NewWave

D5.1 – Development of new plywood resins

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Executive Summary

This report summarizes the experimental work performed in the period M1-M12 in sub-task 5.1 “Lignin characterization” and 5.2 “Resin screening tests”. Four lignin samples were received from BTG and have been analyzed. The samples have been characterized in sub-task 5.1 by measuring the necessary parameters for the implementation and subsequent replacement of phenol in the resin screening tests in sub-task 5.2. Parameters such as the; water content, density, viscosity, pH, % of phenol, elemental analysis (C,H,N), GPC & metal content have been analyzed. Furthermore, to be able to understand the reactivity of the samples, thermal degradation, calorimetry scanning differential and curing ramp analyses were performed as well. Noteworthy is that during the analysis and testing the samples showed to be very homogeneous, which is not always the case with lignins and lignin derived materials. Subsequently in sub-task “5.2 Resin screening test”, a recipe was developed, and a 100 % phenol-formaldehyde resin was synthesized to be used as a blank to compare with resins with incorporated lignin to replace the phenol. The different lignin samples provided by BTG were tested as phenol substitutes in amounts/percentages of 25, 50 & 75%. All the resin synthesis reactions could be carried out without problems in the polymerization step, except for resins with 75% phenol substitution by the solid lignin samples. Due to the solid lignin, the viscosity became too high in the reactor during resin synthesis, hindering polymerization. The synthesized resins have been analyzed to obtain information required for evaluation in following sub-tasks. The replacement of 100% of the phenol in the resin by the different lignin’s provided by BTG is still ongoing.

Introduction

Introduction and Objectives of NewWave

NewWave will contribute to building a circular economy by introducing sustainable raw materials in different manufacturing lines (ML's), replacing toxic chemicals, and lowering the environmental footprint of the products. The four manufacturing lines (see Figure 1) will produce engineered wood panels, furan base-chemicals, polyols and polyurethanes, and modified/engineered wood. These lines are not chosen 'at random', rather they evolved from previous research and technology development work and will reach TRL-6 by the end of the project. The products produced in the manufacturing lines will be used to enhance the sustainability of building materials in the construction industry. NewWave aims at wood-based materials including Cross Laminated Timber (CLT) to replace steel and concrete as structural components, modified/engineered wood to replace tropical hardwood or chemically treated wood for outdoor use, and Medium Density Fibreboard (MDF) and plywood for interior usage. Toxic chemicals like formaldehyde and creosote will be replaced by non-toxic, bio-based alternatives. Within the project, a small demonstration project will be built with these materials to show the products and test their durability.

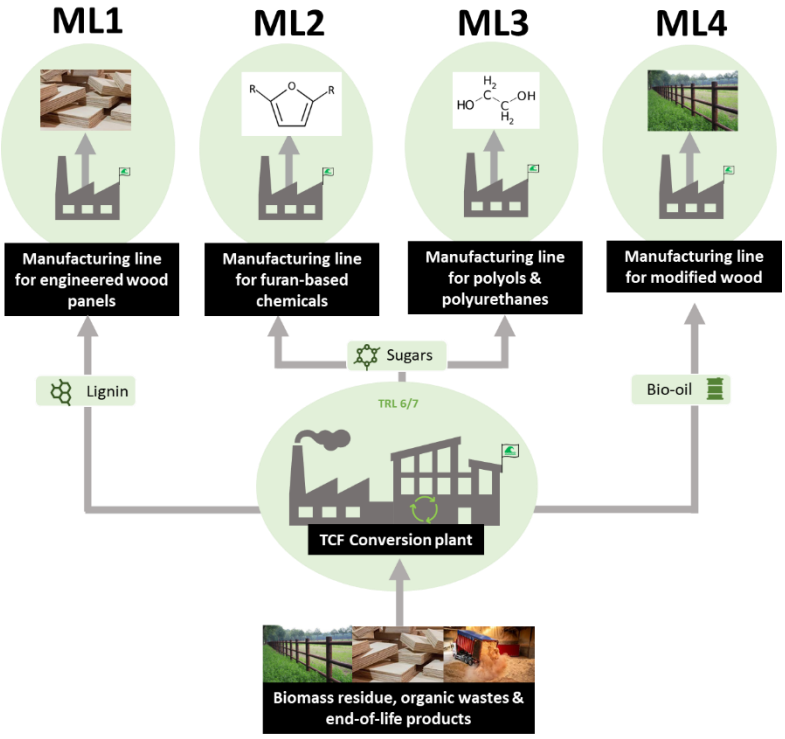


Figure 1: Schematic overview of the NewWave ML's

Thermo-Chemical Fractionation & pyrolytic lignin production

The sustainable raw materials used in the manufacturing lines are obtained by Thermo-Chemical Fractionation (TCF) of biomass residues and end-of-life products. TCF is an innovative, two-step conversion process to transform different bio-resources into sustainable raw materials and is currently at a TRL-6/7. In the TCF process biomass is first converted by fast pyrolysis into Fast Pyrolysis Bio-Oil (FPBO). Subsequently, the FPBO is fractionated -based on chemical functionality- yielding a reactive lignin fraction and a sugar-rich fraction, both being excellent starting materials to produce sustainable, bio-based chemicals & materials. The selected product lines fully exploit the unique chemical functionalities already present in the biomass feeds. Moreover, the lines are interlinked, and output from one line will further improve the sustainability of the other. Wastewater treatment and water re-use is integral part of the NewWave concept. Combined with end-of-life recycling options and efficient use of byproducts this results in essentially waste-free manufacturing processes.

The liquid pyrolytic lignin (LPL) obtained in BTG's TCF process is a highly viscous liquid and still contains some water and organic acids, among other things. For some applications it is necessary that this LPL is further processed to solid pyrolytic lignin (SPL) to obtain certain specifications properties. During this LPL processing step, a small stream rich in different types of lignin-derived mono-phenols is produced. The LPL, SPL and mono-phenols (MP) stream will be used in the development of plywood resins by Foresa Tech, and they will further optimize the process of manufacturing the Plywood and the MDF and methods to maximally incorporate the amount of lignin in these resins, while the properties remain on spec. In sub-task 2.3, BTG provided Foresa Tech with liquid lignin, solid lignin and the mono-phenolics for analysis and testing in WP5. The solid lignin and mono-phenolics are obtained after post-treatment of the liquid lignin.

Task 5.1: Lignin characterization

Foresa Tech received four different lignin samples from BTG in May 2022 and January 2023.

▪ Sample name: BTG NW SPL1 (A)	Sample code: 2022-394 (on 25/05/2022) Sample code: 2023-399 (on 11/01/2023)
▪ Sample name: BTG NW SPL2 (B)	Sample code: 2022-395 (on 25/05/2022) Sample code: 2023-400 (on 11/01/2023)
▪ Sample name: BTG NW LPL (C)	Sample code: 2022-2548 (on 25/05/2022) Sample code: 2023-2641 (on 11/01/2023)
▪ Sample name: BTG NW MP (D)	Sample code: 2022-2549 (on 25/05/2022) Sample code: 2023-2640 (on 11/01/2023)

Figure 2. Photography of differents lignins.

In this task, the objective is to characterize the different lignin samples to obtain as much information as possible in view of manufacturing, synthesis, and reactivity.
The results are shown below.

Basic analysis

The % moisture, pH, viscosity and density were analysed, which are basic parameters for the subsequent introduction of these samples in the resin. Moisture content variations were observed between the different types of samples; a low percentage was found in the SPL samples (0,3%) and relative high content was found in the LPL (17,5%), but within manufacturing parameters.

The pH of the liquid samples showed to be low and thus acidic (2,5-2,95), the solid samples were not analysed.

Noteworthy is that during the analysis and testing the samples showed to be very homogeneous.

Table 1. Results of the basic analysis of the lignins from the first batch.

Lignin	Aspect	Moisture (%)	pH, 25ºC	Viscosity, 25ºC (cP)	Density, 25ºC (g/cm^3)
BTG NW SPL1	Dark brown solid	0.3	Not available	Not available	Not available
BTG NW SPL2	Dark brown solid	0.3	Not available	Not available	Not available
BTG NW LPL	Highly viscous dark brown liquid	17.5	2.95	Not available	1.329
BTG NW MP	Dark brown liquid	2.6	2.51	35	1.127

Table 2. Results of the basic analysis of the lignins from the second batch.

Lignin	Aspect	Moisture (%)	pH, 25ºC	Viscosity, 25ºC (cP)	Density, 25ºC (g/cm^3)
BTG NW SPL1	Dark brown solid	0.3	Not available	Not available	Not available
BTG NW SPL2	Dark brown solid	0.3	Not available	Not available	Not available
BTG NW LPL	Highly viscous dark brown liquid	17.4	2.94	Not available	1.335
BTG NW MP	Dark brown liquid	2.4	2.45	33	1.123

Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) analyses were performed to evaluate the molecular weight of each sample and to be able to analyse its subsequent impact on the synthesis of resins. The highest molecular weight was obtained for the SPL1 and SPL2 samples ranging from 2700 to 3000 Da, 900 Da was obtained for the LPL sample and 450 Da for the MP`s sample. The repeatability between the different batches was also confirmed, obtaining very similar values. The values obtained have been calculated using the same calibration that is used for the analysis of the resins, using the IR channel. The current samples have a high signal intensity in the UV channel, so new calibration will be carried out to adjust as much as possible to the chemical characteristics of the samples.

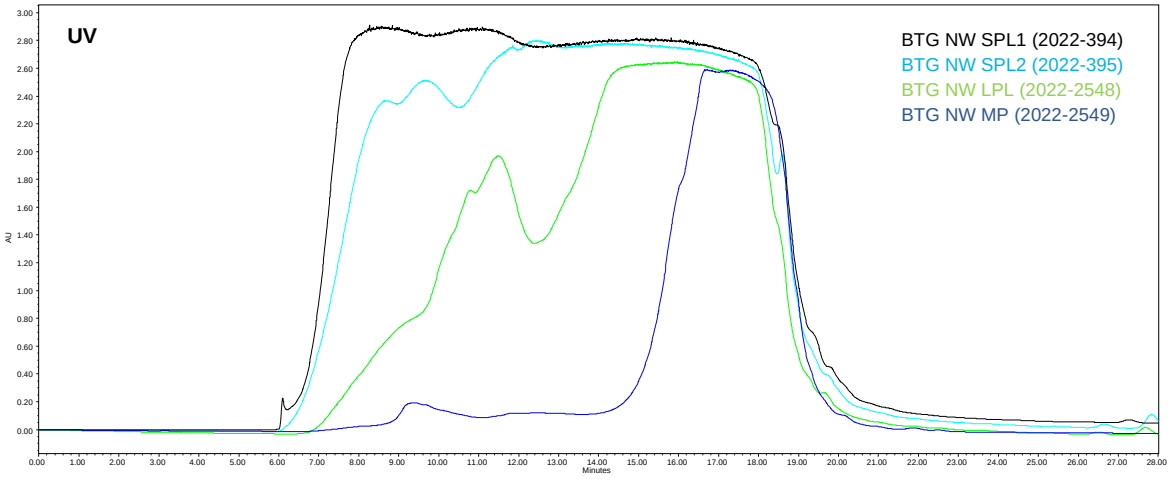


Figure 3. Molecular weight distribution of the lignins from the first batch using the UV detector.

