Supplementary Information (SI) for Green Chemistry. This journal is © The Royal Society of Chemistry 2025

Supporting information

3D printable lignin-caprolactone material

Banchamlak Bemerw Kassaun^{1,2}, Luyao Wang², Oskar Backman², Chunlin Xu^{*2}, Pedram Fatehi^{*1,2}

¹Department of Chemical Engineering, Lakehead University, 955 Oliver Road, Thunder Bay, ON P7B 5E1,

Canada, ²Laboratory of Natural Materials Technology, Faculty of Science and Engineering, Åbo Akademi

University, Turku, Finland.

*corresponding authors: chunlin.xu@abo.fi, pfatehi@lakeheadu.ca

Page number: (S1-S15)

Equation: (S1-S12)

Table: (S1-S7)

Figure: (S1-S7)

1. Yield calculation for ethanol fractionation

$$Yield(\%) = \frac{Wt}{Wo} \times 100$$
_____(S1)

Wt is the final weight, and Wo is the initial lignin (g) weight.

2. Design of experiment-RMS-Box-Behnken

$$xi = \frac{Xi - X_c}{\Delta x_i}, i = 1, 2, 3 \dots Z_{z_i}$$

xi, dimension less value of an independent variable: Xi is the real value of an independent variable, X_c is the actual value of an independent variable at the center point, and ΔXi is the step change of the real value of the variable "i".

$$N = 2p(p-1) + C_{p------}$$
(S3)

N is the number of experiments, p is the number of factors, and Cp is the number of center points,

$$Y = f(x_{1,} x_{2,} x_{3,...} x_{c,+e} - ... (54)$$

Where f is the actual response function of an unknown format, and e is the error that illustrates the differentiation. The behavior of the response surface was examined for the response function of Y sing the second-order polynomial equation.

$$Y = \beta_o + \sum_{a=1}^{c} (\beta_a x_a) + \sum_{a=1}^{c} (\beta_{aa} x_a^2) + \sum_{b \le 2} a \sum_{b \le 2}^{c} \beta_{ab} x_a x_b + e_a$$
------(S5)

Y is the response; x_a and x_b are variables (a and b range from 1 to c) β_0 is the model intercept coefficients; β_a , β_{aa} , and β_{ab} are interaction coefficients of linear, quadric, and second-order terms, respectively; c is the number of independent parameters (c=3 in this study); e_a is the error.

3. Grafting on the hydroxyl group of lignin

$$\alpha = \frac{L_{OH} \ _LPCL_{OH}}{L_{OH}} \times 100$$
 (S6)

LOH -concentration of lignin hydroxyl groups, LPCLOH- concentration of L-PCL hydroxyl groups, and α - the percentage of [CL] grafting ¹.

4. Degree of polymerization using ¹H-NMR

$$n = (\frac{lb}{la} + 1)$$
(57)

Ib and Ia correspond to the PCL chain's repeating and terminal ¹H NMR methylene intensities ².

Table S1. The main ¹³C-¹H correlation signals of birch ALs substructures and interunit linkages detected by HSQC NMR.

5. Quantification of linkages

- -

Besides the semi-quantitative strategy, another quantitative strategy is based on HSQC spectra, which selected "aromatic units" as IS. Particularly, the method uses a cluster of signals representative of all C9 units, i.e., IS. The choice of the 0.5IS2,6 + IG2 signals as IS is for hardwood lignin ³. The results expressed how much linkage (<1.0) per aromatic ring.

IC9 units = 0.5IS_{2,6} + IG₂ (hardwood lignin)-----(**\$8**)

Where IS2,6 is the integration of S2,6, including S and S', IG2 is the integral value of G2. IC9 represents the integral value of the aromatic ring. According to the internal standard (IC9), the amount of IX% could be obtained by the following formula,

IX% = IX/IC9 × 100%------(**S9**)

Where IX is the integral value of the α -position of A (β -O-4), B (β - β), C (β -5), and D (β -1), the integration should be in the same contour level.

 Table S1. Minimum and maximum levels of three factors in terms of coded and uncoded symbols.

Factor	Nama	Unite	Tuno		Std.		
	Name	Units	Туре	-1	0	+1	Dev.
A	CL/OH	Mmol g ⁻ 1	Numeric	0.86	1.73	2.60	0.6152
В	Reaction time	Minutes	Numeric	120	420	720	212.13
С	Catalyst Conc	Wt. %	Numeric	0.50	0.75	1.00	0.1768

Table S 2 Optimization parameters conditions limit and response parameters desirable goals.

