3D Printing of Starch, PLA & Lignin

Authors: Shery Rose Quieng, José Bolaños, Gabriel Dauchot, Pedro Antonio Navarro, Sudip Sharma
Supervisors: Dr. Yevgen Karpichev, Dr. Aurore Richel, Quentin De Roover, Eric Haubruge & Sofiene Abdellaoui

Bioceb – European Master in Biological and Chemical Engineering for a Sustainable Bioeconomy

Contact:
srquieng@gmail.com

1 Introduction

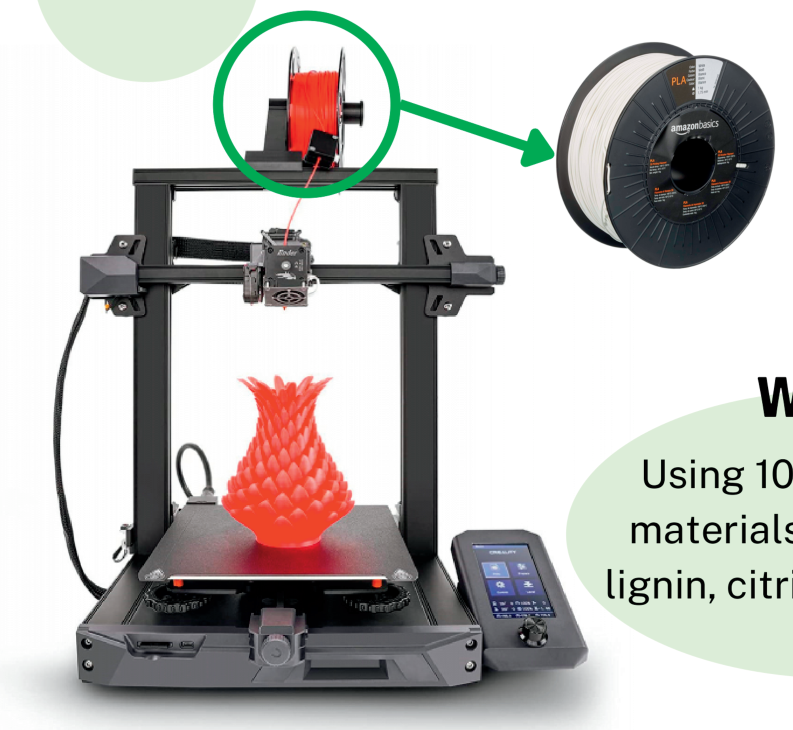

Figure 1. 3D printer with PLA filament

WHY?
Reducing the environmental impacts of 3D printing materials, often fossil-based plastics

WHAT?
Using 100 % biobased materials : starch, PLA, lignin, citric acid, glycerol

HOW?
Formulating optimal filament compositions, assessing their thermo mechanical properties

2 Materials & Methods

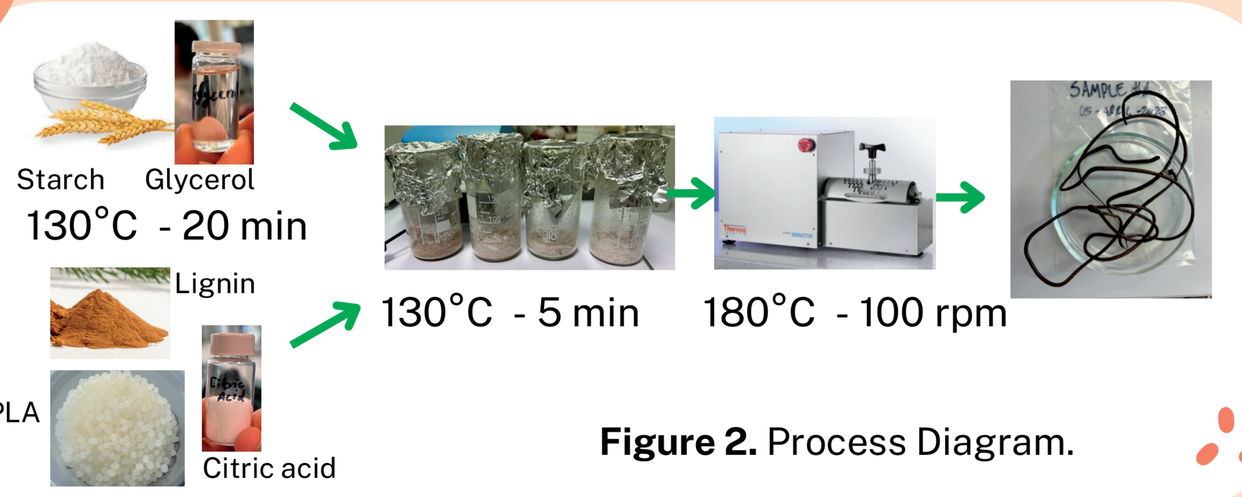

Figure 2. Process Diagram.