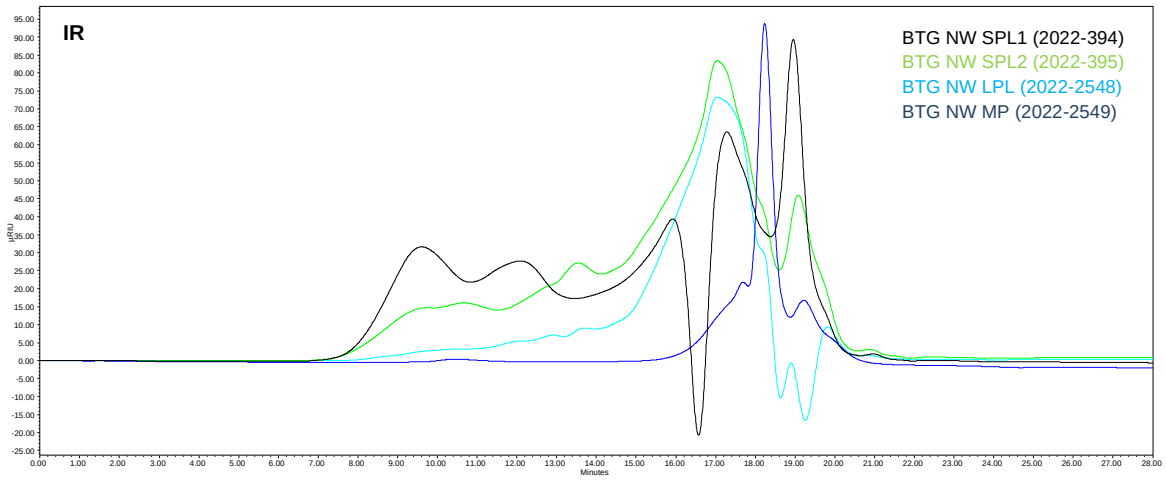


Figure 4. Molecular weight distribution of the lignins from the first batch using the IR detector.

Table 3. Results of molecular weights of the lignins from the first batch.

Lignin	Mn (Da)	Mw (Da)	MP (Da)	Mz (Da)	Mz+1(Da)	PDI	Mz/Mw
BTG NW SPL1	870	3,089	439	29,559	73,706	3.55	9.57
BTG NW SPL2	801	2,953	434	19,492	51,863	3.20	8.39
BTG NW LPL	672	887	448	1,240	1,700	1.32	1.40
BTG NW MP	531	641	421	798	991	1.21	1.24

Mn: Number average molecular weight, Mw: Weight average molecular weight, MP: Peak molecular weight, Mz & Mz+1: Higher average molecular weights, PDI: Polydispersity.

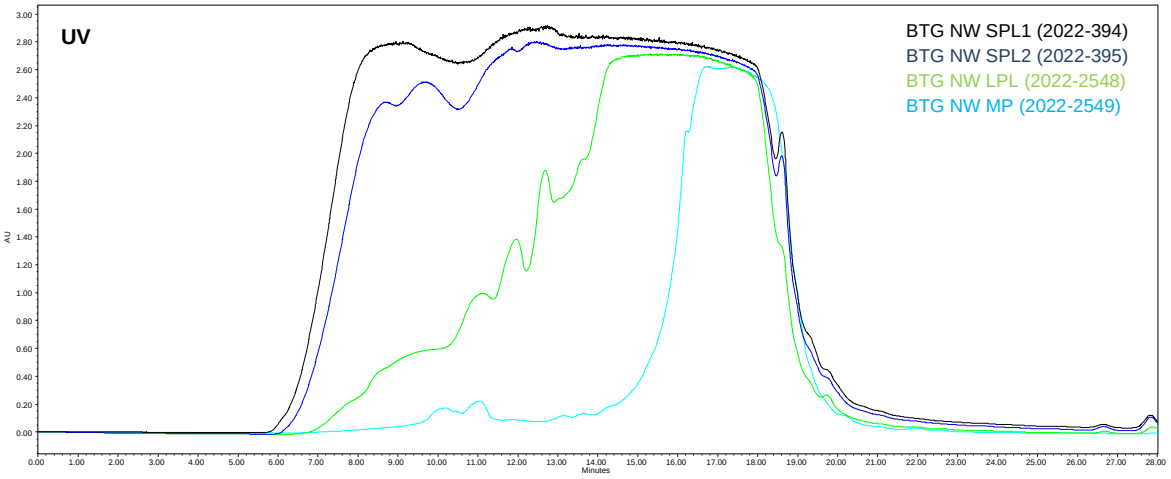


Figure 5. Molecular weight distribution of the lignins from the second batch using the UV detector.

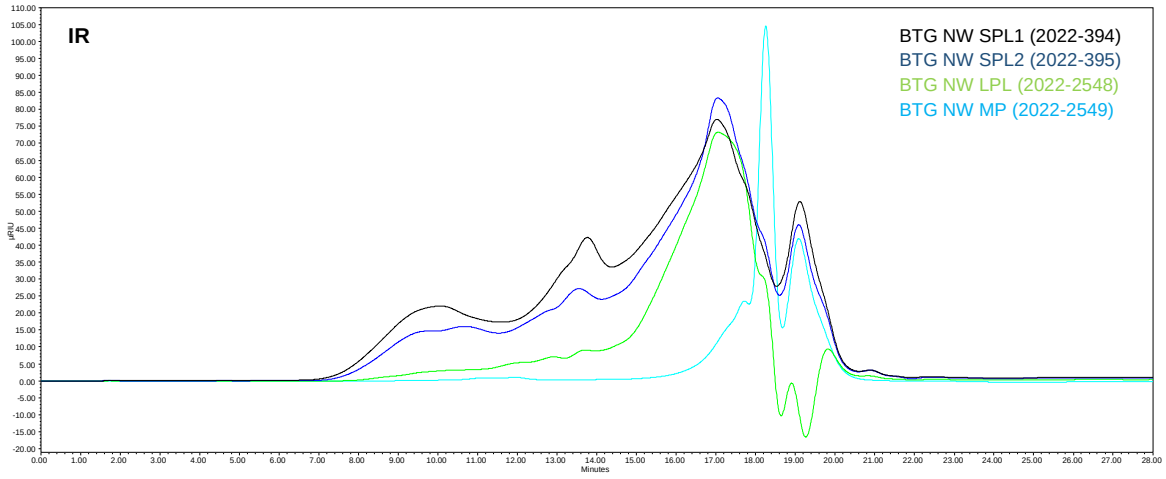


Figure 6. Molecular weight distribution of the lignins from the second batch using the IR detector.

Table 4. Results of molecular weights of the lignins from the second batch.

Lignin	Mn (Da)	Mw (Da)	MP (Da)	Mz (Da)	Mz+1(Da)	PDI	Mz/Mw
BTG NW SPL1	906	2,912	456	28,173	81,283	3.72	9.82
BTG NW SPL2	824	2,727	441	2,094	53,607	3.28	8.99
BTG NW LPL	691	913	473	1,527	2,049	1.27	1.47
BTG NW MP	548	650	438	893	892	1.15	1.32

Mn: Number average molecular weight, Mw: Weight average molecular weight, MP: Peak molecular weight, Mz & Mz+1: Higher average molecular weights, PDI: Polydispersity.

GC-MS (Agilent Technologies 6890-5973N) – Phenol determination

When the liquid lignin is further processed to obtain the solid lignin, the percentage of phenol in the sample becomes lower, as can see in the following tables. Obviously, the number for the mono-phenolics fraction is the highest. No large differences were found between the first and second batch.

Table 5. Results of phenol analysis of the lignins from the first batch.

Lignin	% Phenol
BTG NW SPL1	0.014
BTG NW SPL2	0.021
BTG NW LPL	0.034
BTG NW MP	0.249

Table 6. Results of phenol analysis of the lignins from the second batch.

Lignin	% Phenol
BTG NW SPL1	0.015
BTG NW SPL2	0.019
BTG NW LPL	0.032
BTG NW MP	0.252

Elemental analysis (CNH)

The nitrogen analysis is used to evaluate possible amine functional groups susceptible to reacting with formaldehyde. In these samples the percentage is low, not significantly influencing the reaction.

Table 7. Results of carbon, hydrogen and nitrogen percentage of the lignins from the first batch.

Lignin	% C	% H	% N
BTG NW SPL1	68.32	6.46	0.49
BTG NW SPL2	66.54	6.26	0.56
BTG NW LPL	55.63	7.25	0.37
BTG NW MP	59.92	7.20	0.29

Table 8. Results of carbon, hydrogen and nitrogen percentage of the lignins from the second batch.

Lignin	% C	% H	% N
BTG NW SPL1	70.23	6.38	0.43
BTG NW SPL2	67.99	6.11	0.54
BTG NW LPL	52.95	7.40	0.35
BTG NW MP	59.59	7.24	0.27

ICP-OES (Agilent)

The ICP-OES analysis showed very low amounts of metals in the samples (<1 ppm). These low concentrations do not affect polymerization or generate problems in the final application of the product.

Table 9. Results of metal analysis of the lignins from the first batch.

Lignin	BTG NW SPL1	BTG NW SPL2	BTG NW LPL	BTG NW MP
Ag (ppm)	0.00	0.0	0.00	0.00
Al (ppm)	0.06	0.04	0.02	0.02
As (ppm)	0.02	0.02	0.01	0.02
B (ppm)	0.00	0.00	0.02	0.02
Ba (ppm)	0.03	0.01	0.00	0.00
Be (ppm)	0.00	0.00	0.00	0.00
Ca (ppm)	0.55	0.49	0.41	0.56
Cd (ppm)	0.00	0.00	0.00	0.00
Co (ppm)	0.00	0.00	0.00	0.00
Cr (ppm)	0.00	0.00	0.00	0.00
Fe (ppm)	0.05	0.04	0.08	0.36
K (ppm) – 766.491 nm	0.11	0.13	0.15	0.10
K (ppm) – 769.897 nm	0.00	0.00	0.00	0.00
Mg (ppm)	0.11	0.10	0.09	0.13
Mn (ppm)	0.01	0.00	0.00	0.00
Mo (ppm)	0.00	0.00	0.00	0.00
Na (ppm) – 588.995 nm	0.25	0.29	0.37	0.23
Na (ppm) - 589.592 nm	0.00	0.00	0.00	0.00
Ni (ppm)	0.01	0.01	0.01	0.02
P (ppm) – 213.618 nm	0.02	0.01	0.01	0.00
P (ppm) – 214.914 nm	0.00	0.00	0.00	0.00
Pb (ppm)	0.00	0.00	0.00	0.00
S (ppm) – 180.669 nm	0.09	0.0	0.05	0.18
S (ppm) – 181.972 nm	0.22	0.20	0.16	0.39
Sb (ppm)	0.00	0.00	0.00	0.00
Se (ppm)	0.01	0.01	0.02	0.02
Si (ppm)	0.29	0.29	0.27	0.29

Sr (ppm)	0.00	0.00	0.00	0.00
Ti (ppm)	0.00	0.00	0.00	0.00
Tl (ppm)	0.00	0.00	0.00	0.00
Va (ppm)	0.00	0.00	0.00	0.00
Zn(ppm)	0.03	0.04	0.05	0.08

Table 10. Results of metal analysis of the lignins from the second batch.

