Session: Novel polymers
Presentation by: Tijs Nabuurs, *DSM Coating Resins*

Title: **High performance bio-based wall paints**

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Curriculum:
Tijs Nabuurs studied organic chemistry at the University of Nijmegen and obtained his PhD at the Technical University of Eindhoven on the copolymerization of alkyd-acrylic hybrid emulsions. In 1995 he started working for Zeneca Resins, which was acquired by DSM in 2005. He is now working for DSM Coating Resins. His topics of special interest are emulsion polymerization, biorenewable materials, and biocides. As of January 2017, he operates as science manager for the Decovery® program, which aims at creating a biobased and sustainable product portfolio.

Abstract:
The depletion of the earth's natural resources is forcing us to develop binders for use in paints and coatings based on plant-based raw materials. A very versatile and bio-renewable monomer is itaconic acid. Amongst use in other chemistries, it can be readily applied in emulsion polymerization yielding water-based, partially plant-based binders that can be used in wall paints. As all other diesters of itaconic acid, due to its low kp, dibutyl itaconate will polymerize slower than acrylate and methacrylate monomers, which it is intended to replace. The effect of this can, however, be mitigated by choosing effective comonomers. Binders containing dibutyl itaconate, for use in wall paint formulations were thus prepared with a biocontent of 48 %.

The wall paints produced using such binders show performances – judging from typical wall paint properties - mostly comparable to those of the ones based on fossil fuel-based binders. Chemical resistances of the plant-based paints are somewhat better than those of the fossil fuel-based types, which is attributed to the higher hydrophobicity of dibutyl itaconate compared to butyl acrylate and butyl methacrylate.

High performance biobased wall paints

(including update glue reed project)

Tijs Nabuurs, Maud Kastelijn, Derrick Twene

Wageningen, June 2018

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“We cannot be successful in a society that fails”

Feike Seibesma; CEO DSM

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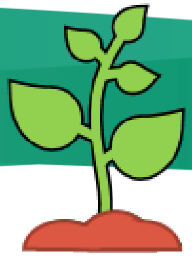
What does this mean for our strategy regarding coatings ?



No toxic materials

- APEO
- biocides
- Sn

Reduced Carbon Foot Print

- green energy
- optimized processing

Use of plant-based renewable resources

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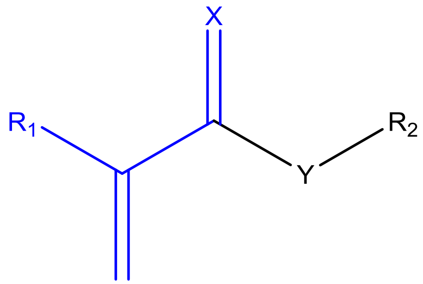
Biobased polymers:

	biobased content	
Alkyds	30-70 %	Depending on oil length; slow curing and dark yellowing
Polyesters	< 30 %	Mostly glycerol and succinic acid
Urethanes	< 30 %	Only polyols based on polyesters or polyethers
Acrylics	0 %	Until recently, no commercial sources available

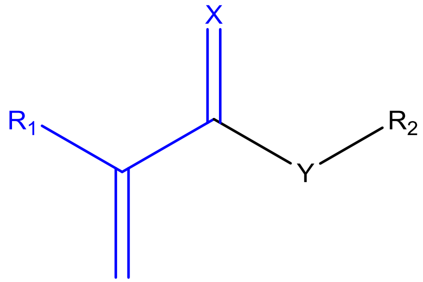
But, acrylic emulsions provide an interesting base set of properties:

- Fast drying
- Non-yellowing
- Good outdoor durability
- Good chemical resistances

