

SUPPORTING INFORMATION

Section 1. Conditions of the process of modification with inorganic nanoparticles for the different lignin formulations

Table SI1. Conditions used for the different formulations of the lignins modified with inorganic nanoparticles

Formulation	Glyoxalated lignin	Inorganic phase (%) ^A	Mixture conditions
LG3A	LG3	5	---
LG3B		---	5
LG6A	LG6	5	---
LG6B		---	5

^AContent of inorganic phase expressed in percentage respect to lignin amount

Section 2. FTIR spectroscopy analysis of the lignins

Table SI2. FTIR analysis of the pristine lignin samples

Range of wavelength (cm ⁻¹)	Assignments	Identified bands (cm ⁻¹)	
		LAS	LMP
3410-3400	O-H stretching	3408	3401
3000-2850	C-H stretch methyl and methylene groups	2933	2930
1710-1680	C=O stretching	1697	1701
1600-1500	C=C vibration aromatic ring	1596, 1508	1597, 1508
1460-1440	C-H bending in methyl and methylene groups	1458	1458
1430-1420	C-H deformation vibrations aromatic ring	1423	1423
1270-1260	C-O stretching in guaiacol ring		1266
1230-1210	C-C, C-O and C=O stretching	1218	1218
1150-1140	C-H deformation in guaiacol ring		1139
1120-1110	C-H deformation in syringyl ring	1119	
1035-1030	C-H aromatic in plane deformation	1031	1030
850-815	C-H aromatic out of plane deformation in G and S groups	829	857, 815

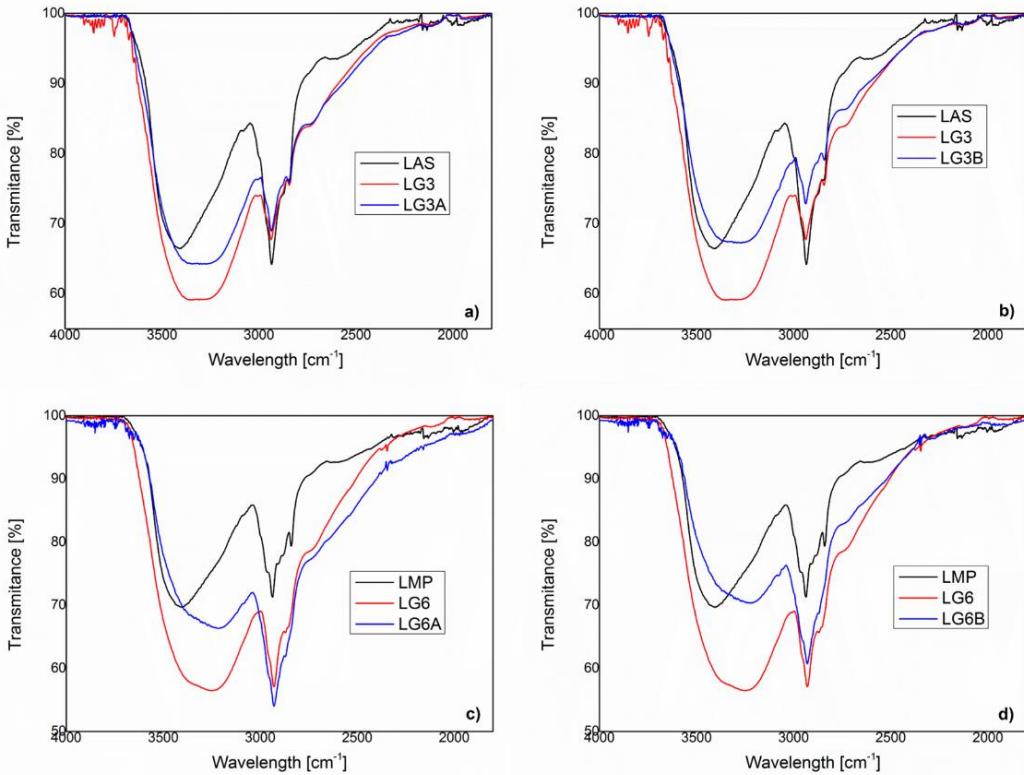


Figure SI1. Comparison of the band corresponding to OH groups between glyoxalated lignins (LG3, LG6) and lignins modified with inorganic nanoparticles (LG3A, B and LG6A, B).