Lignin	BTG NW SPL1	BTG NW SPL2	BTG NW LPL	BTG NW MP
Ag (ppm)	0.00	0.0	0.00	0.00
Al (ppm)	0.07	0.03	0.02	0.02
As (ppm)	0.03	0.02	0.01	0.01
B (ppm)	0.00	0.00	0.03	0.03
Ba (ppm)	0.04	0.01	0.00	0.00
Be (ppm)	0.00	0.00	0.00	0.00
Ca (ppm)	0.57	0.47	0.40	0.59
Cd (ppm)	0.00	0.00	0.00	0.00
Co (ppm)	0.00	0.00	0.00	0.00
Cr (ppm)	0.00	0.00	0.00	0.00
Fe (ppm)	0.05	0.03	0.09	0.39
K (ppm) – 766.491 nm	0.12	0.14	0.15	0.10
K (ppm) – 769.897 nm	0.00	0.00	0.00	0.00
Mg (ppm)	0.12	0.10	0.09	0.14
Mn (ppm)	0.02	0.00	0.00	0.00
Mo (ppm)	0.00	0.00	0.00	0.00
Na (ppm) – 588.995 nm	0.24	0.30	0.39	0.21
Na (ppm) - 589.592 nm	0.00	0.00	0.00	0.00
Ni (ppm)	0.01	0.01	0.01	0.02
P (ppm) – 213.618 nm	0.02	0.01	0.01	0.00
P (ppm) – 214.914 nm	0.00	0.00	0.00	0.00
Pb (ppm)	0.00	0.00	0.00	0.00

S (ppm) – 180.669 nm	0.09	0.0	0.05	0.18
S (ppm) – 181.972 nm	0.24	0.19	0.18	0.42
Sb (ppm)	0.00	0.00	0.00	0.00
Se (ppm)	0.01	0.01	0.03	0.03
Si (ppm)	0.31	0.31	0.28	0.27
Sr (ppm)	0.00	0.00	0.00	0.00
Ti (ppm)	0.00	0.00	0.00	0.00
Tl (ppm)	0.00	0.00	0.00	0.00
Va (ppm)	0.00	0.00	0.00	0.00
Zn(ppm)	0.03	0.05	0.06	0.10

FT-IR (Agilent)

Infrared spectroscopy was used to characterize the different batches and to assess the reproducibility of the different batches. Once again, the homogeneity of the samples between different batches was confirmed.

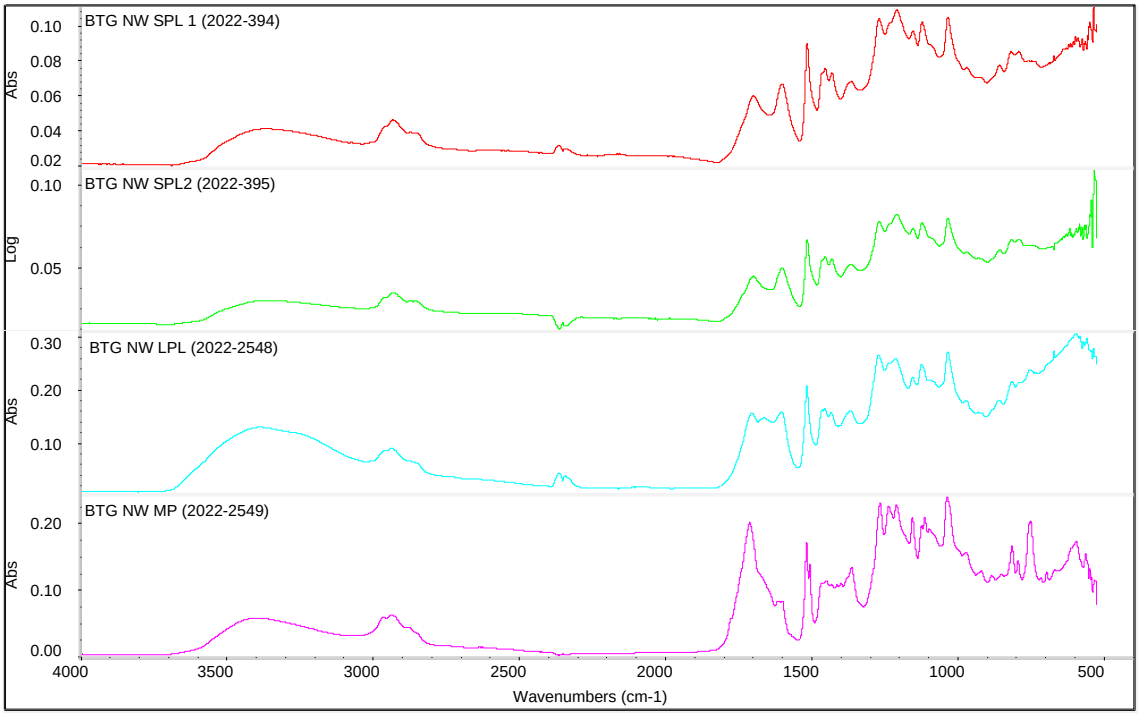


Figure 7. Characterization by FT-IR of the lignins from the first batch.

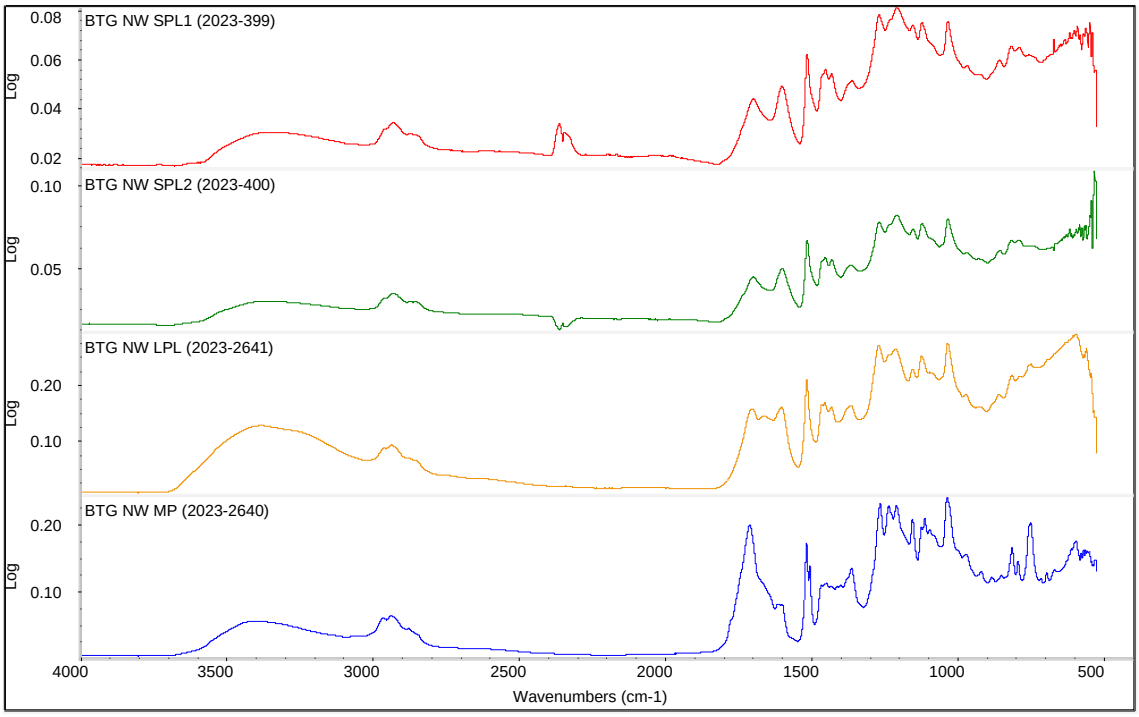


Figure 8. Characterization by FT-IR of the lignins from the second batch.

Thermogravimetric analysis (TGA)

A temperature ramp was carried out to study the behavior (weight loss) of the samples against temperature increase. The ramps indicated that the MP sample had the lowest degradation temperature and that its composition was more uniform since the degradation was carried out in a single slope. The other samples gave a gentler slope indicating greater heterogeneity in their composition. The SPL1 sample did not completely degrade at 900ºC, maintaining between 15-20% of its initial weight. The differences between batches are minimal.

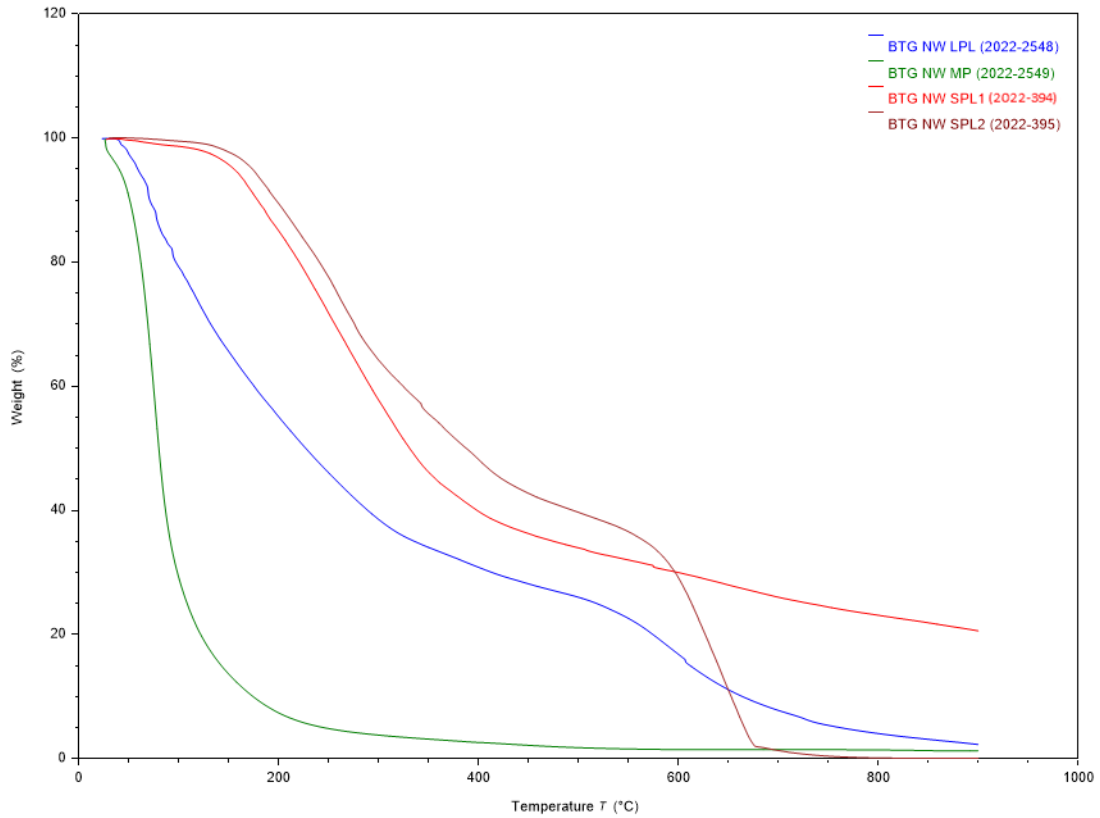


Figure 9. TGA degradation of the lignins from the first batch.

Table 11. Results of TGA degradation of the lignins from the first batch.

