Fully biobased epoxy resins from fatty acids and lignin

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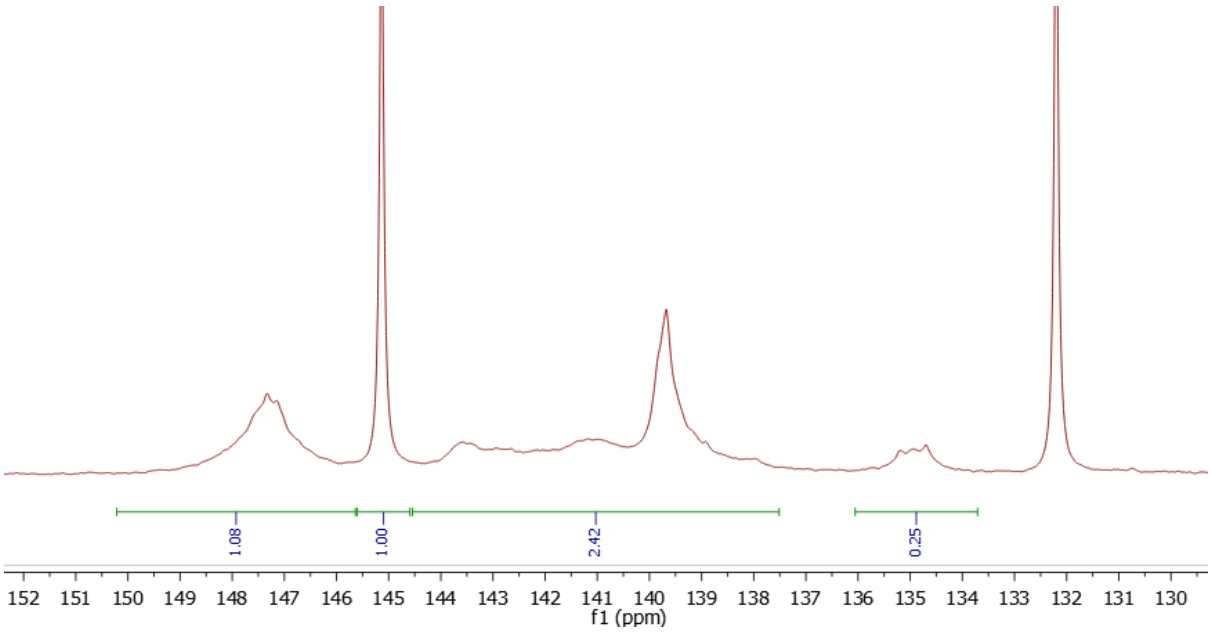
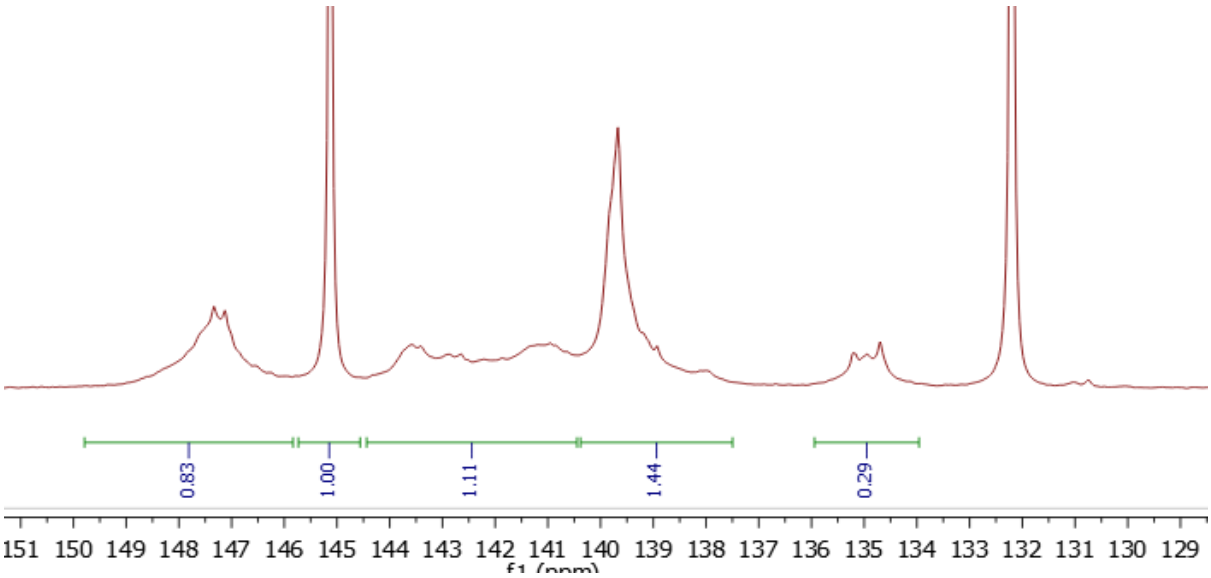
Characterization of lignins

