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Compatibilization of lignin/PLA composites for 3D printing

Ellen Sundström & Oskar Backman
Laboratory of Natural Materials Technology
Åbo Akademi University

Content

- Background/Introduction
- Esterification of lignin
- Preparation of lignin/PLA composites
- Quantifying compatibility of lignin with PLA
- 3D-printing of lignin/PLA composites

Compatibilization of lignin/PLA composites

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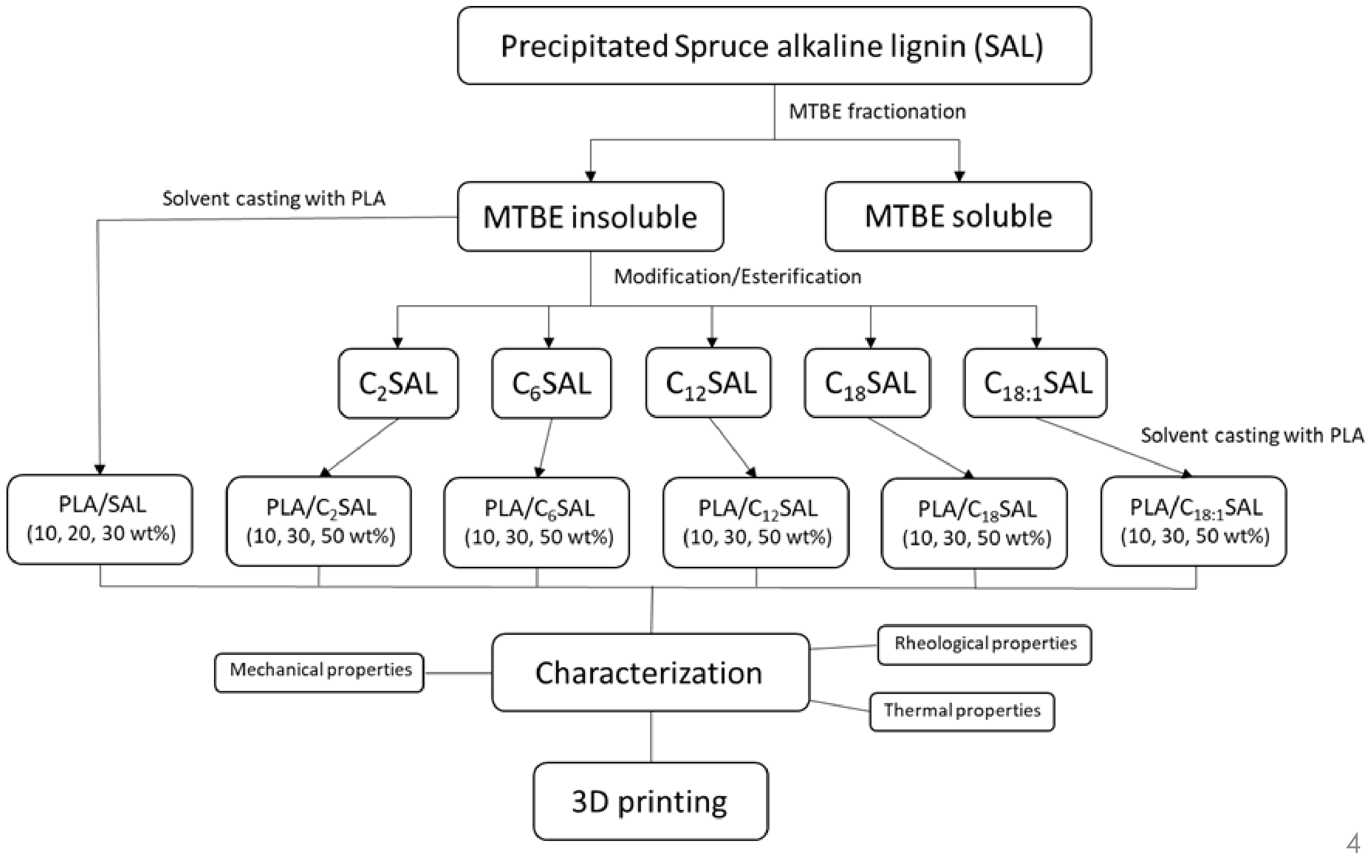
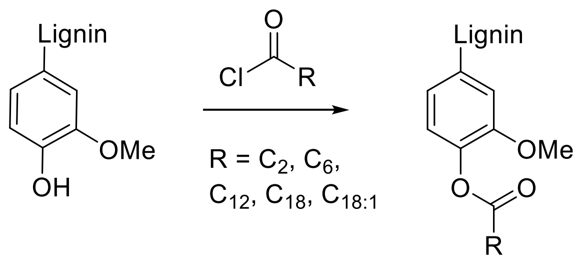
- Esterification of lignin to improve properties and compatibility with PLA
- Blending with PLA
- 3D printing



Acyl chloride esterification of spruce alkaline lignin (SAL)

- Five different acyl chlorides were used C2, C6, C12, C18, C18:1
- Characterized by NMR analysis



SAL　C_2SAL　C_6SAL

C_{12}SAL　C_{18}SAL　$C_{18:1}$SAL

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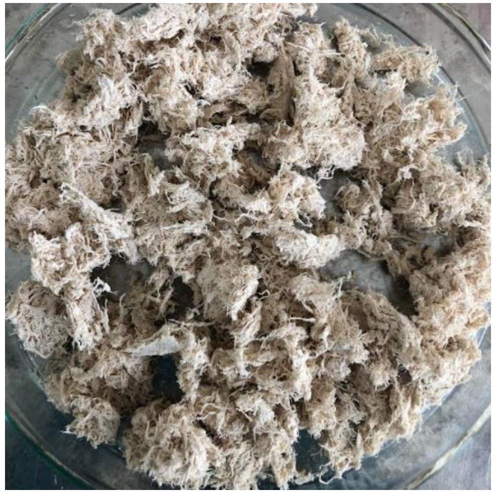
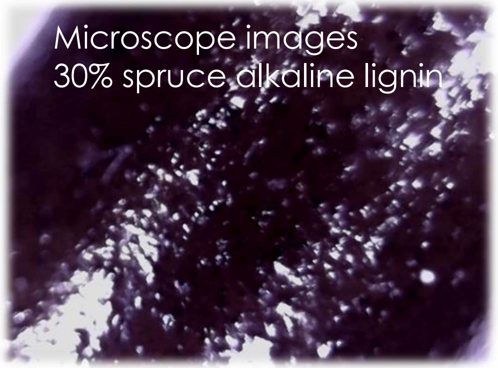
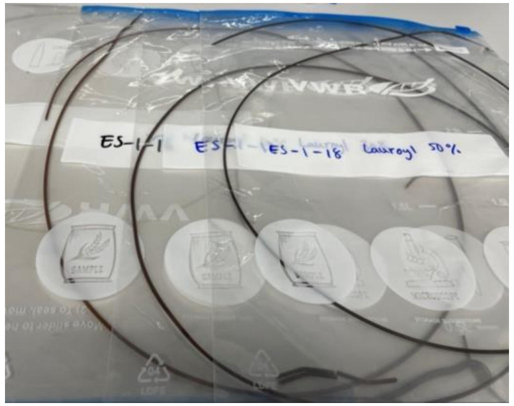
Preparation of lignin/PLA blends by solvent casting