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
CL/OH	in range	0.86	2.6	1	1	3
Reaction time	in range	120	720	1	1	3
Catalyst Con.	minimize	0.5	1	1	1	3
Viscosity	maximize	194.2	10287	1	1	3
Melt Temperature	maximize	45	110	1	1	3
DP	maximize	3.52	10.13	1	1	3

Label	Birch alkaline lignin δ _c /δ _μ (ppm)	Groups
-OCH ₃	(54.6-57.2)/(4.1-3.2)	C-H in -OCH3 (methoxy)
-OCH ₃ (cond.)	(59.7)/(3.18-3.90)	Methoxy from 2/6 condensed units
Β _β	(53.8-54.5)/(3.1-2.9)	B in resinol β-β units
C _β	53.0/3.47	B in phenylcoumaranan β-5 units
A _r	60/3.4	Ύ in β-Ο-4
B	62.8/3.7	C _. -H _. in phenylcoumarane β-5 ՝
X2	72.6/3.04	2 in β -D-xylopyranoside
X3	73.8/3.24	3 in β-D-xylopyranoside
X4	75.3/3.57	4 in β-D-xylopyranoside
X1	101.7/4.29	1 in β-D-xylopyranoside
Β _α	85.0/4.68	α in resinol β-β units
AG_{α}	70.9/4.75	α in β-O-4 linked to G units
AG _γ	63.4/3.47	C_{γ} -H $_{\gamma}$ in aryl glycerol unit
C _α	84.9/4.62	$C_{\alpha}^{-}C_{\alpha}^{-}$ in resinol β-β units
S _{2,6} (etherified)	103.3/6.72	2 and 6 in syringyl unit
S _{2,6} (free phenolic)	105.7/6.49	2 and 6 in non-etherified syringyl unit
S 2,6	106.1/7.22	2 and 6 in $C_{\alpha}^{}$ oxidized syringyl unit
G ₂	110.6/6.7	2 in guaiacyl units
G ₂ '	108.8/7.04	2 in non-etherified guaiacyl units
FA ₂	115.1/6.94	2 in ferulic acid (ester)
pCA _{2,6}	130.4/7.51	2,6 in p-coumaric acid (ester)
pCA_{β}/FA_{β}	116.3/6.45	β in p-coumaric acid (ester) (pCA\beta) and ferulic acid (ester) (FAβ)
G ₅	115.9/6.7	5 in guaiacyl units
G ₆	119.1/6.7	6 in guaiacyl units
G6'	122.9/7.5	6 in oxidized (C _{α} =O) guaiacyl units
		\propto in p-coumaric acid (ester) (pCA $_{_{lpha}}$) and ferulic acid
pCA $_{\alpha/}$ FA $_{\alpha}$	144.9/7.51	(ester) (FA $_{\alpha}$)
M _∝	111.95/6.13	\propto in aryl enol ether
D _β	126.3/6.8	$\boldsymbol{\beta}$ in cinnamaldehyde end groups
H	127.1/7.1	C2,6-H2,6 in p-hydroxybenzoate unit

 Table S3.
 The birch alkali lignin interunit linkages ppm and groups from HSQC analysis.

Coded variable				Real varia	ables	Response					
Run	А	В	С	A: CL/OH	B: reaction time	C: catalyst con.	Viscosity	Melt temp.	DP		
				[mmol g ⁻¹]	[minutes]	[wt.%]	[P]	[°C]			
L _E P1	-1	0	-1	0.86	420	0.5	194.2	108	3.52		
L _E P2	+1	0	-1	2.6	420	0.5	546.83	48	7.02		
L _E P3	0	-1	-1	1.73	120	0.5	250.27	47	5.54		
L _E P4	+1	+1	-1	2.6	720	0.75	1519.5	52	7.82		
L _E P5	0	0	0	1.73	420	0.75	1505.6	50	5.91		
L _E P6	-1	0	1	0.86	420	1	3210.6	53	4.6		
L _E P7	0	0	0	1.73	420	0.75	3337.6	50	7.82		
L _E P8	+1	-1	0	2.6	120	0.75	734.55	48	7.6		
L _E P9	0	+1	+1	1.73	720	1	10287	50	6		
L _E P10	-1	-1	0	0.86	120	0.75	546.45	100	3.86		
L _E P11	-1	+1	0	0.86	720	0.75	2720.9	110	5.6		
L _E P12	0	0	0	1.73	420	0.75	330.61	50	4.74		
L _E P13	0	+1	-1	1.73	720	0.5	1231.1	100	6.83		
L _E P14	0	0	0	1.73	420	0.75	1323.3	50	5.61		
L _E P15	+1	0	+1	2.6	420	1	1200.4	54	10.13		
L _E P16	0	-1	+1	1.73	120	1	5323.8	45	5.93		
L _E P17	0	0	0	1.73	420	0.75	4748.2	55	7.69		

