Stereolithography 3D Printing of Lignin-reinforced Composites with Significantly Enhanced Mechanical Properties

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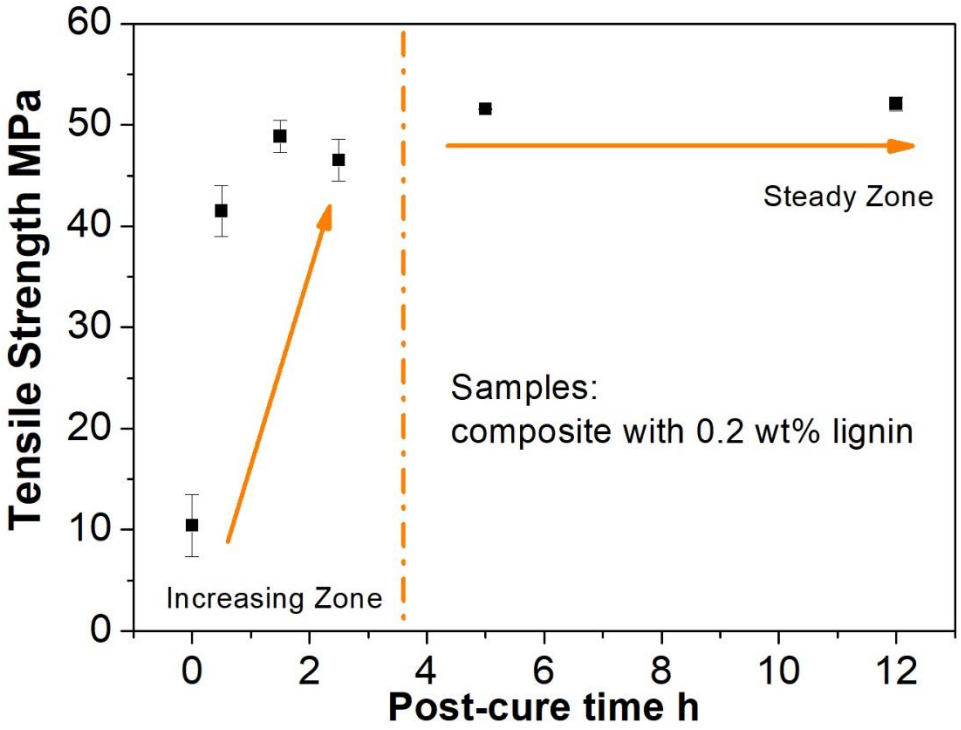

Figure S1. The influence of post-curing time in the Young's modulus of printed samples with 0.2 wt% lignin

The hydroxyl contents on the softwood kraft lignin was characterized by ^{31}P NMR[1] in the supporting information. Quantitative hydroxyl group determination of Kraft lignin samples was performed based on the published methods.[1] The purified Kraft softwood lignin (20.0 mg) used for printing was dissolved in 0.60 mL solution of pyridine/ $CDCl_3$ (v/v=1.6/1). The solution contained $Cr(acac)_3$ as a relaxation reagent and *endo*-N-hydroxy-5-norbene-2,3-dicarboxylic acid imide (NHND) as the internal standard. Then 70 µl of chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane (TMDP) was added to the sample solution for the phosphitylating reaction. The ^{31}P NMR spectrum was recorded on a Varian 500 MHz spectrometer with 90º pulse angle, 25 s pulse delay and 64 scans.

Table S1. Quantification of different types of hydroxyl groups in softwood Kraft lignin

aliphatic	C_5 substituted	guaiacyl	*p*-hydroxyphenyl	acid	total
1.01	1.09	1.19	0.17	0.41	3.86