Lignin/PLA in THF

Ethanol







Solvent casting
- Lignin/PLA precipitation in ethanol

Lignin/PLA blends
- 30% spruce alkaline lignin

Compounding
- 180 °C

Protocol to assess the compatibility of lignin with PLA through microscope imaging

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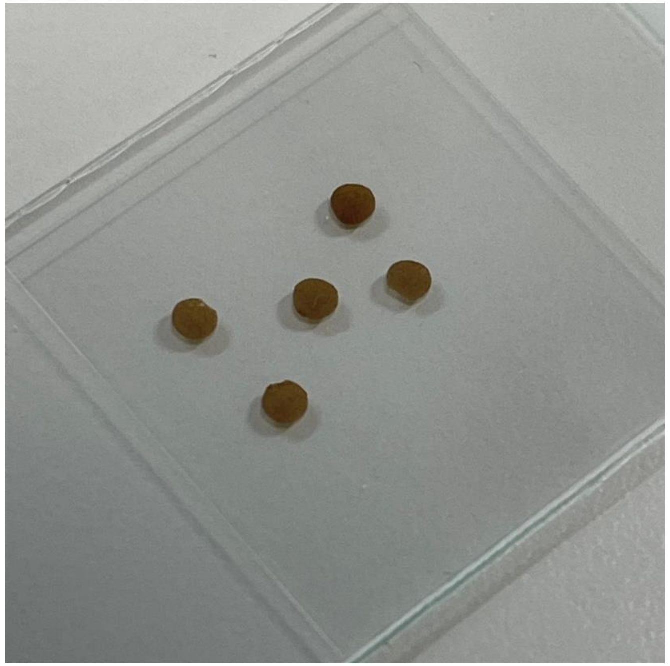
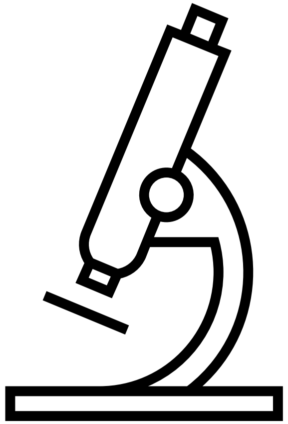
3D printed microtome device



Slice thickness of 0.06-0.09 mm



Microscope imaging

Compatibility of technical lignin (20%) with PLA

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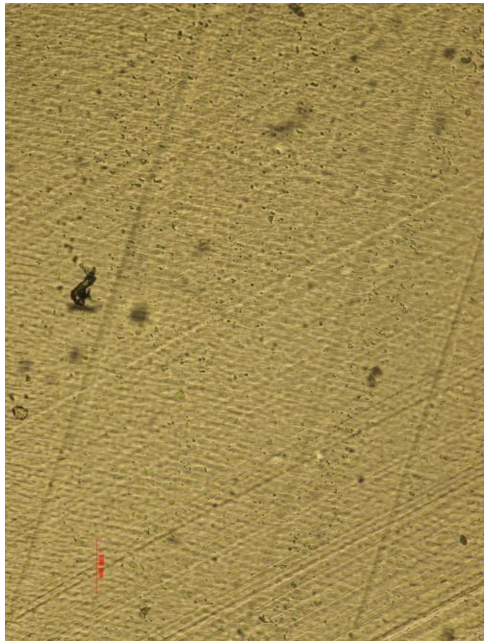
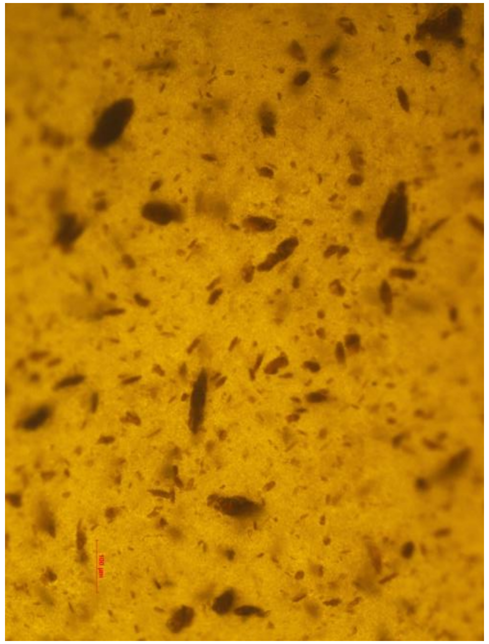
- Kraft lignin (softwood) and enzymatic hydrolysis lignin (softwood) have poor compatibility with PLA

