Wood modification with DMDHEU – State of the art, recent research activities and future perspectives

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[1]University of Goettingen – Wood Biology and Wood Products

Background

late 1940s

Originally:

- Textile modification
- Easy-care finishing of cotton

late 1970s

Development of formaldehyde-reduced and formaldehyde-free reagents for textile application

2000 - 2009

Joint research effort:
UGOE, Wood Biology and Wood Products and BASF AG, Ludwigshafen, Germany

→ Solid wood

→ Wood-based composites

BASF The Chemical Company

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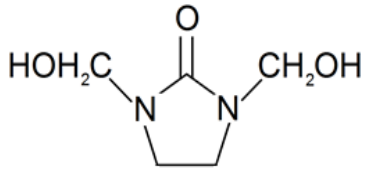
Past

late 1950s

Wood modification with crosslinking reagents

→ **Dimensional stability**

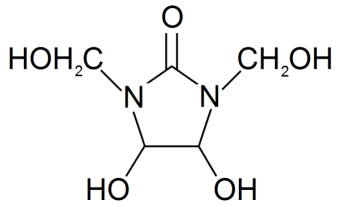


1980s/1990s

Wood modification with DMDHEU

→ Dimensional stability confirmed

\+ **Durability**



since 2000

Fundamental and applied research

→ Research group at UGOE

→ **Upscaling**

→ **Belmadur®Technology**

→ Belmadur®Pine

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Background

2006

BASF: Arising cooperations with companies from the wood-working industry

- Window joinery
- Outdoor furniture
  → Formed plywood
- Decking boards

Rademacher *et al.* 2009

Status quo

- Market penetration not reached
- Production operation currently ceased

State of the art

2010

Belmadur®Pine

- First products reached market maturity
- Acceptance and licensing for window joinery

2011

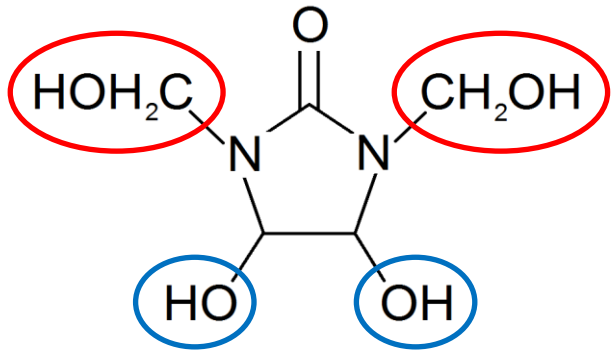
BASF stopped production operation

→ Pilot plant dismantled

…Future perspectives?

Chemical reagents

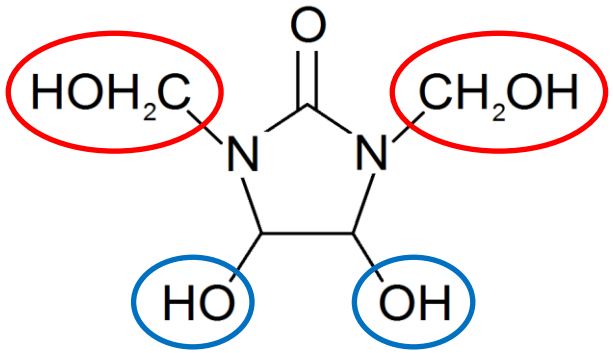
- Water-based monomer impregnation solution
  - Reagent with two reactive functional groups (Ashaari *et al.* 1990; Militz 1993)



Hydroxymethyl group Hydroxy group

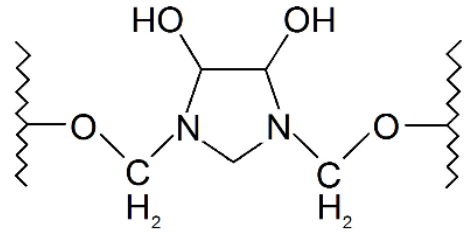
Chemical reagents – Mode of action (Krause 2006)

- Water-based monomer impregnation solution
  - Reagent with two reactive functional groups (Ashaari *et al.* 1990; Militz 1993)



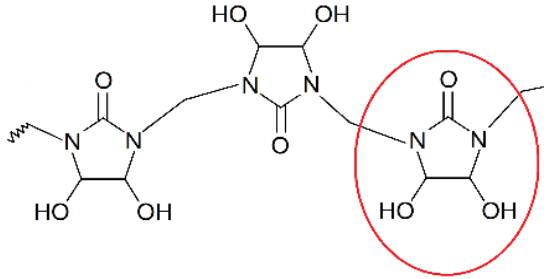
Hydroxymethyl group Hydroxy group

→ Crosslinking



+ H_2O

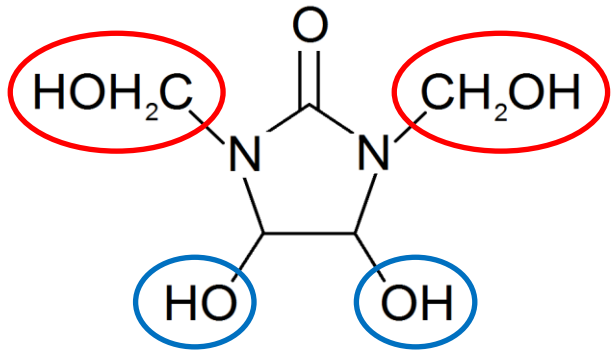
→ Autocondensation



+ H_2O + CH_2O

Chemical reagents and catalysts

- Water-based monomer impregnation solution
  - Reagent with two reactive functional groups (Ashaari *et al.* 1990; Militz 1993)



Hydroxymethyl group Hydroxy group

  - Catalyst screening (Krause 2006)
    - Most suitable catalyst for wood application: $MgCl_2$
    - Later investigations: $Mg(NO_3)_2$ (Dieste Märkl 2009; Leitch 2016; Emmerich 2016)

