
Supplementary Material: Optimization of the Electrospray Process to Produce Lignin Nanoparticles for PLA-based Food Packaging

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Table S1. Range and levels of independent process variables used in the experimental design.

Trial	Bloc	Lignin concentration	Flow rate	Applied voltage	Tip-to-collector distance
1	1	0	0	0	0
2	1	-1	1	0	0
3	1	-1	0	0	1
4	1	0	-1	0	1
5	1	0	1	0	1
6	1	0	0	1	-1
7	1	1	0	0	-1
8	1	0	-1	0	-1
9	1	-1	0	-1	0
10	1	1	0	1	0
11	1	0	-1	-1	0
12	1	1	1	0	0
13	1	1	0	-1	0
14	1	1	-1	0	0
15	1	0	0	0	0
16	1	0	-1	1	0
17	1	-1	0	1	0
18	1	0	1	0	-1
19	1	0	1	-1	0
20	1	0	0	-1	1
21	1	1	0	0	1
22	1	0	0	-1	-1
23	1	-1	0	0	-1
24	1	-1	-1	0	0
25	1	0	0	0	0
26	1	0	0	1	1
27	1	0	1	1	0
28	2	0	0	0	0
29	2	0	1	-1	0
30	2	-1	0	1	0
31	2	-1	0	0	-1
32	2	0	-1	-1	0
33	2	0	0	0	0
34	2	0	1	0	-1
35	2	0	0	-1	-1
36	2	-1	-1	0	0
37	2	0	0	-1	1
38	2	1	0	0	1
39	2	0	1	0	1
40	2	0	0	1	1
41	2	1	0	-1	0
42	2	0	-1	1	0
43	2	0	1	1	0
44	2	-1	1	0	0
45	2	1	1	0	0

46	2	0	-1	0	-1
47	2	1	-1	0	0
48	2	0	0	0	0
49	2	1	0	0	-1
50	2	1	0	1	0
51	2	0	-1	0	1
52	2	0	0	1	-1
53	2	-1	0	0	1
54	2	-1	0	-1	0

Table S2. Condition design using the response surface methodology with the Box–Behnken design and experimental/predicted data of the response.

