Johan Gadolin
PROCESS CHEMISTRY CENTRE

Åbo Akademi University

Value-added products from hemicellulose - opportunities and boundary conditions

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Åbo Akademi University

Possibilities of hemicellulose in biorefining – webinar by XAMK
06. April. 2022

cxu@abo.fi

Laboratory of Natural Materials Technology 2019-

naturmaterialteknik

Prof. X.Y. & Dr. Jan Gustafsson
Fibre and Cellulose Technology
www.abo.fi/fct
Biomass engineering & topochemistry


Prof. Chunlin Xu & Dr. Anna Sundberg
Wood and Paper Chemistry
www.abo.fi/traochpapperskemi
Molecular process technology & analysis


Prof. Martti Toivakka & Dr. Mari Nurmi
Paper Coating and Converting
www.abo.fi/LPCC
Surface engineering for functional natural fiber-based products


- ~20 active doctorate students
- ~6 post doc researchers
- 40 peer-reviewed journal articles/year
- ~45 PhD-degrees during 2010-2020
- 2 previous Academy of Finland Centers of Excellence:
  - Process Chemistry Center
  - Center for Functional Materials

Education at NMT:

- Biomass chemistry and modification
- Biorefinery technology
- Paper and board coating, converting, and printing

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Wood and Paper Chemistry
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Molecular process technology & analysis

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Surface engineering for functional natural fiber-based products

Fibre and Cellulose Technology
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Biomass engineering & topochemistry

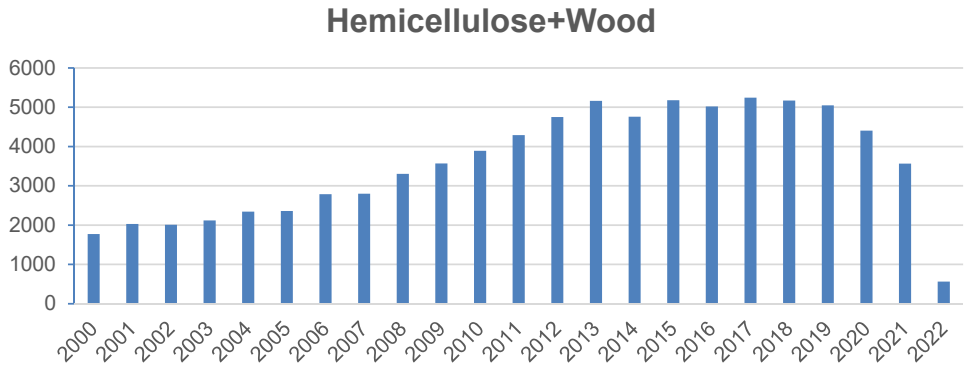
List of contents

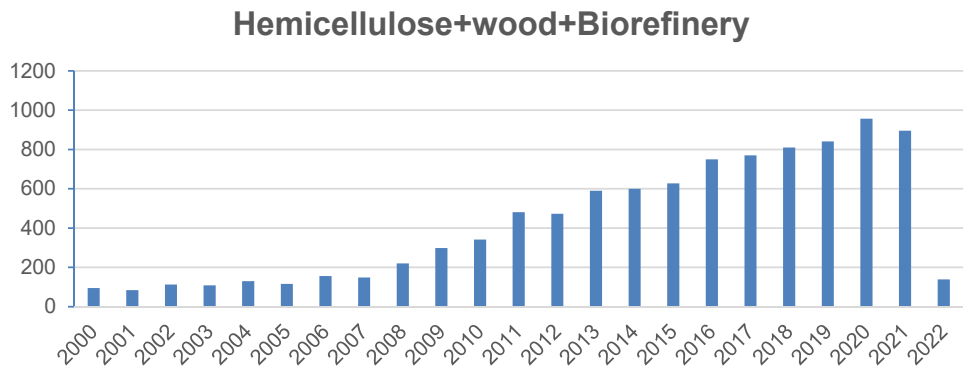
- Background on hemicellulose research
- Overview of hemicelluloses research at Åbo Akademi
- Fractionation of hemicelluloses
- Solution properties
- Application in packaging
- Application in 3D printing

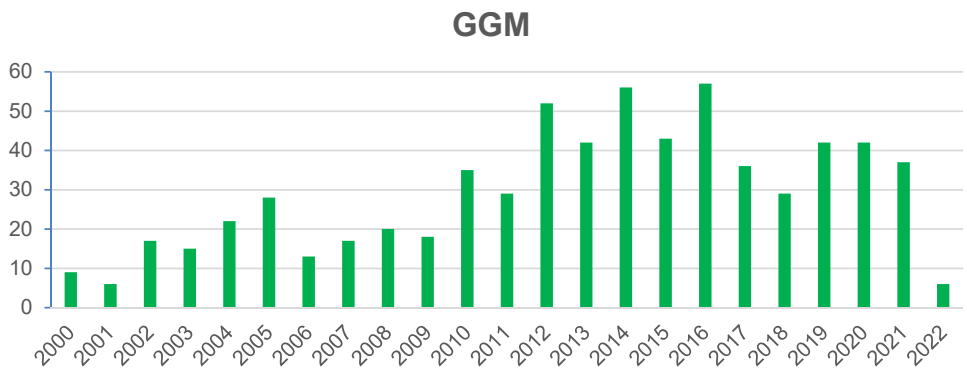
Hemicelluloses and availability

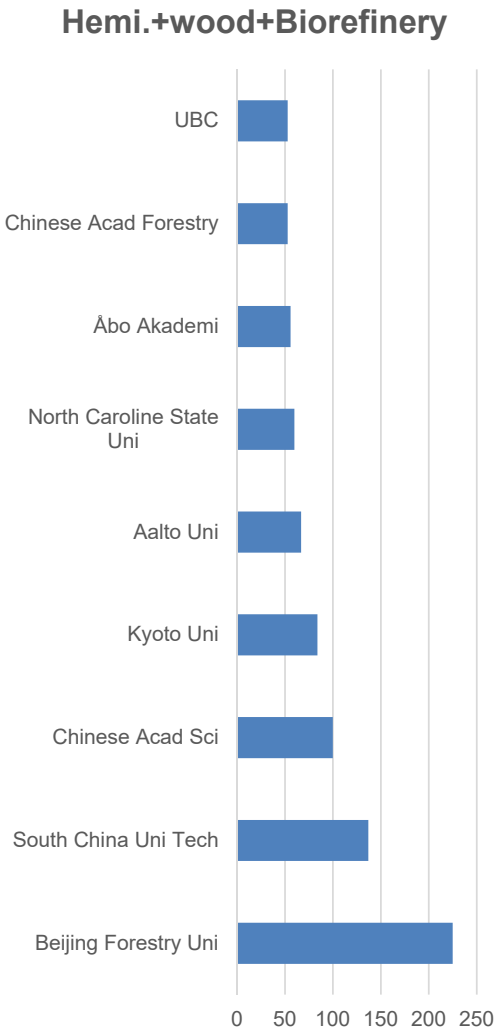
- **Mannans**
  - O-acetyl-galactoglucomannans (GGM) in softwoods, 20-25%
  - Glucomannans in hardwoods, only 2-5%
- **Xylans**
  - Arabino-4-O-methylglucuronoxylan in softwoods, 5-10%
  - O-acetyl-4-O-methylglucuronoxylan in hardwoods, 15-30%

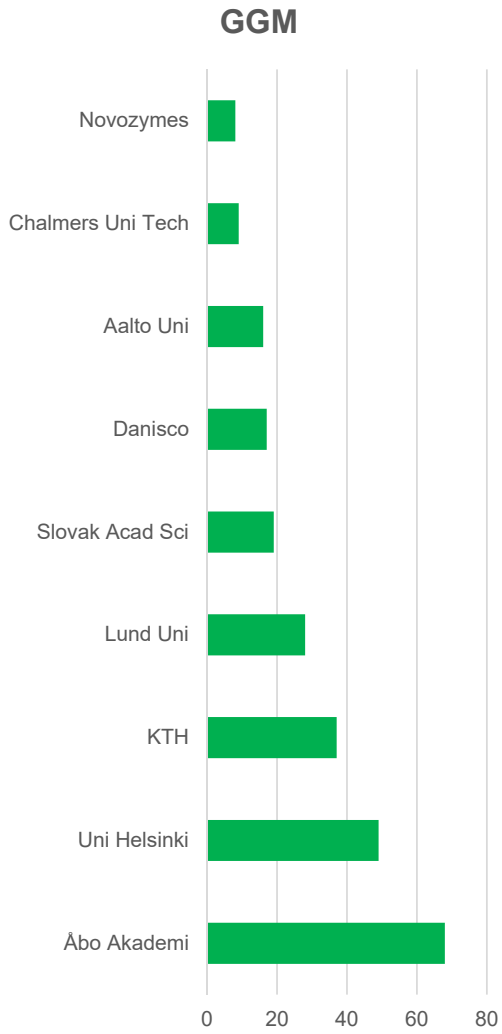
- Wood pulp production in Finland in 2019: **11.595 mill. tons**
  - Mechanical pulp: 3.275 mill. tons
  - Chemical pulp: 8.320 mill. tons
  - Bleached softwood pulp: 4.628 mill. tons
  - Other pulp: 3.692 mill. tons
- Forest stock volume in 2016: 2464 mill.m^3
  - Annual Increment: 110 mill.m^3
  - Sustainable felling potential: **84 mill.m^3**
  - Current commercial consumption: 73.6 mill.m^3


