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1 **Chemical Modification of Plasticized Lignins Using Reactive Extrusion**

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11 **Keywords: Plasticizing, kraft lignin, esterification, ³¹P NMR, DMSO, polyol**

Chemical Modification of Plasticized Lignins Using Reactive Extrusion

12 **Abstract:**

13 The reaction of esterification of plasticized Kraft lignin (KL) with succinic and maleic anhydrides
14 using reactive extrusion (REX) was studied in detail. DMSO, glycol and glycerol were found to be
15 efficient plasticizers for lignin. The chemical structure of these new lignin esters was determined
16 using Solid-state ^{13}C CP-MAS NMR and FT-IR analysis. ^{31}P NMR analysis of phosphitylated lignins
17 showed that the aliphatic OH groups of lignin had superior reactivity under the reactive extrusion
18 reaction conditions. The formation of monoesters was confirmed by HSQC NMR spectroscopy.
19 Molecular weight changes after extrusion process were studied using GPC/SEC chromatography.
20 Thermal properties of these polymers were assessed by TGA analysis. The results were compared to
21 lignin esters modified in classical batch conditions. These results show that REX can be used as a
22 new fast, solvent free and continuous process for lignin valorization.

23 **1 Introduction**

24 Lignin constitutes one of the main chemical families in plant biomass (Gandini, 2011). Lignins are a
25 polymeric form of variously methoxy-substituted phenylpropane monomeric units. Due to its general
26 abundance (up to 20-30% in hardwood) and its slow biodegradability, lignin is likely to be one of the
27 most abundant biopolymers on earth (Smolarski, 2012). Surprisingly apart from energy production in
28 paper factories lignin finds very few industrial applications (Zakzeski et al., 2010). Production of
29 high value added products such as vanillin has been obtained from lignin (Salvesen et al., 1948;
30 Fache et al., 2016). The aromatic phenylpropane nature of lignin offers some similarity with aromatic
31 polymers. Unfortunately, as its complex mixed structure depends on the extraction process, lignin
32 processing is difficult to carry out and not conducive to chemical process development. Moreover,
33 the difficulty in solubilizing and fractionating renders lignin difficult to process at the industrial level

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34 (in non-aqueous media). Various examples of lignin chemical modification have been developed in
35 order to adapt the properties to specific applications (Glasser and Jain, 1993; Laurichesse and
36 Avérous, 2013; Konduri et al., 2015; Ryohei et al., 2017; Sakai et al., 2018; Szabó et al., 2019).
37 Modification of the aliphatic and aromatic hydroxyl groups of lignin via esterification is a typical
38 approach (Laurichesse and Avérous, 2013). Several esterification agents have been applied to
39 synthesize new lignin derivatives: acetic, propionic and butyric anhydrides (Fox and McDonald,
40 2010); maleic, succinic and phthalic anhydrides (Chen et al., 2014); palmitic and lauric acid chloride
41 (Hult et al., 2013). Thielemans and Wool (2005) showed that in unsaturated thermosetting
42 composites, incorporated butyrate kraft lignin plays a role in reinforcing, plasticizing, and
43 influencing on the cure kinetics of the polymerizing resin. Maleated lignin was successfully mixed
44 with recycled polystyrene showing higher miscibility than native lignin (Schorr et al., 2015) and
45 slightly higher thermal stability compared to native polystyrene (Lisperguer et al., 2013).

46 Reactive extrusion (REX) is a fast developing technique that shows high potential in producing
47 chemically modified bio-sourced polymeric material from small to large scale (Berzin and Hu, 2004;
48 Formela et al. 2018; Milotskyi and Bliard, 2018a). It can be applied to a wide range of highly viscous
49 materials. Reactive extrusion itself can be considered as a green manufacturing process as compared
50 to conventional chemical modification processes: it does not require solvents; it is very energy
51 efficient; it allows clean reaction processes with fast kinetics, even when applied to large scales. Only
52 a few examples of REX modified lignin can be found in the literature (Bridson et al., 2013;
53 Fernandes et al., 2014; Luo et al., 2016). In this paper we describe the chemical modification of
54 lignin with maleic and succinic anhydrides using the REX. Both maleic and succinic anhydrides have
55 the potential to be synthesized from biomass-based feedstocks (Li et al., 2018; Bechthold et al.,
56 2008). Moreover, after anhydride opening and reaction with lignin, the free carboxyl group formed

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57 can be used for self-polyesterification to form biobased thermosetting polyester coatings (Scarica et
58 al., 2018). More specifically, the main objective of this work was to intensify the process of lignin
59 esterification and investigate the influence of reaction parameters on lignin conversion during REX.
60 New plasticizer systems were developed for lignin processing with relatively low temperature (140
61 °C).

62 **2 Experimental**

63 **2.1 Materials**

64 Two Lignins: KL pH6 (“Lignin, alkali” Aldrich 370959, insoluble in water) which will be noted KL
65 in this work and KL pH10.5 (“Lignin, alkali”, low sulfonate content, Aldrich 471003, soluble in
66 water) which will be noted KLS were provided by Sigma - Aldrich (St. Louis, USA). Succinic
67 anhydride (SA) and maleic anhydride (MA) were purchased from Alfa Aesar (Karlsruhe, Germany).
68 Glycerol, ethylene glycol and DMSO were purchased from VWR International (Fontenay-sous-Bois,
69 France). The reactor used in this study was the “Minilab Rheomex CTW5” (RHEO S.A., Champlan,
70 France). This apparatus is designed for compounding polymers in a thermostated heat block with a
71 production capacity of 100 g/h. It is also designed for analyzing the rheological behavior of polymer
72 melts on small scale. The system is based on a conical, twin-screw compounder. Two different types
73 of screw geometry (co- and counter- rotating) can be used in order to study the reaction differences
74 according to the mixing mode. Due to a particular design only very small sample amounts (10 g) are
75 needed in its integrated backflow channel. In this study, the conical co-rotating screws mode was
76 chosen over the counter-rotating one because of its superior mixing ability (Milotskyi and Bliard,
77 2018b). The extruder was operated at a screw speed of 60 rpm in the direct and recirculation (loop)
78 modes. The melt-mass flow-rate is determined by weighting extrudates in known time intervals.