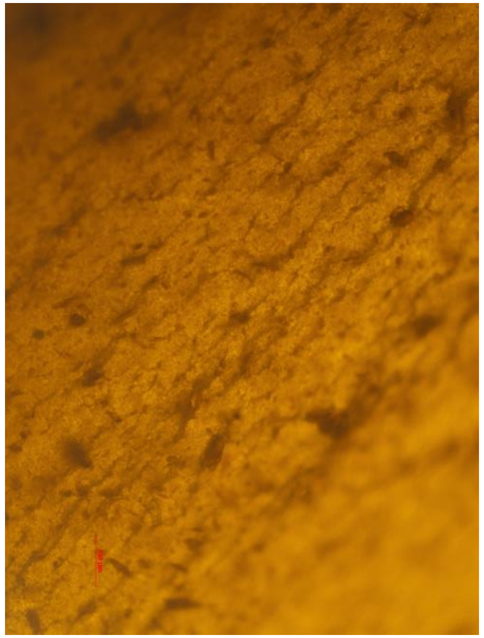
PLA



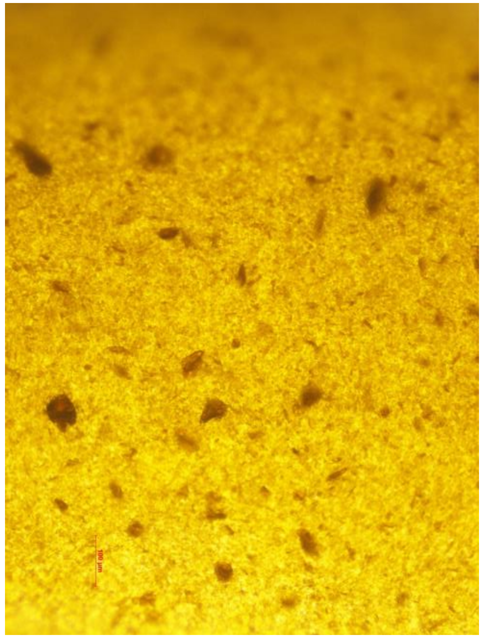
Kraft lignin 1



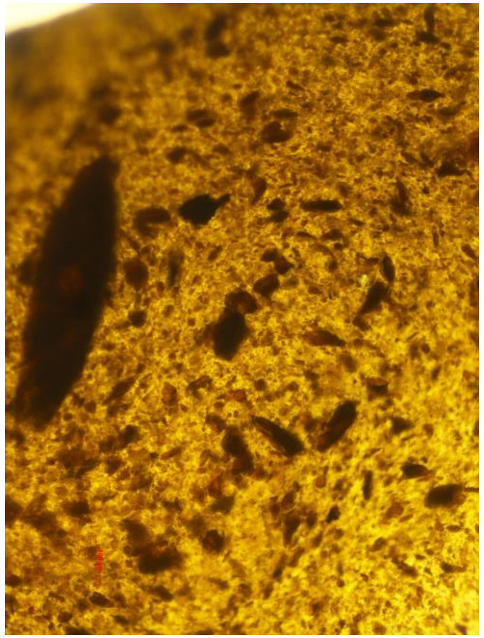
Kraft lignin 2



Enzyme treated KL



Enzymatic hydrolysis lignin



Compatibility of technical lignin (20%) with PLA

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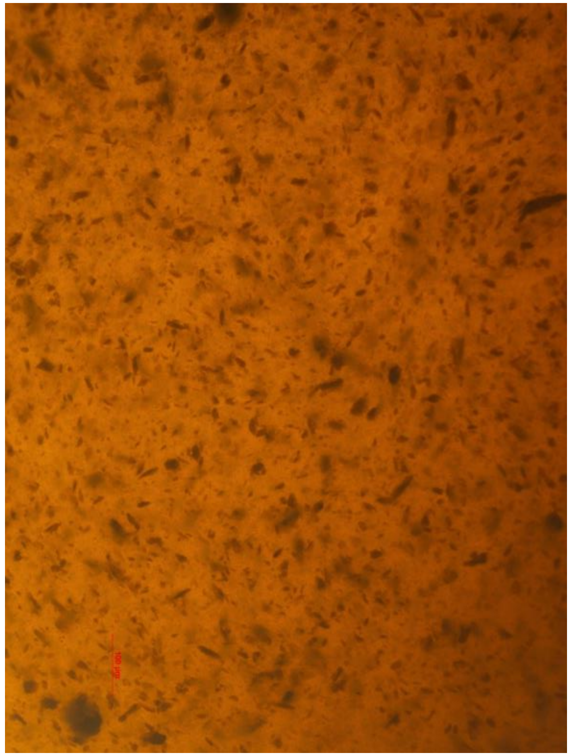
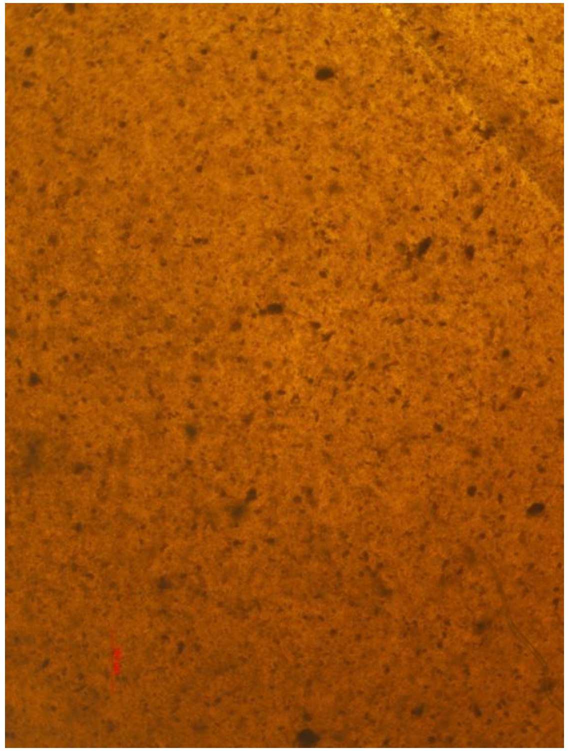
- Unmodified birch alkaline lignin exhibited the best compatibility with PLA than others

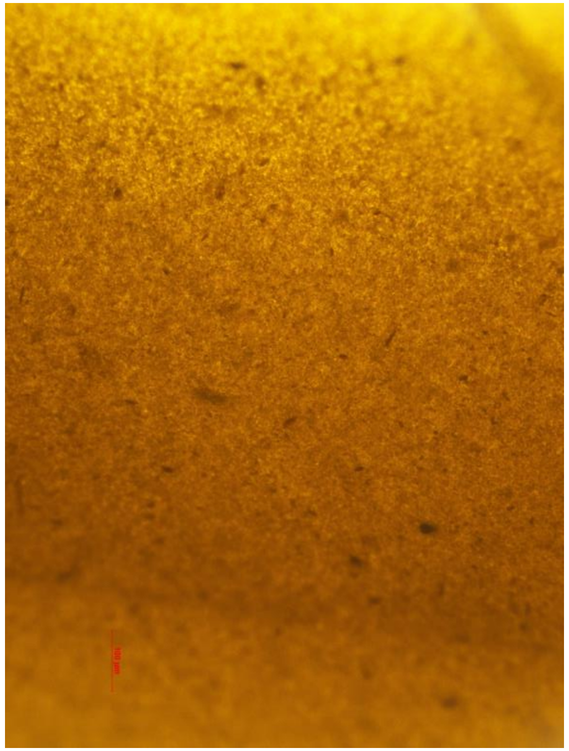
Spruce alkaline lignin



Wheat straw alkaline lignin



Birch alkaline lignin



Improving the compatibility of spruce alkaline lignin (30%) with PLA through esterification

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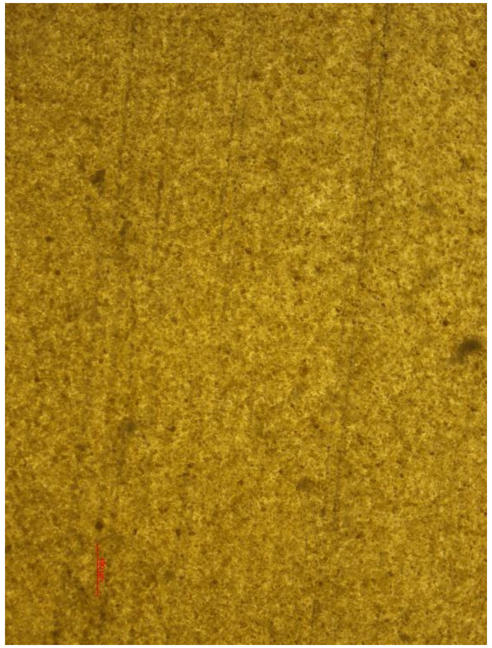
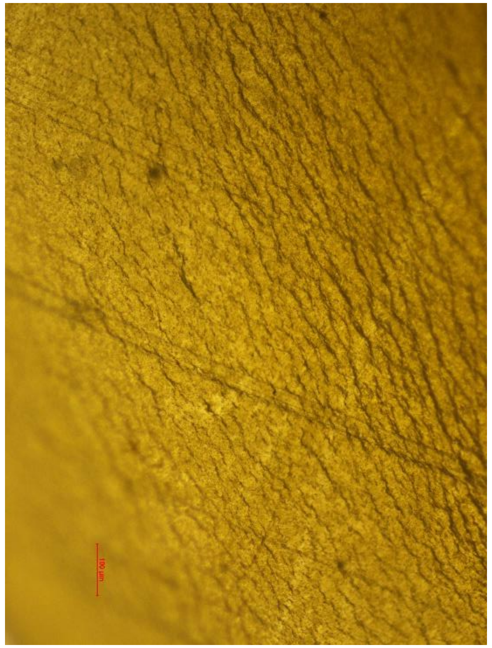
- The compatibility of lignin with PLA was improved by **lignin esterification** with a carbon chain length longer than C2, except for C18 stearoyl chloride