Hemicellulose+Wood
6000
5000
4000
3000
2000
1000
0
2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022


Hemicellulose+wood+Biorefinery
1200
1000
800
600
400
200
0
2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022


GGM
60
50
40
30
20
10
0
2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022

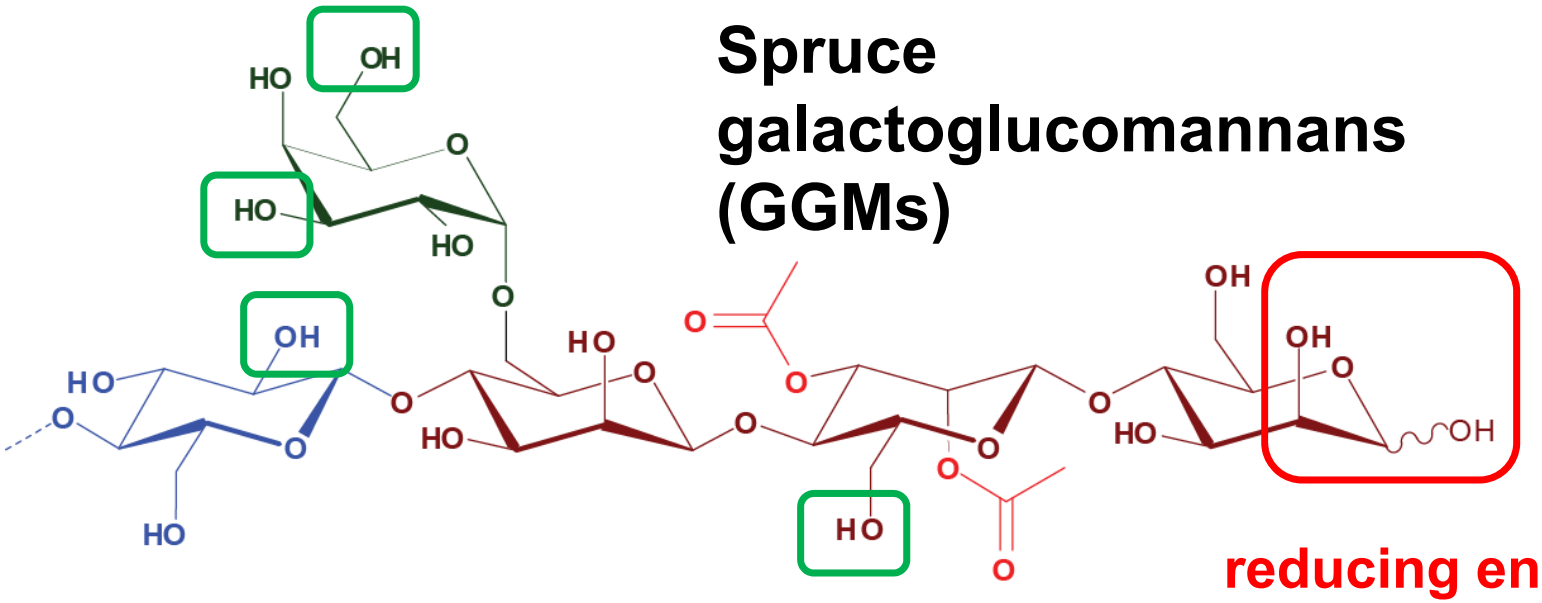

Hemi.+wood+Biorefinery
UBC
Chinese Acad Forestry
Åbo Akademi
North Caroline State Uni
Aalto Uni
Kyoto Uni
Chinese Acad Sci
South China Uni Tech
Beijing Forestry Uni
0 50 100 150 200 250


GGM
Novozymes
Chalmers Uni Tech
Aalto Uni
Danisco
Slovak Acad Sci
Lund Uni
KTH
Uni Helsinki
Åbo Akademi
0 20 40 60 80

Projects involving hemicelluloses

- Wacheup - new concepts for upgrading pulp mill waste streams to values - added chemicals, EU FP6-NMP, 2005-2008 (PI Bjarne Holmbom)
- HEBIKA - Biodegradable films from hemicelluloses – production and properties, Tekes, 2004-2006 (PI Stefan Willför)
- FunMan - Targeted Functionalization of Spruce Galactoglucomannans with Aid of Galactose Oxidase, Academy of Finland, 2007-2010 (PI Stefan Willför)
- HemU - Extraction of Hemicelluloses from Wood with Pressurised Water (HemU), Tekes, 2008-2011(?) (PI Bjarne Holmbom)
- FuBio “Forestcluster Ltd. Future Biorefinery”, Tekes, Forestcluster Ltd. & industry, 2009-2011 (PI Stefan Willför)
- FuBio JR2 “Forestcluster Ltd. Future Biorefinery: FuBio Joint Research 2 Research Program”, Tekes, FIBIC Ltd. & industry, 2011-2014 (PI Stefan Willför)
- BITE - Novel biomass-based solutions for technical emulsions, Tekes, 2015-2018 (PI Stefan Willför)
- TuneScaffolds - Design of biobased extracellular matrix-mimicking scaffolds with tuneable rigidity for 3D cell culture and potential tissue engineering, Academy of Finland, 2016-2020 (PI Stefan Willför)
- Healing the wounds with the Finnish Woods: Conductive hydrogel scaffolds of cellulosic nanomaterials and polysaccharide biopolymers for delivery of bioactive cues in soft tissue engineering, JAES, 2019-2022 (PI Xiaoju Wang)
- SUSBINCO - Sustainable Binders and Coatings, Business Finland, 2021-2023 (PI Chunlin Xu)
- AI-4-LCC - Exploiting Lignin-Carbohydrate Complex (LCC) through Artificial Intelligence, Academy of Finland, 2021-2025 (PI Chunlin Xu)

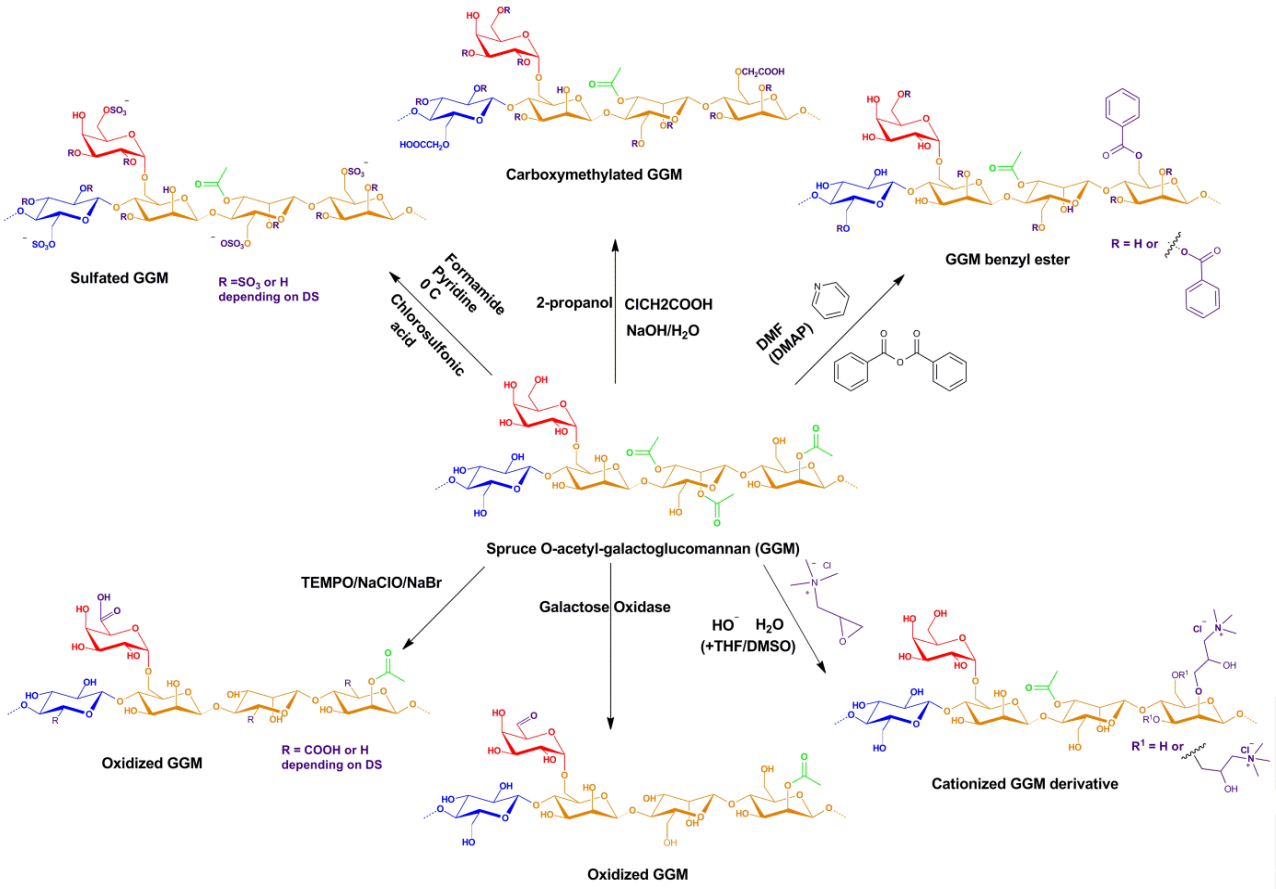
Wood biopolymer: hemicelluloses



Man : Glc : Gal ~ 4 : 1 : 0.5

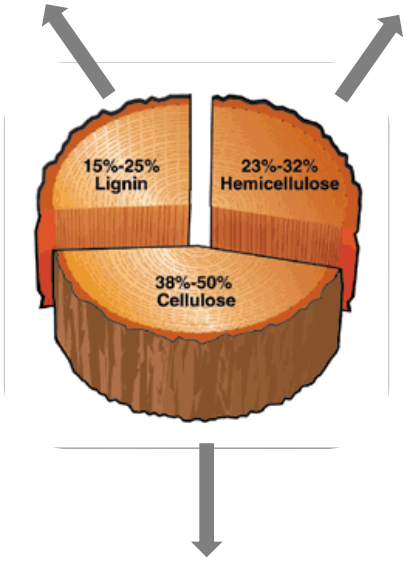
Chemistry as a tool: Derivatization of hemicelluloses