Table SI3. Ratios of relative absorbance for the different glyoxalated lignins

Samples	OH-aromatic*	OH-total*	GI
LG1	1.95	6.04	2.09
LG2	3.24	10.44	2.31
LG3	3.44	12.11	2.53
LG4	1.78	5.32	1.99
LG5	2.54	10.37	3.09
LG6	2.13	11.28	4.29

*These ratios were expressed as percentage of area contribution to the total area under the spectra curves

Section 3. ^1H -NMR spectroscopy analysis of the lignins

Table SI4. Assignment of the main signals detected in the ^1H -NMR spectra of the lignins before and after modification

Chemical shift (ppm)	Assignment
0.8-1.6	Aliphatic protons of saturated chains
1.24	Aliphatic protons of oxidized lignin
2.5	DMSO
3.35	Water
3.75	Protons from methoxyl groups
4.6	Protons H_β from β -O-4 structure
4.5	Hydroxyl proton from hydroxymethyl groups
4.7	Protons H_α from β - β structure
4.85	Protons H_α from β -O-4 structure
4.9-5.25	Protons from methylene or glyoxalene groups
5.3-5.4	Protons H_α from β -5 structure
6.6-6.7	Aromatic protons from syringyl units
6.9-7.0	Aromatic protons from guaiacyl units
8.1-8.3	Phenolic proton from syringyl units
8.7-9	Phenolic proton from guaiacyl units
9.3-9.4	Formyl protons from glyoxal and glyoxal oligomers
9.6	Formyl proton from cinnamaldehyde
9.8	Formyl proton from benzaldehyde

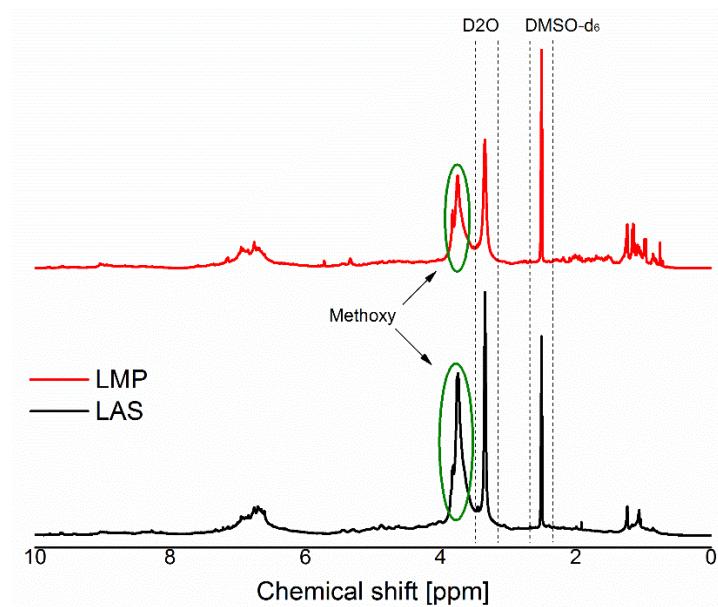


Figure SI2. Comparison of the pristine lignins (LAS and LMP) regarding the peaks corresponding to methoxy groups.

