Thermoplastic silicone elastomers: an endless story

F. GANACHAUD

Université de Lyon, Ingénierie des Matériaux Polymères, CNRS UMR 5223,

IMP@INSA, Villeurbanne, France

francois.Ganachaud@insa-lyon.fr

Elasto-Plast final meeting, remotely, 16 March 2021

Dedicated to the memory of Jean-Pierre PASCAULT

WARNING

Silicone TPEs are hardly commercialized at the moment so this speech mainly cover academic works

- F. Ganachaud, *Thermoplastic silicone elastomers: an endless story*, L'actualité Chimique, n°456-458, 74-81 (2020/2021) (in French)
  Submitted to *JAST* (2021) (in English)

- B. Yi et al, *Dynamic siloxane materials: from molecular engineering to emerging applications,* Chemical engineering Journal, 405, 127023 (2021).

- Z. Wang et al, *Preparation, characterization and properties of intrinsic self-healing elastomers*, Journal of Materials Chemistry B, 7, 4876-4926 (2019).

Focus mainly on mechanical properties

Speech overview

- ✓ **Context**

  Supramolecular chemistry and silicone TPEs

- ✓ **Silicone urea (co)polymers**

  Functional silicones, multiblock copolymers, self-healing

- ✓ **New chemistries**

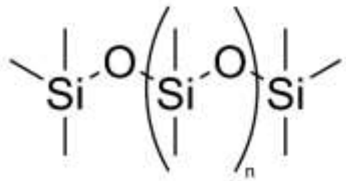
  Ionic pairing, metal-ligand,(covalently-reversible) vitrimers

- ✓ **Applications**

  Electronics, antifouling, shape memory….

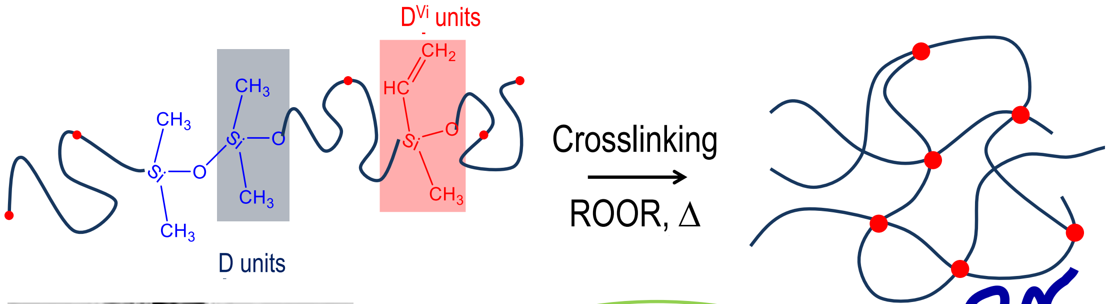
Context

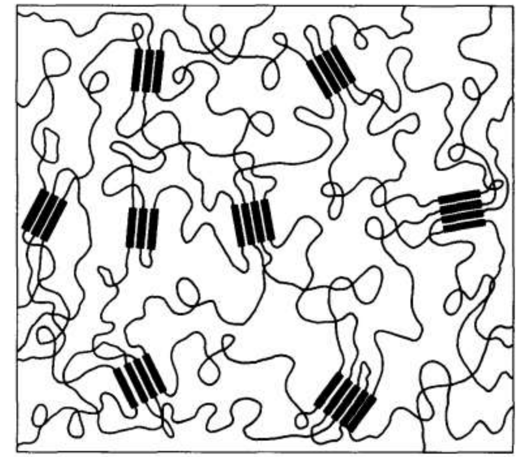
Silicone elastomers

- ✓  : High flexibility, $T_g < -120°C$
- ✓ **Rubber**-like, semi-organic materials, filled with silica
- ✓ Chemically inert, **biocompatible**, high gas permeability
- ✓ **Low modulus** (few MPa), **hyperelasticity**, large **strain at break** (>1000%)

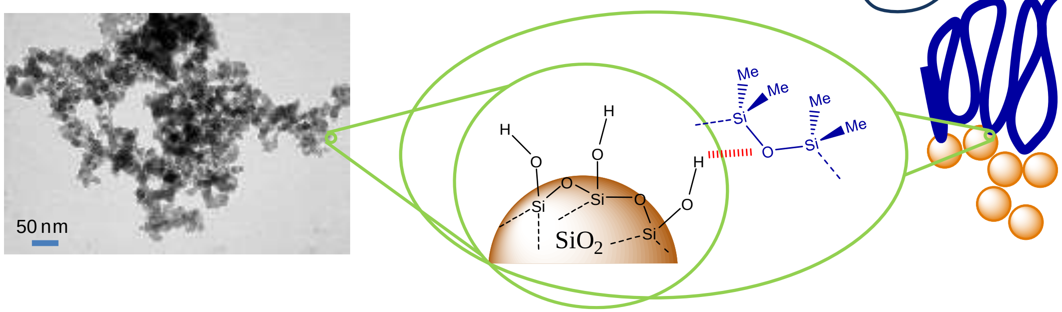
Conventional silicone elastomers vs TPE

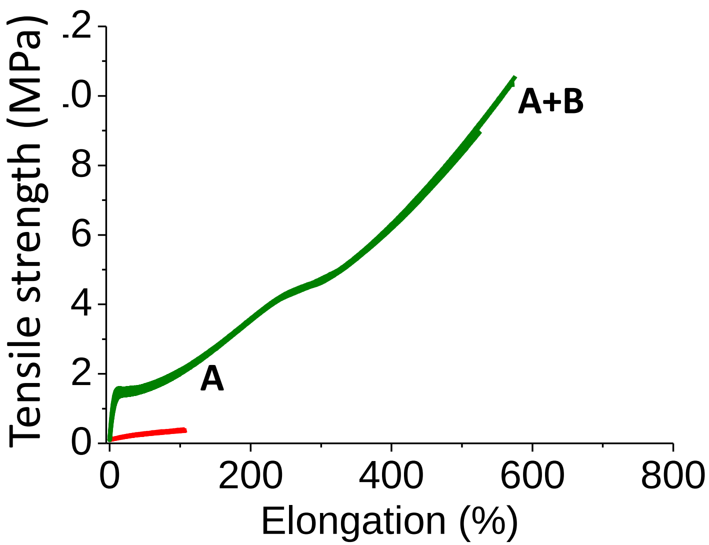
A

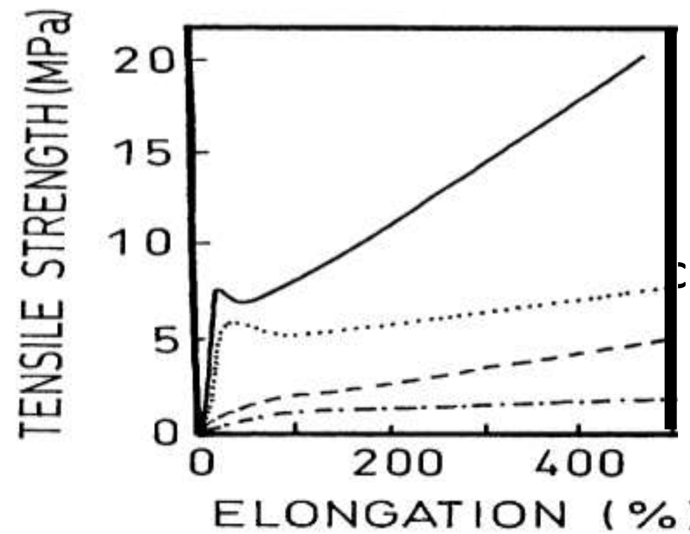




B







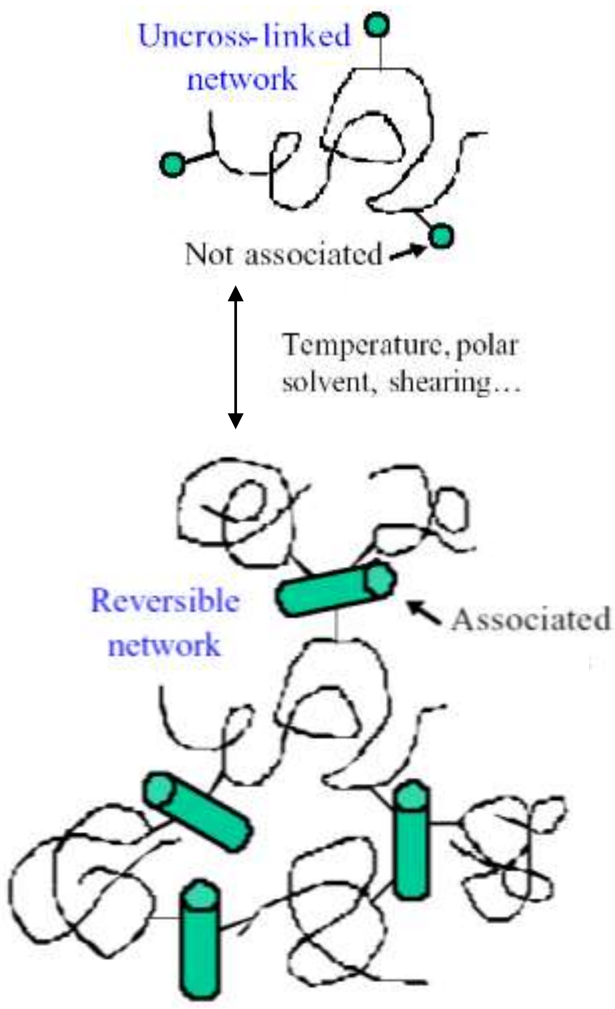
Supramolecular chemistry

Covalent bond		200 - 400 kJ/mol
Physical interactions	ion - ion	100 - 350 kJ/mol
	ion - dipole	50 - 200 kJ/mol
	H bonding (alcohol – acid)	5 - 120 kJ/mol (15 – 60kJ/mol)
	dipole - dipole	5 - 50 kJ/mol
	π - stacking	0 - 50 kJ/mol
	Van der Waals	0 - 5 kJ/mol