 Table S4. Coded and actual levels of reaction parameters (caprolactone to lignin hydroxyl concentration, reaction time, and catalyst concentration) and response variable (viscosity and melt temperature).

Table

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	5.040e ⁺⁰⁷	3	1.680e ⁺⁰⁷	3.88	0.0350	significant
A-CL/OH	8.917e ⁺⁰⁵	1	8.917e ⁺⁰⁵	0.2060	0.6574	
B-Reaction time	9.909e ⁺⁰⁶	1	9.909e ⁺⁰⁶	2.29	0.1542	
C-Catalyst Conc	3.960e ⁺⁰⁷	1	3.960e ⁺⁰⁷	9.15	0.0098	
Residual	5.627e ⁺⁰⁷	13	4.328e ⁺⁰⁶			
Lack of Fit	4.375e ⁺⁰⁷	9	4.861e ⁺⁰⁶	1.55	0.3552	not significant
Pure Error	1.252e ⁺⁰⁷	4	3.130e ⁺⁰⁶			
Cor Total	1.067e ⁺⁰⁸	16				

Source	Sum of Squares	df	Mean Square	F-value	p-value		
Model	10421.03	9	1157.89	11.31	0.0021	significant	
A: CL/OH	6384.50	1	6384.50	62.37	< 0.0001		
B: Reaction time	648.00	1	648.00	6.33	0.0400		
C: Catalyst Conc	242.00	1	242.00	2.36	0.1680		
AB	9.00	1	9.00	0.0879	0.7754		
AC	4.00	1	4.00	0.0391	0.8489		
BC	576.00	1	576.00	5.63	0.0494		

S6. Analysis of variance (ANOVA) for melt temperature quadratic model.

A²	2227.37	1	2227.37	21.76	0.0023	
B²	51.58	1	51.58	0.5039	0.5007	
C ²	151.58	1	151.58	1.48	0.2631	
Residual	716.50	7	102.36			
Lack of Fit	696.50	3	232.17	36.43	0.9914	not significant
Pure Error	20.00	4	5.00			
Cor Total	11137.53	16				

R²=0.936, adjusted R²=0.946,

 Table S7. Analysis of variance (ANOVA) for degree of polymerization linear model.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	31.22	3	10.41	10.12	0.0010	significant
A-CL/OH	28.09	1	28.09	27.31	0.0002	
B-Reaction time	1.38	1	1.38	1.34	0.2679	
C-Catalyst Conc	1.76	1	1.76	1.71	0.2138	
Residual	13.37	13	1.03			
Lack of Fit	6.08	9	0.6757	0.3708	0.9004	not significant
Pure Error	7.29	4	1.82			
Cor Total	44.59	16				

R²=0.7002, adjusted R²=0.631,



Fig. S1. Preparation of L-PCL (a) and Schematic representation of lignin-polycaprolactone (L-PCL) synthesis using DBDTL as a catalyst, lignin as a micro initiator, and caprolactone (CL) monomer (b).



Fig. S2. Substitution of hydroxyl groups of L-PCL polymers after grafting caprolactone into lignin.



Fig. S3. ¹H NMR spectra for all the polymers generated using the BBD-RSM design and reference commercial PCL sample.



Fig. S4. Viscosity at the melt temperature for all the polymers was generated using the BBD-RSM design.



Fig. S5. Contour graphs of two-factor interactions of CL/OH, reaction time, and catalyst concentration on viscosity (a), melt

temperature (b), and degree of polymerization (c).



Fig. S6. The three-dimensional (3D) plots of CL/OH, reaction time, and catalyst concentration on viscosity (a), melt temperature (b), and degree of polymerization (c).



Fig. S7. The appearance of LPO filament (a), the appearance of LPO when melted to make a film (b).