Modification process (Schaffert 2006)

dry

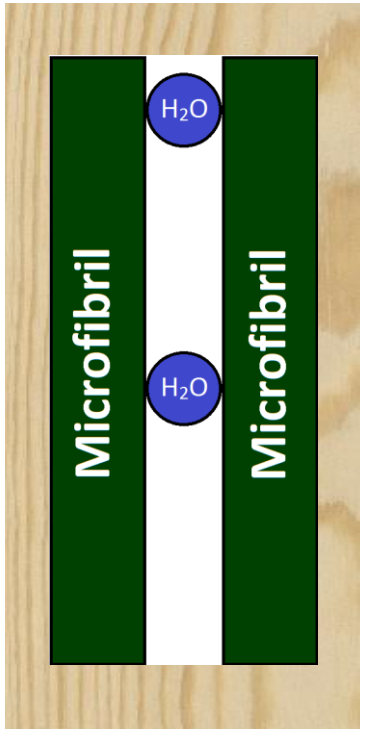
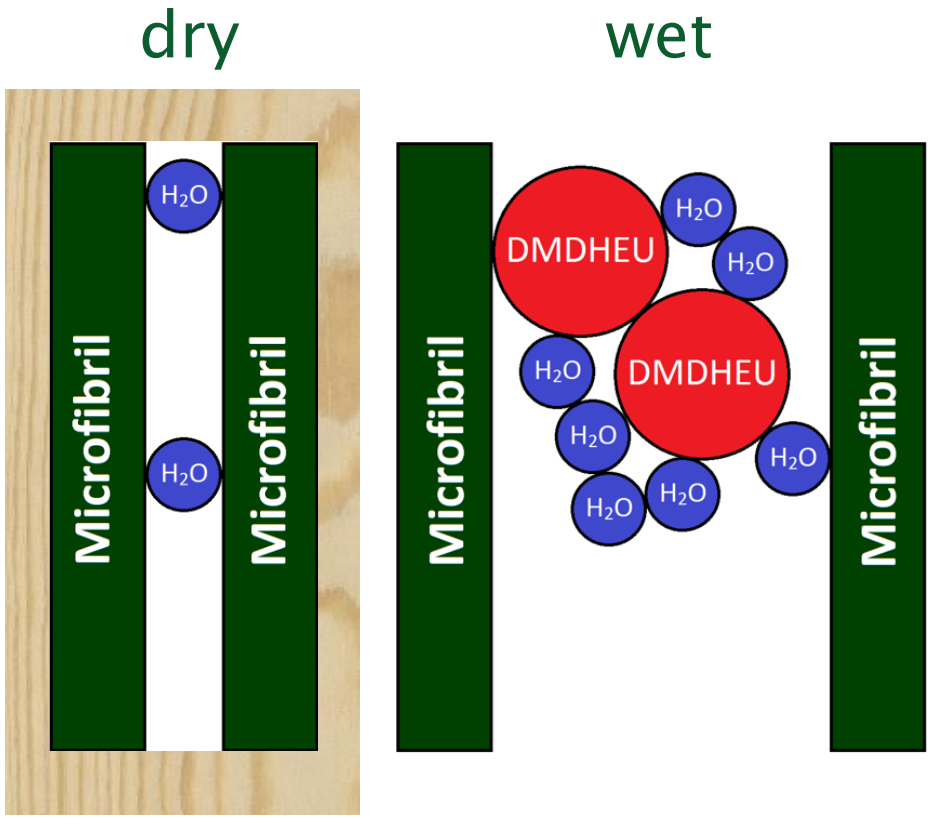


Figure: Krause 2006, adapted

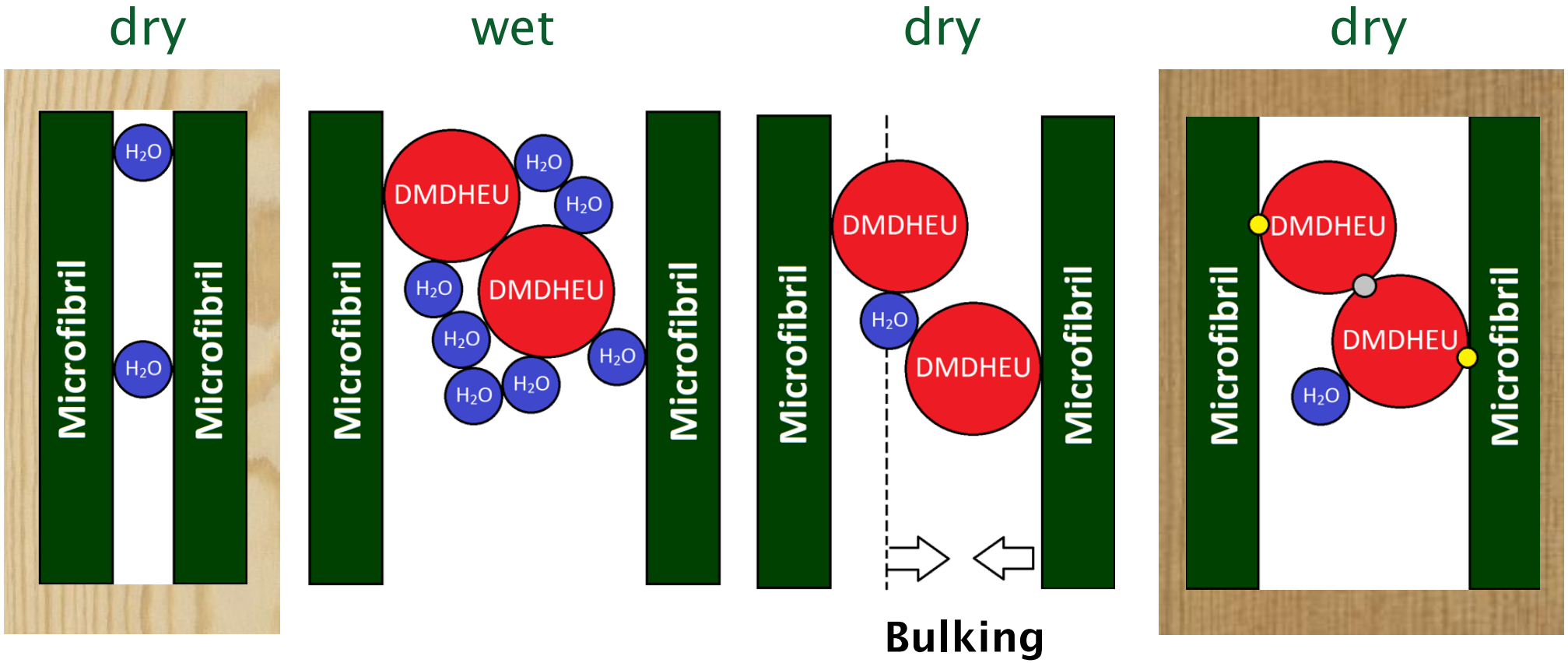
Modification process (Schaffert 2006)



