cidetec
surface engineering

CANs_ Covalent adaptable networks

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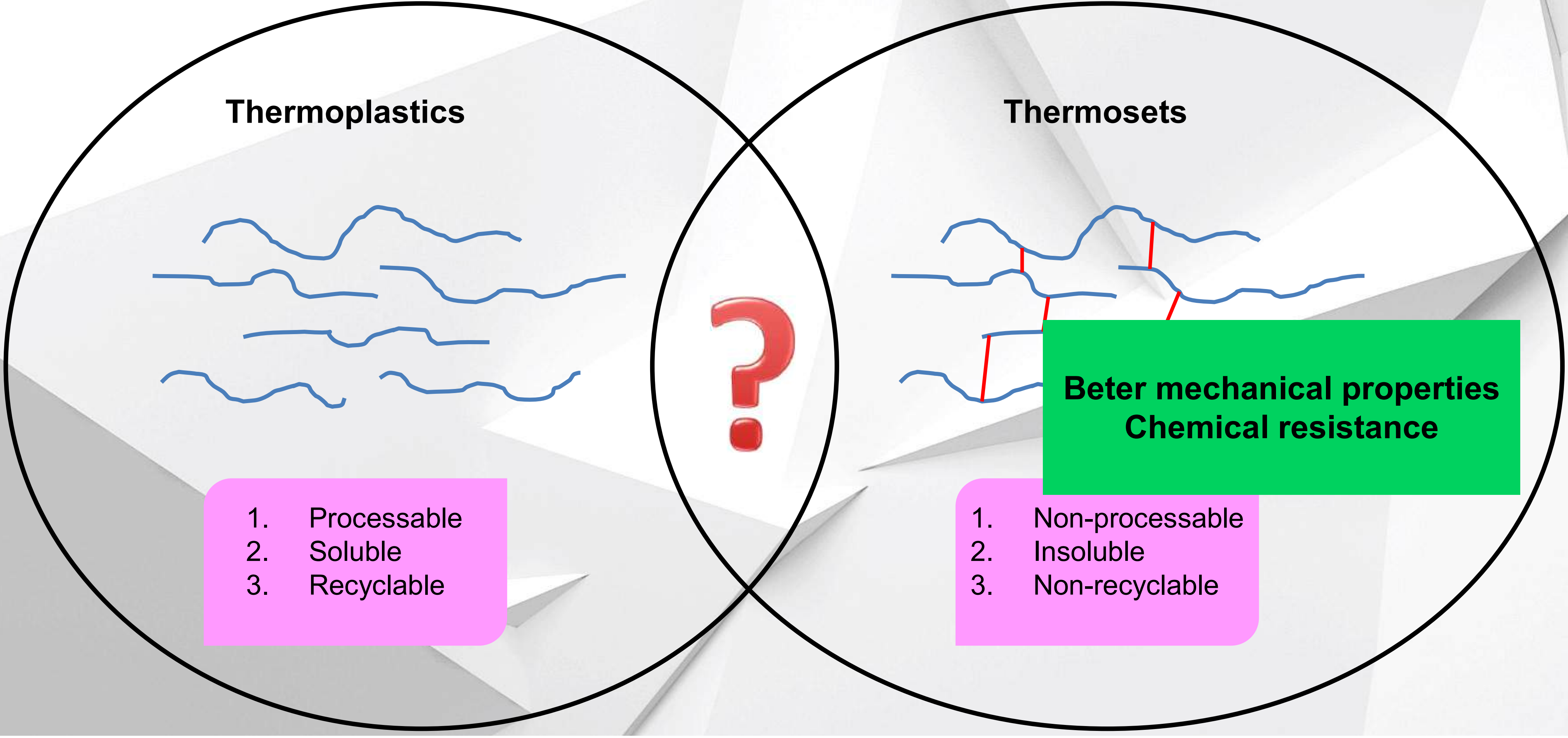
CUBIC
NOVEL BIOBASED MATERIALS TO IMPROVE CIRCULARITY

Outline

1. Introduction & concepts
2. Type of CANs
3. Chemistry of Associative CANs and Vitrimers
4. Characterization of Associative CANs and Vitrimers
5. Application of associative CANs and vitrimers
6. Underlying mechanism of aromatic disulfide exchange
7. Self-healing PUU elastomers
8. Epoxy vitrimers based on aromatic disulfide

Thermoplastic *vs.* Thermoset polymers



Thermoplastics

1. Processable
2. Soluble
3. Recyclable

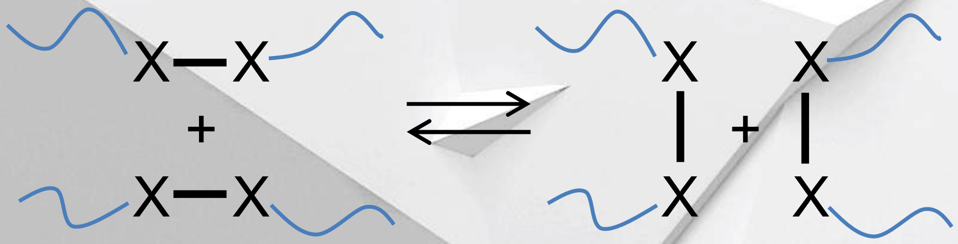
Thermosets

Beter mechanical properties
Chemical resistance

1. Non-processable
2. Insoluble
3. Non-recyclable

Equilibrium in reversible reactions

- **Non-reversible** reaction: $A + B \longrightarrow A\text{-}B$
- **Reversible reaction**: Dynamic equilibrium $A + B \rightleftarrows A\text{-}B$
- **Reversible exchange** reactions:



What would happen if we create a polymer network crosslinked with dynamic bonds in equilibrium?

DYNAMIC COVALENT CHEMISTRY (DCC)

Reversible/Dynamic chemistries used for the design of self-healing polymers

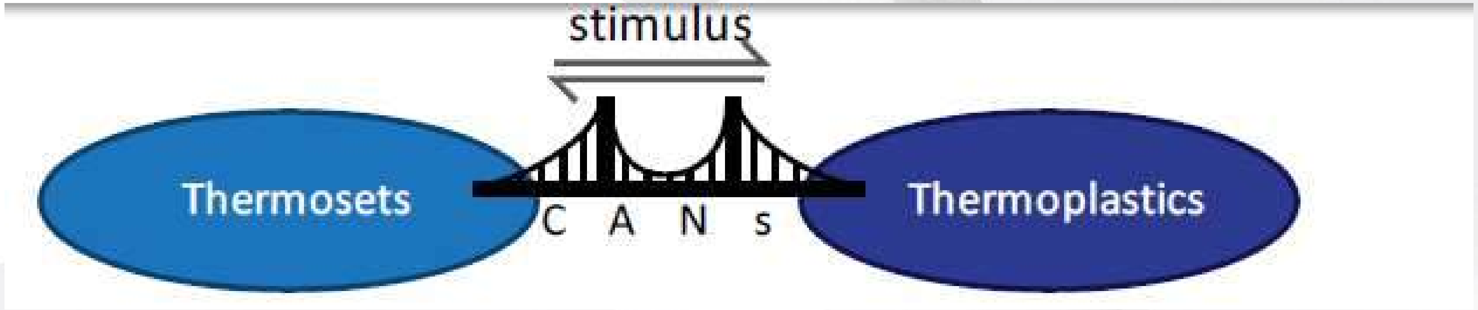
- **Supramolecular interactions**
    - ✓ H-bonding
    - ✓ $\pi-\pi$ stacking
    - ✓ Chain entanglement
    - ✓ Metal coordination
    - ✓ Etc.
- **Dynamic covalent bonds**
    - ✓ Disulfide metathesis
    - ✓ Diels-Alder
    - ✓ Transesterification

    - ✓ Etc.

Required stimulus

- Heat
- UV light
- Catalysts
- …

1. Introduction & Concepts

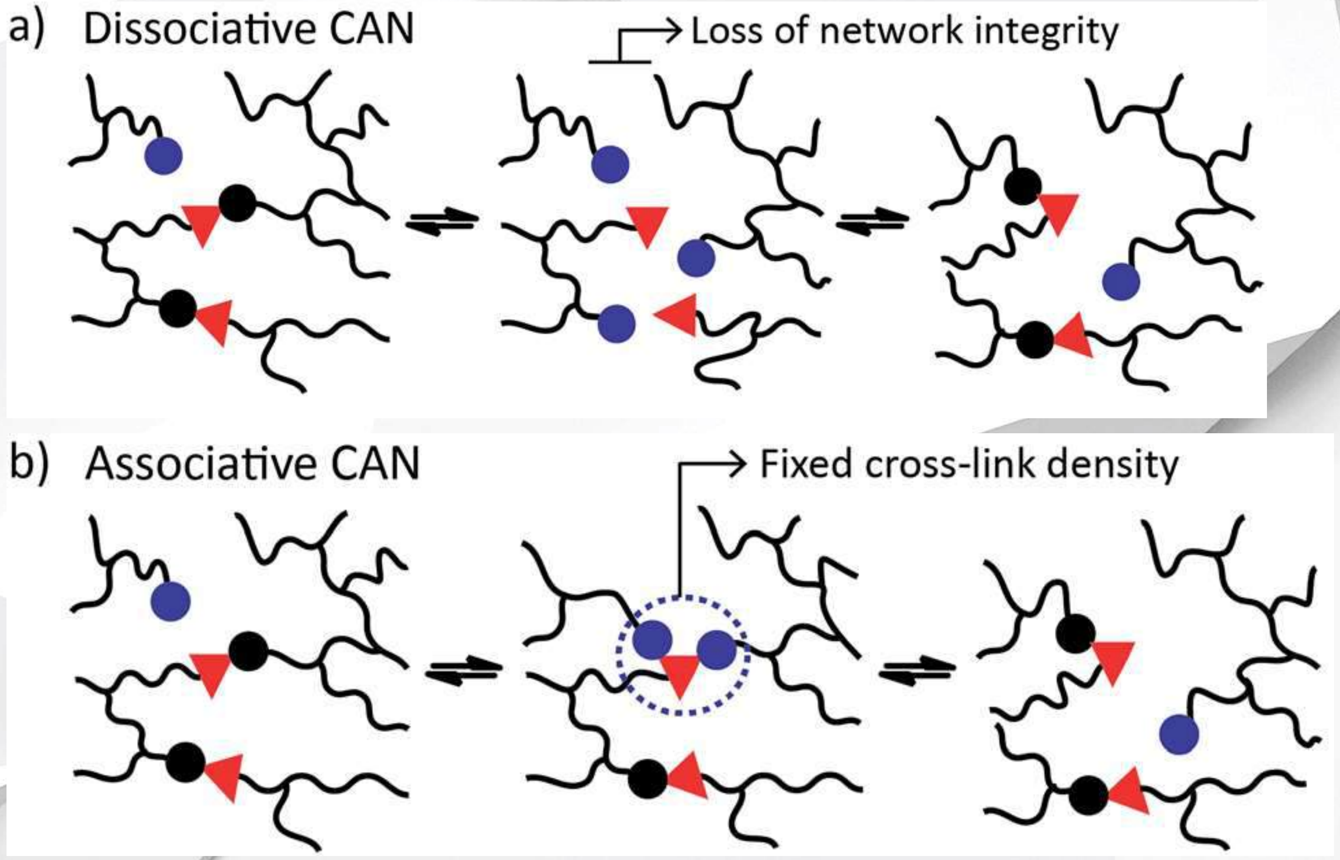


- Implementation of DCC in polymers yields materials with unprecedent applications.
- Incorporation of DCC in polymers aims to find balance between swift and triggerable reactivity with high degree of intrinsic robustness and stability.

