SUSMATx
Sustainable matrices for structural composites
processing and mechanical performance
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Girona - Spain

Dual-curing vitrimers
A novel material design concept

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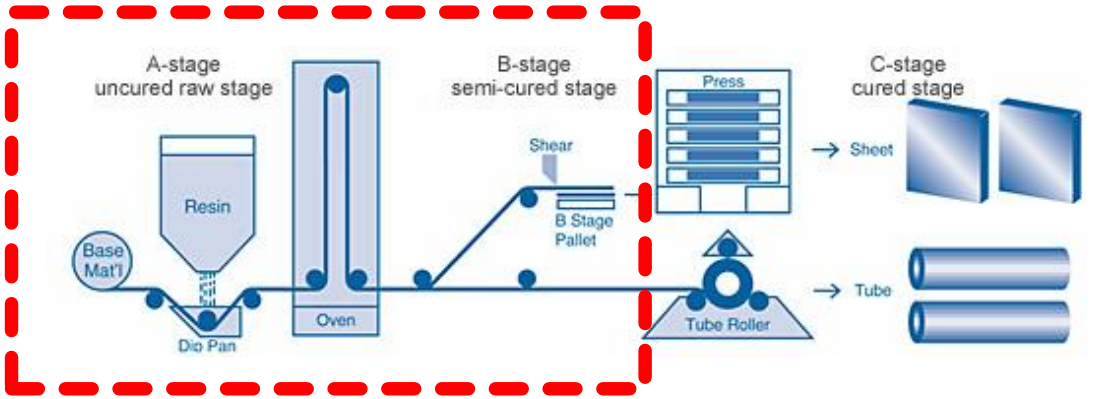
Motivation

1) Multi-stage processing with controlled intermediate properties & stability



Tight time & temperature constraints!!

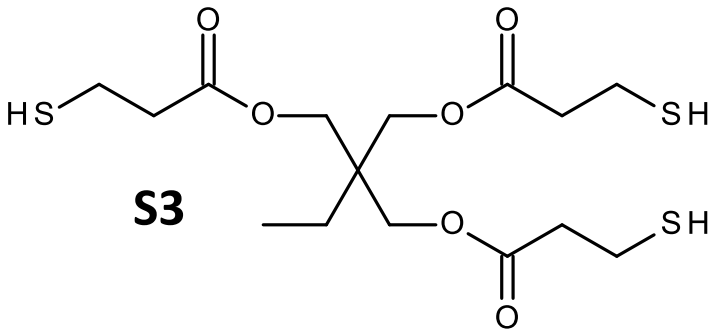
2) Management of waste composite parts after EOL

Limited reuse & recycle capabilities!!

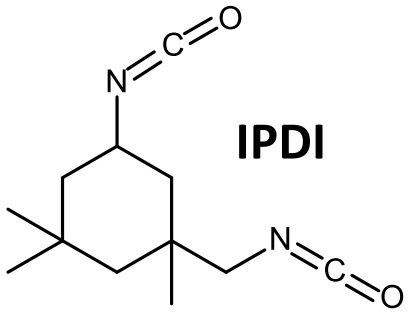
Dual-curing vitrimers?

Dual-curing thiol-isocyanate-epoxy networks

Thiol curing agent

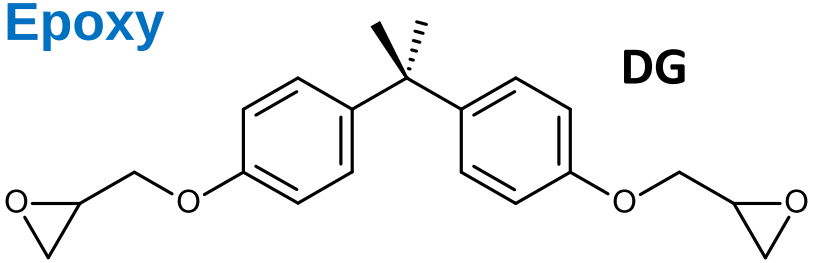


Isocyanate



Equal number of thiol and isocyanate + epoxy groups (stoichiometric)

Epoxy



Composition parameter

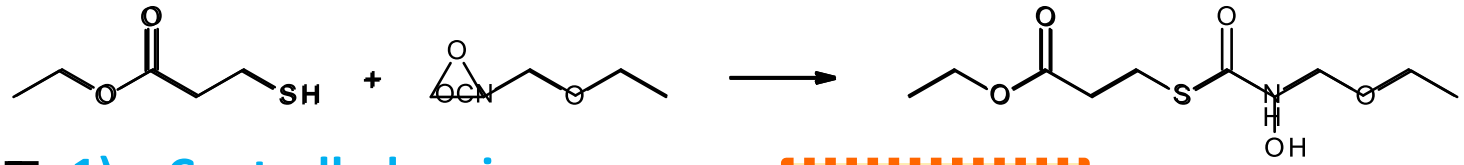
$$r_{NCO} = \frac{[NCO]_0}{[SH]_0}$$

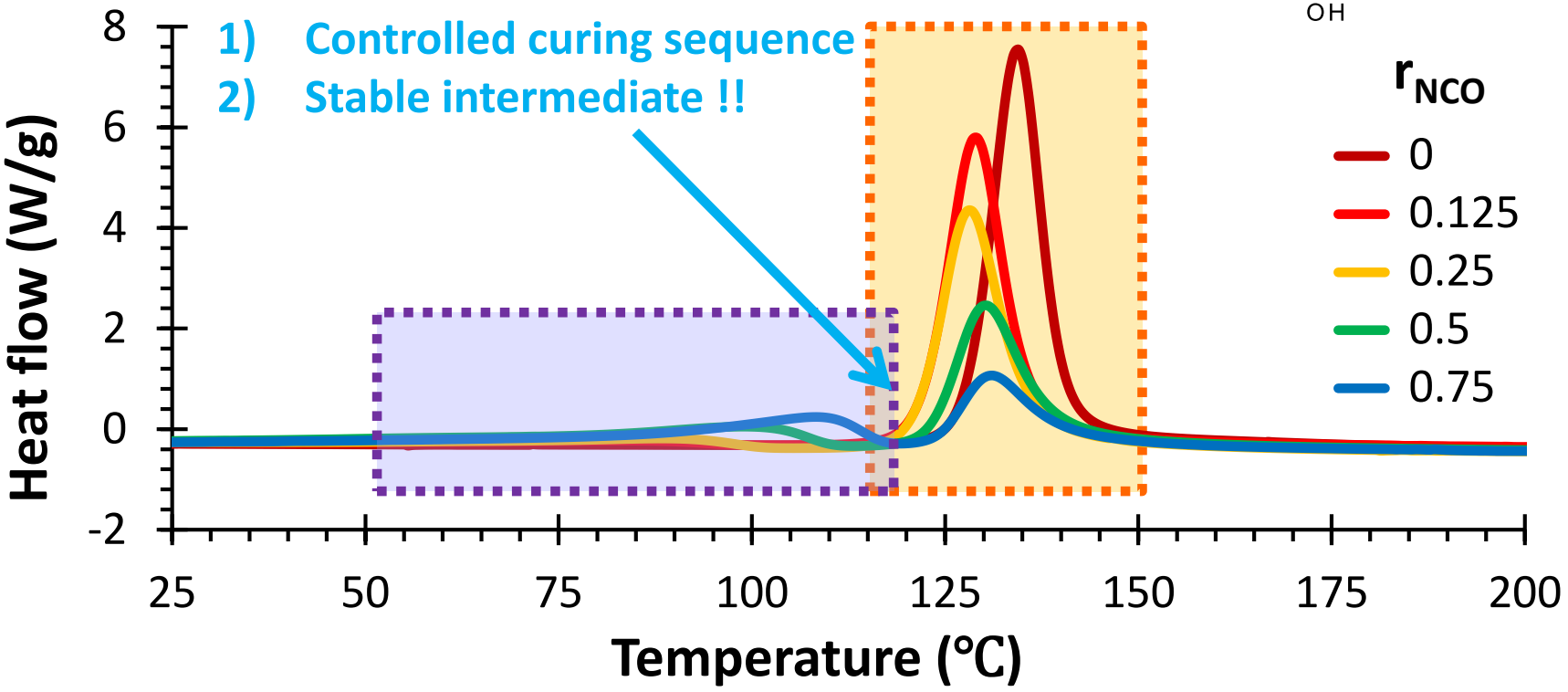
+ base catalyst (latent / non-latent tertiary amine)