Run	TypeP t	Bloc	LC (mg/mL)	FR (mL/h)	HV (kV)	TCD (cm)	Z-Ave (d. nm)		PdI		ZP (mV)	
							EXP	PRED	EXP	PRED	EXP	PRED
1	0	1	27.5	0.75	20	17.5	250.0	212.3	0.278	0.363	-31.1	-30.9
2	2	1	5	1	20	17.5	478.6	548.5	0.504	0.446	-33.6	-32.2
3	2	1	5	0.75	20	25	667.2	668.6	0.497	0.548	-14.8	-25.3
4	2	1	27.5	0.5	20	25	462.4	381.4	0.451	0.324	-21.4	-27.4
5	2	1	27.5	1	20	25	577.2	596.1	0.488	0.655	-30.3	-29.9
6	2	1	27.5	0.75	30	10	455.4	567.2	0.289	0.515	-26.0	-30.2
7	2	1	50	0.75	20	10	384.9	518.3	0.639	0.508	-29.5	-25.2
8	2	1	27.5	0.5	20	10	352.2	256.5	0.63	0.546	-28.4	-30.8
9	2	1	5	0.75	10	17.5	636.4	477.4	0.383	0.426	-34.6	-38.1
10	2	1	50	0.75	30	17.5	490.7	431.9	0.431	0.442	-29.9	-33.7
11	2	1	27.5	0.5	10	17.5	278.2	319.0	0.517	0.420	-30.0	-32.4
12	2	1	50	1	20	17.5	839.8	648.3	0.751	0.559	-28.9	-28.3
13	2	1	50	0.75	10	17.5	712.6	639.8	0.218	0.441	-22.4	-24.8
14	2	1	50	0.5	20	17.5	218.2	271.6	0.203	0.303	-28.1	-28.9
15	0	1	27.5	0.75	20	17.5	173.1	212.3	0.226	0.363	-33.7	-30.9
16	2	1	27.5	0.5	30	17.5	334.4	330.7	0.406	0.433	-31.9	-26.2
17	2	1	5	0.75	30	17.5	723.4	681.7	0.693	0.532	-32.0	-24.9
18	2	1	27.5	1	20	10	487.3	507.9	0.213	0.428	-29.2	-30.6
19	2	1	27.5	1	10	17.5	512.7	565.6	0.651	0.485	-23.5	-29.6
20	2	1	27.5	0.75	10	25	767.2	675.6	0.537	0.464	-33.1	-30.3
21	2	1	50	0.75	20	25	522.6	541.5	0.498	0.392	-33.7	-33.0
22	2	1	27.5	0.75	10	10	367.5	349.0	0.414	0.481	-32.5	-32.7
23	2	1	5	0.75	20	10	409.4	478.7	0.401	0.428	-48.4	-37.3
24	2	1	5	0.5	20	17.5	334.4	458.9	0.359	0.491	-31.1	-29.4
25	0	1	27.5	0.75	20	17.5	134.2	212.3	0.860	0.363	-32.8	-30.9
26	2	1	27.5	0.75	30	25	438.5	453.7	0.528	0.537	-29.0	-28.4
27	2	1	27.5	1	30	17.5	700.3	550.3	0.591	0.580	-34.9	-31.4
28	0	2	27.5	0.75	20	17.5	146.7	212.3	0.182	0.363	-31.7	-30.9
29	2	2	27.5	1	10	17.5	549.5	565.6	0.526	0.485	-31.8	-29.6
30	2	2	5	0.75	30	17.5	857.3	681.7	0.703	0.532	-9.03	-24.9
31	2	2	5	0.75	20	10	674.6	478.7	0.517	0.428	-31.3	-37.3
32	2	2	27.5	0.5	10	17.5	212.3	319.0	0.515	0.420	-29.8	-32.4
33	0	2	27.5	0.75	20	17.5	462.3	212.3	0.343	0.363	-24.9	-30.9
34	2	2	27.5	1	20	10	484.1	507.9	0.375	0.428	-29.4	-30.6
35	2	2	27.5	0.75	10	10	426.7	349.0	0.478	0.481	-31.6	-32.7
36	2	2	5	0.5	20	17.5	305.6	458.9	0.305	0.491	-30.1	-29.4
37	2	2	27.5	0.75	10	25	766.7	675.6	0.496	0.464	-35.4	-30.3
38	2	2	50	0.75	20	25	383.7	541.5	0.319	0.392	-29.8	-33.0
39	2	2	27.5	1	20	25	564.2	596.1	0.590	0.655	-23.7	-29.9
40	2	2	27.5	0.75	30	25	295.4	453.7	0.542	0.537	-31.8	-28.4
41	2	2	50	0.75	10	17.5	469.9	639.8	0.295	0.441	-29.6	-24.8
42	2	2	27.5	0.5	30	17.5	346.2	330.7	0.346	0.433	-27.0	-26.2
43	2	2	27.5	1	30	17.5	497.0	550.3	0.471	0.580	-35.4	-31.4

44	2	2	5	1	20	17.5	473.1	548.5	0.505	0.446	-34.0	-32.2
45	2	2	50	1	20	17.5	657.4	648.3	0.612	0.559	-28.0	-28.3
46	2	2	27.5	0.5	20	10	331.5	256.5	0.655	0.546	-32.6	-30.8
47	2	2	50	0.5	20	17.5	393.1	271.6	0.213	0.303	-29.3	-28.9
48	0	2	27.5	0.75	20	17.5	103.6	212.3	0.277	0.363	-30.8	-30.9
49	2	2	50	0.75	20	10	555.4	518.3	0.615	0.508	-24.9	-25.2
50	2	2	50	0.75	30	17.5	466.6	431.9	0.494	0.442	-32.6	-33.7
51	2	2	27.5	0.5	20	25	464.8	381.4	0.425	0.324	-29.7	-27.4
52	2	2	27.5	0.75	30	10	418.8	567.2	0.562	0.515	-29.3	-30.2
53	2	2	5	0.75	20	25	715.9	668.6	0.455	0.548	-34.3	-25.3
54	2	2	5	0.75	10	17.5	344.9	477.4	0.391	0.426	-40.3	-38.1

LC: lignin concentration, FR: flow rate, HV: applied voltage, EXP: experimental, PRED: predicted, TCD: tip-to-collector distance, d: Sizes of nanoparticles, PdI: polydispersity index, ZP: Zeta potential.

