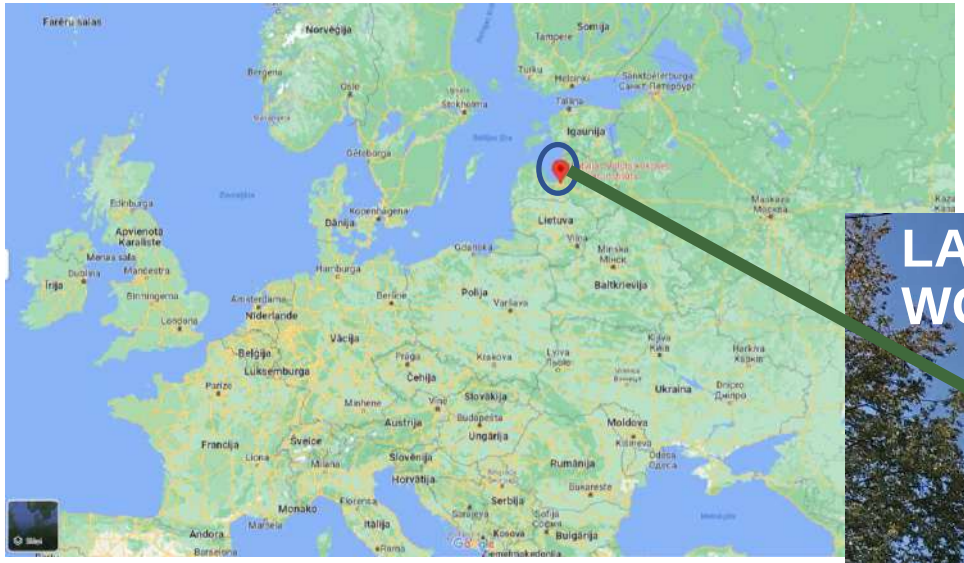
15 min

Birch bark extractives and their potential

Janis Rizikovs,
Latvian State Institute of Wood Chemistry

http://www.kki.lv/



- Founded in 1946
- 101 employees;
- 42 Dr.
- turnover 2022 – 4.5 mill. EUR

Mission

Development of knowledge-based, environmentally friendly low-waste technologies for obtaining competitive materials and products from wood and other plant biomass for sustainable utilisation of natural resources for economic, social and ecological benefits.

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the logo has been changed

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Strategy

Industrial, research, innovation and bioeconomy policies, R&D requirements from forest, agricultural and wood processing industries, which allows identifying three excellences

Wood Materials

Wider use of wood and wood-based materials in building and construction:

improving the durability properties and providing a predictable service life. In the studies, ecological and economical products and technologies are sought for improvement of biodurability and ageing resistance.

Biorefinery

The valorization of European and local plant biomass:

mainly wood and its by-products, considering biorefinery and wasteless conceptions, is the vital conditions for the development of bioeconomy. The advanced analytical tools for chemical analysis of natural products and processes of their obtaining are directed to complete sustainable use of raw materials, through designing of a multi product or feedstock portfolio.

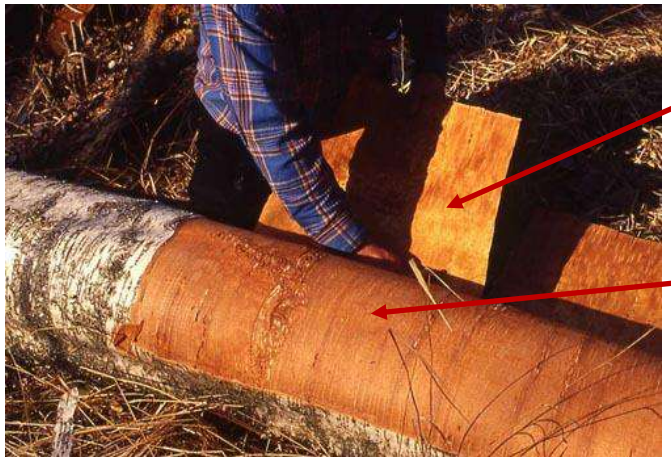
Green Chemistry

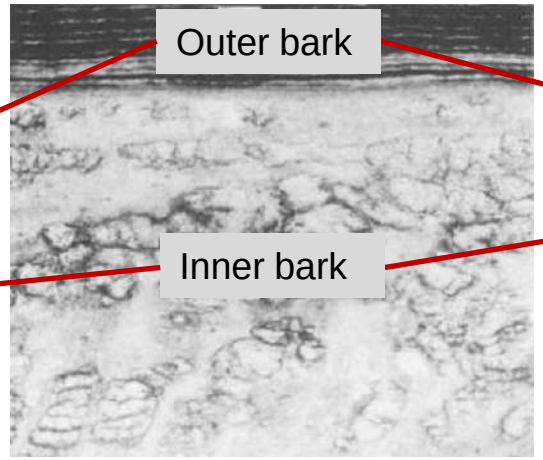
Renewable feedstock as raw materials for synthesis and production of chemicals and polymers:

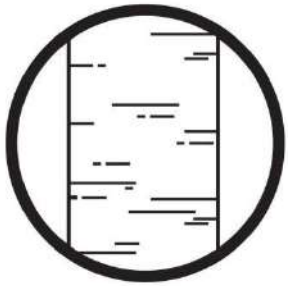
which substitute petrochemical origin materials. Ecologically and economically viable polymers synthesis method, up-scaling of polymer production. Life cycle analysis (LCA) of developed processes.

Birch bark

Silver birch (*Betula pendula*) and downy birch (*Betula pubescens*) are widely used in the furniture, pulp and plywood production







Birch bark – 12.5% of birch log mass

Outer bark - 2.0–3.4% of birch log mass

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BIRCH BARK IN PLYWOOD INDUSTRY

700 000 m³/year

Plywood production

By-product

Energy

Realization

350 000 m³/year - **50%**

Veneer shorts and edges, sawdust, cut-off ends, bark etc.

Boiler house

230 000 m³/year = **17 000-18 000 t/y birch outer bark potential**

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PROBLEM

30 MJ/kg

Synthetic chemicals

Buildings, construction materials, polymers, furniture and finish

Sick building syndrome
Global warming

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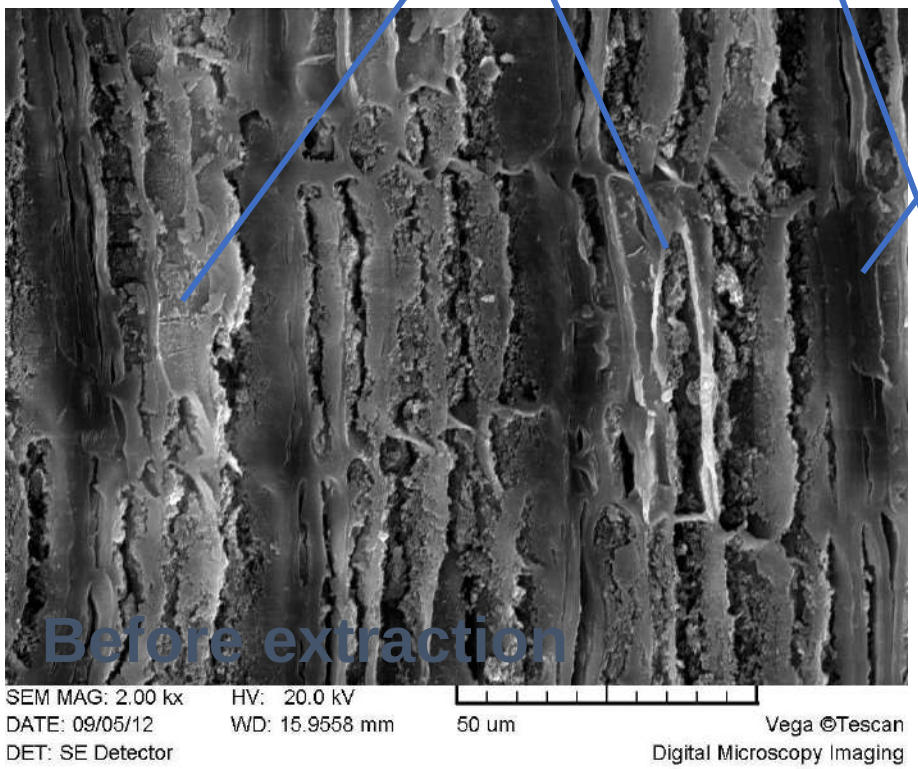
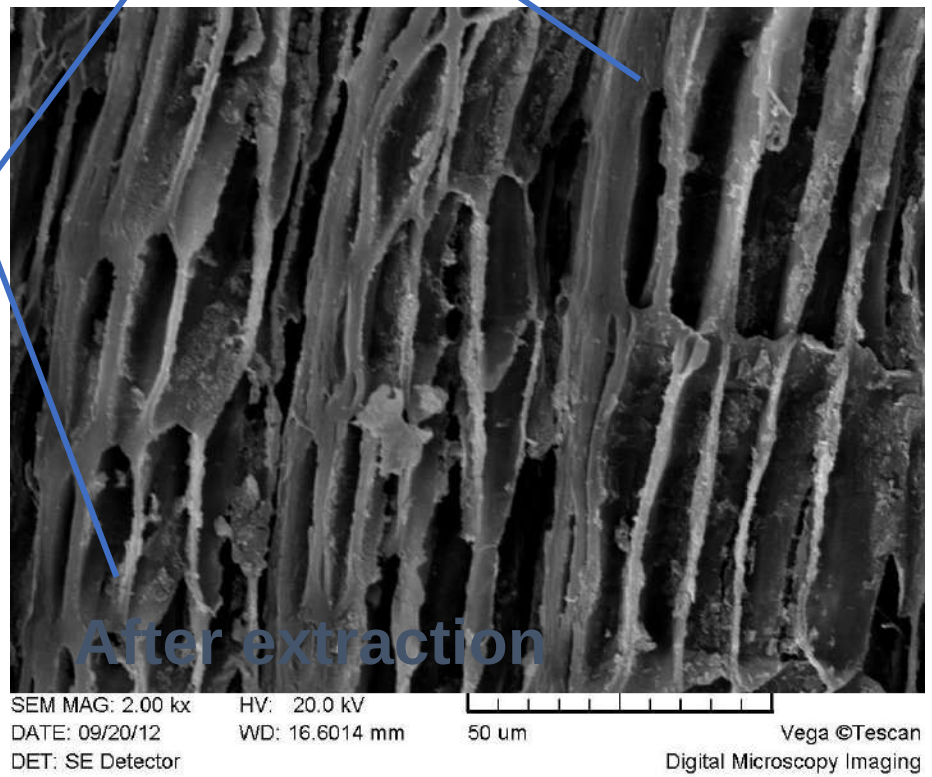
CROSS SECTION OF SILVER BIRCH OUTER BARK (SEM)

Very broad radial dimension cells –deposition of triterpenes

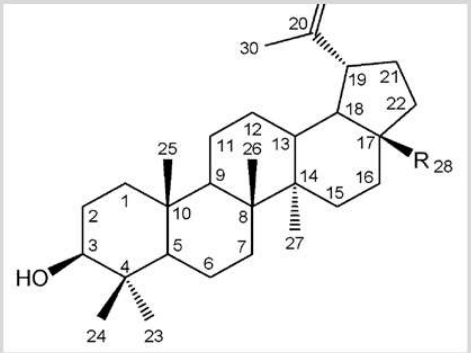
Narrow radial dimension cells- polyphenols containing suberin





BIRCH OUTER BARK CHEMICAL COMPOSITION

Extractives - betulin (30-35%)