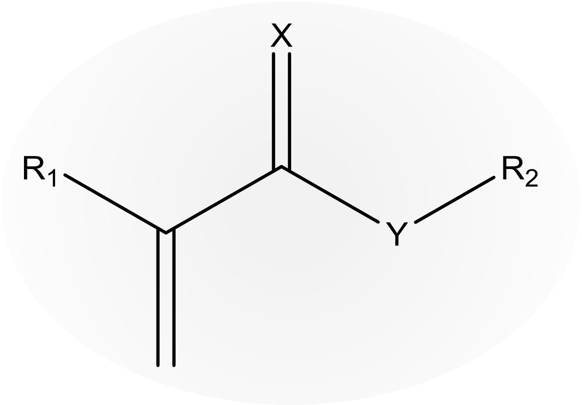
General (co)polymerizable (meth)acrylic structure:



acrylates; R_1 = H



methacrylates; R_1 = CH_3



Y = O or NH

R_2 = $(CH_2)_nH$, n = 0 - …

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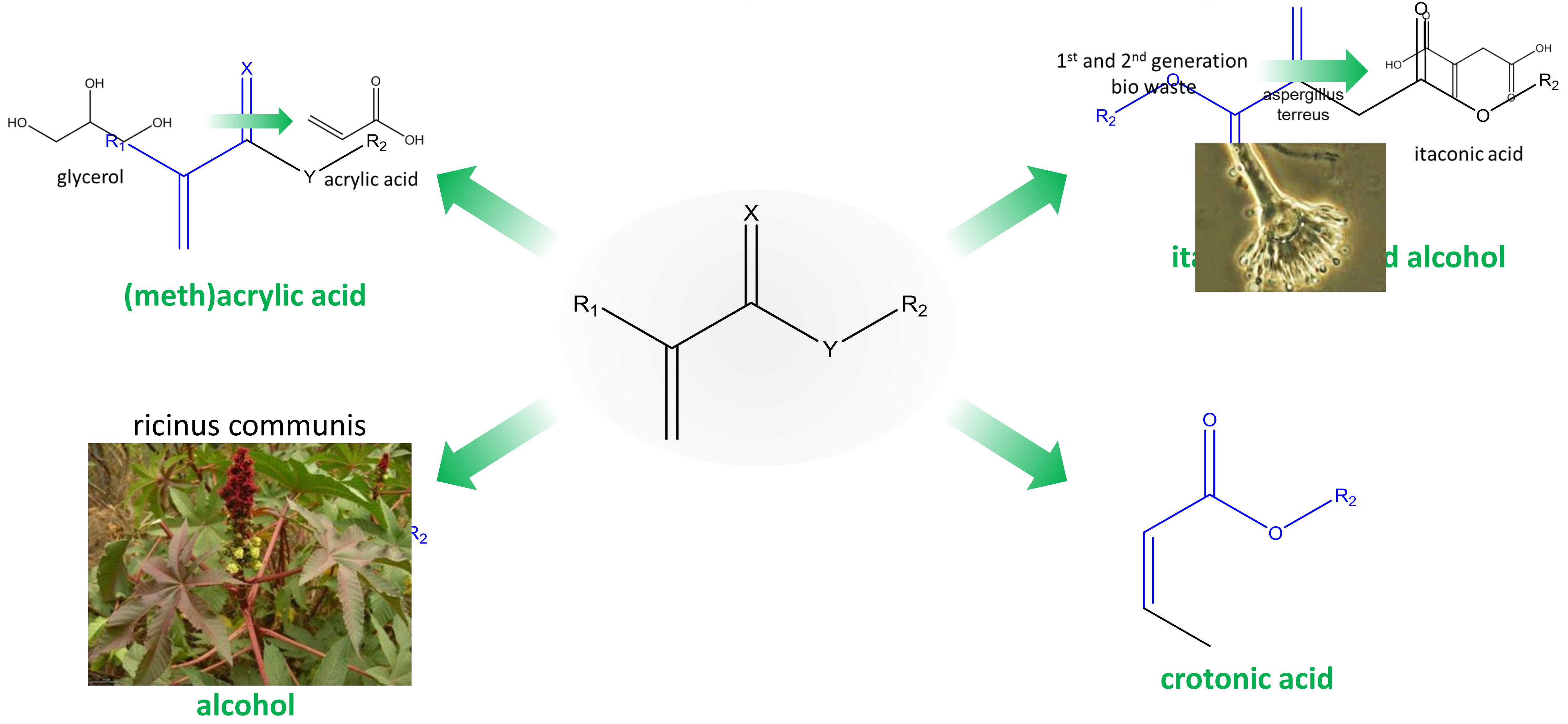
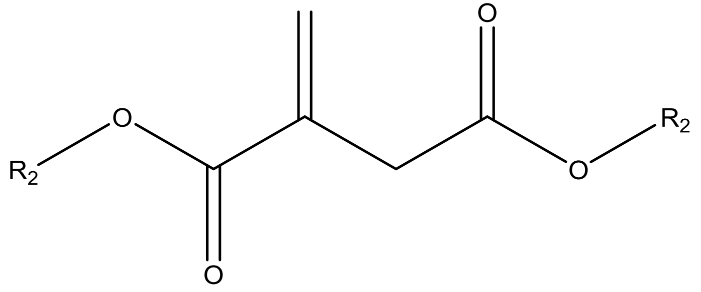
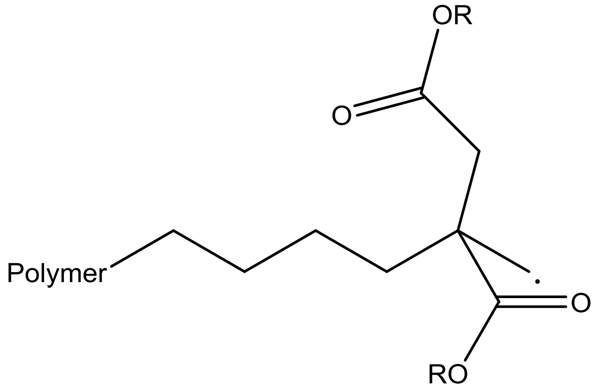
General monomer structure and plant based sourcing:



- Itaconic acid is a very versatile monomer
- Already mostly available as biobased via fermentation [1]

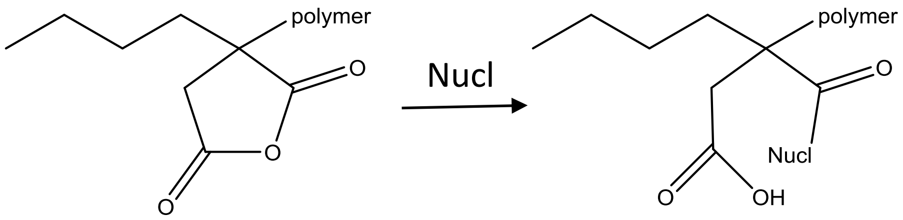


[2]



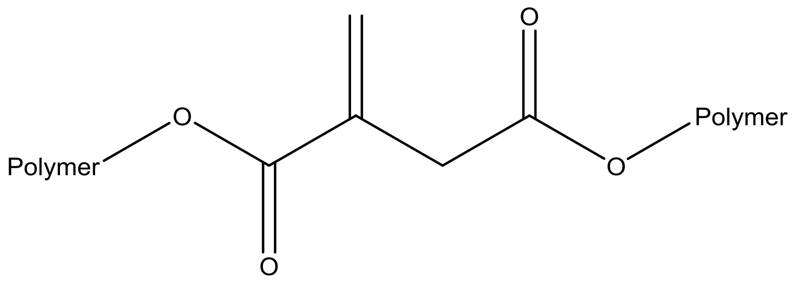
Radical copolymerization

[4]



Chemical modification of anhydride

[3]



Esterification

[1] Steiger et al Front Microbiol, 4, 23 (2013)
[2] Otsu et al Eur Pol J, 29, 167 (1993) ; [3] Robert et al Green Chem, 18, 2922 (2016) ; [4] Milovanovic et al, J. Serb. Chem. Soc. 72(12), 1507 (2007)