- **Chemical and enzymatic modifications:**
  - Carboxymethylation/ dispersants
  - Hydrophobization/barriers for food packaging
  - Regioselective modification e.g. allylation/ molecular anchor for fiber surface modification in paper diagnostics
- **Copolymerization:**
  - Grafting of fatty acids/amphiphilic copolymers in surface coating and as stabilizer for emulsions
  - GGM-based hydrogels for water treatment
  - Scaffold and composites



Fractionation

Biorefinery



Lignin nanoparticles

Functionalized polysaccharide derivatives

Hemicellulose

Lignin

Cellulose

Other biochemicals

Nanocelluloses

Fractionation: Pilot-scale of isolation of GGM

TMP

Paper Machine

Paper

Ultrafiltration

GGM conc.

Speciality products

Effluent treatment

Fractionation of hemicelluloses

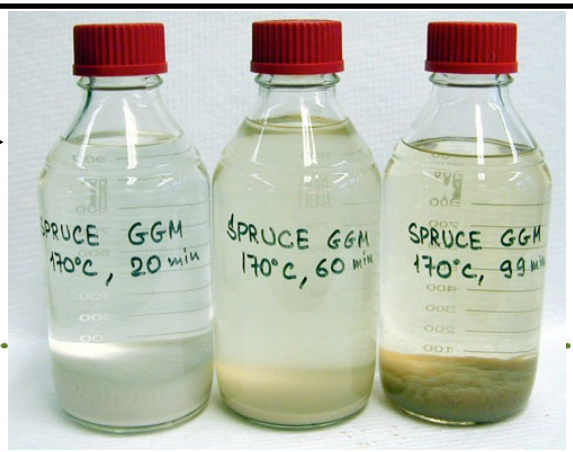
- Sources
  - Wood chips
  - Treated pulps
- Solvent
- pH control
- Temperature control and pressure control
- Treatments
  - Acidic treatment
  - Alkali treatment
  - Addition of surfactants
- Reactor type

Case: Pressurized hot-water extraction of wood

Fresh spruce sapwood

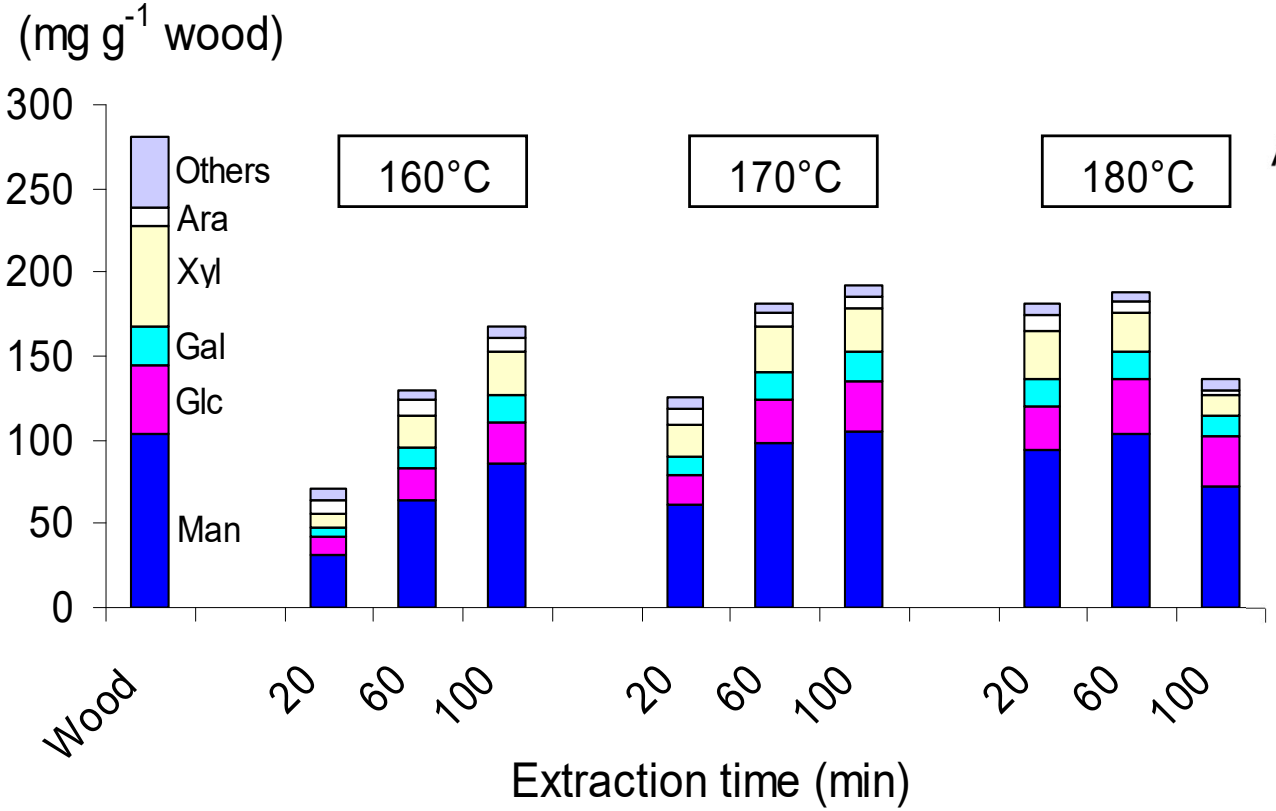
Hand-cut chips or ground wood

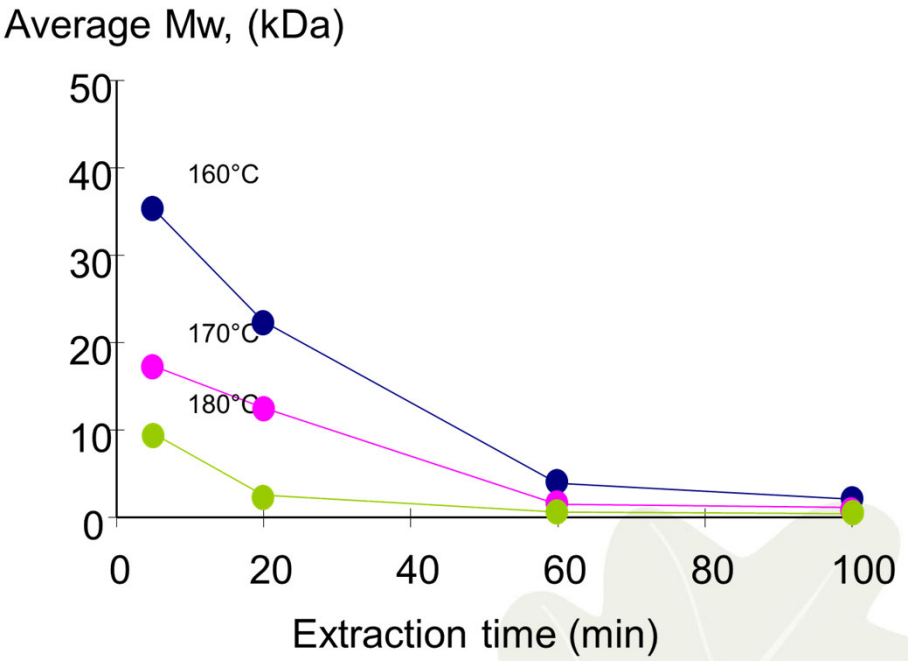
Accelerated Solvent Extractor (ASE)



Analyses

Hot-water extraction of ground spruce wood

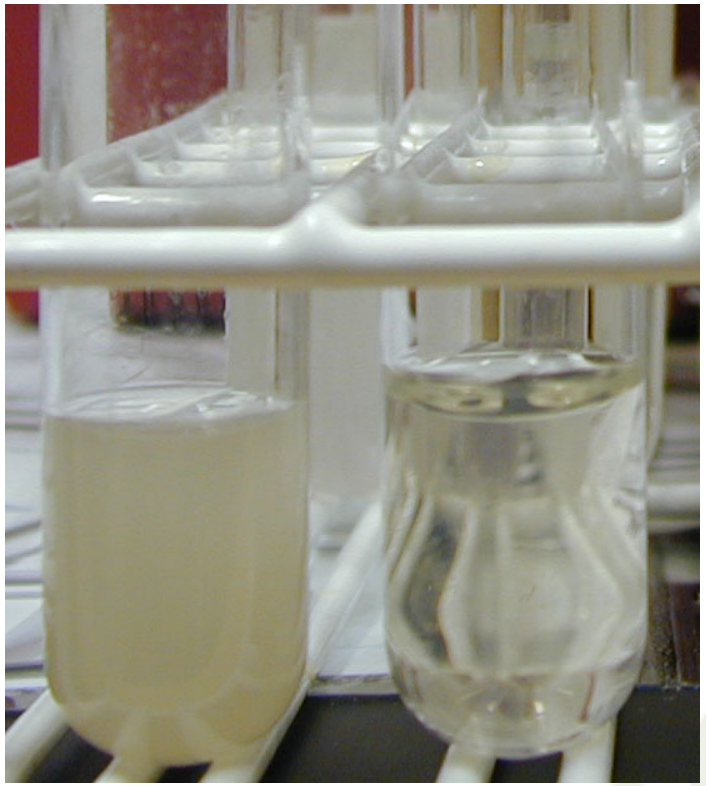




Song et al. 2008, Holzforschung 62, 659-666.