Vacuum-pressure impregnation

Figure: Krause 2006, adapted

Modification process (Schaffert 2006)



Vacuum-pressure impregnation

Temperature > 100 ° C
Superheated-steam curing

Figure: Krause 2006, adapted

Wood species – Solid wood and wood-based composites

- Solid wood
  - Scots pine (*Pinus sylvestris* L.)
    - Krause (2006); Schaffert (2006)
  - European beech (*Fagus sylvatica* L.)
    - Rademacher *et al.* (2009); Bollmus (2011)

Scots pine sapwood (*Pinus sylvestris* L.) (Emmerich 2016)

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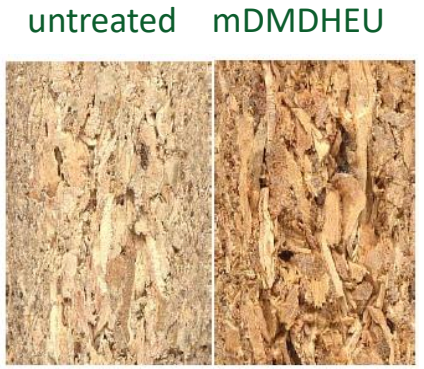
Scots pine sapwood (*Pinus sylvestris* L.) (Emmerich 2016)

- Wood-based composites
  - Plywood (Postel 2006; Wepner 2006; Dieste Märkl 2009)
    - European beech, Scots pine, Birch (*Betula* sp. L.), Spruce (*Picea* sp. Mill.)
  - Particle boards (Bartholme 2005)
    - Scots pine, European beech



Particle boards glued with PMDI (Bartholme 2005)

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    - Rademacher *et al.* (2009), Bollmus (2011)

✓ Scots pine (*Pinus sylvestris* L.) → Upscaling

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    - Scots pine, European beech

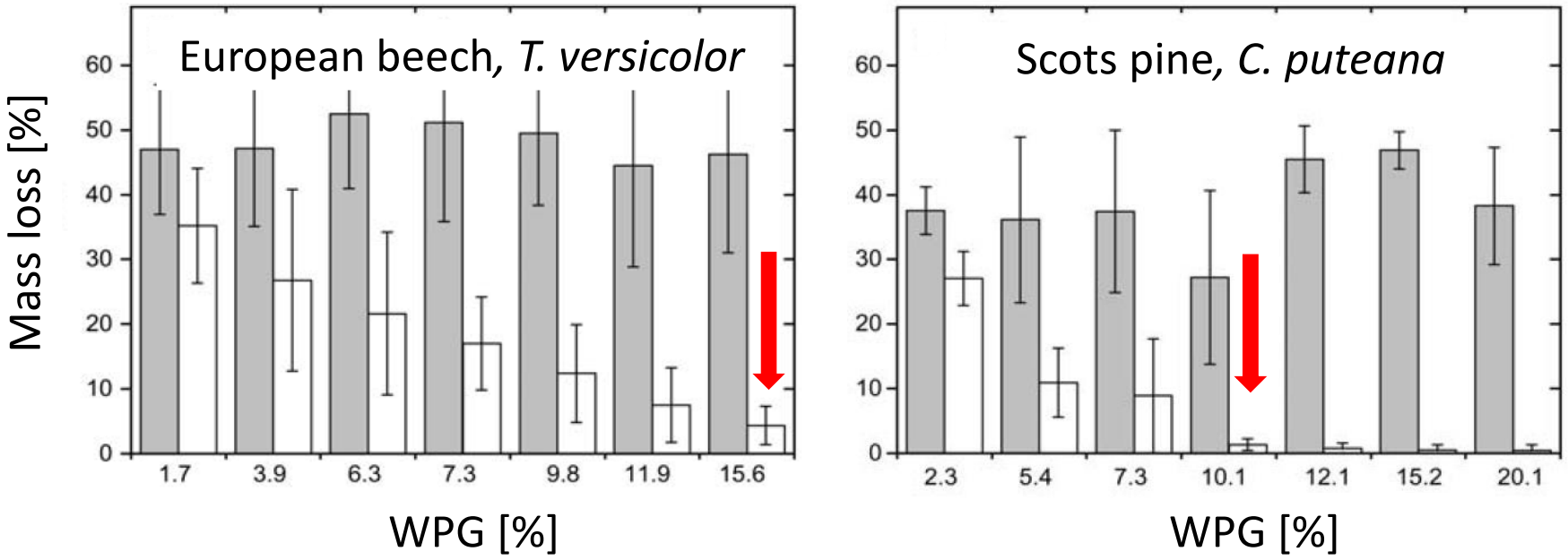
Scots pine (*Pinus sylvestris* L.)
(Emmerich 2016)

Particle boards glued with PMDI (Bartholme 2005)

Characteristic profile – Biological durability

- High resistance against
  - **Brown and white rot fungi**

Verma *et al.* (2009), mini-block test (EN 113)