A large range of available reversible links

Supramolecular materials

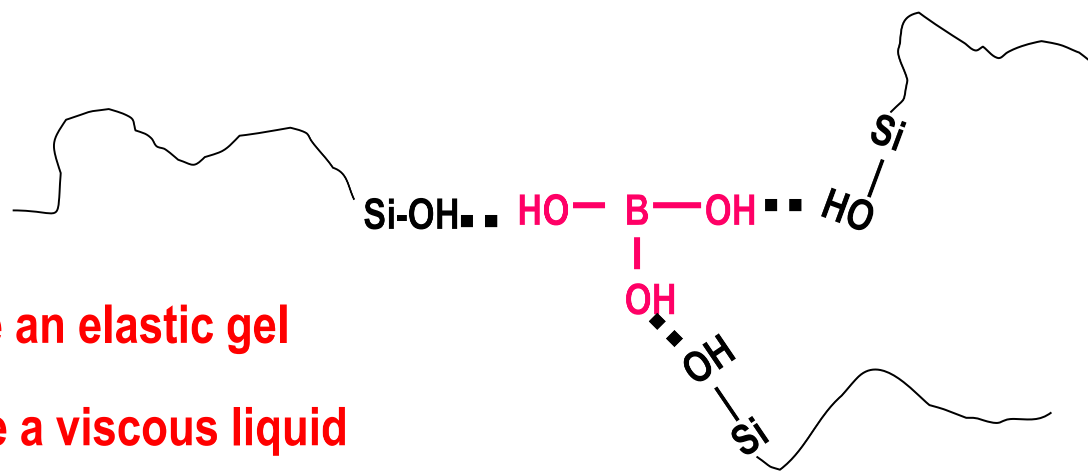
Block copolymer nanostructuration OR association through weak interactions



- Various possibilities
  - H bond ⇨ growing in two directions
  - (Pseudo)-ionic pairs ⇨very stable
  - Others (A/D, π - stacking…) + combinations
- Flexibility and robustness
  - Functional group location
  - Multiple interactions in polymers
  - Phase demixion helps the structuration

Reversibility

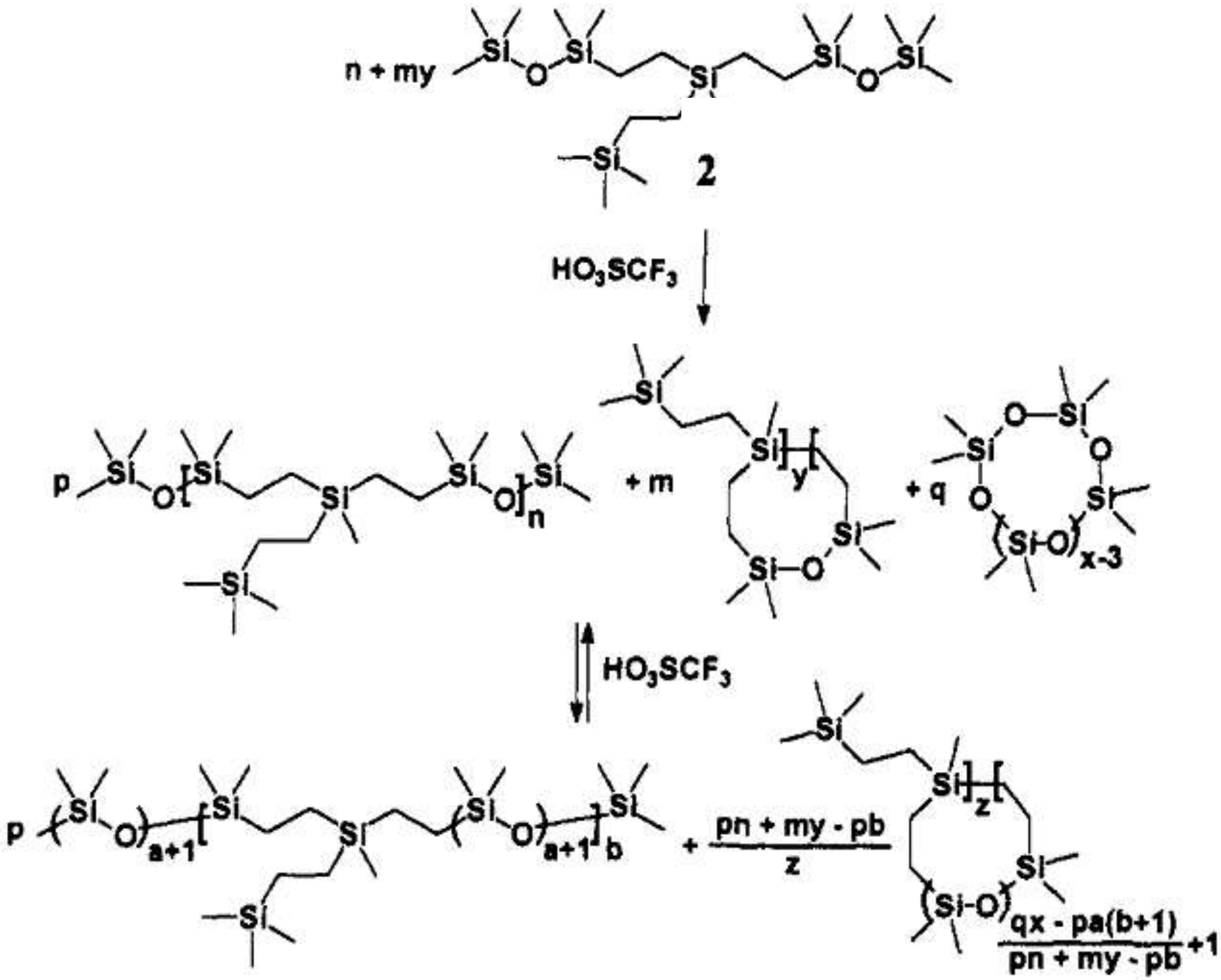
Self-assembly of silicones: « Silly putty » (1943)



Rapid stress ⇨ **behaves like an elastic gel**

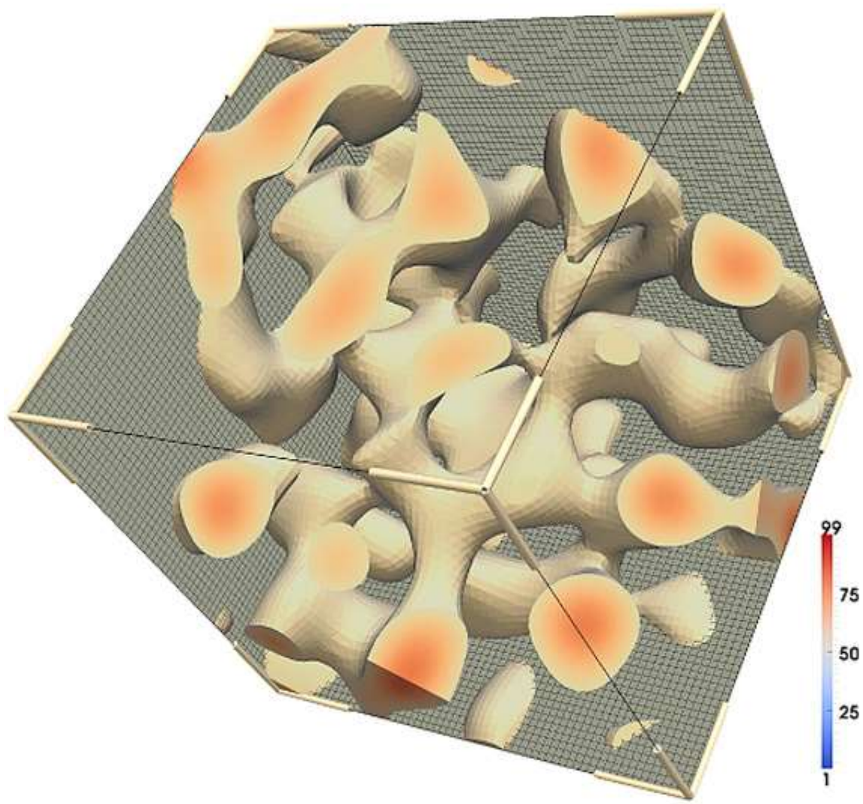
Slow stress ⇨ **behaves like a viscous liquid**

Self healing systems: living polymer network



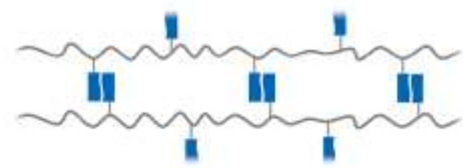
P. S. Chang, M. A. Buese, US patent 5,347,028 /*JACS*, 1993, *115*, 11475-11484.