Solution properties of hemicelluloses

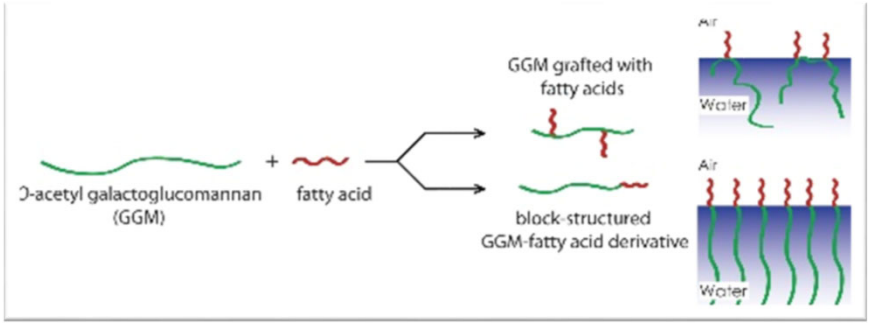
- Solubility
  - Depending on the isolation processes
- Surface activity
  - Surface active when phenolic residues are present
- Modification to tailor the amphiphilicity



Amphiphilic hemicellulose derivatives based on naturally occurring fatty acids

- **Amphiphilic hemicellulose derivatives**
  - Can be prepared by grafting FAs
  - Are surface active
  - Their surface tension can be tailored to meet the dispersing ability need in coating application

Business Finland Co-Innovation: Sustainable Binders and Coatings (SUSBINCO): To produce sustainable compounds and materials from bio-based raw materials for aqueous dispersion coating, 2021-2023

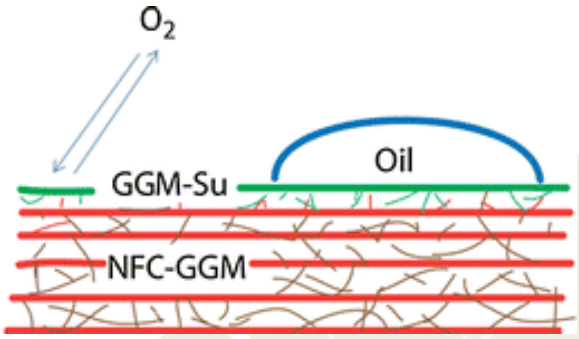


Surfactant	CAC (mg/mL)	γ_{min} (mN/m)	Γ (mol/m²)	A (Å²)
GGM	-	68.8	-	-
GGM-*g*-C9 (0.80)	1.28	55.0	1.5	111
GGM-*g*- C9 (1.53)	1.00	50.0	1.6	102
GGM-*g*- C9 (2.23)	1.22	44.4	1.7	99
GGM-*g*-C14 (0.82)	0.77	57.3	1.2	143
GGM-*g*-C14 (1.14)	ND[a]	<51.2	1.6	102
GGM-*g*-C14 (1.95)	0.78	51.1	1.8	94
GGM-*g*-C18 (0.68)	ND[a]	<56.8	1.4	117
GGM-*g*-C18 (1.07)	ND[a]	<61.3	0.8	214
GGM-*g*-C18 (1.42)	ND[a]	<61.0	0.9	175
GGM-*b*-C9	2.44	44.5	2.3	73
GGM-*b*-C14	1.82	47.11	1.4	111
GGM-*b*-C18	0.88	49.5	1.7	96

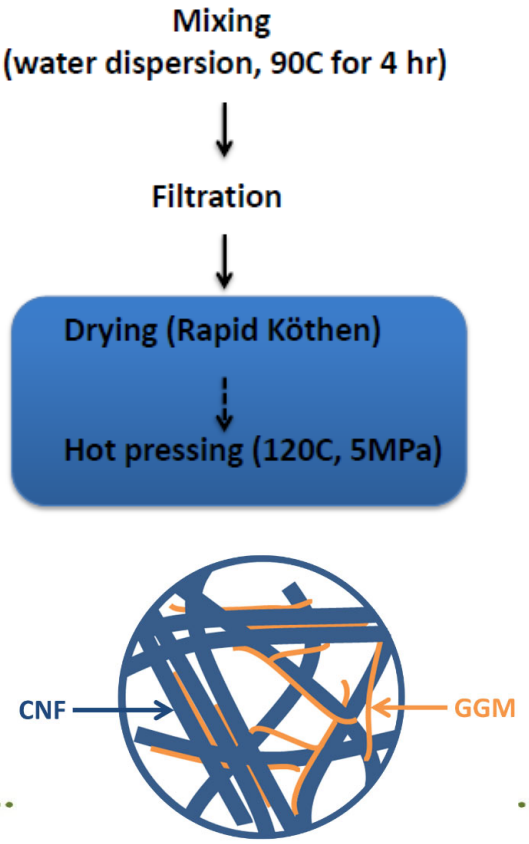
BioResources. 8, 3, p. 3771–3790 (2013)

Hemicelluloses in packaging

- Films of GGM mixed with other polymers have a potential in food packaging
- GGM coating reduce paper porosity and provide excellent grease resistance
- Biomimetic composites of nanocellulose and GGM provide new enhanced properties



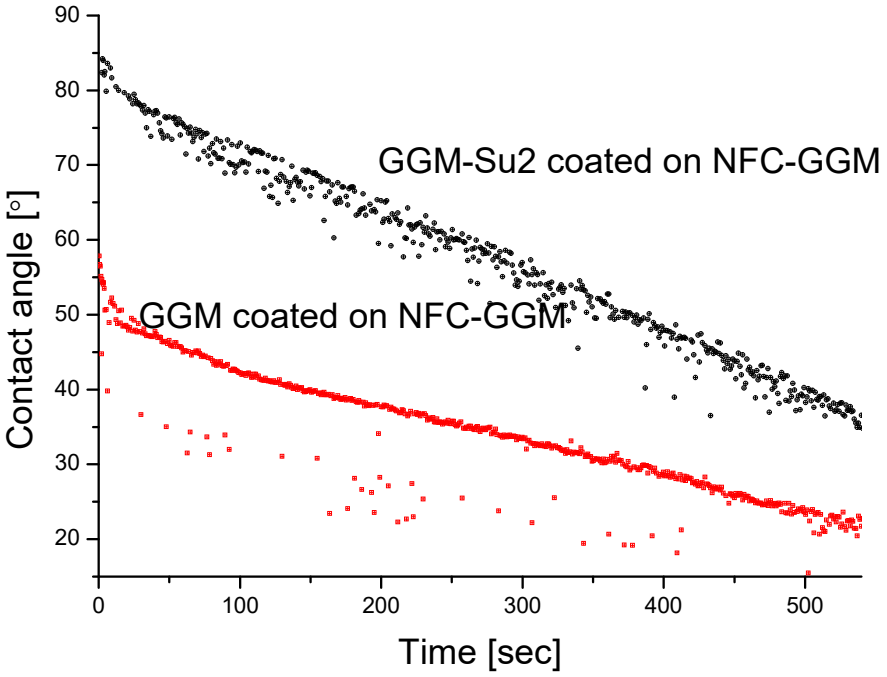
Composites of nanocellulose and spruce GGM