2. Type of CANs

CANs may be further classified into two groups depending on their exchange mechanism:

- **Dissociative CANs**
- **Associative CANs**

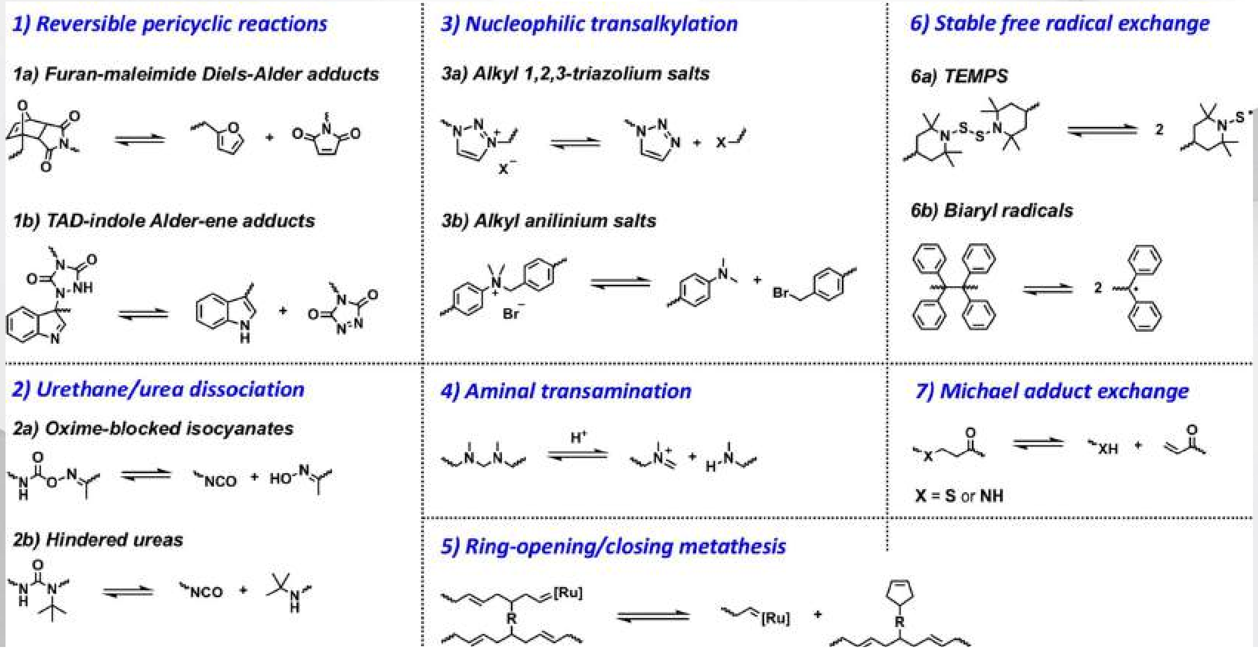


Main consequences: distinct viscoelastic behaviour during the thermal reprocessing step

2. Type of CANs

- **Dissociative CANs**

- Very fast topology rearrangement (stress relaxation and flow)
- Temporary loss of crosslinks results into sudden viscosity drop (similar to thermoplastics).
- Upon cooling the crosslinks are formed again recovering thermoset properties (stiffness and insolubility)
- Reprocessable when heating



2. Type of CANs

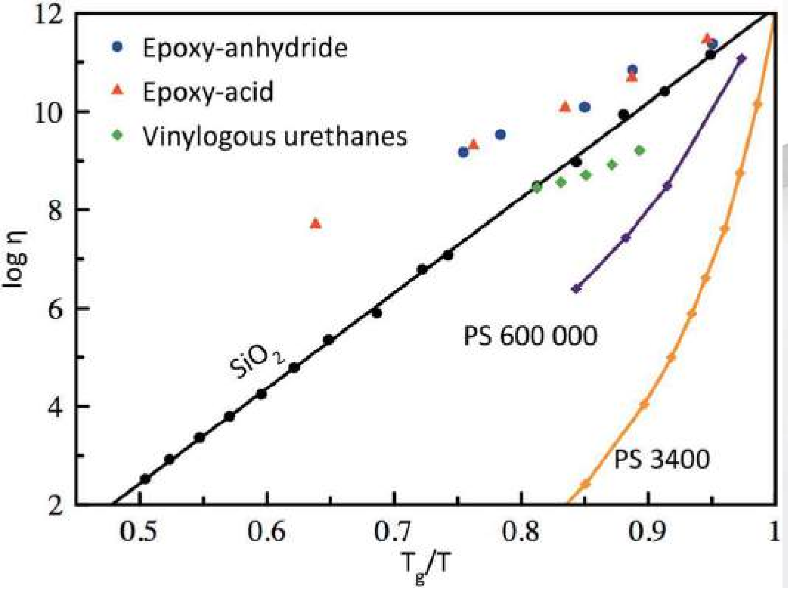
- **Associative CANs**

- Do not depolymerize upon heating.
- They maintain fixed crosslinking density.
- Covalent bonds are only broken when new ones are formed, making these networks **permanent** as well as **dynamic**.
- Gradual viscosity decrease upon heating (similar to silica)
- Also known as **vitrimers**
- **Vitrimers (novel concept introduced for polymers by Ludwick Leibler)**

2. Associative CANS/Vitrimer characteristics

TEMPERATURE BEHAVIUOR

- Thermally malleable network via exchange reactions
- At high temperature vitrimer viscosity is controlled by chemical exchange reactions
- Viscosity decrease follows Arrhenius law as in typical inorganic silica materials
- This latter property distinguishes vitrimers from dissociative CANs and thermoplastic materials because these materials evolve from a solid to a liquid state in a much more abrupt way, following the Williams–Landel–Ferry model (WLF) for thermoplastic polymer melts



2. Associative CANS/Vitrimer characteristics

TEMPERATURE BEHAVIUOR

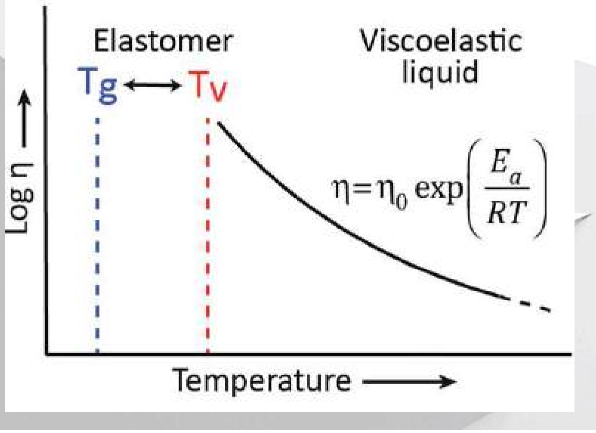
- The viscoelastic behavior of vitrimers can be described using two transition temperatures: Tg and Tv.
- Tg: Glass transition temperature, between glassy and rubbery state.
- **Tv**: topology freezing transition temperature. Tv derives from the network cross-link exchange reactions.
- When the timescale of bond exchange reactions becomes shorter than the timescale of material deformation, the network can rearrange its topology, resulting in flow.
- Tv is defined a temperature where a transition from viscoelastic solid to viscoelastic liquid occurs.
- Tv is conventionally chosen at the point where a viscosity of 10^{12} Pa s is reached.

2. Associative CANS/Vitrimer characteristics

TEMPERATURE BEHAVIUOR

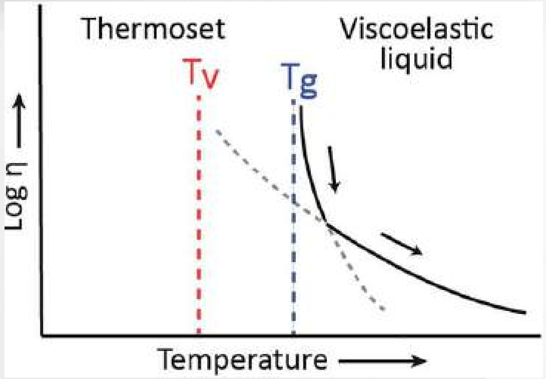
Tg < Tv

- Tg<T<Tv: Material in rubbery state. It wil behave as a elastomer since tha exchange reactions will be very slow and the network structure is fixed.
- Tv<T: exchange reaction speeds up at above Tv, transforming the elastomer toa viscoelastic liquid.
- Flow is mainly controlled by the cross-link exchange kinetics, giving the typical Arrhenian viscosity decrease.



Tv < Tg

- Intrinsically fast exchange reaction is embedded in a rigid polymer matrix where the Tg is higher than expected Tv.
- Tv can be calculated via extrapolation of stress relaxation or creep experiments.
- Tv is hypothetical: network is not frozen by reaction kinetics, but by the lack of segmental motions associated to Tg.
- T<Tg: no movement, no exchange reaction can occur
- T>Tg: segmental motion is gradually initiated. Exchange reaction are already fast.
- Upon heating, the vitrimer evolves from a glassy solid to a visco- elastic liquid with a viscosity that is first controlled through diffusion (WLF) and then by the exchange kinetics (Arrhenius).



2. Associative CANS/Vitrimer characteristics

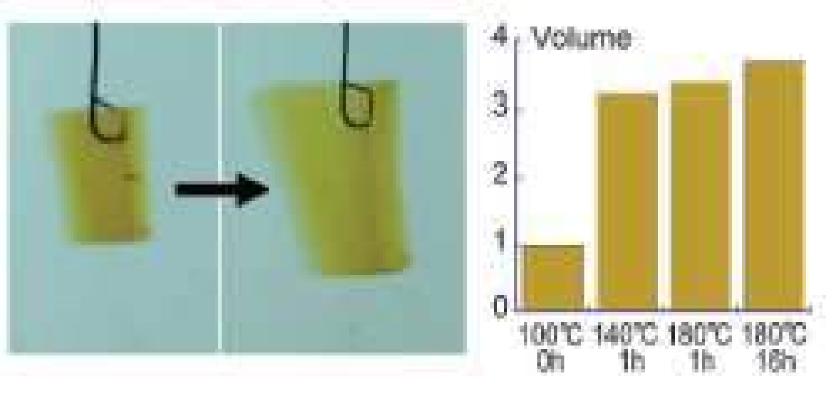
TEMPERATURE BEHAVIUOR

- For the design of vitrimer materials, it is important to consider the two transitions and their corresponding temperatures, **Tg** and **Tv**.
- Tg and Tv, can be controlled through parameters such as the cross-link density, intrinsic rigidity of monomers, the exchange reaction kinetics (e.g. catalyst loading), and the density of exchangeable bonds and groups.
- For most applications vitrimers should behave as classical thermosets in a useful temperature window.

