

100 % bio-based 5-(hydroxymethyl)furfural (HMF) and lignin polymers for Liquid Deposition Modelling (LDM) 3D printing

Eliott Bonnet Martin^{1,2}, Michael Lecourt², Davide Beneventi¹, Aurore Denneulin¹.

¹LGP2 Laboratoire de génie des procédés pour la bioraffinerie, les matériaux bio-sourcés et l'impression fonctionnelle

²Institut technologique FCBA

E-mail: Eliott.BONNETMARTIN@fcba.fr

Michael.LECOURT@fcba.fr

Davide.beneventi@pagora.grenoble-inp.fr

Aurore.denneulin@grenoble-inp.fr

Short abstract

This extended abstract presents the development of novel bio-based non-toxic thermosetting polymers and their implementation in liquid deposition modelling (LDM). Lignin-HMF polymers were investigated. Lignin is a phenolic biobased compound derived as a coproduct of the papermaking process with a global production of around 50 million tons a year, most of which is currently burned for energy. The search to valorise this biproduct is of current importance. If lignin is combined with a bio-based aldehyde, such as HMF, it is possible to produce a bio-based thermosetting polymer with excellent thermal stability. Attention is given to the effect of the HMF/lignin ratio on the thermal properties of the resulting polymers, as well as on their processability in LDM. The results of neat resin characterization will be reported. With addition of fillers LDM printing has been successfully carried out, and the first results are shown.

Keywords: LDM 3D printing, Bio-based materials, Thermoset, Lignin

1. Introduction and background

Bakelite is widely considered as the first synthetic thermosetting polymer, obtained through the polycondensation of formaldehyde and phenol (Pizzi, 2003). Nowadays, phenol-formaldehyde resins are extensively used, particularly in the wood panel industry, due to their excellent mechanical performance and durability. However, increasing concerns about the carcinogenic nature of formaldehyde have prompted searches for a safer and sustainable alternative. Furthermore, both phenol and formaldehyde are conventionally derived from non-renewable petroleum resources, which depletion and rising costs favour the transition toward bio-based materials. In this context, lignin, which is an abundant coproduct of the papermaking industry, has been identified as a promising substitute for phenol in phenolic resins for more than 60 years (Apel and Riehm, 1960). More recently, 5-hydroxymethylfurfural (HMF) derived from lignocellulosic biomass, namely cellulose and hemicelluloses (Eid et al., 2021), has emerged as an available bio-based alternative to formaldehyde. HMF contains a highly reactive furan ring, as well as both an aldehyde in C2 and an alcohol in C5 positions, enabling its participation in condensation reactions with phenolic compounds. These reactions can occur either directly via the aldehyde group or after hydration leading to the formation of levulinic and formic acids under certain conditions (Rosenfeld et al., 2020).

Beyond the abovementioned applications for such resins, emerging opportunities are being explored in additive manufacturing, particularly in liquid deposition modelling (LDM). Although still in its early stages, the use of bio-based thermosetting polymers in 3D printing has attracted growing interest and shows significant potential for the development of sustainable, high-performance materials (Bonnet Martin et al., 2026).

This work presents the development and characterization of lignin–HMF thermosetting resins, with a particular focus on their thermal properties and printability. The influence of formulation parameters, including HMF/lignin ratio and filler content, is being investigated in relation to processability in liquid deposition modelling. Finally, a proof of concept of 3D printing is demonstrated and discussed.

2. Materials and methods

2.1 Materials

Hardwood lignin was obtained from the precipitation of kraft black liquor. The initial liquor, with a pH of approximately 9-10, was acidified to pH 2 at 40°C using sulfuric acid (H₂SO₄). The resulting lignin precipitate was then filtered and washed. The purity of the recovered lignin was 93.1% with a weight-average molecular weight (M_w) of 4100 g·mol⁻¹.

Commercial grade HMF was used for all the formulations. Olive pomace powder was incorporated as a filler for the LDM printing to increase the viscosity of the resin as well as diminishing shrinkage during post-curing.