Lignin extraction
- *Raw material:* Barley straw (BS)
- *Process:* Ethanol Organosolv

Lignin characterization
- Klason lignin
- Fourier-transform Infrared Spectroscopy (FTIR)
- 2D Heteronuclear Single Quantum Coherence (HSQC)
- Nuclear Magnetic Resonance (NMR)
- Differential Scanning Calorimetry (DSC)

(Jõul et al., 2022)

Biocomposite formulation
- Modified starch (35.6% - 55.7%)
- PLA (44% - 0%)
- lignin (4%)
- citric acid (16.4%)

Biocomposite Characterization
- Scanning Electron Microscopy (SEM)
- Polarized optical microscopy (POM)
- Tensile properties
- DSC

(Ju et al.,2022; Zhang et al., 2020)

3.1 Results & Discussion

A. LIGNIN EXTRACTION & CHARACTERIZATION

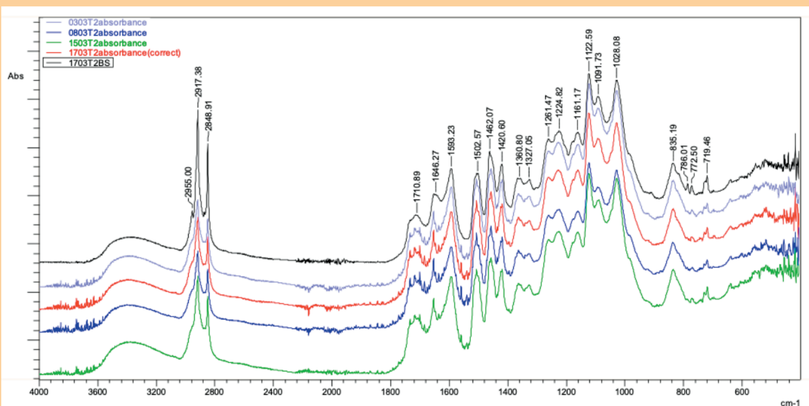

Figure 3. FTIR spectra of ethanol-extracted lignin samples from various batches of BS.

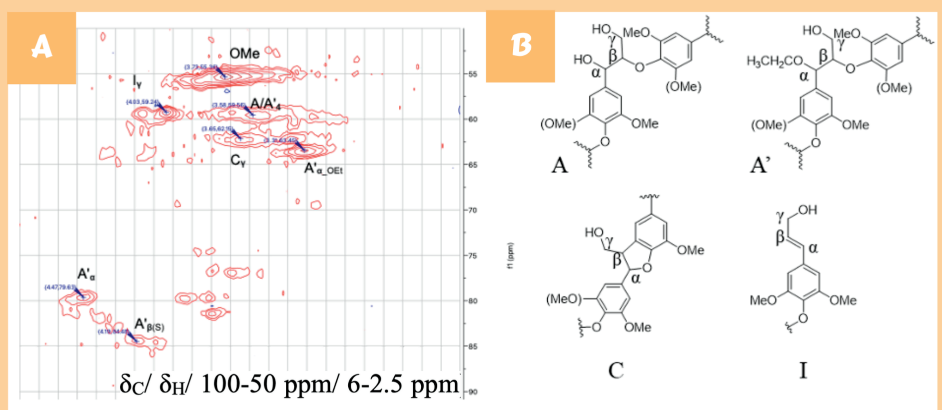

Figure 4. (a) 2D HSQC for aliphatic region of extracted lignin from BS; (b) structures of the monolignols

Method	Results & Discussion	Reference
Klason Lignin	86.3% purity of sample; 3.7% impurities	(Jõul et al., 2022)
FTIR	Same lignin core structure → Homogeneous lignin	(Jõul et al., 2022)
2D HSQC NMR	Linkages between monolignols (H, G, S, PCA, Fer, T): β-O-4 & β-α-O linkages, cinnamyl alcohol ending groups	(Wen et al., 2013) (Jõul et al., 2022)

Specific lignin composition → implications for its properties & potential applications
Hence, this knowledge can help find suitable applications for the bio-composite.