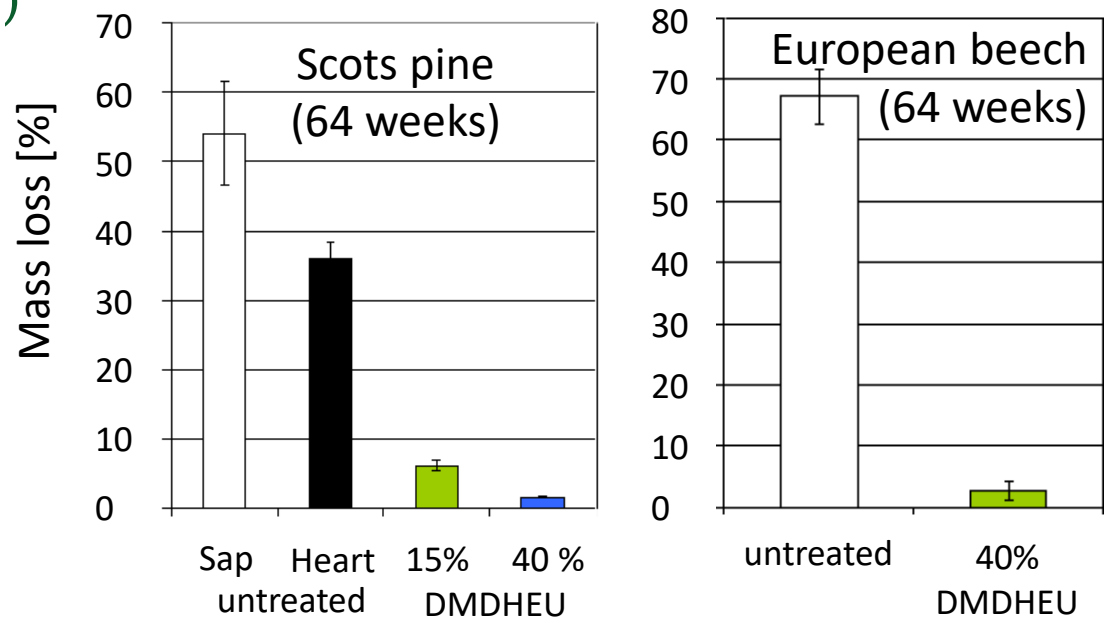


Biological Durability

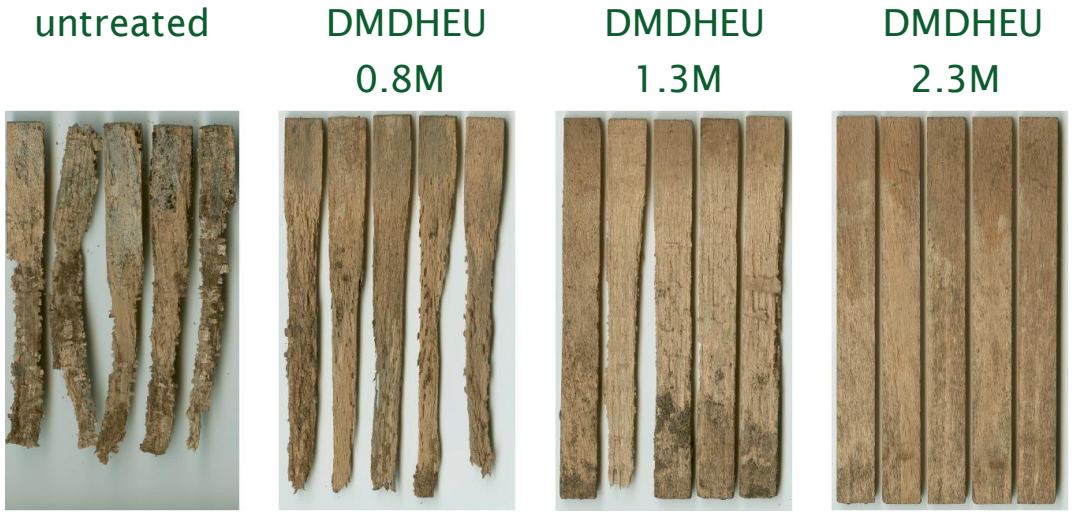
Krause (2006)
ENV 807

- High resistance against
  - Brown and white rot fungi
  - **Soft rot fungi**
  - Scots pine, European beech
  - Laboratory and field tests
    - Europe (e. g. Krause 2006; Schaffert 2006)
    - Australia (Militz and Norton 2013)

→ **Durability class 1 following CEN/TS 15083-1 can be reached**



Bollmus (2011), European beech

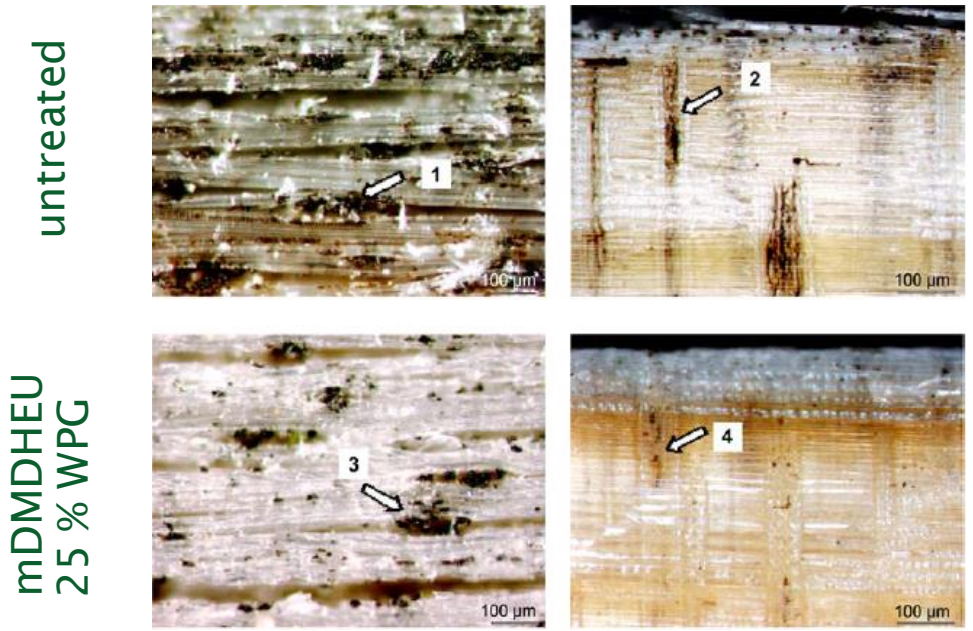


Durability test in ground contact following DIN V ENV 807 (152 weeks)