Gamardella et al., *Polymer.* **2019**, *174*, 200–209
Moradi et al, *Eur. Polym. J.* **2023**, *196*, 112290
Moradi et al., *under preparation*

Control of curing sequence

2nd reaction: base-catalyzed thiol-epoxy addition (high T)





Gamardella et al., *Polymer.* **2019**, *174*, 200–209
Moradi et al, *Eur. Polym. J.* **2023**, *196*, 112290
Moradi et al., *under preparation*

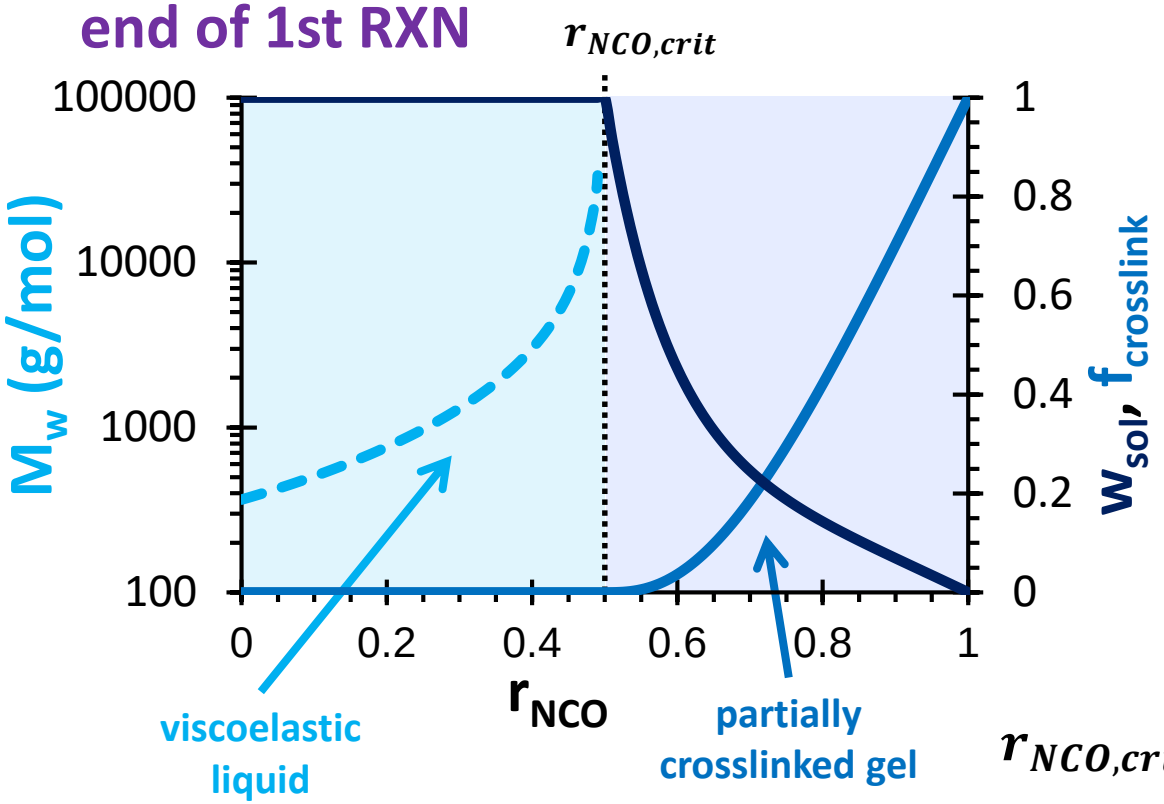
Intermediate structure analysis

Fine-tuning of intermediate material properties

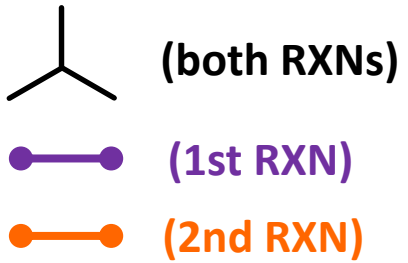
1) **Controlled curing sequence**
2) Monomer feed ratio
3) Monomer functionality/structure

?

end of 1st RXN



Network build-up analysis (Macosko-Miller)



$$r_{NCO,crit} = \frac{1}{(f_{NCO} - 1) \cdot (f_{SH} - 1)}$$

Belmonte et al., *Mater. Des.* **2017**, *113*, 116–127
Moradi et al., *under preparation*

