PURеSmart

PolyUrethane Recycling Towards
a Smart Circular Economy

Smart design

Towards foam-to-foam recycling via the use of Covalent Adaptable Networks

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dissemination workshop
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Strategic Place within PUReSmart Project

- **Smart Sorting:**

  separate end-of-life PU foam waste streams (by chemical class)

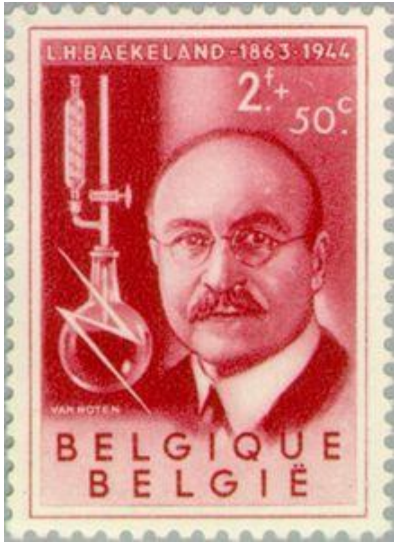
- **Smart Chemolysis:**

  turn PU waste into new PU building blocks (chemical recycling)

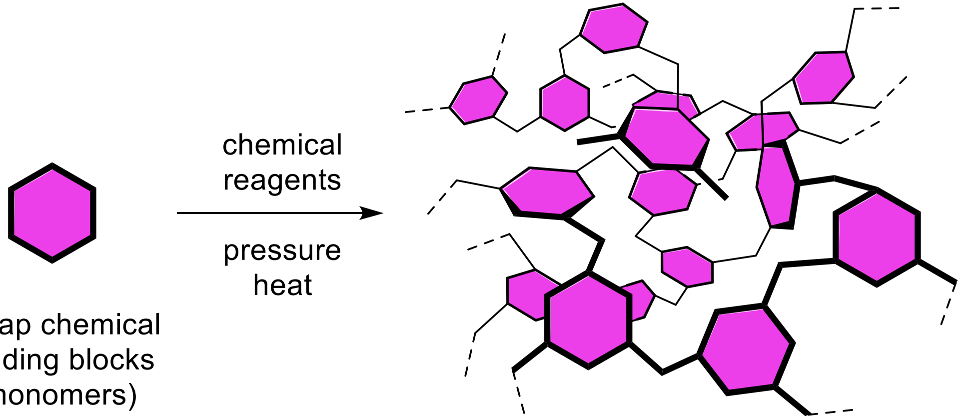
- **Smart Design:**

  (re)design PU foam products that can be re-used as raw material

Intro: Synthetic Thermosetting Materials



Leo Baekeland, inventor of synthetic thermoset materials



cheap chemical building blocks (monomers)