79 2.2 Synthetic procedure

80 2.2.1 Preparation of samples for extrusion

81 At first, the processability of the two lignins KL and KLS in REX conditions was studied. All
82 attempts to extrude the lignins without any added plasticizer resulted in blocking the extruder due to
83 excessive torque value, exceeding the machine parameters. To address this problem the plasticizing
84 of lignins by using different plasticizers: DMSO, glycerol, ethylene glycol was studied.

85 Each lignin was milled with a mortar and pestle and then mixed with the corresponding amount of
86 plasticizer at room temperature. The mixture was then introduced into the extruder through the feed
87 hopper and extruded in re-circulation mode to obtain melt viscosity information. The conditions and
88 results of plasticizing are discussed further in this article.

89 2.2.2 Esterification of lignins using REX

90 To carry out the esterification reaction, 7 g of the plasticized KL was weighed and a corresponding
91 mass of maleic or succinic anhydride calculated with respect to the dry mass of lignin (without
92 plasticizer) was added. The mixture was introduced into the reactor preheated to the selected
93 temperature and was then extruded using the direct mode. In order to evaluate reproducibility, each
94 experiment was repeated at least three times except when noted. The amount of ester reagent (SA or
95 MA) was 0.1, 0.2 and 0.3 equivalents per average phenylpropane unit (Molar mass 178 g/mol,
96 average of the molecular weights of the three monomeric units *p*-coumaryl, coniferyl and sinapyl
97 alcohol). A reference sample named KL_{ref} was extruded with 25% DMSO without reagents at an
98 extrusion temperature of 140°C and a screw speed of 60 rpm using the direct mode.

99

100 **2.2.3 Purification of Reacted Extrudates**

101 The KL was purified as follows to remove residues of free maleic or succinic acid or their anhydrides
102 possibly present in the final mixture:

103 The reaction mixture of KL was crushed in a mortar and the obtained powder was purified with a
104 method adapted from (Chen et al., 2014) with some modifications: washing with distilled water and
105 sodium bicarbonate for 24 h with agitation. The resulting powder was then recovered by filtering off
106 the aqueous phase on Whatman filter paper. The modified lignin was dried for 24 hours at room
107 temperature in open air, and then overnight in a vacuum oven at 60°C.

108 **2.2.4 Esterification of lignins in batch**

109 1 g of kraft lignin (KL) was dissolved in 50 mL pyridine and 0.1/0.2/0.3 equivalent of acylating
110 reagent -succinic anhydride or maleic anhydride- was added to the solution. The reaction was kept
111 for 24 h at room temperature. The obtained product was collected after pouring the solution into 500
112 mL acetone, and dried in a vacuum drying oven at 70 °C for 24 h.

113 **2.3 Specific mechanical energy (SME)**

114 Specific mechanical energy (SME) is the amount of mechanical energy (work) transferred to the
115 melted mix and dissipated as heat inside the material, expressed per mass unit of the material. SME is
116 calculated using eq. 1 according to (Li, Hasjim, Xie, Halley & Gilbert, 2014) as follows:

$$117 \text{ SME (J/kg)} = (\text{Screw speed (rpm)} \times \text{Torque (N x m)} \times 60) / (\text{Feed rate (kg/h)}) \quad (1)$$

118

119

120 **2.4 Elemental analysis (C, H, S, N)**

121 A Perkin Elmer 2400 Series II-CHNS / O Elemental Analyzer was used to determine carbon,
122 hydrogen, nitrogen and sulfur contents by catalytic combustion. The oxygen content was estimated
123 on the assumption that the samples contained only C, H, N, S and O. The samples were dried in
124 vacuum at 80°C prior to the analyses.

125 **2.5 Fourier Transform InfraRed spectroscopy (FTIR)**

126 The FTIR analysis was carried out in absorption mode on KBr pellets mixed with the powdered
127 samples. The spectra were obtained on a Nicolet FT-IR 470 spectrophotometer (Nicolet Instrument
128 Corporation, USA) at 4000-400 cm^{-1} at a resolution of 4 cm^{-1} . The number of accumulated spectra is
129 32.

130 Samples synthesized in batch conditions were analyzed using Thermo Fisher Scientific Nicolet iS10
131 (Thermo Fisher Scientific, Inc., Tokyo, Japan) spectrophotometer equipped with an attenuated total
132 reflection (ATR) unit. The number of accumulated spectra is 64.

133

134 2.6 Nuclear Magnetic Resonance Spectroscopy

135 The HSQC NMR spectra were obtained in DMSO- d_6 as a solvent. The recording was tuned for a one
136 bound coupling of 145 Hz. The number of scans was 48; the acquisition time 0.14 s and the
137 relaxation delay 5s. The data matrix was 256/2048 (covering 22640 Hz in F1 and 7100 Hz in F2).