Lignin		1st degradation	2nd degradation	Final
BTG NW SPL1	Tª (ºC)	43.80 / 494.97	-	900
	m n d (%)	99.83 / 34.19	-	20.68
BTG NW SPL2	Tª (ºC)	110.45 / 430.66	509.29 / 713.51	900
	m n d (%)	99.40 / 44.40	39.18 / 0.98	0.00
BTG NW LPL	Tª (ºC)	41.92 / 382.22	382.22 / 679.09	900
	m n d (%)	99.16 / 32.02	32.02 / 9.01	2.32
BTG NW MP	Tª (ºC)	27.10 / 352.32	-	900
	m n d (%)	99.00 / 3.14	-	1.29

Tª (ºC): T_{start}/T_{end}, m n d (%): Weigth at T_{start}/Weight at T_{end}

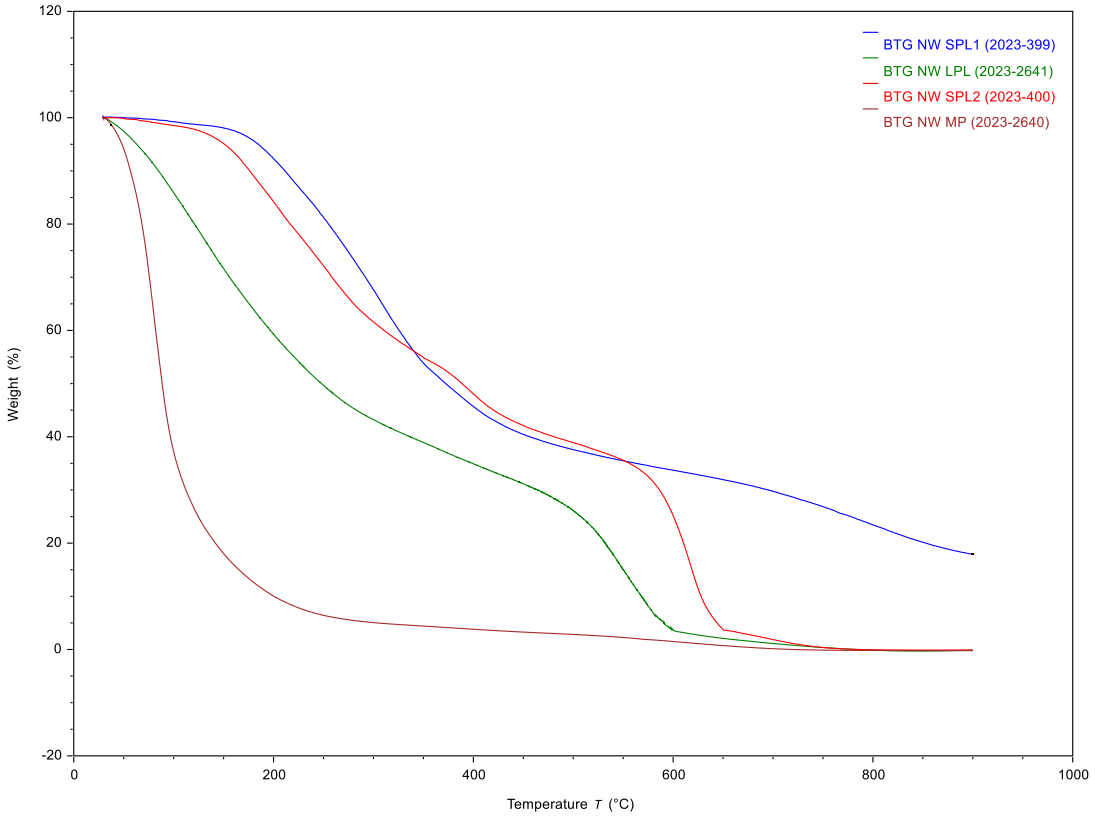


Figure 10. TGA degradation of the lignins from the second batch.

Table 12. Results of TGA degradation of the lignins from the second batch.

Lignin		1st degradation	2nd degradation	Final
BTG NW SPL1	Tª (ºC)	123.10 / 400.67	-	900
	m n d (%)	98.72 / 45.60	-	17.90
BTG NW SPL2	Tª (ºC)	79.15 / 363.05	504.53 / 681.91	900
	m n d (%)	99.11 / 53.57	38.642 / 2.576	0.00
BTG NW LPL	Tª (ºC)	51.95 / 353.98	419.75 / 638.62	900
	m n d (%)	97.11 / 38.62	33.410 / 2.365	0.00
BTG NW MP	Tª (ºC)	35.13 / 321.94	-	900
	m n d (%)	99.25 / 4.74	-	0.00

Tª (ºC): T_{start}/T_{end}, m n d (%): Weigth at T_{start}/Weight at T_{end}

Curing ramp (Rheometer)

To evaluate the modulus generation capacity, a curing ramp analysis was carried out in a rheometer at 20 ªc/min. The results indicated that the modulus of the LPL and MP samples did not increase with temperature. Therefore, there was no mechanical curing. SLP1 and SPL2 samples could not be tested, due to their solid nature.

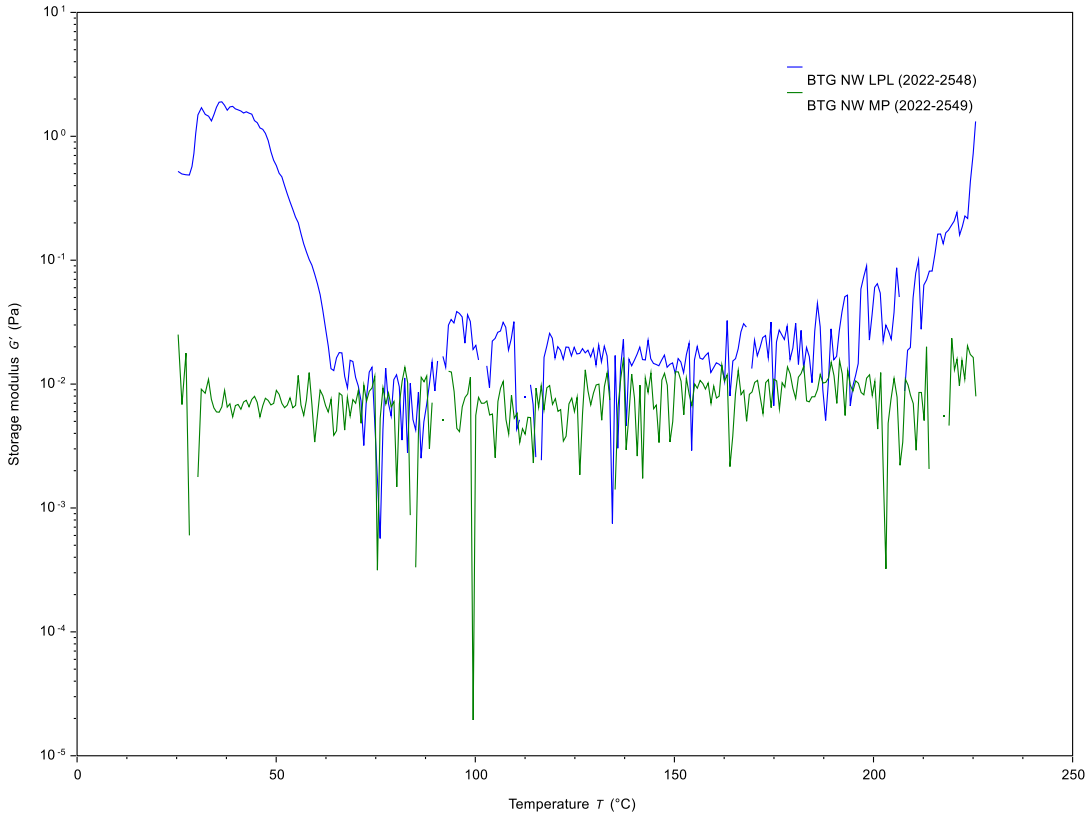


Figure 11. Curing ramp by rheometer of the lignins from the first batch.

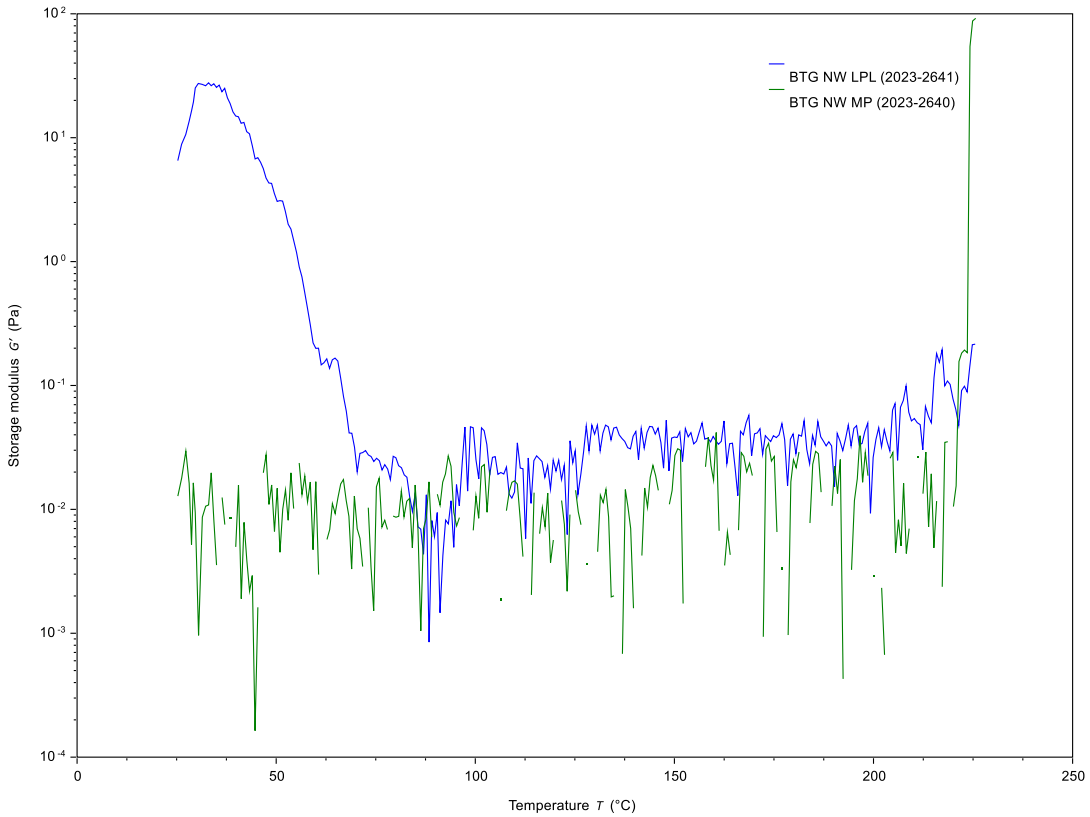


Figure 12. Curing ramp by rheometer of the lignins from the second batch.

Differential scanning calorimetry (DSC)

For the subsequent use of the samples in polymerization it is necessary to know the possible reactivity of the samples at temperatures between 60 and 90 ºC. A ramp at 20 °C/min was performed in DSC. The results showed a slight enthalpy increases outside the reactivity ranges. This does not create any problem in the manufacture of replaced resins.