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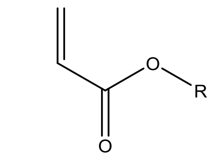
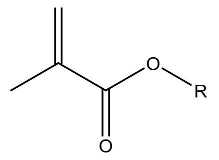
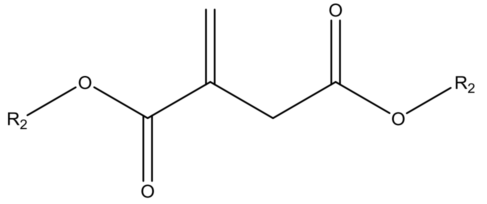
- Comparison (meth)acrylates and itaconates – glass transition temperature

	acrylate (°C)	methacrylate (°C)	itaconate[1] (°C)
Methyl	10	105	95
Ethyl	- 25	65	58
Butyl	- 50	20	12
Octyl	- 50	-10	-16



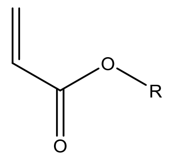


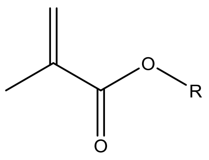


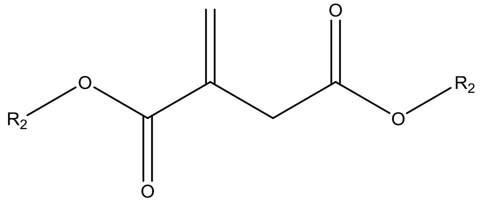
[1] Cowie et al Polymer, 18, 612 (1977)

- Comparison (meth)acrylates and itaconates – water solubility[1]

	acrylate (mg/L)	methacrylate (mg/L)	itaconate (mg/L)
Methyl	4.9E04	1.5E04	1.4E04
Ethyl	1.5E04	5.4E03	1500
Butyl	2.0E03	800	16
Octyl	100	6	



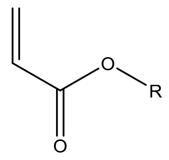


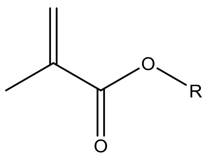


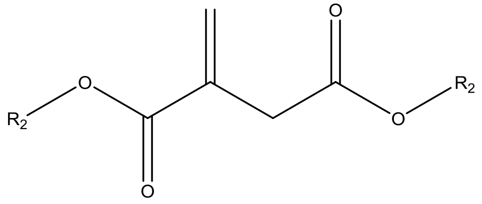
[1] Data taken from Chemspider.com

- Comparison (meth)acrylates and itaconates – propagation rate constants

	acrylate[1] ($L.mol^{-1}.s^{-1}$)	methacrylate ($L.mol^{-1}.s^{-1}$)	itaconate[2] ($L.mol^{-1}.s^{-1}$)
Methyl	3.2E04	1.3E03	10
Ethyl	5.0E04	1.4E03	8
Butyl	4.8E04	1.6E03	6
Octyl	3.8E04		3







$$R_p = k_p.[M].[R\cdot]$$

[1] Coevreur et al Macromol Symp, 174, 197 (2001)
[2] Tomic et al Macromol Chem Phys, 200, 2421 (1999)

- How to cope with reduced reactivity of itaconates ?

$R_p = k_p.[M].[R\cdot]$

- Increase temperature; k_p will be 1300 $L.mol^{-1}.s^{-1}$ at 314 °C
- Reduce instantaneous itaconate concentration (starved fed)
  - Very long process times
- Optimize copolymerization conditions
  - Find suitable comonomers

$$k_p = A\, e^{-E_{act}/RT}$$

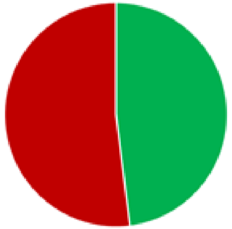
$$r_n = \frac{k_{nn}}{k_{nm}}$$

Monomer 1	Monomer 2	r_1	r_2
DBI	MMA	1.0	1.0
	MA	1.9	0.5
	Sty	0.4	0.4

Optimal comonomers:
- acrylates – good copolymerization, high k_p

- Optimizing process conditions and copolymer composition resulted in:

- Solid content 45 %
- Viscosity 50 mPa.s
- pH 8.0
- MFFT < 5 °C
- particle size 115 nm
- Biobased content 48 %
  (dibutyl itaconate)



- Which was formulated in a wall paint:

- Paint formulation
  - PVC = 58 %
  - Gloss (20°/60°/85°) = 1/3/5 % (satin)
  - Solid content = 60 %
  - VOC = 2.4 g/L

- Paint properties:

Property		Biobased wall paint
Hardness	1 day	52
	1 week	52
Film formation @ RT		ok
Film stress		3
Scrub resistance		2 (8 µm)
Chemical resistance	Water 16 hrs	5
	Ethanol 1 hr	3
	10 % Acetic acid 1 hr	3
	10 % Ammonia 2 mins	5
	10 % Ammonia 1 hr	4
	Detergent 16 hrs	3
	Red wine 6 hrs	1
	Coffee 16 hrs	1

- Paint properties:

Property		Biobased wall paint	Ref. wall paint 1	Ref. wall paint 2	Ref. wall paint 3
Hardness	1 day	52	45	38	52
	1 week	52	45	39	55
Film formation @ RT		ok	ok	ok	Ok
Film stress		3	3	1	3
Scrub resistance		2 (8 µm)	2 (8.6 µm)	2 (24.5 µm)	2 (10.6 µm)
Chemical resistance	Water 16 hrs	5	3	0	2
	Ethanol 1 hr	3	2	0	0
	10 % Acetic acid 1 hr	3	2	2	1
	10 % ammonia 2 mins	5	3	0	1
	10 % ammonia 1 hr	4	2	0	0
	Detergent 16 hrs	3	3	0	1
	Red wine 6 hrs	1	1	1	1
	Coffee 16 hrs	1	1	1	1

Conclusions – part 1:

- At 48 % biocontent, film properties of wall paint are comparable to those of reference, fossil fuel based, wall paints
  - Hardness
  - Film stress (cracking)
  - Scrub class
- Chemical resistances of the biobased paint are improved compared to fossil fuel based wall paints
  - The reason for this is the more hydrophobic nature of dibutyl itaconate

Conclusions – part 2:

- Biocontents of Decovery® grades are currently between 30 and 50 %, based on carbon
- Itaconate monomers currently prepared from 1st generation bio sources, until scale makes use of 2nd generation possible
- All other plant-based monomers can be prepared from bio waste
- Performance of all Decovery grades at least comparable to that of fossil fuel alternatives

Glue Reed: Reed fibre boards based on bio-based and biocompatible water-borne polymer resins

Cor Koning (DCR), Aad Lansbergen (DCR), Martien van den Oever (FBR), Edwin Keijsers (FBR), Jan van Dam (FBR), Yannes Koning (Natuurmonumenten) en Harald van den Akker (Natuurmonumenten)

Objectives

- The development of a new and sustainable board material based on multiannual reed for use in building and/or furniture industries.
- The development of a formaldehyde- and isocyanate-free resin system, based on biocompatible and renewable resources, suitable as a binder for lignocellulose fibres.