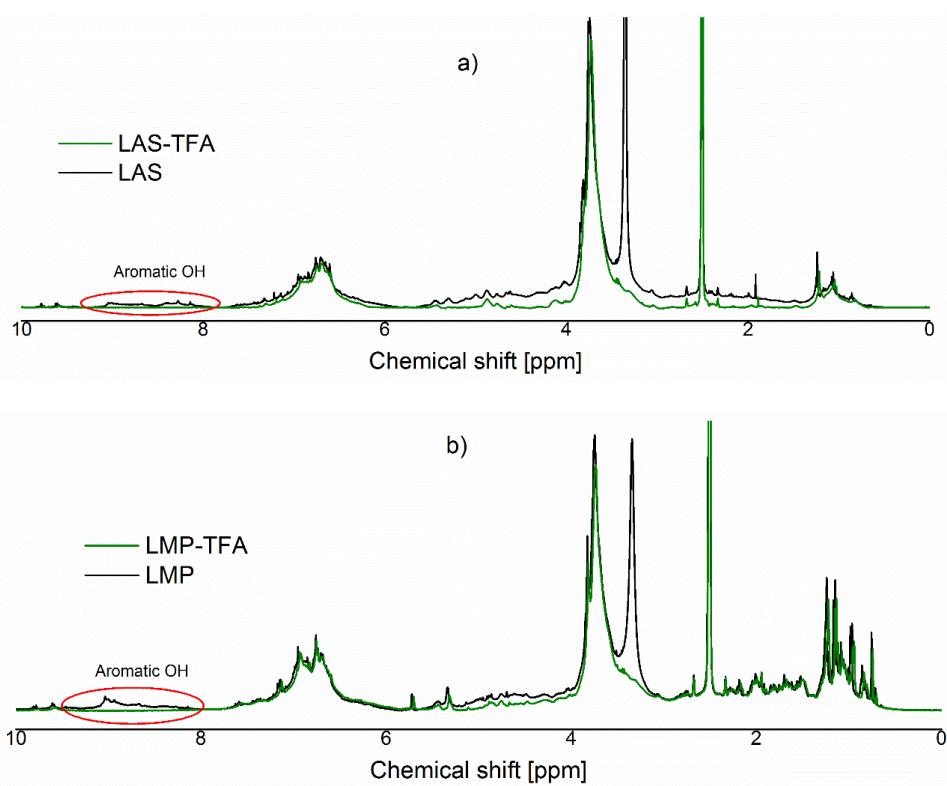


Figure SI3. Determination of the peaks of protons from hydroxyl groups: a) pristine lignin from almond shells (LAS) and b) pristine lignin from maritime pine (LMP).

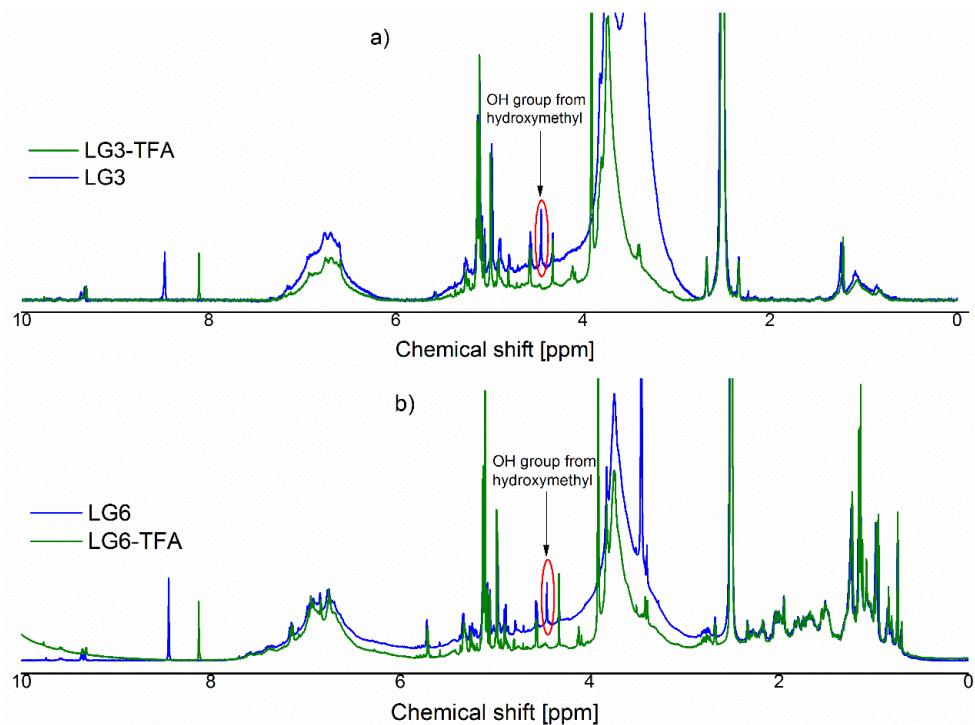


Figure SI4. Determination of the peaks of protons from hydroxyl groups: a) glyoxalated lignin from almond shells (LG3) and b) pristine lignin from maritime pine (LG6).

