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Circular High-performance Aza-Michael Polymers as Innovative materials Originating from Nature

CHAMPION
circular bio-based polymers

Bio-based polymer synthesis and scale-up

Stakeholder Event "Bio-based Innovations for Industrial Applications"

April 24th, 2024, Brussels

Rolf Blaauw

BBI JU

Horizon 2020
European Union Funding
for Research & Innovation

Bio-based Industries
Consortium

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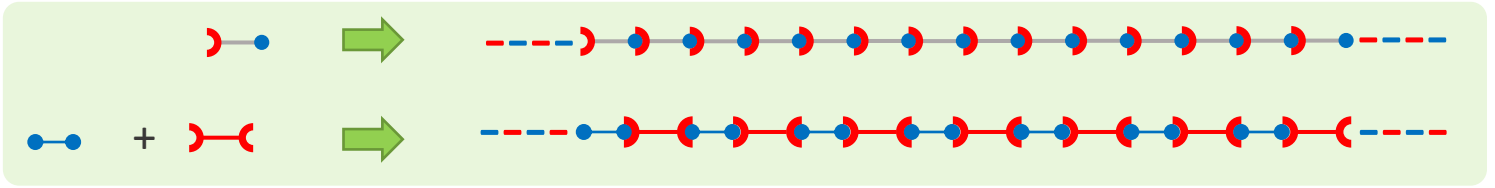
Outline

- **Introduction**
  - Thermoplastic versus thermoset materials
  - Reactive thermoset formulations: two major aspects for improvement

- **The CHAMPION project**
  - The *aza*-Michael (AM) reaction applied to thermosets
  - AM reaction between bio-based diamines and two types of bio-based Michael acceptors:
    - polyester diacrylates
    - unsaturated polyesters (UPE)
  - Optimization of AM thermoset formulations

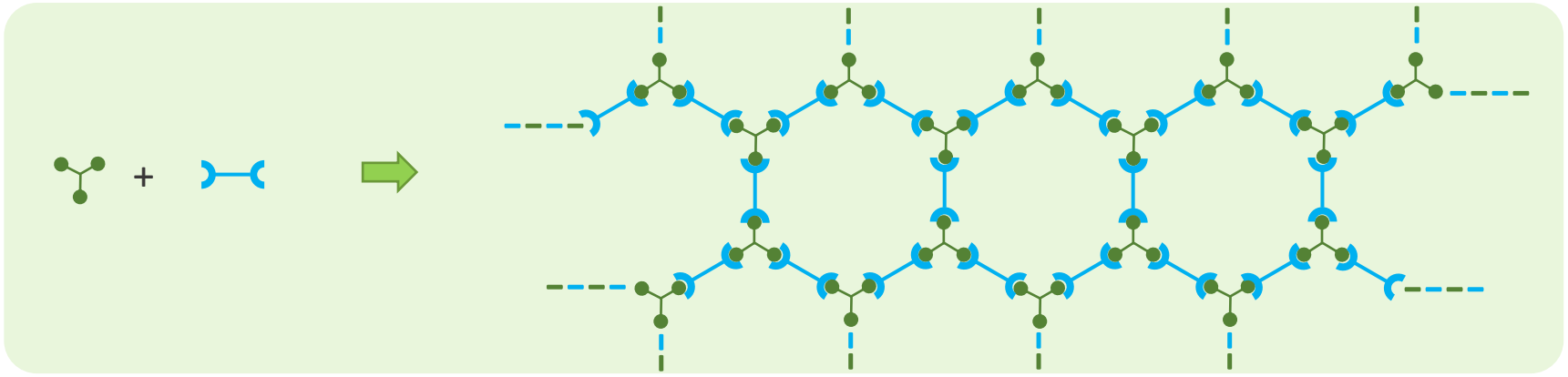
- **Take home messages**

Thermoplastic vs thermoset materials



- **Thermoplastic materials**
  - long **linear** polymer chains
  - can be (re)melted / reshaped by heating;
    limited mechanical stability at high temperatures, but **easier to recycle**
  - main applications: packaging, building & construction