138 Phosphorus-31 NMR spectrometry was used in order to quantify aliphatic and aromatic hydroxyl
139 groups as well as carboxylic acid groups in lignins. In order to carry out the analysis it was necessary
140 to phosphitylate the lignins with 2-chloro-4,4,5,5-tetramethyl-dioxaphospholane as the
141 phosphitylating reagent prior to recording. This reagent was synthesized in our laboratory from
142 pinacol and phosphorus trichloride and purified by distillation according to the method described by
143 (Zwierzak, 1967) as follows. A solution of pinacol (0.2 mole) and distilled triethylamine (0.4 moles)
144 in cyclohexane (150 mL) was added dropwise to a solution of phosphorus trichloride (0.2 mole) in
145 cyclohexane (200 mL) at 5-10 ° C with efficient stirring and cooling. The mixture was kept for 1 h at
146 room temperature and filtered. The resulting triethylamine hydrochloride crystals were filtered off
147 and washed with cyclohexane (200 mL). Evaporation of the filtrate and careful vacuum distillation of
148 the residue gave pure 2-chloro-4,4,5,5-tetramethyl-dioxaphospholane. The yield after distillation was
149 36%.

150 The solvent used for ^{31}P NMR was a mixture of pyridine and deuterated chloroform (1.6:1 v:v)
151 protected from moisture using a 4 Å dry molecular sieve. A solution of relaxation agent was prepared
152 by mixing 5 mg of relaxation reagent (chromium III acetylacetonate) in one milliliter of the prepared
153 solvent. The internal standard solution was prepared with 10.85 mg / ml of cyclohexanol in prepared
154 solvent. For this experiment, 30 mg of lignin was accurately weighed into a 1 mL volumetric flask.

155 The sample was then dissolved in 0.5 mL of the above solvent mixture. 2-Chloro-4,4,5,5-tetramethyl-

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156 dioxaphospholane (50 μ L) was then added, followed by the internal standard and the relaxation agent
157 solution (100 μ L each). Finally, the solution was filled to 1 mL with more solvent mixture. The
158 volumetric flask was closed and stirred to ensure complete mixing. The spectra were obtained at
159 202.45 MHz with inverse-gated decoupling. The pulse lengths corresponded to a 30° pulse. The
160 number of scans was 128, the acquisition time 0.55 s, the relaxation delay 12 s, the spectral widths
161 294 ppm, the carrier frequency 140 ppm.

162 Solid-state ^{13}C CP/MAS NMR spectra were obtained at 10 kHz on a ECX-500II spectrometer (JEOL
163 Ltd., Tokyo, Japan). At least 4096 scans were averaged for each spectrum. In the case of sample
164 “Batch KL0.3MA” the number of scans was increased to 10000 to obtain a spectrum with high
165 resolution. A single contact time of 2 ms, a delay of start of 1.01 s, and proton preparation pulse of
166 2.71 μ s were used. Lignin methoxyl peak (52 ppm) was used as a reference. The DS is calculated
167 using eq. 2 as described by (Bridson et al., 2013),

$$168 \quad \text{DS} = I_1 / (I_2 * n) \quad (2)$$

169 where I_1 is the sum of grafted maleic anhydride carbonyl (165 ppm) and CH integrals (126 ppm), I_2 is
170 the methoxyl integral (assuming a stoichiometric number of methoxyl groups), n is the number of
171 maleate carbons (4). The corresponding reaction efficiency (RE) was calculated using eq. 3:

$$172 \quad \text{RE} = \text{DS} / (\text{MA} / \text{L}) * 100\% \quad (3)$$

173 where DS is the degree of substitution obtained from eq. 2 and MA / L is the mole ratio of maleic
174 anhydride (MA) to lignin C_9 unit.

175

176 **2.7 GPC/SEC chromatography**

177 The molecular weight of native and modified lignins was determined by size exclusion
178 chromatography (SEC, Prominence UFLC system, Shimadzu Co., Kyoto, Japan) based on
179 polystyrene standards. All GPC/SEC measurements were carried out at 40°C using TSK gel α -M
180 (Tosoh Co., Tokyo, Japan). Samples were dissolved in DMF containing 0.01% of LiBr. The final
181 concentration was 1 mg of polymer in 1 ml of solvent. Before injection, the samples were filtered
182 through a 0.2 μ m syringe PTFE filter. The same solvent was used as eluent at the flow rate of 1.0
183 ml/min. RID-10A Refractive Index Detector (Shimadzu Co., Kyoto, Japan) was used in this study.

184 **2.8 Thermogravimetric analysis**

185 The TA Instruments 2950 Thermogravimetric Analyzer (TGA) 2950 was used to determine the
186 degradation temperature of native and modified lignin samples under nitrogen flow. The samples
187 were analyzed up to a temperature of 650°C at a rate of 10°C/min.

188 **3 Results and discussion**

189 **3.1 Lignins processing**

190 At first, the processability of the two native lignins without plasticizer was tested in the extruder
191 within the 140-180°C temperature range. In this case, no melt behavior was observed for both lignins
192 in the chosen range of temperatures. Three plasticizers DMSO, ethylene glycol and glycerol were
193 then studied as potential plasticizers. Results of lignin plasticization using the different plasticizers
194 are given in Table 1. The extrusion temperature was fixed at 140°C with a screw speed of 60 rpm
195 during 5 min using recirculation mode.