NMR

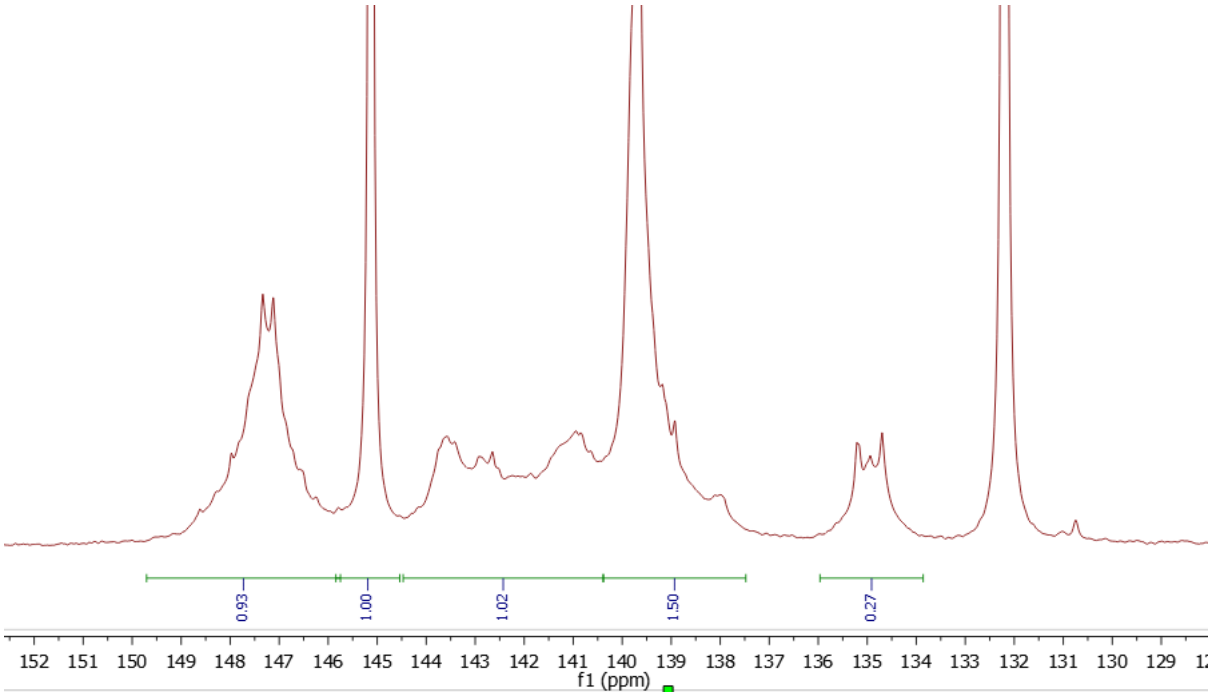
S1 Kraft lignoboost



S2 Acetone extracted Kraft

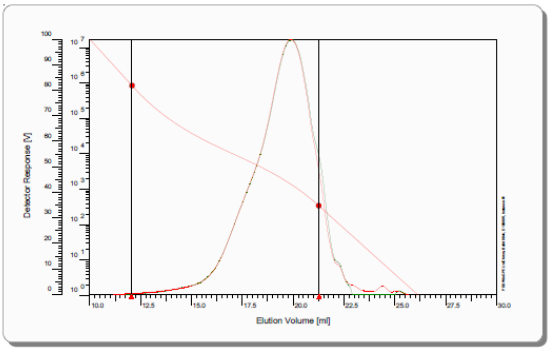


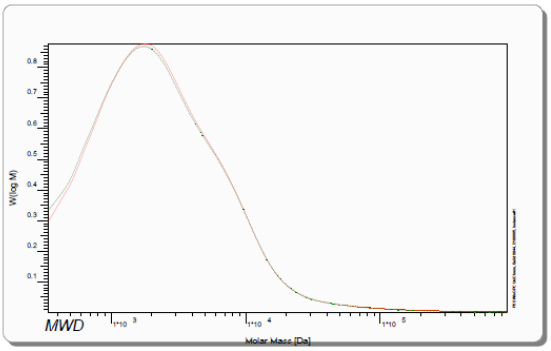
S3 MeOH extracted Kraft



GPC

S4 Lignoboost KL





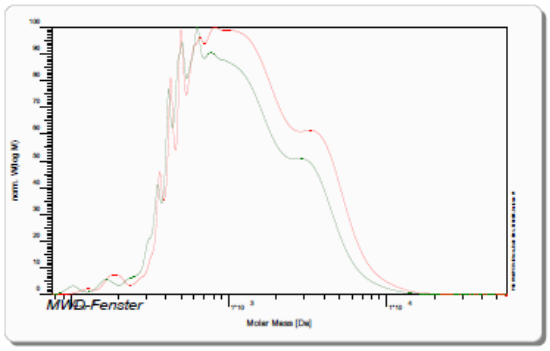
Operator:	WinGPC01
Sample name:	Vial 23: 190626-0164 KL - 1
Project file:	C:\wingpc_8#1\GPC1\BioHart.LDX
Calibration:	CalibTHF20190626HR3-4.cal (created 28.6.2019, 08:01)

Inject date:	Thursday, 27.06.2019 00:06:00				
Concentration:	2,000 g/l				
Baseline from:	11,165 ml	**to:**	25,678 ml	**Integration from:**	12,054 ml **to:** 21,276 ml
Int. Standard:	---			**at:**	50,000 ml

Eluent:	THF		
Pump:	LC-20AT	**Flowrate:**	0,80 ml/min