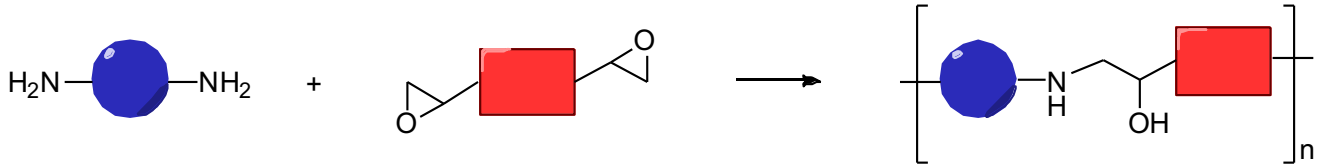
- **Thermoset materials**
  - made from chemicals that react when heated to form a **cross-linked** polymer network
  - cannot be remelted / reshaped by heating; good mechanical stability at high temperatures, but **difficult to recycle**
  - main applications: building & construction, automotive, CASE (coatings, adhesives, sealants, elastomers)



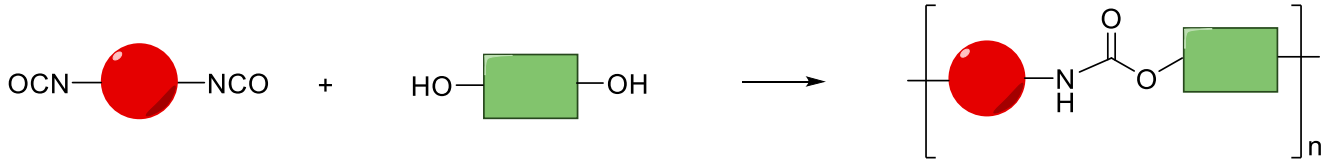
Thermoset chemistry today

Current systems: **non-reversible** polymers, **toxicity** issues with (residual) monomers