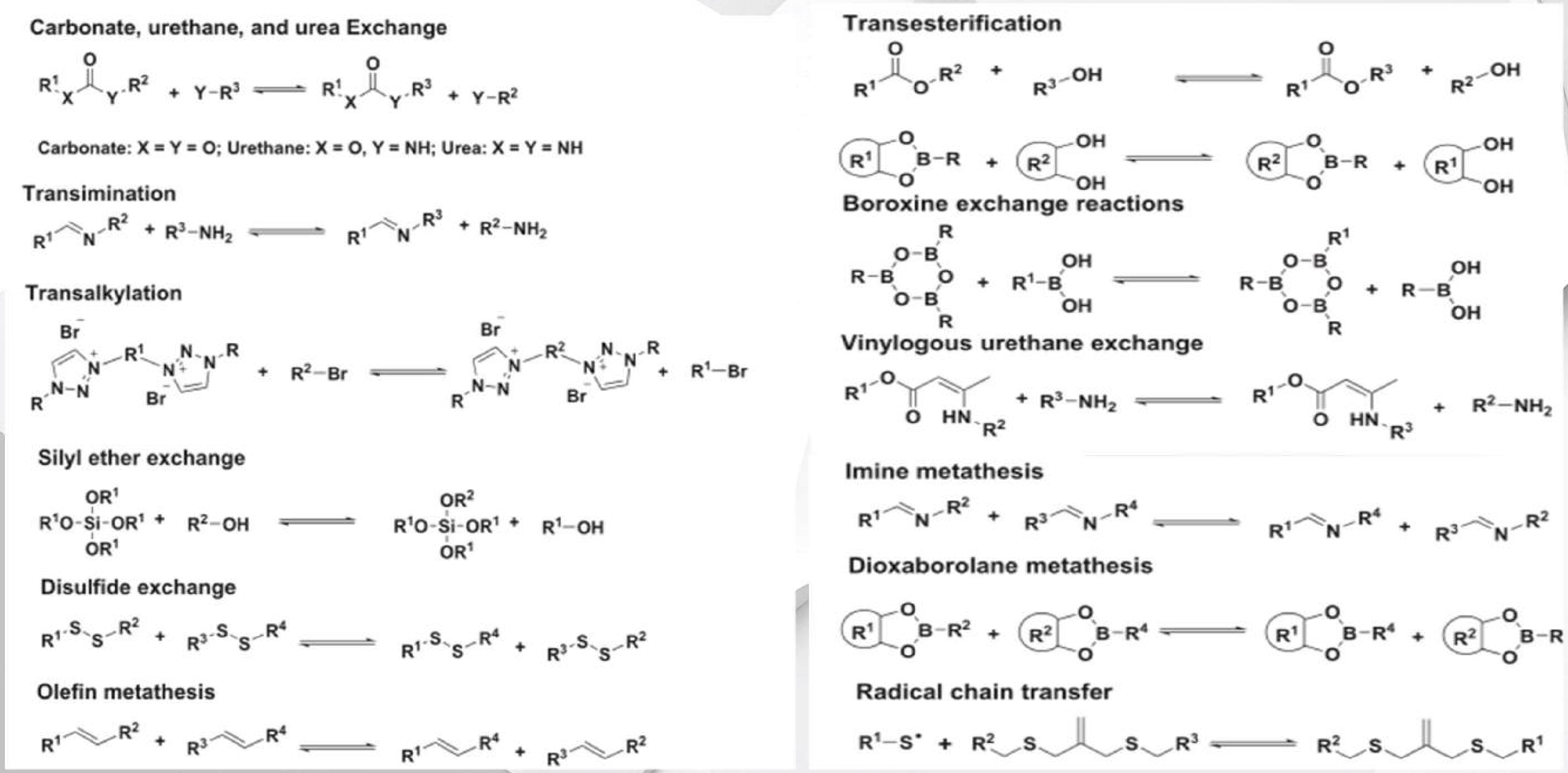
2. Associative CANS/Vitrimer characteristics

SOLVENT RESISTANCE

- As vitrimers are permanent networks with a permanent connectivity at all temperatures (excluding degradation), these *materials swell but do not dissolve in chemically inert solvents, even when heated.*
- In contrast to classical polymer networks, swelling ratios are higher since the elastic retractive forces, opposing the increase in entropy and heat of mixing associated with polymer swelling, can be relaxed due to topology rearrangements.



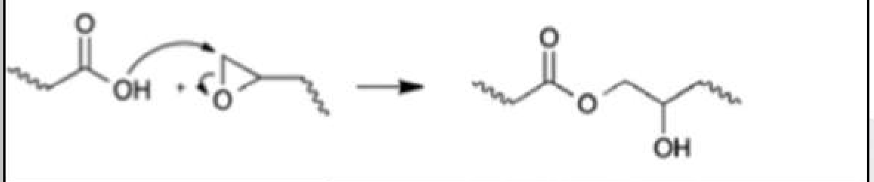
3. Chemistry of Associative CANs and Vitrimers



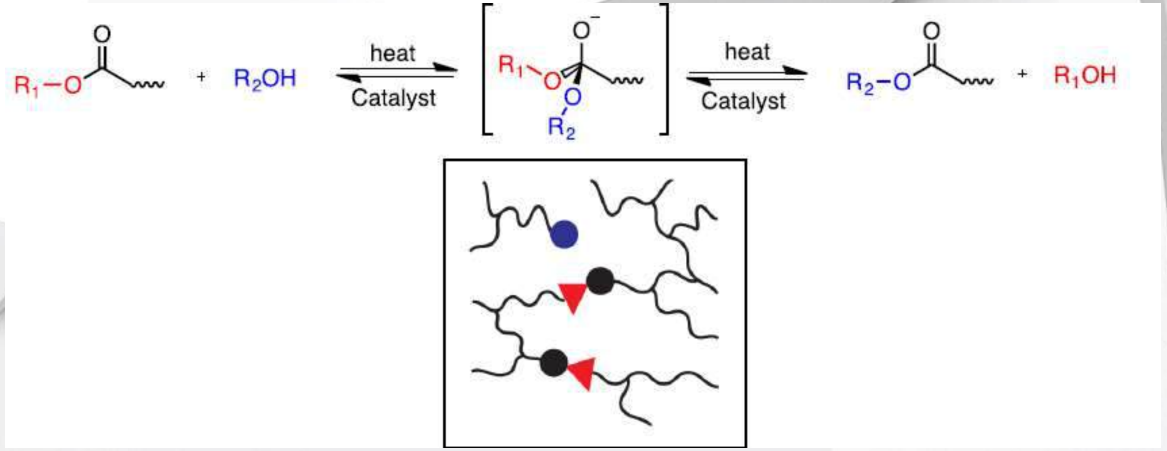
3. Chemistry of Associative CANs and Vitrimers

- **TRANSESTIRIFICATION**

- Leibler and co-workers demonstrated the concept of vitrimers by using carboxylic acid-based transesterification reactions, promoted by a catalyst.
- Organic group of an ester is exchanged with the group of an alcohol. This reaction is typically catalysed by Brønsted acids, organo-metallic complexes or organic bases,
- Exchange reaction kinetics can be easily controlled with a catalyst
- Changing the amount and nature of catalyst, the activation energy (Ea) and Tv can be tuned.
- Advantages: Good reprocesability, long term stability, *insoluble,* availability of monomers, easy synthesis.
- Disadvantages: catalyst (in)solubility, catalyst leaching, ester hydrolysis, *insoluble*



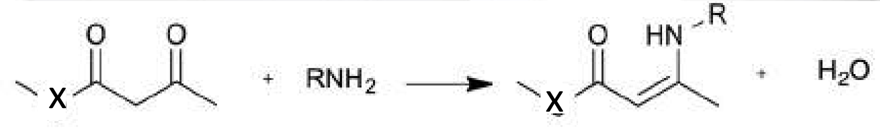
Reaction between epoxides and carboxilic acid. The resulting repeating unit contains both an ester and hydroxyl function



Montarnal, D., Capelot, M., Tournilhac, F., **Leibler**, L. *Science* **334,** 965–968 (2011).

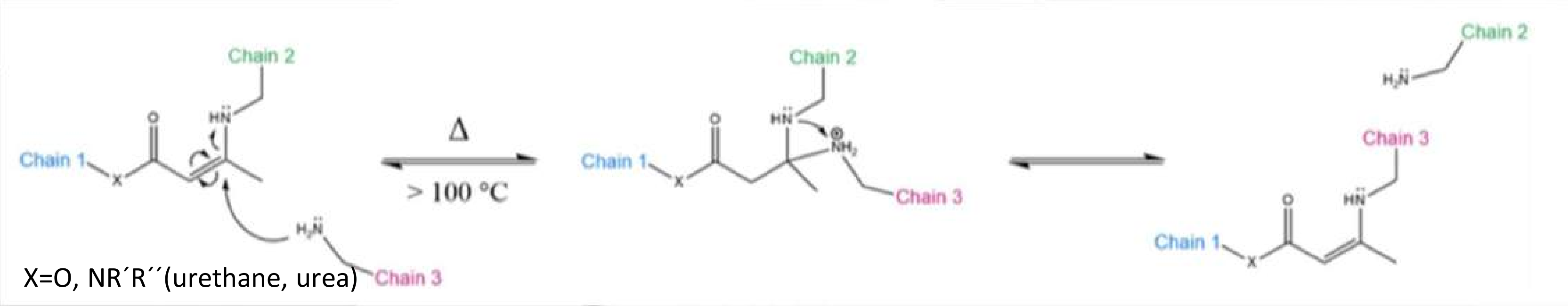
3. Chemistry of Associative CANs and Vitrimers

- **Transamination of Vinylogous Acyls**
- Catalyst free exchangeable vitrimers
- Condensation reaction between acetoacetate (vinylogous urethane) or acetoamide (vinylogous urea) and amine monomers.



X=O, NR´R´´(urethane, urea)

- Introduction of a vinylic bond inserted between the electron-donating nitrogen and the electron-withdrawing moiety confers Michael-type reactivity. The exchange reaction can proceed without catalyst at 100 °C or above via the Michael addition pathway.
- The nucleophilic attack is performed by a free amine group
- Advantages: Stable towards hydrolysis, no catalyst, good mechanical properties
- Disadvantages: release of water in the synthesis, restricted chemistry and requires care in material preparation.