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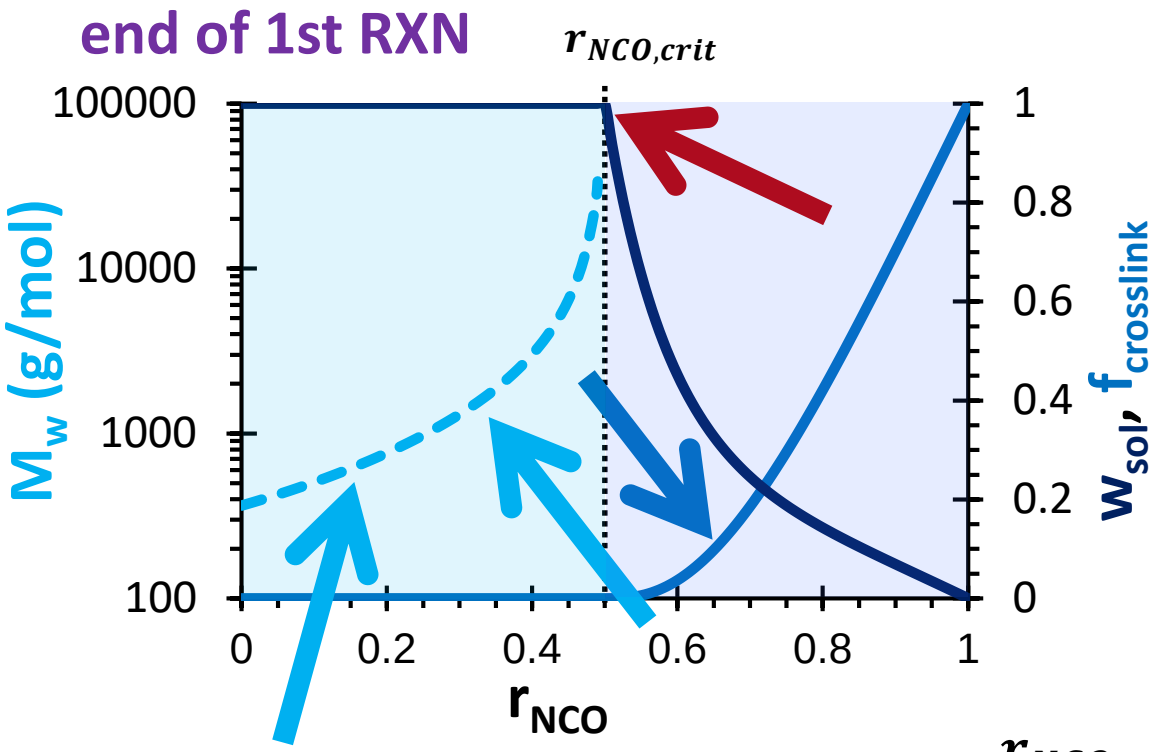

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Belmonte et al., *Mater. Des.* **2017**, *113*, 116–127
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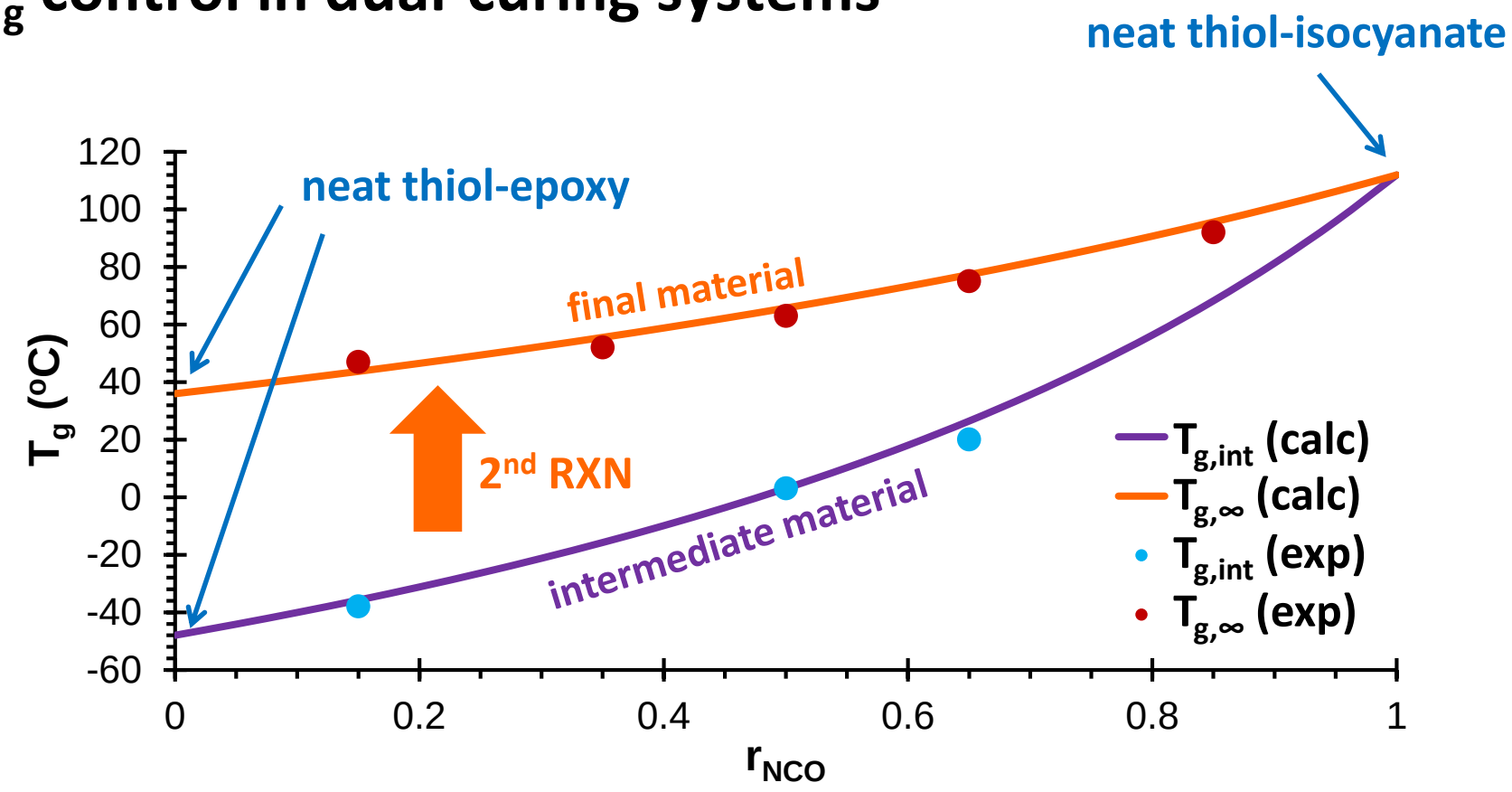
T_g control in dual-curing systems

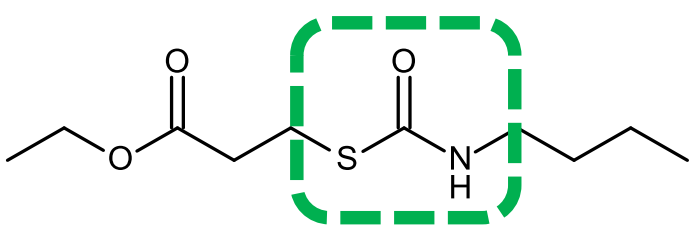


Easily predictable properties intermediate and final properties (Fox equation) !!!