196

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197 Table 1: Results of lignins plasticization with different plasticizers

Lignin/Plasticizer system	Torque (N×m)	SME (kJ/kg)	Melt viscosity (Pa.s)
KL 15 % DMSO	3.3	237	4.9×10^3
KL 20 % DMSO	2	144	1.2×10^3
KL 25 % DMSO	1.8	130	4×10^2
KLS 20% DMSO	1.7	122	8.96×10^3
KLS 20% Et Glycol	1.4	101	2.5×10^3
KLS 20% Glycerol	1,5	108	2.4×10^3

198

199 In the case of the sample where 15% DMSO was used, extrusion is characterized by fairly high SME
200 values; as the maximum torque for the Minilab Rheomex CTW5 is 5.5 N×m, below 15% DMSO the
201 extrusion was not possible on this extruder due to excessive torque values. The addition of
202 supplementary amounts of plasticizer decreased SME and melt viscosity. The melt viscosity values
203 for mixtures prepared with ethylene glycol and glycerol were similar. In conclusion, DMSO gave the
204 best results in providing lignin with a good melting behavior. The two other plasticizers used in this
205 study, polyols -ethylene glycol and glycerol-, were only tested with KLS lignin as they were
206 previously studied for KL lignin (Bouajila et al., 2006). DMSO was then chosen as a main plasticizer
207 as it is compatible with lignin and it has a relatively high boiling point (191°C) compatible with the
208 extrusion conditions and does not interfere with the reagents. In addition, to our knowledge, it had
209 not yet been studied for lignin plasticization applications.

210 3.2 Esterification of lignins by reactive extrusion

211 At first reactive extrusion of native KL (without plasticizer) with MA and SA was tested at a
212 temperature of 175 °C, without plasticizer, as described by (Bridson et al., 2013). A molar ratio of
213 0.2 of MA and SA was used for this test. However, no fusion was observed in our case, indicating
214 that the addition effect of the anhydrides did not improve the melting behavior of KL lignin. REX
215 esterification of lignin was then conducted using previously plasticized KL lignin with 25% of
216 DMSO at 140 °C.

217 3.3 Elemental and FTIR analysis

218 In both ester types, elemental analysis showed a decrease in the amount of analyzed carbon in all
219 esterified products, compared to unmodified lignins. For example, the carbon content of native KL
220 before extrusion was 63.42% (± 0.11), after extrusion of KL with 0.1 maleic anhydride, it decreased
221 to 62.01% (± 0.02) and to 60.02% (± 0.13) after extrusion with 0.3 MA. The decrease in carbon
222 content was observed for KL modified with SA, from 61.88% (± 0.04) for KL0.1SA to 58.86%
223 (± 0.24) for KL0.3SA. This result confirms the addition of succinic and maleic groups to the lignin,
224 which contain a lower proportion of carbon. FTIR results show that in both cases, a band of carbonyl
225 groups is present at 1722 cm^{-1} for 0.1, 0.2 and 0.3 MA and SA, the intensity of this band increases
226 with the quantity of anhydride added (Figure 1). All these results confirm the substitution of OH
227 groups in lignins and their transformation into esters. FTIR spectra of samples synthesized in batch
228 are presented in supporting information (Figure S1 and Figure S2).

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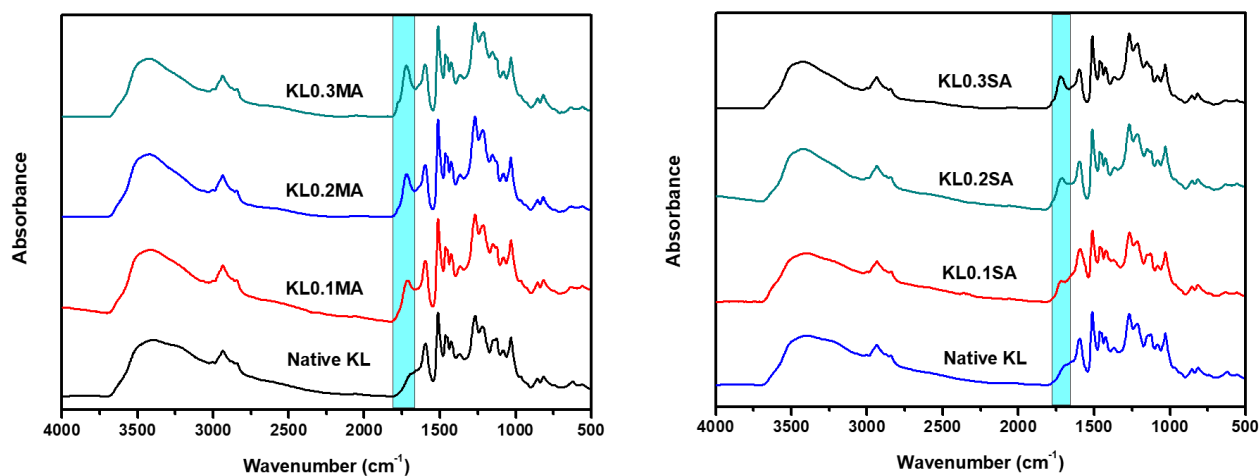
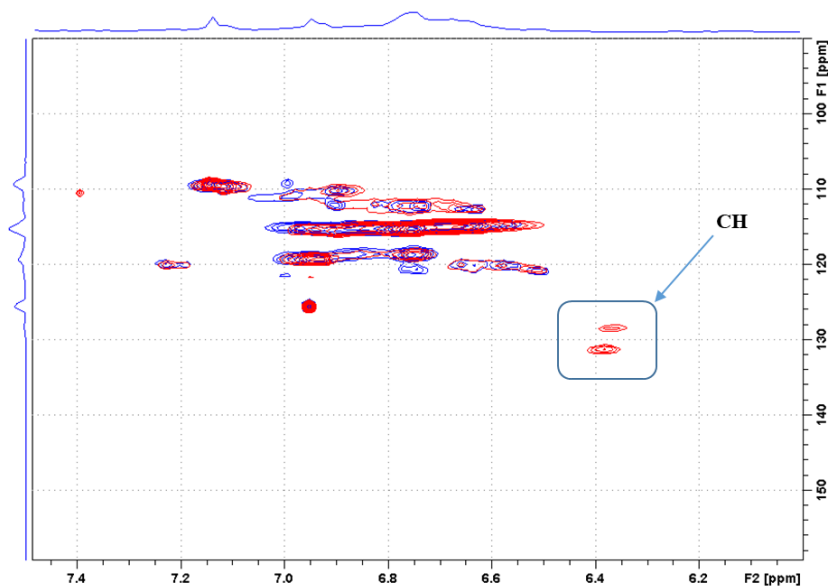


