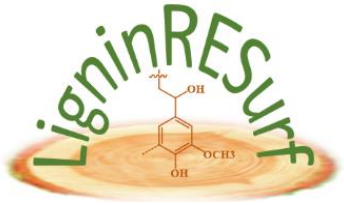


Lignin copolymers

Rupali Bhadane

Åbo/Turku, February 6th, 2024





Novel Fiber Surfaces Functionalized by Lignins Refined and Engineered from Finnish Biorefinery Processes (LigninReSurf).



Lignin copolymers

- Significance and Applications
- Sustainable Alternatives in Polymer Industry
- Environmental Impact
- Potential Applications of Lignin Copolymer
e.g., Plastics, 3D print, Adhesives, Coatings)

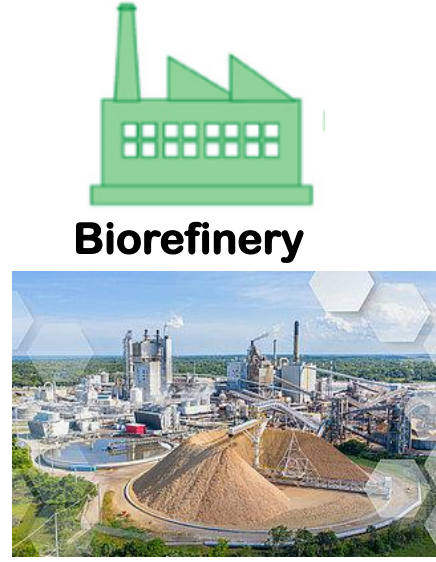
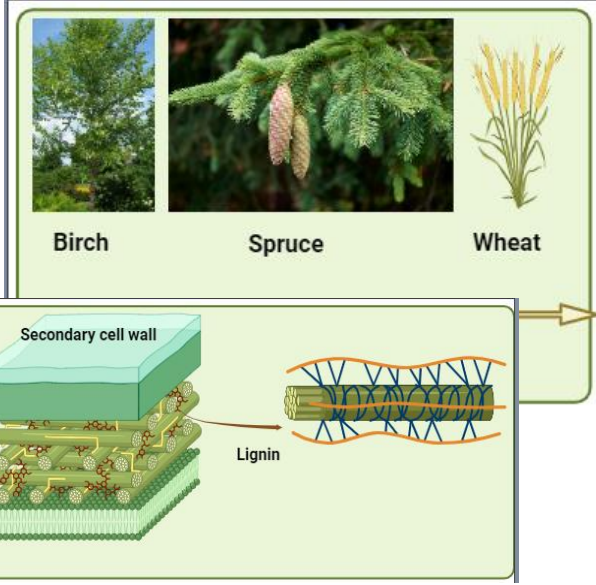
OUR MISSION

Solutions for the necessary transition can be found in interdisciplinary research in new technologies.

In our research, we enable efficient and sustainable utilization of renewable resources instead of fossil ones.



Lignin for LigninReSurf project work



Pulp and paper industry
<https://www.hydac.com/en-us/industry-solutions/pulp-paper-industry/>