Belmonte et al., *Mater. Des.* **2017**, *113*, 116–127
Konuray et al., *Eur. Polym. J.* **2019**, *116*, 222–231
Russo et al., *Eur. Polym. J.* **2019**, *112*, 376–388
Gamardella et al., *Polymer.* **2019**, *174*, 200–209

Bond exchange reactions

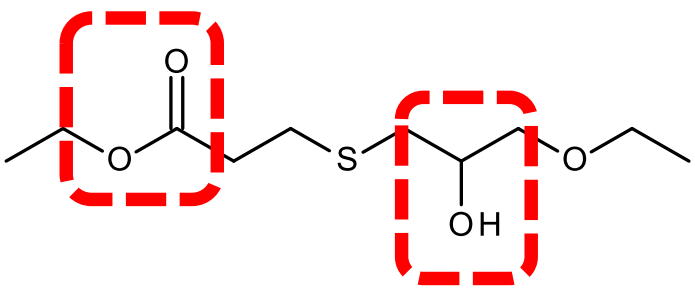
Thiol-isocyanate network



Trans-thiocarbamoylation

(“fast”, base catalyzed)

Thiol-epoxy network



Transesterification (+ others)

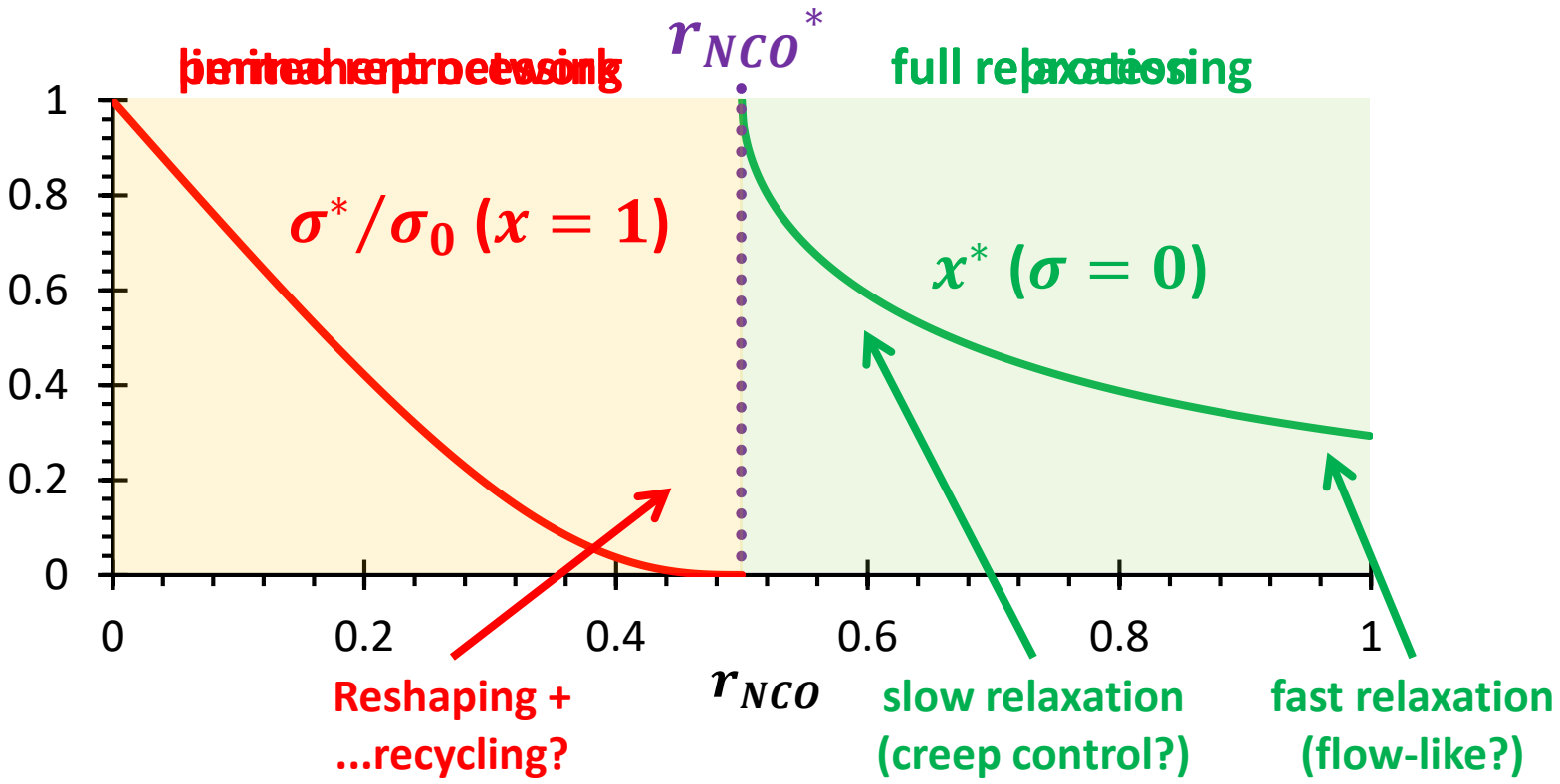
(“slow”, base catalyzed)

What is the effect of composition on stress relaxation kinetics and reprocessing scenarios?

Li et al., *Macromolecules* **2018**, *51*, 5537–5546
Li et al., *Macromolecules* **2019**, *52*, 8207–8216
Gamardella et al., *Polymers* **2020**, *12*, 2913.
Moradi et al. *Eur. Polym. J.* **2023**, *196*, 112290.

Relaxation map

1) Only trans-thiocarbamoylation takes place!!
2) Thiol-epoxy bonds are permanent