Figure 1: FTIR spectra of KL modified with different ratio of maleic (left) and succinic (right) anhydrides

3.4 HSQC NMR analysis

The disperse and complex structure of lignin makes ^1H and ^{13}C NMR analysis very difficult. On the other hand, 2D NMR spectroscopy yields spectra that provide more useful information. HSQC analyses of lignins (in $\text{DMSO-}d_6$) were performed. The signal of DMSO was set at 2.5 ppm for ^1H and 39.5 ppm for ^{13}C . The HSQC spectra of native KL and KL modified with 0.2MA were compared. As can be seen in the enlargement of this spectrum (Figure 2: blue signals for native KL CH or CH_3 and red/pink signals for KL 0.2MA CH or $\text{CH}_3 / \text{CH}_2$), two new spots appeared at (1) 6.37 ppm (^1H); 128.7 ppm (^{13}C) and (2) 6.39 (^1H); 131.3 (^{13}C). These signals are attributed to the CH groups of the grafted maleic anhydride. These signals are absent for the native KL. In addition, they do not correspond to the signals of MA or maleic acid that could be formed during the washing of samples with water. The appearance of two spots and not only one is due to the different chemical environment of these two CH groups: ester on one side and carboxylic acid on the other. This trend is observed for all samples (0.1; 0.2 and 0.3 MA). This confirms that the esterification reaction has occurred. In this case, the reaction is a mono-esterification. This result is in good agreement with the elemental and FT-IR analysis.

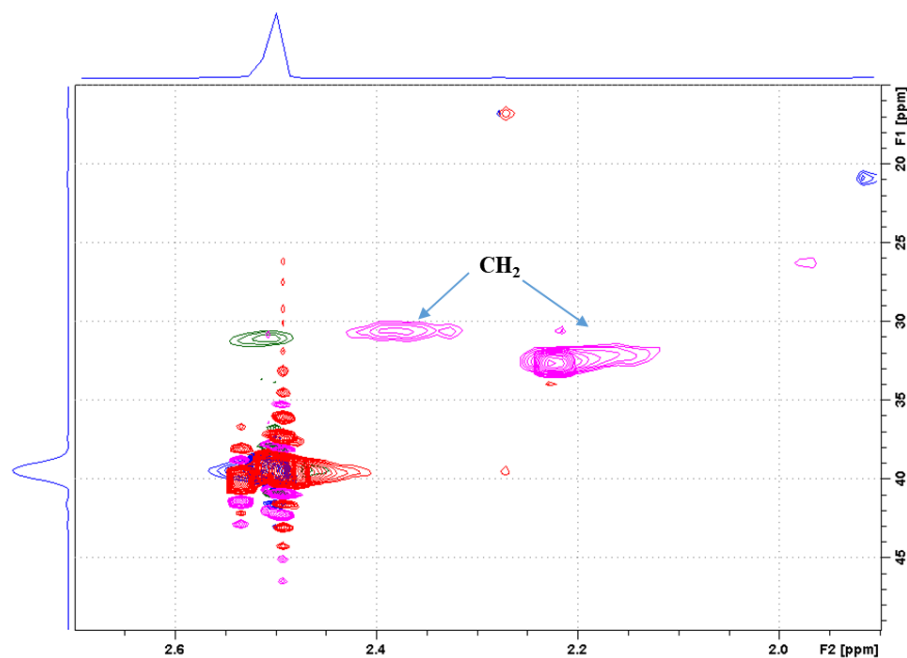


247

248 Figure 2 HSQC spectrum of native KL and KL0.2MA in DMSO, aromatic zone

249

250 In the same manner, the HSQC spectra of native and succinic anhydride modified lignin 0.2SA KL
251 were superimposed (Figure 3) -blue/green signals: CH or CH₃ / CH₂ for the native KL; Red/pink
252 signals: CH or CH₃ / CH₂ for KL0.2SA-. As in the case of MA, the HSQC enlargement of SA
253 modified KL confirms the appearance of two new signals (pink) corresponding to CH₂ groups with
254 different chemical environment. Full HSQC spectra for KL0.2MA and KL0.2SA are available in
255 supporting information (Figure S3 and S4).



256

257 Figure 3: HSQC spectrum of native KL and KL0.2SA in DMSO, aliphatic zone

258 **3.5 Phosphorus NMR analysis**

259 The obtained proportions of the different hydroxyl and carboxylic acid groups (in mmol/g) for both
 260 MA and SA modified KL are summarized in Table 2. For both anhydrides, the total amount of
 261 hydroxyl decreases during the reaction. After esterification, the hydroxyl content decreased by 34%
 262 (KL0.3MA). This also confirms that the esterification has taken place. The carboxylic acid content
 263 increased after esterification. Aliphatic and aromatic hydroxyls show a different reactivity. A 48%
 264 decrease was observed for the aliphatic hydroxyl content while only 23% of the phenolic hydroxyl
 265 reacted. Therefore, esterification was more effective on aliphatic hydroxyl groups than on phenolic
 266 hydroxyl groups. This trend was also observed by Ahvazi et al. (2011) during the esterification of
 267 kraft lignin with MA in batch. On the other hand, Bridson et al. (2013) described the possible
 268 decrease in aliphatic hydroxyl and carboxylic acids after extrusion of kraft lignin without plasticizer.

