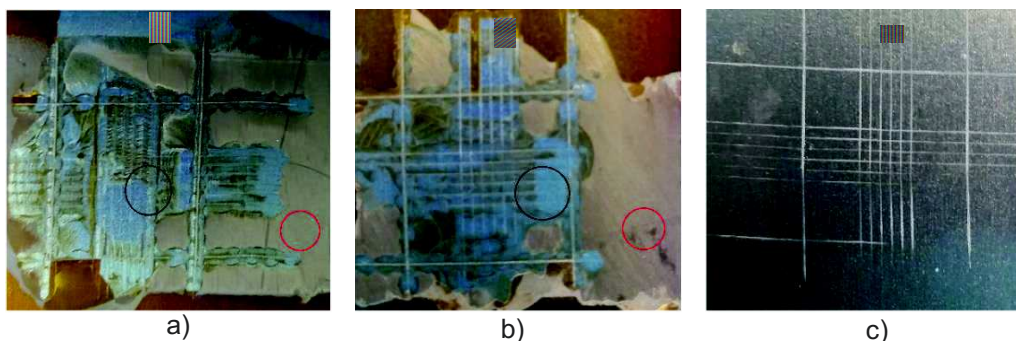


Figure 3. Digital images of double layer coatings after adhesion crosscut measurements. (a) PU on OL-TEP-180, (b) PU on KL-TEP-180 and (c) PU coating on iron-phosphated steel.

In order to study the adhesion of a polyurethane topcoat with lignin coatings of OL-TEP-180 and KL-TEP-180, the crosscut adhesion measurements were also conducted on the lignin coatings that also contained a layer of PU coating with comparable thicknesses of 30 μm . Furthermore, a PU coating that was directly applied onto iron-phosphated steel surface with a similar thickness value was used as reference. Digital images of the surfaces after the measurements are displayed in Fig. 3. As can be observed, the PU sample that was directly applied to surface demonstrates the best adhesion, unlike samples that contain lignin coatings of OL-TEP-180 (Fig. 3, a) and KL-TEP-180 (Fig. 3, b) that completely peel-off from the surface, to leave behind two different regions that either contain a layer of lignin coating (red circles, Fig. 3) or regions where the lignin coating is partially detached from the surface along with the PU top-coat (black circles,

Table 3. Results obtained from crosscut adhesion measurements of lignin coatings. Based on ISO 2409, best adhesion performance is represented as 0 and adhesion failure as 5 (EN ISO 2409, 2013)

No.	Sample designation	Adhesion results (scale: 0–5)
#1	OL	2
#2	OL-TEP-90	2
#3	OL-TEP-180	2
#4	KL	1
#5	KL-TEP-90	2
#6	KL-TEP-180	2

Table 4. Results obtained from crosscut adhesion measurements with double layer coatings of lignin-PU topcoat and steel-PU topcoat reference

Samples' code	Adhesion results (scale: 0–5)
PU on steel	0
PU on OL-TEP-180	5
PU on KL-TEP-180	5

Fig. 3). Magnified OM images of these regions can be seen in Fig. 4 and the related adhesion results are detailed in Table 4.

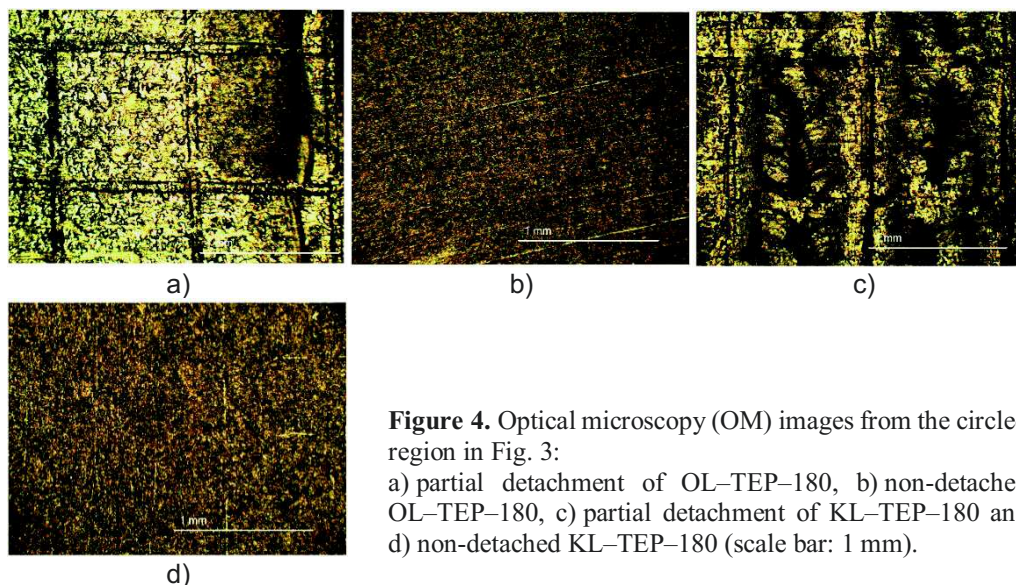


Figure 4. Optical microscopy (OM) images from the circled region in Fig. 3:

a) partial detachment of OL-TEP-180, b) non-detached OL-TEP-180, c) partial detachment of KL-TEP-180 and d) non-detached KL-TEP-180 (scale bar: 1 mm).

The difference in adhesion behaviour between the two layers suggests that when the underlying lignin coatings are not mechanically stressed, the adhesion between the steel and lignin is higher than that of lignin with PU topcoats, therefore separation occurs at the interface between lignin and PU. However, when the surface is damaged (by the cutting tool in this case) the underlying lignin coating loses the adhesion to the steel substrate and detaches along with the PU topcoat. This adhesion loss of lignin coatings from the substrate might be related to the brittle nature of lignin (Kai et al., 2012), which results in the cracking of coatings after the application of an external stress.

Based on these findings, neither kraft lignin nor organosolv lignin coatings that are crosslinked with TEP provide a reliable adhesion to the PU topcoat and therefore are not suitable for use as a primer coating in the investigated system. Nevertheless, the enhanced performance of KL-TEP-180 as a single layer protective coating or a primer for other organic coatings types, e.g. epoxies, could be a subject for further investigation.

CONCLUSIONS

In this study, a high-performance anticorrosion coating was obtained from the crosslinking of triethyl phosphate (TEP) with kraft lignin (KL) after heat-treatment of samples at 180 °C. Although an aggressive electrolyte (5% NaCl) was used for long-term corrosion tests, the KL-TEP coatings maintained the anticorrosion capabilities. Although satisfactory adhesion performance of this coating with a polyurethane topcoat was not obtained, this investigation demonstrates the possibility to further enhance the corrosion protection of sustainable coatings by use of 100% kraft lignin as a component.

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