Silicone ureas



Brief survey

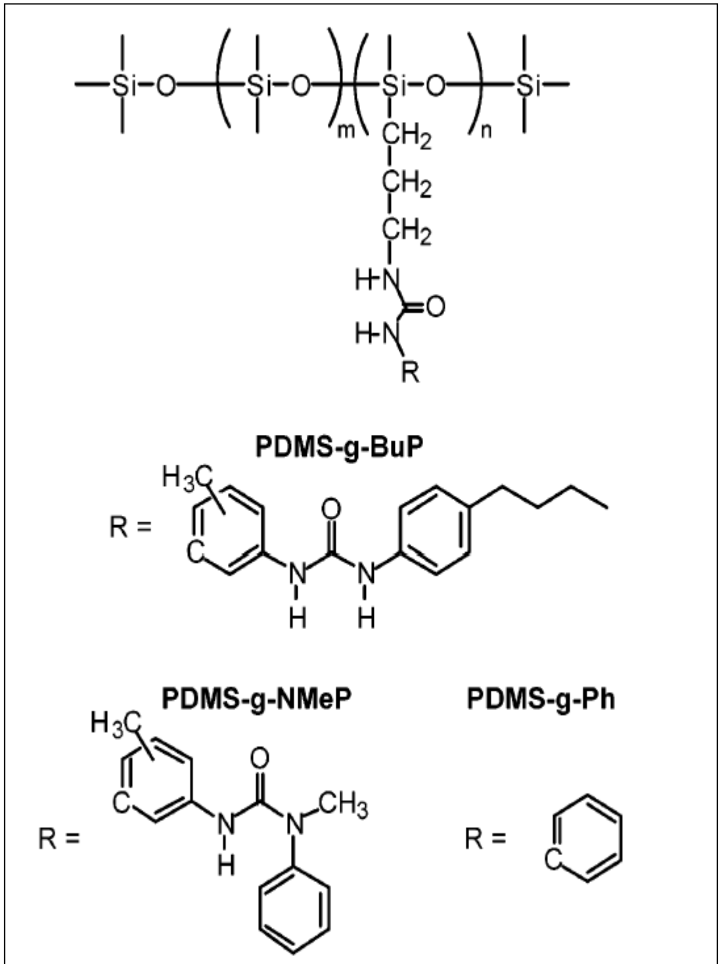
- ✓ **Inspired from polyurethane TPEs**
  - Seminal work of Yilgor and Yilgor
- ✓ **Two main categories**
  - Modified silicone backbone vs multiblock copolymers

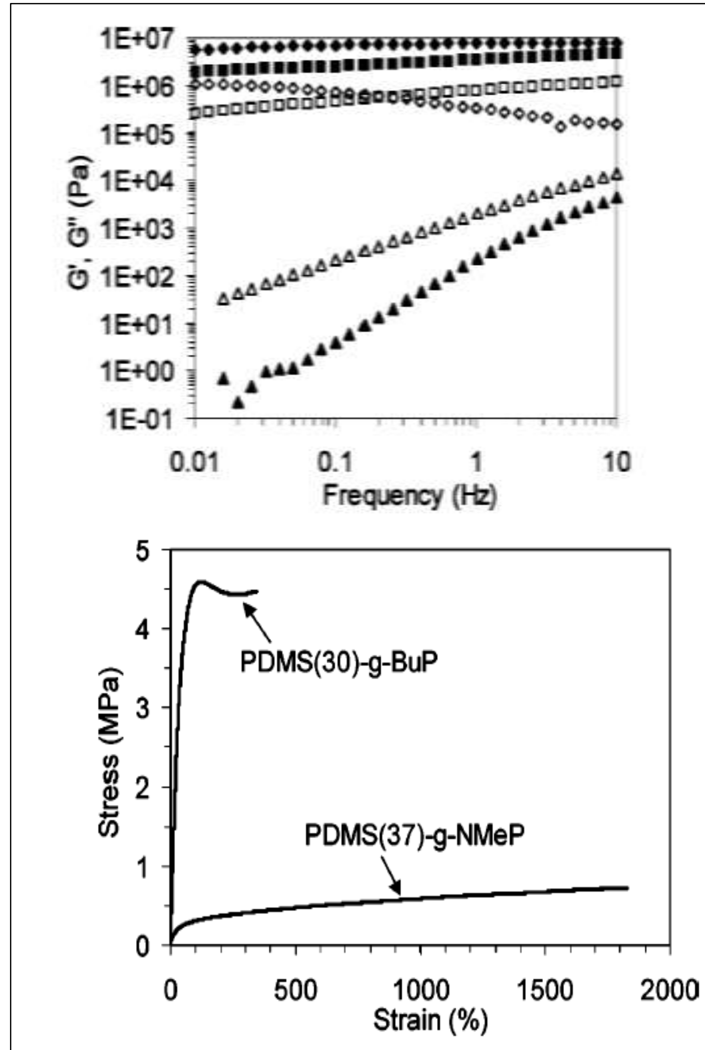


- ✓ **Versatile chemistry**
  - Amine + various diisocyanates…

	Soft segment	Urea content (%)	Tensile strength (MPa)	Strain at break (%)
PSU-DY-20	PDMS	20	7.9	205
PSU-HM-20	PDMS	205	8.1	195
PSU-ED-19	PDMS	19	8.3	180
PEU-DY-20	PEO	20	25.4	1320
PEU-HM-20	PEO	20	25.8	1325
PEU-ED-19	PEO	19	26.5	1450