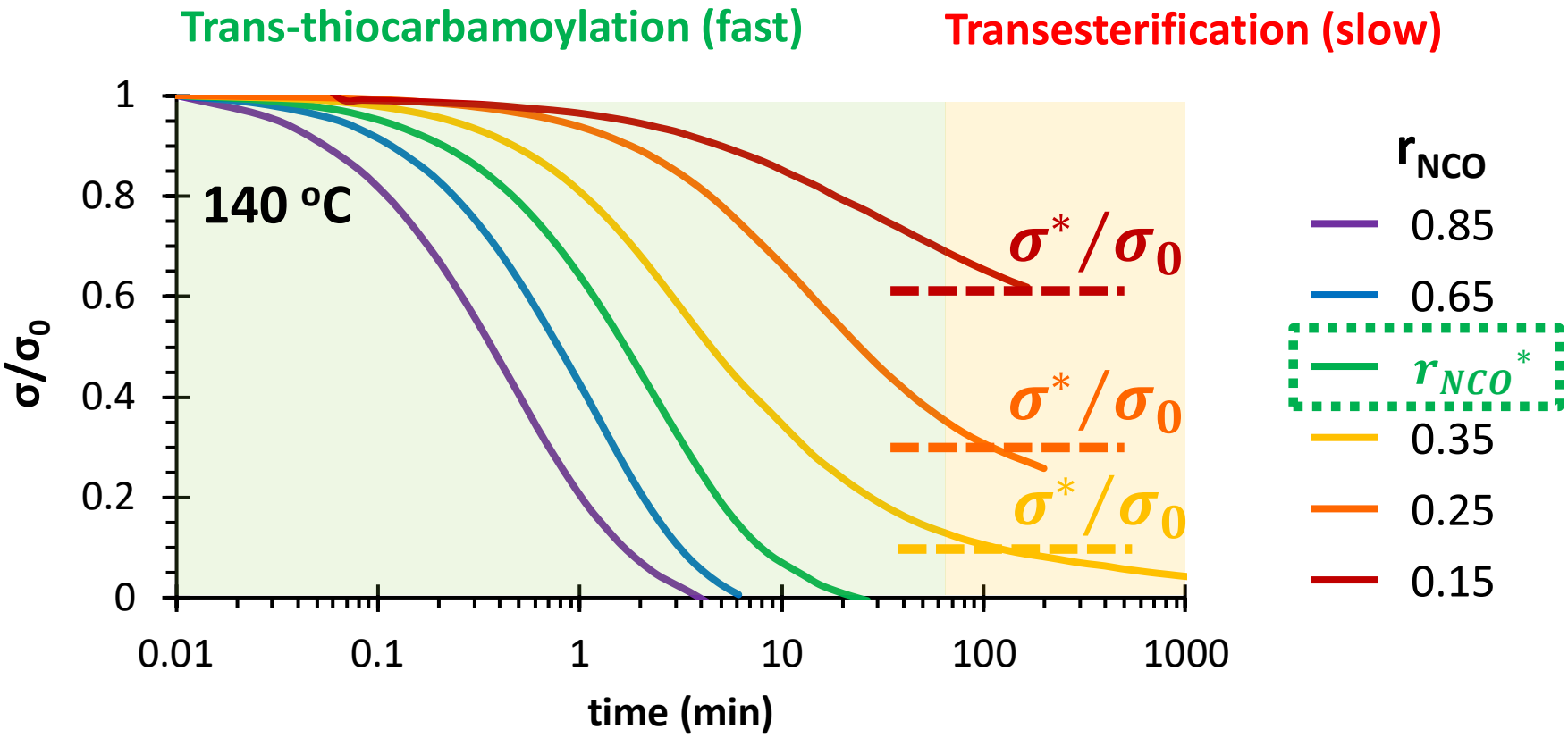


Easily predictable behavior depending on the functionality of the static / permanent components of the network structure !!

$$r_{NCO}{}^* = 1 - \frac{1}{(f_{SH} - 1) \cdot (f_{DG} - 1)}$$

Macromolecules **2018**, *51* (15), 5537–5546 (permanent network concept)
Macromolecules **2023**, *56* (13), 4855–4873

Stress relaxation

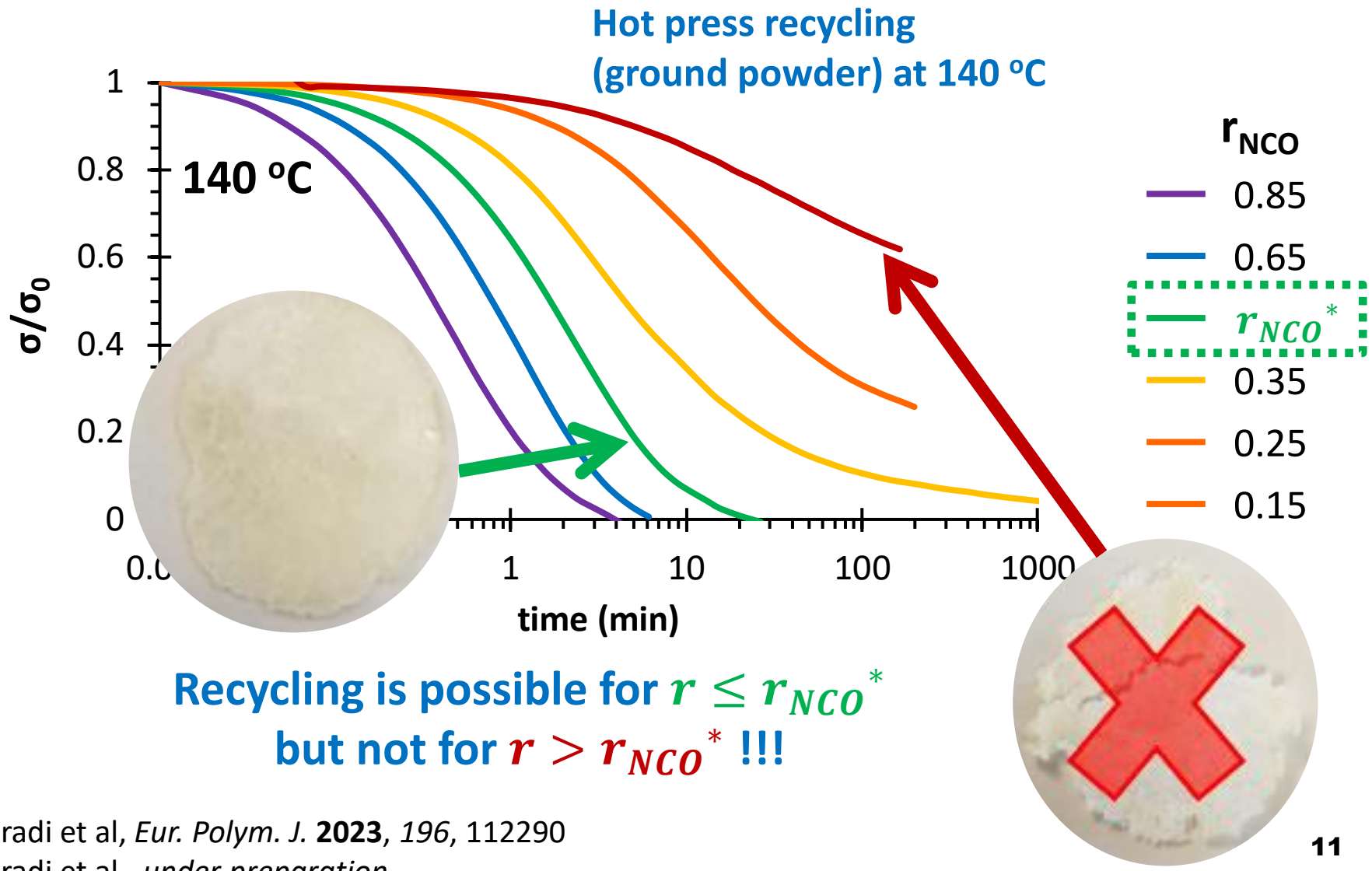


Materials relax completely at $r_{NCO} \geq r_{NCO}^*$ by transthiocarbamoylation !!

Permanent network effects (slow transesterification) appear at $r_{NCO} < r_{NCO}^*$!!