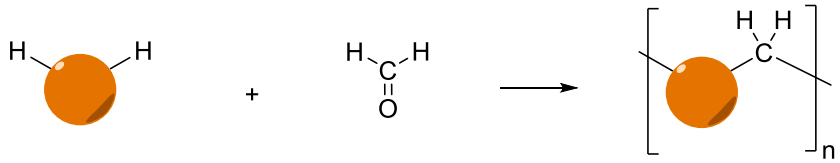
- Epoxy resins



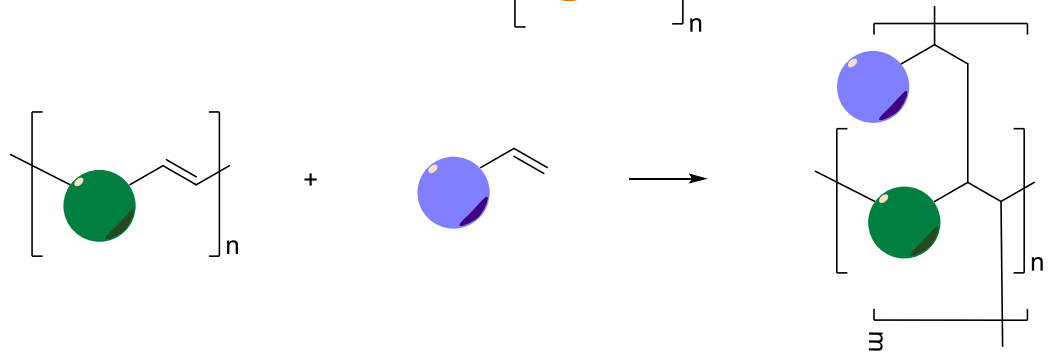
- Polyurethanes



- Formaldehyde resins



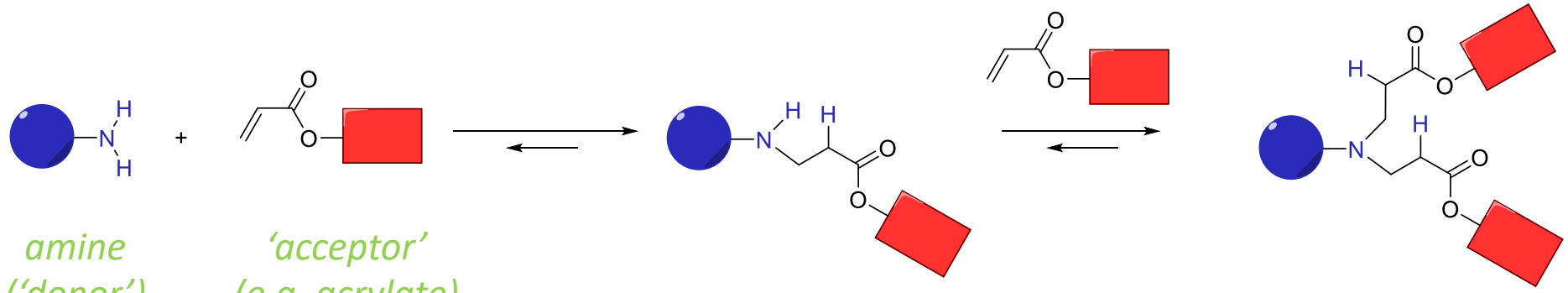
- Unsaturated polyester resins



Note: simplified and idealised structures for comparison only

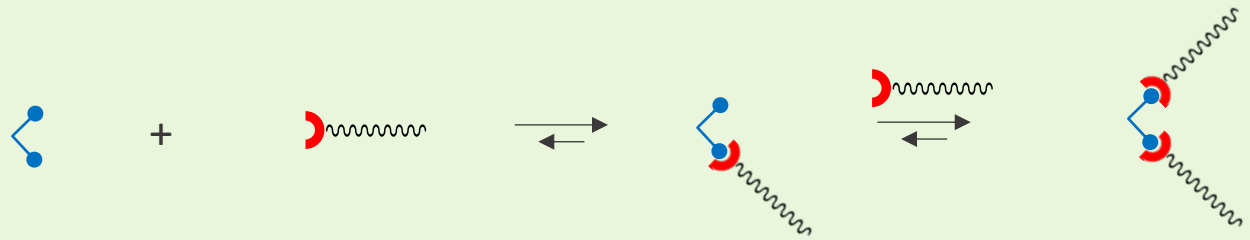
Thermoset chemistry in CHAMPION: *aza*-Michael (AM) addition

- *aza*-Michael C-N bond formation:



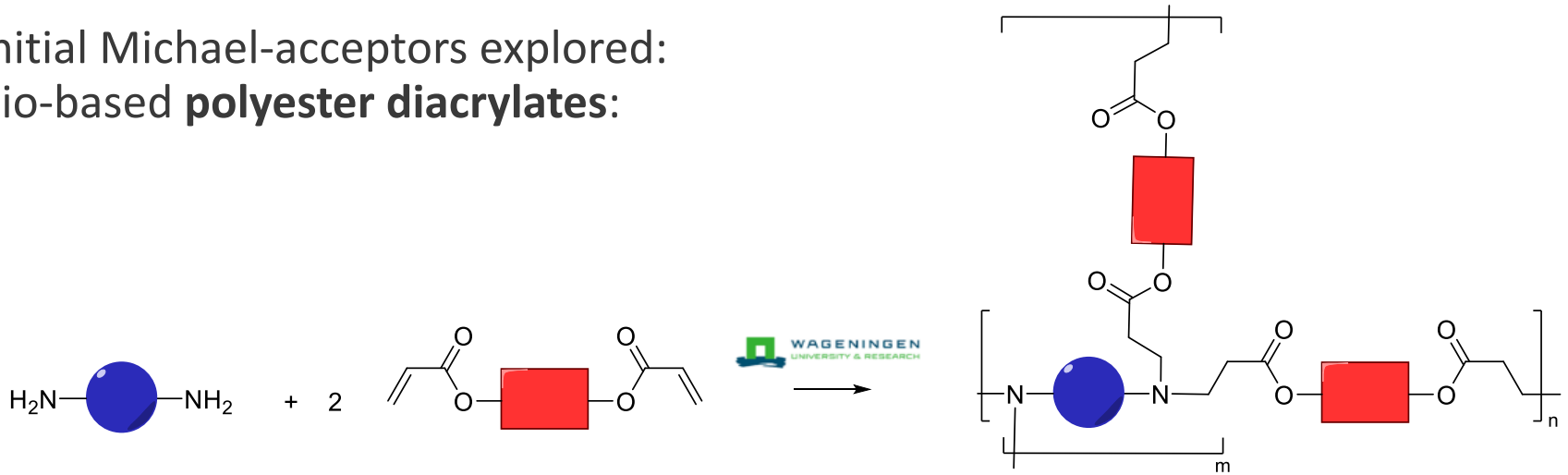
amine ('donor') *'acceptor' (e.g. acrylate)*

- Simplified representation:



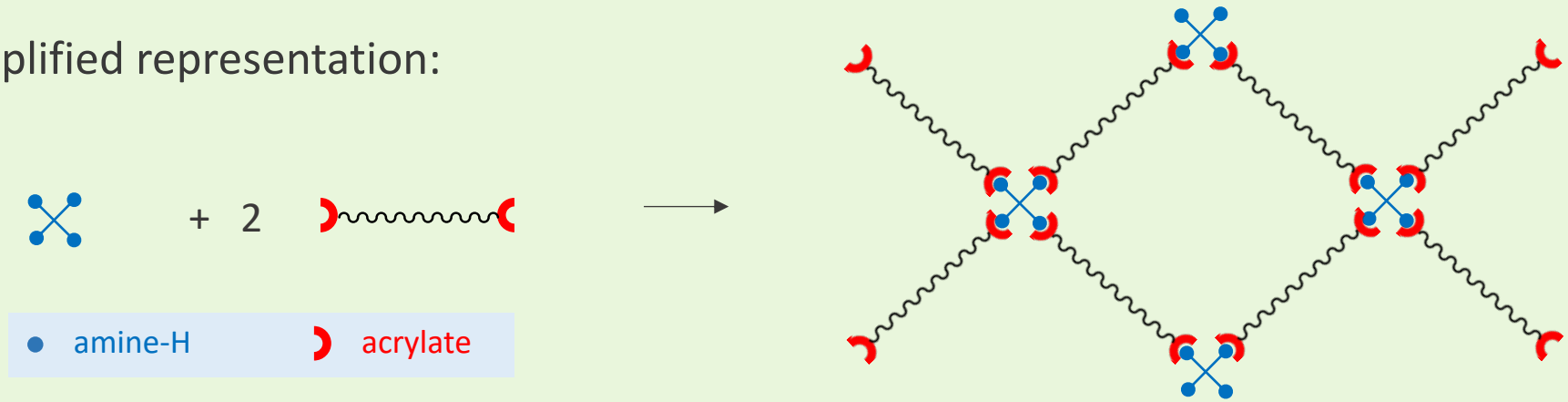
AM thermosets from diamines and polyester diacrylates

- Initial Michael-acceptors explored:
  bio-based **polyester diacrylates**:



diamine *polyester diacrylate* *thermoset material*

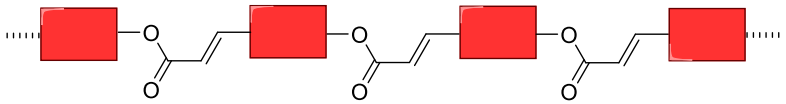
- Simplified representation:



Findings with polyester diacrylate acceptors

- Most polyester diacrylates were **solids** → formulation difficulties (liquid components required)
- Those that *were* liquid resulted in very soft, gel-like *aza*-Michael products
  - not fit for targeted applications (**strong flexible and hard coatings, structural adhesives**)

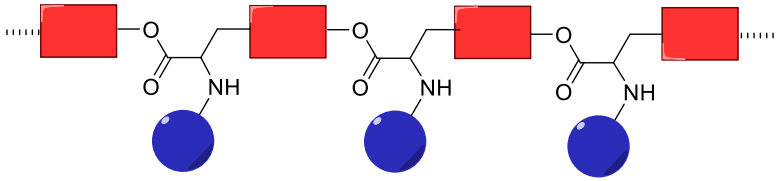
- **DECISION**: switch from diacrylates to **unsaturated polyesters (UPE)**
  - UPE were already developed in the project for **home care applications**:



unsaturated polyester

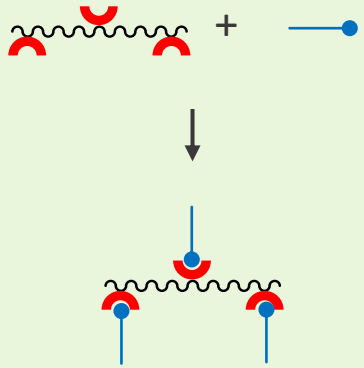
+

amine



water-soluble polymers

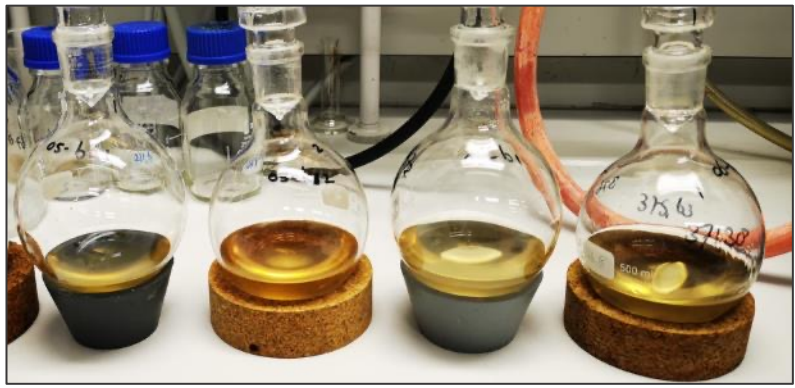
Simplified:

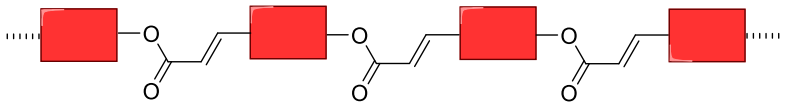


- amine-H or -NH_2
- *α,β-unsaturated ester*

AM thermosets from diamines and unsaturated polyesters

- By balancing type of monomers and molecular weight, **liquid UPE** were obtained by polycondensation of bio-based diols and diacid(s) esters
- These UPE could be mixed with bio-based diamines and cured to thermoset products

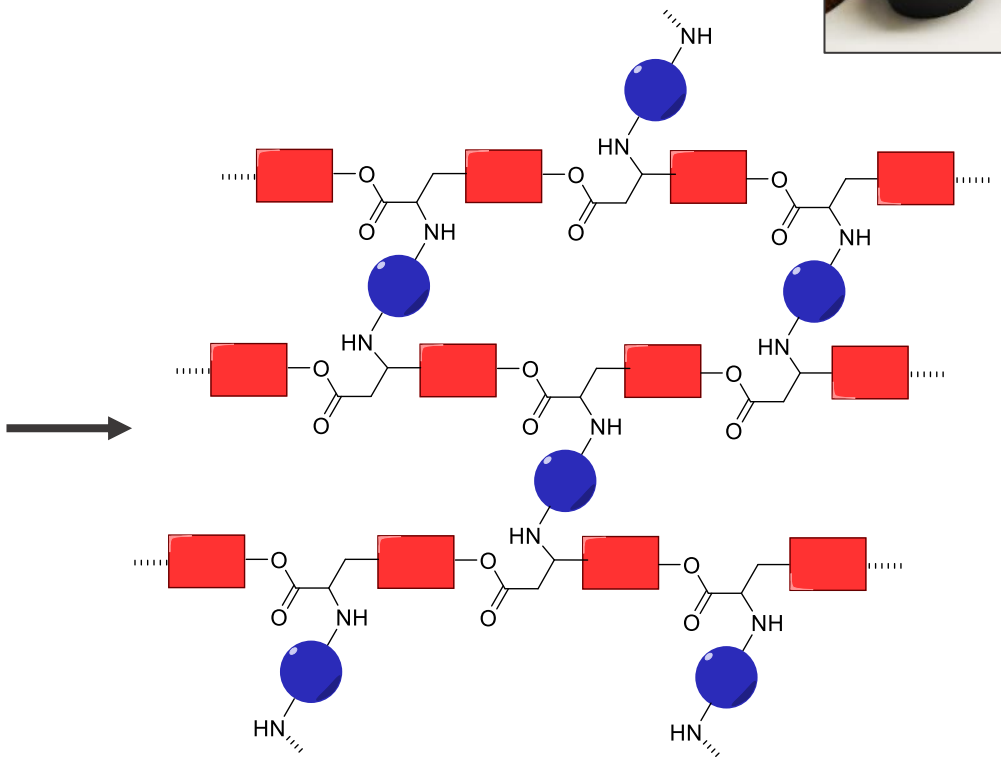




unsaturated polyester

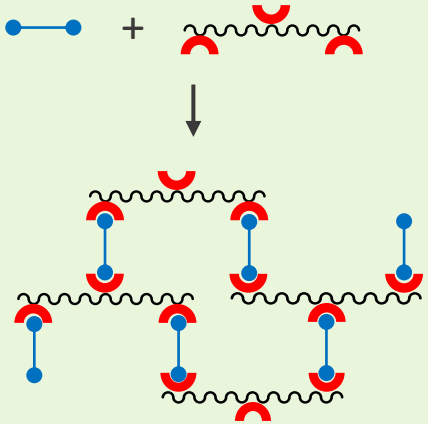
+

diamine



thermoset material

Simplified:



Illustrative lab-scale *aza*-Michael mixing and curing for thermosets

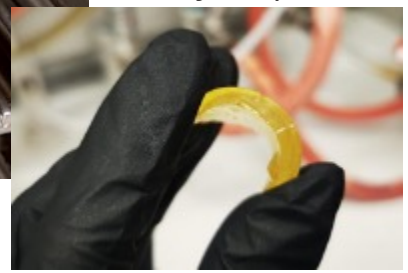
- **Novel bio-based diamines** and **bio-based UPE** mixed after pre-heating of UPE (reduce viscosity)
- Mixture transferred to silicon mould
- Let cure for 24 h at room temperature
- Post-curing for 2 h at 80°C

t = 0

t = 24 h @ RT

post-curing 2 h @ 80°C

final product

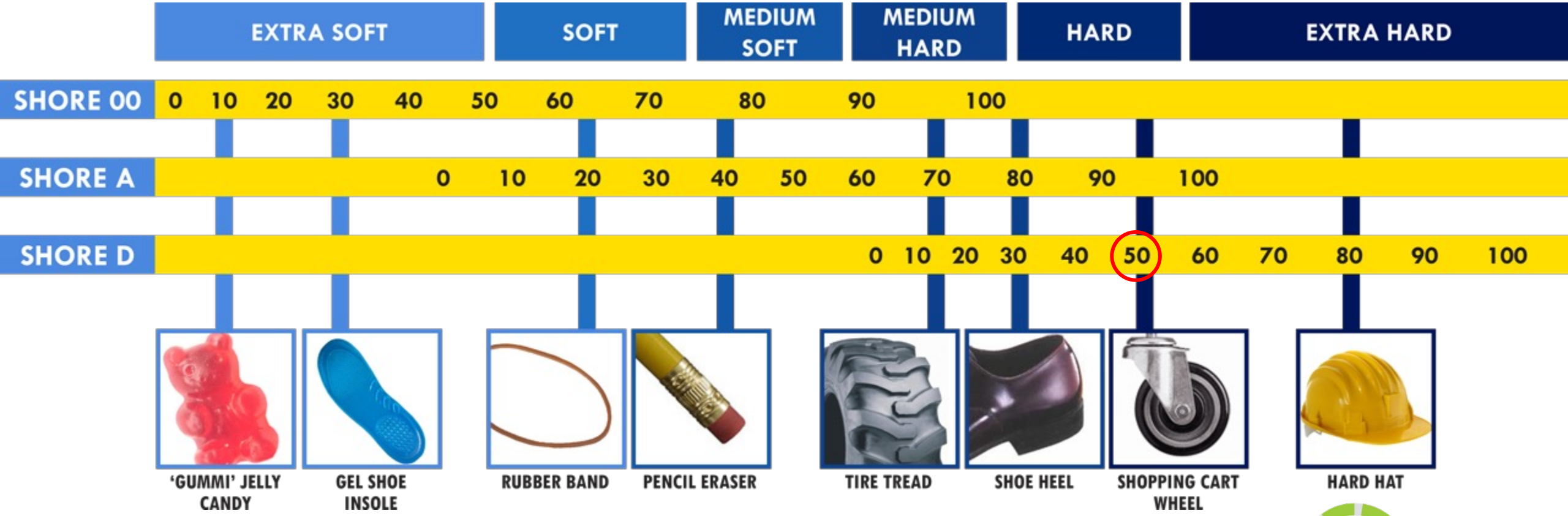


Shore D hardness

automotive interior coatings

rigid coatings, structural adhesives

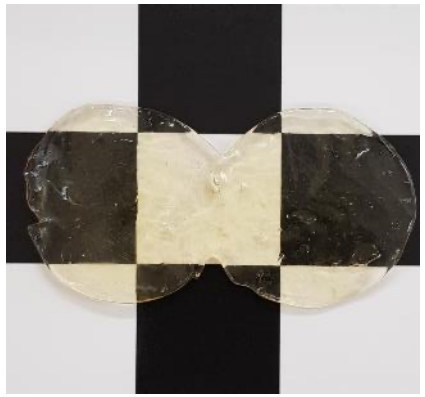
Stahl → ORINEO, Scott Bader →



Aza-Michael thermosets: general findings

- Depending on the diamine and UPE used, both strong **flexible** as well as **hard** materials could be obtained
- At a given reactant ratio, **diamine structure** also influences material hardness, with ‘rigid’ diamines leading to harder products
- Two issues were encountered:
  1. **Too high viscosity of the UPE** for easy mixing with diamine
  2. In a few cases: **flow** of cured materials at RT, for certain diamines
     - Solved by using primary diamines and optimized UPE/diamine ratios

1. High resin viscosity



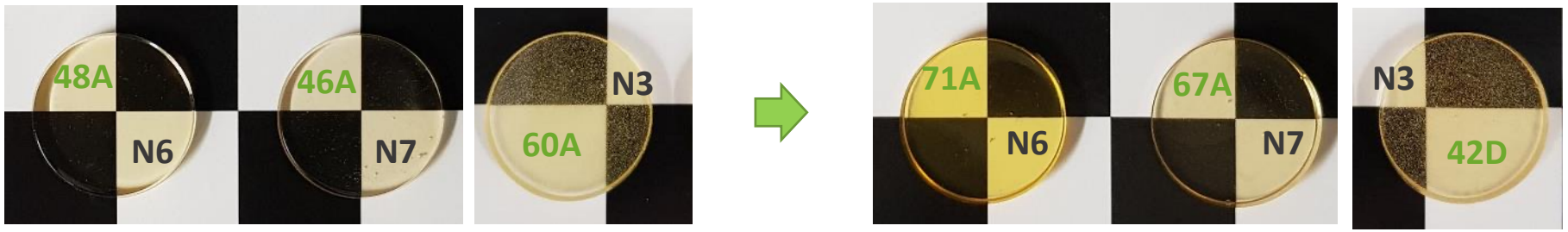
2. Merging of two samples

Lowering UPE viscosity with reactive diluents