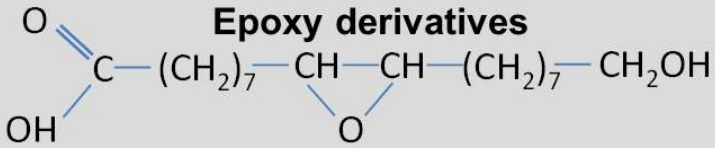


R= CH_3	Lupeol
R = CH_2OH	Betulin
R = COOH	Betulinic acid

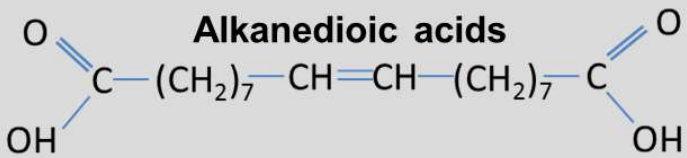
- ✓ **Biological activity**
- ✓ **Cosmetics – emulsifier, antioxidant, preservative**
- ✓ **Remedy against the development of cancerous cells**
- ✓ **Positive results against virus infections**
- ✓ **Against obesity – weight loss**
- ✓ **Anti-inflammatory effect**
- ✓ **Decreases holesterin level in blood**

Residue - suberin (40-50%)

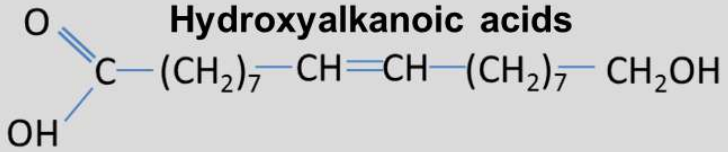
Epoxy derivatives



Alkanedioic acids



Hydroxyalkanoic acids



- ✓ **Rarely formed in nature**
- ✓ **Very difficult to obtain synthetically**
- ✓ **Interesting raw material for organic synthesis**
- ✓ **Cosmetics - skin smoothing**
- ✓ **Adhesives for wood based panels**
- ✓ **Polymer industry - glues, coating agents, epoxides, emulsifiers**

15-20% of outer birch bark components are sugars, polyphenols, tannins, cellulose and lignin

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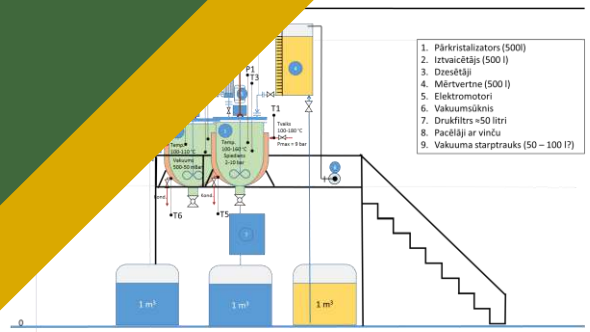
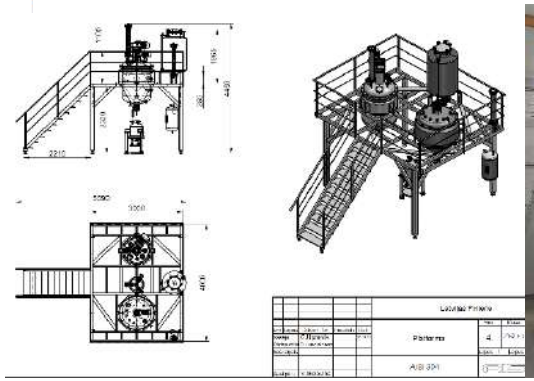
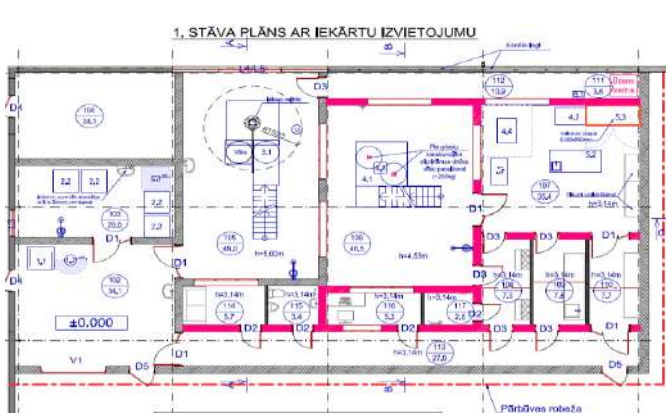
Extractives - betulin







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Contractual research

TRL4-6

- ✓ Technology developed to an industrial level **(500 L)**,
- ✓ An experimental production laboratory **«Betulin Lab»** has been completed
- ✓ Pilot plant regimes adapted for industrial production
- ✓ https://www.youtube.com/watch?v=LyGnc_X45aw

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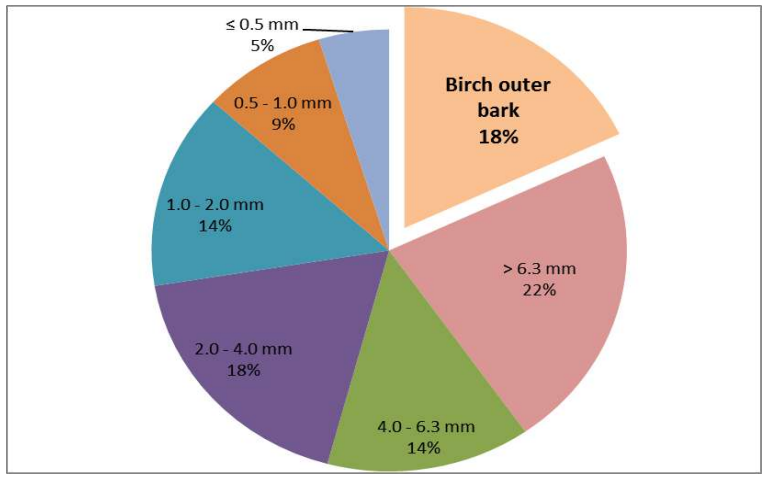
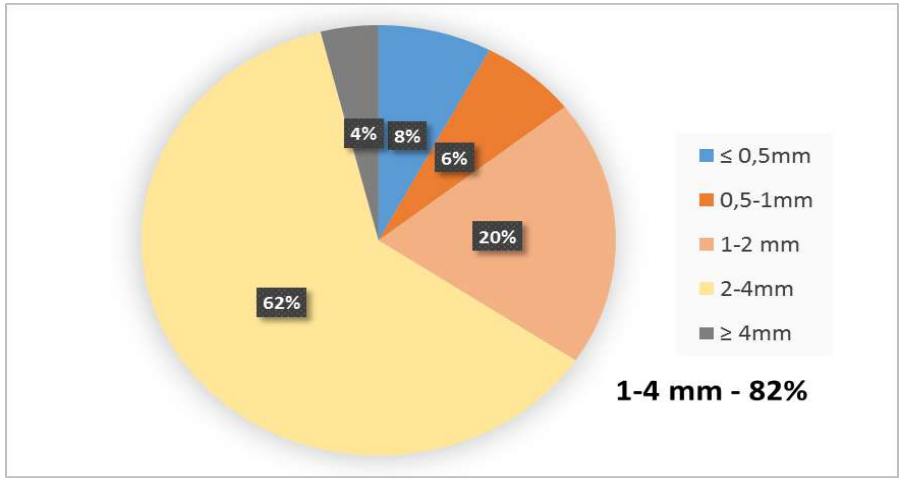
Raw material and experimental

Birch bark



Birch outer bark 18% from bark

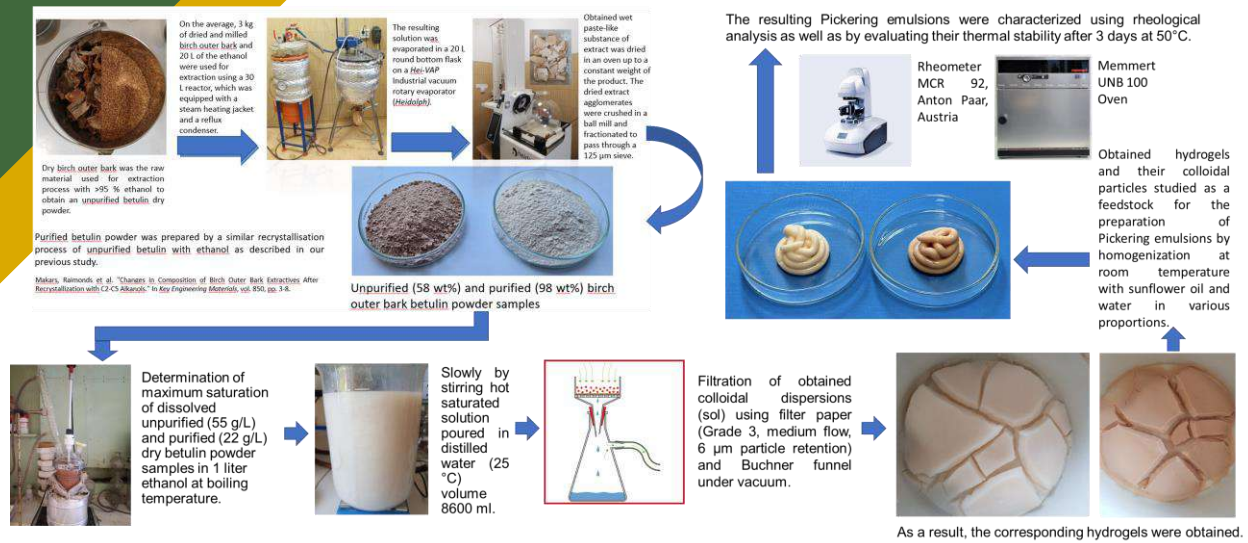
Milled outer bark

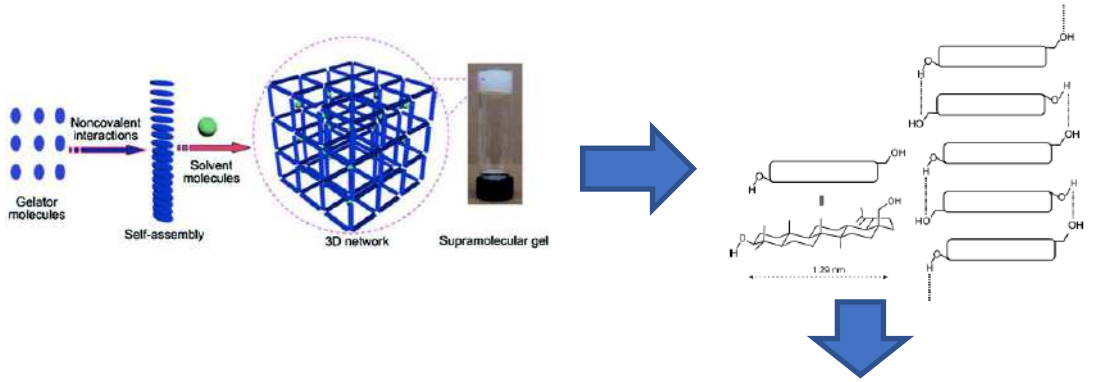


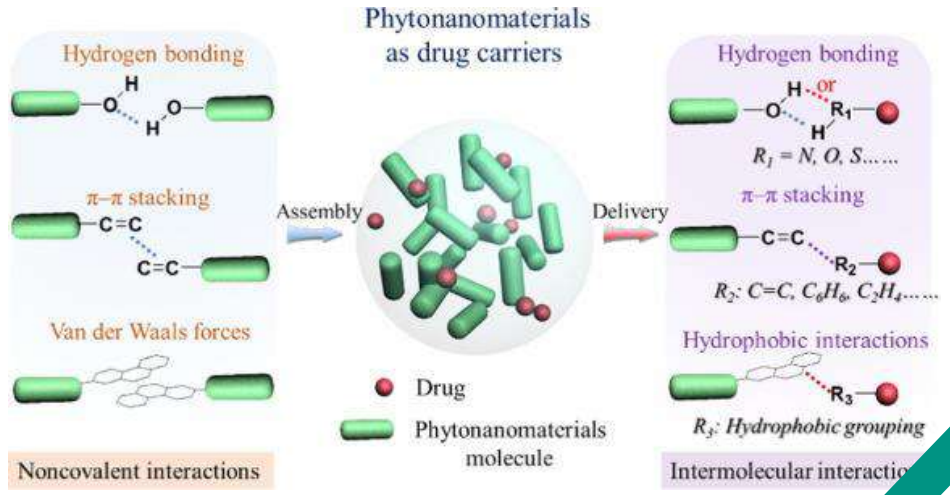
Main experimental steps:

- ✓ **Fraction 1-4 mm was taken for experiments – 82%**
- ✓ **Ethanol extraction was carried out to isolate extractives**
- ✓ **Depolymerization was performed in alkaline solution**
- ✓ **Acidification with mineral acids**
- ✓ **Filtration and rinsing operations to remove mineral salts**
- ✓ **Fractionation, purification and application**

Betulin, hydrogels and emulsions







- ✓ It is possible obtain homogeneous Pickering emulsions from purified and unpurified betulin hydrogels.
- ✓ great potential to be used in medicine, food, cosmetics and nano-catalysis or as drug carriers.