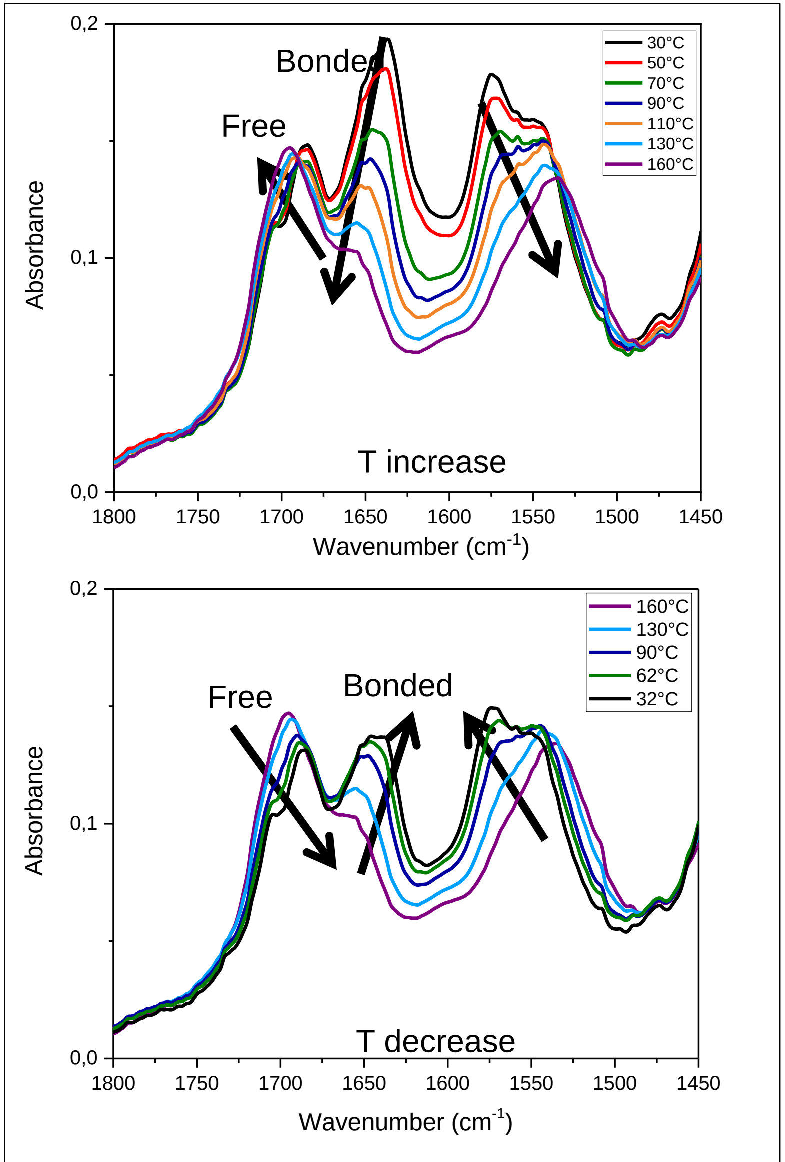
Functional silicones

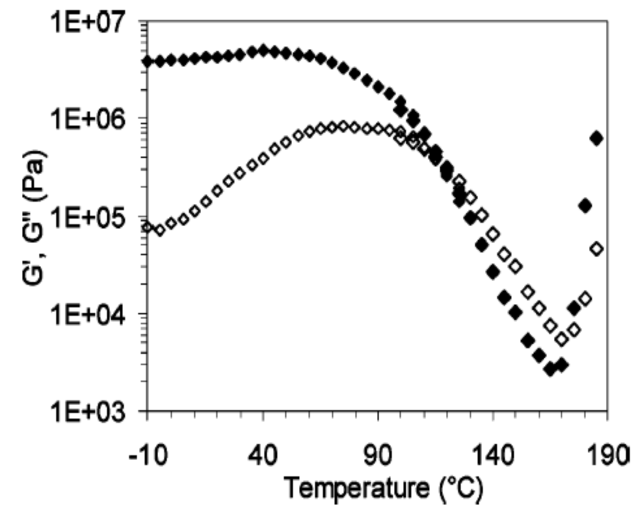




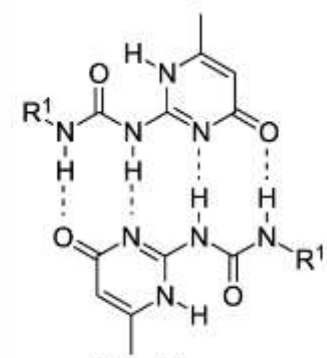
O. Colombani et al *Macromolecules* **2005**, *38,* 1752

Functional silicones (bis)



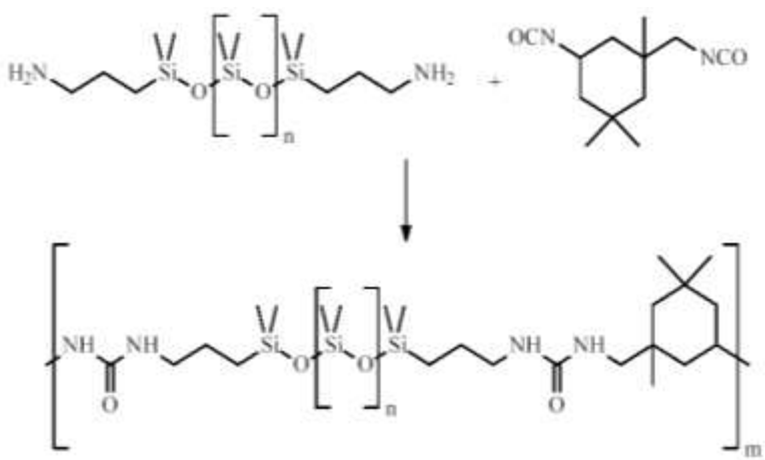


Degradation of the material above 180°C
=> Chemical cross-linking

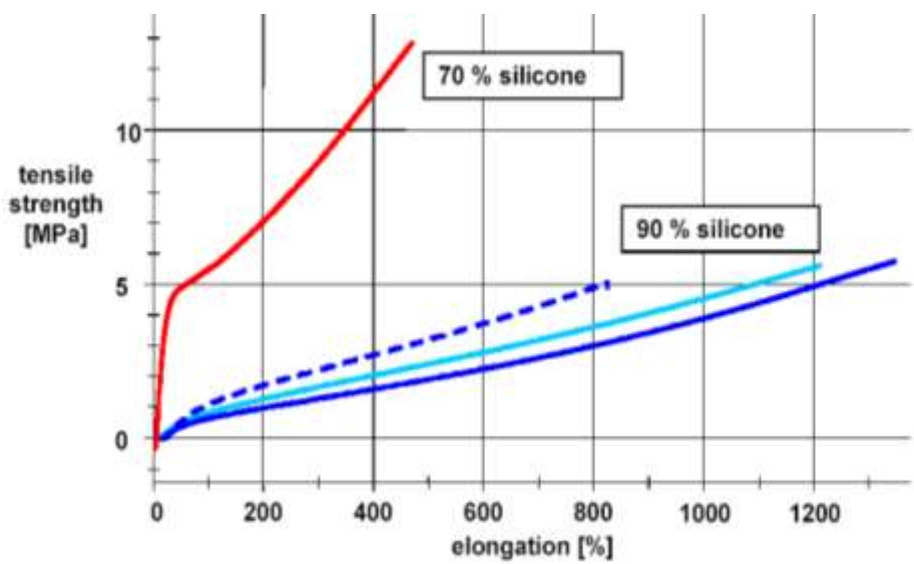


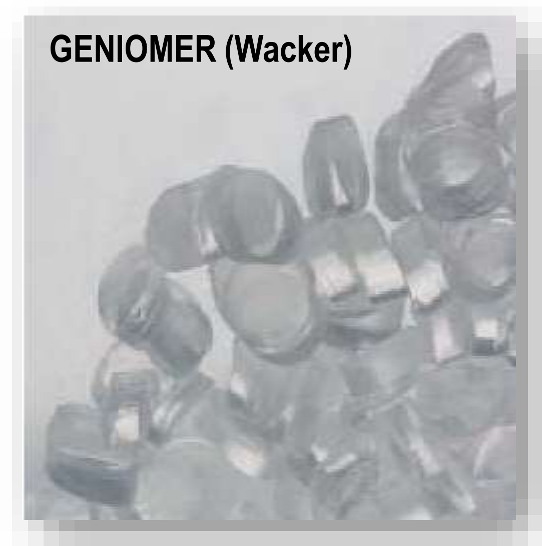
UPy dimer

Silicone ureas' copolymers



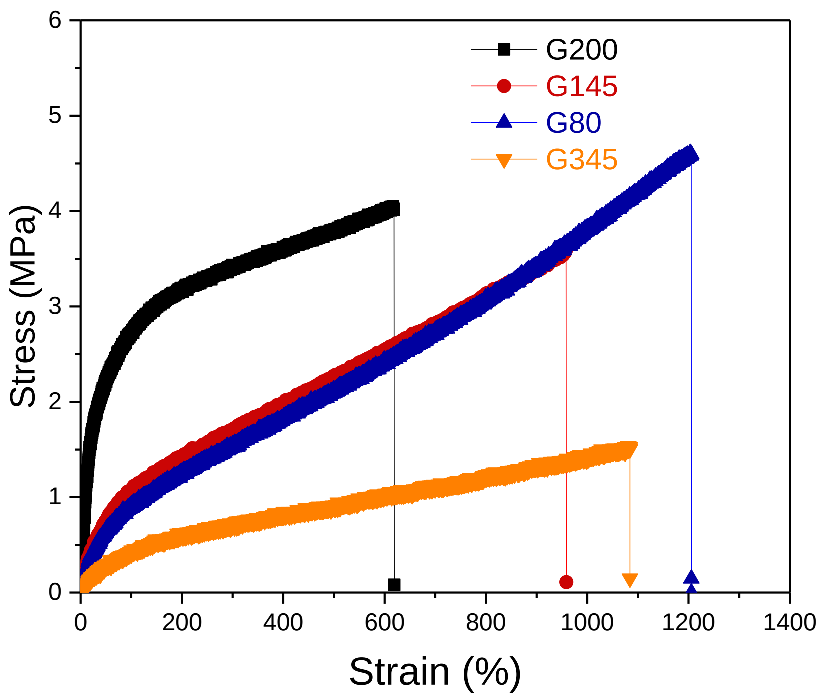
Synthesis in solution (IPA)
or in reactive extrusion