- A class of promising non-toxic reactive diluents (RD) was found, facilitating handling/formulation
- At RD levels of ≈ 10 wt%, some reduction of hardness observed, but still in good range
- These RDs have not yet been described in (patent) literature about UPE formulations

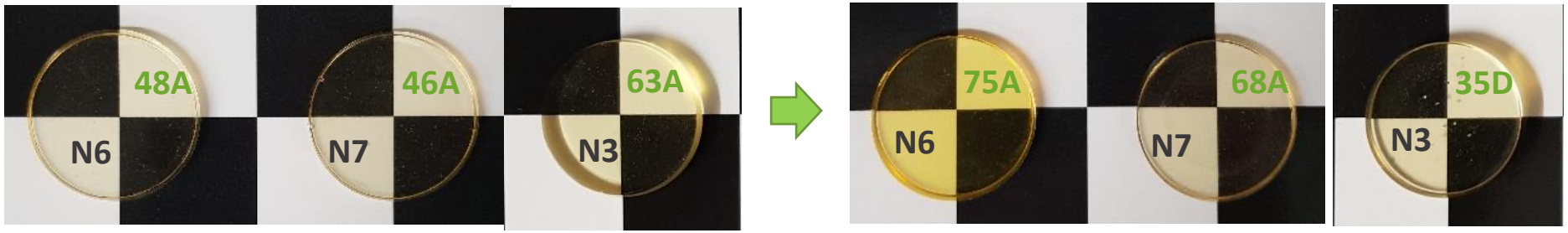
Shore hardness values *read after 10 seconds:*

RD-1



N3 = rigid diamine
N6 = flexible diamine, unsaturated
N7 = flexible diamine

RD-2



t=24h@RT

t=24h@RT+ 2h@80°C

Take home messages

- Two-component reactive resin formulations based on Michael addition between diamines and liquid UPE have been developed
- These may serve as safe and circular alternatives for PU and epoxy systems
- Aza-Michael thermoset formulations show promise in end-use applications such as surface coatings and home care formulations
  - ➡ see presentation "*End-user Application Testing of Polymers in CHAMPION*" by Thomas Farmer

Thank you!

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Acknowledgement

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- Particular thanks to Janice Lofthouse and Thomas Farmer for their excellent project and scientific management, respectively.

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