C2 Acetyl

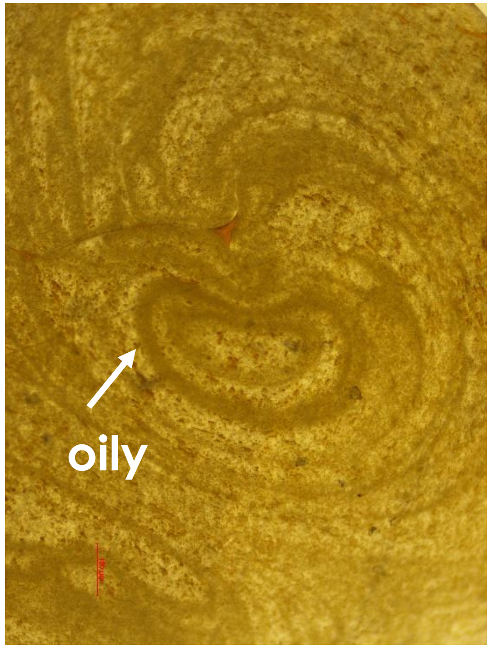
C6 Hexanoyl



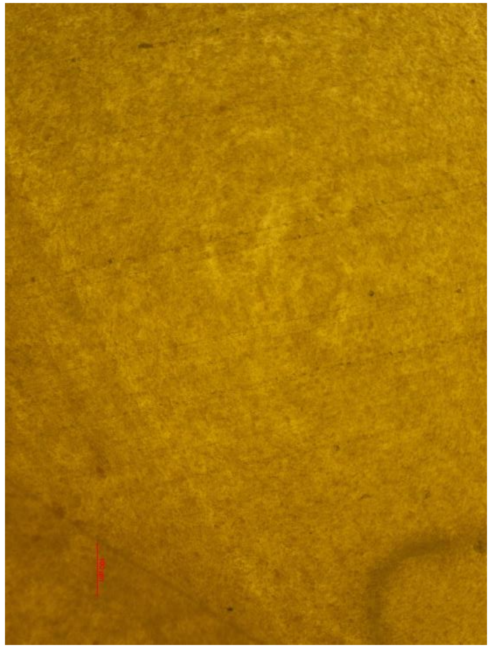
C12 Lauroyl



C18 Stearoyl



C18:1 Oleoyl



Quantifying compatibility using Image J - Microscopy image analysis

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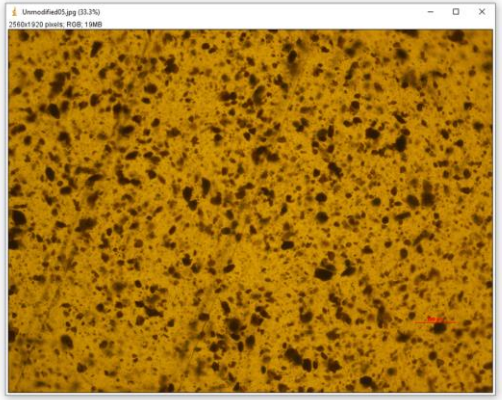
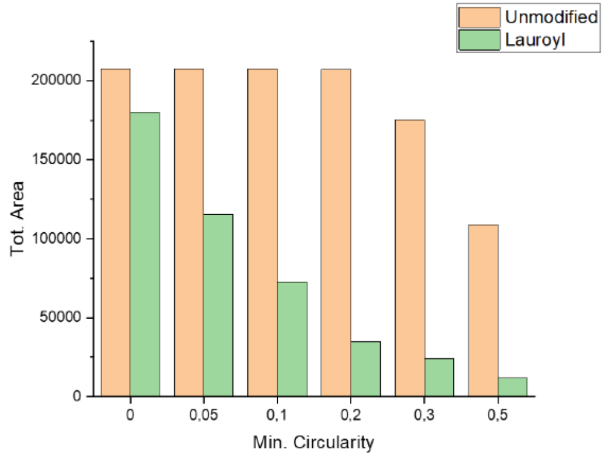
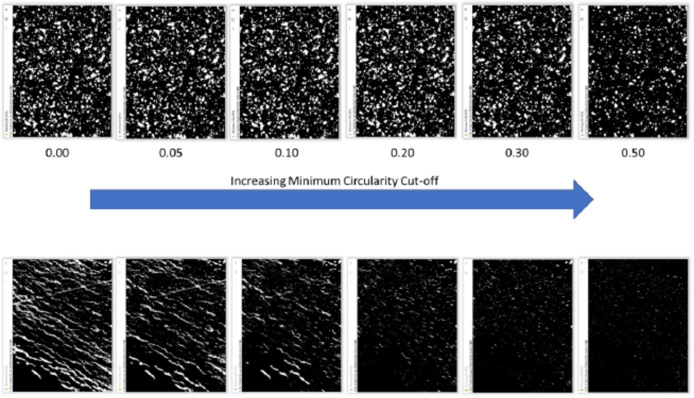
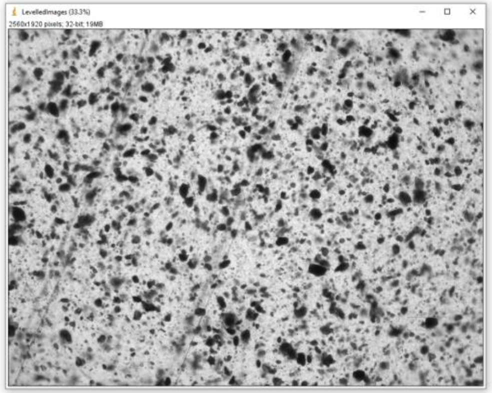
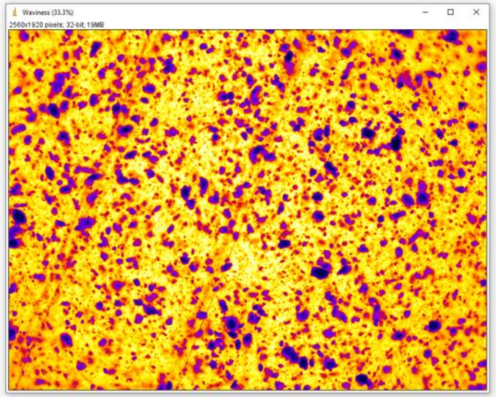