Injector:	SIL-20AC	**Inj. Vol.:**	100,00 µl
Interface:	PSS/UDC 810 CH		
Column 1:	Styragel Guard Column		
Column 2:	Styragel HR1		
Column 3:	Styragel HR0.5		
Detector 1:	SPD-20A UV	**Delay:**	0,000 ml
Detector 2:	RID-10A	**Delay:**	0,130 ml

Detector	*1*	*2*
Name:	**SPD-20A UV**	**RID-10A**
Mn [Da]:	1.450	1.420
Mw [Da]:	5.370	5.200
Mz [Da]:	99.600	89.000
Mv [Da]:		
D:	3,713	3,662

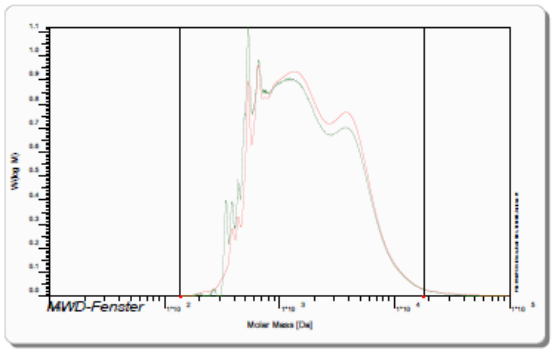
S5 Lignoboost KL – MeOH extracted



Eluent:	THF		
Pump:	LC-20AT	Flowrate:	0,80 ml/min
Injector:	SIL-20AC	Inj. Vol.:	25,00 µl
Interface:	PSS/UDC 810 CH		
Column 1:	Ultrahydrogel Guard Column		
Column 2:	Ultrahydrogel 500		
Column 3:	Ultrahydrogel 120		
Detector 1:	SPD-20A UV	Delay:	0,000 ml
Detector 2:	RID-10A	Delay:	0,000 ml