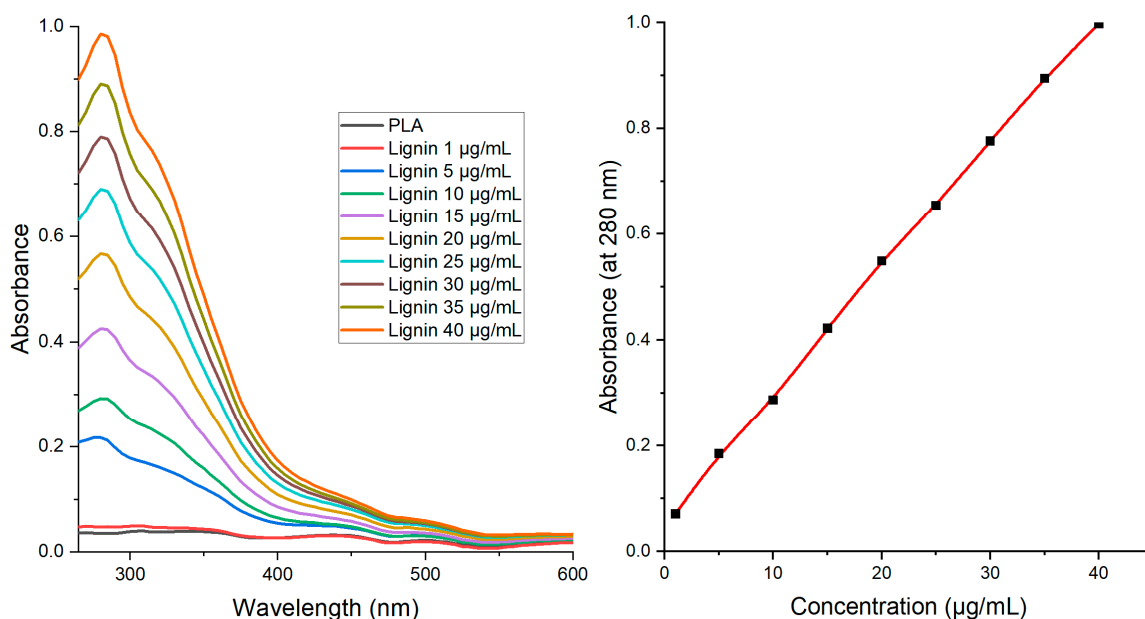


Figure S1. UV-Visible absorbance spectra of lignin nanoparticles in ethanol solutions at different concentrations (left) and calibration curve obtained by plotting the absorbance at 280 nm as a function of lignin concentration.

Table S3. Initial thermal degradation temperature (°C) and glass transition temperature (°C). The lignin content is 10 wt.%.

Sample	T _{5%}	T _g
Lignin	-	164
Lignin nanoparticles	-	165
PLA	378.7	64.2
Lignin-PLA	374.8	62.7
LNPs-PLA	368.0	63.2
LNPs-PLA/PLA	379.3	62.7

T_{5%}: Temperature at which the mass loss of the sample is 5% less than its mass loss at 50 °C via TGA;
T_g: glass transition temperature determined by DSC.