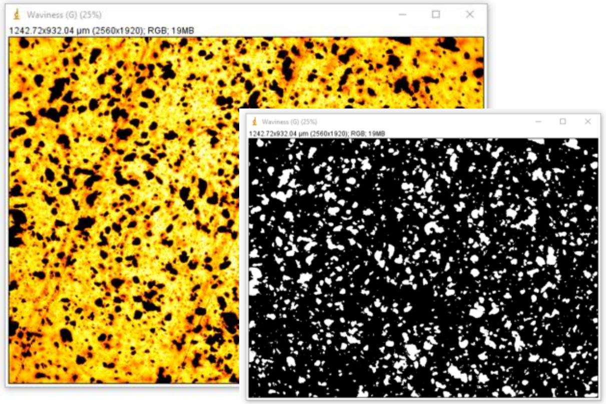
Image Processing





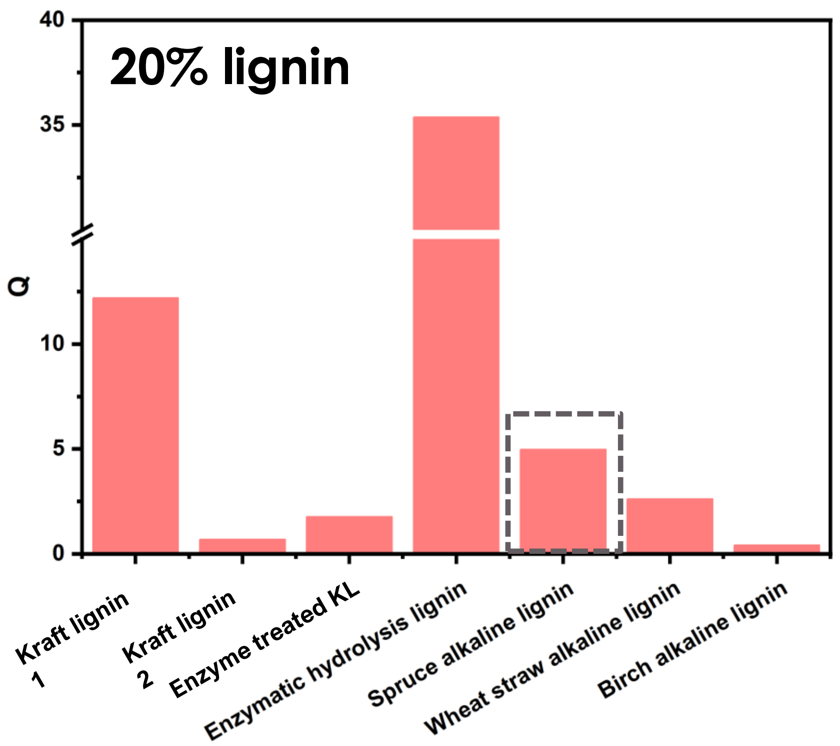


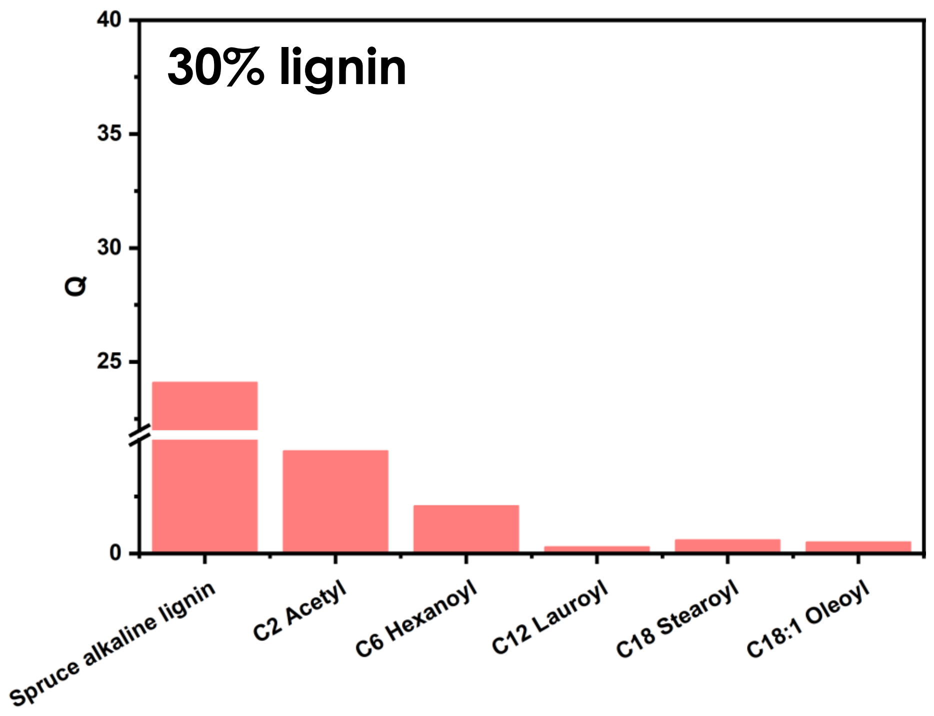




Quantifying compatibility using Image J
- Microscopy image analysis

- Q was used to indicate compatibility, $Q = 10^{-6} * TotArea * AveSize$
- Quantitative results align well with microscope images → Reliable protocol