Weathering performance (Xie 2006)

- Photodegradation decreased
- Colonization by sapstaining fungi
  - Time-delayed but still apparent
  - Penetration more shallow

Xie *et al.* (2008)

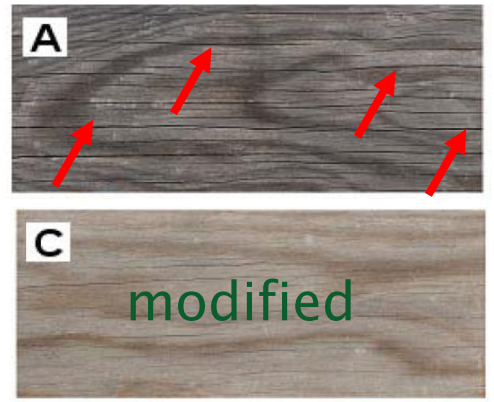


Weathering performance (Xie 2006)

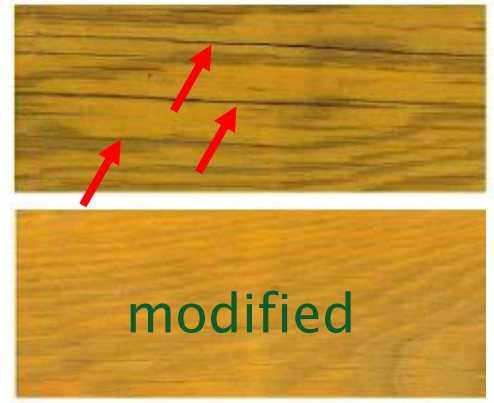
- Photodegradation decreased
- Colonization by sapstaining fungi
  - Time-delayed but still apparent
  - Penetration more shallow
- Surface erosions, deformations & crack formation
  - Reduced in the long-term (Xie *et al.* 2008; Mai *et al.* 2009)
  - Extended service lives of coating systems (Xie *et al.* 2008)
  - **Beginning of exposure: Increased crack sensitivity**

    (Rademacher *et al.* 2009; Emmerich 2016)

Mai *et al.* (2009)



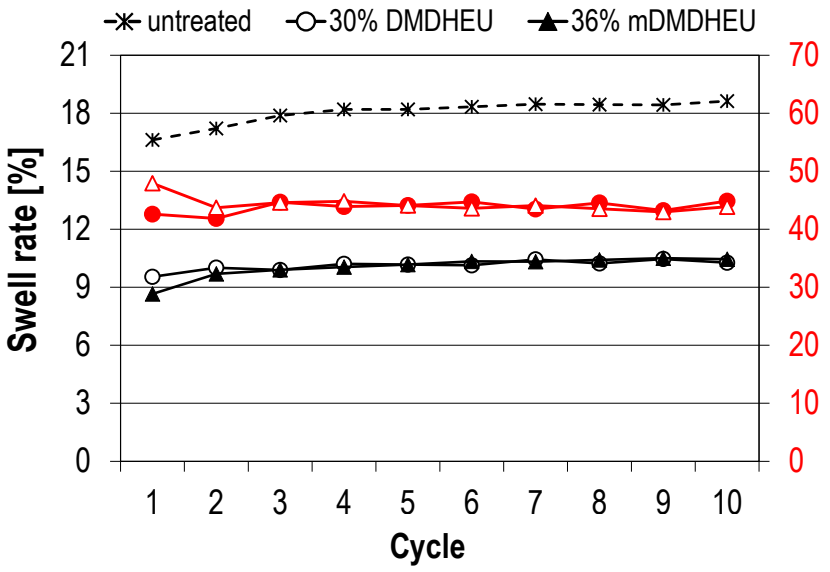
Xie *et al.* (2008)



Moisture behaviour - Dimensional stability

- Impact factors regarding dimensional stability (up to 70 % ASE)

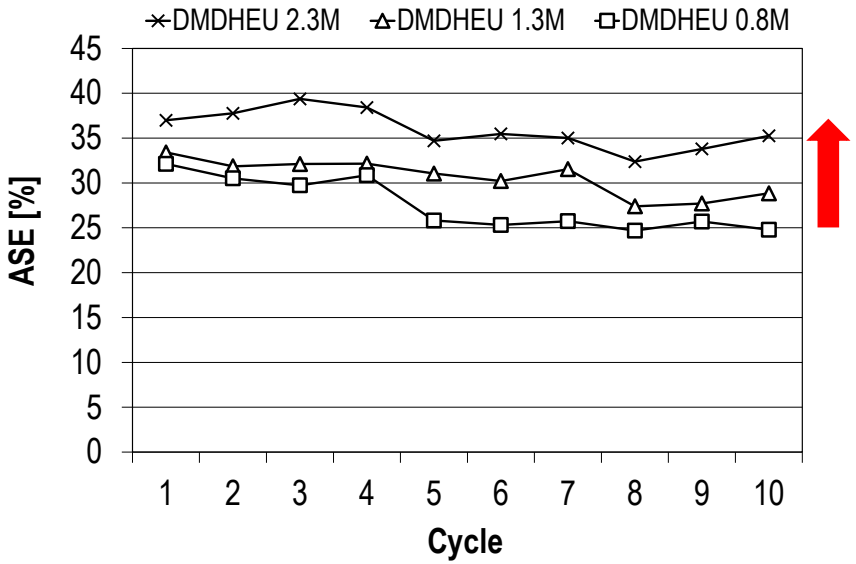
I. Modification agent



Emmerich (2016)

Scots pine sapwood (*Pinus sylvestris* L.)