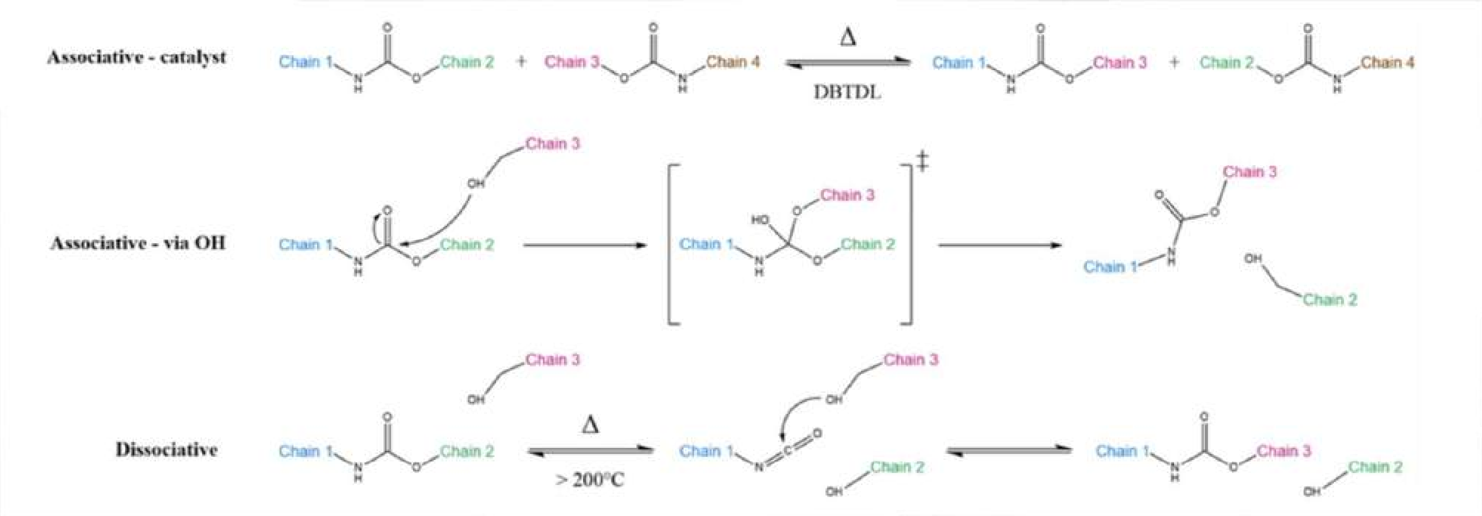
X=O, NR´R´´(urethane, urea)

Denissen, W.; Rivero, G.; Nicolay, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. dv. Funct. Mater. **2015**, 25 (16) 2451– 2457.
Wim Denissen, Ives De Baere, Wim Van Paepegem, Ludwik Leibler, Johan Winne, Filip E. Du Prez. *Macromolecules* **2018,** *51* (5) , 2054-2064

3. Chemistry of Associative CANs and Vitrimers

- **Transcarbamoylation**

- Transcarbamoylation of carbamate groups in polyurethanes may take different pathways, depending on the chemical units involved

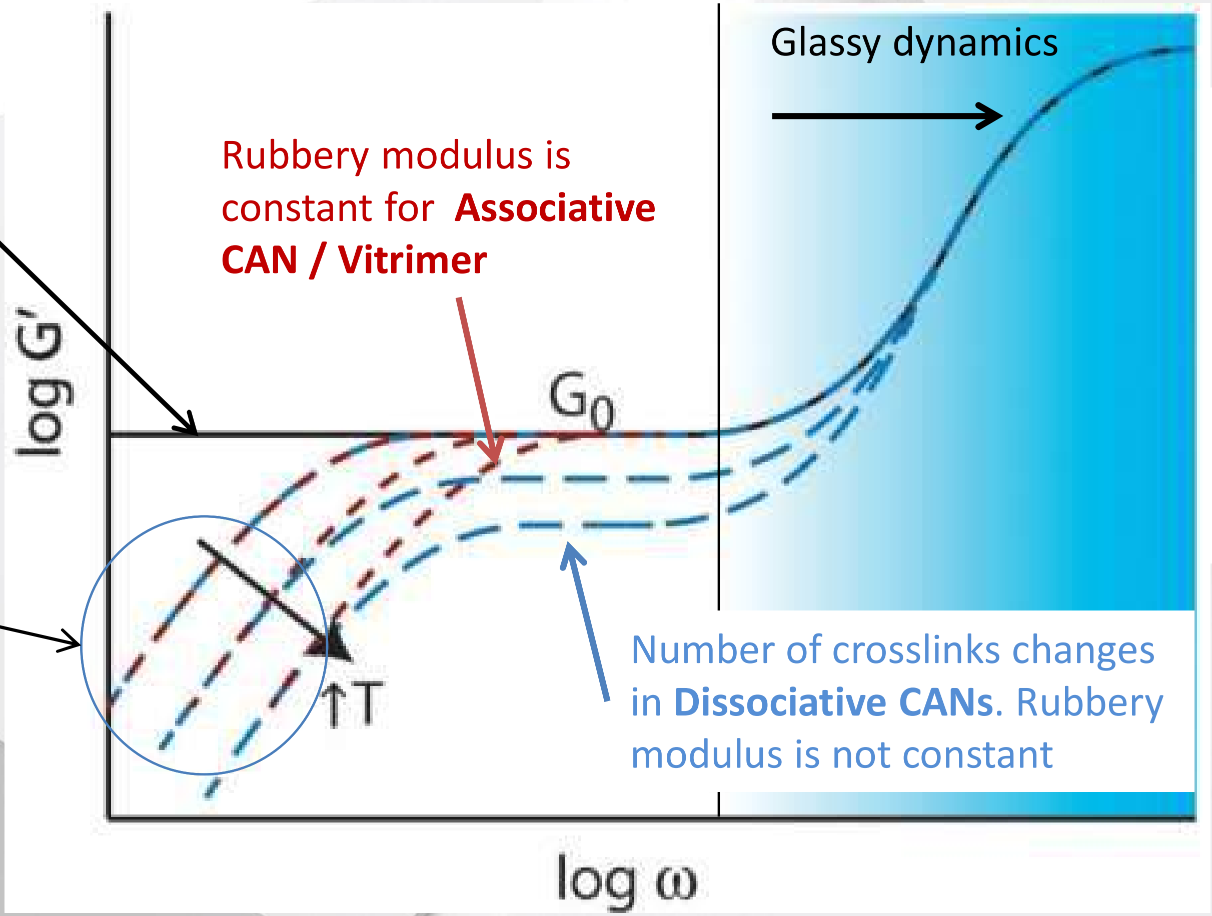


- Challenging exchange reaction due to high Ea and secondary reactions that led to degradation of materials
- Advantages: Availability of monomers, easy and well known synthesis.
- Disadvantages: Slow exchange kinetics, degradation

Zheng, N.; Fang, Z.; Zou, W.; Zhao, Q.; Xie, T.. Angew. Chem. **2016**, 55, 11421–11425
Elizalde, F.; Aguirresarobe, R. H.; Gonzalez, A.; Sardon, H. *Polymer Chemistry* **2020**, *11*, 5386-5396.

4. Characterization of Associative CANs and Vitrimers

- **Rheological characterization**



Covalently crosslinked network

Rubbery modulus is constant for **Associative CAN / Vitrimer**

Relaxation in a covalently corsslinked network

Number of crosslinks changes in **Dissociative CANs**. Rubbery modulus is not constant

- Polymeric materials experience a rapid increase in modulus at high frequency related to the small length-scale glassy dynamics.
- -All covalently crosslinked materials have a modulus, G_0, that is related to crosslink density.
- Both dissociative and associative type CANs exhibit liquid like stress relaxation at low frequency (long time-scales).

C.J. Kloxin and C.N. Bowman *Chem. Soc. Rev.*, 2013, **42**, 7161--7173

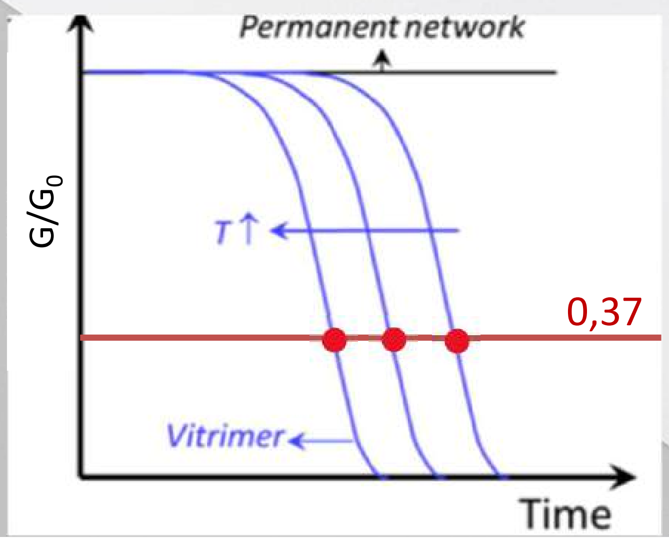
4. Characterization of Associative CANs and Vitrimers

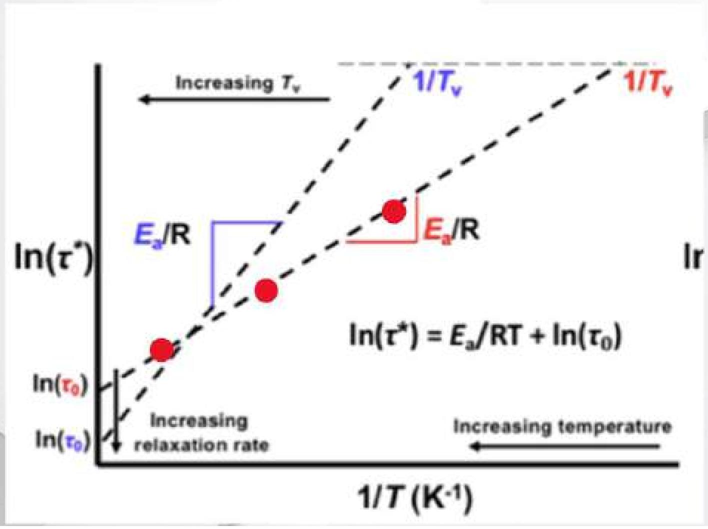
• Rheological characterization: Stress relaxation

- Stress–relaxation behaviour of vitrimers can be described by the Maxwell law: $G_t/G_0=\exp(-t/\tau)$
- Relaxation times (τ*) are calculated following the Maxwell model which defines it as the time needed for the modulus to decrease to 37% of its initial value (G/G0 = 1/e)
- τ* data as a function of the temperature follows the Arrhenius' law

$$\boxed{\tau(T) = \tau_0 e^{\left(\frac{Ea}{RT}\right)}}$$

where | is the relaxation time at each temperature, Ea is the activation energy, R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature.

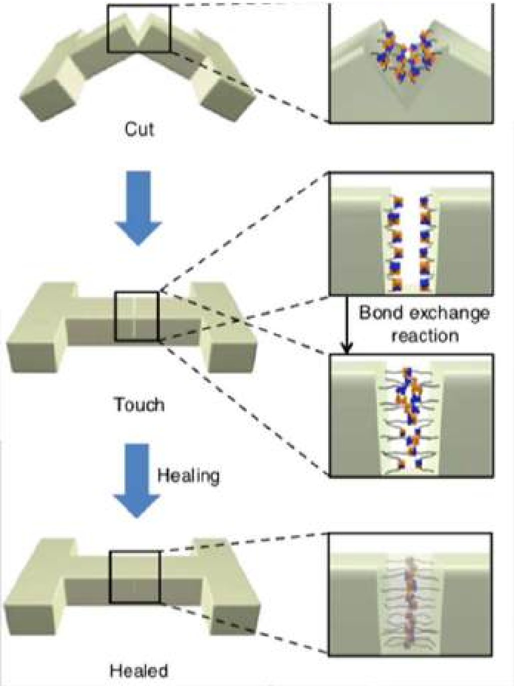




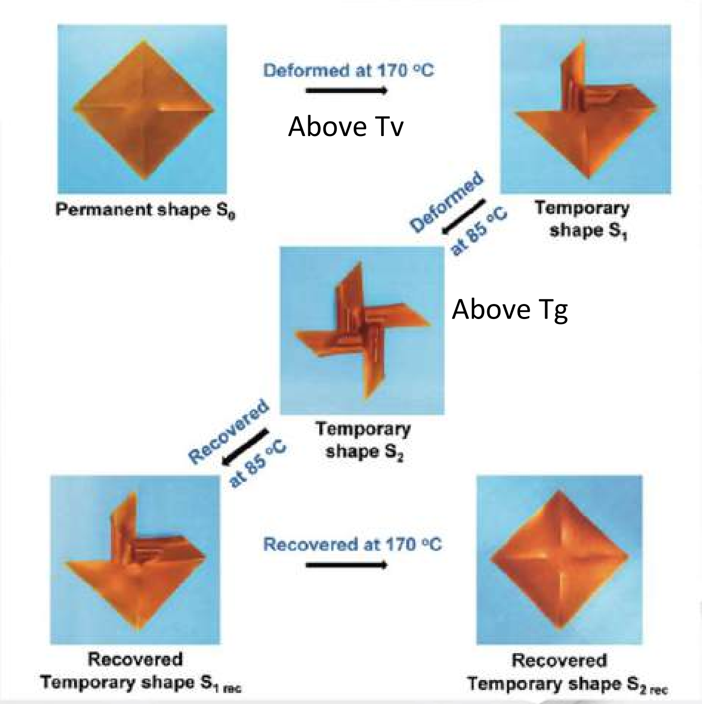
- Ea: activation energy of Exchange reaction or activation energy of viscous flow.
- Describes the sensitivity of of the viscosity to T changes.
- High Ea fast decrease of viscosity when heating.
- High Ea improved dimensional stability at service temperatures.
- τ0 prefactor is extrapolated to infinite T, can be interpreted as a characteristic relaxation time if the network rearrangement is barrierless