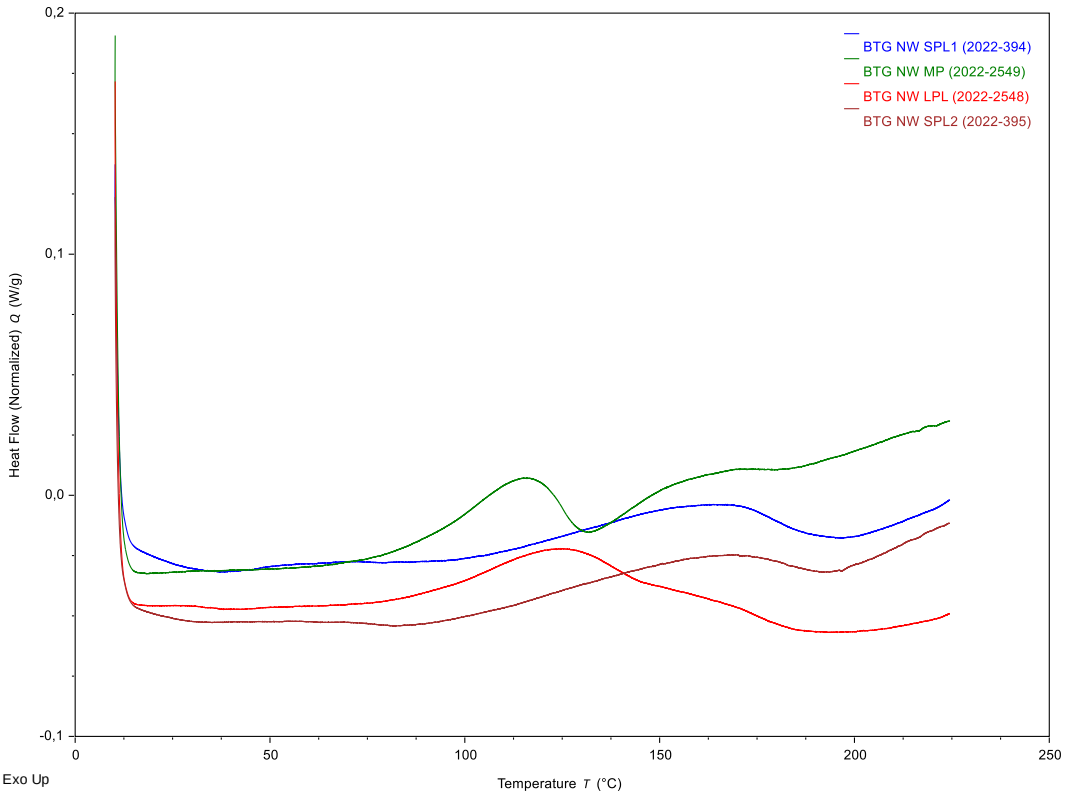


Figure 13. DSC thermograms of the lignins from the first batch.

Table 13. Results of enthalpy of the lignins from the first batch.

Lignin	Peak Tª (ºC)	Enthalpy (J/g)
BTG NW SPL1	161.40	25.73
BTG NW SPL2	153.12	19.26
BTG NW LPL	125.50	46.30
BTG NW MP	114.55	20.27

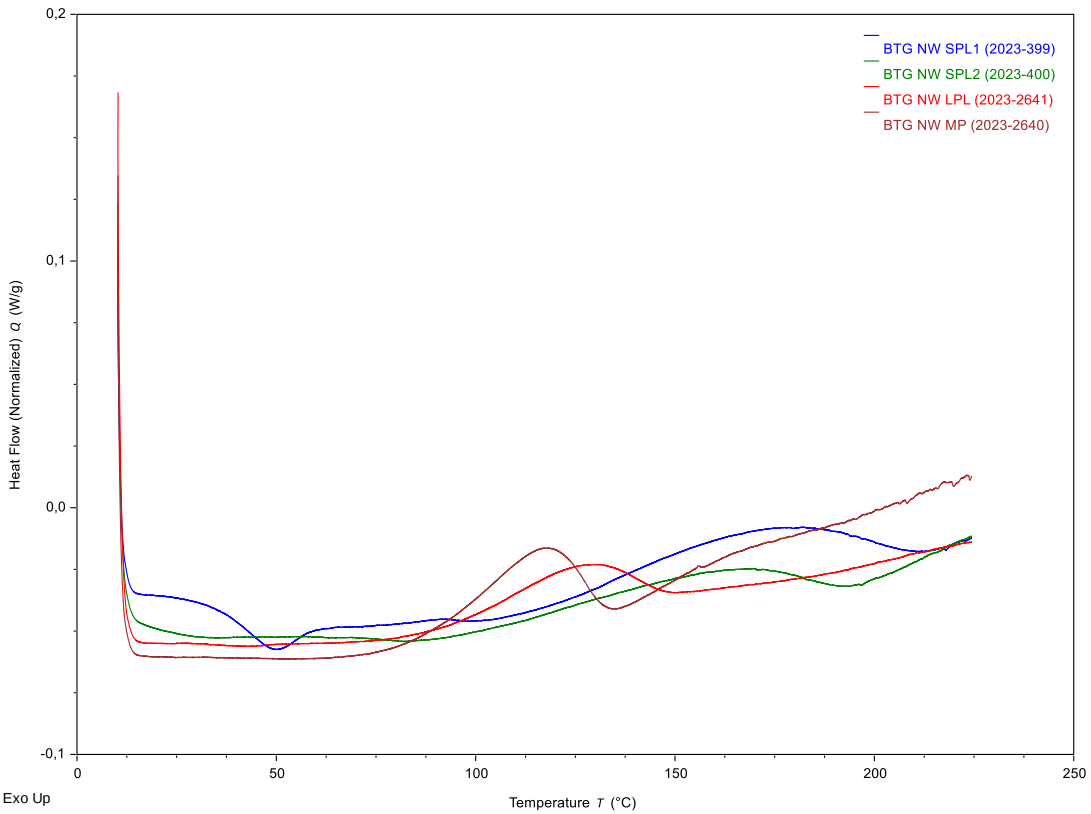


Figure 14. DSC thermograms of the lignins from the second batch.

Table 14. Results of enthalpy of the lignins from the second batch.

Lignin	Peak Tª (ºC)	Enthalpy (J/g)
BTG NW SPL1	168.58	20.90
BTG NW SPL2	158.01	18.95
BTG NW LPL	126.94	16.24
BTG NW MP	117.07	22.77

Task 5.2: Resin screening test

The objective of this task is to compare the behaviour of the different samples and obtain information to enable the production of specific resins for the manufacture of plywood and MDF boards. A specific (standard) recipe was synthesized that allowed phenol to be replaced by different percentages of lignin and that could be used to see trends in the final characteristics of the resins obtained.

Foresa Tech started with a reference recipe:

Phenol + Formaldehyde + Base → Polymer + Free Phenol + Free Formaldehyde

Then Foresa Tech modified the recipe in which a part or all of the phenol was replaced by pyrolytic lignin:

Pyrolitic Lignin + Phenol + Formaldehyde + Base→ Polymer + Free Phenol + Free Formaldehyde

Task 5.2.1: Substitution of phenol for bio-phenol in a generic resin

In this first step, Foresa Tech made a sweep to investigate the reaction initial temperature for complete dissolution of the lignins. The study was based on dissolving (on a small scale) water, sodium hydroxide and lignin at temperatures of: 20, 30, 40 and 60 ºC. Results showed that all lignins need a minimum temperature of 60 ºC to be completely dissolved.

Regarding the reaction, the first step is the addition of lignin is the ability to dissolve it.

At this point, Foresa Tech made a reaction of a generic reference resin and three different degrees of substitution, being: 25%, 50% and 75%. For each test, the resin was prepared three times. All the resins were analysed to measure the different properties.

All the resin synthesis reactions could be carried out without problems in the polymerization step, except for resins with 75% phenol substitution by the solid lignin samples. Due to the solid lignin samples, the viscosity became too high in the reactor during resin synthesis, hindering polymerization.

Figure 15. Photo of the different resins prepared.

Figure 16. Photo of reisn reactor.

Task 5.2.2: Characterization resins

In the table below, the physical & chemical properties of the prepared resins are given. For each resin this was done threefold, the average values for each property are given in the table.

Table 15. Description of the analysis of each resin.

	Lignin	Replaced	η, cP (25ºC)	P 25ºC (g/cm³)	pH (25°C)	Hardening time (min)	Solid Content (%)	Miscibility	Free Formaldehyde (%)	Free Phenol, (%)
x̄ (E0)		0%	322	1.206	11.5	53.6	49.7	1,000	0.00	2.09
x̄ (AE1)	BTG NW SPL1	25%	337	1.232	11.2	43.4	53.1	1,000	0.09	0.62
x̄ (BE1)	BTG NW SPL2	25%	348	1.218	11.6	50.5	49.4	1,000	0.00	0.58
x̄ (CE1)	BTG NW LPL	25%	344	1.206	11.4	51.2	52.5	1,000	0.05	0.92

x̄ (DE1)	BTG NW MP	25%	307	1.211	11.3	51.1	49.4	1,000	0.04	0.90
x̄ (AE2)	BTG NW SPL1	50%	365	1.215	11.6	42.5	52.5	1,000	0.16	0.11
x̄ (BE2)	BTG NW SPL2	50%	377	1.226	11.6	49.3	50.9	1,000	0.14	0.00
x̄ (CE2)	BTG NW LPL	50%	322	1.223	11.2	51.3	51.1	1,000	0.24	0.10
x̄ (DE2)	BTG NW MP	50%	295	1.205	11.1	48.1	49.4	1,000	0.23	0.02
x̄ (AE3)	BTG NW SPL1	75%	The high viscosity of the lignin, does not allow to finish the reaction.							
x̄ (BE3)	BTG NW SPL1	75%	The high viscosity of the lignin, does not allow to finish the reaction.							
x̄ (CE3)	BTG NW LPL	75%	402	1.221	11.2	34.4	52.1	1,000	0.51	0
x̄ (DE3)	BTG NW MP	75%	263	1.208	11.1	60.8	53.6	1,000	0.53	0.04

Viscosity

It was observed that for all resins the final viscosities were in the same range (300 – 350 cP). This was due to the fact that all the resins were synthesized according to the same recipe, and that the polymerization was stopped in the same range of viscosity. In the case of the solid lignin (BTG NW SPL1) replacing 75% of phenol (AE3), the initial viscosity was very high, and the reaction could not be finished.

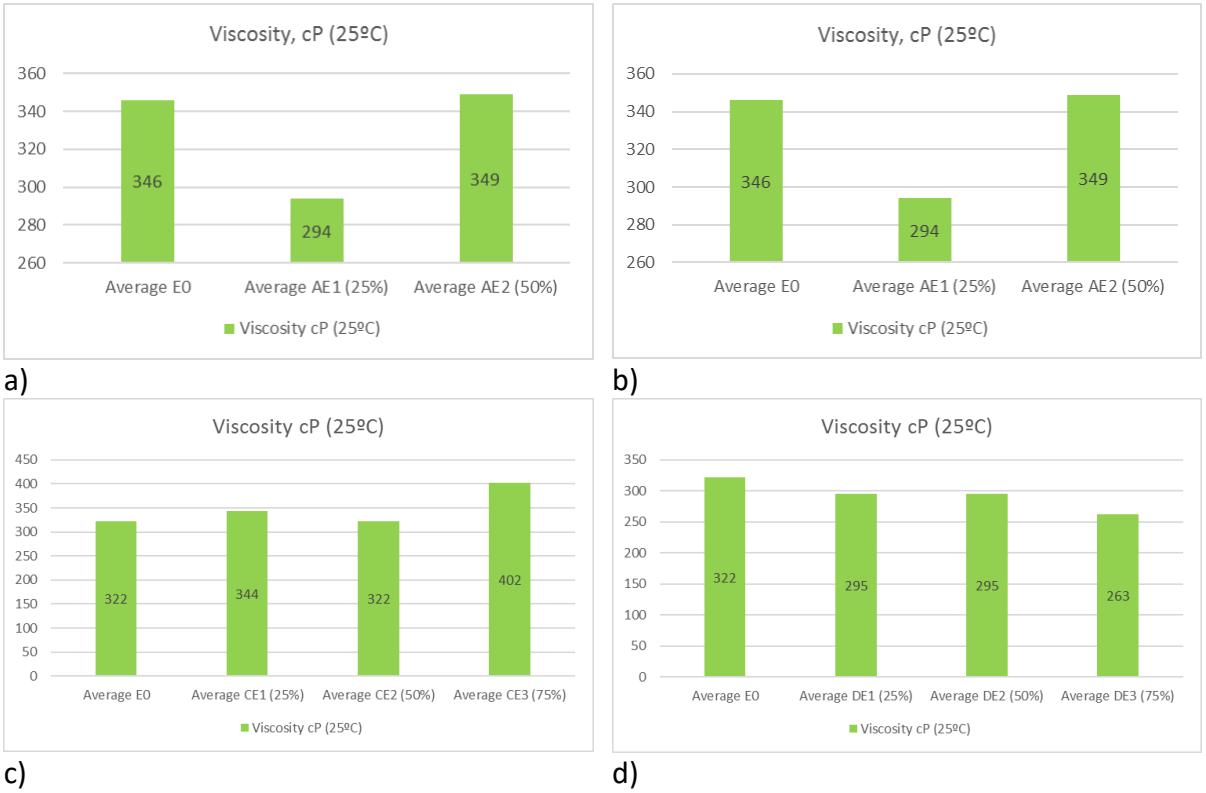


Figure 17. Viscosity of a) reference resin (E0), lignin BTG NW SPL1 resin with replaced 25% (AE1) and 50% (AE2); b) reference resin (E0), lignin BTG NW SPL2 resin with replaced 25% (BE1) and 50% (BE2); C) reference resin (E0), lignin BTG NW LPL resin with replaced 25% (CE1), 50% (CE2) and 75% (CE3); d) reference resin (E0), lignin BTG NW MP resin with replaced 25% (DE1), 50% (DE2), 75% (DE3).