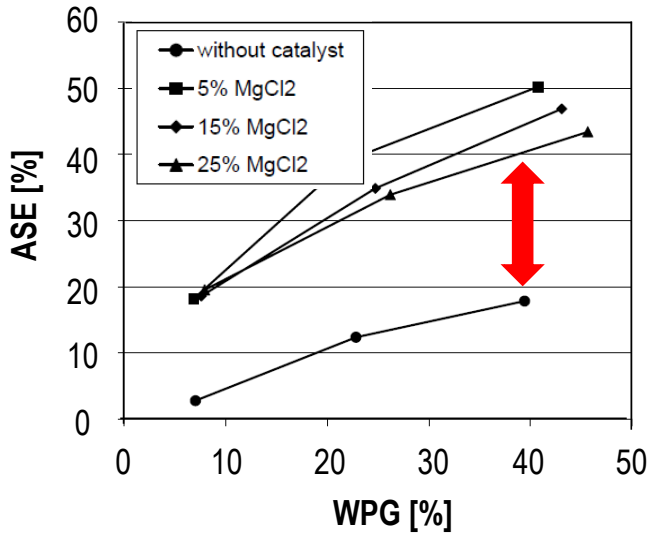
II. Concentration



Bollmus (2011)

European beech (*Fagus sylvatica* L.)

III. Catalyst



Krause (2006)

Scots pine sapwood (*Pinus sylvestris* L.)

Moisture behaviour

- Water vapor adsorption reduced

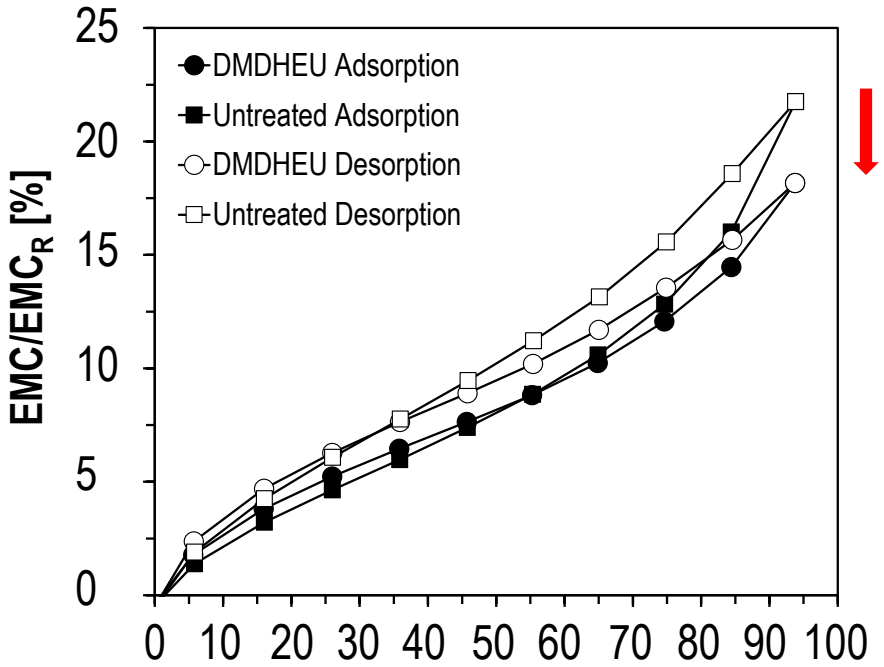
  (Bollmus 2011)
- Water uptake reduced

  (Krause 2006; Xie 2006; Bollmus 2011)
- *FSP* reached at *RH* < 100 %

  (Wepner 2006; Xie 2006; Dieste Märkl 2009)
- EMC_R reduced at high RH-level

  (Bollmus 2011; Lopes 2013; Emmerich 2016)

Emmerich (2016)



Adsorption and desorption isotherms of untreated (squares) and 30% DMDHEU modified (circles) Scots pine sapwood (*Pinus sylvestris* L.) measured at 25 °C within the RH range between 0 and 95 %

Strength properties

- Hardness, Compression strength ⬆

  (Krause 2006; Wepner 2006; Bollmus 2011; Xie *et al.* 2014)

- Bending strength, MOE ⟷

  (Schaffert 2006; Bollmus 2011; Xie *et al.* 2014)

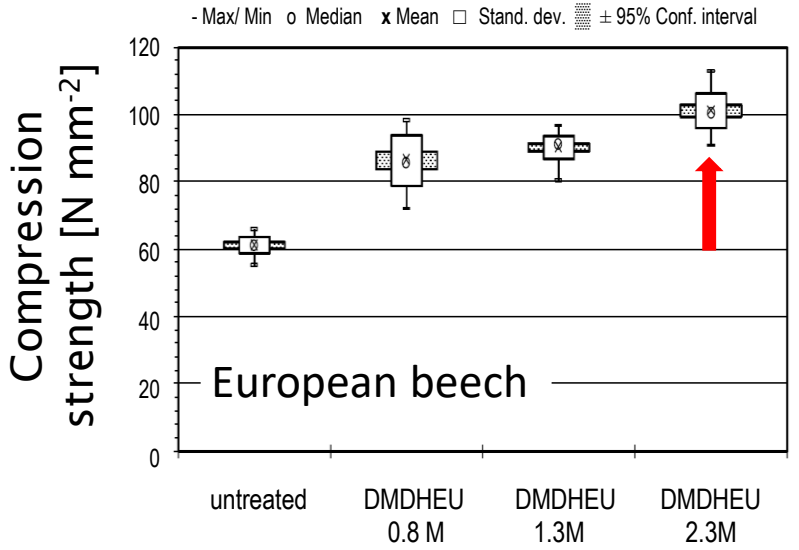
- Tensile strength ⬇

  (Wepner 2006; Bollmus 2011; Wessel 2013; Leitch 2016)