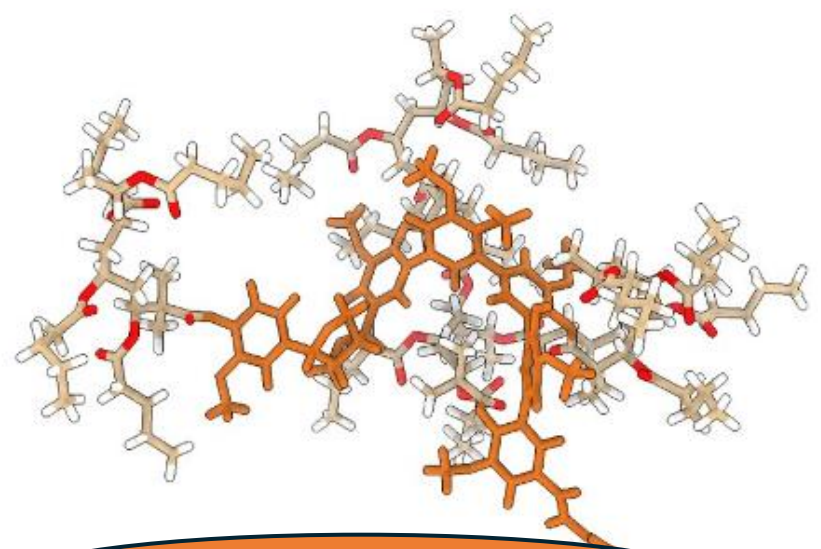
Side stream product



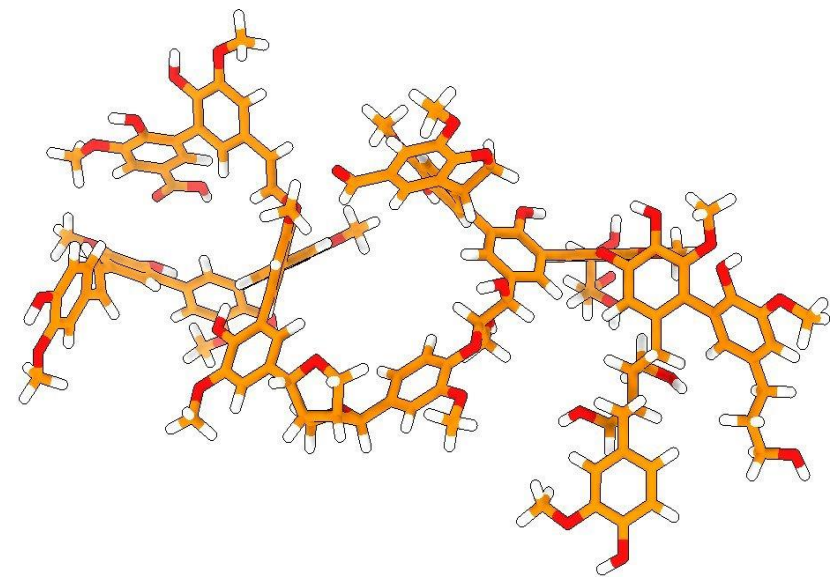
Black liquor



Lignin



LIGNIN COPOLYMER



- **Aim (WP3, LigninReSurf)**

Modified lignin and lignin copolymer for the development of sustainably designed coatings, 3D printing and membrane applications

- **Objectives**

We focused on three types of polymerization reactions

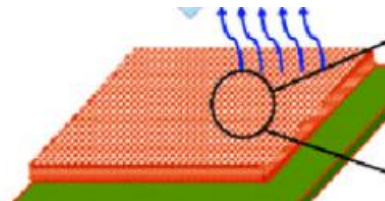
- Ring opening polymerization (ROP)
- Atom transfer radical polymerization (ATRP)
- Direct polymerization