Detector	1	2
Name:	SPD-20A UV	RID-10A
Mn [Da]:	939	820
Mw [Da]:	1.880	1.610
Mz [Da]:	3.870	3.430
Mv [Da]:		
D:	2,004	1,959

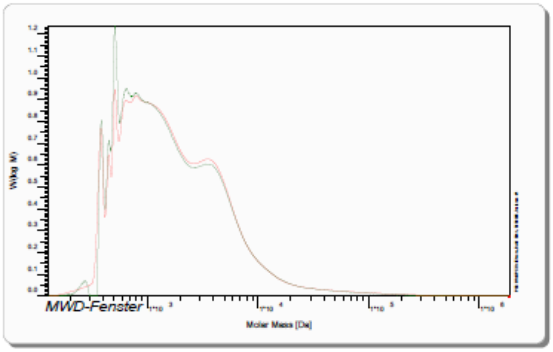
S6 Lignoboost KL – Acetone extracted



Eluent:	THF		
Pump:	LC-20AT	Flowrate:	0,80 ml/min
Injector:	SIL-20AC	Inj. Vol.:	100,00 µl
Interface:	PSS/UDC 810 CH		
Column 1:	Styragel Guard Column		
Column 2:	Styragel HR1		
Column 3:	Styragel HR0.5		
Detector 1:	SPD-20A UV	Delay:	0,000 ml
Detector 2:	RID-10A	Delay:	0,110 ml

Detector	1	2
Name:	SPD-20A UV	RID-10A
Mn [Da]:	1.240	1.140
Mw [Da]:	2.740	2.540
Mz [Da]:	8.420	7.120
Mv [Da]:		
D:	2,206	2,216

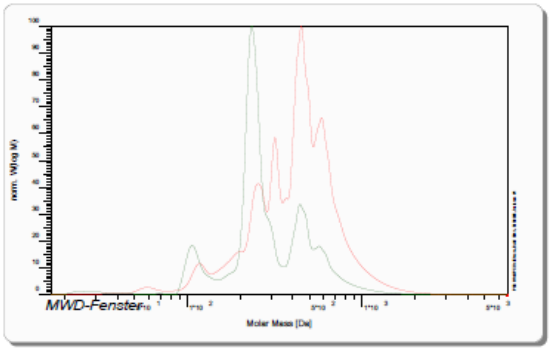
S11 West Fraser KL



Eluent:	THF		
Pump:	LC-20AT	Flowrate:	0,80 ml/min
Injector:	SIL-20AC	Inj. Vol.:	100,00 µl
Interface:	PSS/UDC 810 CH		
Column 1:	Styragel Guard Column		
Column 2:	Styragel HR1		
Column 3:	Styragel HR0.5		
Detector 1:	SPD-20A UV	Delay:	0,000 ml
Detector 2:	RID-10A	Delay:	0,110 ml

Detector	1	2
Name:	SPD-20A UV	RID-10A
Mn [Da]:	1.090	1.090
Mw [Da]:	4.570	4.080
Mz [Da]:	94.800	69.800
Mv [Da]:		
D:	4,170	3,751