European Regional Development Fund project No. 1.1.1.1/20/A/071"Research of the production and application of high specific surface birch outer bark betulin particlesin dispersed systems".

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Extracted birch bark potential for suberinic acids

Birch outer bark

Extraction

On the average, 3 kg of dried and milled birch outer bark and 20 L of the ethanol were used for extraction using a 30 L reactor, which was equipped with a steam heating jacket and a reflux condenser.

Cosmetic
Food suuplements
Medicine

Betulin extractives

Extracted birch outer bark

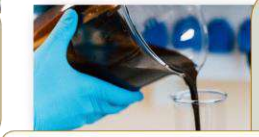
- Fractional composition;
- Higher heating value;
- Residual extractives (in ethanol);
- Suberin content from TGA.

Depolymerization

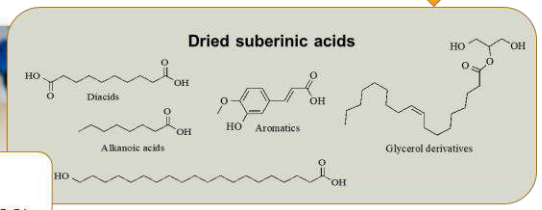
T=80°C;
t= 60 min;
KOH – 0.65M;

Acidification

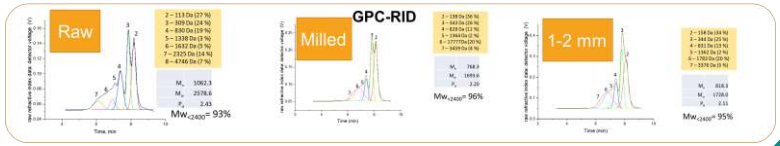
Rinsing

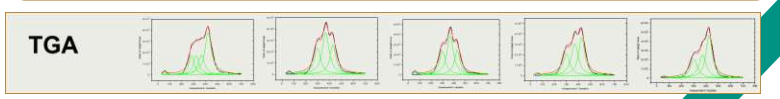


- Yield of SFAs;
- GPC-RID,
- SFA thermal behaviour (DSC).



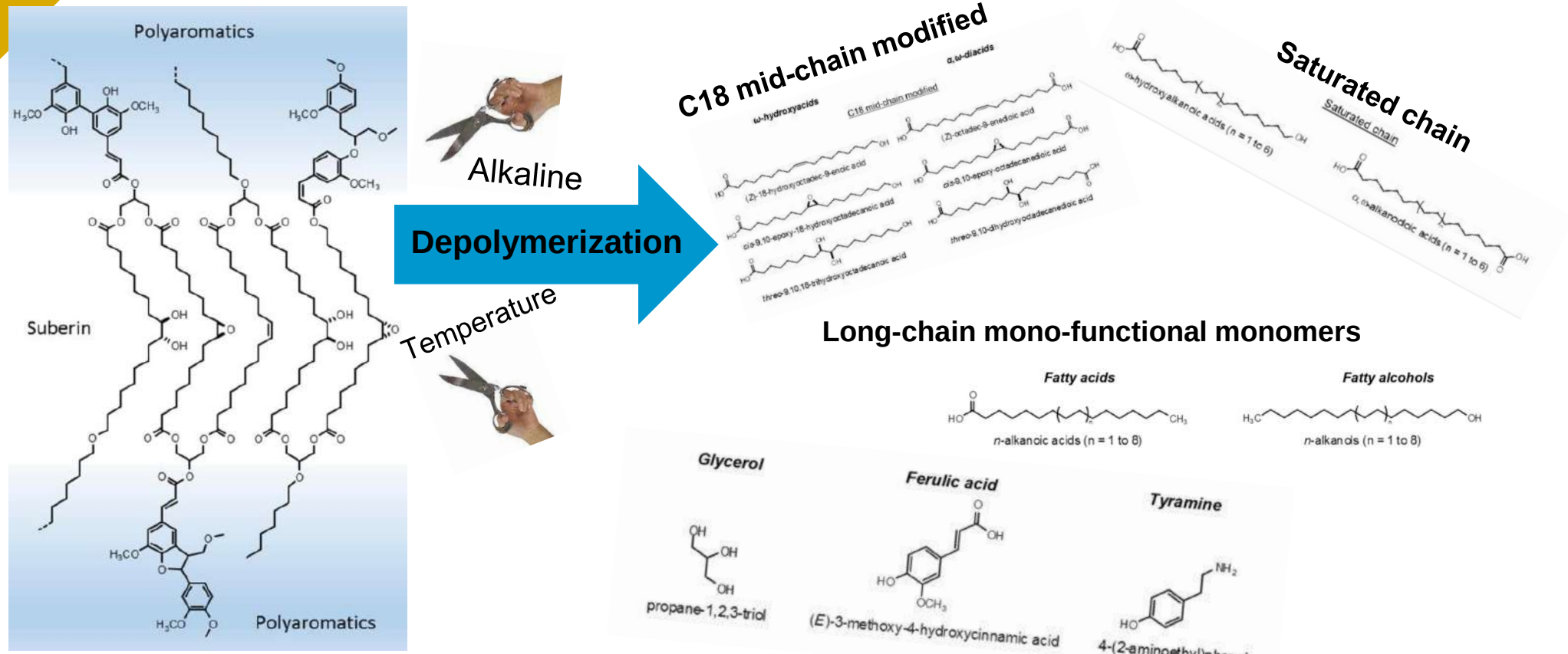
Fractional of extracted and milled birch outer bark					
Fr., mm	**≤0.25**	0.25–0.5	0.5–1	**1–1.4**	**1.4–2**
Higher heating value, Q					
Q_{raw}, MJ/kg	**27.04**	26.57	25.73	**27.85**	**29.28**
Residual extractives (Ex)					
Ex %	**12.83**	8.10	7.43	**9.50**	**11.02**
Higher heating value after isloation of residual extractives, Q					
Q_{ex}, MJ/kg	**26.04**	25.54	24.47	**26.74**	**28.31**
Suberin content by TGA					
Sub, %	**37.5**	22.4	21.5	**32.7**	**40.0**
Extracted birch outer bark (EBOB) content					
EBOB, %	**58.1**	53.3	43.1	**64.7**	**79.7**





- **Fractions 1-1.4 and 1.4-2.0 mm were the most suitable**
- **Not significant improvement to the yield**
- **Suberin fatty acids qualitty was improved in terms of total suberin content – less impurities.**

SUBERIN depolymerization



- ✓ **Suberin is a polyester biopolymer possessing a mixture of monomers with hydroxyl and carboxylic acid functionalities.**
- ✓ **Mid-chain modifications in the C18 ω-hydroxyacids and α,ω-diacids are dominant**

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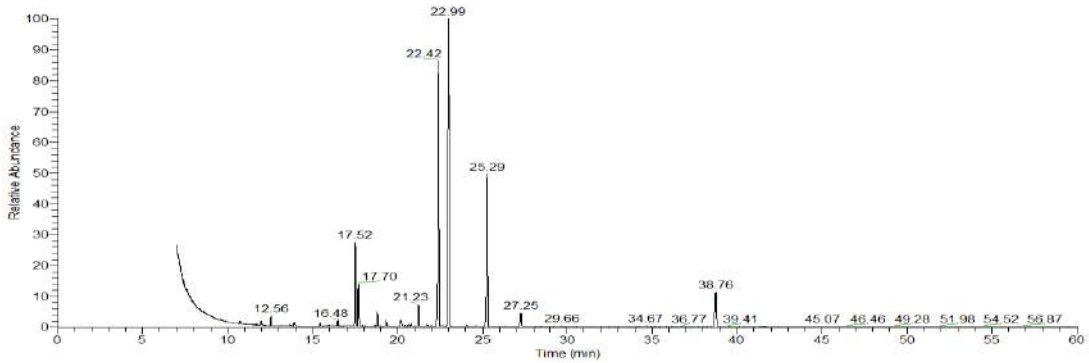
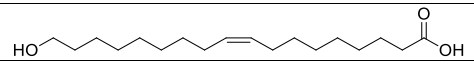
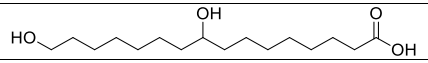
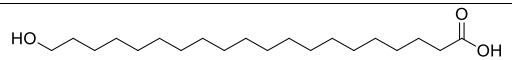
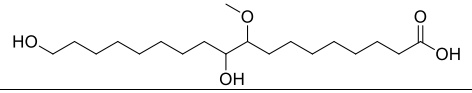
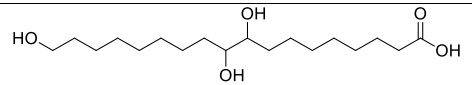
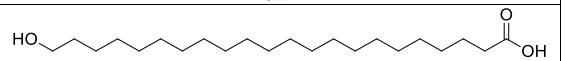
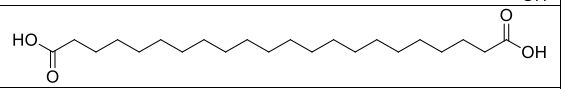
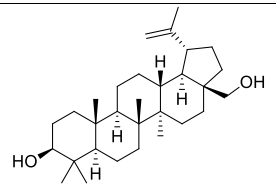
CHARACTERIZATION



Isolation by methanolysis

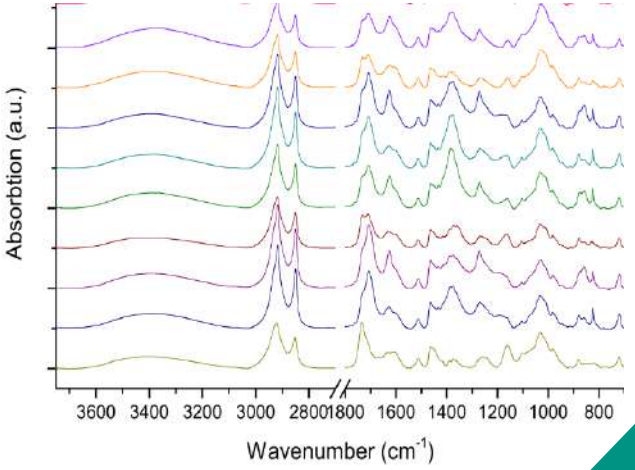
Silylation with BSTFA

GC/MS analysis in *Thermo Scientific TRACE 1300*

nr.	Retention time, min	Compound	Structural formula
1.	17,52	ω-hydroxy-C18:1 acid	
2.	17,70	ω,x-dihydroxy-C16 acid	
3.	21,23	ω-hydroxy-C20 acid	
4.	22,42	9-methoxy-10,18-dihydroxy-C18 acid	
5.	22,99	9,10,18- trihydroxy-C18 acid	
6.	25,29	ω-hydroxy-C22 acid	
7.	27,25	α,ω- C22 dioic acid	
8.	38,74	Betulin	