- **Targeted applications (WP4, LigninReSurf)**

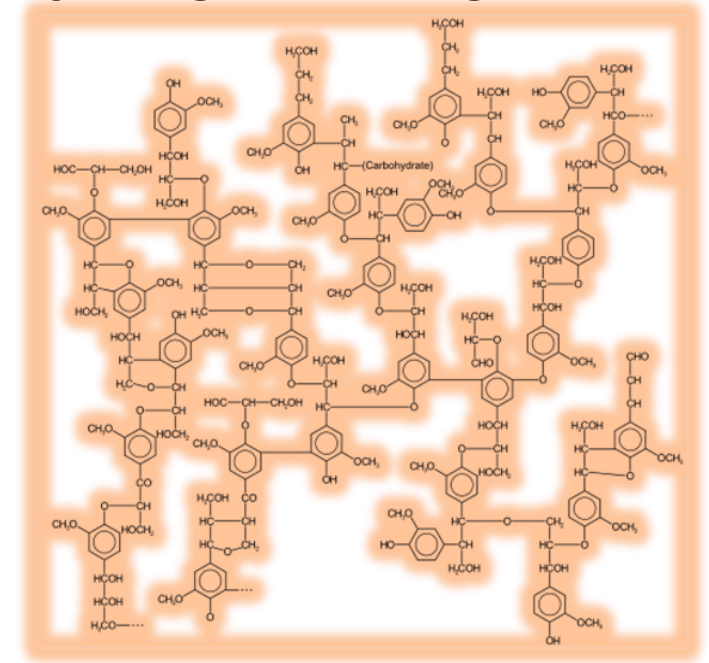
Thermoplastics



Membrane fabrication



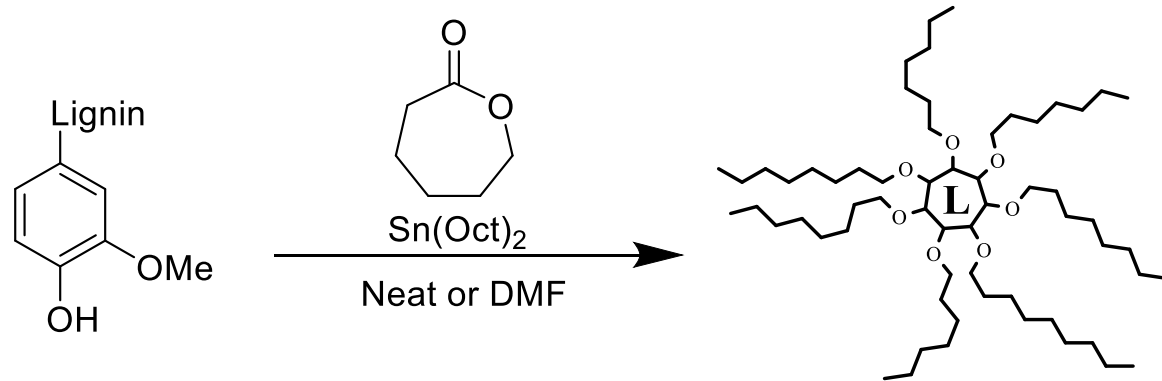
Resins and Adhesives



Karol Głęb pl.wiki: [Karol007](https://pl.wikipedia.org/wiki/Karol007)

1. Ring opening polymerization (ROP)

ROP offers controlled polymerization and allows for the incorporation of specific monomers.



- Star-like polycaprolactone polyesters
- Ring-opening polymerization (ROP) for targeted application as a thermoplastic for 3D printing application

Characterization of Lignin-g-PCL copolymers

- NMR analysis : successful formation of Lignin-g-PCL copolymers.
- TGA : Investigate thermal stability and degradation behaviour.
- DSC: to explore thermal properties.



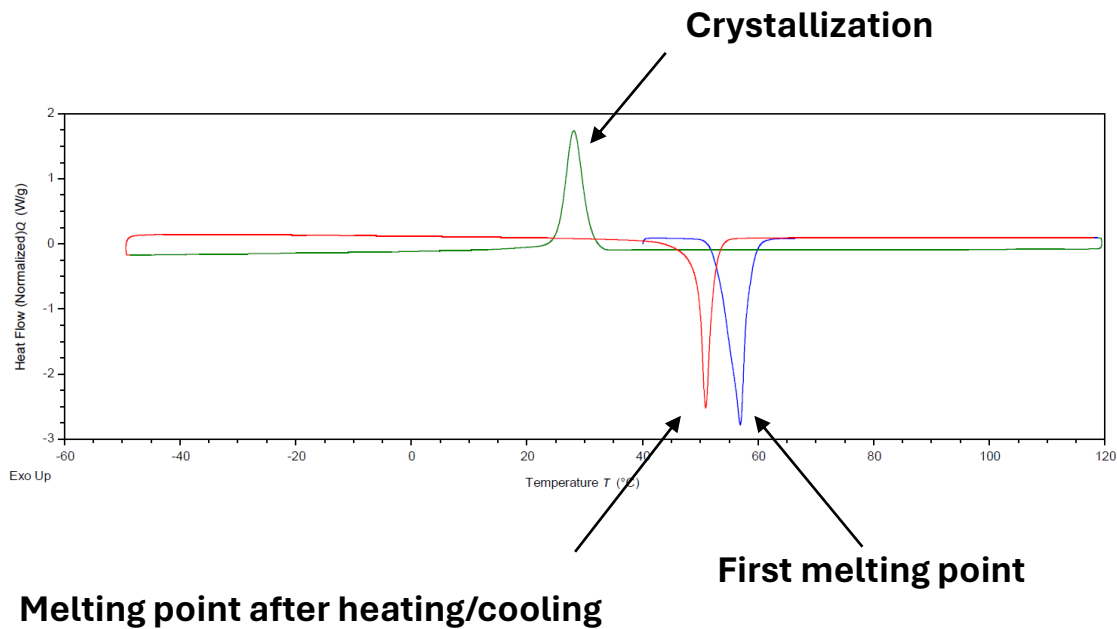
Photographs of BAL-PCL copolymers with DP 2.5, 5, 10 and 100 and lignin-PCL copolymers using Metgen AP70, Metgen AP10-70, and Kraft lignin V4 with DP 10 (from left to right).