S12 BCD, solvent extracted eucalyptus lignin



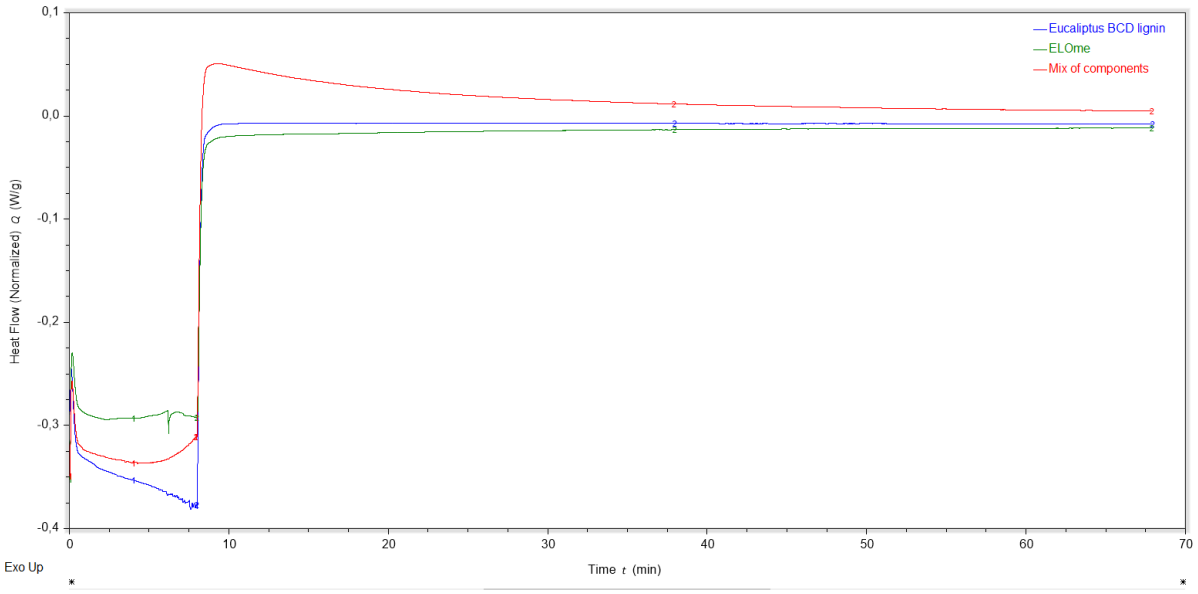
Eluent:	THF		
Pump:	LC-20AT	**Flowrate:**	0,80 ml/min
Injector:	SIL-20AC	**Inj. Vol.:**	40,00 µl
Interface:	PSS/UDC 810 CH		
Column 1:	Styragel Guard Column		
Column 2:	Styragel HR1		
Column 3:	Styragel HR0.5		
Detector 1:	SPD-20A UV	**Delay:**	0,000 ml
Detector 2:	RID-10A	**Delay:**	0,000 ml

Detector	*1*	*2*
Name:	**SPD-20A UV**	**RID-10A**
Mn [Da]:	321	220
Mw [Da]:	466	327
Mz [Da]:	638	483
Mv [Da]:		
D:	1,451	1,485

Curing mechanism

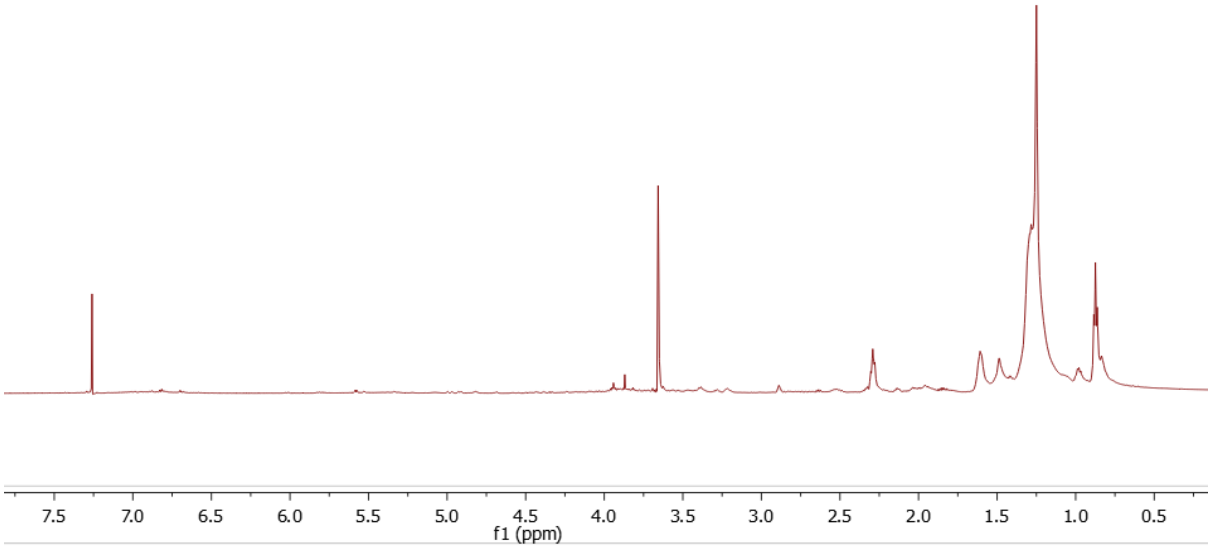
S7 Proof of reaction of lignin with the epoxy groups of ELO_{me} by DSC