FTIR analysis

- **Aliphatic chains**
- **Epoxy groups**
- **Carboxyl groups**
- **OH groups**
- **Saturated**
- **Unsaturated**
- **C18-C22**



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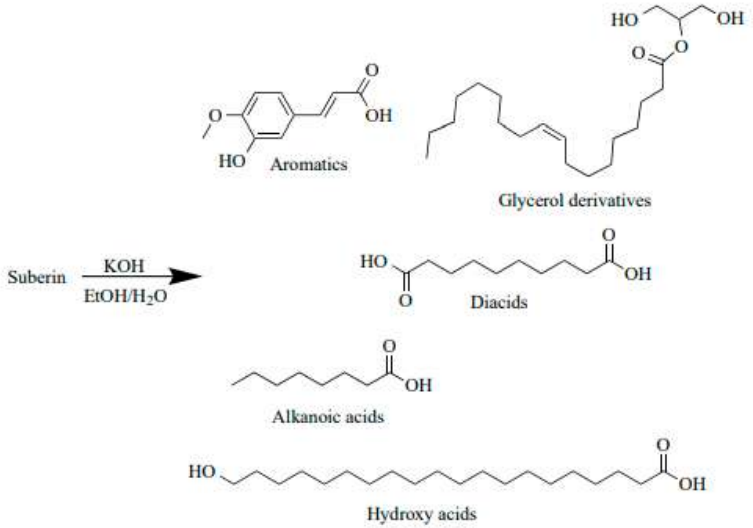
Suberinic acids (SA) Obtaining and properties



Untreated

Treated

Sample	Acid number, mmol·g^{-1}	Epoxy groups, mmol·g^{-1}	TPC, %	Yield, %
SA_U	1.57	0.59	2.3	29.3
SA_T	1.77	0.66	1.5	24.7

- In both SA samples **different fatty acids and their corresponding esters were identified**. The most common fatty acid in both SA samples was **ethyl stearate, octadecanedioic acid, hydroxy-decenedioic acid, sebacic acid and 22-hydroxy-docosanoic acid.**
- Pentacyclic triterpenoids such as **lupeol and betulin**.
- Both SA samples contain **not only monomeric fractions but also oligomeric/polymeric fractions** of compounds which cannot be detected with GC-MS.

molecules

Article

Analytical method cluster development for comprehensive characterisation of suberinic acids derived from birch outer bark

Daniela Godina[1*], Raimonds Makars[1,2], Aigars Paze[1], Janis Rizikovs[1]

GPC and MALDI-Tof

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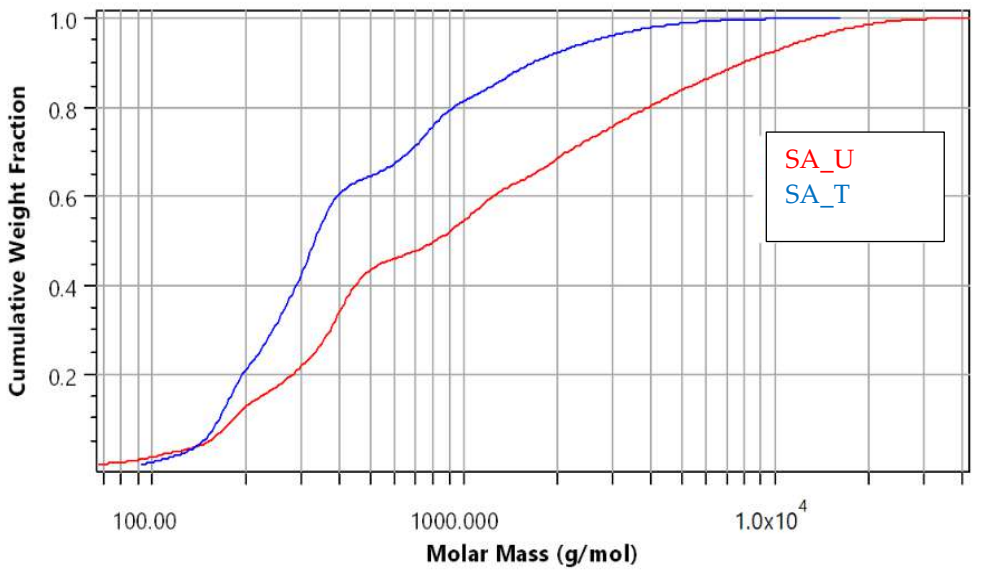

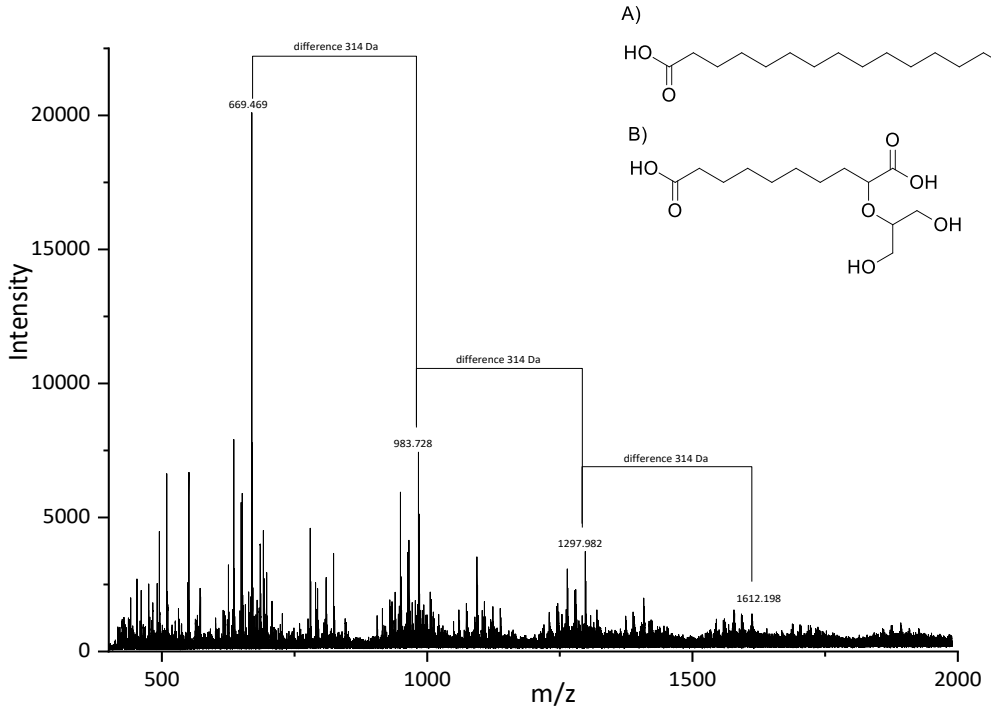

Sample	Molar mass range, Da						
	100–200	200–500	500–800	1000–2500	2500–3000	3000–5000	>10 000
	Relative area percentage, %						
SA_U	19	14	14	10	17	19	7
SA_T	24	23	22	10	16	5	-

Corresponds with GC-MS results after depolymerization where hydroxyacids (C10 – sebacic acid) and diacids (C18 - 1,18-octadecanedioic acid) were the dominant type of compounds found in the sample.

- Using **$FeCl_3$ not only TPC but also some higher molecular fractions** of SA were removed from the sample.

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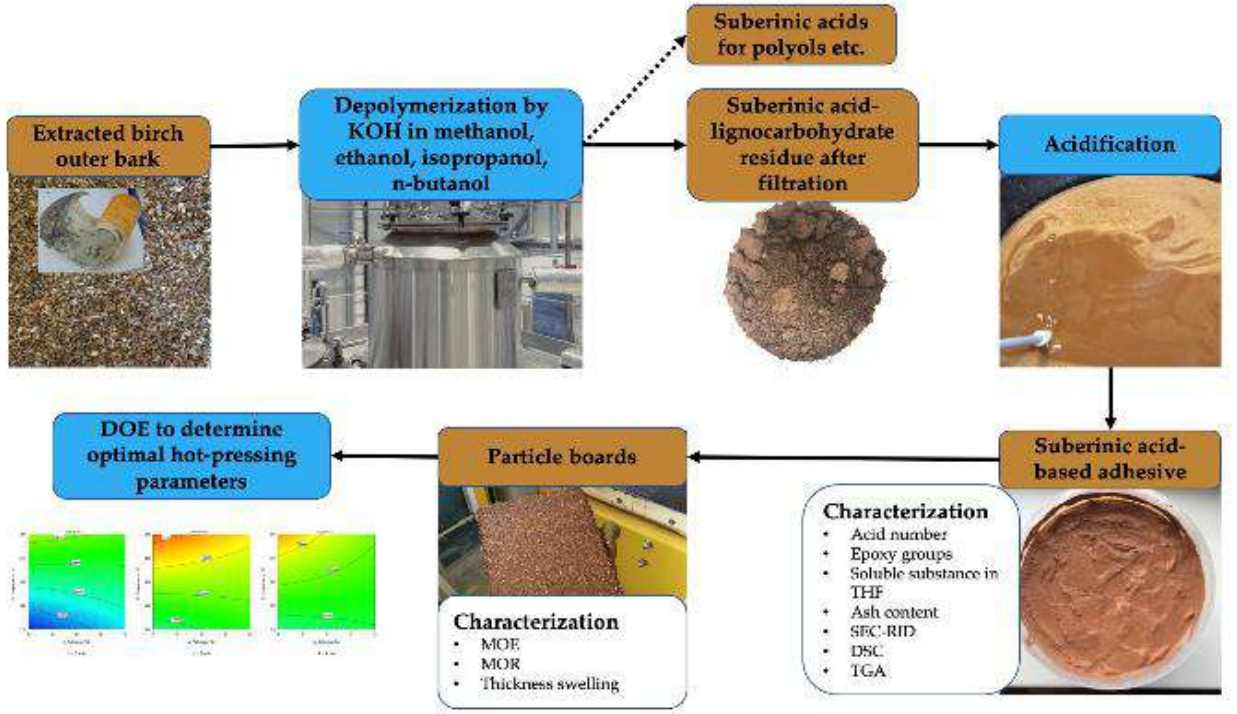
Suberinic acids adhesives



The SA-bonded particleboards, produced with a SA content of 21% and processing conditions of 226 °C for 5 minutes, **exhibited properties** (bending strength - 17.1 MPa) within the range s**pecified by the EN 312 standard for type P3 particleboards – moisture resistant**

In **plywood SA acted** as well **as an excellent binder to obtain moisture resistant samples** (bending strength 177-189 N/mm^2 and shear strength 1.7-1.8 N/mm^2), **which conforms to class F 80 and to the 3rd moisture resistance class**, which is the highest moisture resistance class for the materials used in unprotected exterior conditions over sustained periods.

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Suberinic acids adhesives

SUBERBINDER

ADVANTAGES

Environmentally friendly

The suberinic acids binder is a by-product obtained from renewable natural resources and is completely ecological.

Health friendly

The binder does not contain phenol-formaldehyde resins or other substances harmful to human health.

Efficiency

Much more expedient use of wood resources to obtain a widely used material.

Moisture resistance

Suberinic acids are hydrophobic substances, so they are suitable for use in moist outdoor conditions.

Innovative material

Innovation in the industry with new and simple manufacturing technology.

Good mechanical properties

Particle boards with the suberinic acids binder are characterized by high bending strength, strength of internal bonds and form stability.