6. The BBD-RSM modeling for the lignin-caprolactone polymers

The BBD-RSM in design expert software optimized the reaction conditions and created a lignin caprolactone polymer with the required melt temperature and flow properties. Based on the model analysis, the data for the response viscosity is fitted in a linear model, as presented in **Table S3**. The relationship between viscosity and the experimental parameters (CL/OH, reaction time, and catalyst concentration) is shown in **Eq. S10**. The coefficient of determination (R²) is the ratio of the explained variation to the total variation and measures the degree of fit.⁴ A good model fit that can predict the response variable using a predictor variable shows an R² closer to 1.⁵ This means that the response model evaluated in this study can explain the effect of experimental parameters on viscosity with an R² of 0.847, an adjusted R² of 0.895, and a confidence interval of 95%. In addition, the model's significance is evidenced by an F-value (3.88) and a low probability value (P=0.03). A P-value lower than 0.05 indicates that the model is statistically significant, whereas a value higher than 0.1 indicates that the model is not significant. In this case, the linear effect of catalyst concentration is a considerable model term. The Lack of fit F-value of 1.55 implies the lack of fit is insignificant relative to the pure error. The relationships between the viscosity and CL/OH, melt temperature, and DP are shown in **Fig. S6**a and **Fig. S5**a. Each plot shows the effects of two variables within their studied ranges, with the other variable fixed to zero level. The shape of the contour plot shows the nature and extent of the interactions between factors. An elliptical contour plot indicates a prominent interaction, whereas a negligible effect appears as a circular contour plot.⁶

As can be seen from the plots, the viscosity increased with increasing catalyst concentration. The role of a catalyst in the viscosity of a lignin caprolactone polymer has yet to be investigated. However, the literature on the polymerization of lignin caprolactone polymer indicates that a catalyst plays a role in activating the reaction between lignin and the cyclic caprolactone polymer.⁷ Metal complexes with unoccupied p, d, or f orbital functions are coordination catalysts rather than anionic initiators. These catalysts facilitate the synthesis of polymers with large molecular weights via the coordination/insertion process.⁸ The molecular weight of L_EP6 is higher than L_EP5 (**Table 3**). Even though the CL/OH ratio is higher for L_EP5, the catalyst concentration of L_EP6 is higher, which leads to higher molecular weight and viscosity (**Table 3**).

$$Viscosity(P) = -5274.2 - 383.7 \frac{CL}{OH} \left(\frac{mmol}{g}\right) + 3.709 \ reaction. \ time(min) + 8899.7 \ Catalyst \ con.(wt.\%) --- ($10]$$

Melt temperature (°*C*)

$$= 2.14.3 - 138.6 \frac{CL}{OH} \left(\frac{mmol}{g}\right) + 0.13 reaction time (min) - 106.8 catalyst con.(wt.%) - 0.0057 \frac{CL}{OH} \left(\frac{mmol}{g}\right)$$

reaction time(min) + 4.59 $\frac{CL}{OH}$ catalyst con.(wt.%) - 0.16 × reaction time(min) × catalyst con.(wt.%) + 30.4 $\frac{CL}{OH} \left(\frac{mmol}{g}\right)^2$ + 0.000039 reaction time(min.)² + 96 catalyst con.(wt.%)²

----(S11)

$$Degree \ of \ polymerization(DP) = 0.54 + 2.2 \frac{CL}{OH} (mmol/g) + 0.001 reaction \ time \ (min) + 1.88 catalyst \ con.(wt.\%) = ---$$

-----(\$12)

Based on the model analysis, the data for the melt temperature can be fitted in a quadratic model, as presented in **Table S5**. The relationship between melt temperature and the experimental parameters (CL/OH, reaction time, and catalyst concentration) is shown in **Eq. S11**. The response model evaluated in this study can explain the effect of experimental parameters on melt temperature with an R²= 0.936, adjusted R²=0.946, and a confidence interval of 95%. In addition, the model F-value of 11.31 and P-values were less than 0.05, implying that the model is significant. The effect of the CL/OH ratio, reaction time, the interaction of reaction time and catalysis concentration, and the square of the CL/OH ratio are significant. The lack of fit F-value of 36.43 implies that the lack of fit is insignificant.