3-dimensional network material = one big solid molecule

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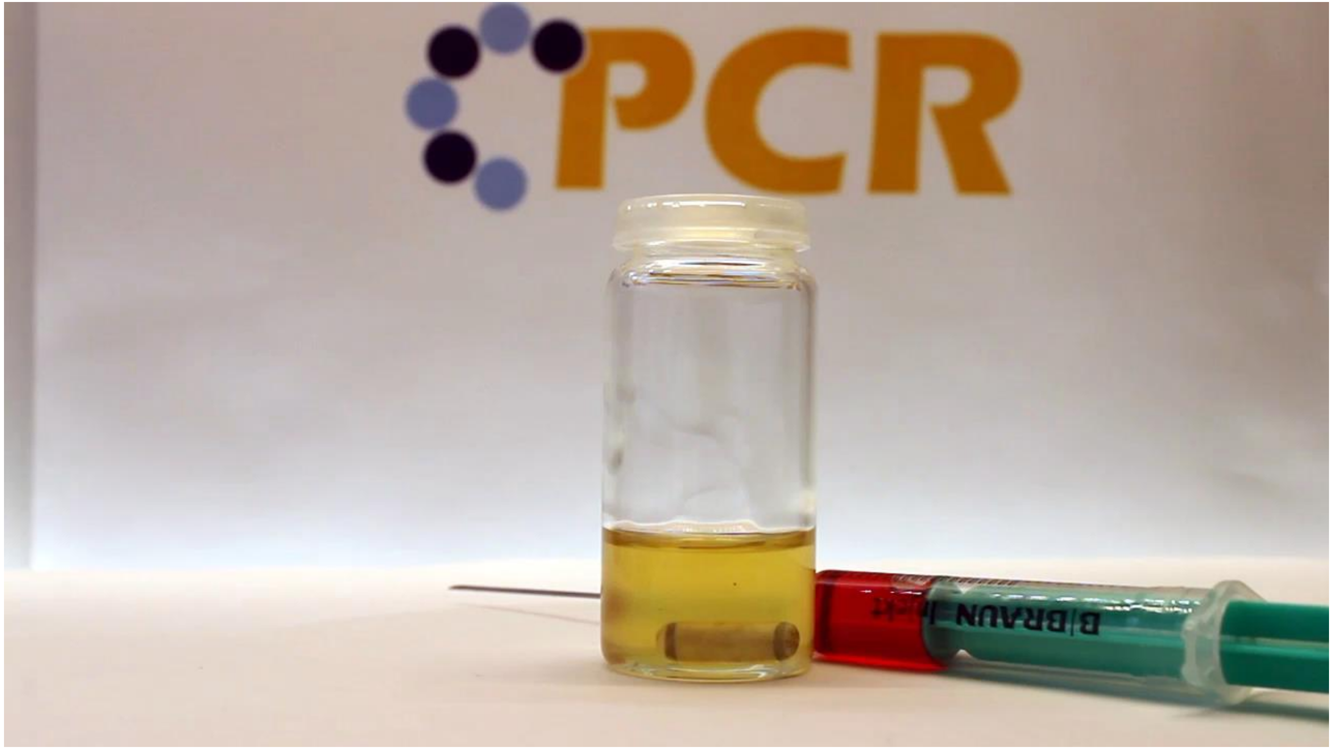
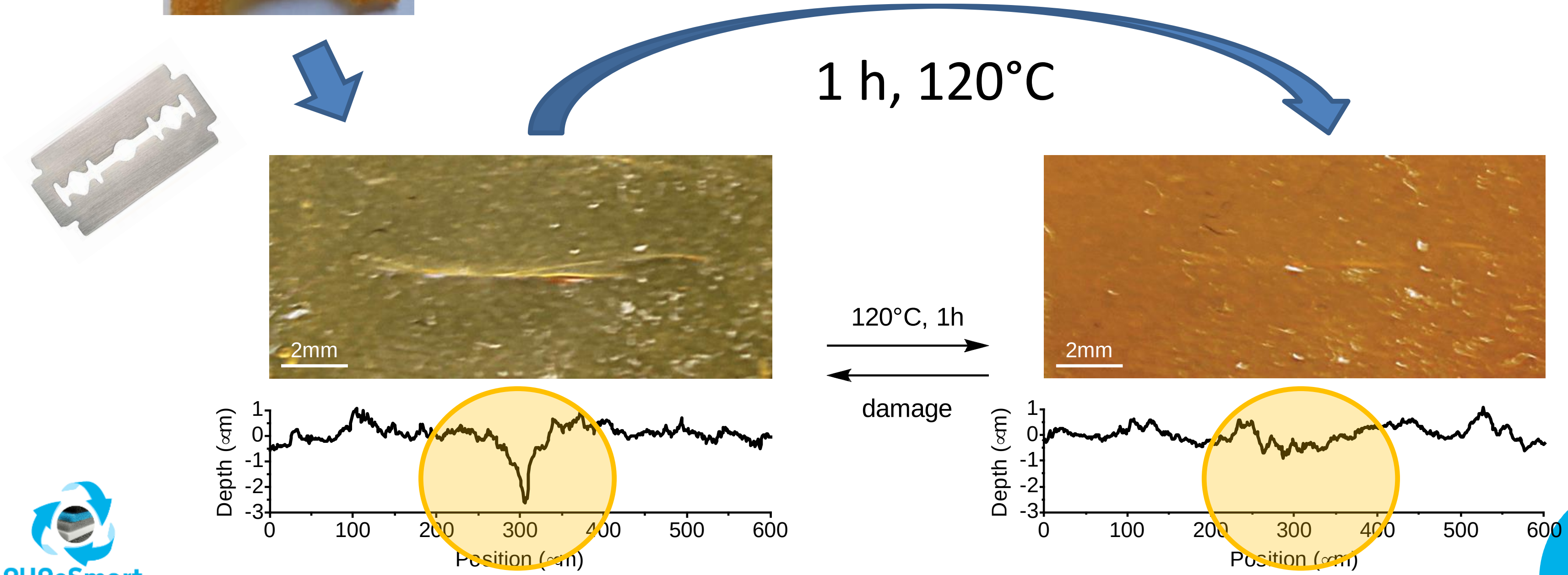
Main concept: Covalent Adaptable networks