Mechanical properties of lignin (30%)/PLA filament - 3-point bending test

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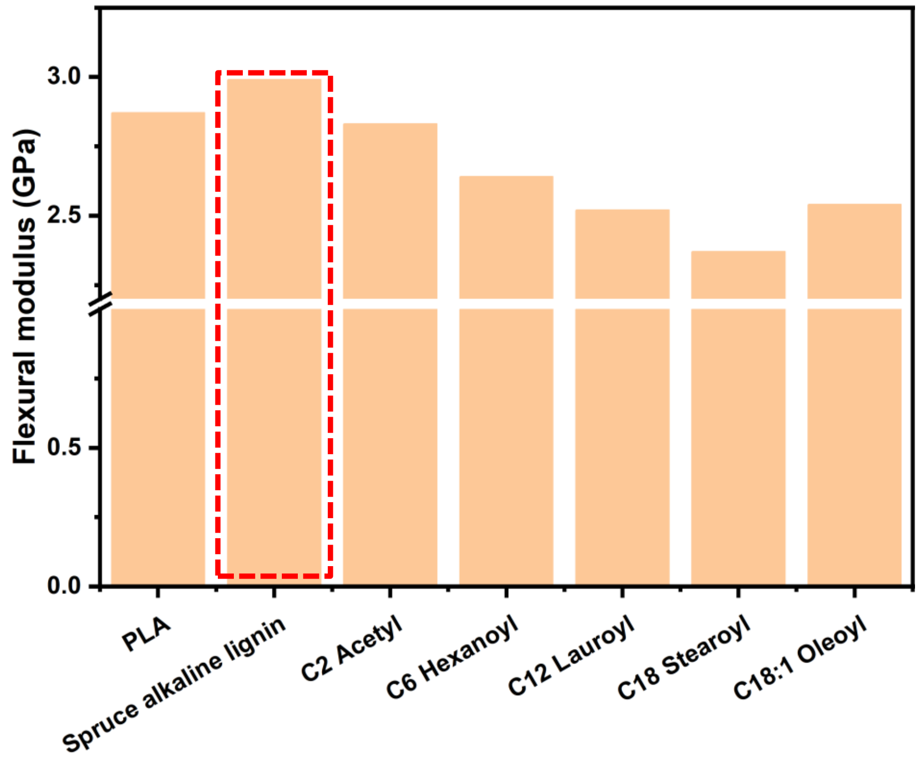
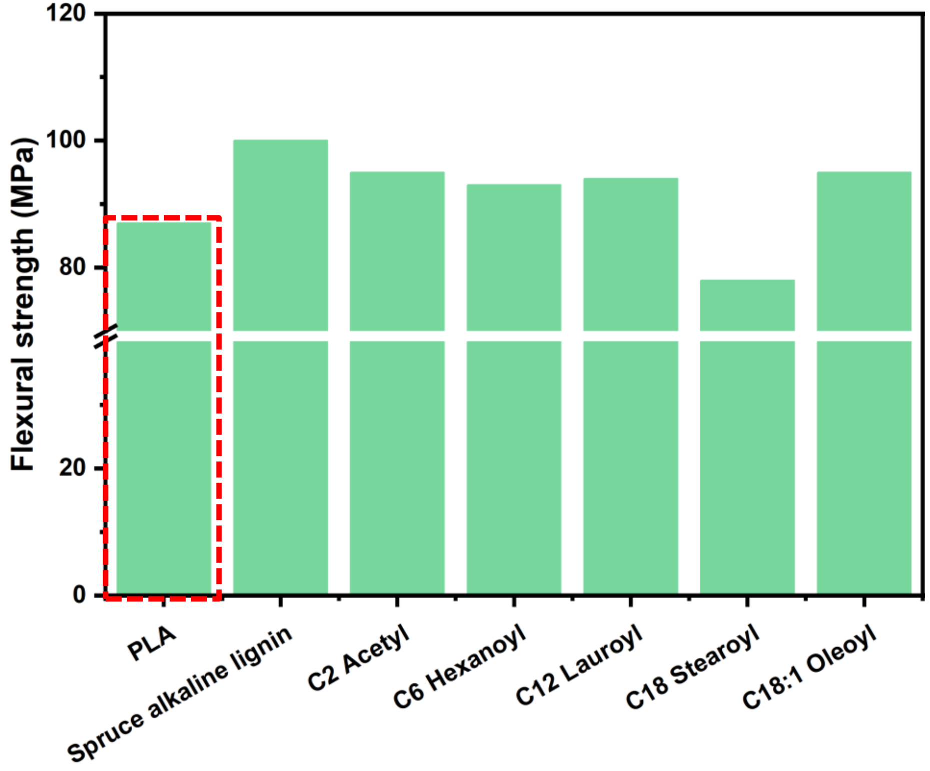
- Flexural modulus: Lignin esterification increased the flexibility of lignin/PLA blends compared to unmodified lignin
- Flexural strength: Unmodified lignin and esterified lignin increased the impacting forces that PLA can withstand, except for C18 stearoyl chloride





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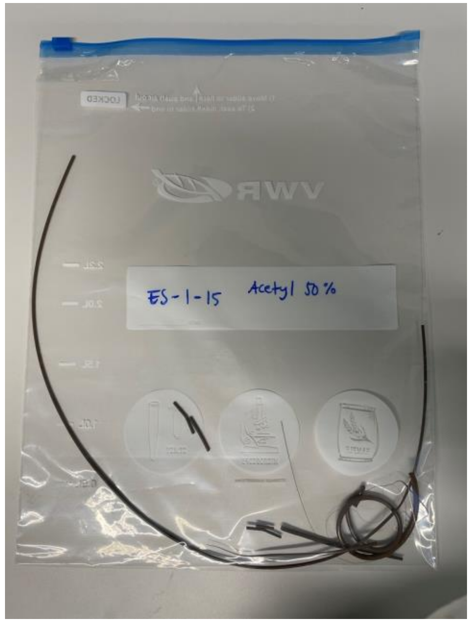
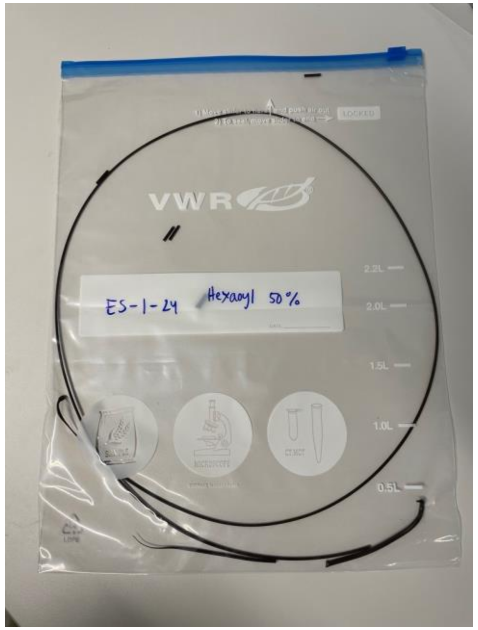
Preparation of PLA filaments containing 50% esterified spruce alkaline lignin

C2 Acetyl (50%)



C6 Hexanoyl (50%)

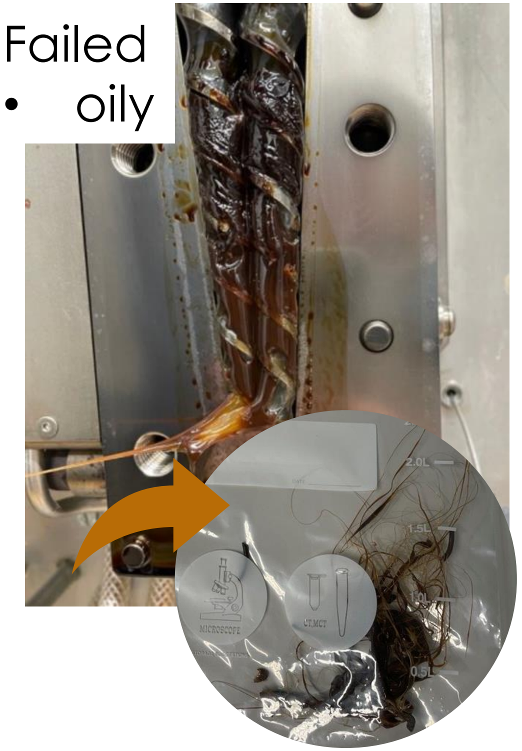


C12 Lauroyl (50%)

C18 Stearoyl (50%)

Failed

- oily



C18:1 Oleoyl (50%)

