3D Printing of Starch, PLA & Lignin

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

1 Introduction

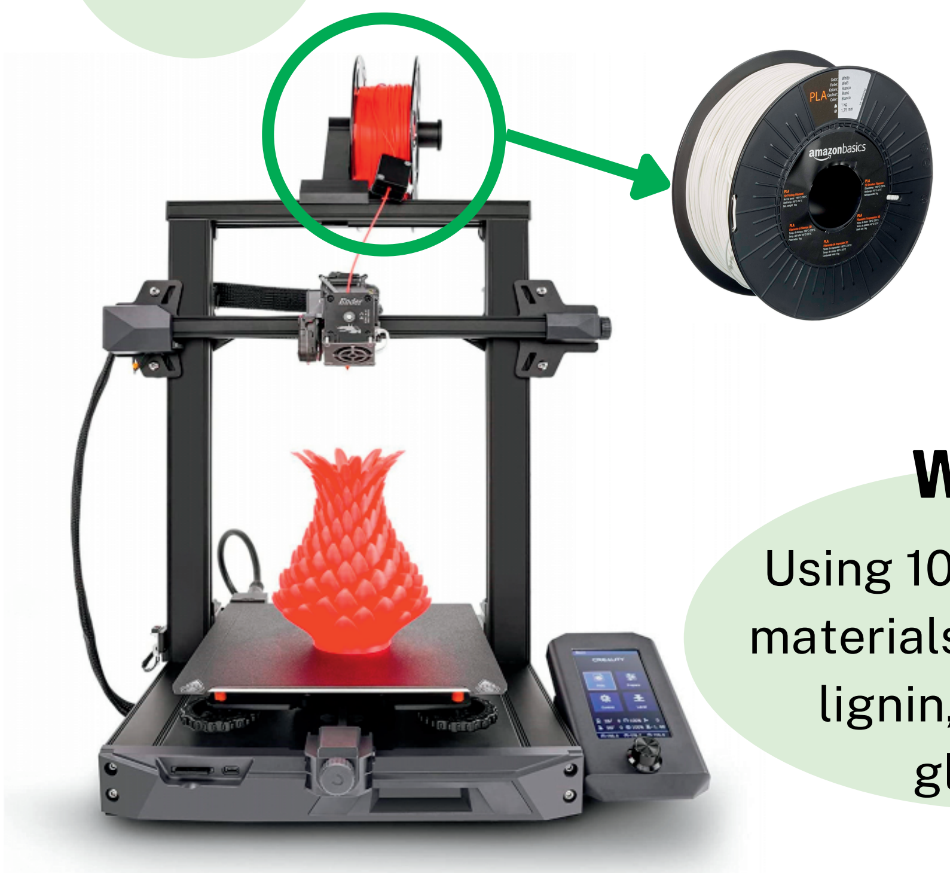


Figure 1. 3D printer with PLA filament

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

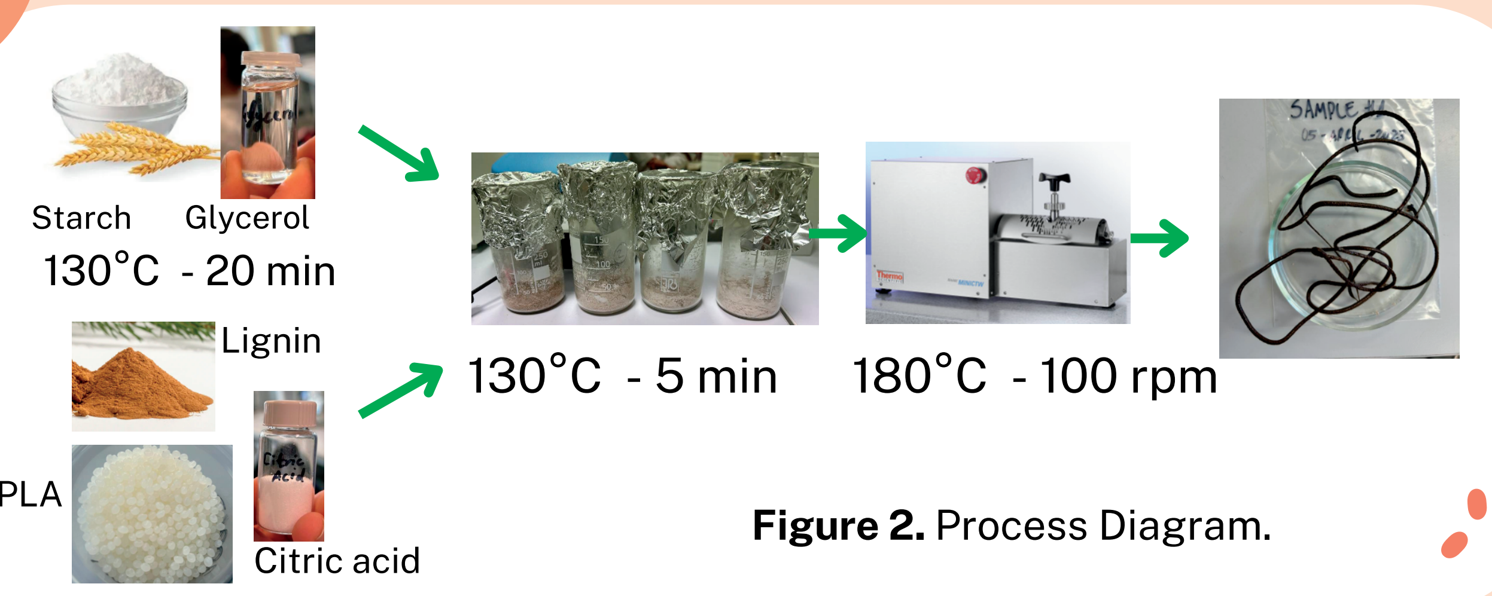


Figure 2. Process Diagram.

Lignin extraction and characterization

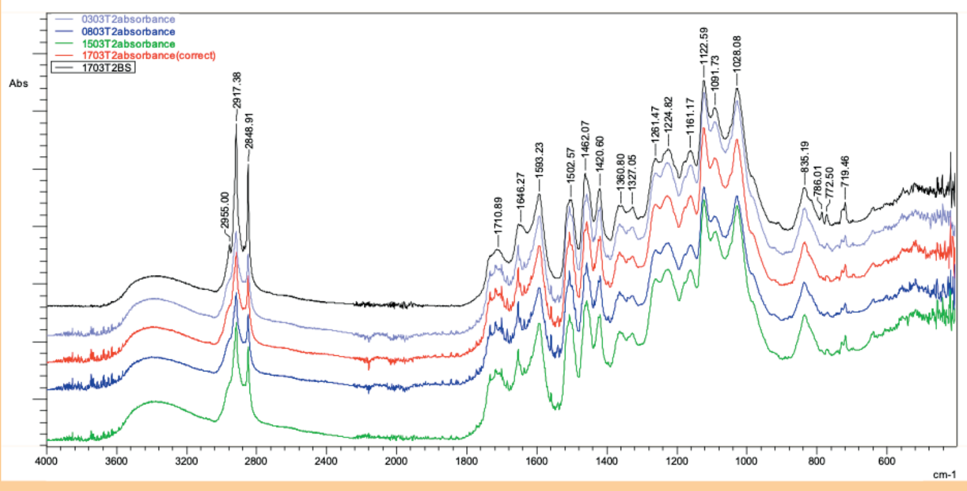
- Lignin was extracted from Barley straw (BS) using organosolv process. Lignin was characterized by Klason lignin, Fourier-transform infrared spectroscopy (FTIR), Heteronuclear Single Quantum Coherence (HSQC) Nuclear Magnetic Resonance (NMR), and differential scanning calorimetry (DSC) (Jõul et al., 2022).

Formulation of composites and characterization.

- The composite was produced following the process in Figure 2, using Modified starch (35.6% - 55.7%), PLA (44% - 0%), lignin (4%), and citric acid (16.4%) (Ju et al.,2022; Zhang et al., 2020).
- The composite/ filament was characterized by Scanning Electron Microscopy (SEM), Polarized optical microscopy (POM), DSC, and tensile properties.