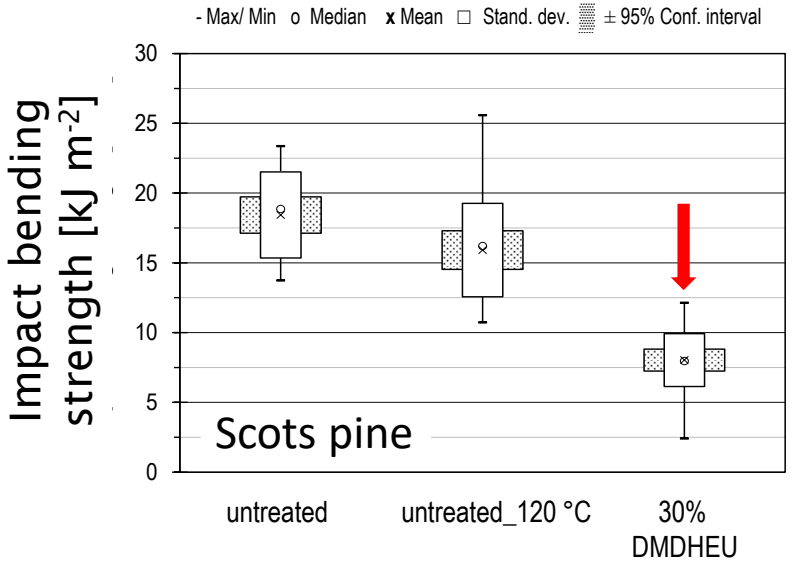
- **Dynamic strength properties**
  → Impact bending strength ⬇⬇

  (Schaffert 2006; Bollmus 2011; Brischke *et al.* 2012; Emmerich 2016; Leitch 2016)

Bollmus (2011)

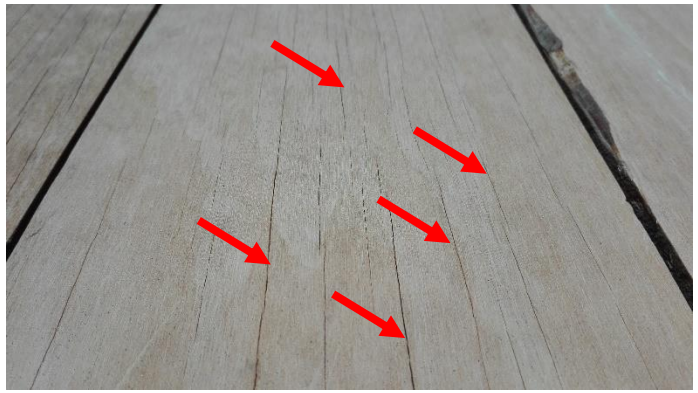


Emmerich (2016)

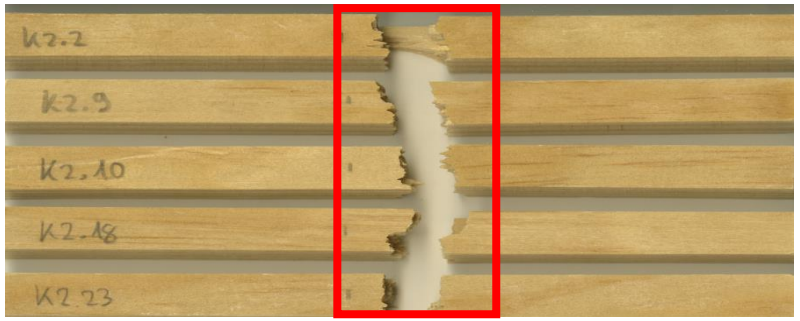


Conclusions - Findings

- **Present challenges**
  - Brittleness (dynamic strength properties)
  - Crack sensitivity of uncoated wood
  - Formaldehyde (CH_2O) emissions



Pinus radiata D. Don: DMDHEU-treatment – Crack appearance after 5 months outside exposure (Photo: Emmerich 2017)



Pinus sylvestris L.: DMDHEU treatment – Fracture patterns (Emmerich 2016)

Future perspectives

Status quo

- Market penetration not reached
- Production operation currently ceased

- …**Future perspectives?**

since 2016

- Joint research effort:
  UGOE, Wood Biology and Wood Products and Archroma Management GmbH

→ **Advancement** of wood modification with DMDHEU and **formaldehyde-free** derivatives
→ Market launch
→ Further **wood-species**

ARCHROMA
LIFE ENHANCED

Recent research activities **Future perspectives**

2015

- Archroma Management GmbH (Reinach, CH) acquired the global textile chemical business of BASF