2.2 Methods

2.2.1 Formulations of lignin-HMF resins.

The resin was synthesized under reflux in a round-bottom flask, HMF was first heated to 65°C with 6 mL of sodium hydroxide (NaOH) at a concentration of 500 g.L⁻¹ in water, in order to obtain a final solid content of 75% by wt. Acid-precipitated lignin was then added to the flask, with an HMF/lignin mass ratio of 1:1.6. After addition of lignin, the mixture was stirred for 15 minutes to ensure proper homogenization. This temperature was then increased to 85°C and maintained for 2 hours to promote the polycondensation reaction. To perform rapid crosslinking assessment and FTIR spectroscopy, the resulting resin was then cured in an oven for 2 hours at 160°C in aluminium cups.

2.2.2 Neat resin characterisation.

Molecular structure of the resin

The FTIR spectra were obtained with a Spectrum 65 (PerkinElmer, Shelton, CT, USA), scanning from 600 to 4000 cm⁻¹. H-NMR will also be performed.

Thermal properties analysis

Dynamic scanning calorimetry was performed using a DSC Q100 (TA Instruments, New Castle, DE 19720, USA). The resin was encapsulated in hermetic aluminium crucible able to sustain a pressure of 2 MPa. The temperature scan was done from 25°C to 300°C with a heating rate of 10°C/min. Thermogravimetric analysis was performed using a TGA/DSC 3+ Star system (Mettler Toledo, Im Langacher, 8606 Greifensee, Switzerland) under an air atmosphere: the temperature scan was performed from 30°C to 900°C with a heating rate of 10°C/min.

2.2.3 Liquid deposition modelling.

The resin was mixed with olive pomace powder for the 3D printing part. For additive manufacturing, a 3D printer equipped with a WASP liquid deposition modelling extruder (WASP 48024 Massa Lombarda RA, Italy) was employed. The paste was pushed into the system through a syringe with compressed air, before being deposited through a 1.5 mm diameter nozzle. The

printed geometries included cylindrical and dumbbell-shaped samples, the latter being designed for mechanical characterisation.

3. Results and discussion

The FTIR spectra of cured phenol-formaldehyde resins show the presence of characteristic absorption peaks at 1465 cm^{-1} and 2925 cm^{-1} , attributed to methylene bridges linking the phenolic units, thereby proving the condensation of the polymer. Additional bands of absorbance at 1070 and 1150 cm^{-1} indicate the presence of methylene ether bridges, representing the second type of bridging formed between phenolic units during the polycondensation of phenol formaldehyde.

In contrast, lignin-HMF polymers display absorption peaks at 1465 cm^{-1} and 2925 cm^{-1} with lower intensity compared to those of phenol-formaldehyde resins, suggesting a reduced formation of methylene bridges. Furthermore, peaks normally characteristic of methylene ether bridges are apparently absent. However, this observation remains difficult to confirm for sure due to the potential overlap of such peaks with the C-O-C stretching vibrations of the furan ring, as well as with the peak at 1125 cm^{-1} associated with syringyl units in lignin. Nevertheless, the FTIR analysis suggests that the reaction mechanism between lignin and HMF significantly differs from that of the conventional phenol-formaldehyde resole resins (Figure 1), likely involving alternative crosslinking pathways.