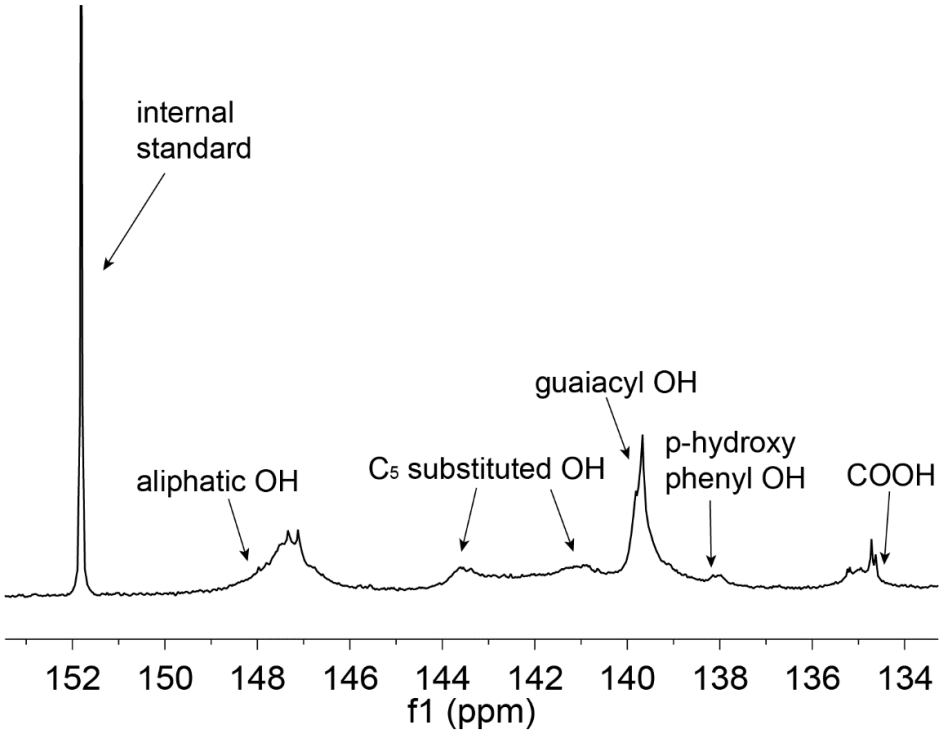

Figure S2. ^{31}P NMR spectra of the derivatized softwood Kraft lignin

To measure the size of lignin in acetone, lignin/acetone dispersion (0.01mg/mL) was measured by dynamic light scattering (DLS) on an ALV Light Scattering System with 22 mW He-Ne laser (wavelength, λ=632.8 nm). An ALV-7004 Multiple Tau Digital Correlator was used to calculate the normalized intensity autocorrelation function and find the average size of lignin particles in acetone. The computed hydrodynamic radius R_h=7830 nm.

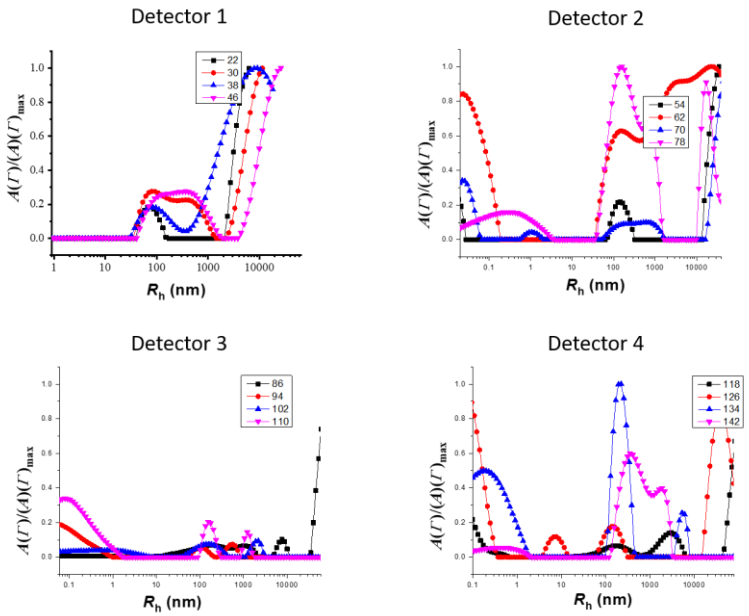

Figure S3. Size distribution of lignin in different

We also observe the lignin particles in acetone on SEM by drop the dispersion of lignin/acetone on silicon grid. Particles sizes are in accord with that by DLS.

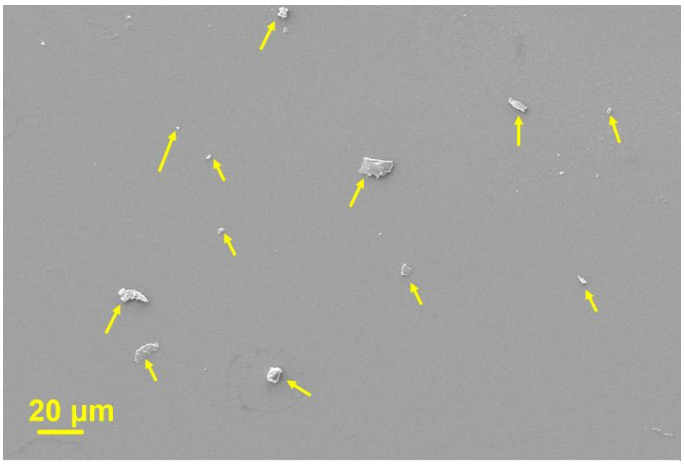

Figure S4. SEM of lignin particles

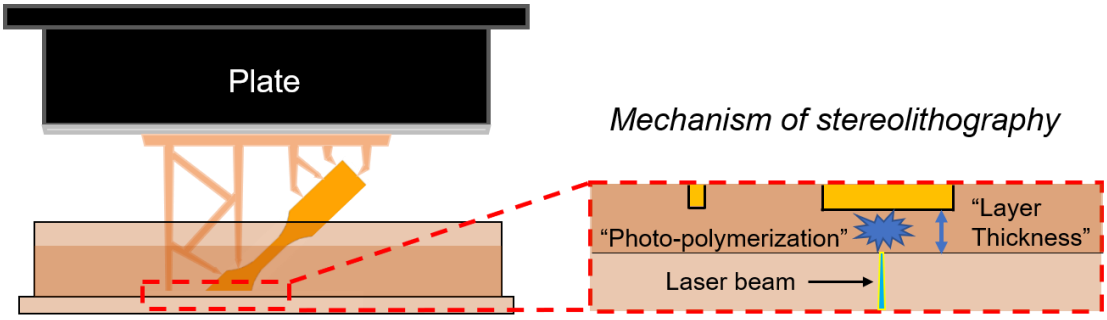

Figure S5. Form 1+ printer and its printing mechanism

Table S2. UV intensity of the UV device[a]