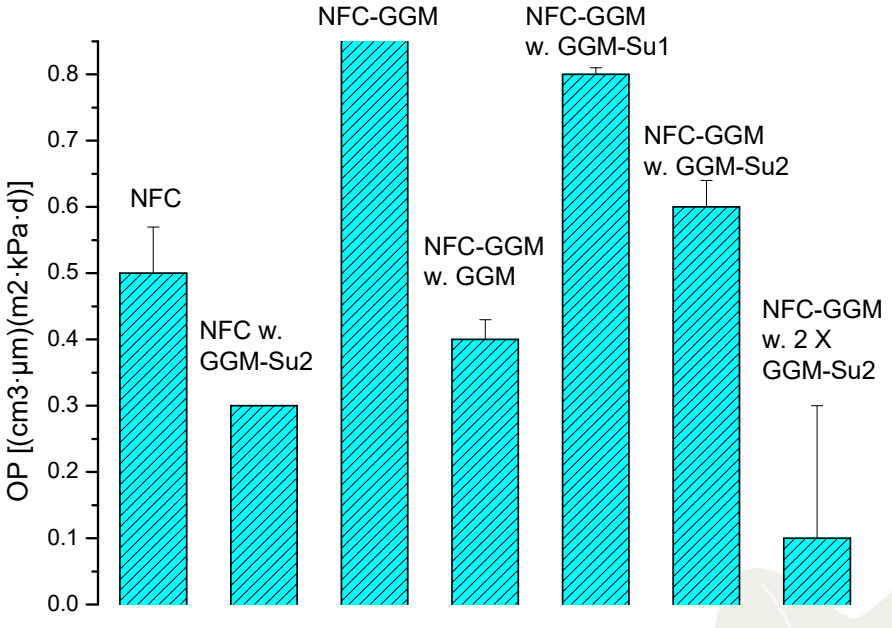


Wet gels	Solid content (%)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation (%)	Work of fracture (kJ/m^3)
CNF	14.9	4.1 (0.5)	0.11 (0.04)	9.2 (2.1)	8.2 (3.0)
CNF/GGM 5.6 wt%	15.1	5.9 (2.2)	0.15 (0.03)	8.3 (1.0)	7.8 (1.7)
CNF/GGM 10.6 wt%	18.0	21.3 (2.0)	0.33 (0.04)	15.8 (3.0)	46.0 (10.1)
CNF/GGM 13.4 wt%	16.9	28.8 (6.6)	0.65 (0.16)	10.9 (1.3)	50.8 (12.8)

J. Materials Science. 50, 22, 7413–7423 (2015)

Composites of nanocellulose and succinic esters of GGM





J. Mater. Sci.,50, 3189-3199.(2015)

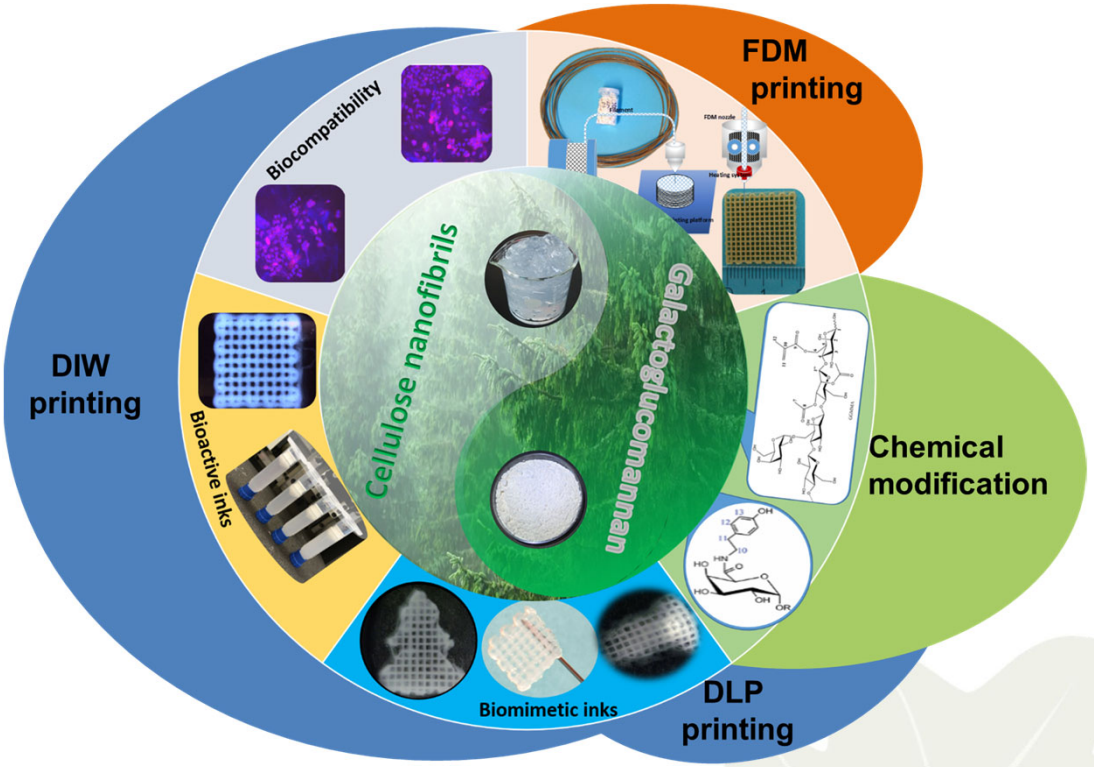
Hemicelluloses in 3D printing

Thermoplastic filaments

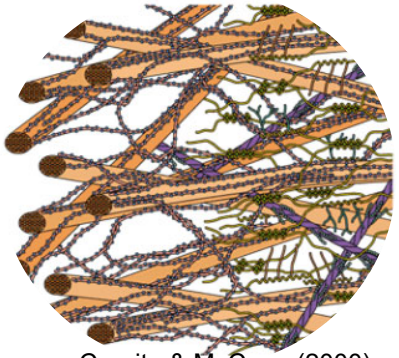
- Fused Deposition Modeling (FDM)

Hydrogel and resins

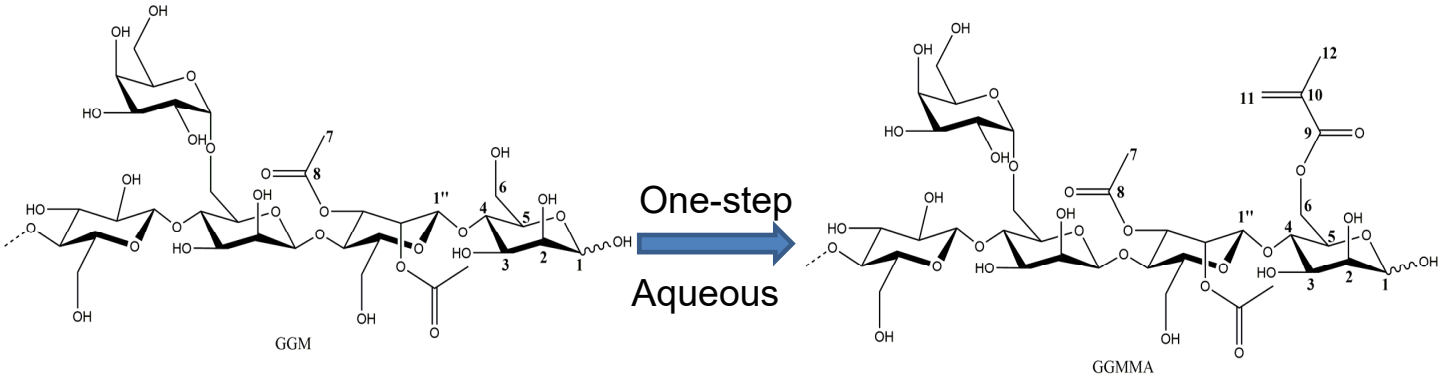
- Direct Ink Writing (DIW)
- Digital Light Processing(DLP)

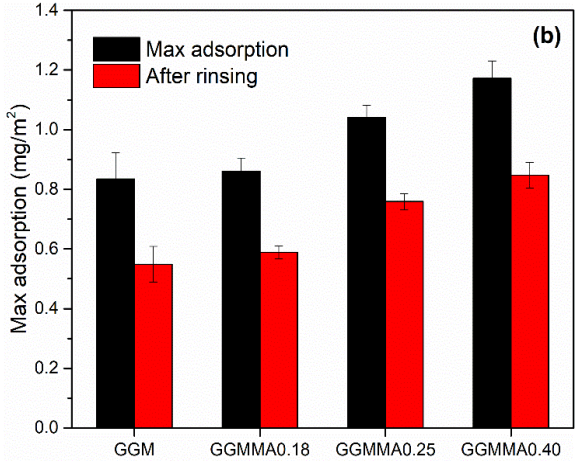


Biomimetic all-wood-ink of CNF and galactoglucomannan methacrylates (GGMMA)



Carpita & McCann (2000)





Woody heteropolysaccharides: Versatile chemical modifications can introduce functional groups such as- aldehyde, -amine, -methacrylate and -thiol groups onto the sugar units

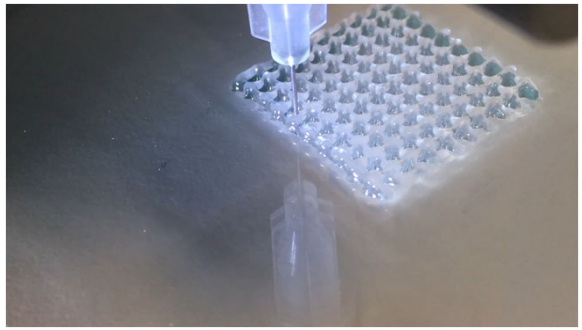
- Aqueous chemistry
- Tunable DS of methacrylation
- Intrinsic affinity to cellulose surface
- Anchoring polymer for engineering the cellulose surface