B. BIO-COMPOSITE FILAMENT CHARACTERIZATION

i. Differential Scanning Calorimetry (DSC)

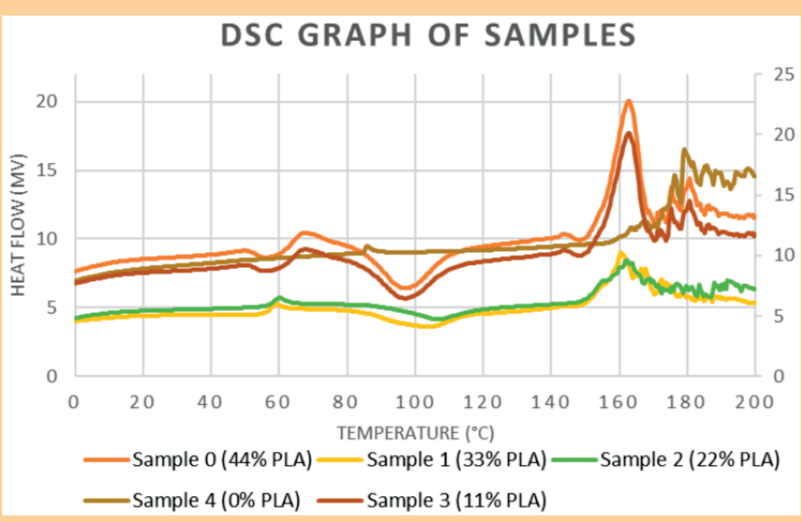

Figure 5. DSC graphs of each samples merged together

- All samples show glass transition around 55°C to 60°C, except Sample 4 (0% PLA).
- Higher peaks observed around 160°C to 170°C (melting point of PLA).
- Smaller peaks beyond the main peak indicate the disintegration or melting of other components (starch, lignin, etc.) (Cuiffo et al., 2017).

3.2 Results & Discussion

ii. Polarized Optical Microscopy and Scanning Electron Microscopy (SEM)

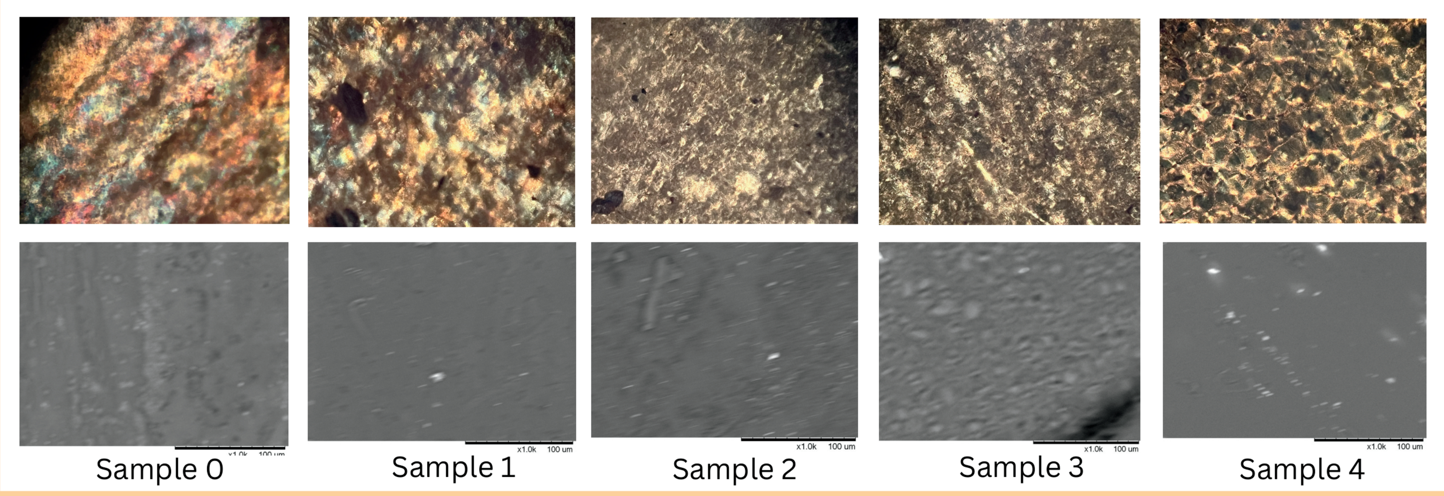

Figure 6. Optical miscroscopy (top) & SEM of each sample (bottom)

- Bright spots, dark spots, and colorful spots observed.
- Darker areas → Amorphous structures
- Colorful areas → Crystalline structures
- Agglomerates formed due to non-uniform ingredient distribution (PLA and MS) → suggests plasticization of starch.
- Native starch forms granular structures.
- Mixing native starch with hydrophilic glycerol at higher T → resulted into microcrystals spreading & separation.