FDM 3D printing of esterified spruce alkaline lignin (50%)/PLA blends

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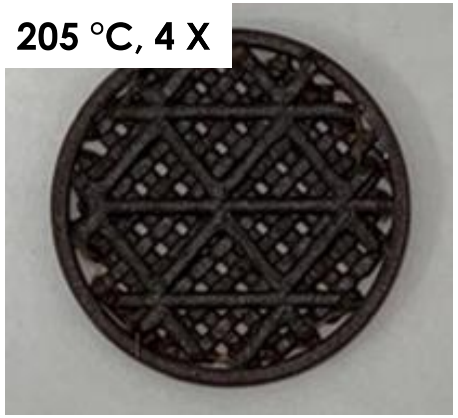
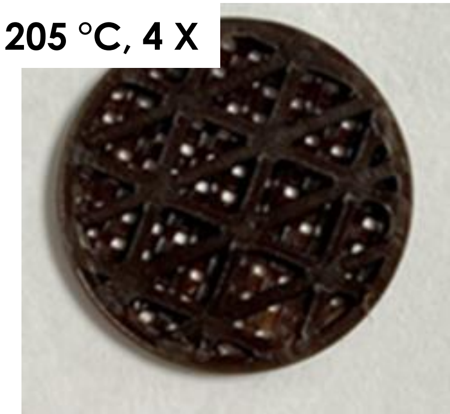
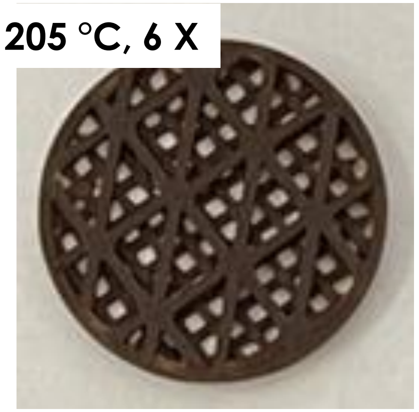
Brinter 3D printer

spruce alkaline lignin (30%)	C6 Hexanoyl (50%)	C12 Lauroyl (50%)	C18:1 Oleoyl (50%)







FDM printing esterified spruce alkaline lignin/PLA - Problematic cases

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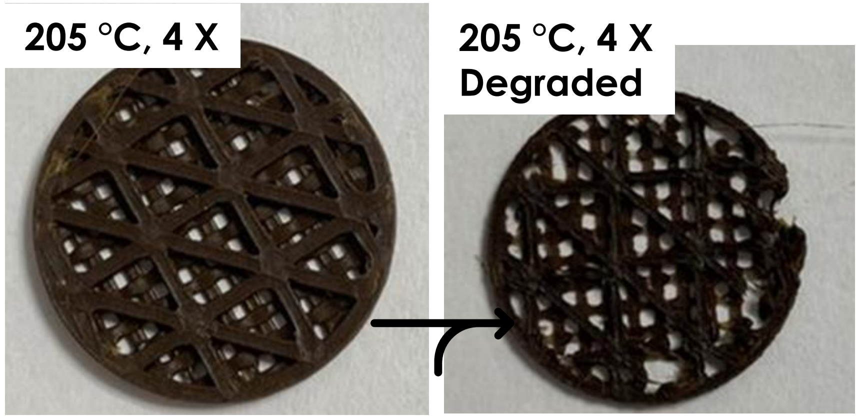
C2 Acetyl (50%)	C12 Lauroyl (50%)	C18 Stearoyl (30%)

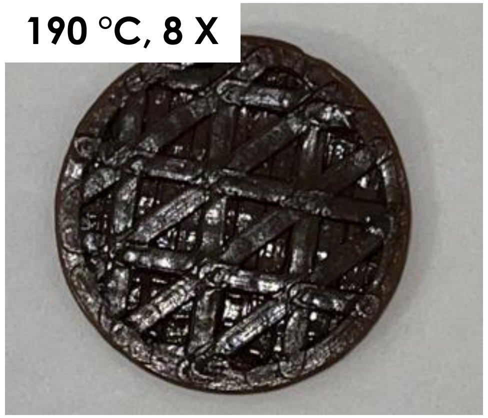
205 °C, 4 X

205 °C, 4 X Degraded



180 °C, 2 X

190 °C, 8 X



- C2 Acetyl (50%)/PLA degraded after some time in the 3D printer at 205 °C
- The materials did not adhere to the printing surface at 180 and 190 °C
- C18 Stearoyl (30%)/PLA becomes liquid like at higher temperature than 190 °C

Conclusion

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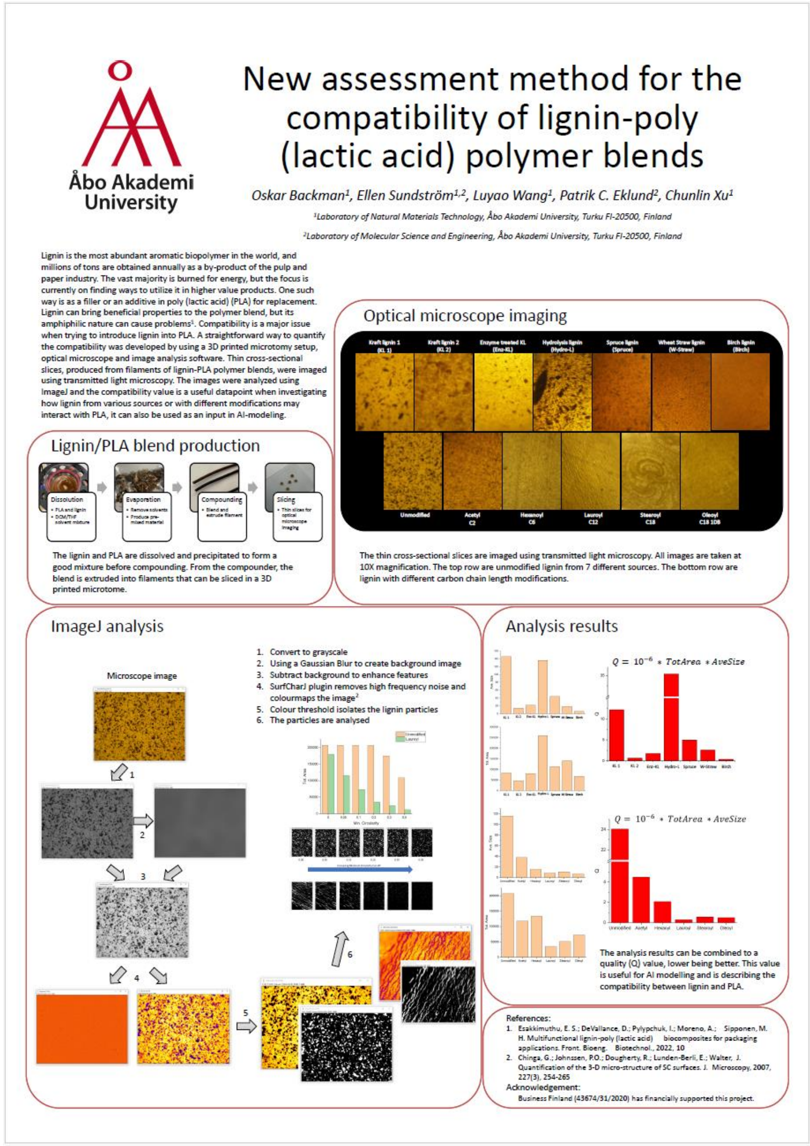
- The compatibility of lignin with PLA was improved by lignin esterification, especially with a carbon chain length of C6, C12, and C18:1
- Lignin esterification increased the flexibility of the lignin/PLA blends, but at the same time increased the impacting forces that PLA can withstand, except for C18
- Up to 30% lignin can be used to replace PLA to make thermoplastic lignin/PLA filaments
- Lignin esterified with C6, C12, and C18:1 are good candidates for lignin/PLA 3D printing

Thank you for your attention!