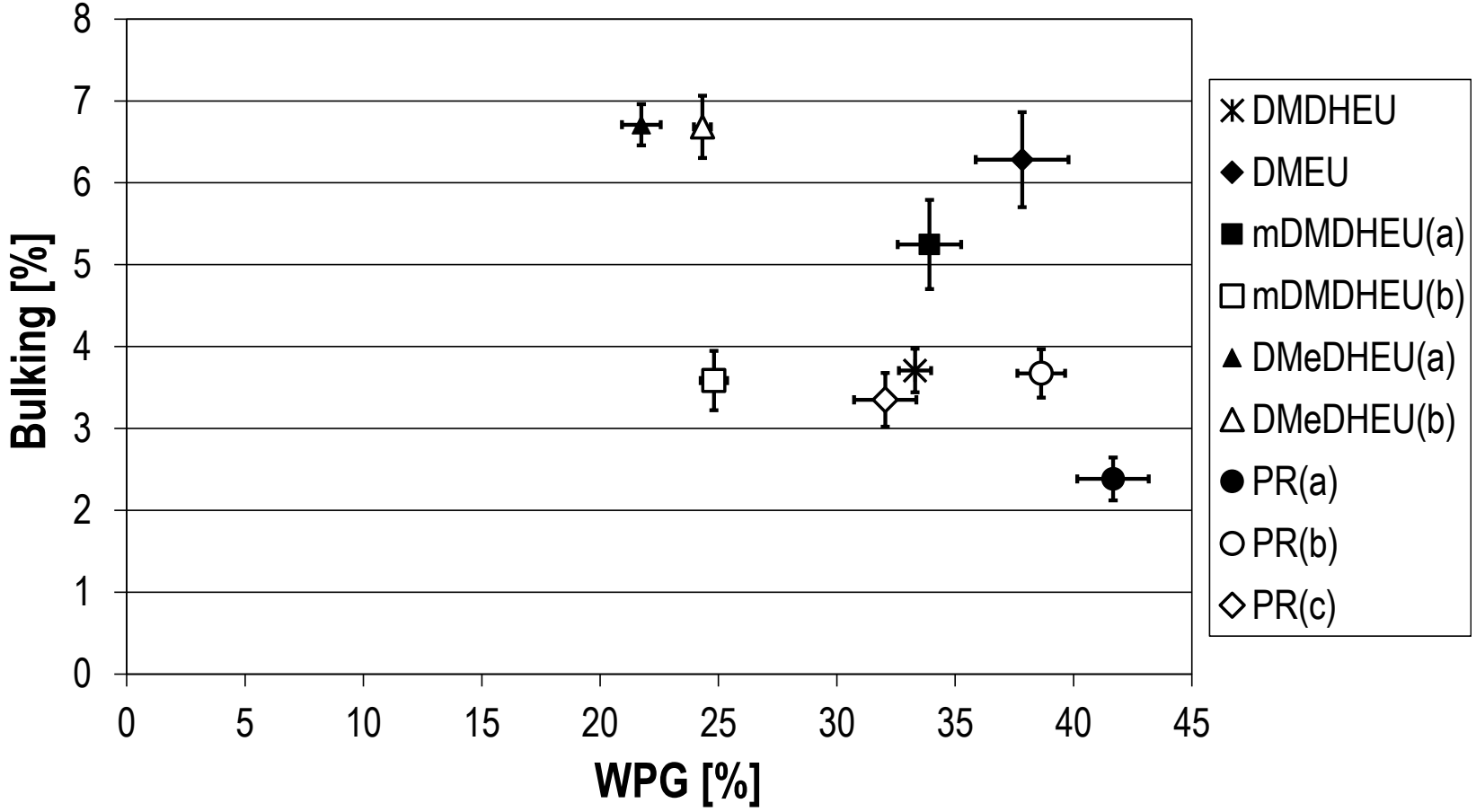
Currently

- Collaboration of TimTechChem International Ltd (New Zealand) with UGOE (Germany)
- Focus: **General applicability** of DMDHEU modification → Radiata pine (large-scale trials)

TimTechChem™
International

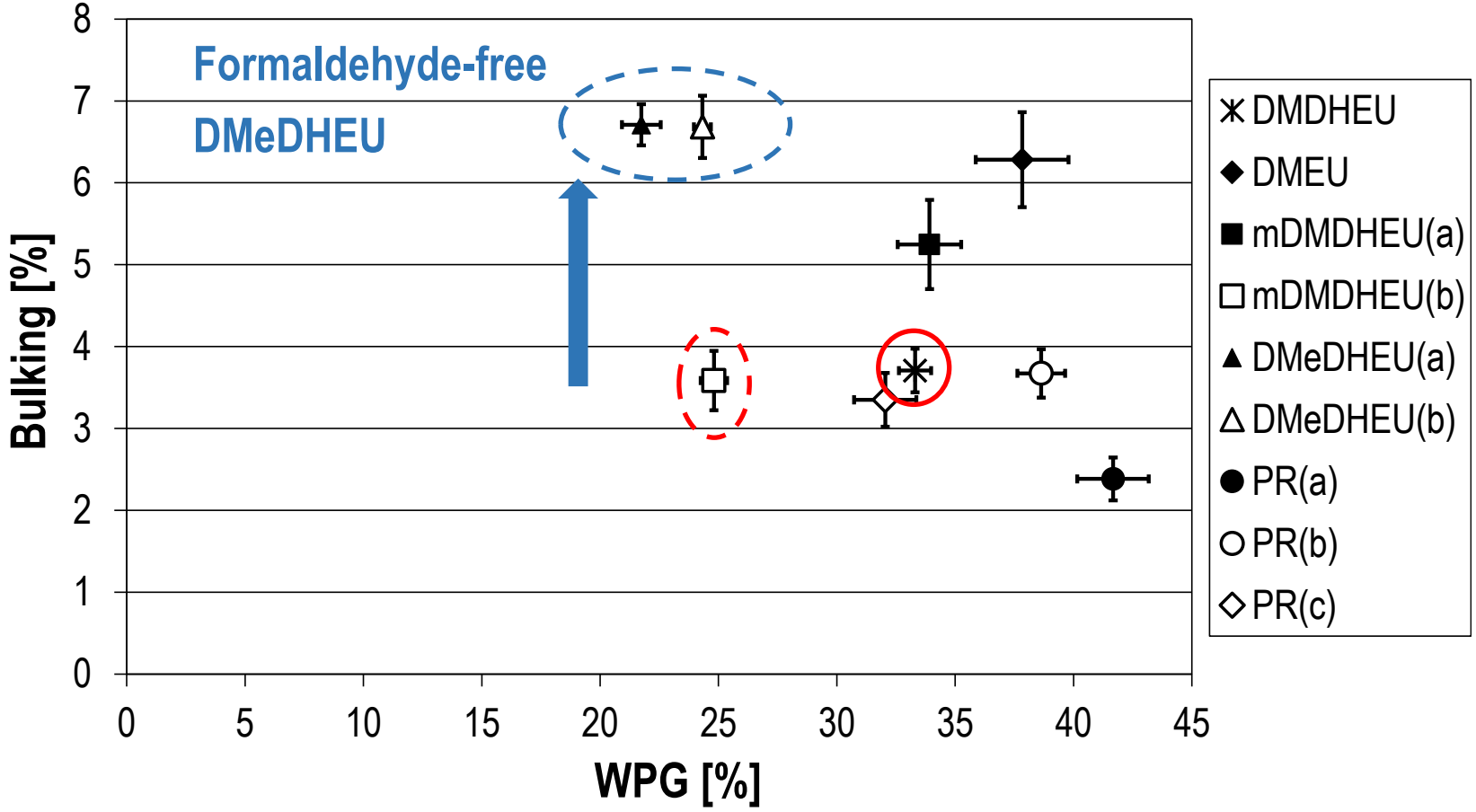
Recent research activities

- ***W**eight **P**ercent **G**ain* [%] – Deposition of modification agent
- *Bulking* [%] - Cell wall penetration



Recent research activities

- ***Weight Percent Gain*** [%] – Deposition of modification agent
- *Bulking* [%] - Cell wall penetration



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Thanks for your attention!