iii. Tensile Strength

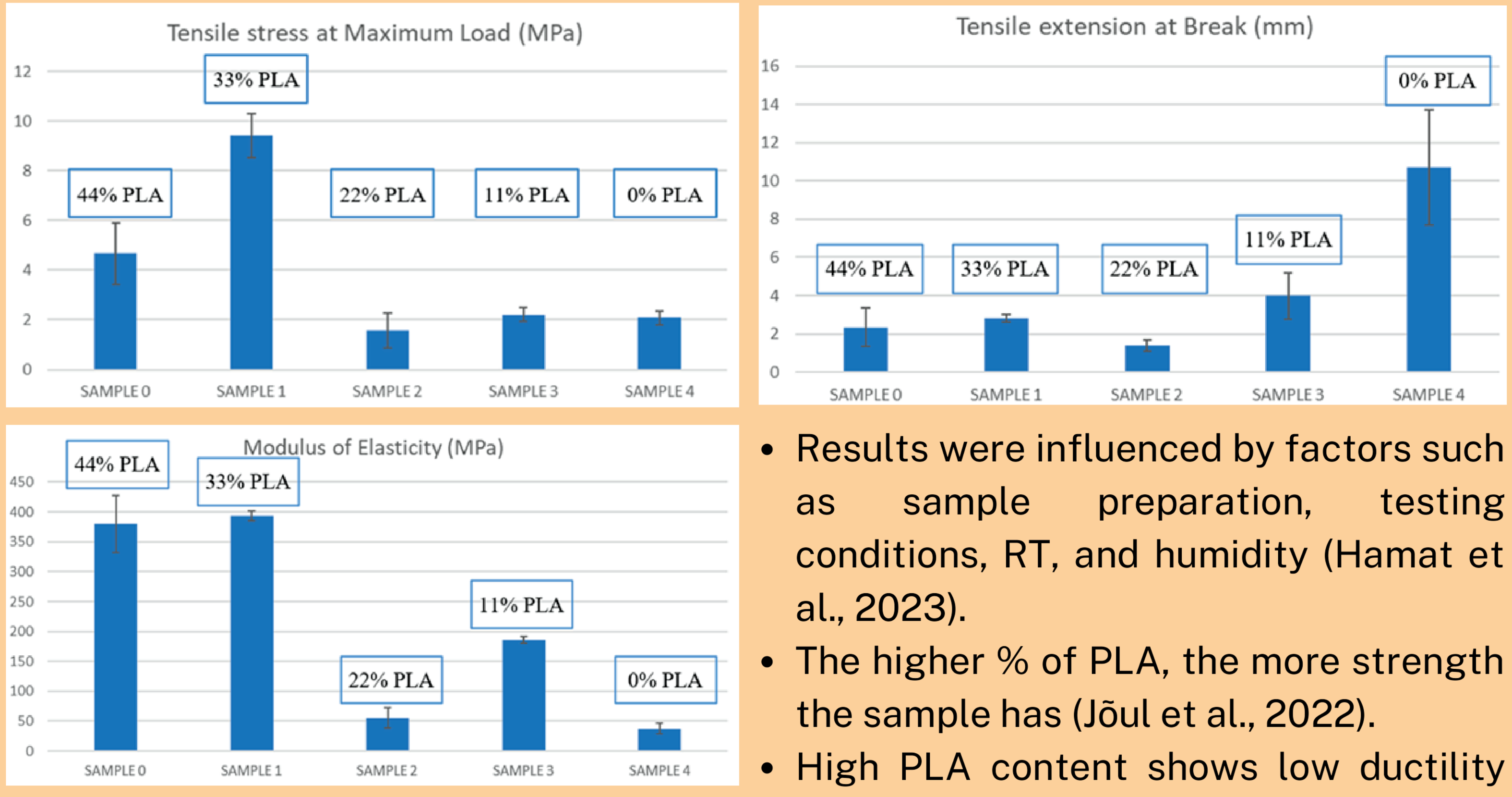

Figure 7. Different tensile properties and measurements.

- Results were influenced by factors such as sample preparation, testing conditions, RT, and humidity (Hamat et al., 2023).
- The higher % of PLA, the more strength the sample has (Jõul et al., 2022).
- High PLA content shows low ductility and high elasticity (Goh et al., 2020).
- Depending on the final product, desired tensile properties will vary accordingly.