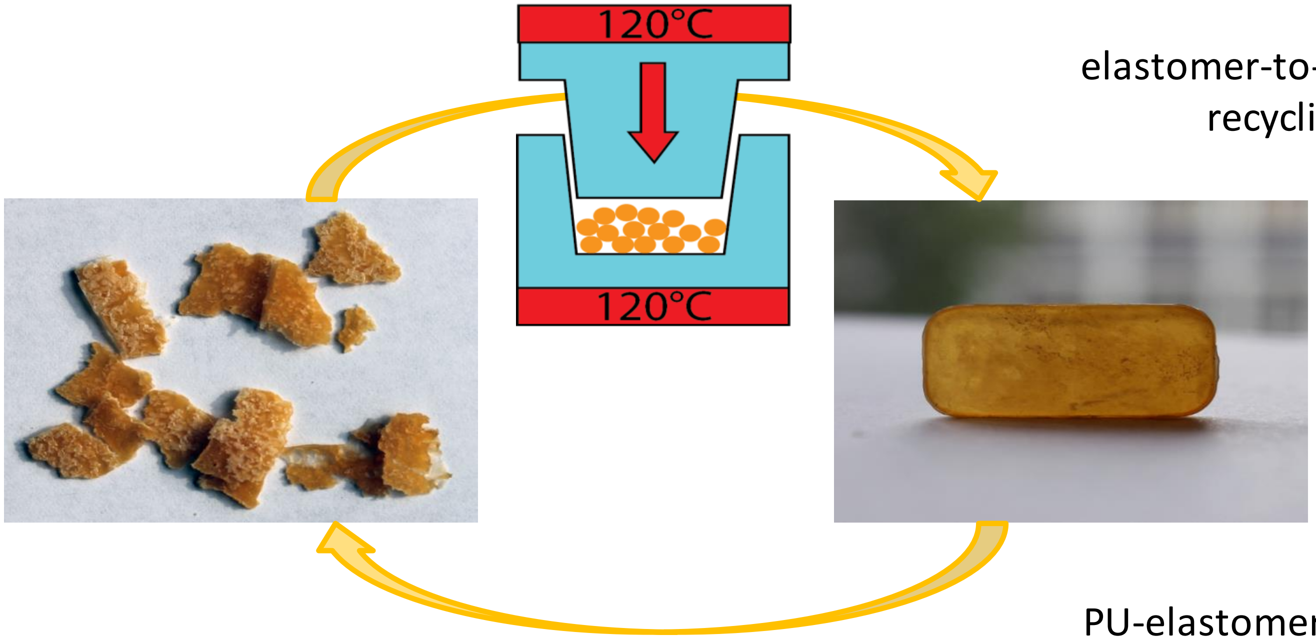


Covalent Adaptable PU: healing

= PU-elastomer with covalent adaptable cross-links (CAPU-elastomer)



Covalent Adaptable PU: recycling



elastomer-to-elastomer
recycling

PU-elastomer retains material
properties through many cycles

Billiet S., De Bruycker K., Driessen F., Goossens H., Van Speybroeck V., Winne J. M., Du Prez F. E.
Nature Chem., **2014**, *6*, 815 – 821.

Smart CAPU foam Design: Main Objectives

- Screen lab-scale technologies for PU thermoset recycling as **covalent adaptable** PU (CAPU) with focus on industrial relevance (no solvent/cheap materials/…)
- Production of PU elastomer sheets for probing mechanical properties and recycling (**elastomer-to-elastomer** reprocessing) for further selection of CAPU technology
- Scale-up the most successful chemical technologies for **CAPU foam** synthesis, with a focus on **foam-to-elastomer recycling** trials (100 gram)
- Use supercritical CO_2-technology for foaming CAPU elastomers: **elastomer-to-foam**
- ScCO_2 -based refoaming process of recycled CAPU foams: **foam-to-foam**
- Pilot scale/industrial demonstration scale production of best CAPU comonomers for larger scale PU foam production with improved intrinsic recycling properties