0.5 grams of BCD Eucaliptus lignin oil was mixed with 0.5 grams of ELO_{me} and stirred for 1 minute at room temperature. Then an aliquot of the mixture was placed in DSC pan and heated at 10°C/min to 120°C. It was maintained at that temperature for 60 min. Reference samples of the ELO_{me} as well as Eucaliptus BCD lignin oil were run at the same conditions Eucaliptus BCD lignin instead of Kraft lignin because it could be mixed with the ELO_{me} without the need of solvents.



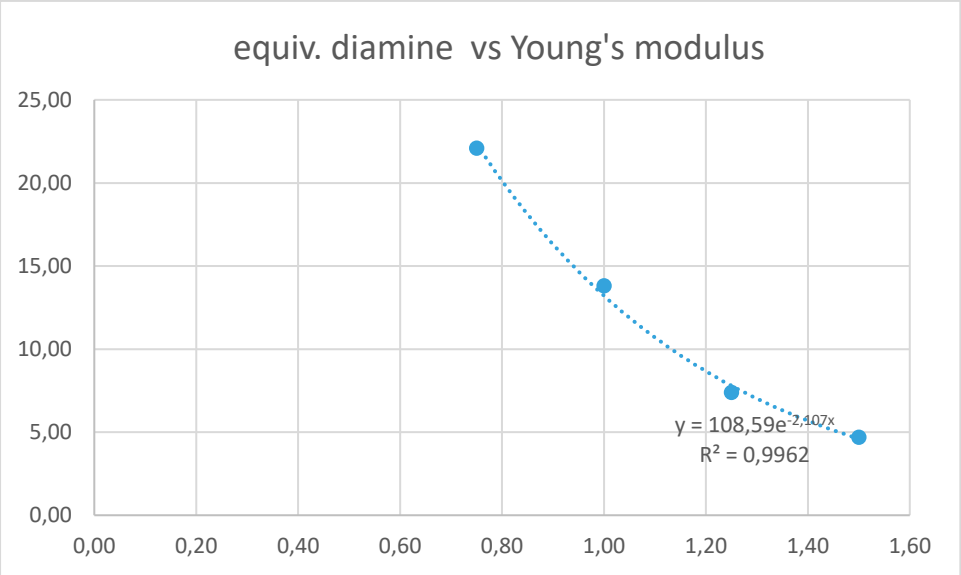
S8 Proof of lignin incorporation in the resin by analyzing the leaching of a fully cured epoxy sample by ^{1}H NMR

150 mg of the fully cured epoxy resin with 22% of KL_{MeOH} was immersed in a vial containing 15 ml of THF and was kept there for 48h. The sample was removed, and the THF evaporated. The residue was analyzed by ^{1}H NMR using $CDCl_3$ as solvent.