4 Life Cycle Assessment

Open LCA 2023, Agribalyse 2022, ReCiPe Mindpoint H (2016)

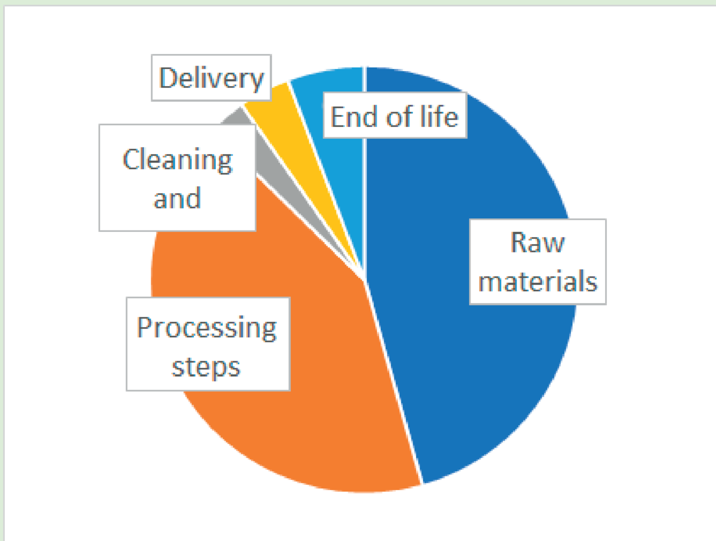

Figure 8. Carbon footprint contribution

Table 1. Environmental impacts

	S.n°3	BBP	PBP	Unit
Carbon footprint	**2,4**	2	2-3	kg.CO2. eq /kg
Water footprint	**54**	1000	0	L/kg
Land use	**1,9**	5	0	m2.crop. eq /kg

Towards sustainable design (by turning electricity greener, scaling up, and using byproducts)

Sample n°3, BioBased Plastics (BBP), PetroBased Plastics (PBP)

(Brizga et al., 2020)

5 Conclusion

- Successful lignin extraction
- Filament extrusion and characterization
- Sustainable design plan

TO DO
- Working on the 3D printability
- Increasing lignin %
- Testing biodegradability

References

Brizga, J., Hubacek, K., & Feng, K. (2020). The Unintended Side Effects of Bioplastics : Carbon, Land, and Water Footprints. One Earth, 3(1), 45-53. / Cuiffo, M., Snyder, J., Elliott, A., Romero, N., Kannan, S., & Halada, G. (2017). Impact of the Fused Deposition (FDM) Printing Process on Polylactic Acid (PLA) Chemistry and Structure. Applied Sciences, 7, 579./ Goh, G. D., Yap, Y. L., Tan, H. K. J., Sing, S. L., Goh, G. L., & Yeong, W. Y. (2020). Process–Structure–Properties in Polymer Additive Manufacturing via Material Extrusion: A Review./ Hamat, S., Ishak, M. R., Sapuan, S. M., Yidris, N., Hussin, M. S., & Abd Manan, M. S. (2023). Influence of filament fabrication parameter on tensile strength and filament size of 3D printing./ Jõul, P., Ho, T. T., Kallavus, U., Konist, A., Leiman, K., Salm, O.-S., Kulp, M., Koel, M.,& Lukk, T. (2022). Characterization of Organosolv Lignins and Their Application in the Preparation of Aerogels. Materials, 15(8), 2861. / Ju, Q., Tang, Z., Shi, H., Zhu, Y., Shen, Y., & Wang, T. (2022). Thermoplastic starch based blends as a highly renewable filament for fused deposition modeling 3D printing. International Journal of Biological Macromolecules, 219, 175–184. / Mirón, V., Ferrándiz, S., Juárez, D., & Mengual, A. (2017). Manufacturing and characterization of 3D printer filament using tailoring materials. Procedia Manufacturing, 13, 888–894. / Wen, J. L., Sun, S. L., Xue, B. L., & Sun, R. C. (2013). Recent advances in characterization of lignin polymer by solution-state nuclear magnetic resonance (NMR) methodology. Materials, 6(1), 359-391./ Zhang, X., Fevre, M., Jones, G. O., & Waymouth, R. M. (2018). Catalysis as an enabling science for sustainable polymers. Chemical reviews, 118(2), 839-885. Zhang, C., Nair, S. S., Chen, H., Yan, N., Farnood, R., & Li, F. (2020). Thermally stable, enhanced water barrier, high strength starch biocomposite reinforced with lignin containing cellulose nanofibrils. Carbohydrate Polymers, 230, 115626.

Université de Reims Champagne-Ardenne · TalTech · AgroParisTech · Aalto University · Liège université

With the support of the Erasmus+ Programme of the European Union