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Smart CAPU foam Design: Hurdles

- NO commercially available (co)monomers that allow large scale CAPU production are known or available at start of project (so their cost is unclear)
- ONLY **elastomer-to-elastomer** reprocessing has ever been demonstrated for CAPU and other covalent adaptable networks (industrially only for high T_g thermosets)

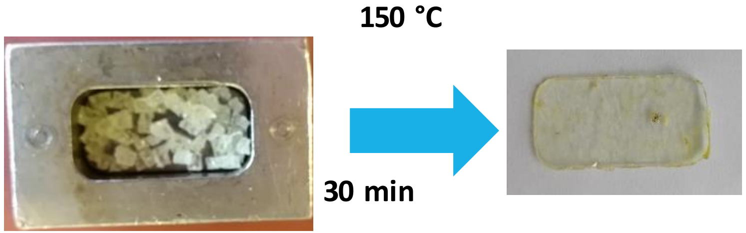
CAPU lab scouting: Main Results

- Over 20 different comonomers were prepared and screened, belonging to all known classes of CAPU chemistries that have potential in PU markets.
- Two main technologies were retained as most promising for scale-up:
  - Thiourethane technology (developed in PUReSmart)
  - TAD-indole technology (developed at UGent, further refined in PUReSmart)
- Selection criteria:
  cost/scalability/PU material properties/recycling properties

Polythiols as CAPU comonomers

- Commercially available polythiols (used in PU coatings)
  - Successful in elastomer recycling trials (less good than TAD-indole)!
  - Technical issues: very rigid elastomers/foams (only low MW)
  - Technical issue: smell

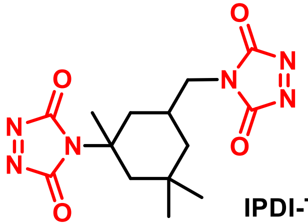
- PUReSmart innovation
  - Prepared non-smelly, less rigid, long chain polythiols from normal PU foam polyols (10 kg)
  - Can be used in flexible foam formulations
  - Technical issue: a bit too dynamic?



TAD-indole based polyol CAPU comonomers

- Known TAD-indole CAPU comonomers (developed previously @UGent)
  - Most promising in PU recycling trials!
  - Technical issues:
    - → higher cost/effort of synthesis!
    - → available TAD-indoles not compatible with flexible PU foam

- PUReSmart innovation
  - First pilot scale synthesis (50kg) of TAD-based cross-linker
  - Stability studies show industrial potential of the monomer/cross-linker
  - First demonstration scale (1 kg) of liquid TAD-indole based polyol
  - Technical issue: polyol too costly to be produced on larger scale



IPDI-TAD

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Polythiol CAPU foam trials

	Ref							
Standard polyol	100	98	95	90	85	80	80	75
Commercial polythiol	0	2	5	10	15	20	20	25
Density (kg/m³)	+	+	+	+	+	+	+	-
CLD hardness 40% (kPa)	+	+	+	+	+	+	+	+
Air resistance (cm H2O)	+	+	+	+	+	+	+	+
Compression set 50% at 70°C (%)	+	+	+	+	+	+	+	-
WCS 50°C at 95%RH (%)	+	+	+	+	+	+	+	+
Ball rebound (%)	+	+	+	+	+	+	+	+
Elongation at break (%)	+/-	+	+	+/-	+/-	+/-	+/-	+/-
Tensile strengh (kPa)	+/-	+	+	+/-	+/-	+/-	+/-	+/-
Tear resistance (N/cm)	+/-	+	+/-	-	-	-	-	-

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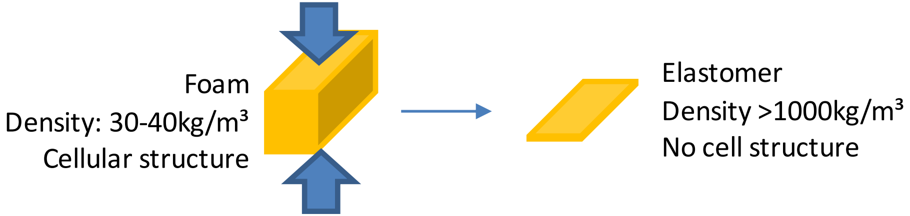
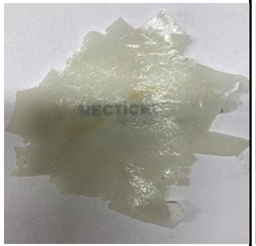
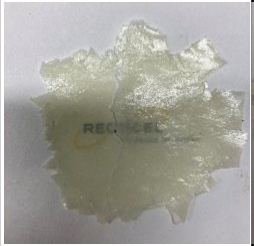
Polythiol CAPU foam-to-elastomer recycling