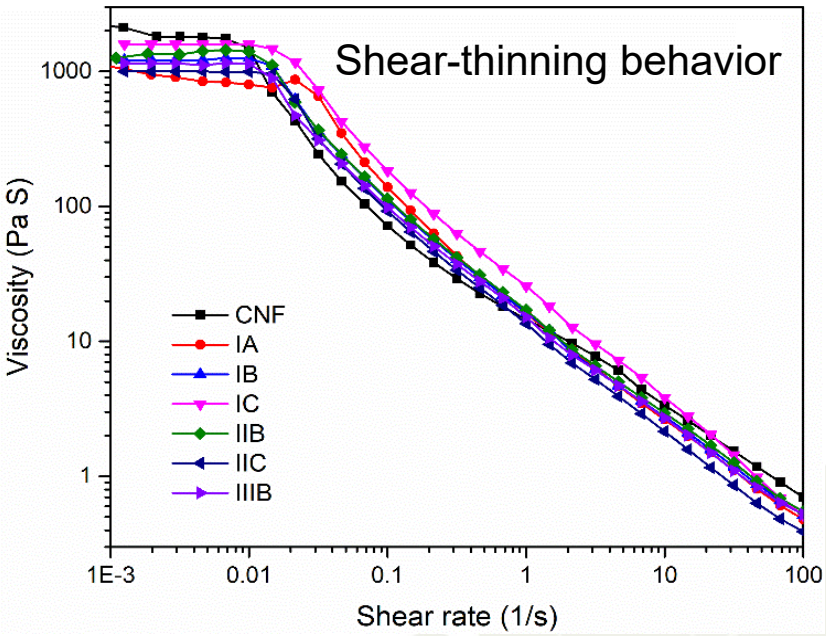
Biomimetic affinity between hemicellulose and nanocellulose is still retained with methacylation in the sugar units

ACS Applied Materials & Interfaces, 11 (13), 12389-12400. (2019)

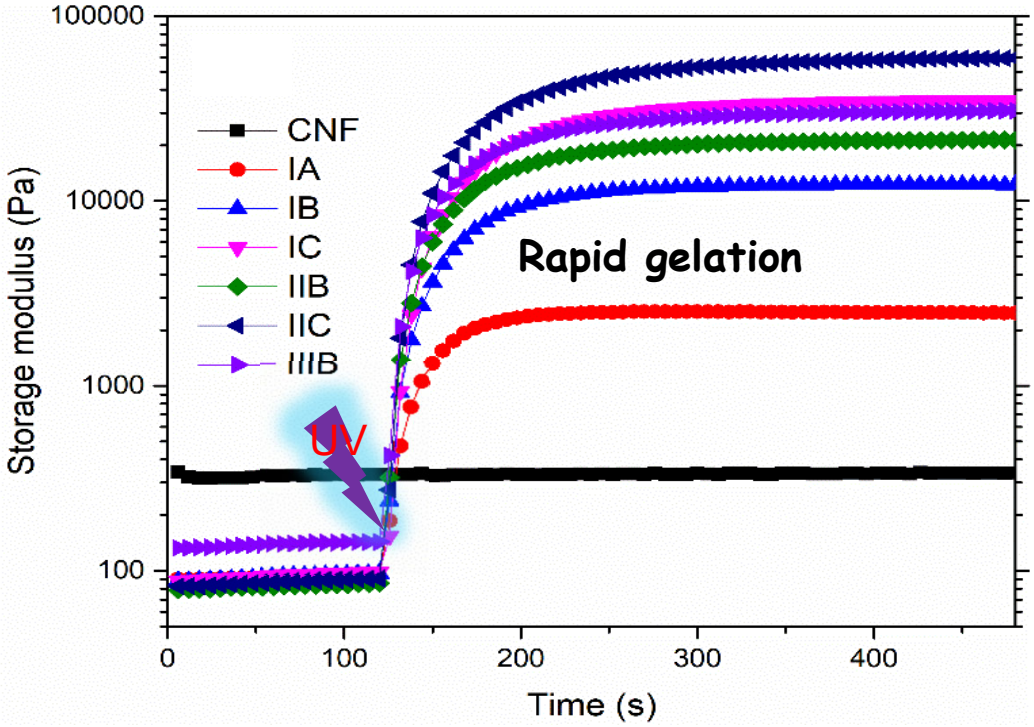
Ink formulation and printablity

Ink	CNF (wt.%)	GGMMA		Compositional ratio of CNF/GGMMA
		Type	Wt.%	
CNF	1		0	-
IA#		GGMMA0.18	1	1:1
IB#			2	1:2
IC#			3	1:3
IIB*		GGMMA0.25	2	1:2
IIC*			3	1:3
IIIB¤		GGMMA0.40	2	1:2

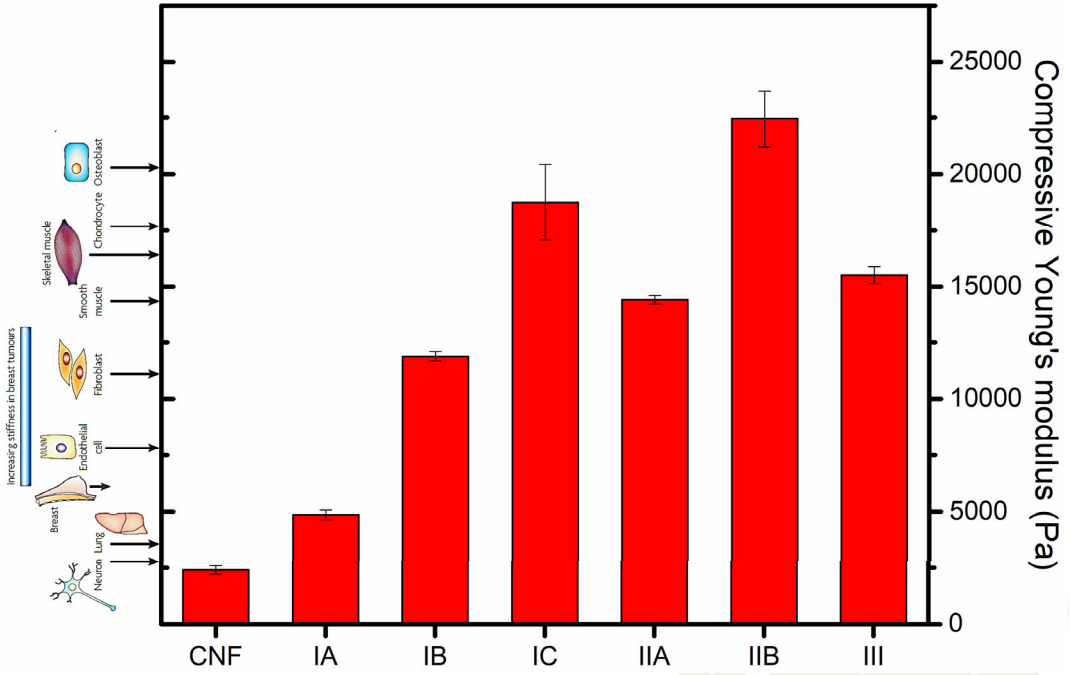




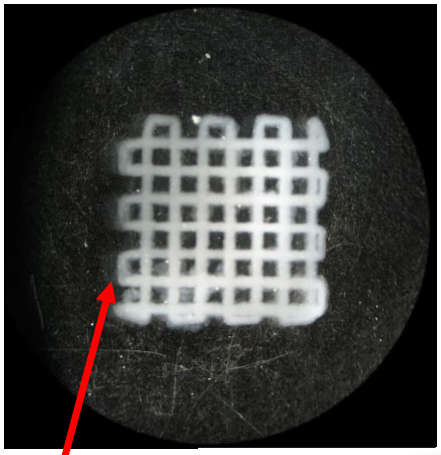
Cross-linking of GGMMA upon UV irrdiation (Photorheology)

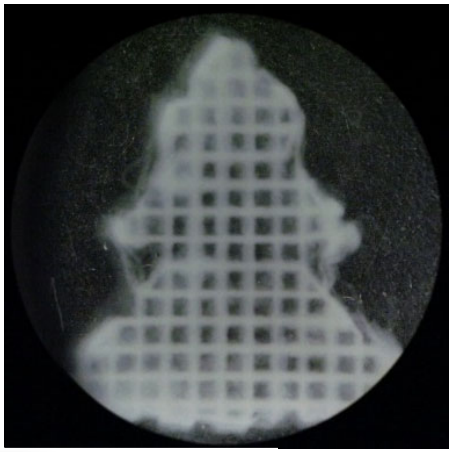


A wide spectrum stiffness suitable for culturing various cell lines in TE context

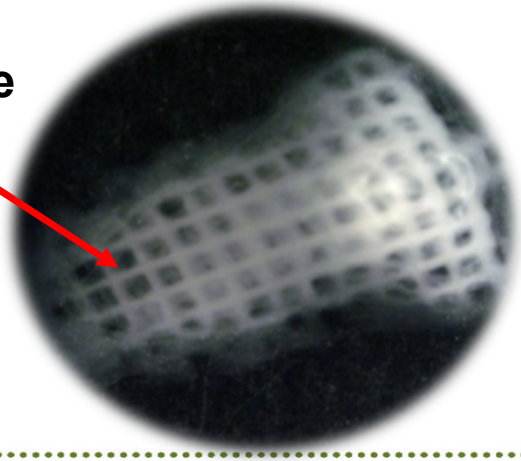


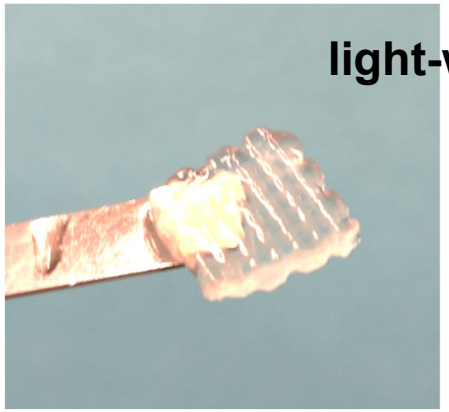
High-resolution printability and light-weight scaffolds