3.1 Results & Discussion

A. LIGNIN EXTRACTION & CHARACTERIZATION



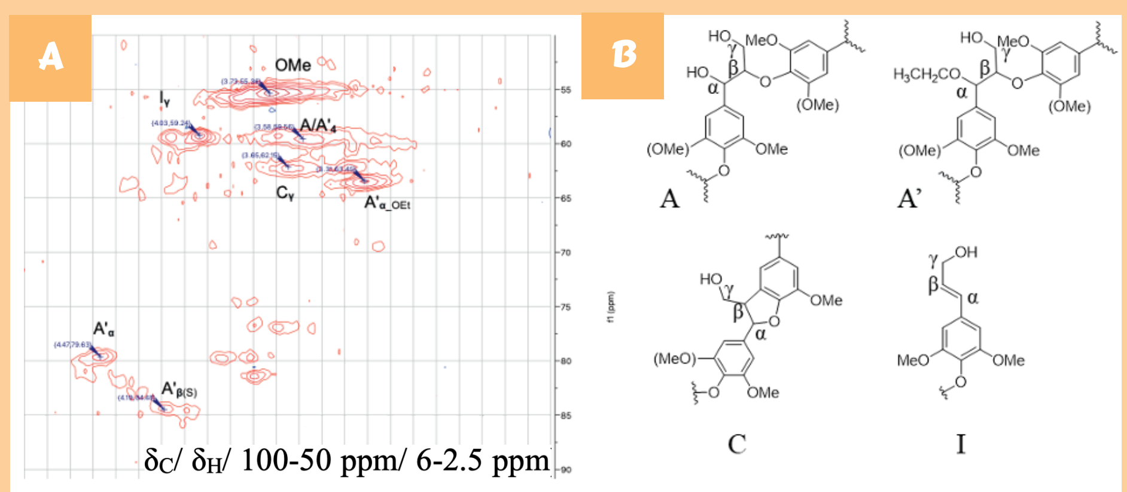


Figure 3. FTIR spectra of ethanol-extracted lignin samples from various batches of BS.

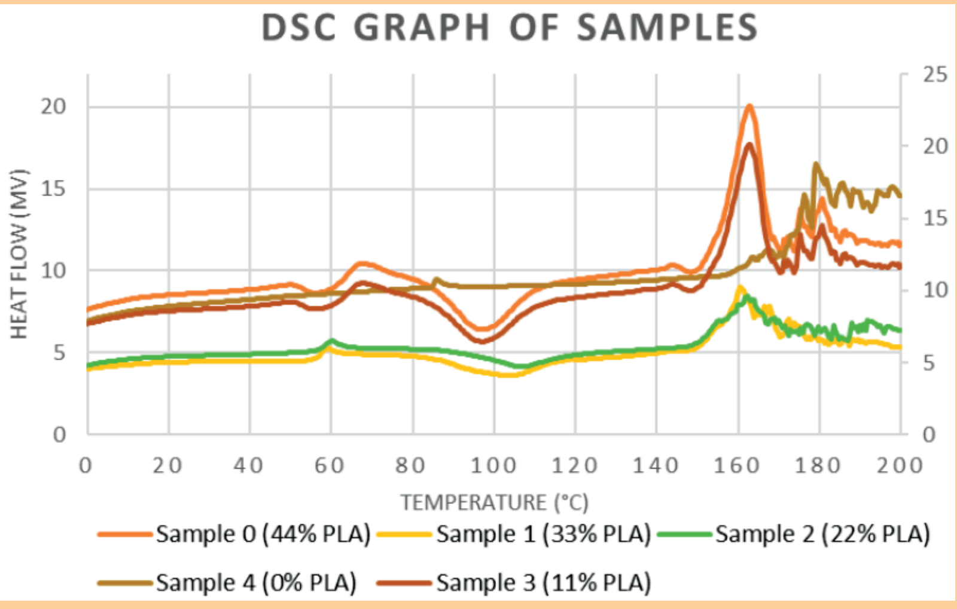
Figure 4. (a) 2D HSQC for aliphatic region of extracted lignin from BS; (b) structures of the monolignols

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)



- 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).