Section 4. DRX analysis of the lignins

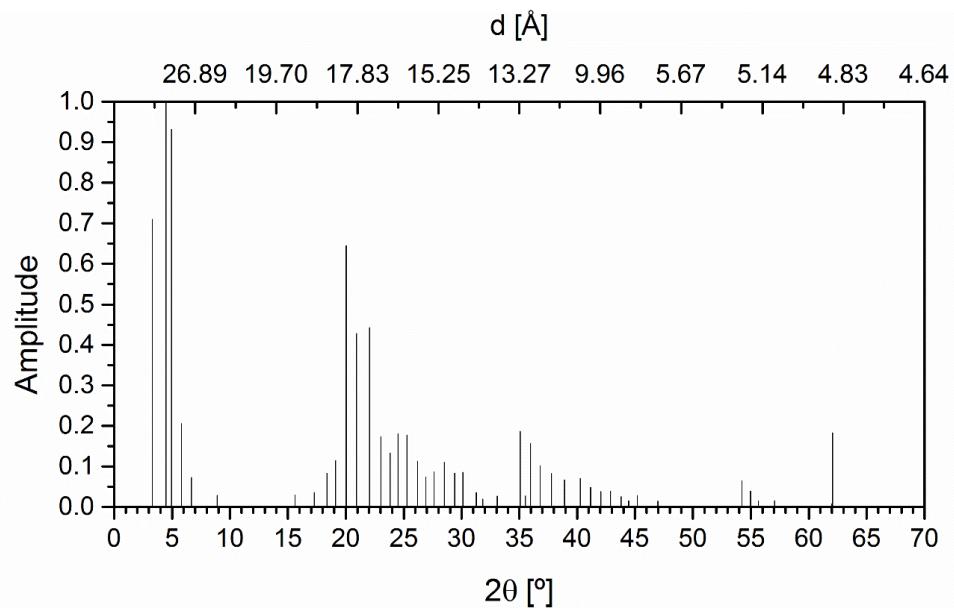


Figure SI5. Diffractogram obtained for the OMMT-Delite43B from the DRX analysis.