New assessment method for the compatibility of lignin-poly (lactic acid) polymer blends

Oskar Backman[1], Ellen Sundström[1,2], Luyao Wang[1], Patrik C. Eklund[2], Chunlin Xu[1]
[1]Laboratory of Natural Materials Technology, Åbo Akademi University, Turku FI-20500, Finland
[2]Laboratory of Molecular Science and Engineering, Åbo Akademi University, Turku FI-20500, Finland

Lignin is the most abundant aromatic biopolymer in the world, and millions of tons are obtained annually as a by-product of the pulp and paper industry. The vast majority is burned for energy, but the focus is currently on finding ways to utilize it in higher value products. One such way is as a filler or an additive in poly (lactic acid) (PLA) for replacement. Lignin can bring beneficial properties to the polymer blend, but its amphiphilic nature can cause problems[1]. Compatibility is a major issue when trying to introduce lignin into PLA. A straightforward way to quantify the compatibility was developed by using a 3D printed microtomy setup, optical microscope and image analysis software. Thin cross-sectional slices, produced from filaments of lignin-PLA polymer blends, were imaged using transmitted light microscopy. The images were analyzed using ImageJ and the compatibility value is a useful datapoint when investigating how lignin from various sources or with different modifications may interact with PLA, it can also be used as an input in AI-modeling.

Lignin/PLA blend production

Dissolution
- PLA and lignin
- DCM/THF solvent mixture

Evaporation
- Remove solvents
- Produce pre-mixed material

Compounding
- Blend and extrude filament

Slicing
- Thin slices for optical microscope imaging

The lignin and PLA are dissolved and precipitated to form a good mixture before compounding. From the compounder, the blend is extruded into filaments that can be sliced in a 3D printed microtome.

Optical microscope imaging

Kraft lignin 1 (KL 1), Kraft lignin 2 (KL 2), Enzyme treated KL (Enz-KL), Hydrolysis lignin (Hydro-L), Spruce lignin (Spruce), Wheat Straw lignin (W-Straw), Birch lignin (Birch)

Unmodified, Acetyl C2, Hexanoyl C6, Lauroyl C12, Stearoyl C18, Oleoyl C18 1DB

The thin cross-sectional slices are imaged using transmitted light microscopy. All images are taken at 10X magnification. The top row are unmodified lignin from 7 different sources. The bottom row are lignin with different carbon chain length modifications.

ImageJ analysis

Microscope image

1. Convert to grayscale
2. Using a Gaussian Blur to create background image
3. Subtract background to enhance features
4. SurfCharJ plugin removes high frequency noise and colourmaps the image[2]
5. Colour threshold isolates the lignin particles
6. The particles are analysed

Analysis results

$Q = 10^{-6} * TotArea * AveSize$

$Q = 10^{-6} * TotArea * AveSize$

The analysis results can be combined to a quality (Q) value, lower being better. This value is useful for AI modelling and is describing the compatibility between lignin and PLA.

References:
1. Esakkimuthu, E. S.; DeVallance, D.; Pylypchuk, I.; Moreno, A.; Sipponen, M. H. Multifunctional lignin-poly (lactic acid) biocomposites for packaging applications. Front. Bioeng. Biotechnol., 2022, 10
2. Chinga, G.; Johnssen, P.O.; Dougherty, R.; Lunden-Berli, E.; Walter, J. Quantification of the 3-D micro-structure of SC surfaces. J. Microscopy, 2007, 227(3), 254-265

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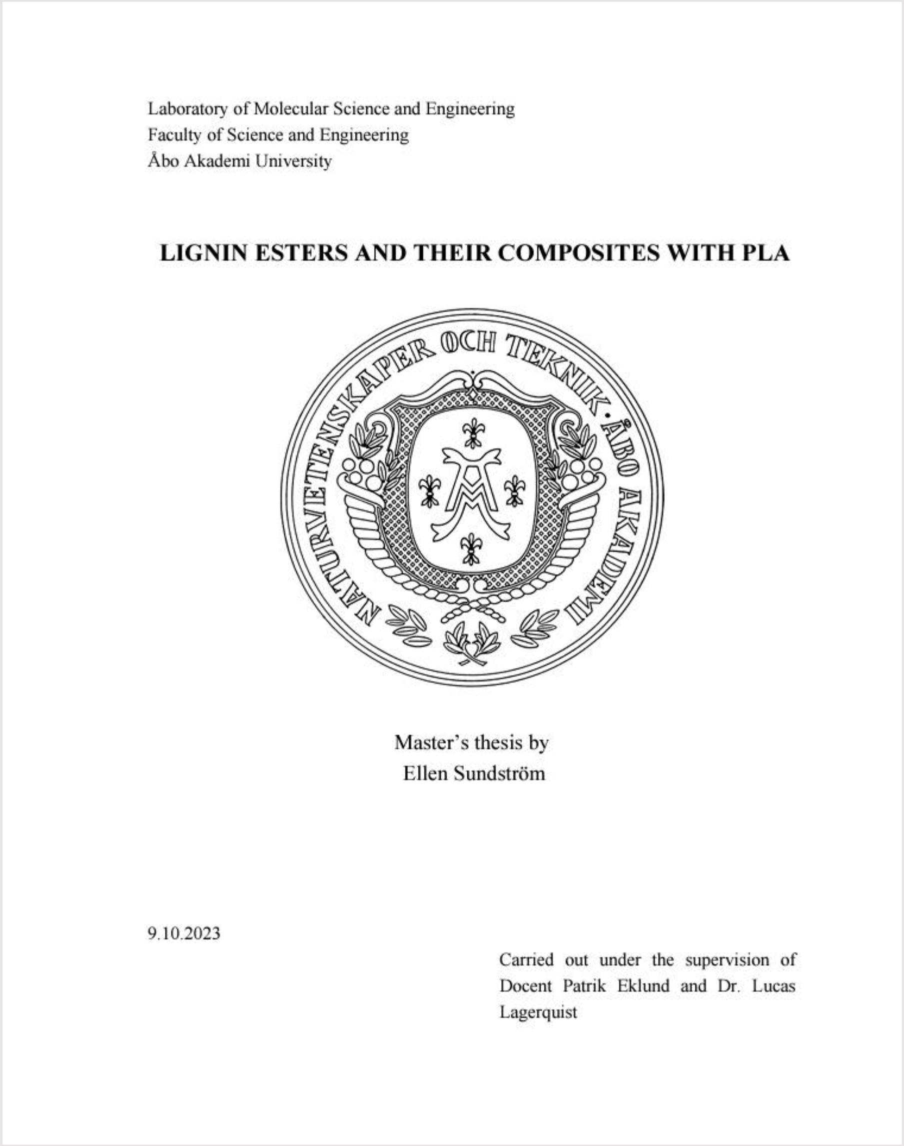

Laboratory of Molecular Science and Engineering
Faculty of Science and Engineering
Åbo Akademi University

LIGNIN ESTERS AND THEIR COMPOSITES WITH PLA

Master's thesis by
Ellen Sundström

9.10.2023

Carried out under the supervision of Docent Patrik Eklund and Dr. Lucas Lagerquist

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Want to know more?

Read the Master's Thesis.

SCAN ME

Can also be found through the LigninReSurf webpage!