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269 According to them, the decrease in hydroxyl levels is probably due to dehydration reactions leading
270 to condensation. These results highlight condensation reactions when using reactive extrusion for
271 lignin chemical modification. Similar results can be observed for the esterification reaction with
272 succinic anhydride. The percentage of hydroxyl decreases after esterification, with the increase in the
273 amount of carboxylic acid. Aliphatic OHs are also more reactive than aromatic OHs. The sample
274 KL0.3SA was not soluble in used solvent system. The reference sample (KL_{ref}) showed a decrease in
275 both aromatic and aliphatic OHs as well as carboxyl groups. Phenolic OH groups decreased from
276 1.81 mmol/g for native KL to 1.42 mmol/g. Aliphatic OHs decreased from 1.54 mmol/g (native KL)
277 to 1.39 mmol/g (KL_{ref}). This result reveals that the structure of lignin changes during the REX
278 process even when no reagent is used. In contrast, the samples of KL modified with MA and SA
279 prepared in batch conditions show very poor solubility in pyridine/deuterated chloroform mixture
280 used for ³¹P NMR, which might further indicate (along with the increase in molecular weight) a
281 possible crosslinking between free carboxyl groups of grafted anhydride and the residual hydroxyl
282 groups still present in lignin.

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283 Table 2: Proportion in mmol/g of lignin, of the different hydroxyl groups and carboxylic acids of
284 native and esterified KL

KL	COOH	G -OH	S -OH	H -OH	Total phenolic -OH	Total aliphatic -OH	Total hydroxyl
Native	0.22	1.43	0.23	0.15	1.81	1.54	3.35
0.1 MA	0.28	1.31	0.18	0.12	1.61	1.3	2.91
0.2 MA	0.34	1.25	0.14	0.1	1.49	1.15	2.64
0.3 MA	0.56	1.2	0.12	0.08	1.40	0.8	2.2
0.1 SA	0.27	1.32	0.2	0.1	1.62	1.25	2.87
0.2 SA	0.42	1.29	0.12	0.08	1.49	1.2	2.69

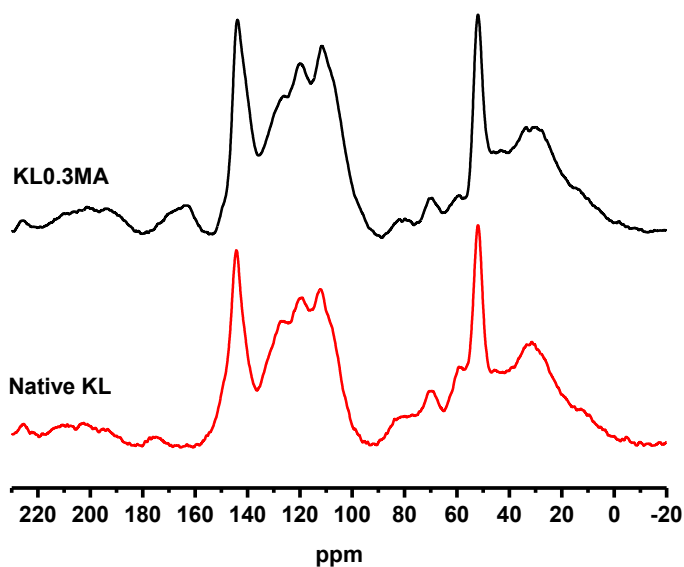
285

286 3.6 Solid-state ^{13}C CP-MAS NMR

287 It was not possible to calculate the DS of esterified lignin samples using ^{31}P NMR due to possible
288 dehydration involving hydroxyl groups of lignin. On the other hand, Solid-state ^{13}C CP-MAS NMR
289 allows us to calculate the DS using the signals of grafted carbonyl groups after esterification. Figure
290 4 shows solid-state ^{13}C CP-MAS NMR spectra of native and modified (KL0.3MA) lignins. It can be
291 seen that after esterification with maleic anhydride the carbonyl group (175 ppm) which is present in
292 native lignin in small quantity increases significantly and shifts to higher field (163 ppm). This shift
293 can be explained by the difference in the chemical environment of carbonyl functions in native and

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294 esterified lignins. The DS of modified sample (KL0.3MA) was found to be 0.18 with a corresponding
295 RE of 60%. The Solid-state ^{13}C CP-MAS NMR spectrum of batch modified KL (Batch KL0.3MA) is
296 shown in supporting Information (Figure S5). The DS of this sample is 0.19 with RE of 63%.