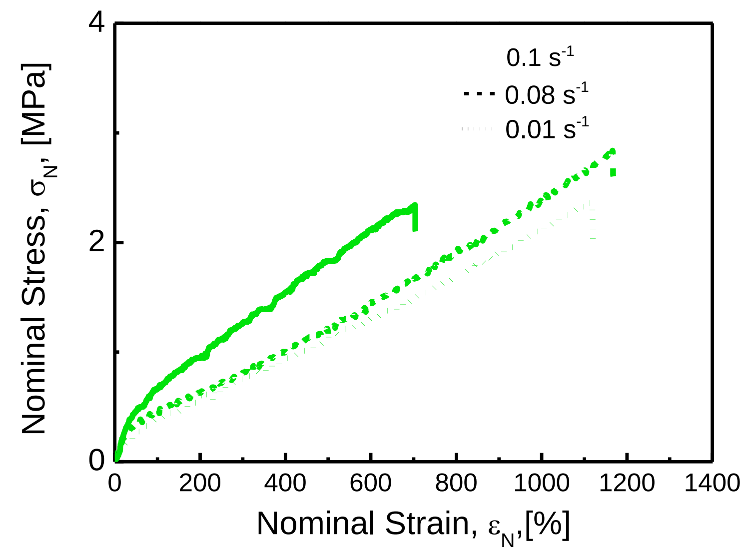


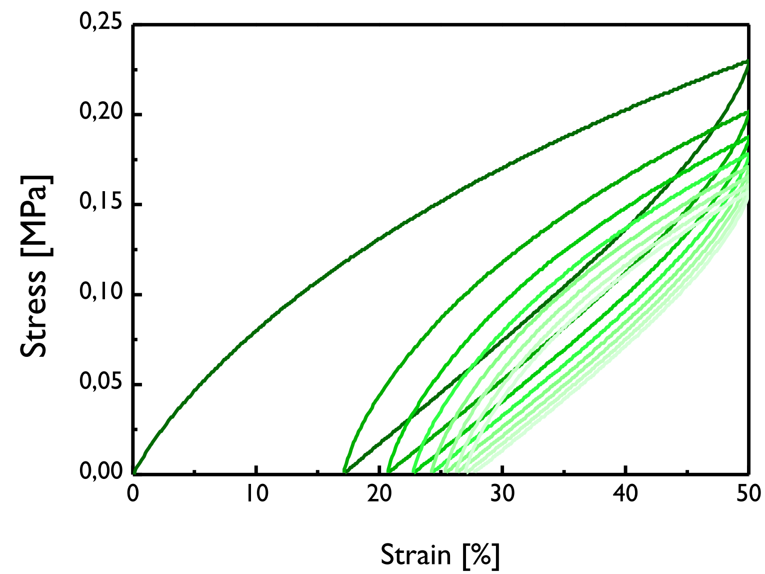


O. Schäfer, J. Weis, S. Delica, F. Csellich, A. Kneissl *Polym. Prep*. **2004**, *45(1),* 714

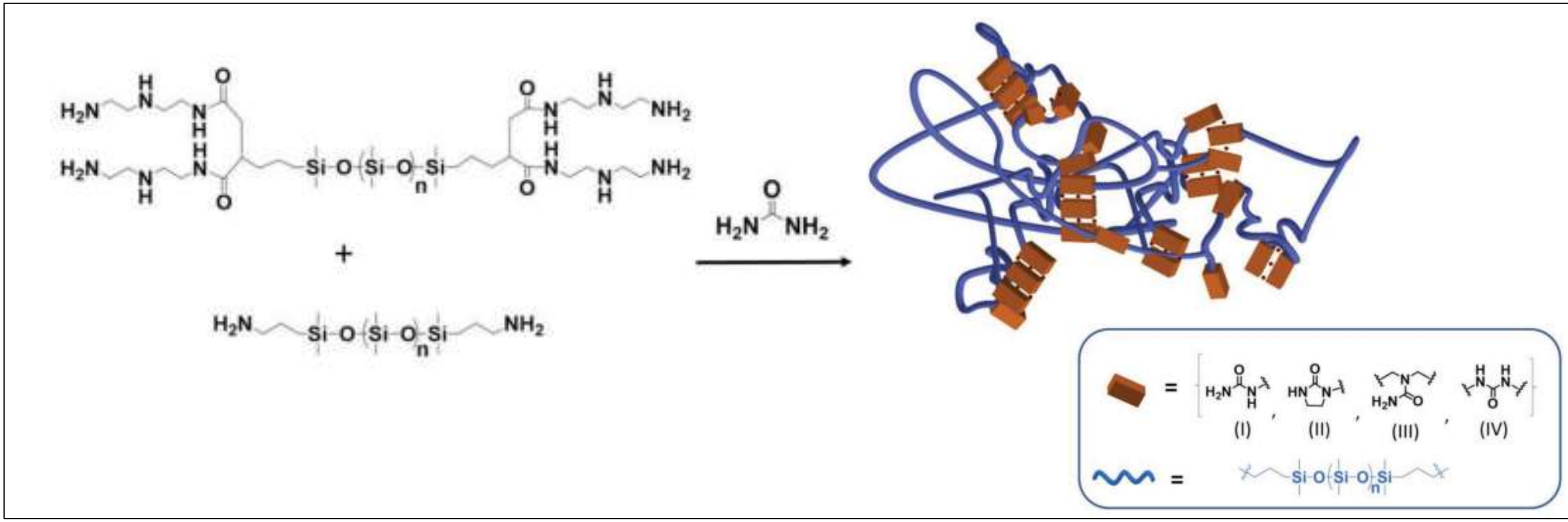
Real life properties

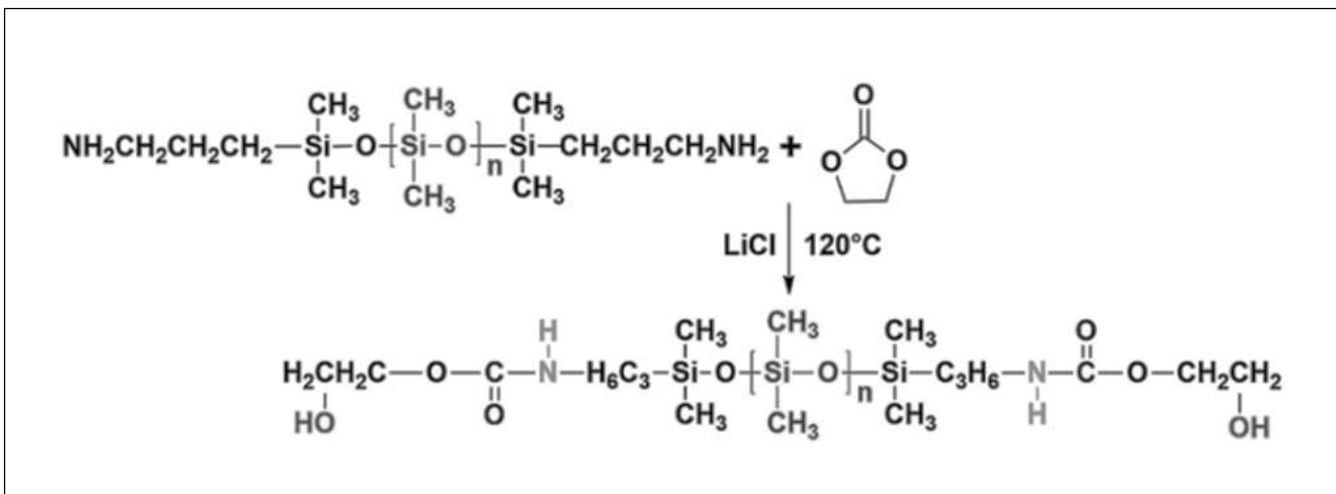




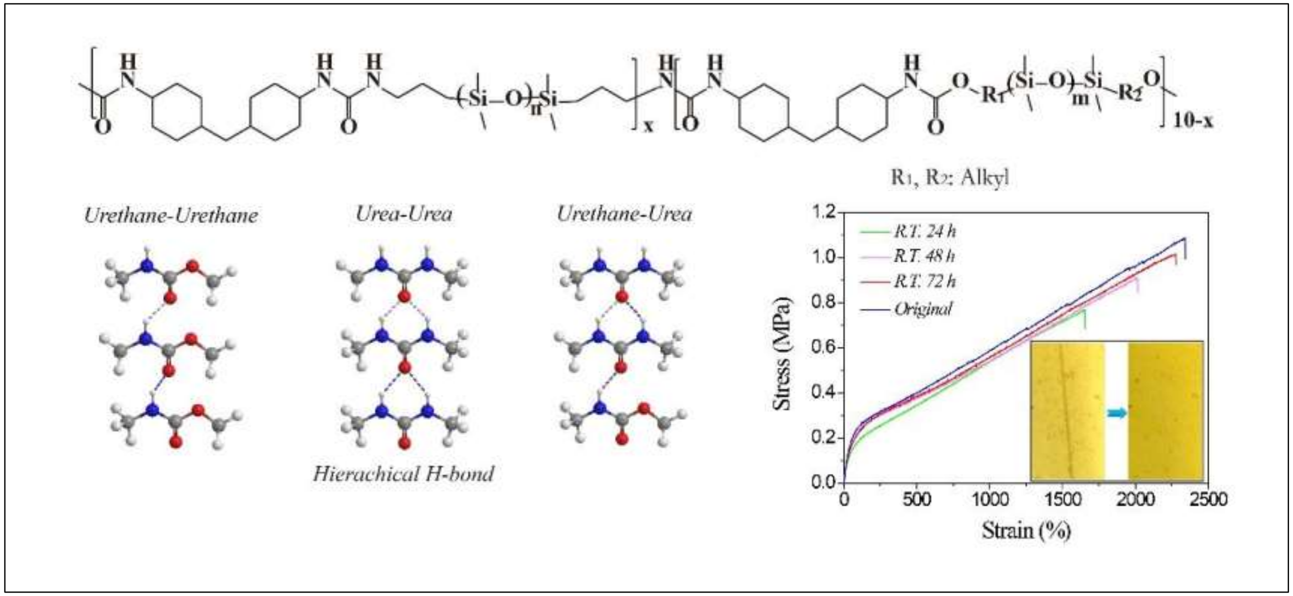


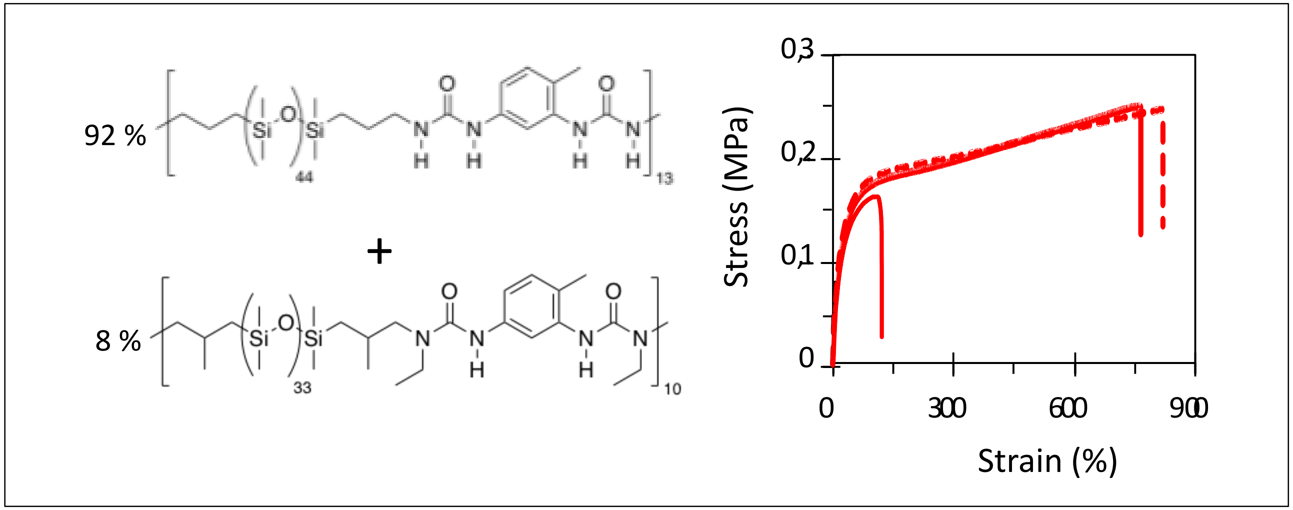
Isocyanate-free silicone urea





Implementing self-healing





Other chemistries