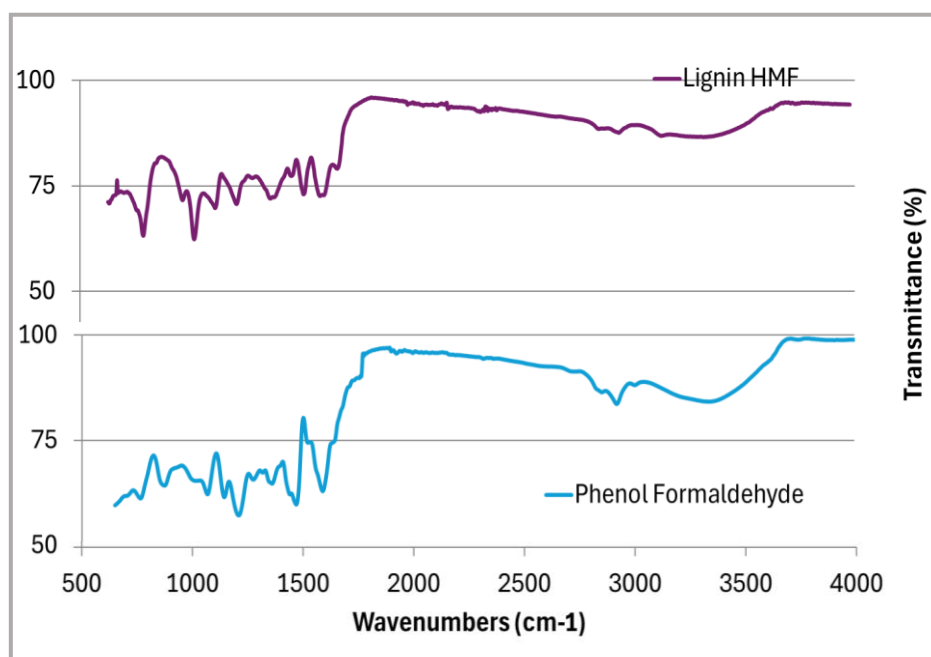


Figure 1: FTIR spectra for 160°C cured phenol formaldehyde resin and the lignin HMF polymer

The curing of phenol-formaldehyde resin occurs in two distinct exothermic steps, as evidenced by differential scanning calorimetry. The first step is the formation of quinone methide intermediates by electrophilic addition of formaldehyde at the C2 position of the phenolic ring, followed by dehydration. These intermediates can then react either with phenol or with other quinone methide species before its dehydration in the condensation step leading to network formation (Pizzi, 2003). The first exothermic peak at 140°C is attributed to the quinone methide formation step while the peak at 170°C corresponds to the condensation reaction.

In contrast, the lignin and HMF resin exhibits a different thermal behaviour with only a single well-defined exothermic peak detected at 250°C . This observation supports the hypothesis of a different reaction mechanism for this polymer compared to phenol-formaldehyde and indicates

the necessity of a higher energy of activation to trigger the resin (Figure 2). Such a shift toward higher curing temperatures is not surprising. Indeed, it is consistent with previous studies on lignin-based phenolic resins, where the incorporation of lignin has been shown to cause a shift in the location of the exothermic curing peak due to steric hinderance effects as well as the presence of alternative reaction mechanism with lignin (Ghorbani et al., 2016).

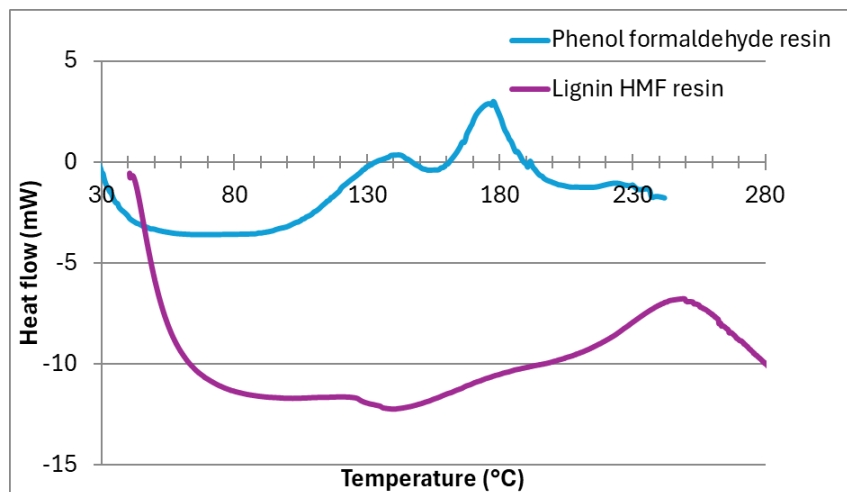


Figure 2: Differential scanning calorimetry results comparing a typical phenol formaldehyde resin with the constructed lignin HMF resin

A proof of concept for the 3D printing of lignin-HMF resin filled with olive pomace powder using liquid deposition modelling was demonstrated by printing two cylindrical structures: one with a single-layer wall and the other with a 2-layer wall structure (Figure 3). 1.5 mm nozzle diameter was chosen to prevent clogging, which systematically occurred when using a 0.5 mm nozzle diameter. A dry matter content of 75 %wt. was tested. Formulations with lower dry matter content were also investigated; however, problems insufficient homogeneity during mixing with the fillers led to some irregularity in extrusion and poor print quality.