5. Applications of Associative CANs and Vitrimers

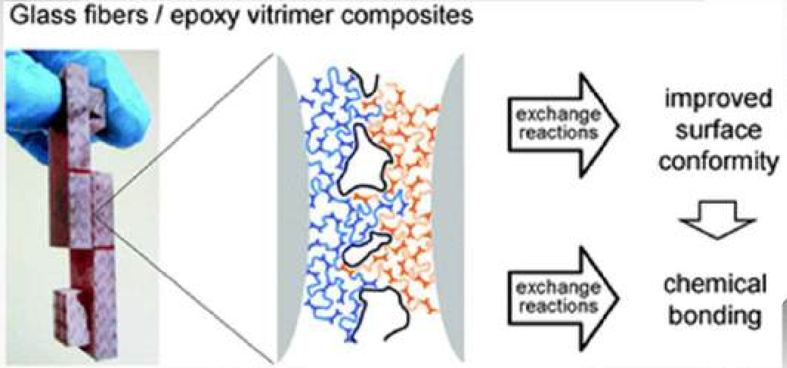
- **Self healing**



- **Shape memory**



- **Welding**



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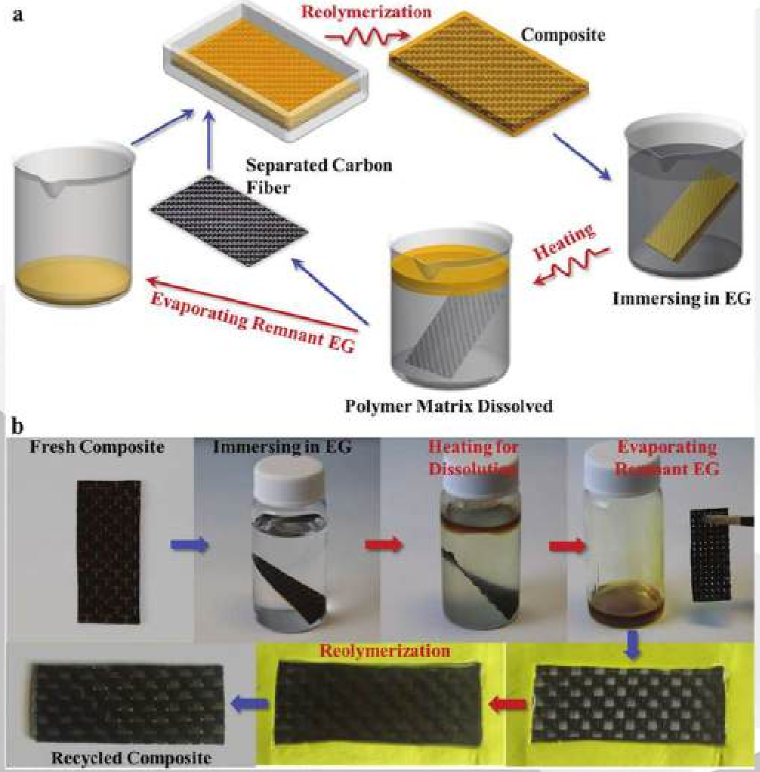
5. Applications of Associative CANs and Vitrimers

- **Recycling**

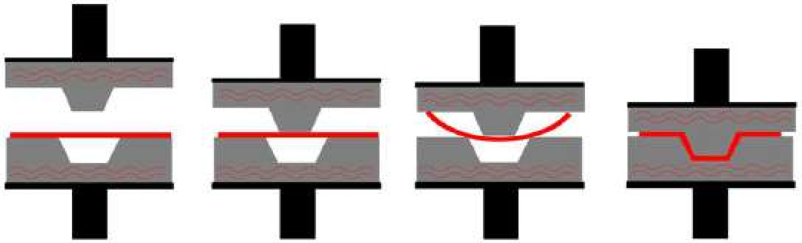


- **Reshaping/thermoforming**

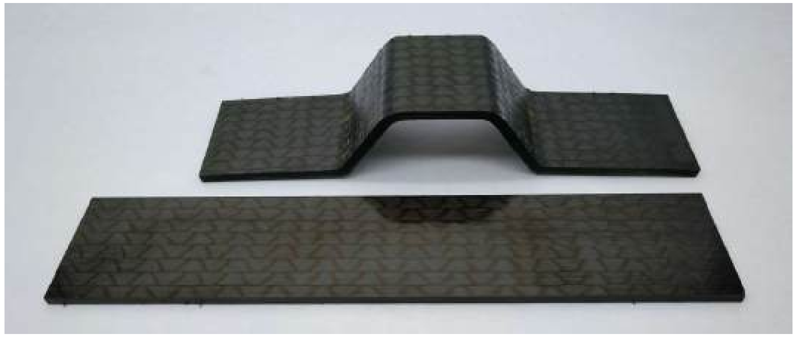
Upper mold approaching > 50 mm/s

Closing 100 N /s until consolidation load (30000 N)

Consolidation load 15 – 120 s



Press forming steps.

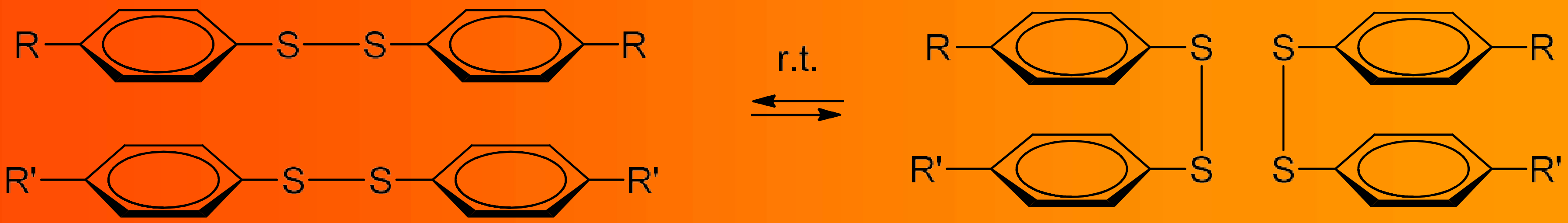


Aromatic disulfidecontaining epoxy vitrimer/CF composite sample before and after thermoforming process

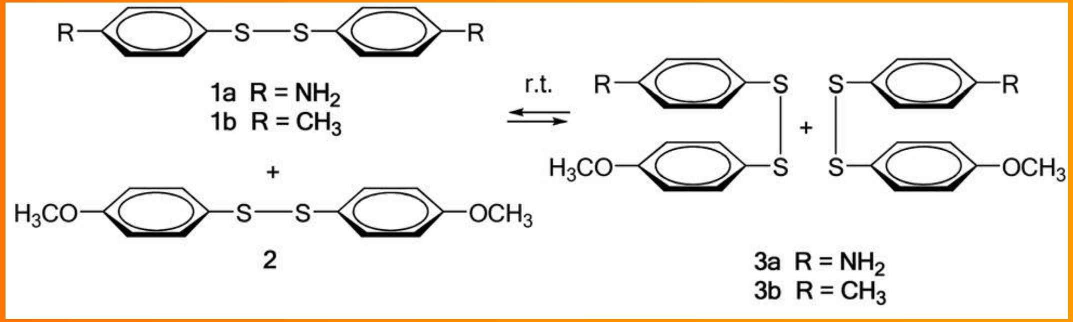
Dynamic networks and composites based on aromatic disulfide exchange

6. Aromatic disulfide exhange

Vitrimers based on **aromatic disulfide exchange**



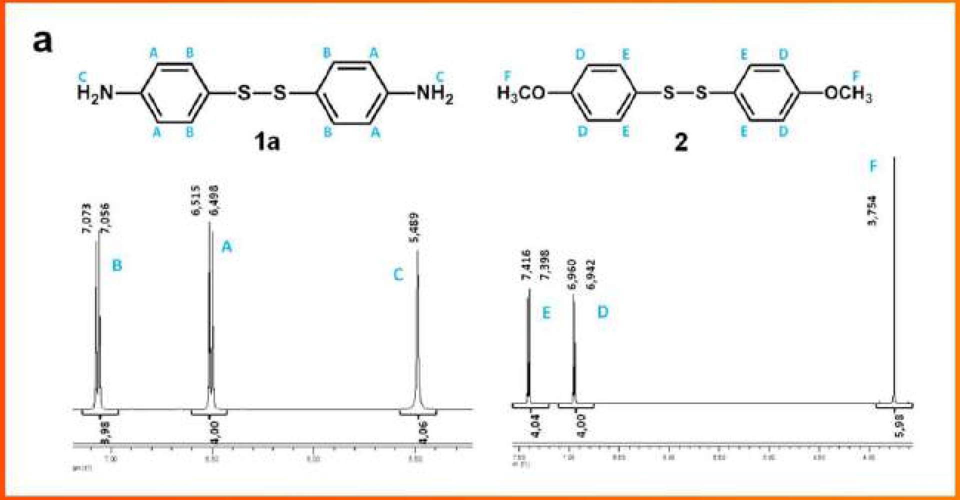
As a model metathesis reaction, we studied the equilibration of equimolar amounts of different aromatic disulfide mixtures by ^{1}H-NMR.