297

298 Figure 4: Solid-state ^{13}C CP-MAS NMR spectra of Native KL and KL modified with 0.3 equivalents
299 of MA

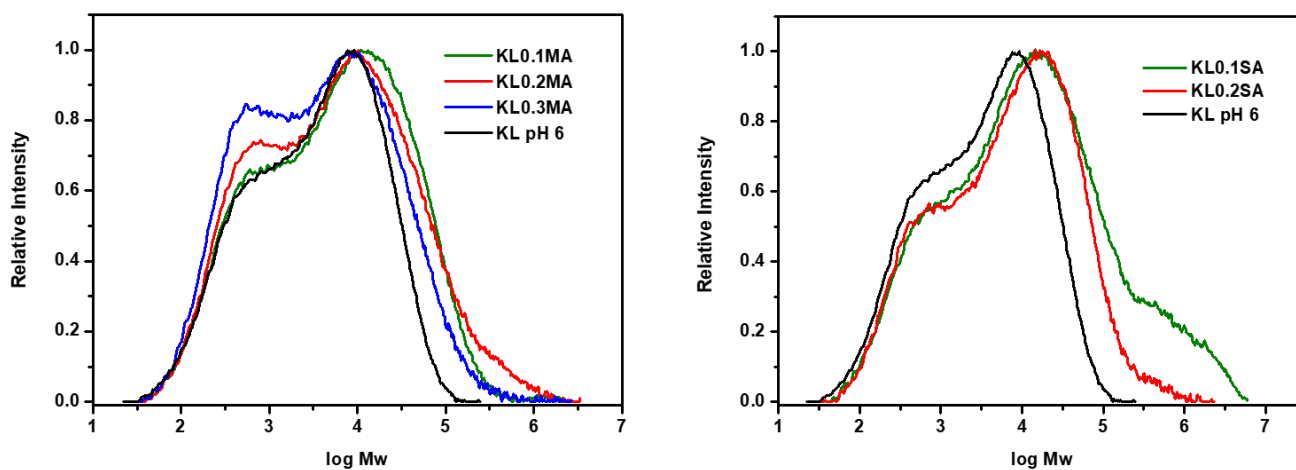
300

301 3.7 GPC/SEC chromatography

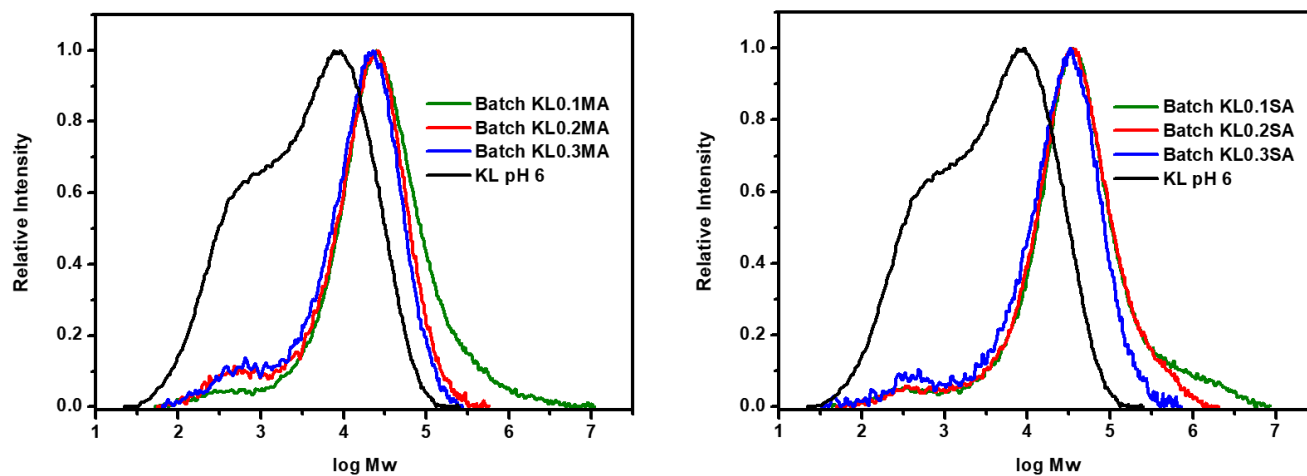
302 Chemical modification of lignin in REX conditions, where shear rate and temperature play essential
303 role, can have a direct influence on molecular weight distribution. It was found that for native lignin
304 M_w is 10800 g/mol with a polydispersity of 8.91. As we can see in Figure 5, after extrusion the
305 polydispersity increases significantly for both MA and SA lignin esters. However, the
306 chromatograms are different for two reagents. In the case of KL modified with MA, a new peak with
307 $M_w = 560$ g/mol appeared in the area of low molecular weight fractions, which increases with
308 increasing ratio of the anhydride. This can be explained by possible lignin chain cleavage during
309 REX conditions (Bridson et al., 2013). The original peak of lignin becomes broader after the reaction.
310 For KL modified with SA, there are no changes in low molecular weight area. At the same time, the
311 original peak is shifted towards higher molecular weight showing higher polydispersity than native
312 KL. These results show that REX can change the structure and properties of lignin. In contrast, KL
313 esterified in batch conditions (Figure 6) shows a shift of molecular weight profiles towards higher
314 molecular weights for both anhydrides. In this case, one possible explanation could be intra- and
315 intermolecular crosslinking between remaining hydroxyls of lignin and free carboxyl groups newly
316 generated after the reaction with the anhydride. As previously mentioned, (section 3.5 Phosphorus
317 NMR analysis), the KL samples esterified in batch show poor solubility in ^{31}P NMR solvent which
318 also indicate the possible crosslinking in the lignin polymer. The crosslinking has an influence not
319 only on lignin molecule but also on the properties of lignin-based materials (Lang et al., 2018).
320 However, the polydispersity decreases in the case of reaction in batch from 8.91 for native KL to 6
321 for Batch KL0.3MA and 7.82 in case of Batch KL0.3SA. This result could be also due to the
322 purification procedure, with the low molecular weight fractions being more soluble in acetone. To
323 highlight the influence of REX parameters on the lignin transformation, the reference sample KL_{ref}

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324 was studied by GPC/SEC. It was found that after extrusion, the molecular weight and polydispersity
325 of lignin increase ($M_w=16700$, $M_w/M_n= 18$). This result confirms that temperature and shear rate
326 have a significant influence on lignin structural changes. The future interest in lignin transformation
327 using REX would be to explore if these changes are directly correlated to SME and if it is possible to
328 control the average molecular weight and polydispersity of the obtained product by the extrusion
329 process parameters.