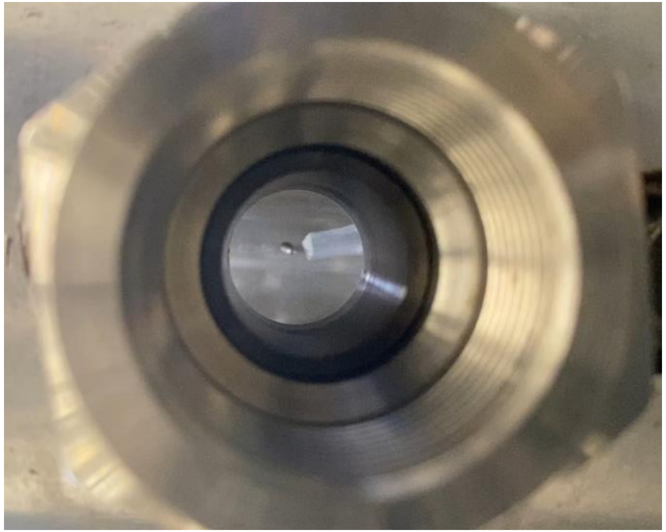
- **Foam-to-elastomer recycling**
  - **Compression molding**
  - **x min, xbar, x° C**

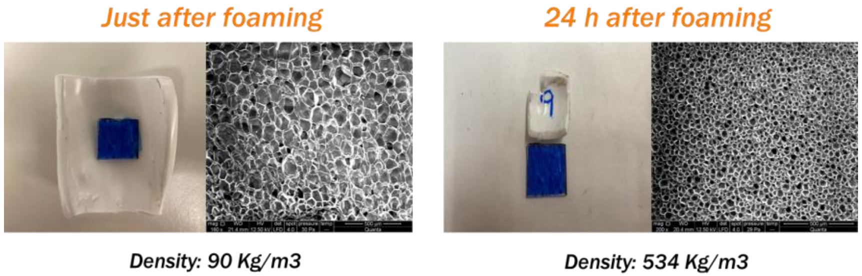


	1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle	6th cycle	7th cycle
Ref							
100% SH							

Polythiol CAPU elastomer-to-foam trials

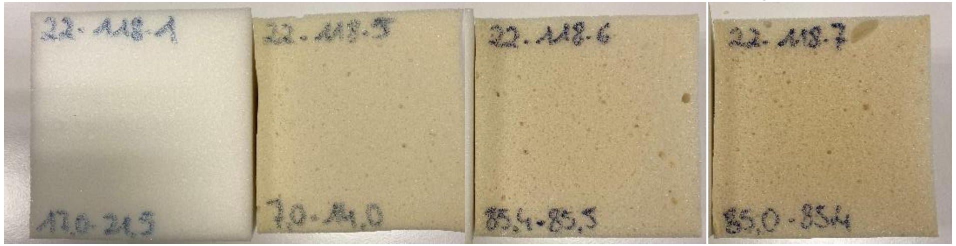
- $scCO_2$ foaming of Thiourethane elastomers (UCLM)
  - Series of elastomers based on PPG1000 + TDI + β-trithiol (commercial small thiol molecule)





TAD-indole CAPU foam trials

Reference | 20p TAD/indole | 30p TAD/indole | 40p TAD/indole



LI 2022-0118			1	5	6	7
Polyol			100	80	70	60
TAD/indole crosslinker v3.0				20	30	40
Blow off		Scale 0-5	4	4	1	1
Settling			no	5,40%	3,30%	2,70%
Density	EN/ISO 875 M1	kg/m³	+	+	+	+
Air resistance	C&TF/T.015.0	cm H2O (min-max)	+	+	-	-
CLD Hardness 40%	EN/ISO 3386/1 M1	kPa	+	+	+	+