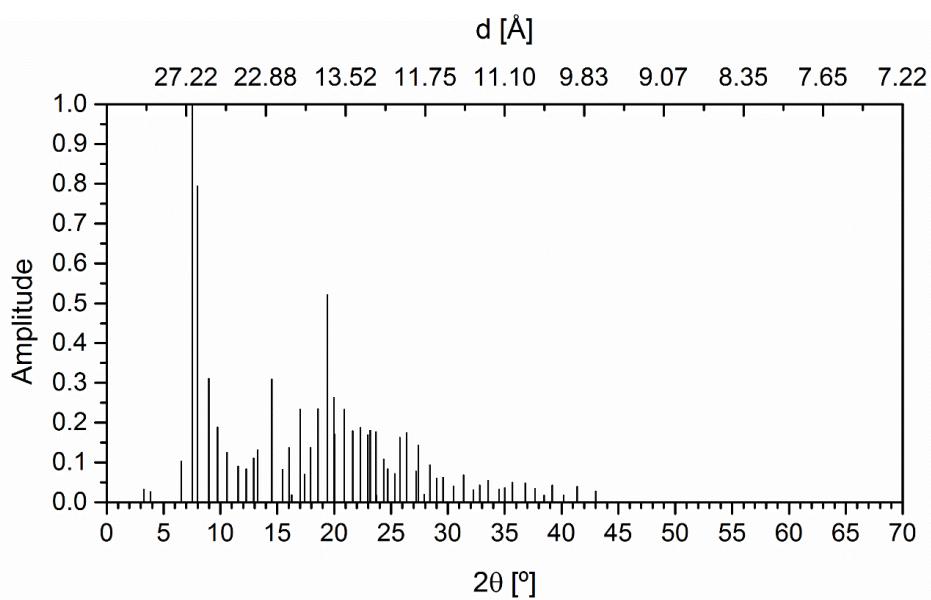


Figure SI6. Diffractogram obtained for the POSS[®]-SO1458 from the XDR analysis

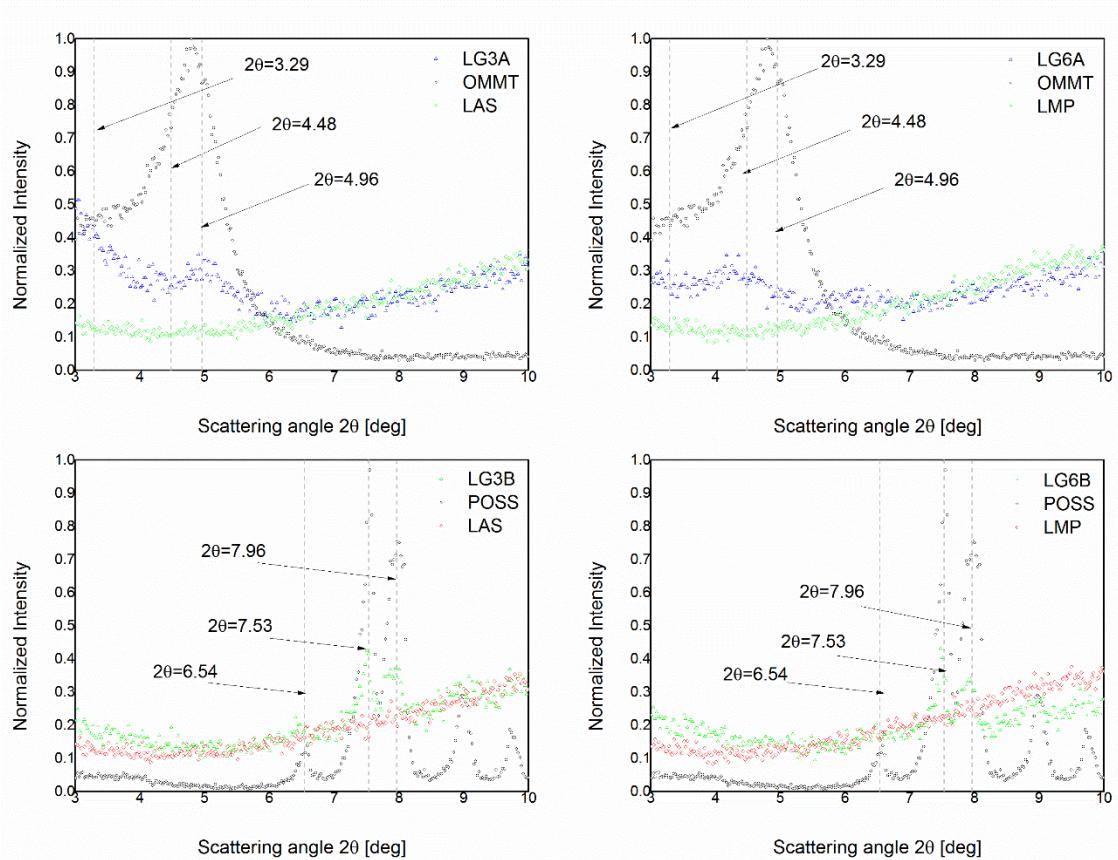


Figure SI7. Insets of the diffractograms showed in the main manuscript in figure 7 (range $2\theta=3-10$ degrees)

Table SI5. Indexing of the different peaks obtained from the DRX analysis for OMMT

Peak	2θ ($^{\circ}$)	Amplitude a.u.	d_{spacing} (\AA)	$h \ k \ l$	Phase	Type of signal	Source
1	3.29	0.71	26.89	0 1 0	MMT ^a	S ^B	Calculated
2	4.48	1.00	19.70	0 1 0	43B ²	VS ^A	Esposito et al. 2015 ¹
3	4.96	0.93	17.83	-1 0 0	MMT ^a	VS ^A	Calculated
4	5.79	0.20	15.25	0 0 1	MMT ^a	VW ^D	Calculated
5	6.66	0.07	13.27			VW ^D	
6	8.88	0.03	9.96	0 0 1		VW ^D	Calculated
7	15.62	0.03	5.67			VW ^D	