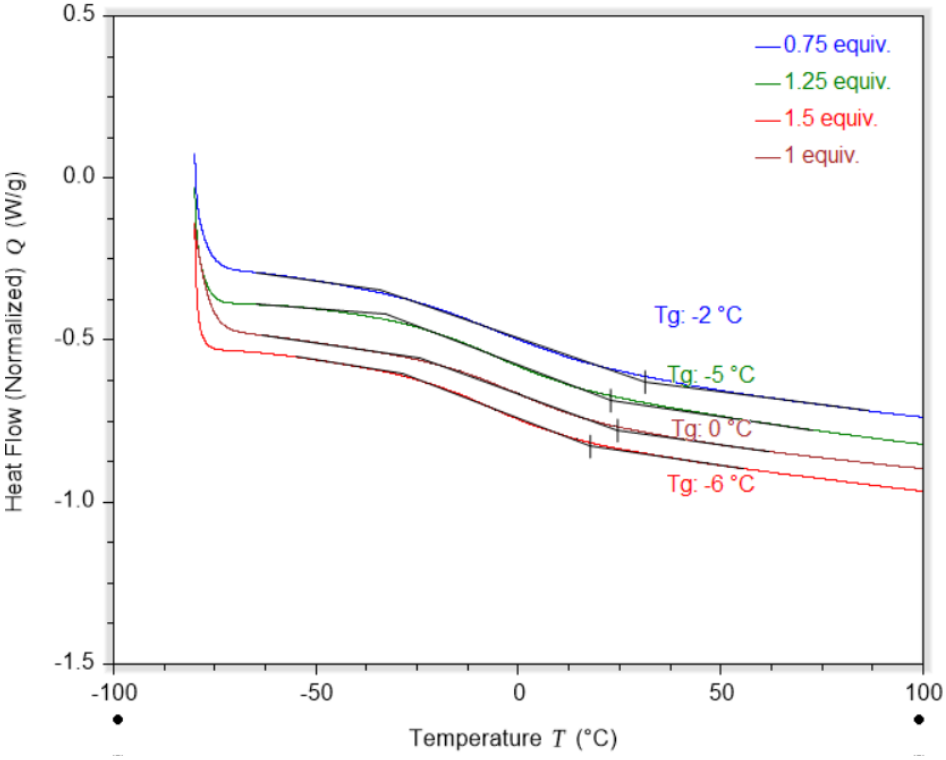
Characterization of cured samples

S9 Plot of equivalents of diamine vs Young's modulus

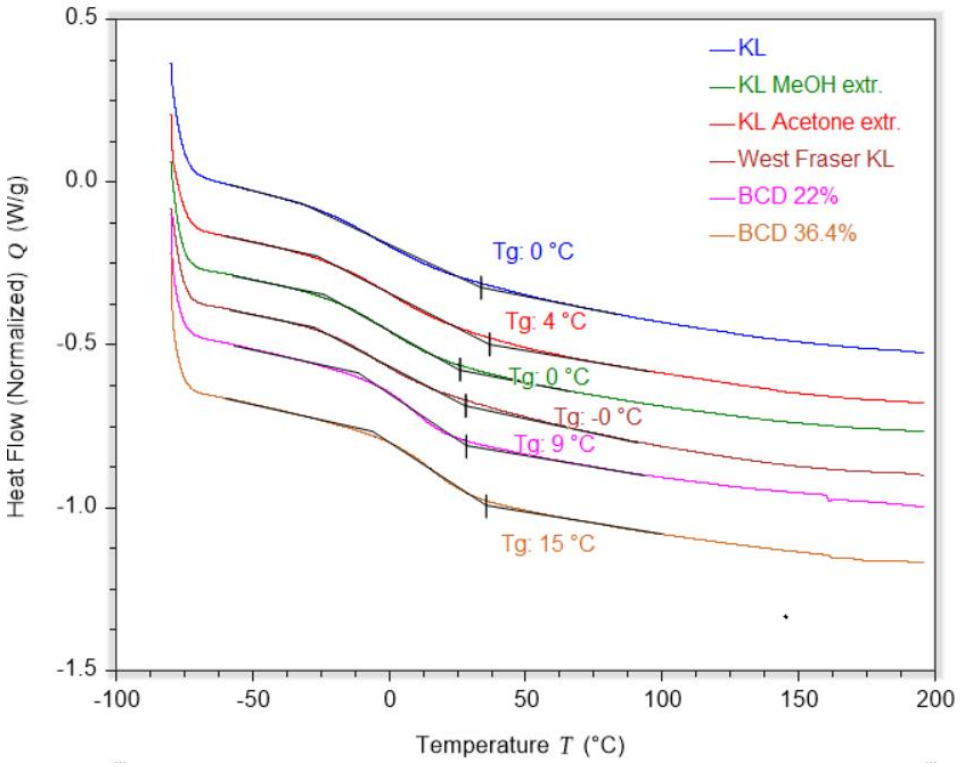


DSC-2nd heating curves

S10 Variable amounts of Dimer diamine



S13 Different types of lignins



S14 TGA