Consequently, the optimisation of formulation/processing parameters is still a major challenge for this novel formulation as the printed objects shown display a partial collapse immediately after extrusion. This highlights an insufficient yield stress and structural build-up of the material, which are critical parameters for shape retention in liquid deposition modelling. Such limitation could be resolved by adjusting using filler content, modifying its particle size distribution, or further tailoring the resin formulation to enhance rheological properties such as viscosity and thixotropy. In particular, increasing the solid fraction or promoting faster structuration after deposition will improve dimensional stability. Additionally, process parameters such as extrusion pressure, printing speed, and layer height could be further optimised to refine print fidelity.

Finally, it is worth noting that the inherent black colour of the lignin-based polymers is an important positive factor for applications where aesthetic considerations are important.

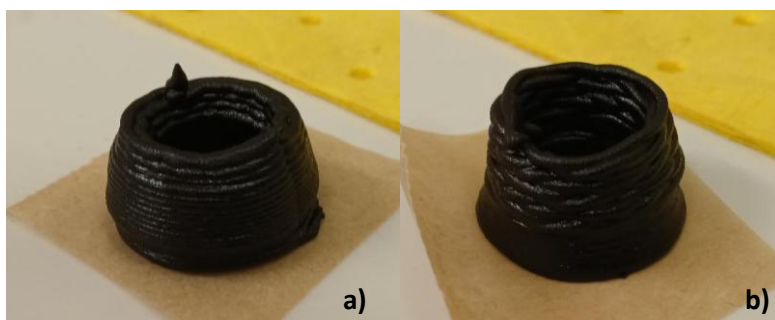


Figure 3: 3D printed cylinder lignin HMF resin and olive pomace powder composite with a) two-layers thick structure b) one-layer thick structure

4. Conclusions

Results demonstrate that the substitution of petroleum-derived phenol and formaldehyde with lignin and HMF constitutes a viable and promising pathway toward the development of sustainable thermosetting resins. Observed differences in chemical structure and curing behaviour indicate that lignin–HMF systems follow a distinct reaction mechanism, resulting in higher curing temperature and altered network architectures. These characteristics support the feasibility of designing fully formaldehyde-free alternatives, as they confirm that effective crosslinking can be achieved without relying on conventional phenol–formaldehyde chemistry.

Furthermore, the successful extrusion and shaping of formulated composites validate their potential for additive manufacturing applications. Despite remaining challenges in terms of printability, dimensional stability, and mechanical performance, the ability to process these materials using liquid deposition modelling, demonstrate that bio-based thermosets can extend beyond conventional uses.

References

- Apel, A., Riehm, T., 1960. LIGNIN-PHENOL-FORMALDEHYDE RESINS, AND METHOD OF PREPARATION.
- Bonnet Martin, E., Denneulin, A., Lecourt, M., Irle, M., Beneventi, D., 2026. The role of bio-based constituents in additive manufacturing with thermosetting polymers and vitrimers: a review. *Mater. Adv.* 7, 1918–1935. <https://doi.org/10.1039/D5MA00585J>
- Eid, N., Ameduri, B., Boutevin, B., 2021. Synthesis and Properties of Furan Derivatives for Epoxy Resins. *ACS Sustainable Chem. Eng.* 9, 8018–8031. <https://doi.org/10.1021/acssuschemeng.0c09313>
- Ghorbani, M., Liebner, F., Van Herwijnen, H.W.G., Pfungen, L., Krahofer, M., Budjav, E., Konnerth, J., 2016. Lignin Phenol Formaldehyde Resoles: The Impact of Lignin Type on Adhesive Properties. *BioResources* 11, 6727–6741. <https://doi.org/10.15376/biores.11.3.6727-6741>
- Pizzi, A. (Ed.), 2003. Handbook of adhesive technology, 2. ed., rev.expanded. ed. Dekker, New York Basel.
- Rosenfeld, C., Konnerth, J., Sailer-Kronlachner, W., Rosenau, T., Potthast, A., Solt, P., Van Herwijnen, H.W.G., 2020. Hydroxymethylfurfural and its Derivatives: Potential Key Reactants in Adhesives. *ChemSusChem* 13, 5408–5422. <https://doi.org/10.1002/cssc.202001539>