Differential scanning calorimetry (DSC)

Formulation of the Lignin-*g*-PCL copolymers and their yield and thermal properties

Macroinitiator	DP/OH	Lignin (g)	ϵ -CL (g)	% lignin	% yield ^b	T _{Crystallization} (°C)	T _{Melting} (°C)
BAL	100	1	72	1	75	24	50
BAL	10	1	7.2	12	86	28	51
BAL	5	1	3.6	22	73	23	49
BAL	2.5	1	1.9	35	51	--- ^a	--- ^a
Kraft lignin V4	10	1	11.8	8	95	28	53
Metnin AP10-70	10	1	6.2	14	89	21	50
Metnin AP70	10	1	6.2	14	85	18	49
BnOH	10	1	10.6	0	68	30	48
BnOH	5	1	10.6	0	51	23	44
BnOH	2.5	1	5.3	0	9	28	51

^anot detectable. ^bMeOH precipitated fraction.



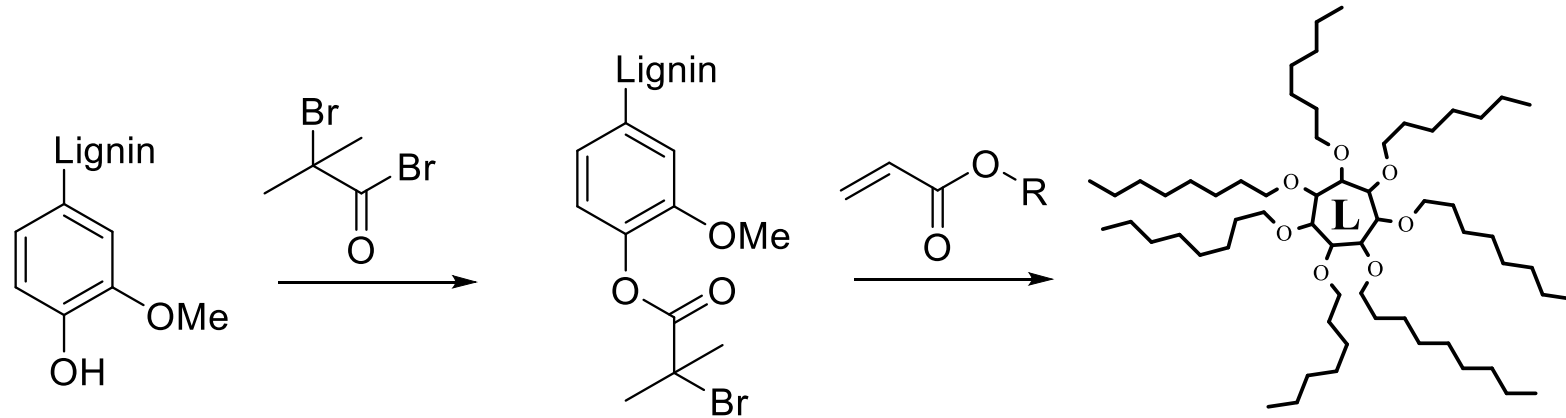
- Heat-cool-heat cycle (40°C ->120°C -> -50°C -> 120°C)
- 10°C/min
- N₂ atmosphere

Conclusion

- **Lignin-g-PCL copolymers exhibit melting temperatures.**
- **Range: 50-60 °C, except for BAL-PCL-2.5DP copolymer.**
- **Potential application as a thermoplastic for 3D printing**

2. Atom transfer radical polymerization (ATRP)

ATRP provides precision in molecular weight control, leading to well-defined copolymers.