Density

In all tests, no large changes in density were observed, all resins had a density of around 1.200 g/cm^3.

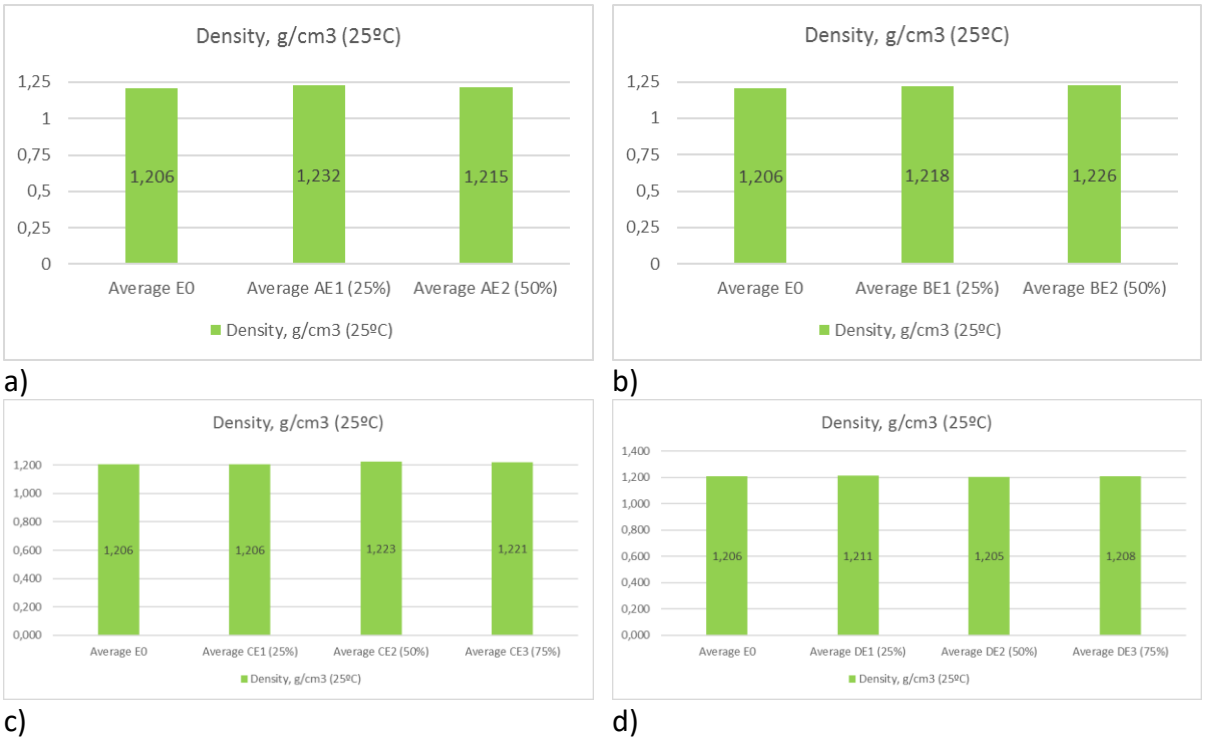
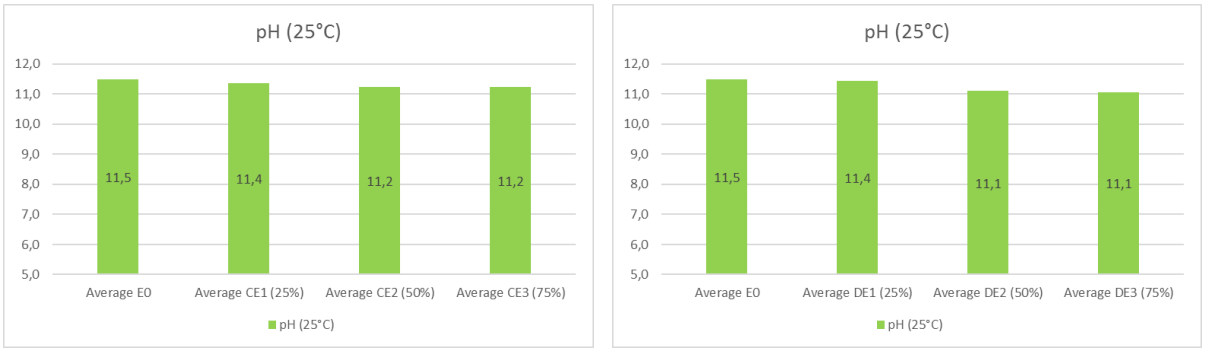


Figure 18. Density of a) reference resin (E0), lignin BTG NW SPL1 resin with replaced 25% (AE1) and 50% (AE2); b) reference resin (E0), lignin BTG NW SPL2 resin with replaced 25% (BE1) and 50% (BE2); C) reference resin (E0), lignin BTG NW LPL resin with replaced 25% (CE1), 50% (CE2) and 75% (CE3); d) reference resin (E0), lignin BTG NW MP resin with replaced 25% (DE1), 50% (DE2), 75% (DE3).

pH

All the resins, including the reference, had a similar pH of around 11. This is normal because the resins condenses with sodium hydroxide and this parameter is fixed in the polymerization.

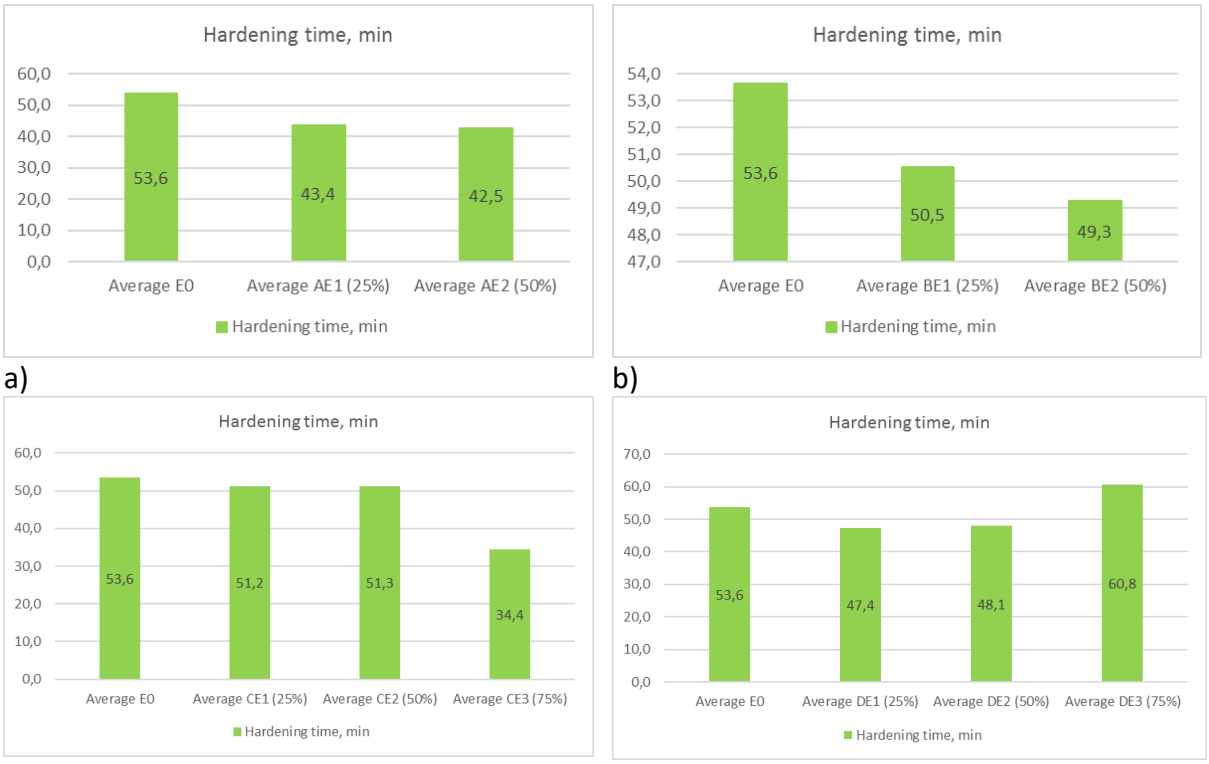


c) d)

Figure 19. pH of a) reference resin (E0), lignin BTG NW SPL1 resin with replaced 25% (AE1) and 50% (AE2); b) reference resin (E0), lignin BTG NW SPL2 resin with replaced 25% (BE1) and 50% (BE2); C) reference resin (E0), lignin BTG NW LPL resin with replaced 25% (CE1), 50% (CE2) and 75% (CE3); d) reference resin (E0), lignin BTG NW MP resin with replaced 25% (DE1), 50% (DE2), 75% (DE3).

Hardening time

The hardening time decreases when increasing the degree of substitution. As the degree of substitution increases, the free formaldehyde increases because lignin samples are less reactive, and more formaldehyde thus remains unreacted in the resin.



a) b)

c) d)

Figure 20. Hardening time of a) reference resin (E0), lignin BTG NW SPL1 resin with replaced 25% (AE1) and 50% (AE2); b) reference resin (E0), lignin BTG NW SPL2 resin with replaced 25% (BE1) and 50% (BE2); C) reference resin (E0), lignin BTG NW

LPL resin with replaced 25% (CE1), 50% (CE2) and 75% (CE3); d) reference resin (E0), lignin BTG NW MP resin with replaced 25% (DE1), 50% (DE2), 75% (DE3).

Solid content

No large variations were observed in the solid content.

