Utilization of softwood lignin as both crosslinker and reinforcing agent in silicone elastomers

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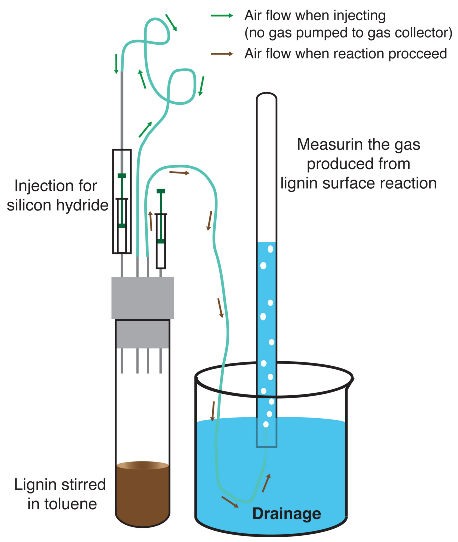
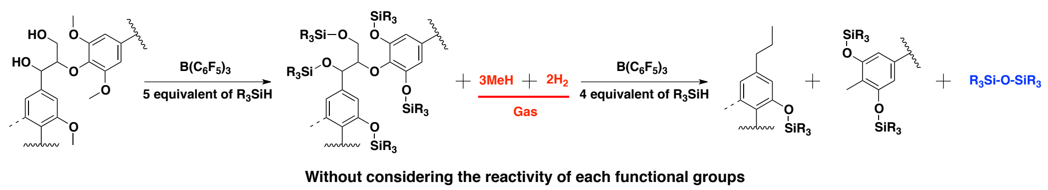
Electronic Supporting Information

Equipment associated with titration of the lignin surface:



Scheme S1. The water displacement method for gas production measurement.

Chemistry associated with titration of the lignin surface:



Scheme S2. The molar ratio of reactive surface functional group to gaseous by-product (5 equiv./4 equiv.)

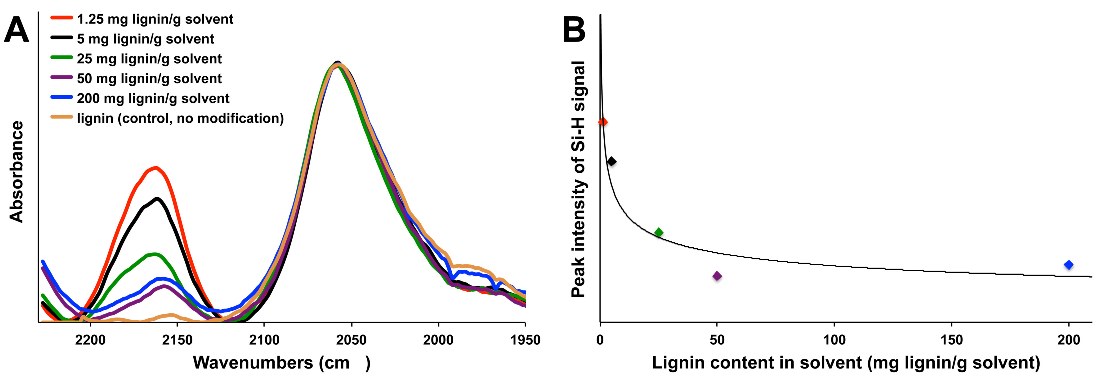


Figure S1. The DRIFT-IR spectrum for lignin particles titrated with different concentration in solvent. (A) and (B) The intensity of "Si-H" peak dropped with the increasing of lignin content in solvent (mg lignin/g solvent).

Demonstrated calculation for optimal formulations: balancing available functional group on lignin with [SiH]:

1. The equivalence of hydride:
    - If 800 mg of lignin was require in 1000 mg of DMS-H31 for ~ 40% weight ratio
    - The hydride that lignin could consume: 800 mg × 0.8 µmol/mg × 2 = 1280 µmol (Note, the reason for "× 2" refers to **Scheme S2**).
2. The hydride of DMS-H31:
    - If 1000 mg of DMS-H31 was required
    - The hydride content: 1000 mg × 0.07 µmol/mg = 70 µmol

3. The 70 µmol of hydride is not enough for 1280 µmol equivalence hydride required for lignin surface reaction, therefore, a co-crosslinker (HMS-301, 501, or 992) was required.

4. The hydride required to be provide by HMS-992:
    - If hydride to reactive surface functional group on lignin was set to 1/2
      The hydride required by HMS-992 = (1280 – 70 × 2)/2 = 570 µmol
      The mass of HMS-992 required = 570 µmol/16.67 µmol/mg = 34.2 mg
    - If hydride to reactive surface functional group on lignin was set to 2/1
      The hydride required by HMS-992 = 1280 × 2 - 70 = 2490 µmol
      The mass of HMS-992 required = 2490 µmol/16.67 µmol/mg = 149.4 mg
    - If hydride to reactive surface functional group on lignin was set to 4/1
      The hydride required by HMS-992 = 1280 × 4 - 70 = 5050 µmol
      The mass of HMS-992 required = 5050 µmol/16.67 µmol/mg = 302 mg

Table S1. Example formulation of lignin (SKL from Weyerhaeuser, 40.9%) as crosslinker/reinforcement in silicone elastomer. a co-crosslinker (HMS-992) was used for keeping the chemical stoichiometry of hydride to surface functional group of lignin close to 1:1.