Moradi et al, *Eur. Polym. J.* **2023**, *196*, 112290
Moradi et al., *under preparation*

Stress relaxation

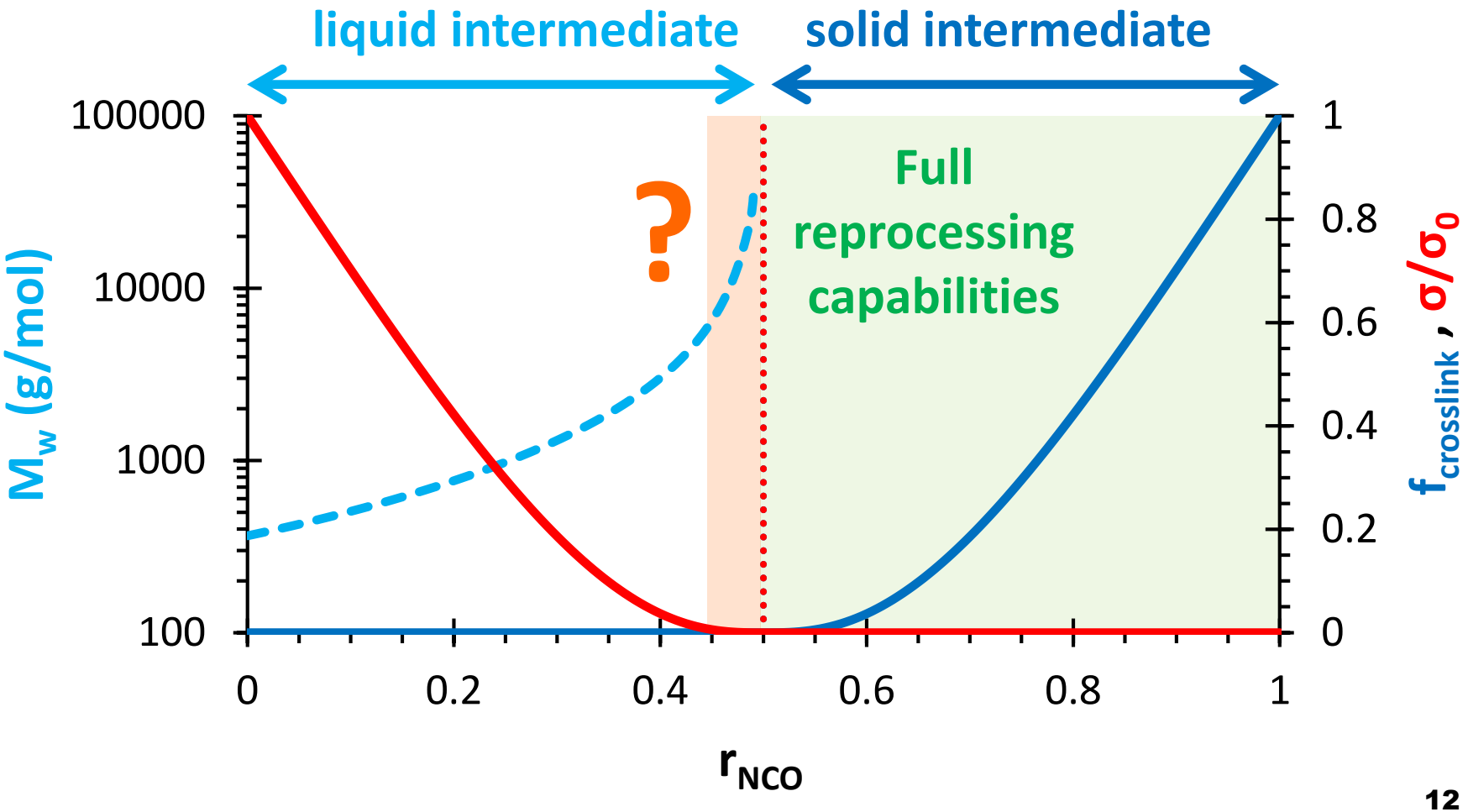


Moradi et al, *Eur. Polym. J.* **2023**, *196*, 112290
Moradi et al., *under preparation*

Processing/reprocessing map

S3 + IPDI + DG

$$r_{NCO,crit} = r_{NCO}^{*}$$

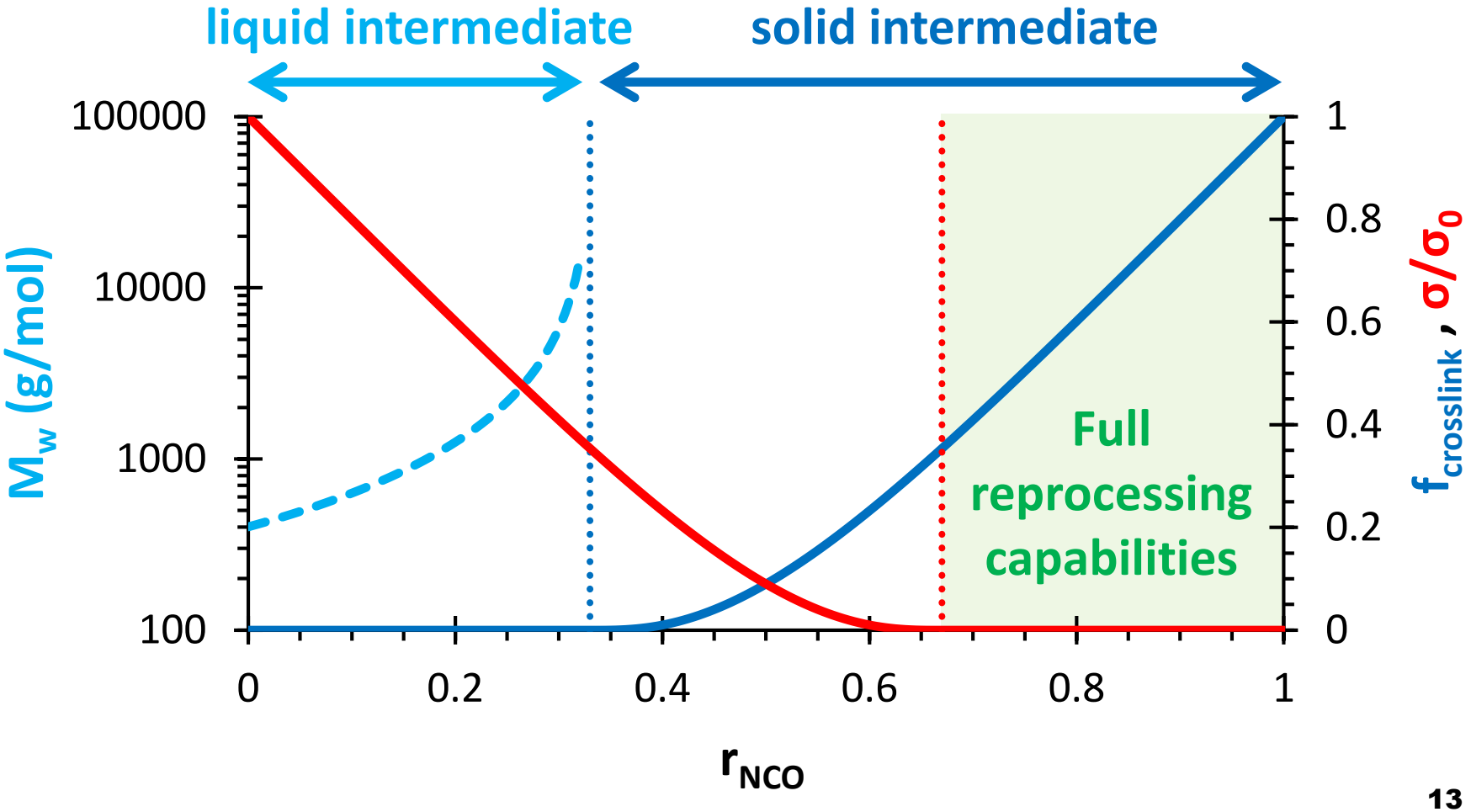


Processing/reprocessing map

S4 + IPDI + DG

$$r_{NCO,crit} < r_{NCO}^{*}$$

(increasing thiol functionality)