Figure 5. DSC graphs of each samples merged together

3.2 Results & Discussion

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

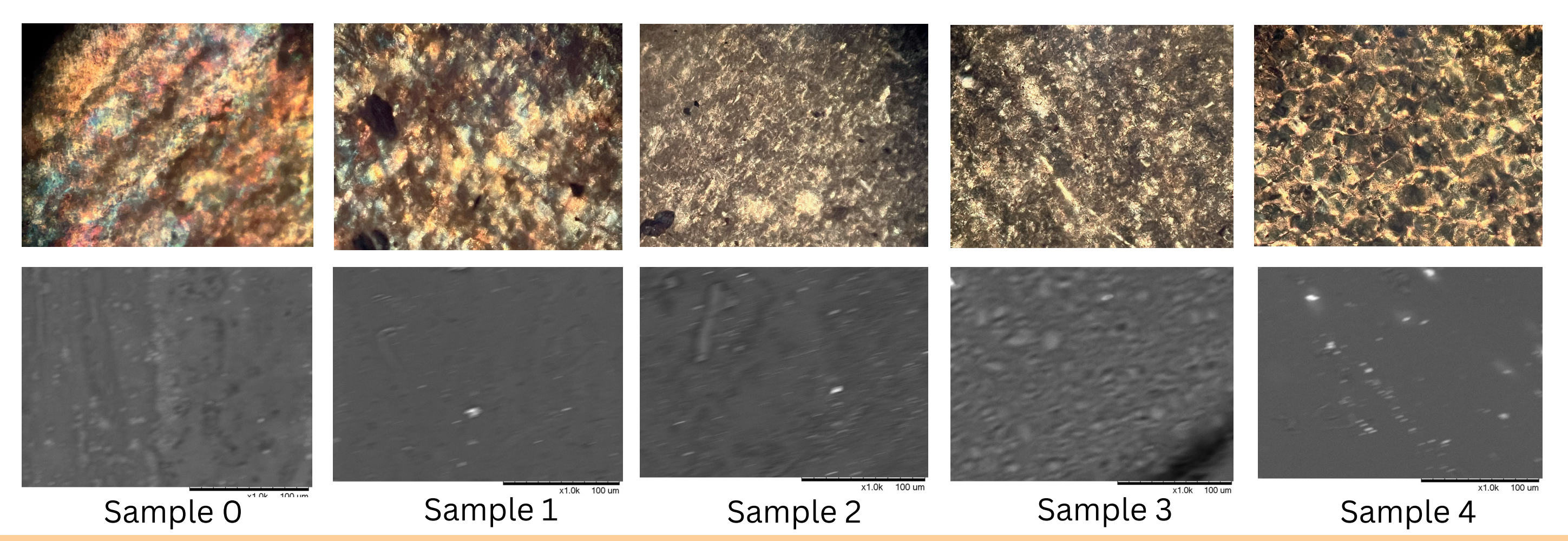


Figure 6. Optical miscroscopy (top) & SEM of each sample (bottom)