Lignin (mg)	DMS-H31 (mg)	HMS-992 (mg)
800	1000	34
		150
		302

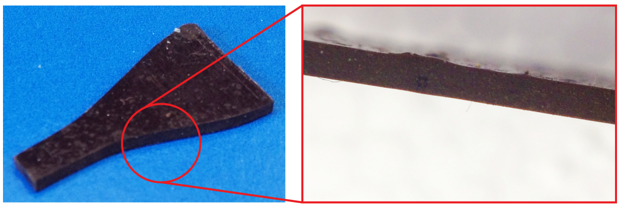
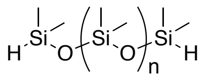
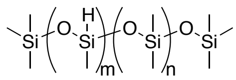


Figure S2. Images of bubble lignin/silicone elastomers made without solvent, right image is the cross-section of elastomer.

Table S2. The hydride content of hydride functionalized silicone with different chemical structures

	Mw (g/mol)	Chemical structure	Hydride content [Si-H], µmol/mg
DMS-H11	1175		1.70
DMS-H21	6000		0.33
DMS-H31	28000		0.07
DMS-H41	62700		0.03
HMS-301	1900-2100		4.36
HMS-501	900-1200		7.46
HMS-992	1800-2100		16.67

Solvent resistance:

Table S3. Solvent resistance of lignin-C/R-elastomer to organic solvents and water

	DMSO	MeOH	H_2O	Acetone	IPA	THF	THF/DMSO (1:1)	Toluene
Initial (g)	0.0285	0.0244	0.0275	0.0224	0.0218	0.0282	0.0203	0.0270
Swelling (g)	0.0748	0.0396	0.0334	0.0409	0.0315	0.0860	0.0332	0.0466
Swelling ratio (%)	162	62	21	83	44	205	64	73
After extraction (g)	0.0289	0.0237	0.0285	0.0231	0.0249	0.0212	0.0155	0.0257
Weight gain/loss ratio (%)[a]	1	-3	4	3	14	-25	-24	-5

[a] The "-" means a weigh loss percentage (loss weight/original weigh × 100%).

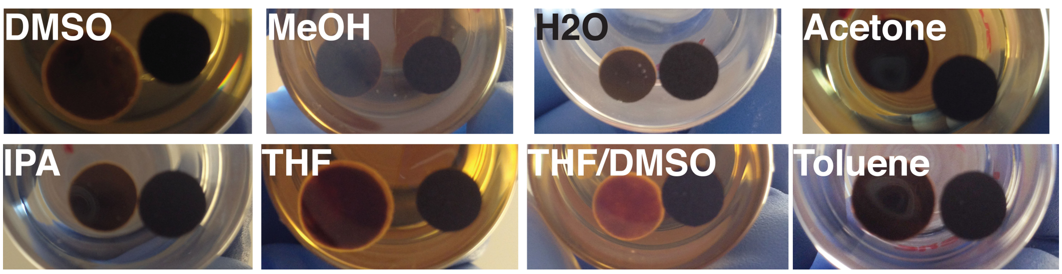


Figure S3. Swelling the lignin-C/R-elastomer with different solvent. The diameter ratios before and after swelling are list sequently: 1.32, 1.14, 1.00, 1.12, 1.00, 1.29, 1.41, 1.23, and 1.24 (left is the elastomer swell in solvent, right is control).

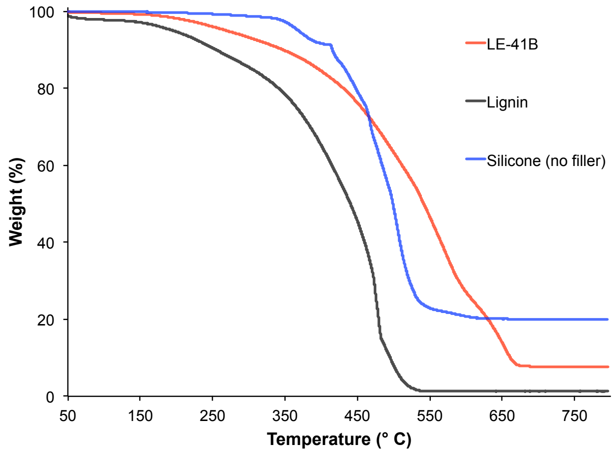


Figure S4. TGA thermograms of LE-41B (red), lignin (blue), and silicone (black) under air atmosphere