- Polybutyl acrylate co-polymers
- Atom transfer radical polymerization (ATRP) for targeted application as a membrane formation

Characterization of Lignin-g-poly(acrylate) Copolymers

- NMR analysis : successful formation of lignin-g-poly(acrylate)copolymers.
- HPSEC: Molecular weight distribution

Sample	Mn(g/mol)	Mw(g/mol)	PD
BLN	1124	1970	1.75
SLN	1520	4239	2.79
WSLN	1095	2120	1.94
BLNBr	1535	4679	3.05
SLNBr	2115	8088	3.82
WSLNBr	1447	5594	3.87
BLNBA2	4625	24158	5.22
BLNBA4	9543	42240	4.43
BLNBA10	12002	68722	5.73
SLNBA4	9343	38104	4.08

Porous Membrane: Lignin copolymers exhibit promising potential for porous membrane fabrication, contributing to water filtration and separation processes.



Collaborators for membrane application

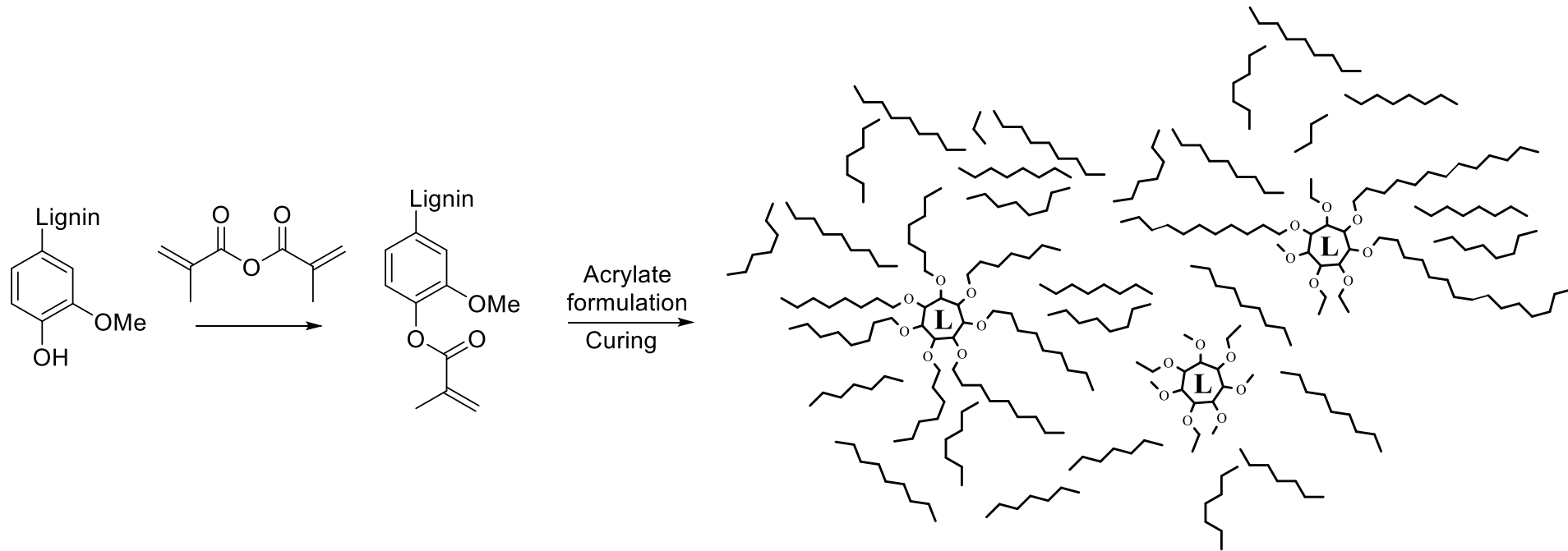
**Institut Européen des Membranes
Montpellier, France**

Conclusion

- **Lignin-g-poly(acrylate) copolymers exhibit different properties with different lignin source**
- **Potential application in membrane formation**
- **Adhesives, sealants**