- 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

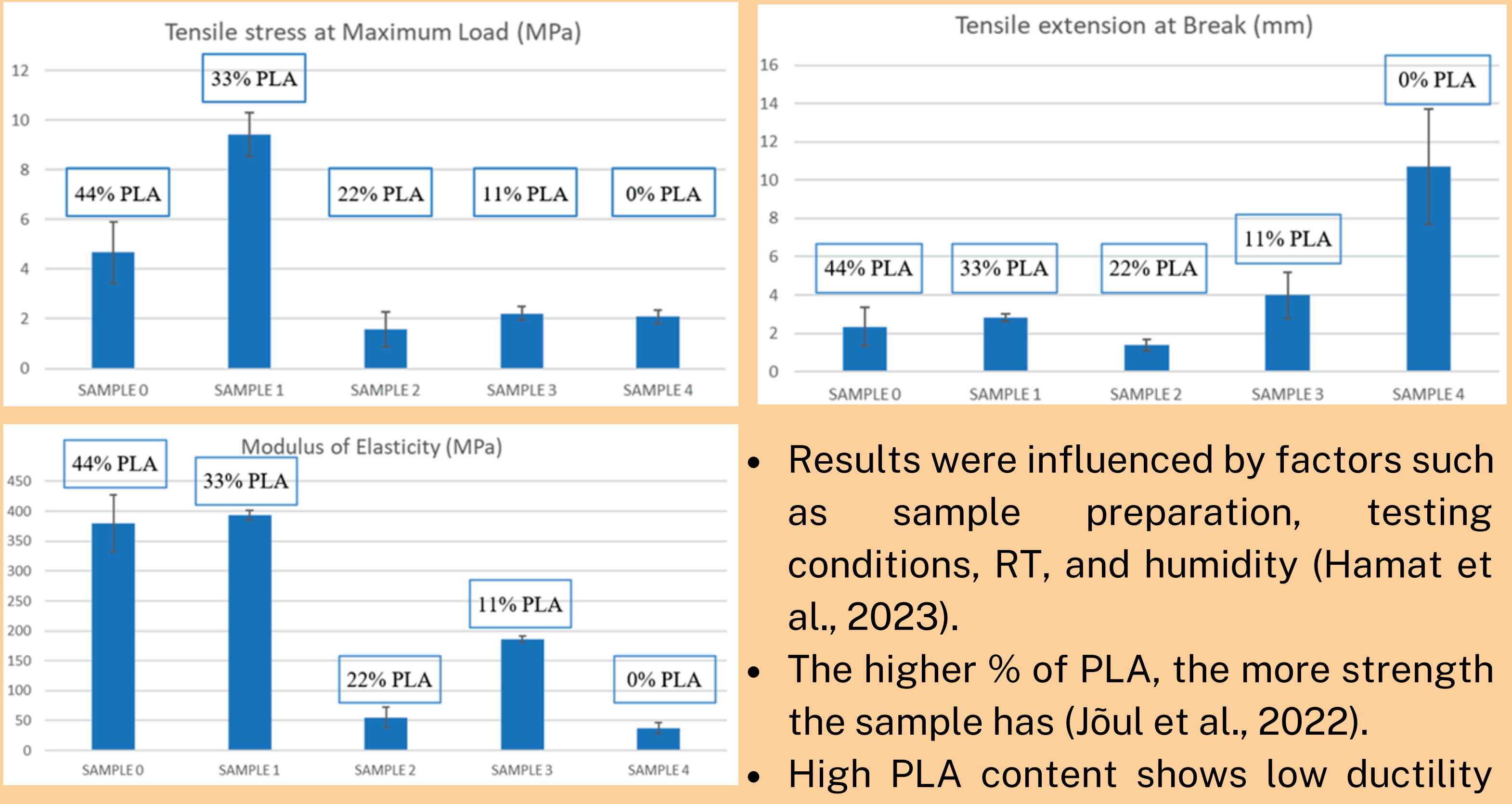


Figure 7. Different tensile properties and measurements.

- 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)

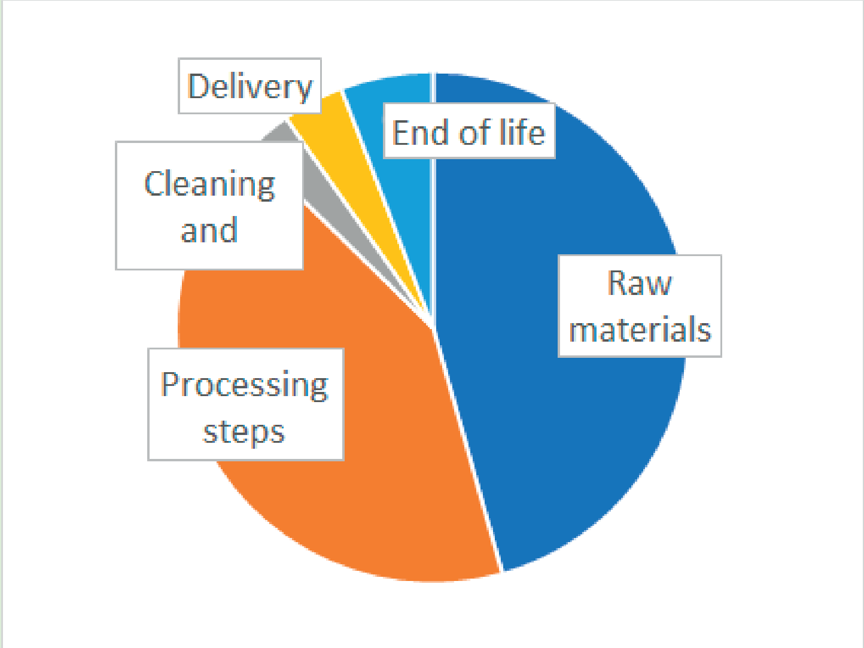


Figure 8. Carbon footprint contribution

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

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