		Measured UV intensity μW/cm^2		
		1st [b]	2nd	3rd
Measured time	1 h[c]	282	277	248
	2 h	308	283	284
	3 h	292	257	274
	4 h	287	274	289
Average[d]			280	
Standard error[d]			16	

a. the UV intensity was measure by Lutron Pocket UV Intensity Meter (SP-82UV). The UV meter was put in the UV device for 4 h and record the UV intensity reading after each hour. The whole process was performed for 3 times.

b. represents the first measurement.

c. at which hour the UV intensity was recorded in a measurement

d. The statistic value was from all the shown data

The basic idea of determining lignin concentration in the printed sample is to determine the weight percentage of lignin in the uncured parts, assuming the lignin concentrations in cured and uncured are the same. For this purpose, the printed sample was cut into small cubes and then soaked in DMSO to separate the uncured (dissolve in the solvent and obtained as supernatant after centrifugation) and cured (undissolved and obtained as precipitate after centrifugation) parts. The lignin concentration in dissolved solution can be found by using the standard curve of UV Absorption-Lignin Concentration in lignin/DMSO solution.

To find the standard curve, five samples with various concentrations (q') was prepared and measured for the UV-absorption (A'). The data was shown in Fig 2 and the relationship was fitted into a linear relationship as:

$$A' = 34.541q' - 0.207 \quad (1)$$

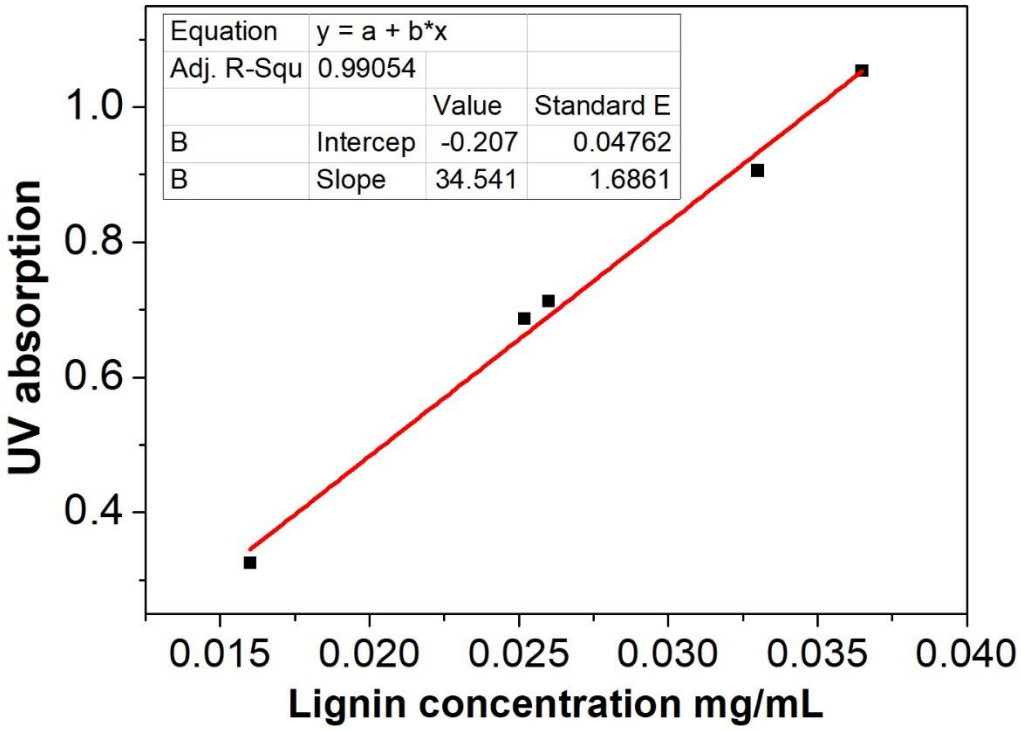

Figure S6. Standard curve of UV absorption against the lignin concentration in lignin/DMSO solution

Then the UV absorption of the supernatant was measured and the concentration can be find by apply Equation 2. To make sure the equation was applied properly, the measure supernatant

was first diluted for *n* times (*n*, the dilution multiplier, was depended on the samples) to make the value of UV-absorption (A) be in the range of 0.4 to 1.0. The lignin concentration in supernatant was calculated for N-0.2%, N-0.4%, N-0.5%, N-0.8% and N-1.0% samples.

$$q = \frac{A+0.207}{34.541} \times n \quad (2)$$

n is the dilution multiplier.

Reference:

1. Li, M.; Pu, Y.; Tschaplinski, T. J.; Ragauskas, A. J. 31P NMR characterization of tricin and its structurally similar flavonoids. *ChemistrySelect*. **2017**, 2, 3557.