Interreg France-Wallonie-Vlaanderen
CoTeSS Elasto-Plast

Brief survey

- ✓ **Ionic interactions put on success**

  As strong bonds as covalent ones

- ✓ **Pairing with metals**

  Direct ion pairing or metal-ligand specific interactions

- ✓ **Reversible covalent bonds**

  Following the trend of vitrimers

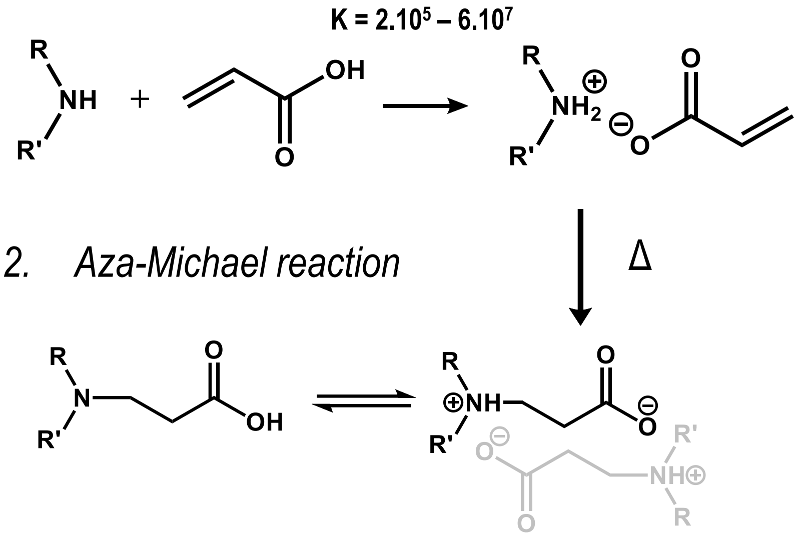
- ✓ **Possibility to add fillers!**

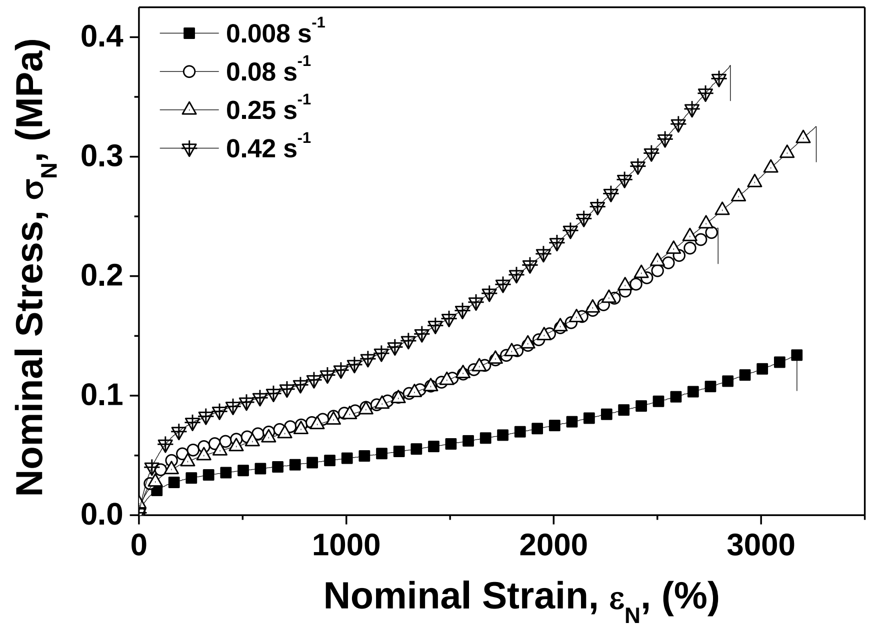
  Little interactions with associating groups