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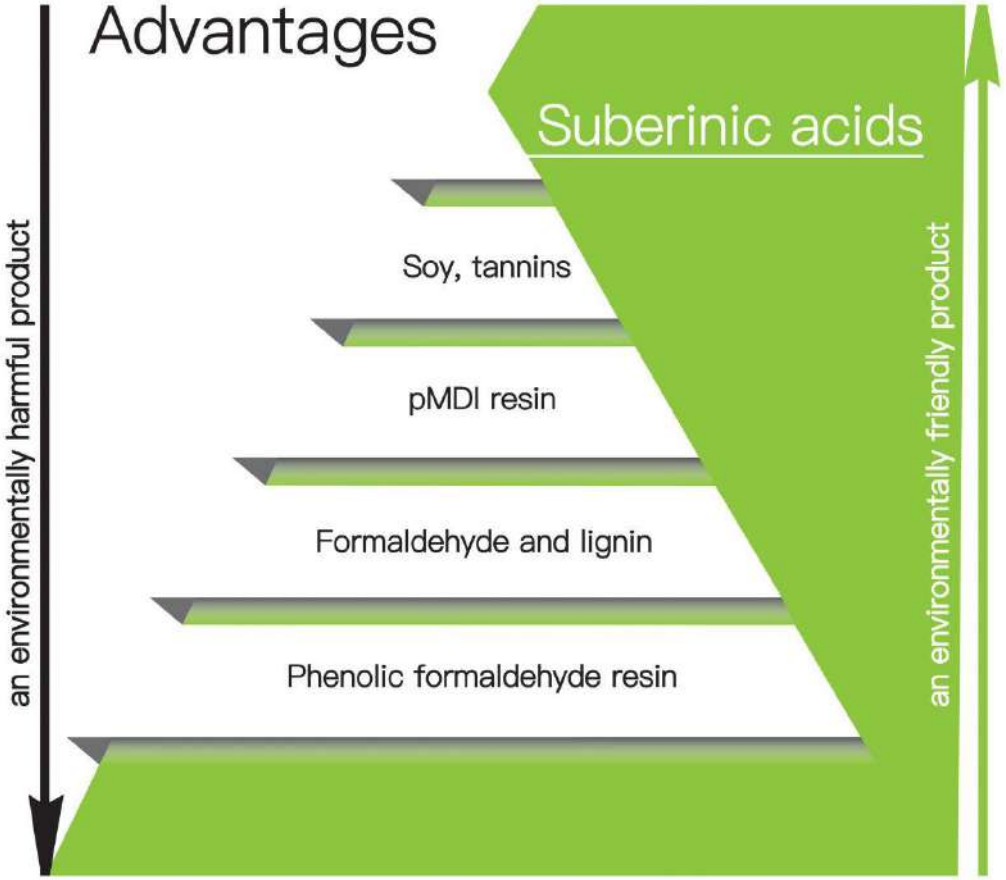
Suberinic acids adhesives

SUBERBINDER



In comparison with other natural binders where synthetic additives are used in production to obtain improved properties, suberinic acids containing ***binder act as it is****, without any additives or modifiers. This means that* ***it is completelly ecological product****.*

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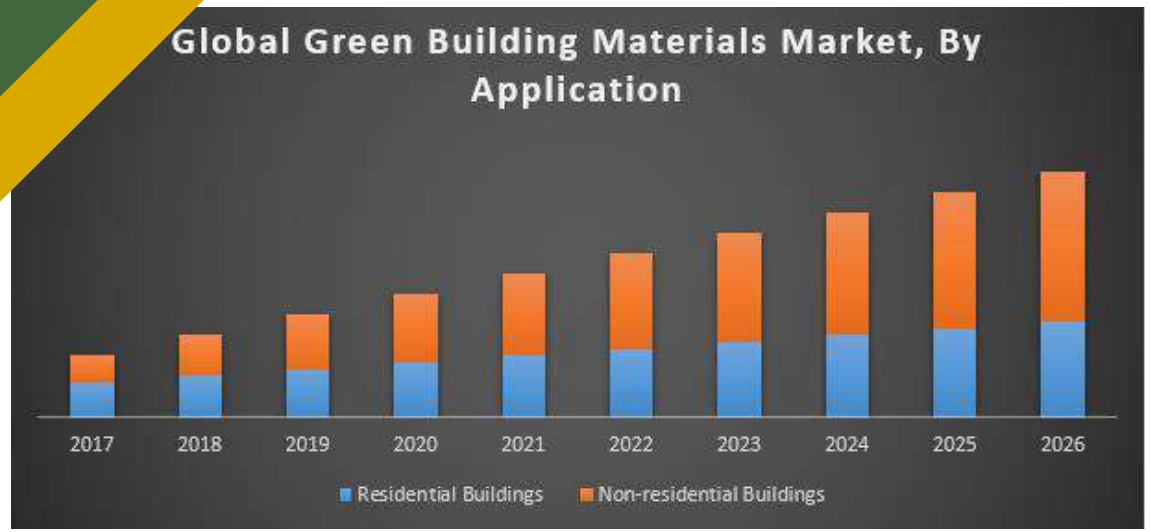
BUSINESS POTENTIAL



The market for building materials for **«green buildings»** in 2017 was estimated at an average of USD 198.5 billion, with a forecast that it will grow to an average of USD 480.5 billion by 2026.

«The adhesives market increase by 5.2% in a year»

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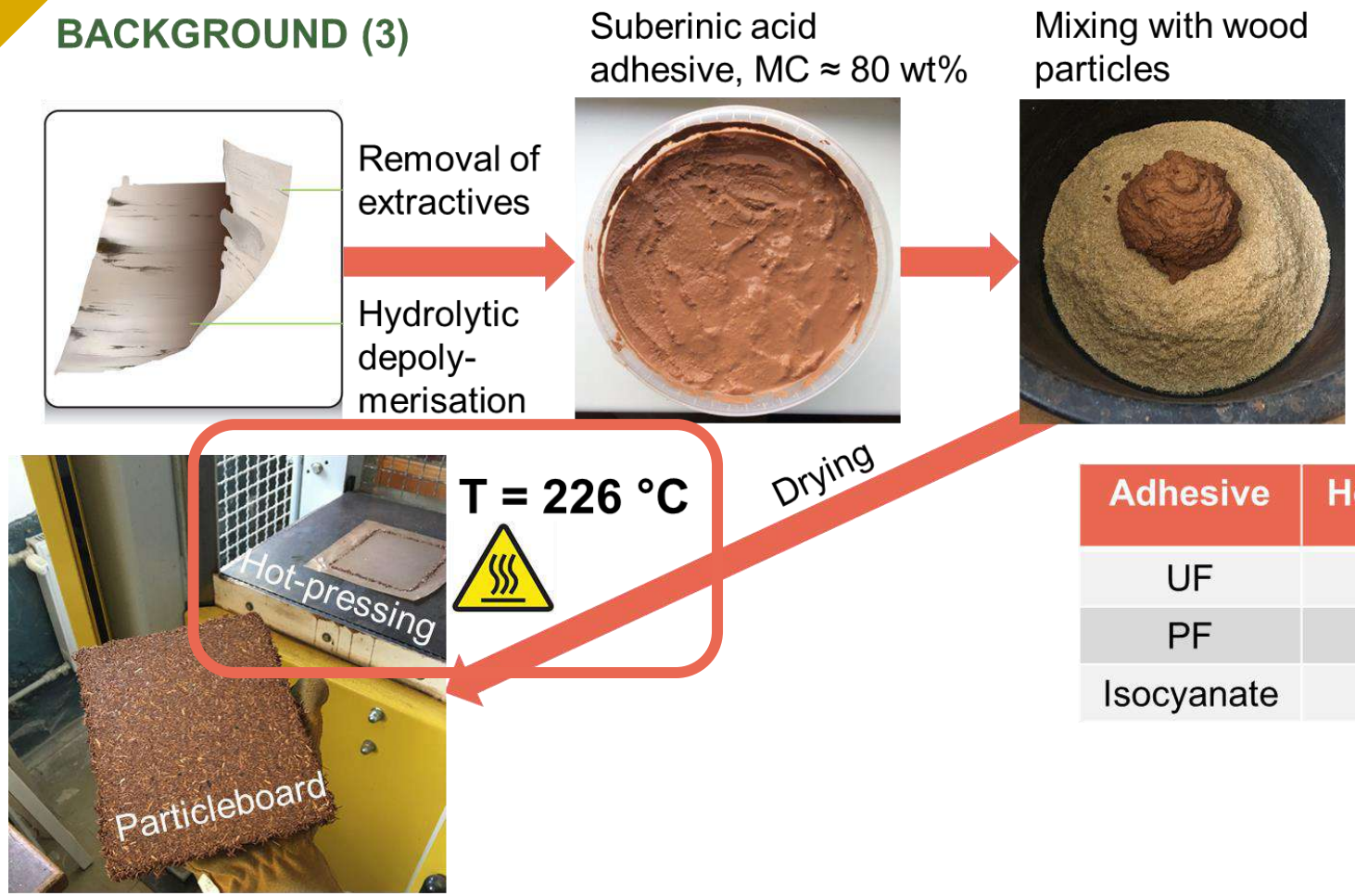
Elevated pressing temperature

BACKGROUND (3)



Adhesive	Hot-pressing T, °C
UF	**120–130**
PF	**170–180**
Isocyanate	**150–160**

R. Tupciauskas, J. Rizhikovs, J. Grinins, A. Paze, M. Andzs, P. Brazdausks, M. Puke, A. Plavniece, Investigation of suberinic acids-bonded particleboard, Eur. Polym. J. 113 (2019) 176–182.
A.H. Iswanto, I. Azhar, Supriyanto, A. Susilowati, Effect of Resin Type, Pressing Temperature and Time on Particleboard Properties made from Sorghum Bagasse, Agric. For. Fish. 3 (2014) 62–66.

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EXPERIMENTAL

Drying

DSC analysis 25→220 °C

Addition of potential catalyst

Group of catalysts	Catalysts
Protonic acids	Sulfanilic acid (SA), p-toluenesulfonic acid (PTSA), 5-sulfosalicylic acid (5-SSA), 2-naphthalenesulfonic acid (2-NSA)
Lewis acids	$Al_2(SO_4)_3$
Tin-based	$SnCl_2$, $SnCl_2$/PTSA, dibutyltin oxide (DBTO), dibutyltin dilaurate (DBTL)
Antimony-based	Sb_2O_3
Amines	Hexamine (HX)
Peroxides	t-Butyl peroxybenzoate (TBPB)