The relationships between the melt temperature and the three factors are shown in **Fig. 6S**b and **Fig. S5**b. Each plot shows the effects of two variables within their studied ranges, with the other variable fixed to zero level. The plots show that the T_m

decreased with increased CL/OH ratio and catalyst concentration, while the increase in reaction time seems to increase the melt temperature. The decrease in T_m with an increase in CL/OH ratio and catalyst concentration might be due to increased initiation and activation of the caprolactone monomer for ROP, resulting in increased chain growth of PCL in the lignin backbone as evidenced by the DP (**Table 3**).^{2, 9} The increase in T_m with an increase in reaction time could be related to increased chain entanglements and stronger intermolecular forces.² Nevertheless, extended reaction durations result in heightened chain branching or degradation, potentially reducing the melting temperature.¹⁰

Based on the model analysis, the data for the DP can be fitted in a linear model, as presented in **Table 6**. The relationship between DP and the experimental parameters (CL/OH, reaction time, and catalyst concentration) is shown in **Eq. S12**. The response model evaluated in this study can explain the effect of experimental parameters on DP with an R²=0.7002, adjusted R²=0.631, and a confidence interval of 90%. In addition, the model F-value of 10.12 and P-values were less than 0.05, implying that the model is significant. In this case, the concentration of CL/OH shows a statistically significant effect on the DP of lignin-PCL polymers, as shown by a P-value of 0.0002. The lack of fit F-value of 36.43 implies that the lack of fit is insignificant.

The relationship between DP and the three factors is shown in **Fig. S6**c and **Fig. S5**c. Each plot shows the effects of two variables within their studied ranges, with the other variable fixed to zero level. Increased CL/OH ratio, reaction time, and catalysis concentration increase the DP. An increased CL/OH ratio means increased polymerization rate and higher DP, while prolonged reaction time allows for more extensive polymerization, leading to higher molecular weight and longer polymer chains, and higher catalyst concentration would lead to faster polymerization rates and higher DP by providing more active sites for the polymer chain initiation. However, excessive caprolactone concentration, longer reaction time, and higher catalyst concentration could have a negative impact on the resultant polymer, leading to the creation of undesired by-product or incomplete polymerization, undesired side reactions such as chain branching/degradation, and crosslinking or gelation, respectively.^{1, 10, 11} Therefore, optimizing the CL/OH ratio, reaction time, and catalyst concentration is crucial to achieving the desired balance between DP, viscosity, and melt temperature.

The primary objective of the experimental analyses was the nature of the L-PCL polymer to be 3D printable. For a polymer to be 3D printable by the extrusion method, shear thinning and melt temperature are important characteristics. Since lignin by itself has shear thickening and doesn't have a melt temperature, the DP of PCL plays a great role in achieving a shear thinning and melt temperature of lignin-caprolactone polymers. Therefore, the optimization function in the design expert software was used to obtain the optimal conditions for the polymerization of lignin-caprolactone polymer reaction conditions, as discussed in the methodology (**Table 2**).

Reference

- 1. J. Tian, Y. Yang and J. Song, Int. J. Biol. Macromol., 2019, 141, 919-926.
- 2. I.-K. Park, H. Sun, S.-H. Kim, Y. Kim, G. E. Kim, Y. Lee, T. Kim, H. R. Choi, J. Suhr and J.-D. Nam, *Sci. Rep.*, 2019, **9**, 7033.
- 3. M. Sette, H. Lange and C. Crestini, *Comput. Struct. Biotechnol. J.*, 2013, 6, e201303016.
- 4. M. Burton and K. C. Kurien, J. Phys. Chem. A., 1959, 63, 899-904.
- 5. J. S. Krueger and M. S. Lewis-Beck, Pol. Anal., 2007, 15, 2-4.
- 6. A. I. Khuri and J. A. Cornell, *Response surfaces: designs and analyses*, CRC press, 2018.
- 7. M. C. Najarro, M. Nikolic, J. Iruthayaraj and I. Johannsen, *ACS Appl. Polym. Mater.*, 2020, **2**, 5767-5778.
- 8. A. Arbaoui and C. Redshaw, *Polym. Chem.*, 2010, 1, 801-826.
- 9. X.-Q. Zhang, M.-J. Chen, C.-F. Liu and R.-C. Sun, J. Agric. Food Chem., 2014, 62, 682-690.
- 10. E. Zhuravlev, J. W. P. Schmelzer, B. Wunderlich and C. Schick, *Polymer*, 2011, **52**, 1983-1997.
- 11. H. Liu, N. Mohsin, S. Kim and H. Chung, J. Polym. Sci. A. Polym. Chem., 2019, 57, 2121-2130.