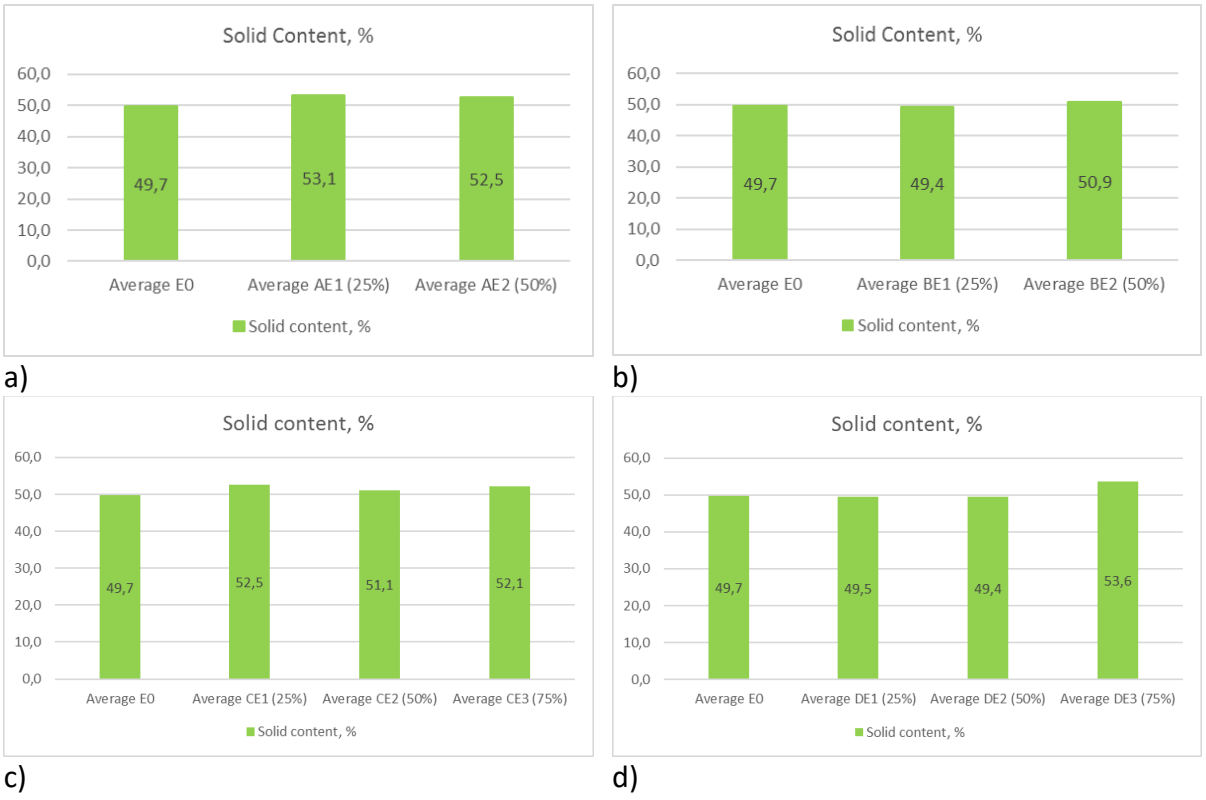


Figure 21. Solid content of a) reference resin (E0), lignin BTG NW SPL1 resin with replaced 25% (AE1) and 50% (AE2); b) reference resin (E0), lignin BTG NW SPL2 resin with replaced 25% (BE1) and 50% (BE2); C) reference resin (E0), lignin BTG NW LPL resin with replaced 25% (CE1), 50% (CE2) and 75% (CE3); d) reference resin (E0), lignin BTG NW MP resin with replaced 25% (DE1), 50% (DE2), 75% (DE3).

Free Formaldehyde and Phenol

Formaldehyde analysis showed that increasing the degree of substitution causes an increase in the percentage of free formaldehyde. Phenol analysis showed that the free phenol content decreases with increasing the percentage of substitution, which is obvious because there is less phenol present in the resin.

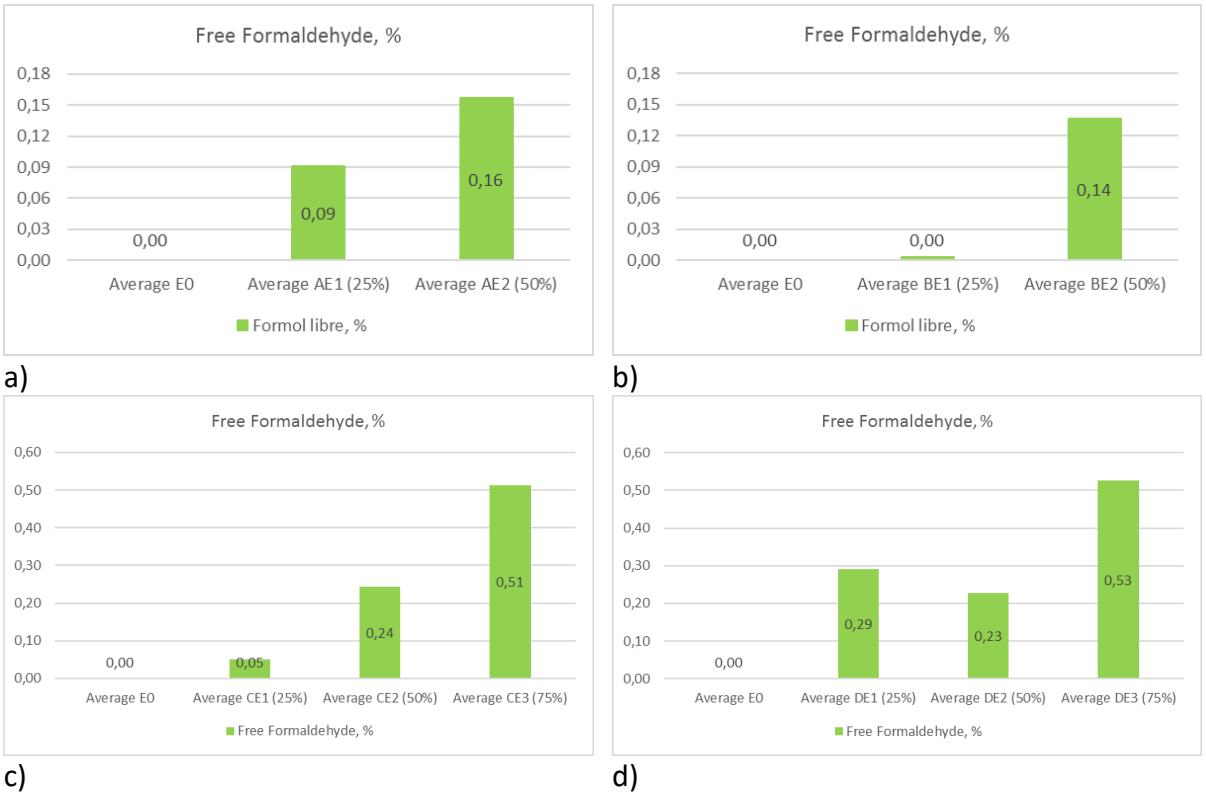
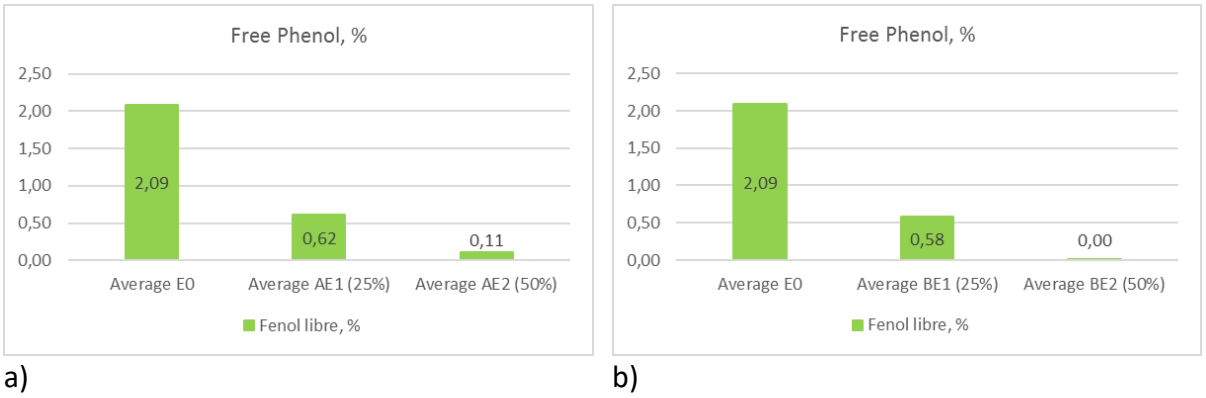
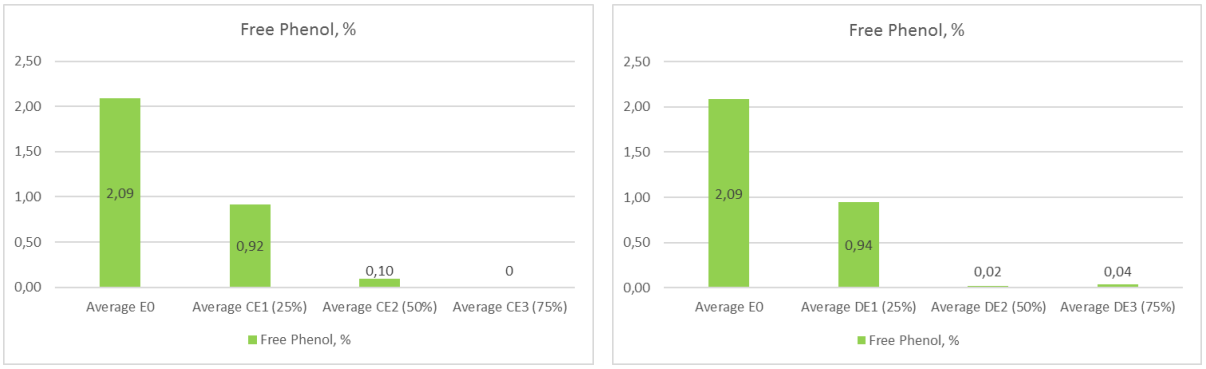


Figure 22. Free Formaldehyde of a) reference resin (E0), lignin BTG NW SPL1 resin with replaced 25% (AE1) and 50% (AE2); b) reference resin (E0), lignin BTG NW SPL2 resin with replaced 25% (BE1) and 50% (BE2); C) reference resin (E0), lignin BTG NW LPL resin with replaced 25% (CE1), 50% (CE2) and 75% (CE3); d) reference resin (E0), lignin BTG NW MP resin with replaced 25% (DE1), 50% (DE2), 75% (DE3).





c) d)

Figure 23. Free Phenol of a) reference resin (E0), lignin BTG NW SPL1 resin with replaced 25% (AE1) and 50% (AE2); b) reference resin (E0), lignin BTG NW SPL2 resin with replaced 25% (BE1) and 50% (BE2); C) reference resin (E0), lignin BTG NW LPL resin with replaced 25% (CE1), 50% (CE2) and 75% (CE3); d) reference resin (E0), lignin BTG NW MP resin with replaced 25% (DE1), 50% (DE2), 75% (DE3).

Gel Permeation Chromatography (CPG)

Gel permeation chromatography (GPC) analyzes were performed to evaluate the molecular weight of the resins. Figure 23 and Figure 24 illustrate the chromatograms of the ultraviolet and infrared detector of the reference resin and resins with 50% replacement. The molecular weight obtained are consistent with the CPG performed on lignin's. The resins prepared with SPL1, SPL2 and LPL have a higher molecular weight than the reference (phenol) resin, because the initial molecular weight is already very high. However, the resin prepared with the MP lignin, had a lower molecular weight compared to the reference. This can be explained by the fact that for the same final polymerization viscosity, the resin with the phenol produces a more cross-linked polymer, resulting in a higher molecular weight.

Table 16. Results of molecular weights of reference resin (E0), BTG NW SPL1 lignin resin with replaced 50% (AE2), BTG NW SPL2 lignin resin with replaced 50% (BE2), BTG NW LPL lignin resin with replaced 50% (CE2), BTG NW MP lignin resin with replaced 50% (DE2).