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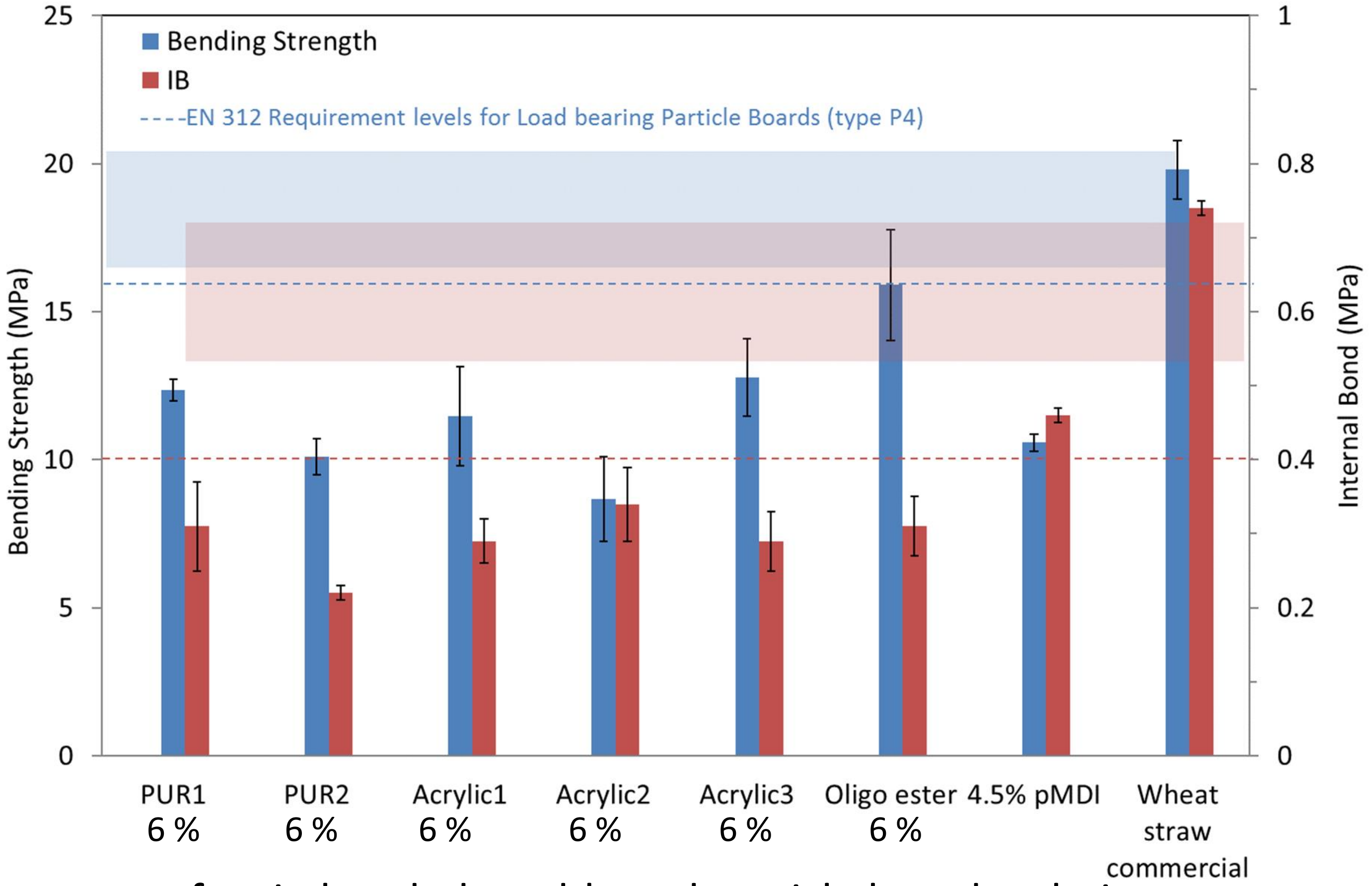
Summary of Glue Reed results obtained so far

Reed-based particle board; Particles prepared using Wanner cutting mill with 5 mm screen.



Performance of resin bonded reed-based particle boards relative to commercial (fossil) pMDI resin bonded reed and commercial wheat straw-pMDI board. The blue and red banners indicate the claimed performance level of the commercial wheat straw-pMDI bonded boards.

Conclusions

Bending strength of reed fiber boards based on novel sustainable binders is close to pMDI-based boards (some systems score even higher).

Internal bond strength needs further improvement (at best 60-70 % of pMDI-based reed boards).

Commercial wheat straw-based board using pMDI as binder outperforms multiannual reed-based boards.

Next steps

Resins will be further optimized to meet high speed industrial scale curing requirements.

Possible better performance of one year old reed w.r.t. multiannual reed will be evaluated.

Acknowledgement

This work is part of the research program Biobased Performance Materials, which is (partly) financed by the Top Sector Chemistry.

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