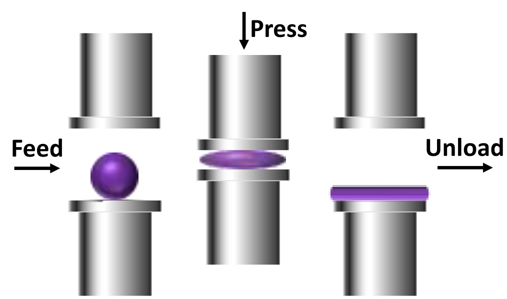
Zwiterionic polymers

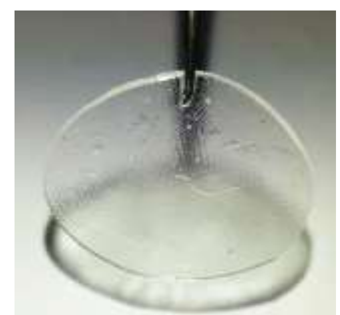
1. *Acid-base reaction*

2. *Aza-Michael reaction*

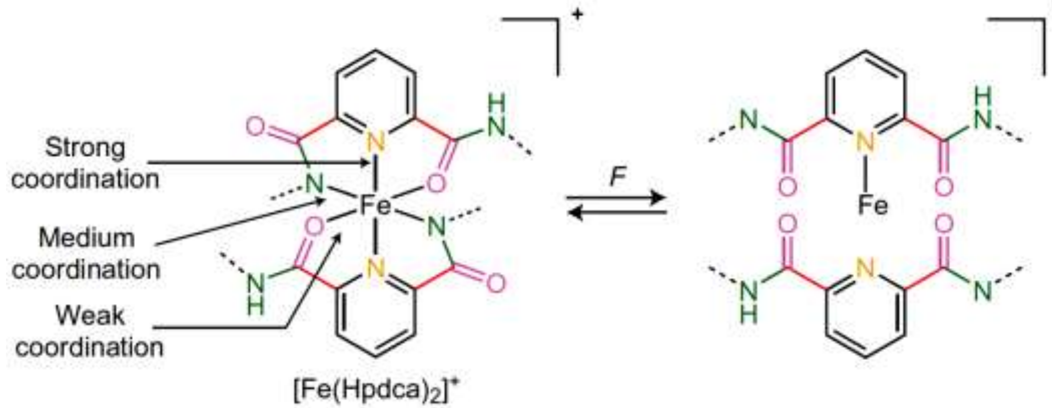


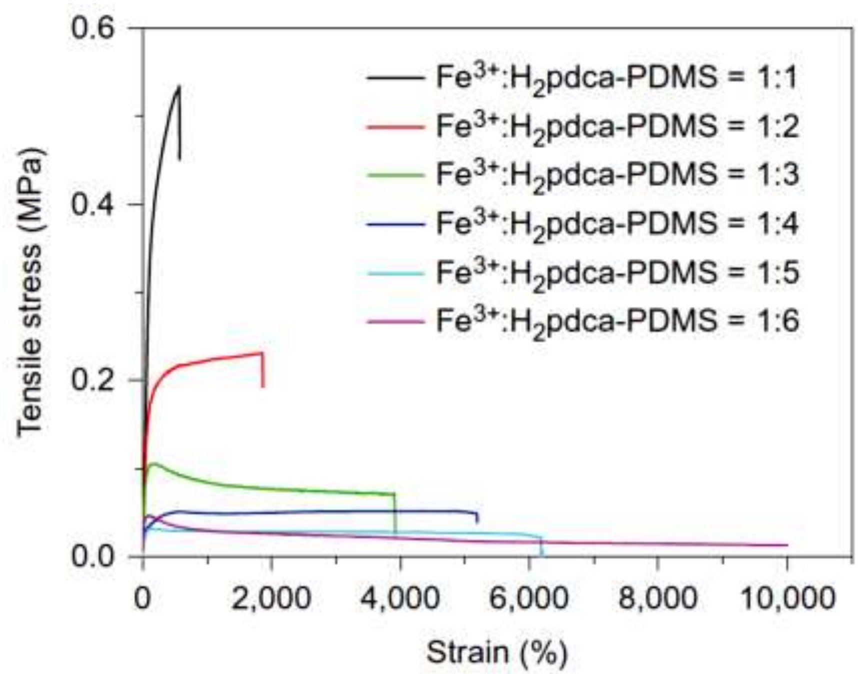






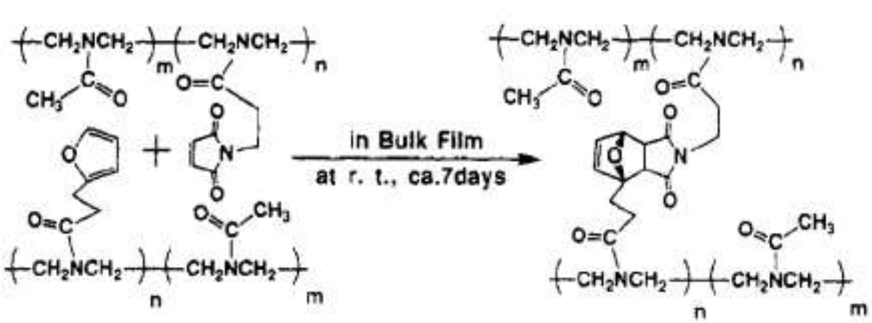
Metal ligand interactions



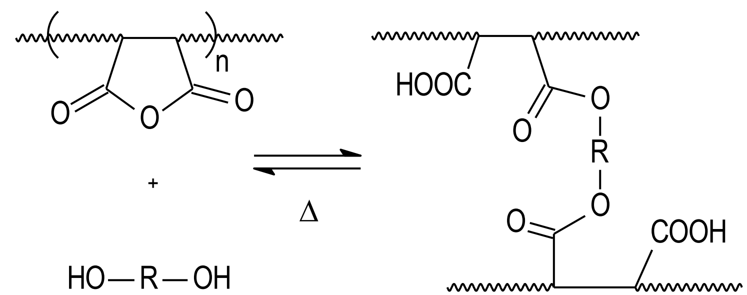


Thermoreversible covalent link (old version)

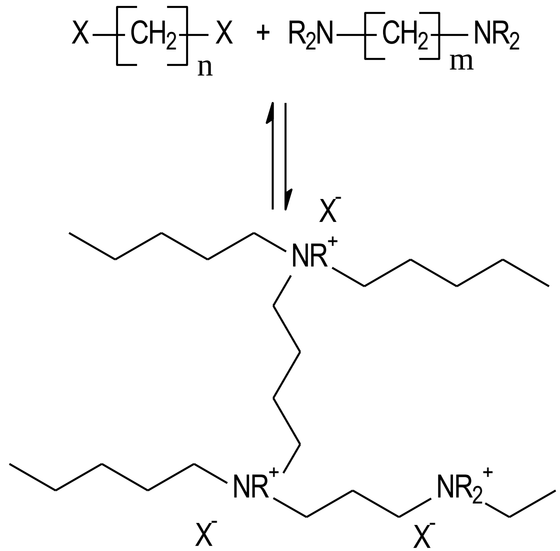
Diels-Alder



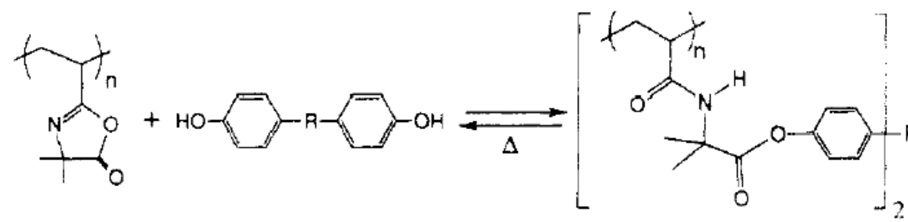
Esters



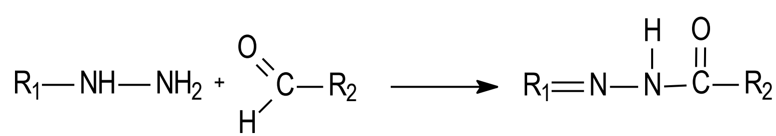
Ionene



Azlactone

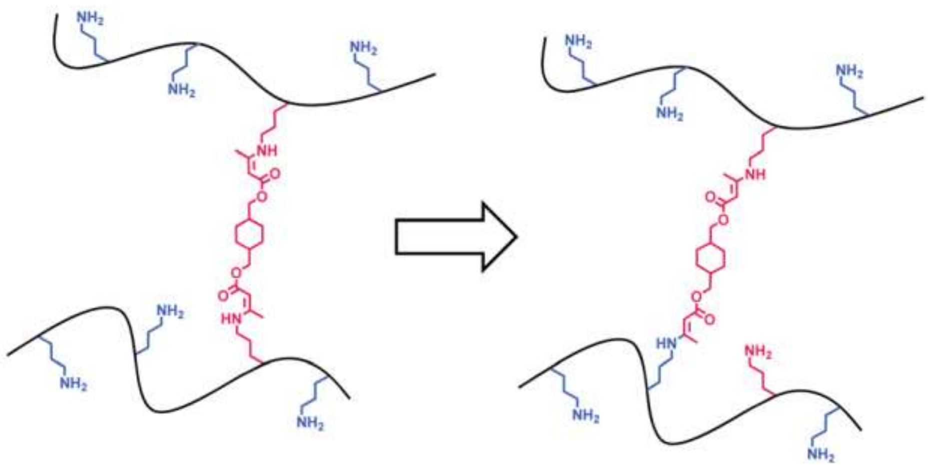


Hydrazone

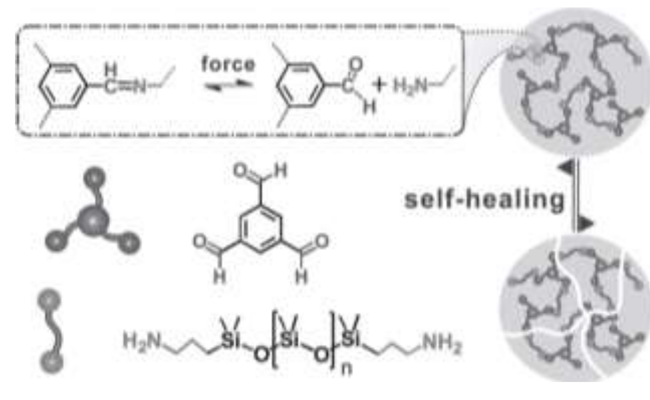


Thermoreversible covalent link (new version)