A. Rekondo, R. Martin, A. Ruiz de Luzuriaga, G. Cabañero, H. J. Grande and I. Odriozola, *Mater. Horiz.*, **2014**, *1*, 237–240

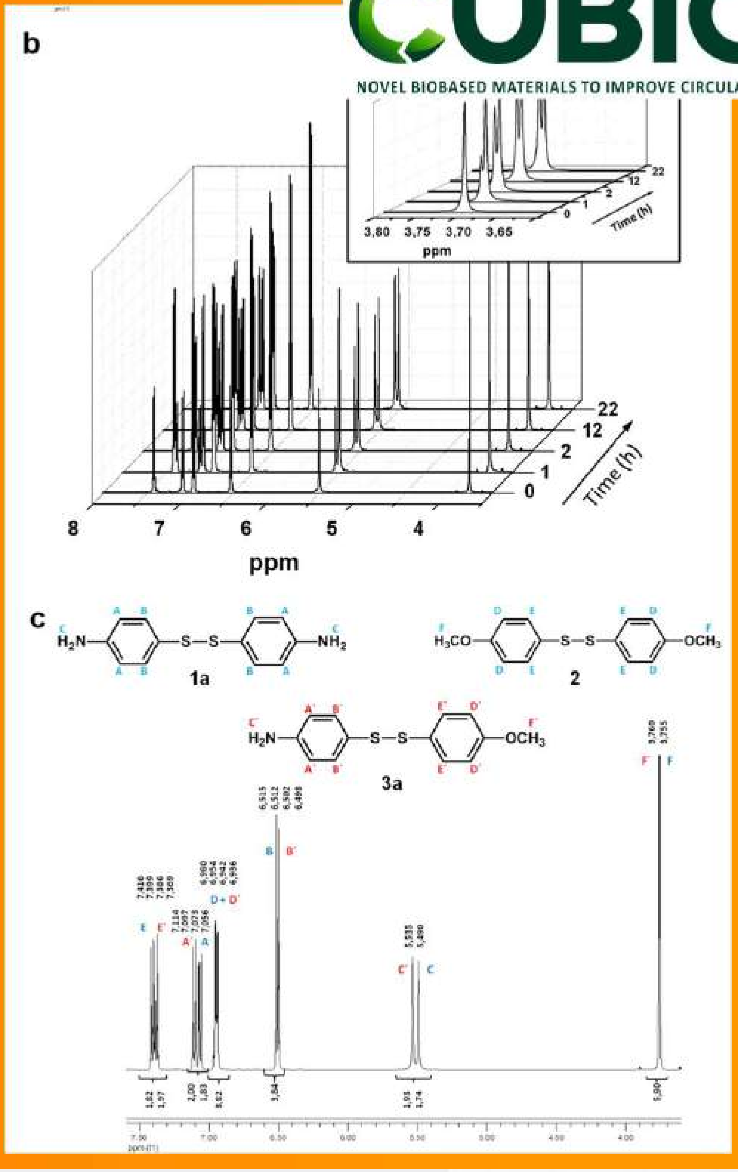
6. Aromatic disulfide exhange

Study of the **aromatic disulfide exchange** by ^{1}H-NMR



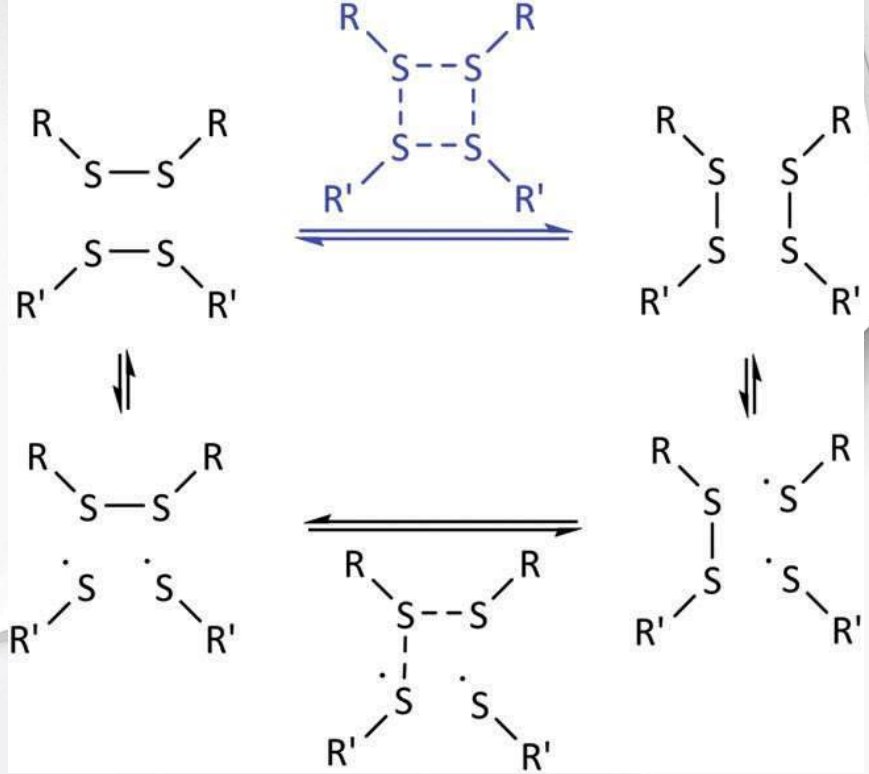
- **In absence of any catalyst metathesis started in less than 1 hour, achieving the equilibrium in 22 hours where a mixture of 1a (25 mol%), 2 (25 mol%) and 3a (50 mol%) was obtained.**

- **When the reaction was performed in the presence of 0.1 equivalents of NEt_3, the equilibrium was reached in less than 1 hour.**



7. Underlying mechanism of aromatic disulfide exchang

- ✓ Both metathesis and a radical-mediated mechanism have been used in the literature to describe the mechanism for disulfide exchange.
- ✓ In the first case, the disulfide bonds would break and form simultaneously.
- ✓ In the radical mediated mechanism, the breaking of one disulfide bond would lead to the formation of sulfur-centered radicals that would eventually attack other disulfide bonds.



Schematic representation of the [2 + 2] metathesis (blue) and [2 + 1] radical-mediated (black) mechanisms.

7. Underlying mechanism of aromatic disulfide exchang

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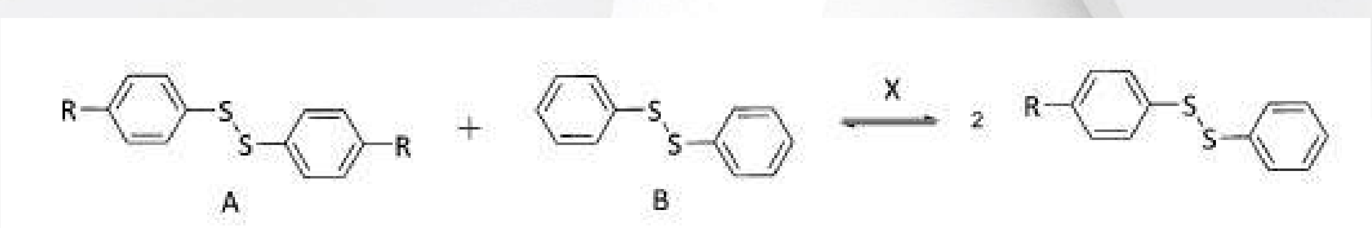
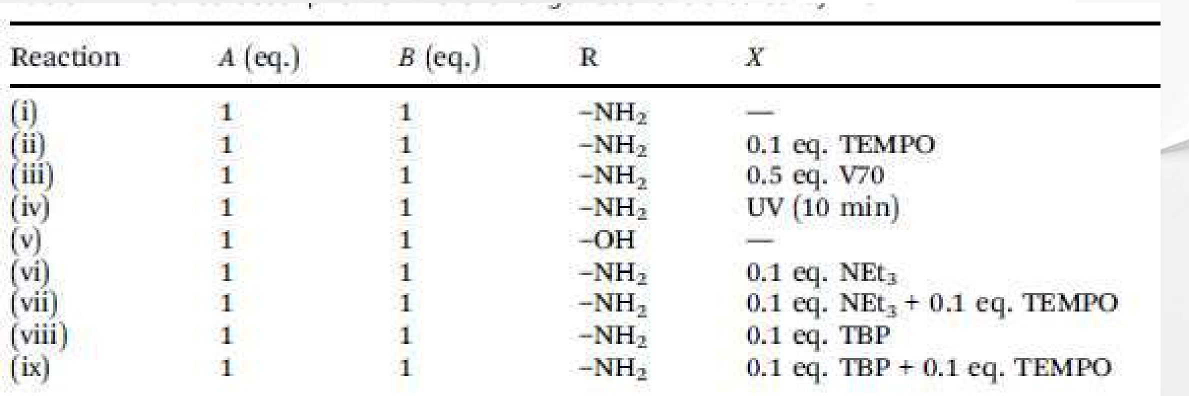
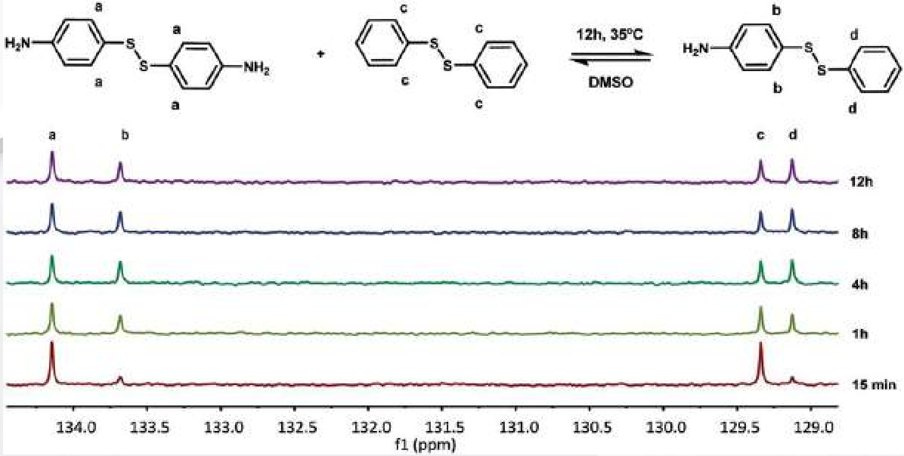
- ✓ **Validation and clarification of the underlying mechanism by studying the kinetics of the exchange of a mixture of aromatic disulfides**
- ✓ **^{13}C NMR study of a model exchange reaction modifying parameters such as initiator, inhibitor, catalyst, UV radiation, etc.**





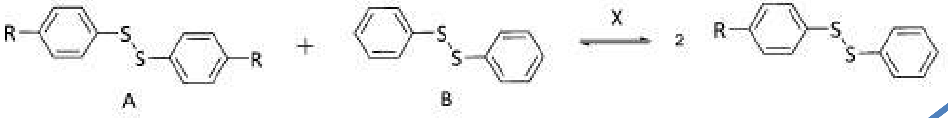
Reaction	*A* (eq.)	*B* (eq.)	R	*X*
(i)	1	1	$-NH_2$	—
(ii)	1	1	$-NH_2$	0.1 eq. TEMPO
(iii)	1	1	$-NH_2$	0.5 eq. V70
(iv)	1	1	$-NH_2$	UV (10 min)
(v)	1	1	$-OH$	—
(vi)	1	1	$-NH_2$	0.1 eq. NEt_3
(vii)	1	1	$-NH_2$	0.1 eq. NEt_3 + 0.1 eq. TEMPO
(viii)	1	1	$-NH_2$	0.1 eq. TBP
(ix)	1	1	$-NH_2$	0.1 eq. TBP + 0.1 eq. TEMPO



S. Nevejans, N. Ballard J. I. Miranda, B. Reckc and J. M. Asua, *Phys.Chem.Chem.Phys.*, **2016**, *18*, 27577

7. Underlying mechanism of aromatic disulfide exchang

✓ ^{13}C NMR study of a model exchange reaction modifying parameters such as initiator, inhibitor, catalyst, UV radiation, etc.