	Mn (Da)	Mw (Da)	MP (Da)	Mz (Da)	Mz+1 (Da)	PDI	Mz/Mw
NewWave E0 (0%)	1,933	268,745	986	36,997,062	137,383,360	139.04	137.67
NewWave AE2 (50%; SPL1)	1,797	578,630	1,088	172,739,964	519,450,441	321.97	298.53
NewWave BE2 (50%; SPL2)	2,051	783,814	1,097	196,895,134	533,169,683	382.17	251.20
NewWave CE2 (50%; LPL)	2,084	365,313	1,094	52,043,203	146,447,173	175.27	142.46
NewWave DE2 (50%; MP)	2,332	183,588	1,079	3,609,061	7,668,460	78.71	19.66

Mn: Number average molecular weight, Mw: Weight average molecular weight, MP: Peak molecular weight, Mz & Mz+1: Higher average molecular weights, PDI: Polydispersity.

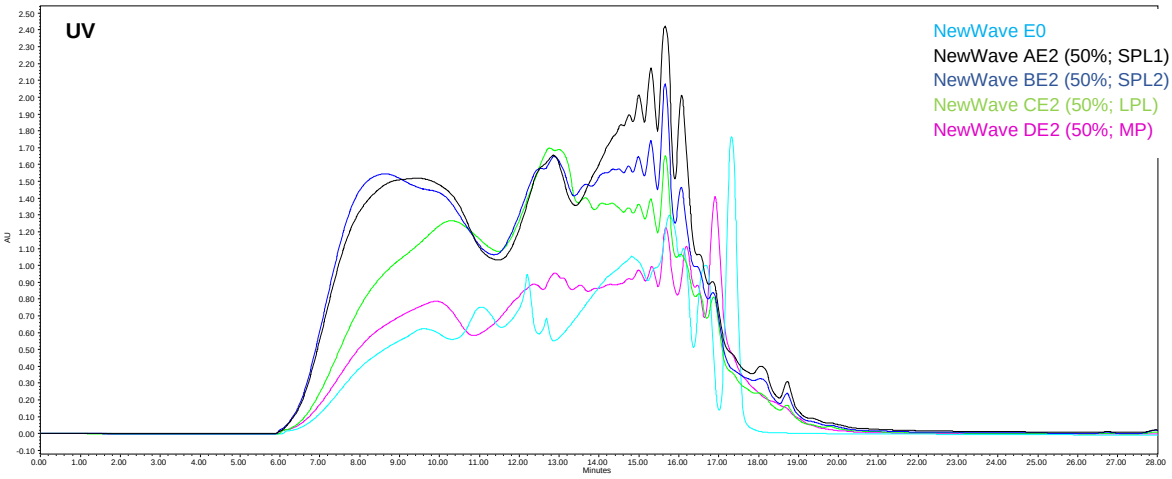


Figure 24. Molecular weight distribution by UV detector of reference resin (E0), BTG NW SPL1 lignin resin with replaced 50% (AE2), BTG NW SPL2 lignin resin with replaced 50% (BE2), BTG NW LPL lignin resin with replaced 50% (CE2), BTG NW MP lignin resin with replaced 50% (DE2).

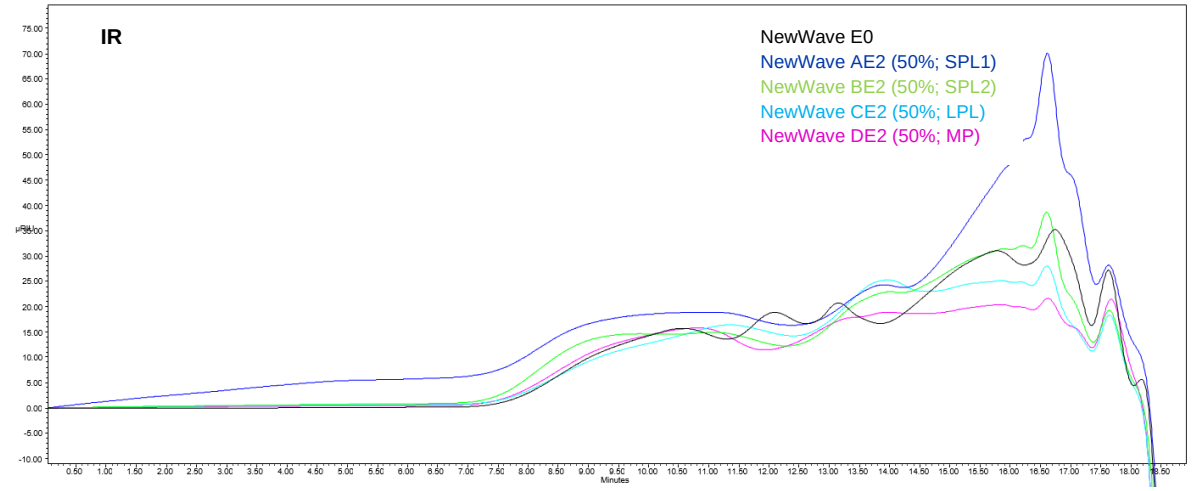


Figure 25. Molecular weight distribution by IR detector of reference resin (E0), BTG NW SPL1 lignin resin with replaced 50% (AE2), BTG NW SPL2 lignin resin with replaced 50% (BE2), BTG NW LPL lignin resin with replaced 50% (CE2), BTG NW MP lignin resin with replaced 50% (DE2).

In Figure 25 and Figure 26 the chromatograms of the ultraviolet and infrared detector of reference resin and resins with 75% replacement for the LPL and MP samples are given. As the calibration used to obtain the molecular weights was being modified, the results obtained are not reliable. Therefore, the provisional plots are shown. The values for the resin DE3 could not be obtained.

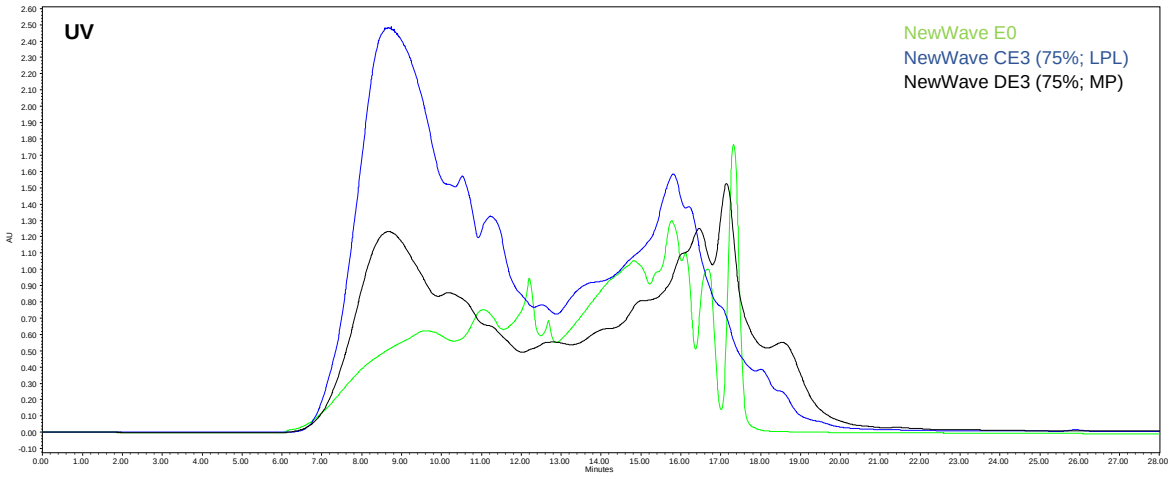


Figure 26. Molecular weight distribution by UV detector of reference resin (E0), BTG NW LPL lignin resin with replaced 75% (CE3), BTG NW MP lignin resin with replaced 75% (DE3).

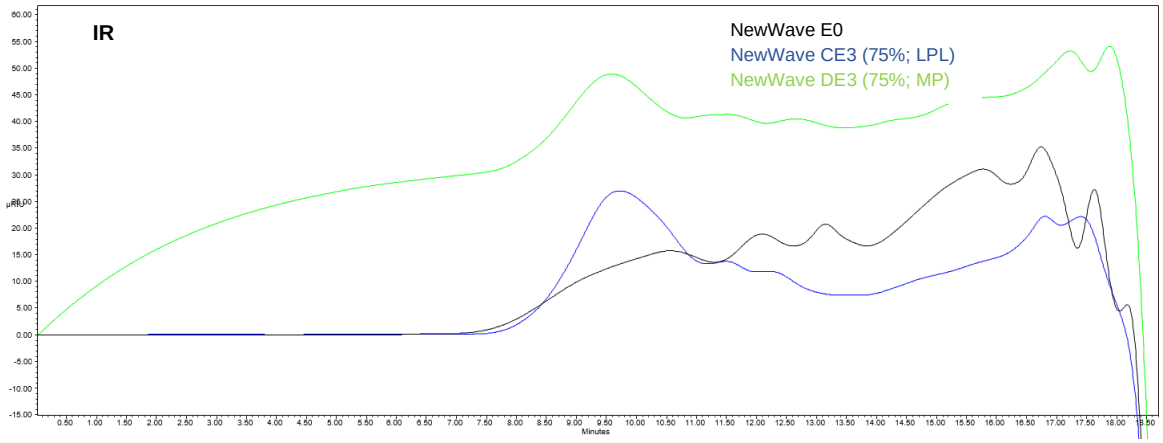


Figure 27. Molecular weight distribution by IR detector of reference resin (E0), BTG NW LPL lignin resin with replaced 75% (CE3), BTG NW MP lignin resin with replaced 75% (DE3).

Table 17. Results of molecular weights of reference resin (E0), BTG NW LPL lignin resin with replaced 75% (CE3), BTG NW MP lignin resin with replaced 75% (DE3).

	Mn (Da)	Mw (Da)	MP (Da)	Mz (Da)	Mz+1 (Da)	PDI	Mz/Mw
NewWave E0 (0%)	1,933	268,745	986	36,997,062	137,383,360	139.04	137.67
NewWave CE3 (75%; LPL)	2,234	237,551	295,408	5,577,981	33,358,763	106.32	23.48
NewWave DE3 (75%; MP)	-	-	-	-	-	-	-

Mn: Number average molecular weight, Mw: Weight average molecular weight, MP: Peak molecular weight, Mz & Mz+1: Higher average molecular weights, PDI: Polydispersity.

Conclusions

D5.1 is the first of two deliverables describing the development of new plywood resins. In sub-task " 5.1 Lignin characterization". Four lignin samples were received from BTG and have been analyzed. Parameters such as the; water content, density, viscosity, pH, % of phenol, elemental analysis (C,H,N), GPC & metal content have been analyzed. Furthermore, to be able to understand the reactivity of the samples, thermal degradation, calorimetry scanning differential and curing ramp analyses were performed as well. Noteworthy is that during the analysis and testing the samples showed to be very homogeneous, which is not always the case with lignins and lignin derived materials. In sub-task "5.2 Resin screening test", a recipe was developed, and a 100 % phenol-formaldehyde resin was synthesized to be used as a blank to compare with resins with incorporated lignin to replace the phenol. The different lignin samples provided by BTG were tested as phenol substitutes in amounts/percentages of 25, 50 & 75%. All the resin synthesis reactions could be carried out without problems in the polymerization step, except for resins with 75% phenol substitution by the solid lignin samples. Due to the solid lignin samples, the viscosity became too high in the reactor during resin synthesis, hindering polymerization. The synthesized resins have been analyzed to obtain information required for evaluation in following sub-tasks. The replacement of 100% of the phenol in the resin by the different lignin's provided by BTG is still ongoing.

NewWave

Funded by
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