8	17.27	0.04	5.14	0 0 2	VW ^D	Calculated
9	18.38	0.08	4.83	1 1 0	VW ^D	
10	19.12	0.11	4.64		VW ^D	Calculated
11	20.04	0.64	4.43	0 2 0	MMT ^a S ^B	Gournis et al 2008 ²
12	20.93	0.43	4.24	1 0 2	W ^C	Calculated
13	22.04	0.44	4.03	-1 1 1	MMT ^a W ^C	Galimberti et al 2009 ³
14	23.04	0.17	3.86		VW ^D	
15	23.81	0.13	3.74		VW ^D	
16	24.52	0.18	3.63		VW ^D	
17	25.29	0.18	3.52		VW ^D	
18	26.19	0.11	3.40		VW ^D	
19	26.91	0.07	3.31	0 2 2	VW ^D	Calculated
20	27.63	0.09	3.23		VW ^D	
21	28.52	0.11	3.13	1 2 2	VW ^D	Calculated
22	29.41	0.08	3.04		VW ^D	
23	30.10	0.09	2.97		VW ^D	
24	31.26	0.04	2.86		VW ^D	
25	31.82	0.02	2.81		VW ^D	
26	33.07	0.03	2.71		VW ^D	
27	35.09	0.19	2.56	-2 0 1	MMT ^a VW ^D	Calculated
28	35.53	0.03	2.53	-1 3 1	MMT ^a VW ^D	Calculated
29	35.99	0.16	2.50		MMT ^a VW ^D	Calculated
30	36.82	0.10	2.44		MMT ^a VW ^D	
31	37.80	0.08	2.38	-2 0 2	MMT ^a VW ^D	Calculated
32	38.90	0.07	2.32	-1 1 4	MMT ^a VW ^D	Calculated
33	40.26	0.07	2.24	1 3 2	MMT ^a VW ^D	Calculated
34	41.16	0.05	2.19	2 0 2	MMT ^a VW ^D	Calculated
35	42.06	0.04	2.15		MMT ^a VW ^D	

36	42.88	0.04	2.11	-2 2 2	MMT ^a	VW ^D	Calculated
37	43.80	0.03	2.07		MMT ^a	VW ^D	
38	44.46	0.02	2.04	0 4 2	MMT ^a	VW ^D	Calculated
39	45.20	0.03	2.01		MMT ^a	VW ^D	
40	46.96	0.01	1.93	2 0 3	MMT ^a	VW ^D	Calculated
41	54.23	0.06	1.69	1 5 0	MMT ^a	VW ^D	Calculated
42	54.97	0.04	1.67	3 1 1	MMT ^a	VW ^D	Calculated
43	55.65	0.01	1.65	0 0 6	MMT ^a	VW ^D	Calculated
44	57.06	0.01	1.61	-1 3 5	MMT ^a	VW ^D	Calculated
45	61.99	0.01	1.50	1 1 6	MMT ^a	VW ^D	Calculated

^aMMT: planes related to monoclinic montmorillonite structure

^b43B: plane related to the organic modifier (dimethylbenzylhydrogenated tallow ammonium)

^AVS: very strong, BS: strong, CW:weak, DVW: very weak

Table SI6. Indexing of the different peaks obtained from the DRX analysis for POSS®

Peak	2θ (°)	Amplitude	d _{spacing}	h k l	Phase	Type of signal	Source
		a.u.	(Å)				
3	6.54	0.10	13.52	1 -1 0	TS-Ph ¹	W ^C	Calculated
4	7.53	1.00	11.75	1 0 -1	POSS ²	VS ^A	Barry et al. 1955 ⁴
5	7.96	0.79	11.10	1 0 -1	POSS ²	VS ^A	Calculated
6	8.99	0.31	9.83	1 1 0	TS-Ph ¹	W ^C	Calculated
7	9.75	0.19	9.07	1 1 -1		VW ^D	Calculated
8	10.59	0.12	8.35	1 1 0	POSS ²	VW ^D	Fu et al. 2001 ⁵
9	11.57	0.09	7.65	2 0 0	POSS ²	VW ^D	Fu et al. 2001
10	12.26	0.08	7.22	2 0 -1	TS-Ph ¹	VW ^D	Calculated
11	12.91	0.11	6.86	2 0 0	POSS ²	VW ^D	Fu et al. 2001 ⁵