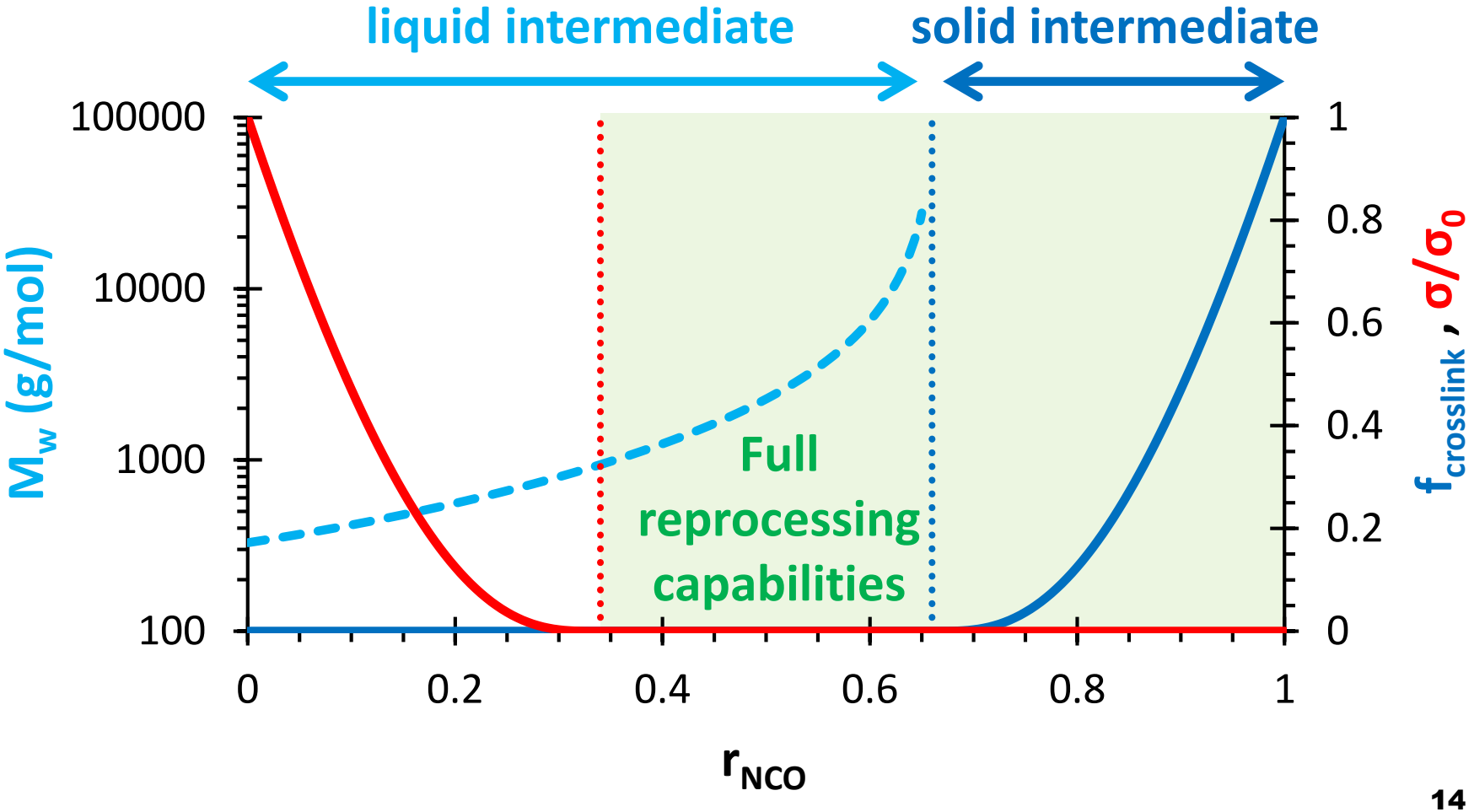


Processing/reprocessing map

S3/S2 + IPDI + DG

$r_{NCO}{}^{*} < r_{NCO,crit}$

(decreasing thiol functionality)



Conclusions

- **Dual-curing CANs** with **controlled processing** and **reprocessing** can be **engineered** and **prepared**.
- **Simple design criteria** can be defined depending on the **feed ratio and functionality** of the network components.
- Crosslinking and relaxation maps can be used to **predict expected behavior** and **design materials** for **target application scenarios: composites**, **adhesives**, **coatings** & **3D-printing** applications…
- **Cost of CANs** can be **optimized** (**reduction of dynamic component!!**)
- **Many other systems** (**complex, non-ideal,…**) can be studied!!

Design methodology based on structure & kinetics analysis with experimental thermoset characterization & modelling

snack thermosets
smart **n**etwork **a**rchitecture
& **c**ontrolled **k**inetics

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https://futur.upc.edu/POLTEPO

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Dailyn Guzmán
Pere Verdugo

Current projects in covalent adaptable networks (CANs)

VI3DUAL (PID2020-115102RB-C22)
DYNETFUN (PID2023-147128OB-C21)

MINISTERIO DE CIENCIA, INNOVACIÓN Y UNIVERSIDADES

AGENCIA ESTATAL DE INVESTIGACIÓN

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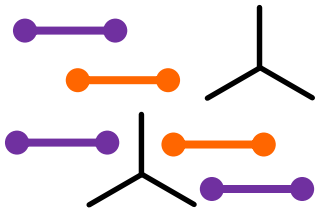
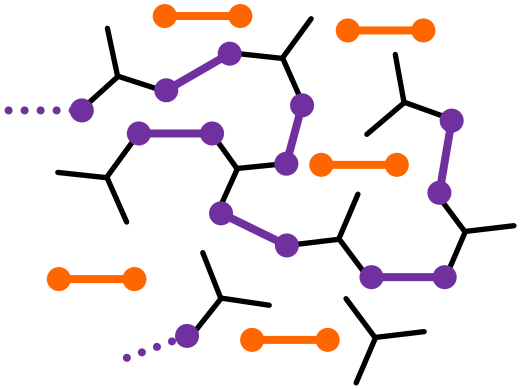
Dual-curing processing