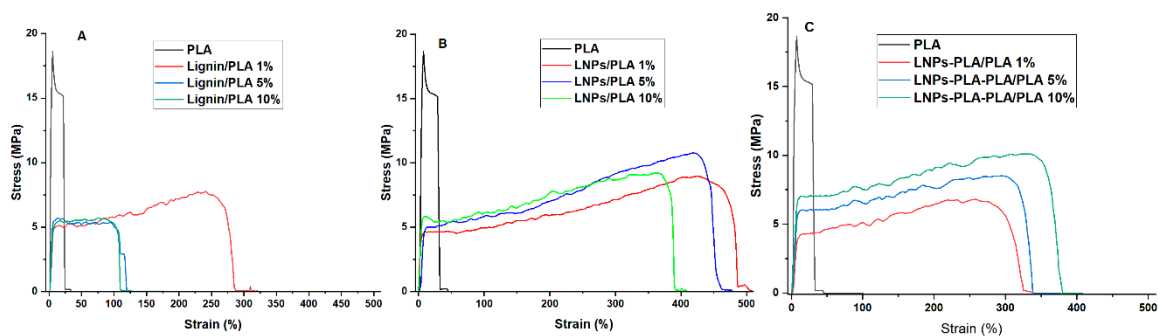


Figure S2. Stress-strain plots for neat PLA and PLA blend films containing different concentrations of lignin (A); lignin nanoparticles (B), and PLA-grafted lignin nanoparticles (C).

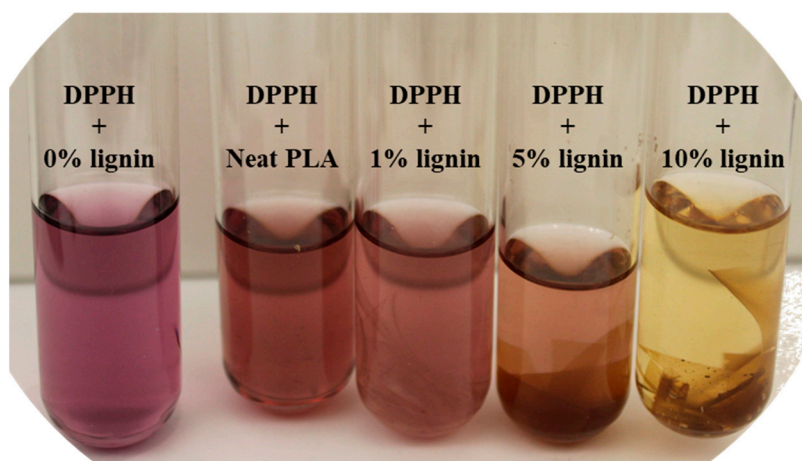


Figure S3. Image of DPPH solution and PLA composite films containing lignin at different concentrations (0-10%) immersed in DPPH solution (25% in methanol) for 4 h. The films are cut into small pieces before placing them into a DPPH solution.

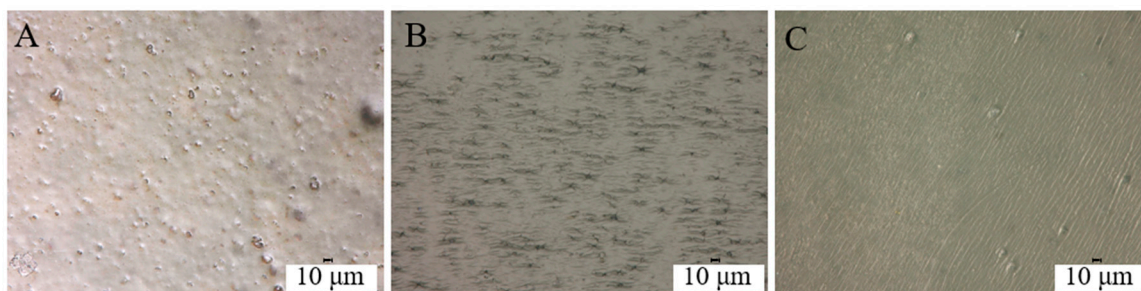


Figure S4. Digital images (thick films) of: (A) lignin-PLA blend, (B) lignin nanoparticle- PLA blend and (C) PLA-PLA-grafted lignin nanoparticle blend. All the blends contain 10 wt.% of lignin.