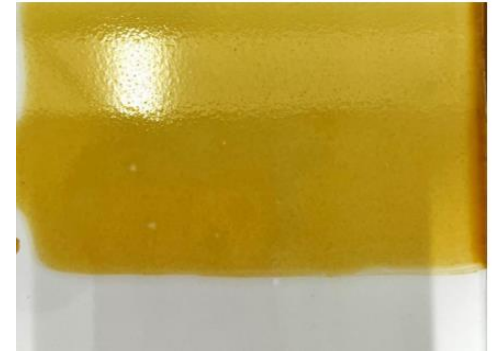
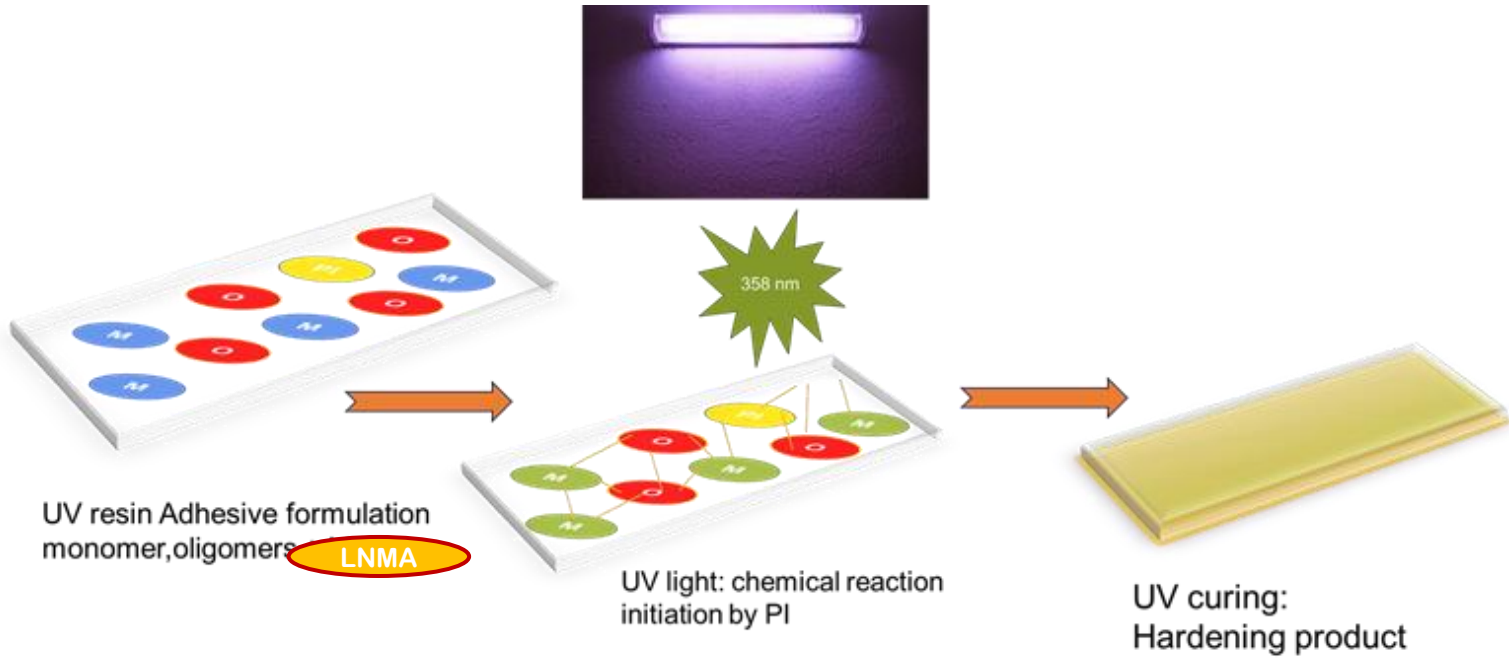
3. Direct polymerisation

Direct polymerization simplifies the process and enhances efficiency.



- **Direct polymerisation of lignin with acrylate for adhesive application**

- **Adhesive application: Master thesis research work of "Ann-Louise Hakalax**



Challenges and conclusion

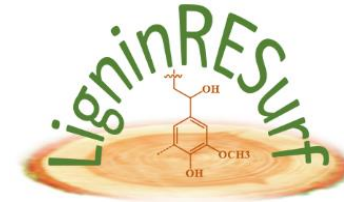
- Variability in lignin sources gives different copolymer
- Different DP shows different physiochemical properties
- Utilizing varied lignin sources with distinct degree of polymerization customize the copolymer for specific applications.

Thank you for your kind attention!



Acknowledgements

- Patrik Christoffer Eklund
- Chunlin Xu
- Lucas Lagerquist
- Teija Tirri
- Jarl Hemming



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**Johan Gadolin
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