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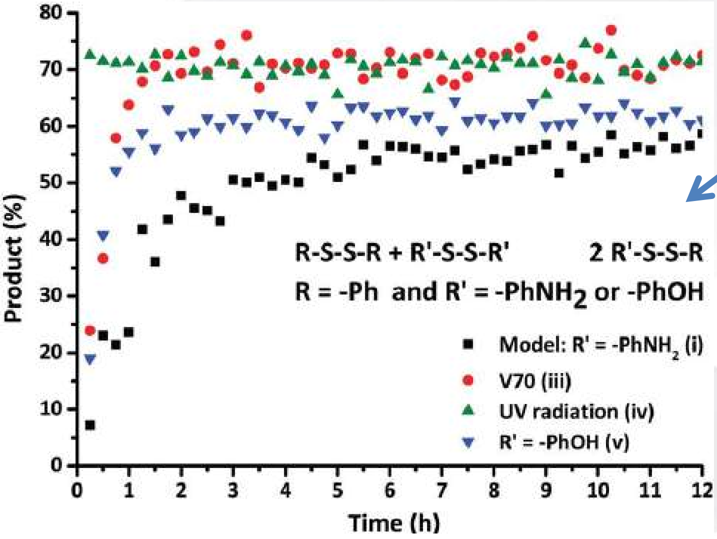
(iii)	1	1	–NH_2	0.5 eq. V70
(iv)	1	1	–NH_2	UV (10 min)
(v)	1	1	–OH	—
(vi)	1	1	–NH_2	0.1 eq. NEt_3
(vii)	1	1	–NH_2	0.1 eq. NEt_3 + 0.1 eq. TEMPO
(viii)	1	1	–NH_2	0.1 eq. TBP
(ix)	1	1	–NH_2	0.1 eq. TBP + 0.1 eq. TEMPO



Formation of the exchange product as a function of time for the exchange reactions (i), (iii), (iv) and (v).

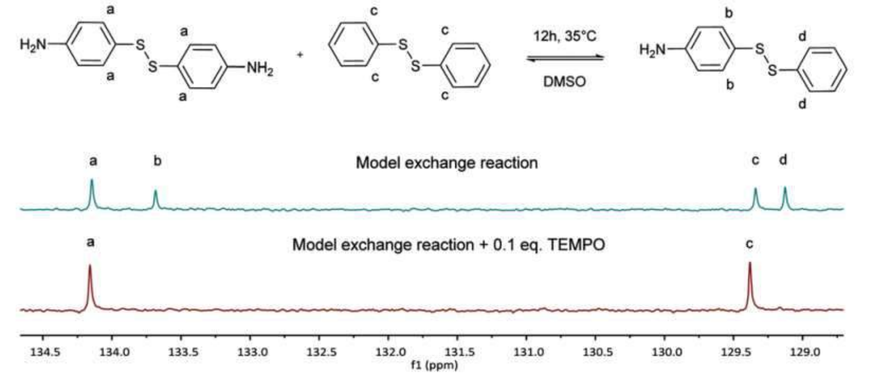
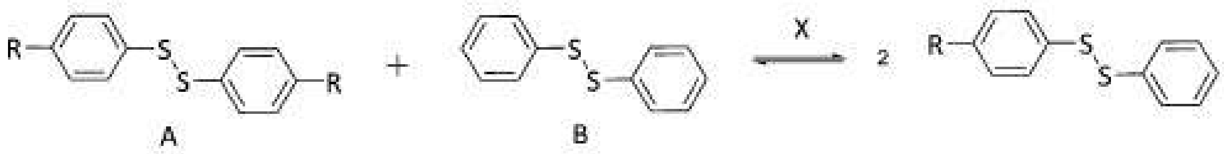


Fig. 5 Formation of the exchange product *via* the model exchange reaction (i) and in the presence of TEMPO (ii) (delay time of 20 s).

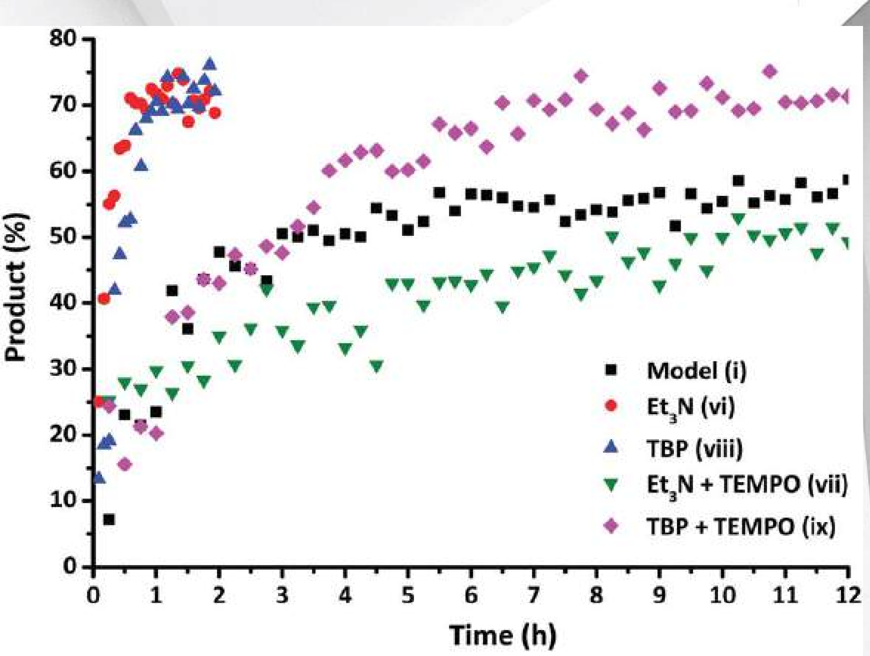
S. Nevejans, N. Ballard J. I. Miranda, B. Reckc and J. M. Asua, *Phys.Chem.Chem.Phys.*, **2016**, *18*, 27577

7. Underlying mechanism of aromatic disulfide exchang

- ✓ ^{13}C NMR study of a model exchange reaction modifying parameters such as initiator, inhibitor, catalyst, UV radiation, etc.



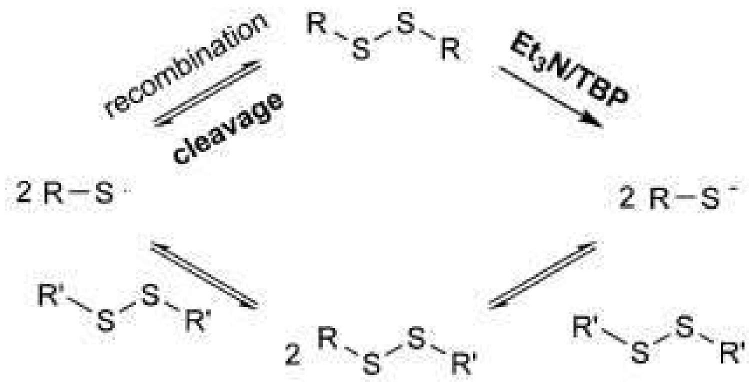
Reaction	*A* (eq.)	*B* (eq.)	R	*X*
(i)	1	1	$-NH_2$	—
(ii)	1	1	$-NH_2$	0.1 eq. TEMPO
(iii)	1	1	$-NH_2$	0.5 eq. V70
(iv)	1	1	$-NH_2$	UV (10 min)
(v)	1	1	$-OH$	—
(vi)	1	1	$-NH_2$	0.1 eq. NEt_3
(vii)	1	1	$-NH_2$	0.1 eq. NEt_3 + 0.1 eq. TEMPO
(viii)	1	1	$-NH_2$	0.1 eq. TBP
(ix)	1	1	$-NH_2$	0.1 eq. TBP + 0.1 eq. TEMPO



Formation of the exchange product as a function of time for the exchange reactions (i), (vi), (vii), (viii) and (ix).

S. Nevejans, N. Ballard J. I. Miranda, B. Reckc and J. M. Asua, *Phys.Chem.Chem.Phys.*, **2016**, *18*, 27577

7. Underlying mechanism of aromatic disulfide exchang

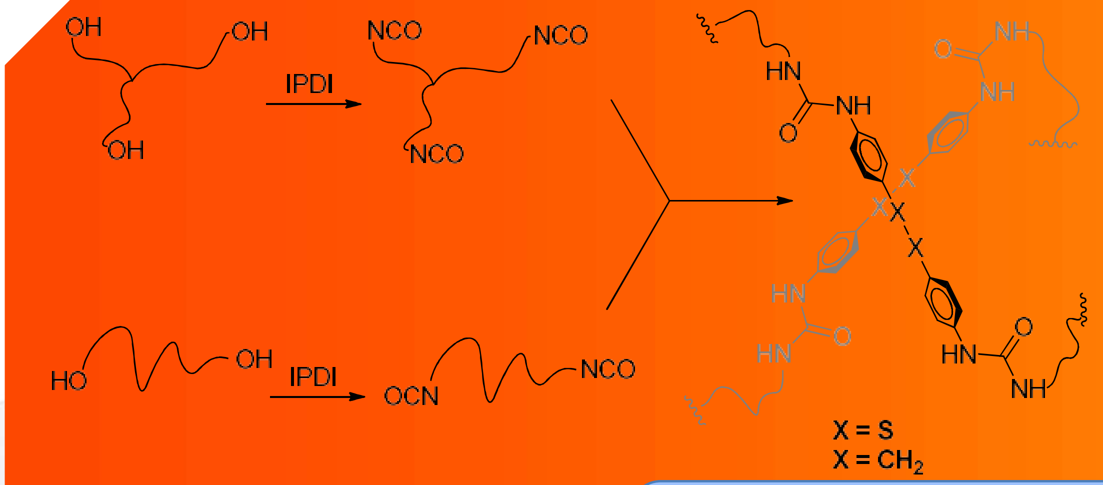


Scheme 2 Disulfide exchange through the formation of sulfur-based radicals and sulfur-based anions.

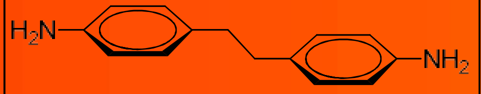
Main conclusions

- ✓ The change in kinetics of the disulfide exchange in the presence of a radical trap and a radical source demonstrate that the mechanism for the disulfide exchange is radical-mediated.
- ✓ NEt_3 and TBP nucleophilic catalyst also increase the exchange rate.
- ✓ Based on these experiments, it would be suggested that in the presence of a catalyst both radical-mediated and thiol-mediated exchanges occur simultaneously

8. Self-healing poly(urea-urethane) (PUU) elastomer



Conventional crosslinker



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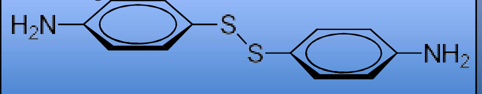

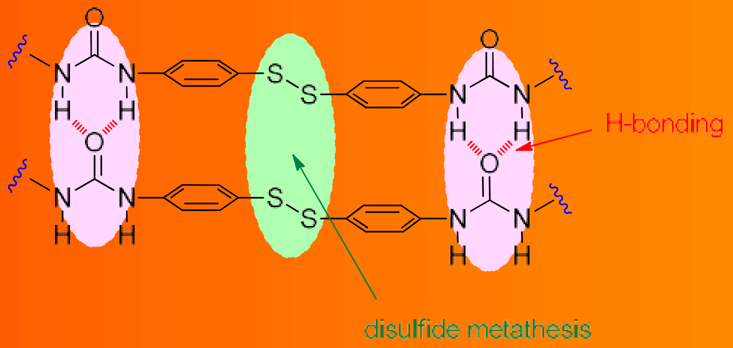

Patent applications:

- PCT/EP2014/053925 - *"Self-healing elastomer and process for its preparation".*

- The remarkable self-healing ability of this system could be attributed to two structural features, which are present in this unique crosslinking unit: (i) the aromatic disulfide which is in constant exchange at room temperature and (ii) two urea groups, capable of forming a quadruple H-bond.