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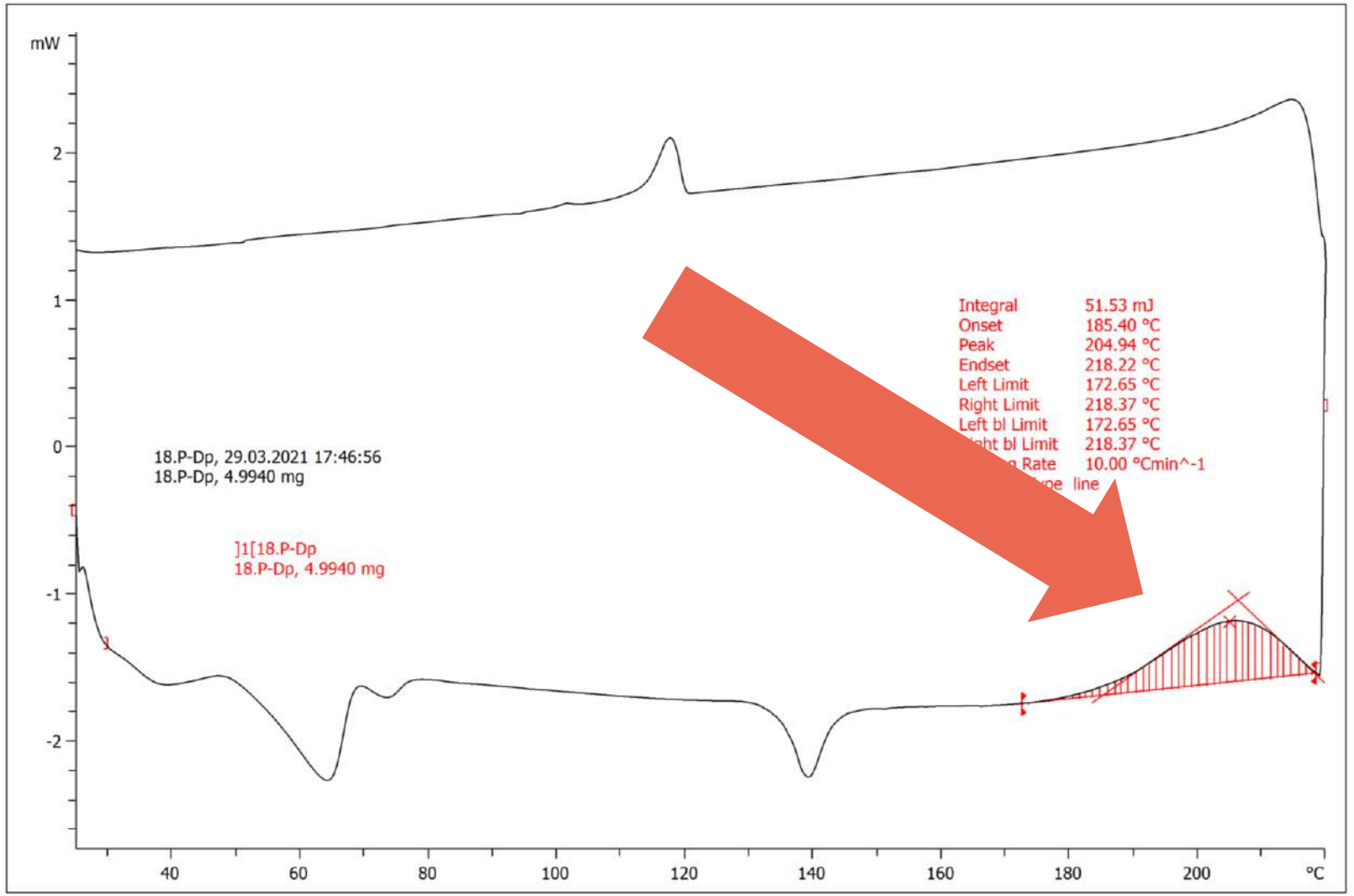
DSC THERMOGRAM (UNTREATED SAMPLE)

- Exotermic peak with an onset value of 185 °C is characteristic to suberinic acid adhesive sample.
- This occurrence is most probably due to thermosetting reactions of adhesive constituents.
- To assess the suitability of potential catalyst, the specific enthalpies of the exothermic reaction were compared.
- Most of the tested catalysts had a positive effect on specific enthalpy of the polymerization.



EXPERIMENTAL – particle board samples

Suberinic acid adhesive, MC ≈ 80 wt%

Addition of potential catalyst:

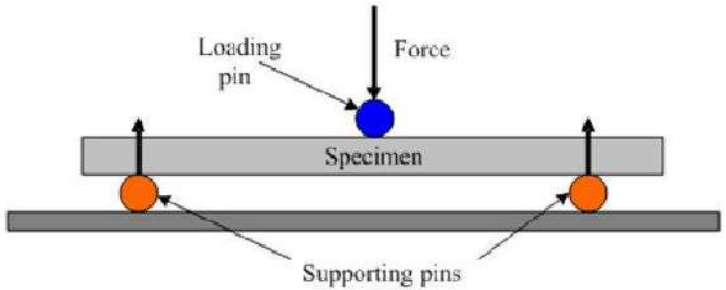
- SA
- PTSA
- $Al_2(SO_4)_3$
- $SnCl_2$
- $SnCl_2$/PTSA
- DBTO

Mixing with wood particles

Drying

Hot-pressing

Designed density — **830 kg m^{-3}**
Designed thickness — **7 mm**
Adhesive (o.d.) — **30 wt%**
p (max) = **3,5 MPa**
T = **200 °C**
t = **10 min**



Three-point bending test (MOE, BS)
N = 9

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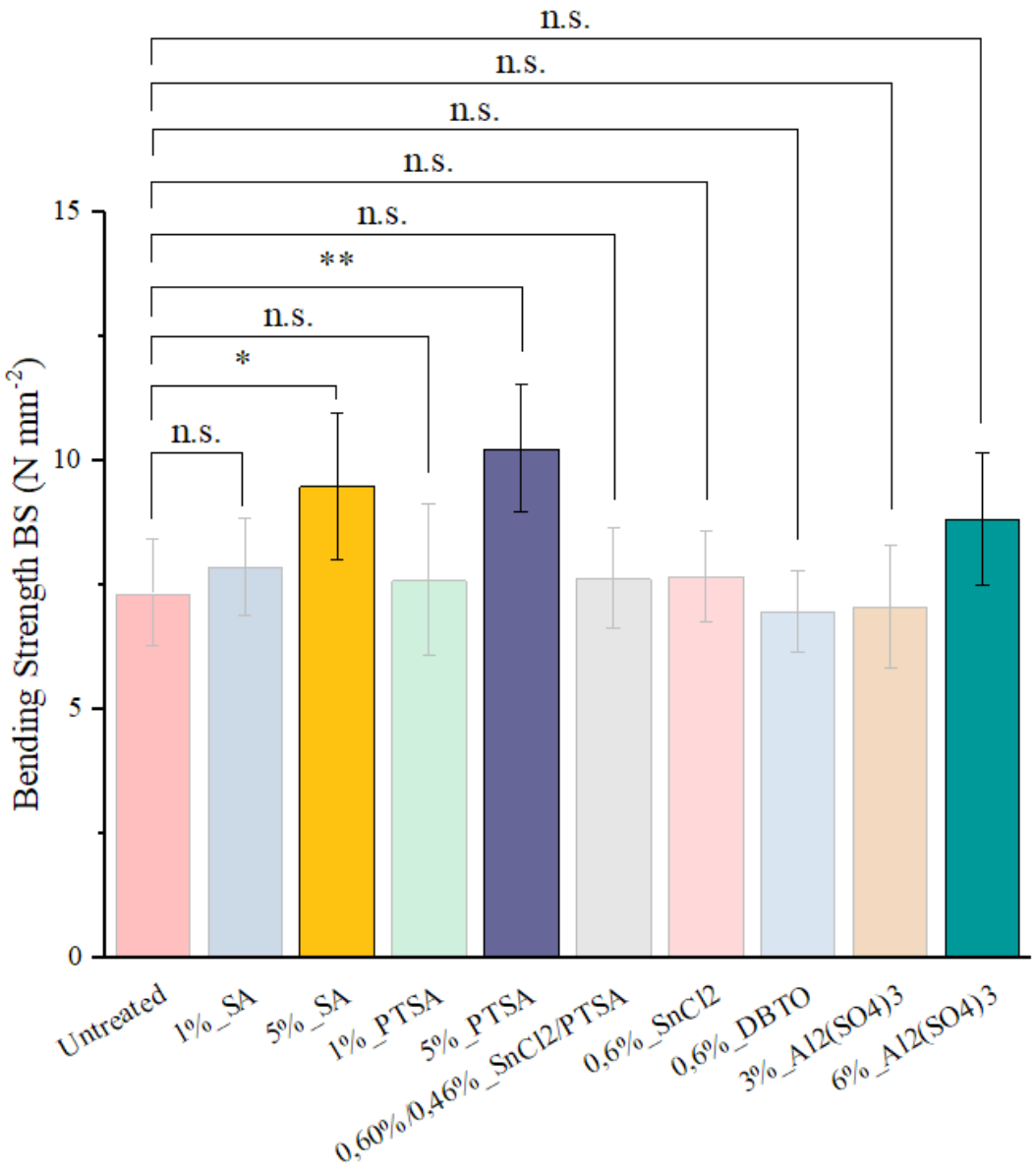
RESULTS (3)

- Increasing catalyst percentage for **Sulfanilic acid** (SA), **p-toluenesulfonic acid** (PTSA) to 5% significantly improved BS value.
- For 6%_ $Al_2(SO_4)_3$ there wasn't significant improvement.
- **It was possible to decrease the pressing temperature to 200 °C**
- **Need to continue the research to reach at least 180 °C.**



* p<=0,01 ** p<=0,001 n.s. not significant

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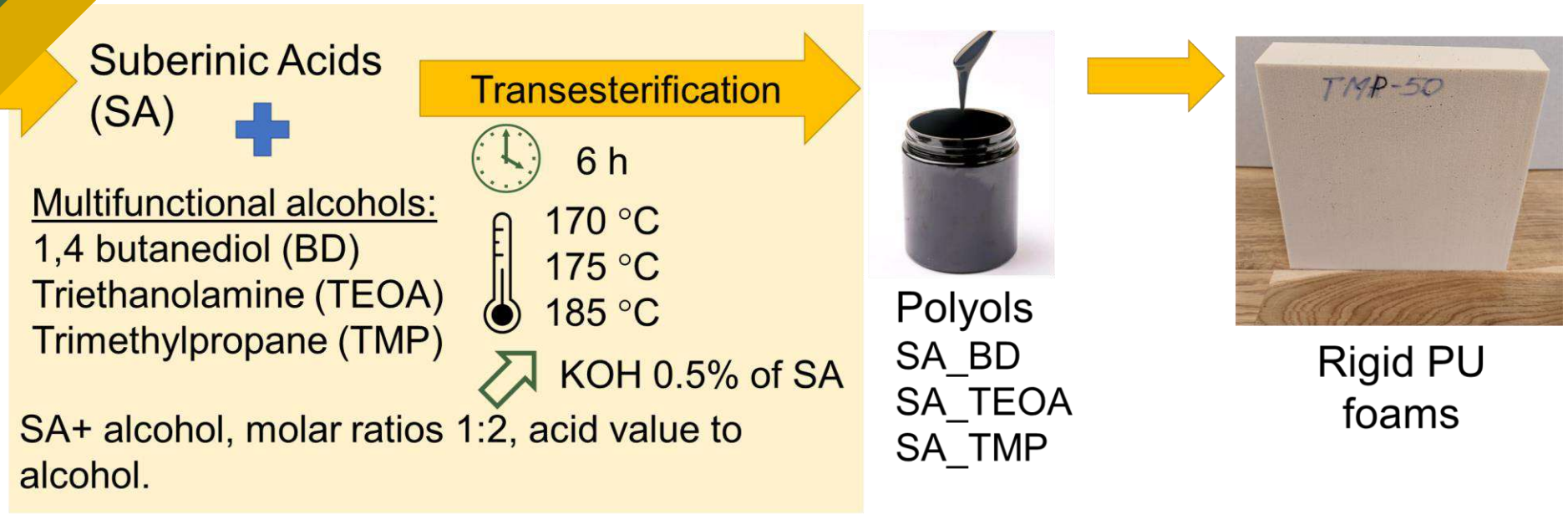
Suberinic acids in bio-polyols for PUR



- ✓ **Total renewable material content of 20 wt.%**
- ✓ SA-based polyol synthesized with TEOA showed **autocatalytic properties**
- ✓ Apparent density (~33 kg/m^3), as well as closed cell content (~94%), compression strength (0.25 MPa, parallel to foaming direction) and thermal conductivity (~0.019 W/(m·K)) **approved** the potential ability of SA-based rigid PUR foam production **as thermal insulation material.**