13	14.53	0.31	6.10	-2 2 1	TS-Ph ¹	W ^C	Calculated
14	15.47	0.08	5.73	2 0 2	POSS ²	VW ^D	Fu et al. 2001 ⁵
17	17.00	0.23	5.22	2 2 0	TS-Ph ¹	W ^C	Calculated
19	17.93	0.14	4.95		POSS ²	VW ^D	
20	18.57	0.23	4.78	2 2 1	POSS ²	VW ^D	Barry et al. 1955 ⁴
21	19.43	0.52	4.57	2 2 -2	TS-Ph ¹	S ^B	Calculated
22	19.98	0.26	4.44	3 0 2	TS-Ph ¹	W ^C	Calculated
24	20.89	0.23	4.25	3 1 -2	POSS ²	VW ^D	Fu et al. 2001 ⁵
26	22.33	0.19	3.98	2 3 0	TS-Ph ¹	VW ^D	Calculated
28	23.19	0.18	3.84	4 0 0	POSS ²	VW ^D	Barry et al. 1955 ⁴
29	23.67	0.18	3.76	4 -1 -1	POSS ²	VW ^D	Fu et al. 2001 ⁵
33	25.33	0.07	3.52	1 2 4	POSS ²	VW ^D	Barry et al. 1955 ⁴
35	26.37	0.17	3.38	3 2 1	POSS ²	VW ^D	Barry et al. 1955 ⁴ , Fu et al. 2001 ⁵
38	27.93	0.02	3.20	3 2 2	POSS ²	VW ^D	Barry et al. 1955 ⁴ , Fu et al. 2001 ⁵
41	29.58	0.06	3.02		POSS ²	VW ^D	
43	31.39	0.07	2.85	4 0 -4	POSS ²	VW ^D	Calculated
45	32.81	0.04	2.73		POSS ²	VW ^D	

^aTS-Ph: planes related to triclinic trisilanol phenyl structure

^bPOSS: planes related to the rhombohedral polyoligomeric silsesquioxane structure

^AVS: very strong, ^BS: strong, ^CW:weak, ^DVW: very weak

Section 5. Thermogravimetric analysis of the lignins

Table SI7. Main thermal degradation parameters of the different lignins sample.

Samples	TGA Analysis		DTGA Analysis (Temperatures of degradation °C)					
	T _{5%} (°C)	T _{50%} (°C)	Residue (%)	1 st Stage	2 nd Stage	3 rd Stage	4 th Stage	5 th Stage
LAS	221.97	456.22	35.89	148.18 ^A	385.84 ^C			
LG3	116.09	477.63	40.22	137.25 ^A	303.94 ^B	360.78 ^C	503.79 ^D	
LG3A	121.43	505.96	42.45	137.23 ^A	293.49 ^B	358.94 ^C	510.78 ^D	
LG3B	122.28	513.44	42.58	137.11 ^A	298.64 ^B	359.84 ^C	507.85 ^D	
LMP	237.23	435.30	33.18	137.05 ^A	258.33	389.72 ^C		
LG6	116.37	481.87	41.54	145.24 ^A	239.15	308.01 ^B	363.45 ^C	458.80 ^D
LG6A	129.89	509.65	42.55	141.02 ^A	250.01	309.61 ^B	376.14 ^C	475.60 ^D
LG6B	131.11	494.54	41.07	142.52 ^A	256.54	309.46 ^B	380.74 ^C	468.85 ^D

^AStage of degradation related to the moisture and volatiles decomposition

^BStage of degradation related to the decomposition of lignin polymers of low molecular weight formed during the glyoxalation

^CStage of degradation related to the decomposition of the main lignin structure

^DStage of degradation related to the decomposition of the condensed structure formed after glyoxalation

SECTION 6. References

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- (5) Fu, B. .; Hsiao, B. .; Pagola, S.; Stephens, P.; White, H.; Rafailovich, M.; Sokolov, J.; Mather, P. .; Jeon, H. .; Phillips, S.; et al. Structural Development during Deformation of Polyurethane Containing Polyhedral Oligomeric Silsesquioxanes (POSS) Molecules. *Polymer (Guildf)*. 2001, 42, 599–611.