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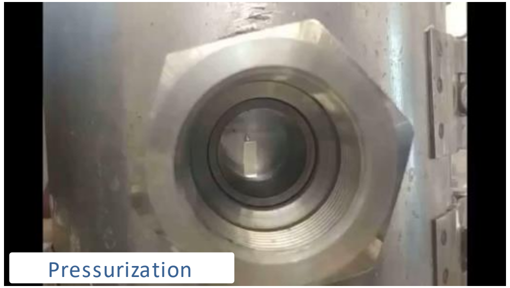
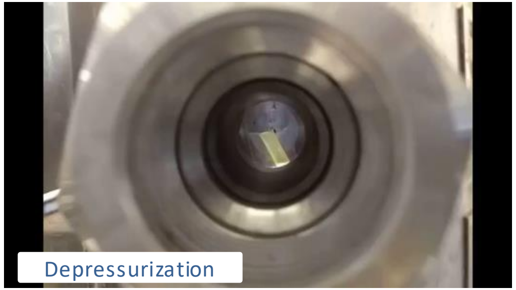
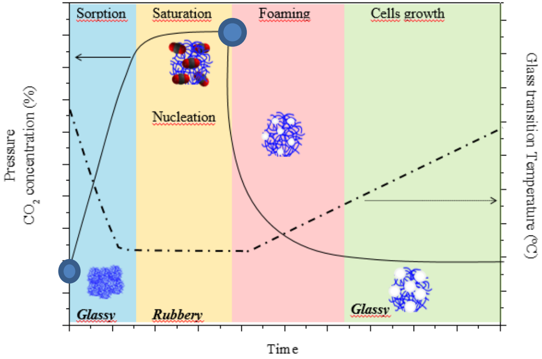
TAD-indole foam-to-elastomer recycling

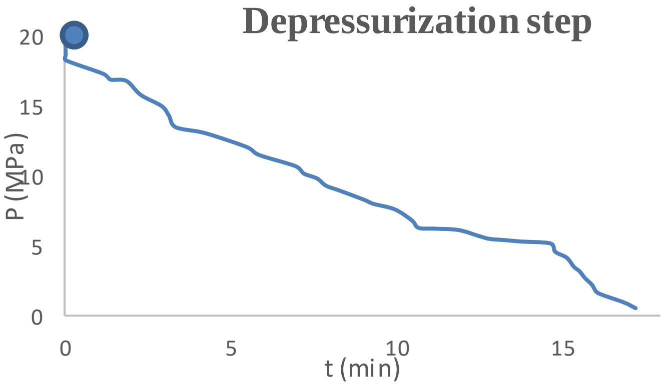
	1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle	6th cycle	7th cycle
Ref							
20/80							
30/70							
40/60							

TAD-indole elastomer-to-foam trials

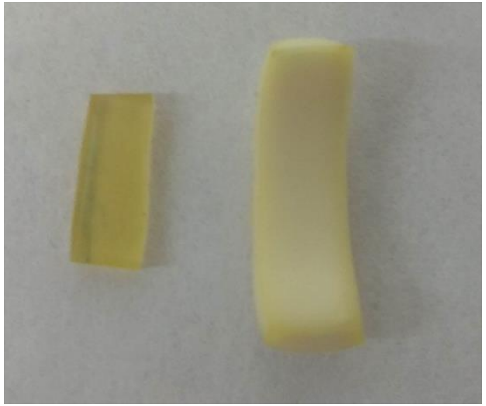








OBSERVABLE FOAMING



Foam to foam?

- Until now, none of the CAPU elastomers obtained from recycling CAPU foams could be re-foamed.
- It seems that the total crosslink density has an influence on the "foamability" of the elastomer
- Due to the trifunctional raw materials and the excess of isocyanates, PU foams are usually highly crosslinked

Conclusions

- Two promising and (in principle) industrially scalable CAPU technologies have been developed for improving the recyclability of PU products
- TAD-indole polyols are found to be best performing but are not cost-effective in PU foams, but can be more cost-effective in other PU or thermoset matrices
- Polythiols are on the PU coating market and have been recognized for their potential to improve intrinsic recyclability of various PU products
- First proof-of-principle for physical blowing of a fully cross-linked PU elastomer opens potential for closing the cycle in thermosetting foam materials.
- Achieving good foam properties is possible, but this comes at the cost of lower recyclability. A balance must be found. The road for industrialization of the CAPU concept may be still long, and can be niche-dependent.

Thank you

Any question?