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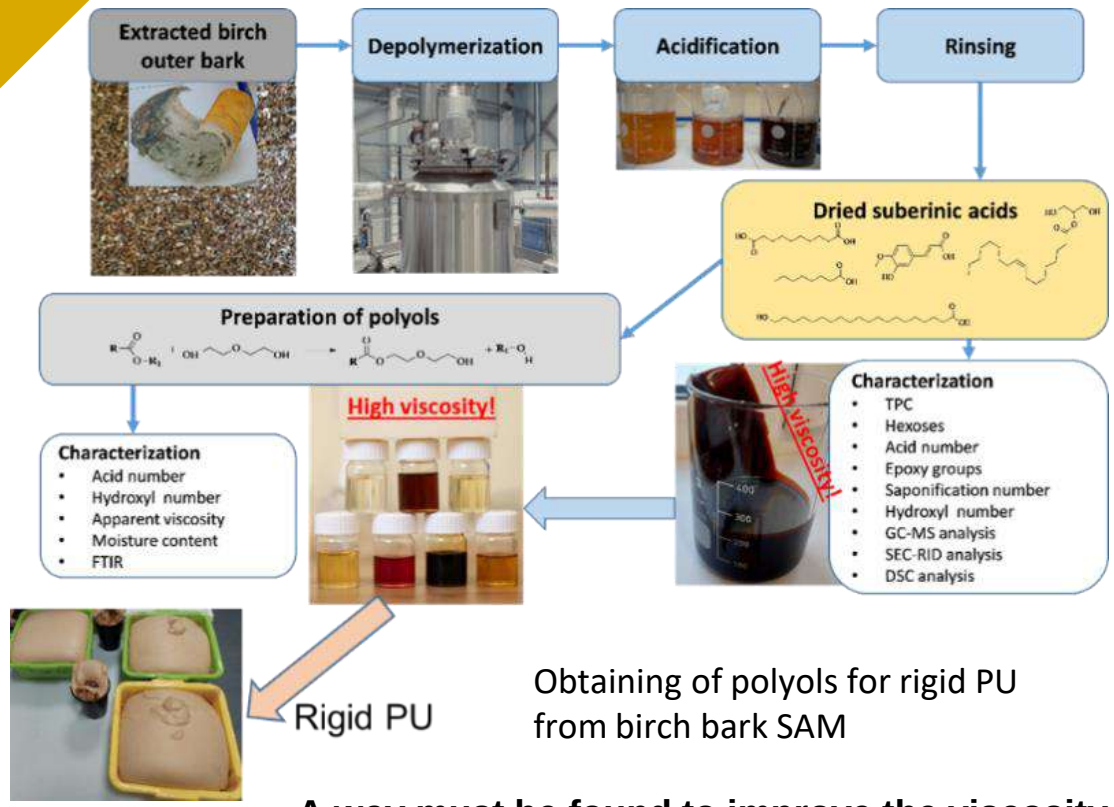
Challenges of SA in polyols

1) **The apparent viscosity of bio-polyols was too high** (15-82k mPa·s at a shear rate 50 1/s at 25°C), which can be explained by a very high molecular weight of the bio-polyols;
2) **The final acid value of the bio-polyols was too high** indicating that synthesis was not completed even after more than 6 hours;
3) **Suberinic acids mixture (SAM) itself was in solid form and sticky state (flowable only at 80-100°C)** with potential problems to operating on the industrial scale**.**



Obtaining of polyols for rigid PU from birch bark SAM

- Heterogeneous composition (containing oligomeric fractions, polyphenols, carbohydrates, triterpenes, KNO_3 and solid particles from inner bark) of the SAM from birch bark.
- After drying SAM is partly copolymerized, with high molecular weight and therefore high viscosity.
- One of the ways to skip the thermal drying was lyophilization and it was concluded that lyophilized SA samples had a higher content of low MW fractions (210 – 840 Da).
- Still, **lyophilization is not the best industrial solution** and also the viscosity of SAM was almost the same due to several admixtures, including triterpenes, solid inner bark particles and KNO_3.

A way must be found to improve the viscosity and integrate SAM into PU formulations keeping the same mechanical and thermal properties, and to substitute petrochemical educts.

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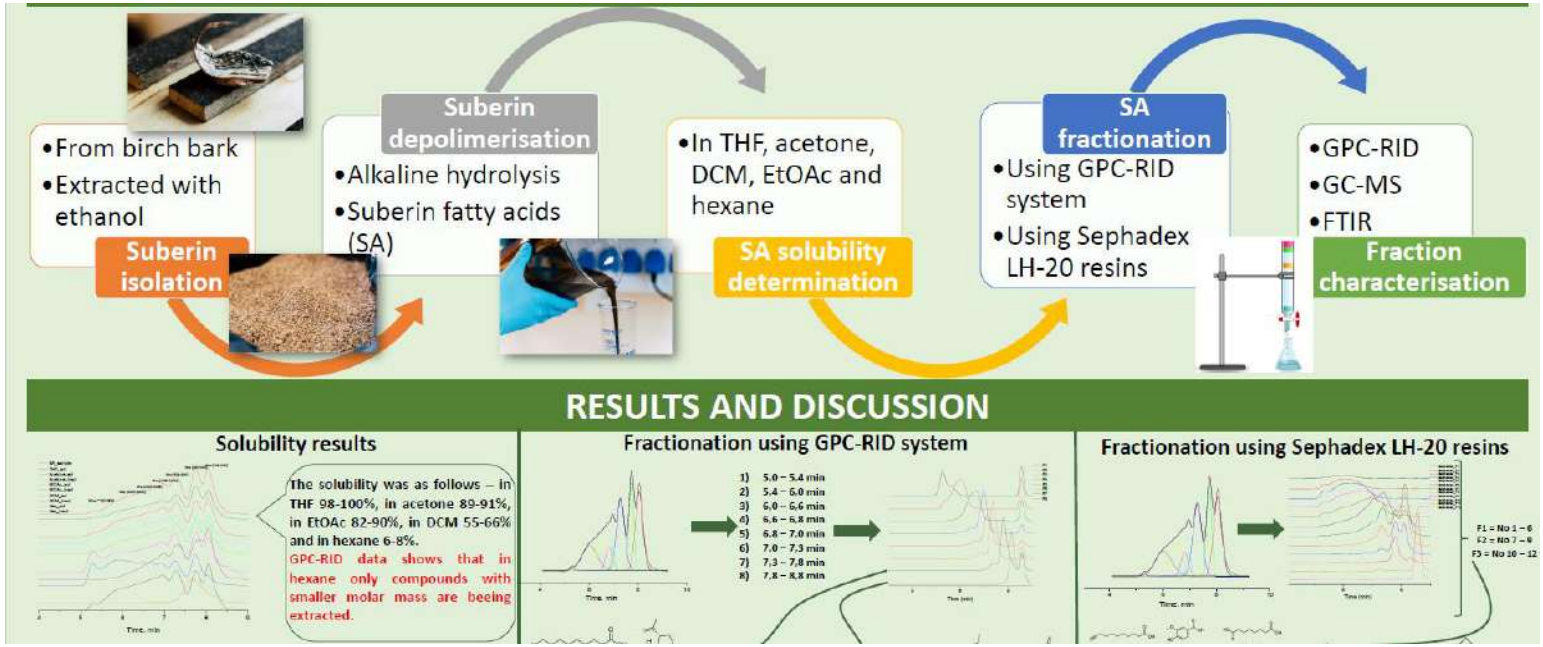
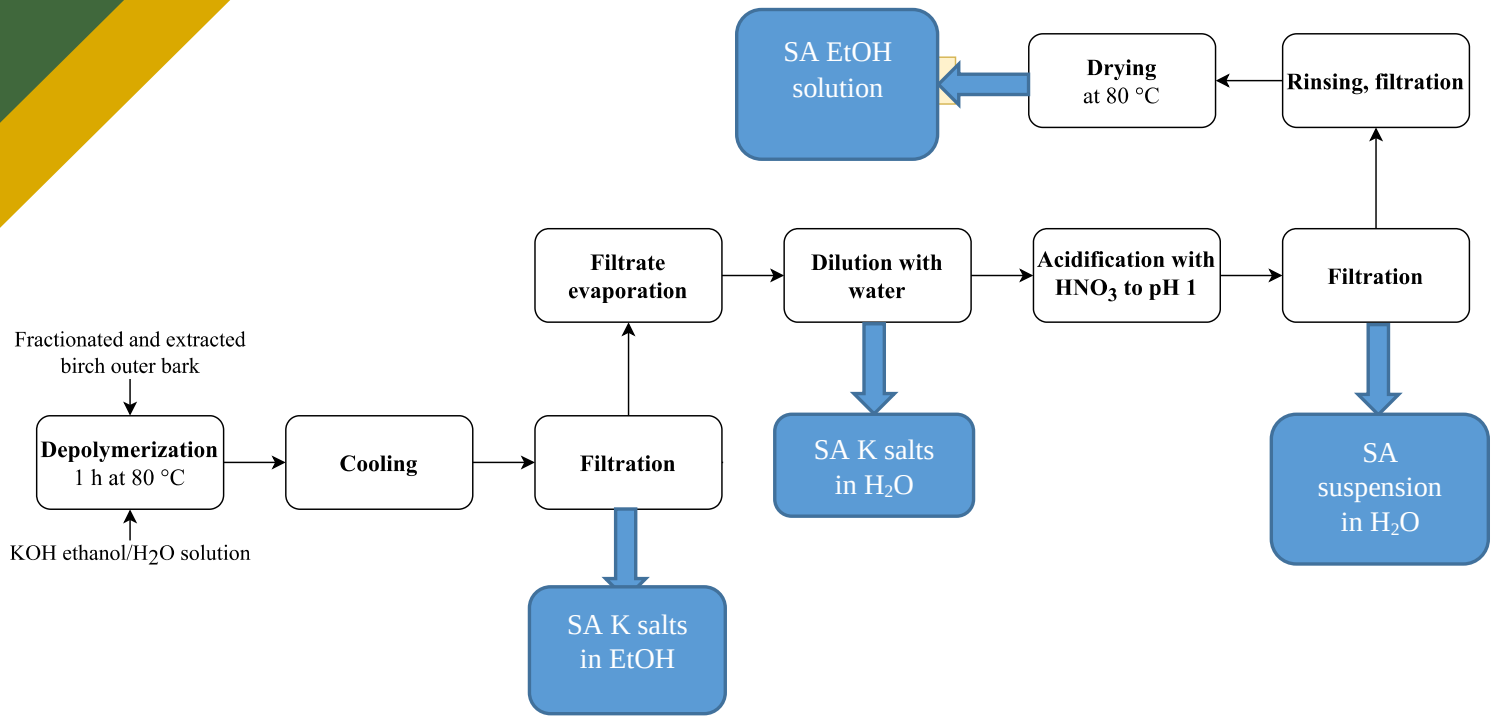
SUBERINIC ACID FRACTIONATION



- ✓ Varying the polarity of solvent it is possible to drastically change the composition of the corresponding fractions
- ✓The use of non-polar solvents allows to separate condensed high molecular weight fraction
- ✓The use of semi-polar solvents separate the low molecular monomeric fraction mostly consisting of free C18 hydroxyl acids, and various phenolic type compounds
- ✓Fractionating sample with Sephadex LH-20 resins, it is possible to obtain fractions with varying molecular weight that can be used in different applications – impregnation, coating or polymeric synthesis

Impregnation



Four SA solution liquid products as samples for impregnation were prepared:

1) SA potassium salts in ethanol (solid content 7%) – SAK-EtOH;

2) SA potassium salts in water (solid content 7-8%) – SAK-H2O;

3) SA suspension in H2O (solid content 7%) – SAS-H2O;

4) Dried SA and diluted in ethanol (solid content 7%) – DSA-EtOH.

For each impregnation 10 *Radiata Pine* (NIBIO) wood samples were chosen with the closest density profile.