Vinylogous



Imine



Disulfide

High performance applications

Brief survey

- ✓ **Playing with specific properties**

  Processability, self-healing, high stretch

- ✓ **High-tech applications**

  Batteries, dielectric actuators, electronic sensors…

- ✓ **Coatings and bulk materials**

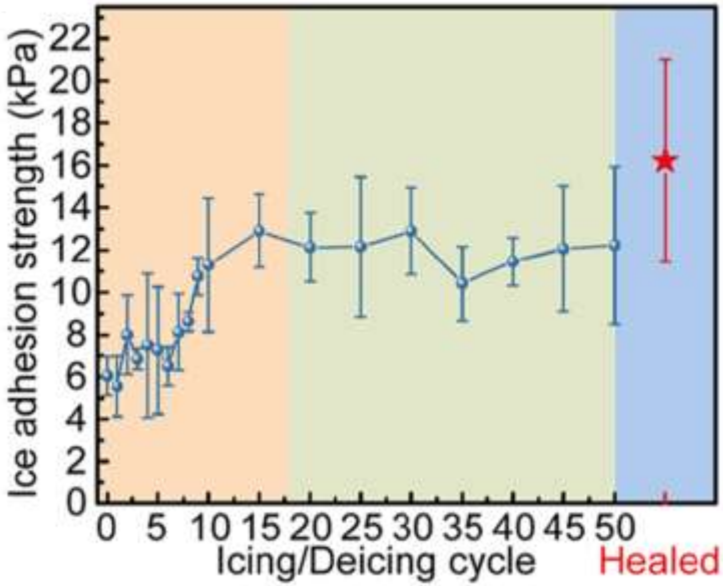
  From anti-icing to shape-memory materials

- ✓ **Challenge: 3D printing**

  Fused deposition modeling

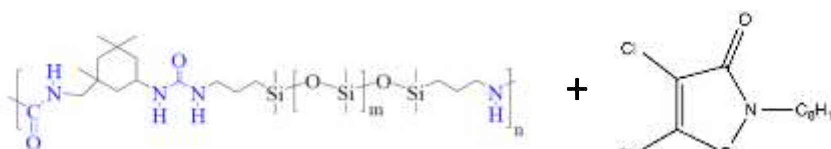
Coatings

Anti-icing



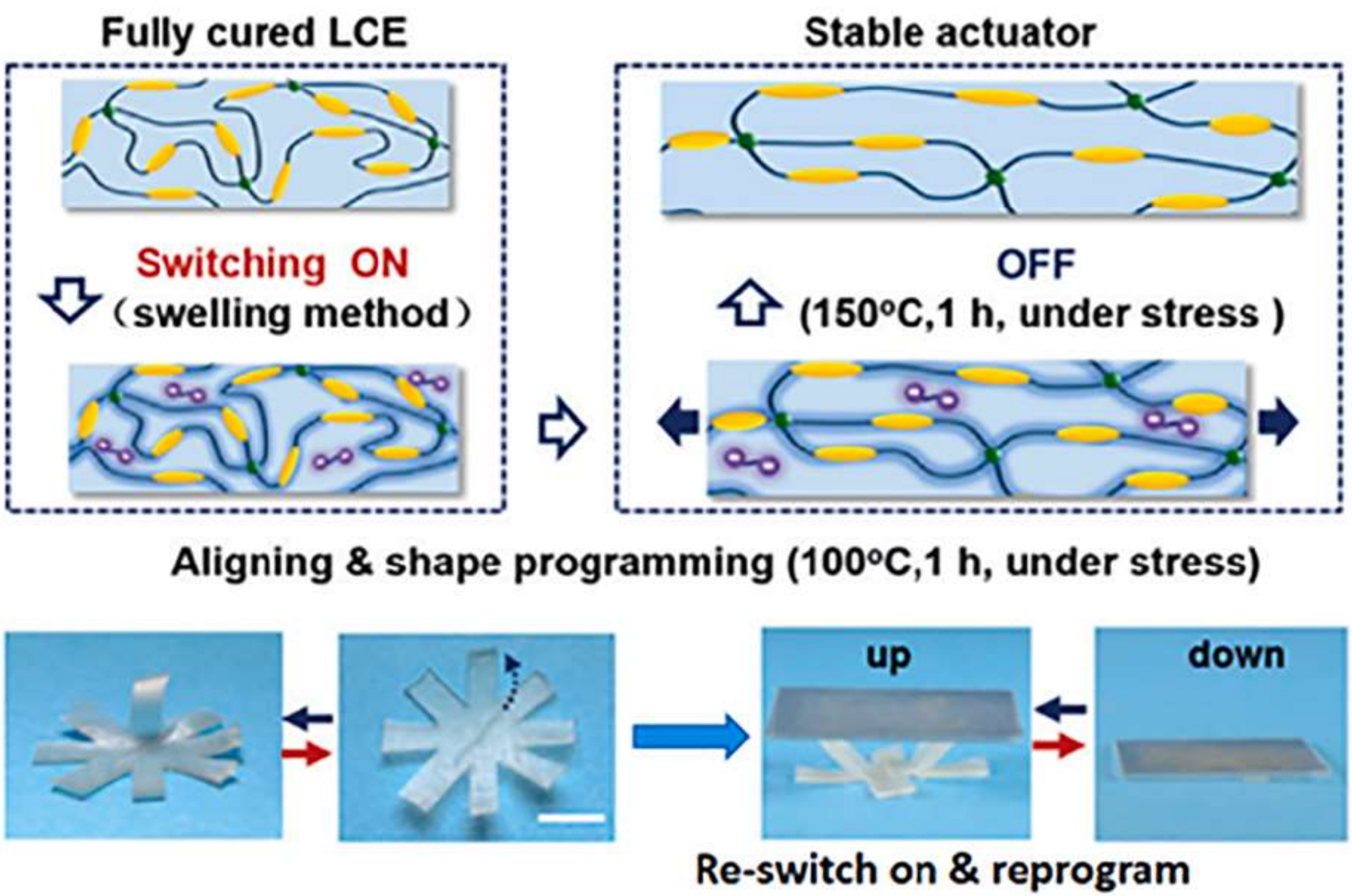
Anti-fouling

Self-healing avoids unwanted adhesion



Materials

Shape memory



Conclusion and prospects

- Silicone is ideal to generate TPEs

  Very low polarity ⇨ efficient demixing and self-assembly

- Versatility of chemical modifications

  From weak forces to disruptable covalent links

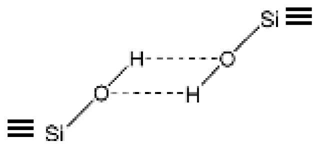
- Still need improvement to compete with silicone elastomers

  Weak mechanical properties ⇨ fillers

  Thermal resistance ⇨ new chemistry?

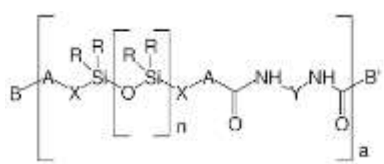
At IMP (if you are interested)

H-Bonding

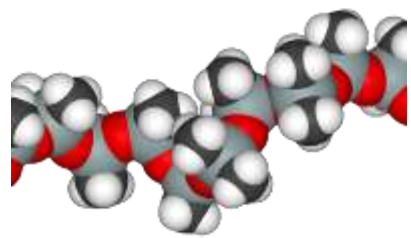


J. Mater. Chem., 2010, 20, 10269-10276.

Chem. Commun., 2016, 52, 6681-6684

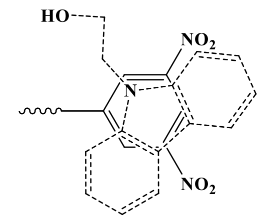


In progress

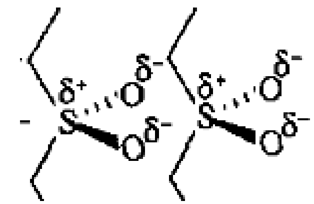


Supra

Others

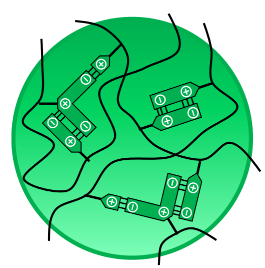


In Silicon Based Polymers, 2008, pp 85-98



FR2912410 (A1)

Ionic pairing



WO 2016102498 A1

J Colloid Interface Sci. 2013, 408, 87-93
+ Patent pending

Thermoplastic silicone elastomers: an endless story

F. GANACHAUD

Université de Lyon, Ingénierie des Matériaux Polymères, CNRS UMR 5223, IMP@INSA, Villeurbanne, France

francois.Ganachaud@insa-lyon.fr