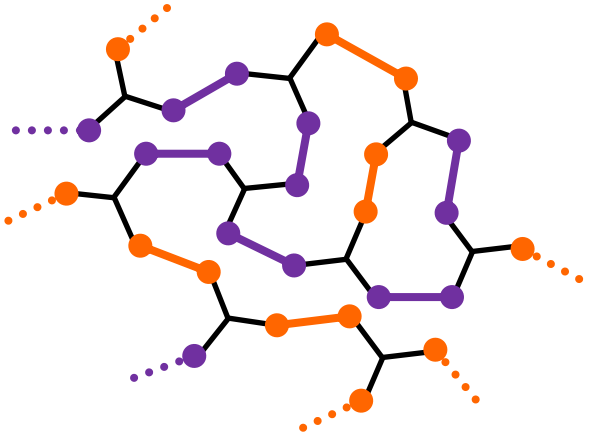
starting monomers

1st RXN



intermediate structure
unreacted monomers

2nd RXN



final network

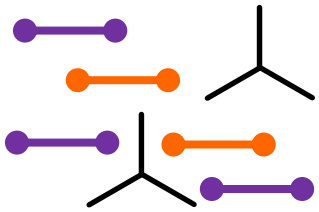
1) Custom-tailored intermediate structure & properties (processing)

2) Ultimate structure & properties (application)

- Control of curing sequence
- Composition

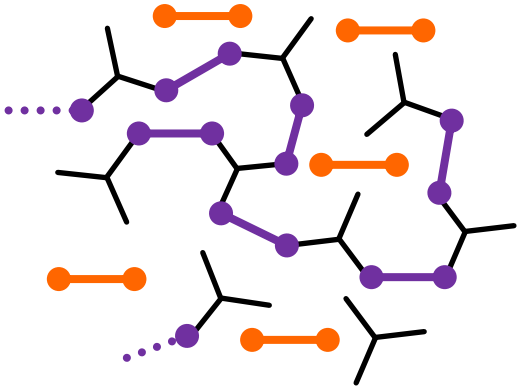
Chapter 16 In *Thermosets: Structure, Properties, and Applications: 2nd Edition,* Elsevier, 2018

Dual-curing vitrimer processing



starting monomers

1st RXN



intermediate structure
unreacted monomers

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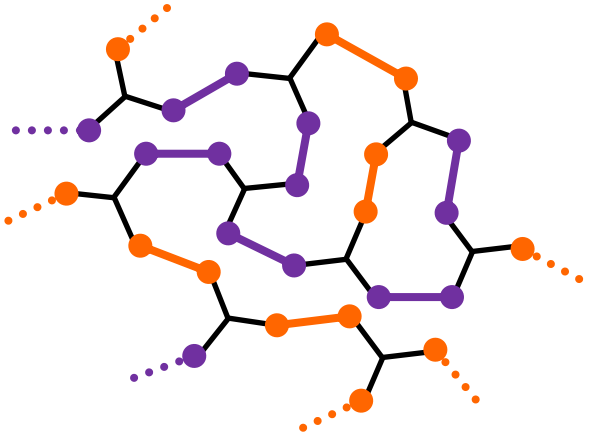


final covalent adaptable network

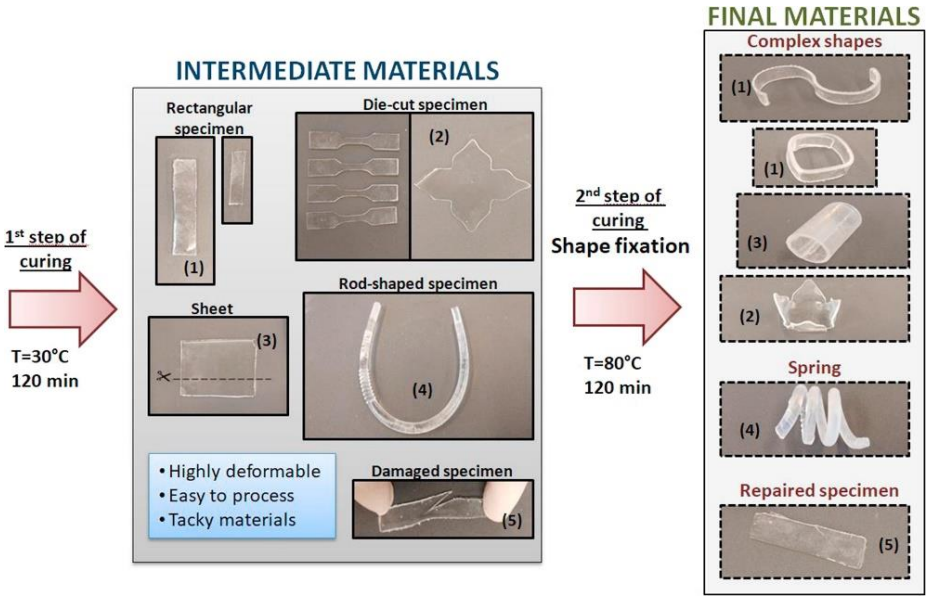
1) Custom-tailored intermediate structure & properties (processing)

2) Ultimate structure & properties (application)

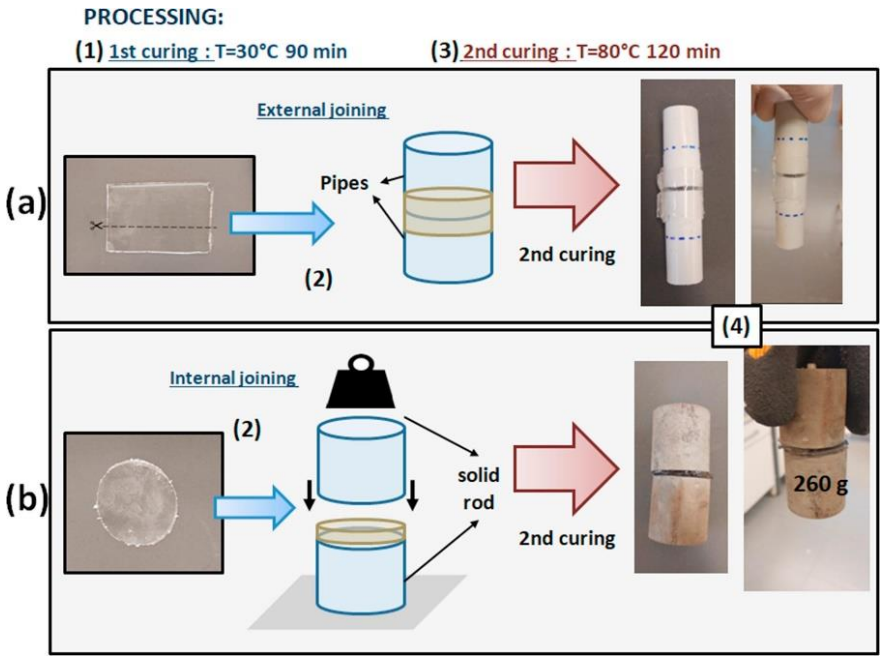
3) Reprocessing capabilities (repair, recycling...)

What for?

Creation of complex geometries from simple solid-like intermediate templates



Structural joints from adhesive intermediates



We can add reprocessing capabilities to the fully cured components !!

Belmonte et al., *Mater. Des.* **2017**, *113*, 116–127
Russo et al., *Eur. Polym. J.* **2019**, *112*, 376–388
Russo et al., *Int. J. Adhes. Adhes.* **2022**, *112* , 102959