“BarkBuild – Tree bark as a renewable source of wood protection materials for building applications (ES RTD/2022/14 within ERA-NET Cofund Action “ForestValue – Innovating the forest-based bioeconomy”). Project Bark- Build is supported under the umbrella of ERA-NET Cofund ForestValue by Valsts izglītības attīstības aģentūra (Latvia), Vinnova (Sweden), Ministry of Education, Science and Sport (MIZS). (Slovenia), Academy of Finland, The Research Council of Norway, and The National Science Centre, Poland. ForestValue has received funding from the European Union's Horizon 2020 re-search and innovation programme under grant agreement N° 773324.

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Impregantion
100-200 mbar, 1 h

BarkBuild
ERA-NET Cofund Action "ForestValue — Innovating forest-based bioeconomy"

Fig. 1. Impregnation samples

Fig.2. Impregnation autoclave and samples

Fig.4. Wood blocks after impregnation prepared for drying (left) and cut samples (right)

Three impregnation liquids seems to penetrate into the sample, **except SAK-H2O**. For this sample most probably the solid salt particles blocked the way, what can be observed by the darker color in the longitudinal direction, and it was not able to penetrate also nor in radial, nor in tangential direction.

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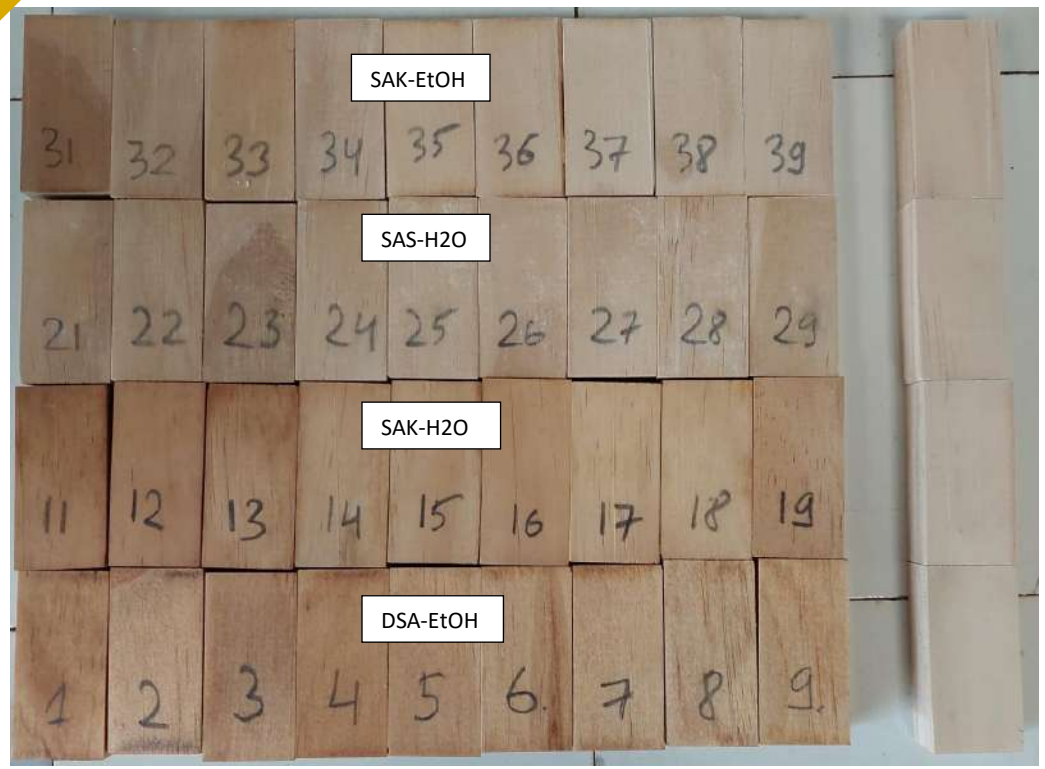
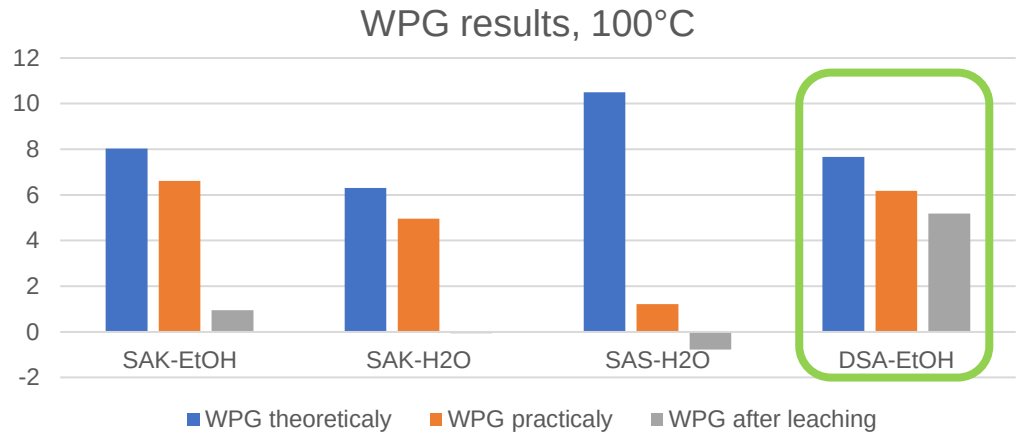
BarkBuild

ERA-NET Cofund Action "ForestValue — Innovating forest-based bioeconomy"

After leaching

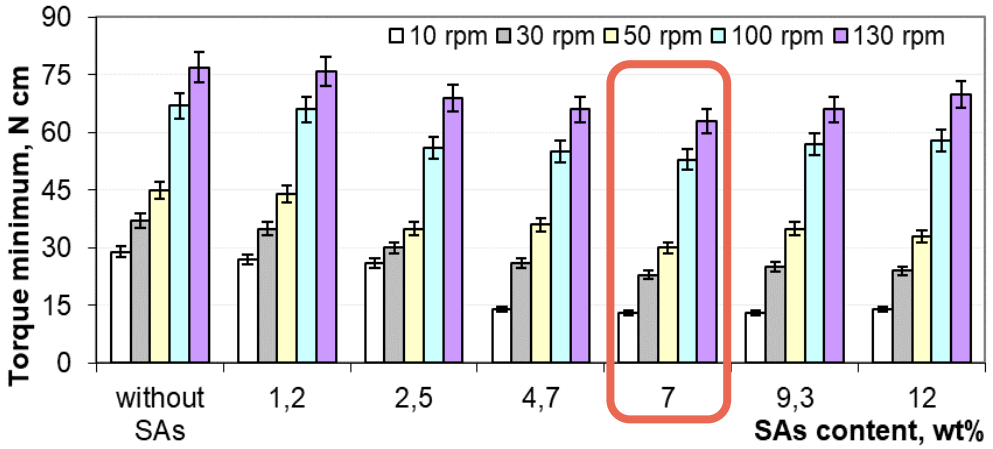




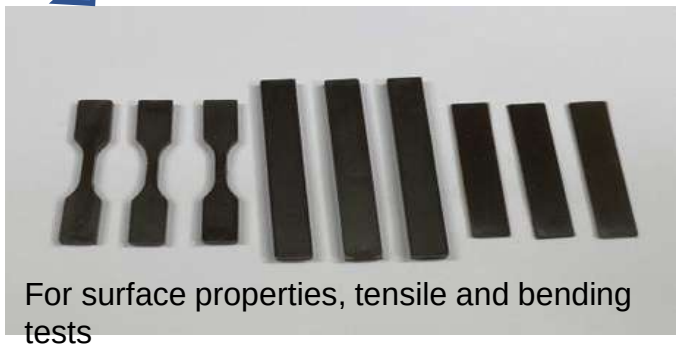
- Salts (SAK-EtOH, SAK-H2O and SAS-H2O) are leached out from the sample.
- SAS-H20 – visually, looks like there are something in the sample, but it is only on the surface. Still maybe this could act as some coating substance
- **DSA-EtOH – the best results – slight mass loss could be explained by the reacting of SA with wood and fixation during drying.**

Suberinic acids in WPC

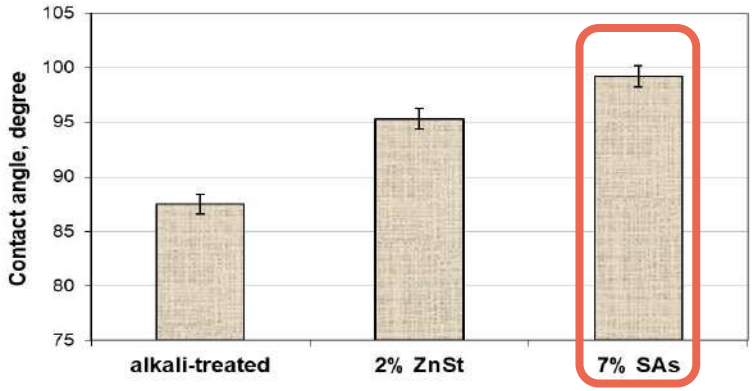
- water suspension with a concentration from 2.5 to 30.0 wt% (dry basis)
- 100 g dried wood particles were processed with 100 ml SAs suspension
- mixed manually for 3-5 min
- dried at 60 °C
- added to the rPP/PLA polymer matrix
- 175 °C and a circulation time of 5 minutes in a two-screw extruder
- injection molding at 120 °C



Extrudates of the biocomposite obtained without (A) and with SAs (B).



For surface properties, tensile and bending tests



- ✓ **More effective lubricant than ZnSt at the optimal content in the WPC sample.**
- ✓ **decrease the wettability of the composite, performing the function of an adhesion enhancer.**

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Potential of suberinic acids

- ✓ Polar and nonpolar adhesion
- ✓ Suberinic acids exhibit good adhesive properties, including high bonding strength, water resistance, and compatibility with various hydrophylic materials
- ✓ The incorporation into polymers can enhance their properties and provide additional functionalities (mechanical strength, enhanced barrier properties, increased thermal stability, and resistance to moisture and chemicals)
- ✓ Exhibit antioxidant and antimicrobial properties
- ✓ Superior friction-reducing agents – lubricant in WPC
- ✓ An interphase modifier between the hydrophilic wood particles and polymer matrix
- ✓ Enhance the dimensional stability of WPCs by reducing the effects of moisture and temperature variations
- ✓ As bio-based additives derived from renewable non-food plant sources, suberinic acids offer an environmentally friendly alternative to conventional additives

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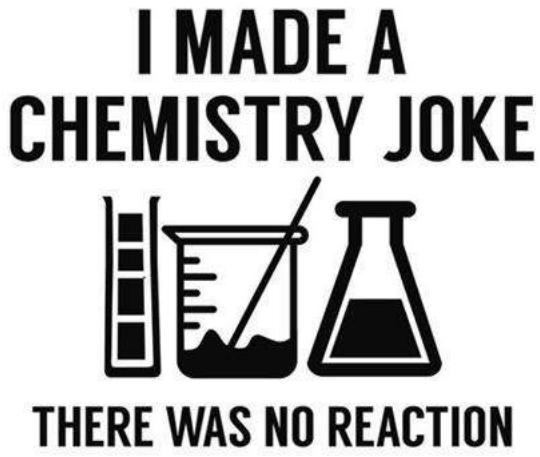
- ✓ Skills
- ✓ Knowledge
- ✓ Experience
- ✓ Infrastructure
- ✓ Research staff
- ✓ Access to academic databases
- ✓ Contacts with industry
- ✓ Ambitions



Hoping for reaction!

- ✓ Eco-Cosmetics - skin smoothing;
- ✓ Bio-Polymer industry - glues, coating agents, epoxides, emulsifiers, plasticizers, polyols, lubricants, 3D inks, WPC.
- ✓ Bio-Based raw material for organic synthesis
- ✓ Bio-composites – plywood, particleboards, fibreboards
- ✓ Eco-Houses

Thank You!

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