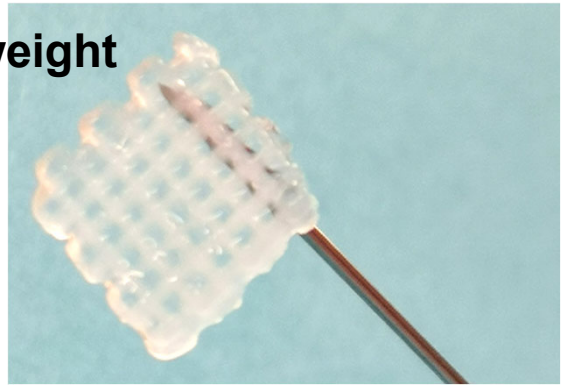


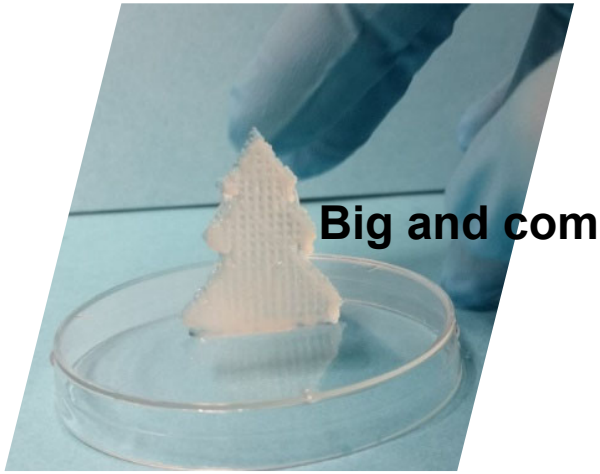
Sharp Edge



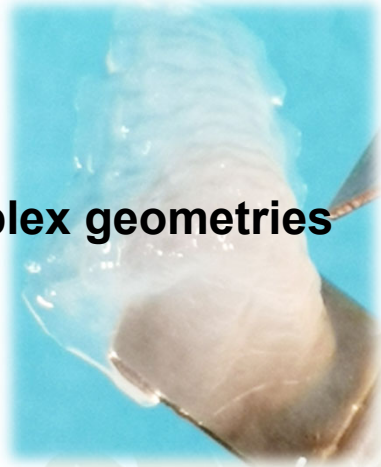


light-weight





Big and complex geometries

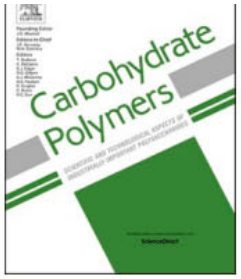


GGMMA-based injectable hydrogels in delivery of therapeutic inorganic ions

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

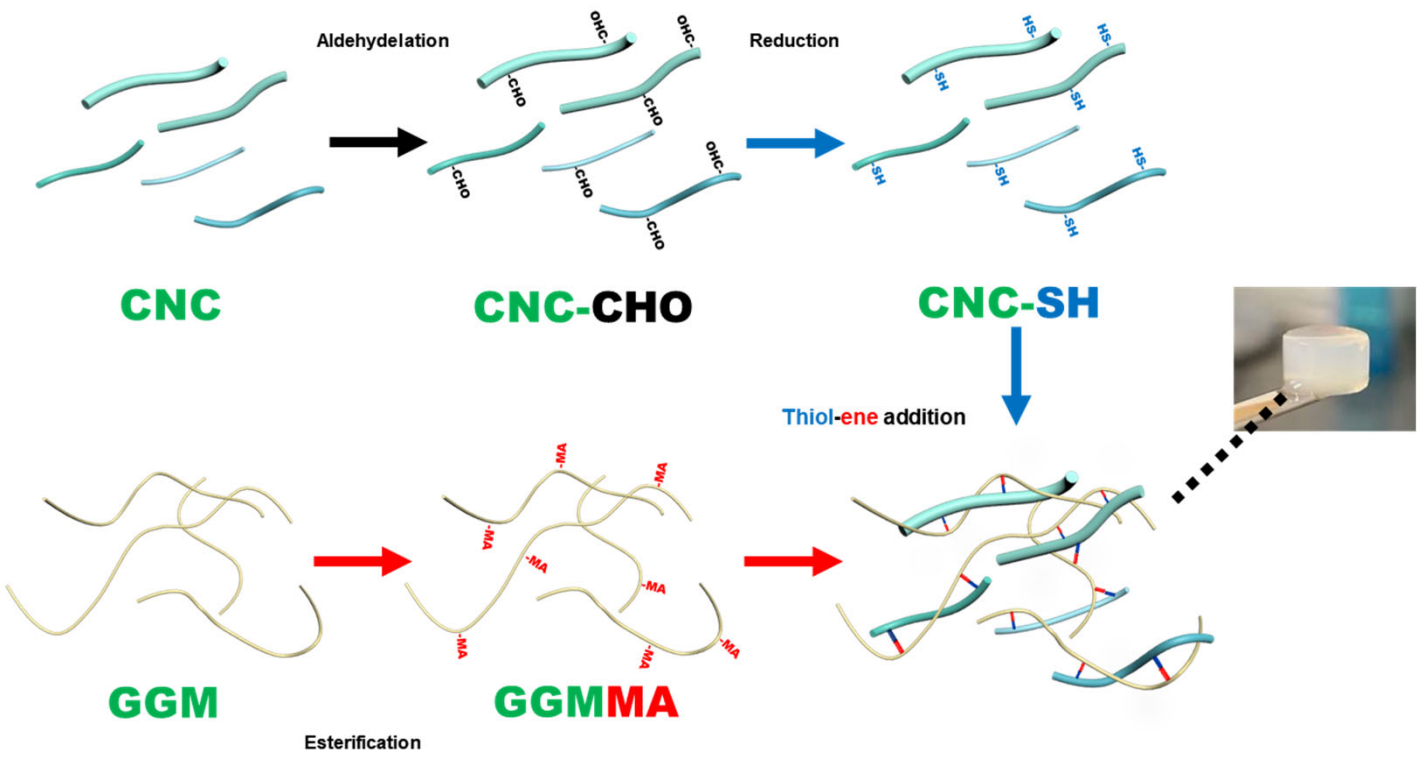


Check for updates

Injectable thiol-ene hydrogel of galactoglucomannan and cellulose nanocrystals in delivery of therapeutic inorganic ions with embedded bioactive glass nanoparticles

Qingbo Wang [a,1], Wenyang Xu [a,1], Rajesh Koppolu [a], Bas van Bochove [b], Jukka Seppälä [b], Leena Hupa [c], Stefan Willför [a], Chunlin Xu [a], Xiaoju Wang [a,d,*]