331 Figure 5: GPC/SEC chromatograms of REX modified KL with maleic (left) and succinic (right)
332 anhydrides

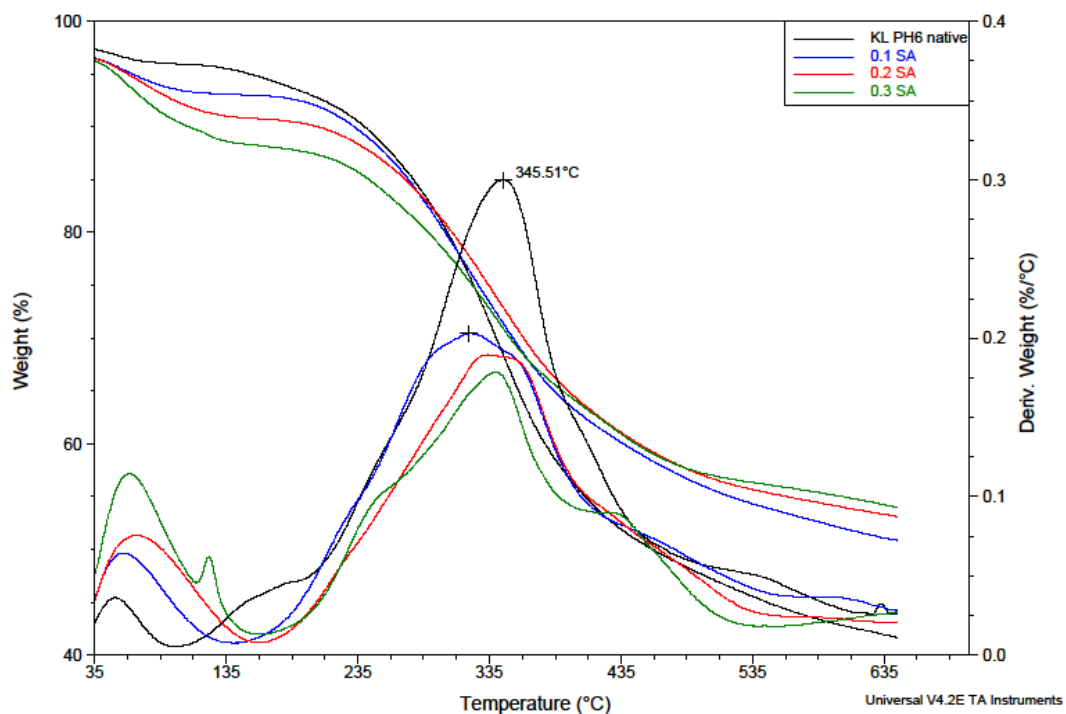


334 Figure 6: GPC/SEC chromatograms of KL modified in batch with maleic (left) and succinic (right)
335 anhydrides

336 **3.8 Thermal analysis of native and modified KL**

337 Native and modified KL were analyzed using TGA (Figure 7). For all samples, a weight loss of about
338 5-8% at temperatures up to 100°C corresponds to water loss. The water loss percentage increases
339 with the increase of succinic anhydride. This result confirms that modified samples become more
340 hydrophilic. During additional heating, the onset of degradation occurred between 135°C and 200°C.
341 Typically, the degradation rate reaches a maximum between 300 and 400°C. During this stage (up to
342 600°C) the pyrolysis of the lignin takes place, resulting in the breaking of the C-C and C-O bonds of
343 the side chains, the condensed bonds and the breaking of the ether bonds (Cao et al., 2013). From
344 600°C, the formation of amorphous carbon residue is observed. The samples of KL modified with
345 succinic anhydride all show a slower degradation compared to native lignin. The same behavior is
346 observed in the case of MA. However, no significant changes in thermal behavior between native KL
347 and the reference sample are observed.

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348

349 Figure 7: TGA and DTG curves (recorded under nitrogen atmosphere) of native kraft lignin and kraft
350 lignin esterified with SA

351

352 **4 Conclusion**

353 In summary, we found that kraft lignin maleic and succinic esters can be prepared in very short
354 reaction time (< 1 minute) in a homogeneous medium and by using low amounts of plasticizer (15-
355 25%) in a reactive extrusion process. Native lignin shows no melting behavior. We showed that small
356 amounts of DMSO renders lignin processable when low extrusion temperature (140°C) is applied.
357 2D NMR spectroscopy revealed that the reaction of lignin transformation via REX is a
358 monoesterification. At the same time, the molecular weight and polydispersity increase in high shear
359 rate + temperature REX conditions resulting in lignin molecules crosslinking. GPC chromatograms
360 after extrusion showed a shift towards higher molecular weights. A similar shift was also observed
361 for samples prepared in batch conditions. In contrast, the polydispersity decreases for lignin esters
362 synthesized in batch. REX esterified lignin samples show slower degradation compared to native
363 lignins. These new lignin derivatives could be used in combination with other polymers to produce
364 new plastics. Due to the presence of a pendant reactive double bond maleated lignin could be used as
365 a macromonomer for further polymerization or copolymerization synthesis.

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371

372 **Declaration of interest:** none

373

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