Fabrication of hydrogel from wood CNC and hemicellulose

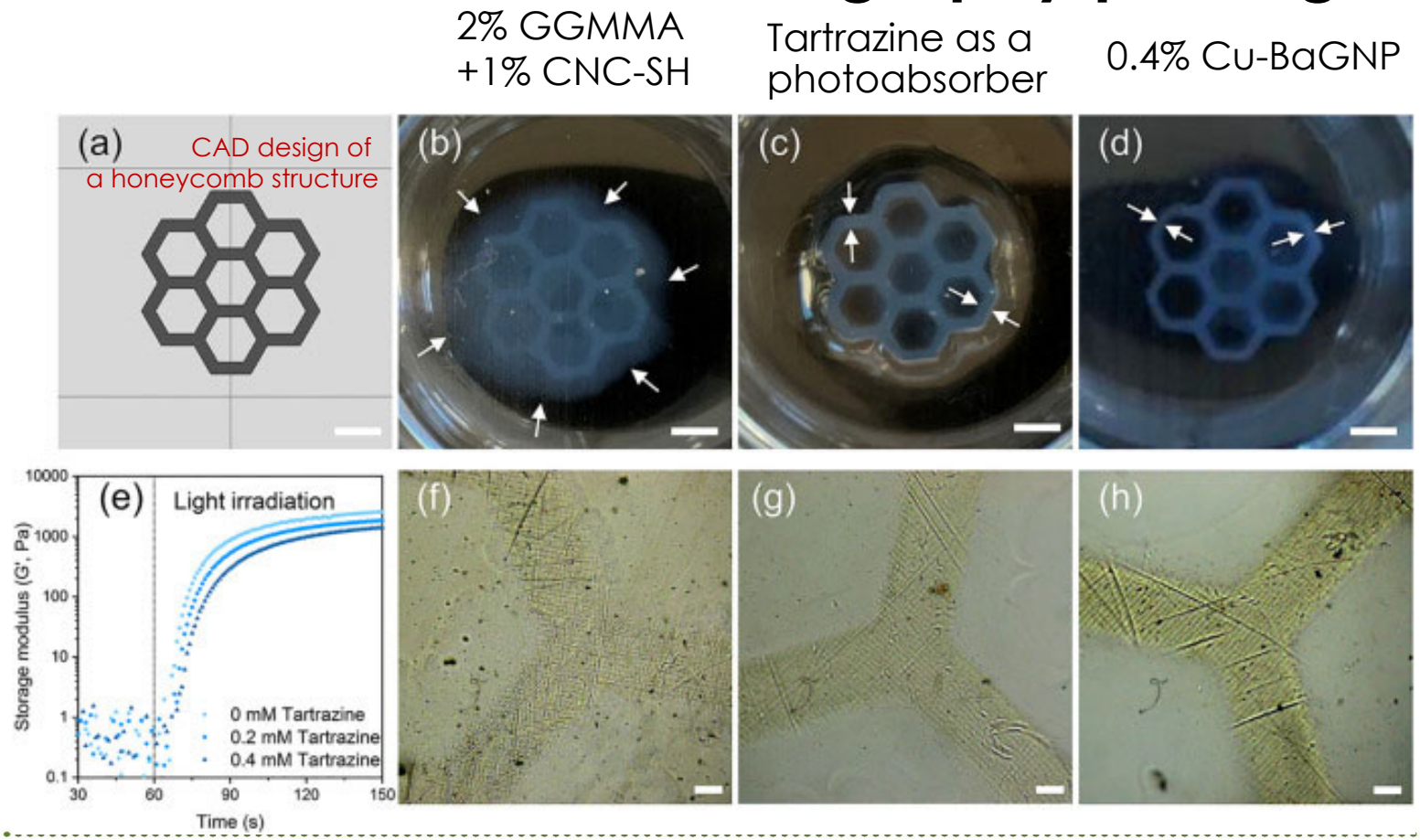


CNC: oxidized to introduce aldehyde, followed by reductive amination to graft SH moiety (L-cysteine)

GGM: esterified to introduce MA moiety

Hydrogel: obtained through light-induced thiol-ene addition.

GGMMA+CNC-SH hydrogel as biomaterial resin in DLP lithography printing

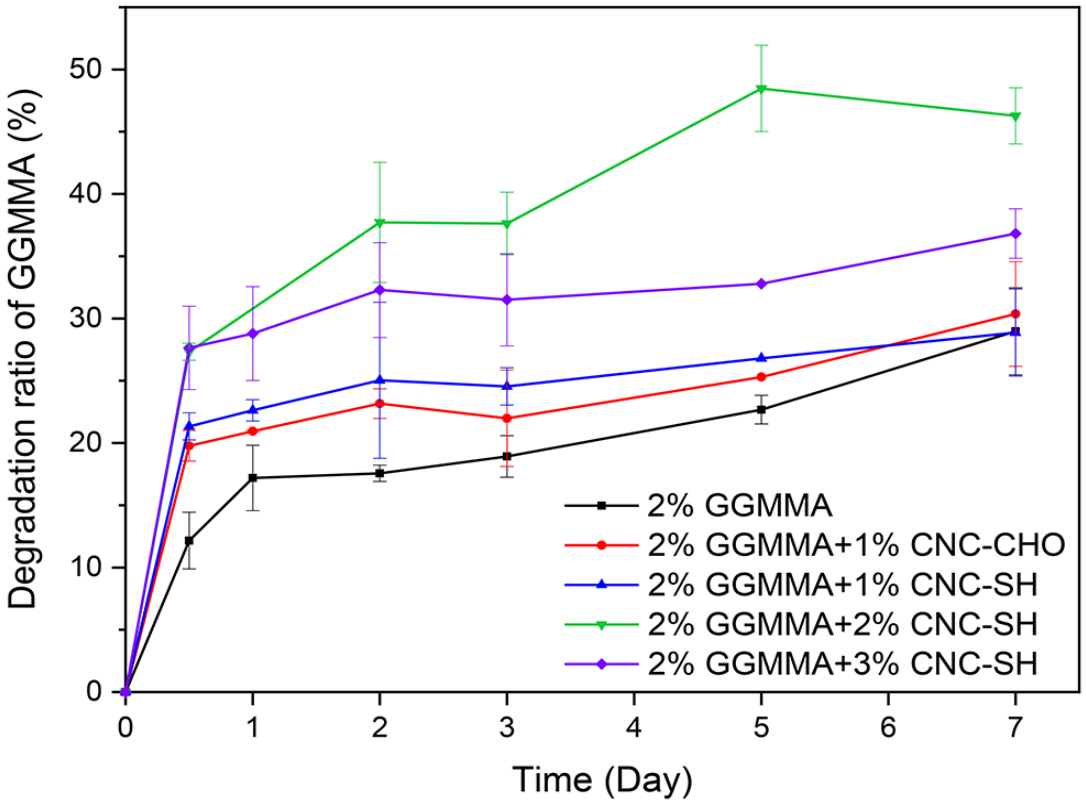


Excess crosslinking was observed in the honeycomb.

Tartrazine was incorporated as a photoabsorber

When encapsulated 0.4% Cu-BaGNP, the printed honeycomb hydrogel with sharp edges also shows good shape fidelity

Mannanase-mediated degradation of the GGMMA/CNC hydrogel

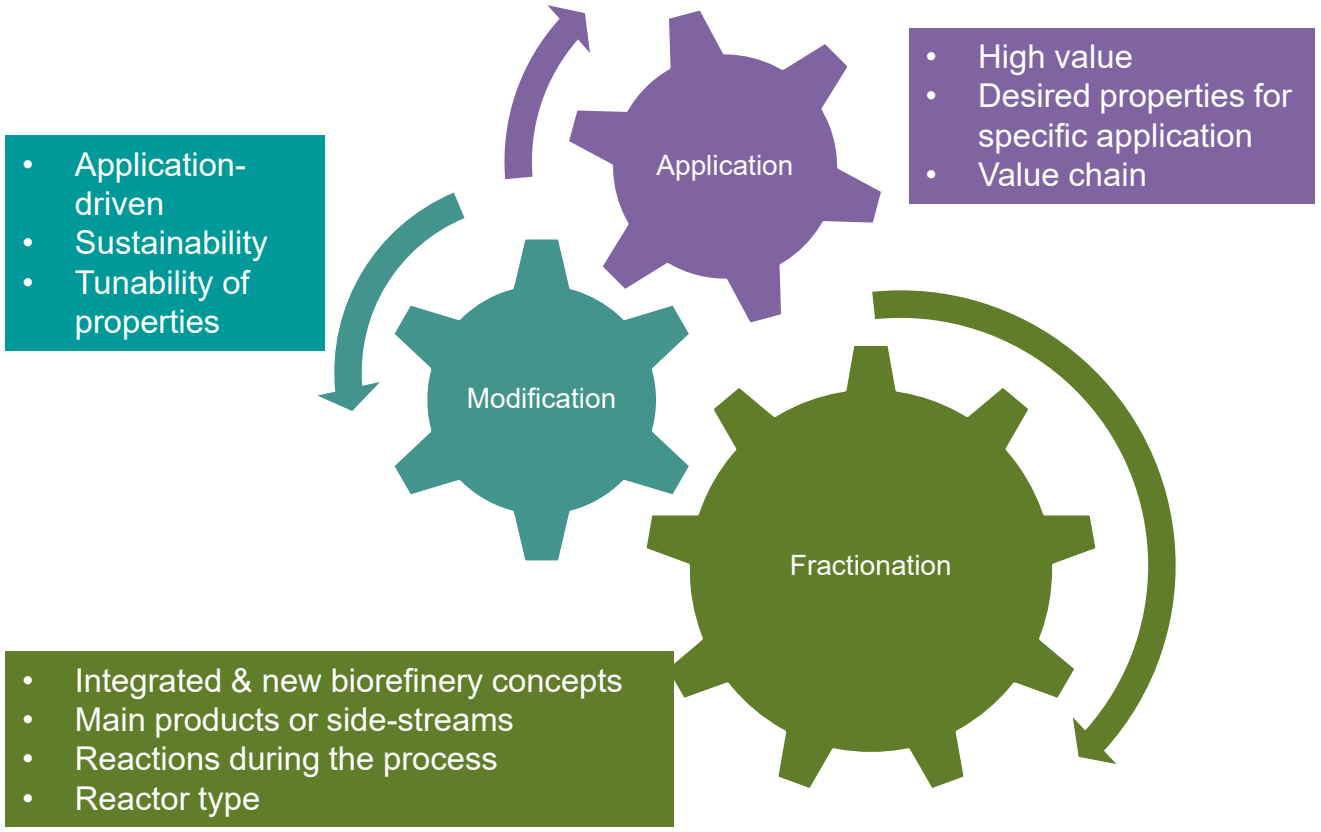


In vitro enzymatic degradation by endo-1,4-β-mannanase

GGMMA/CNC hydrogels presented faster degradation kinetics than the pristine GGMMA hydrogels

The thiol-ene hydrogel of 2% GGMMA+2% CNC-SH presented the fastest hydrolysis kinetic

Concluding remarks



- Abundant quantity
- Currently underutilized
- Rich hydroxyl
- Water-soluble polymer
- Easy to modify
- Compatible as such with fibers
- Renewable
- Biodegradable

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Thank you for your attention!

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