8. Self-healing poly(urea-urethane) (PUU) elastomer

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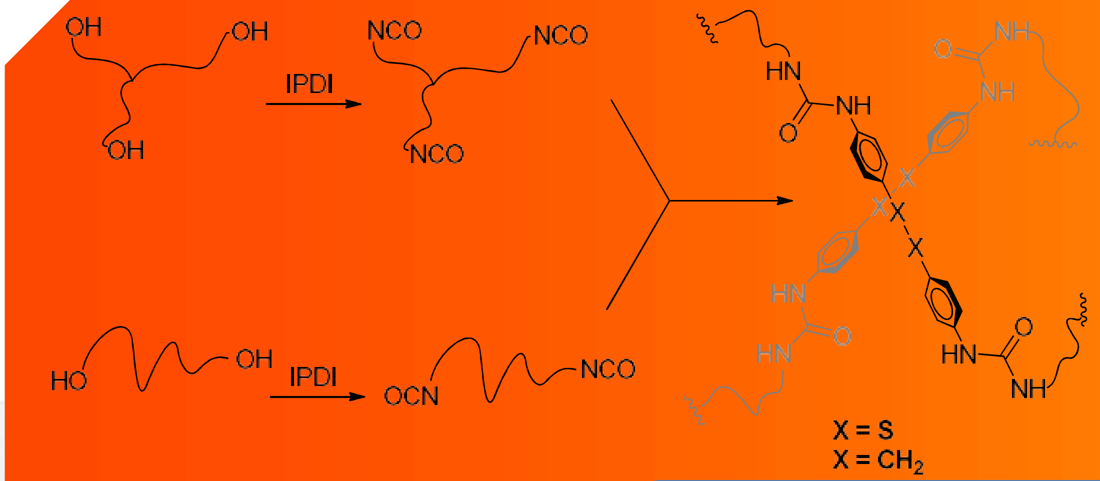
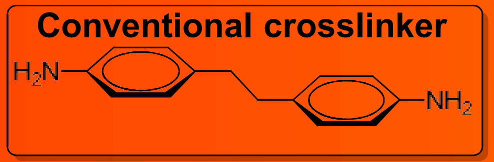


X = S
X = CH_2



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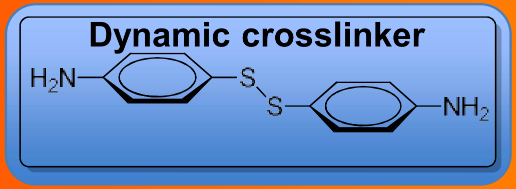

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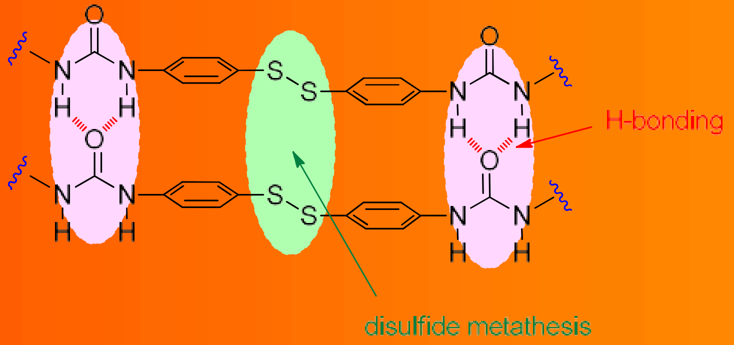
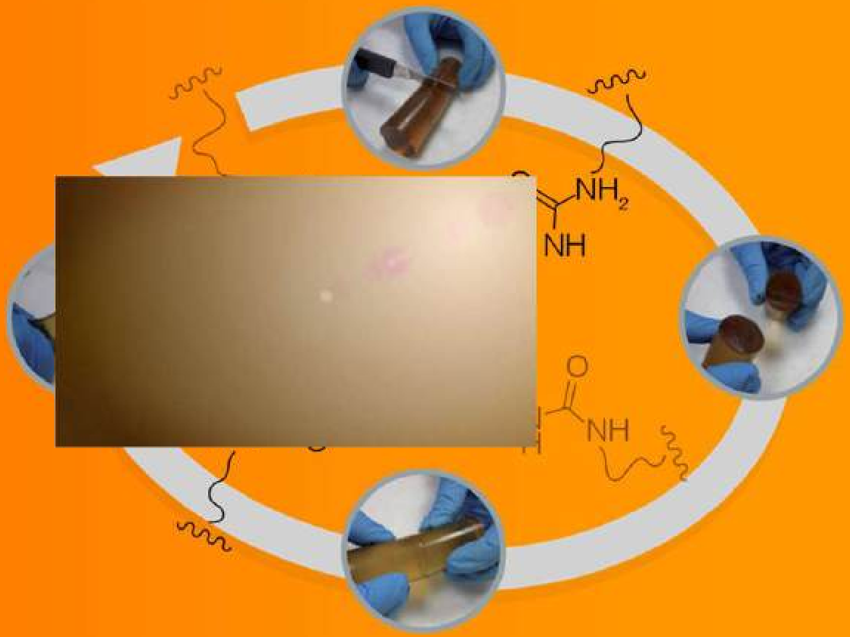


H-bonding

disulfide metathesis



- The remarkable self-healing ability of this system could be attributed to two structural features, which are present in this unique crosslinking unit: (i) the aromatic disulfide which is in constant exchange at room temperature and (ii) two urea groups, capable of forming a quadruple H-bond.

Patent applications:

- PCT/EP2014/053925 - *“Self-healing elastomer and process for its preparation”.*

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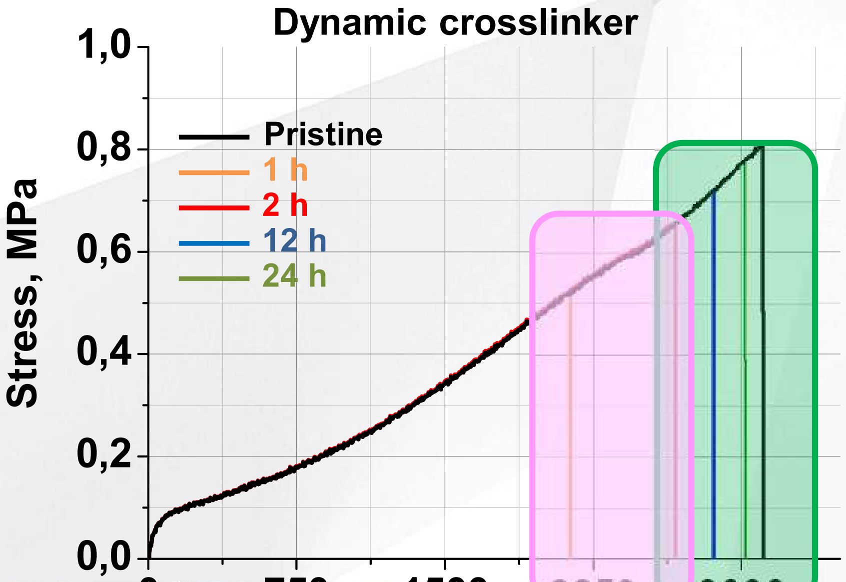
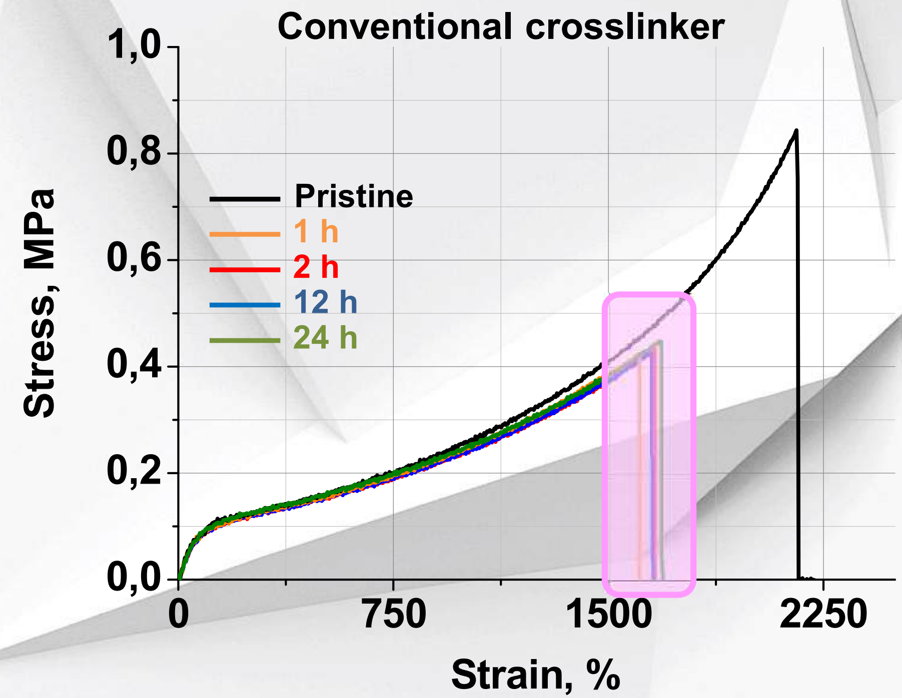
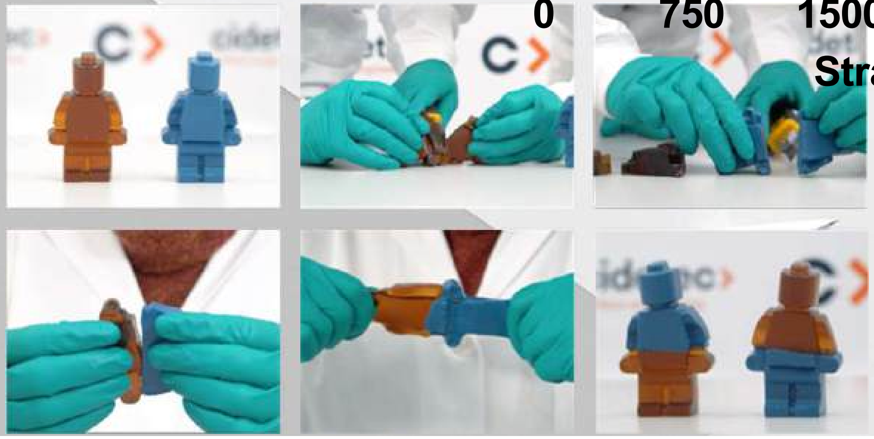
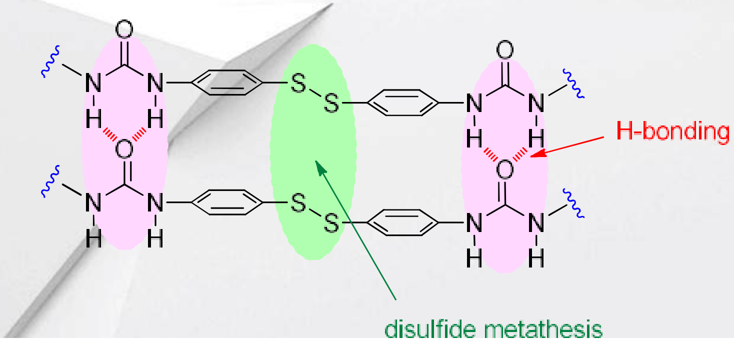
8. Self-healing poly(urea-urethane) (PUU) elastomer

Healing as a function of time determined by tensile strength measurements





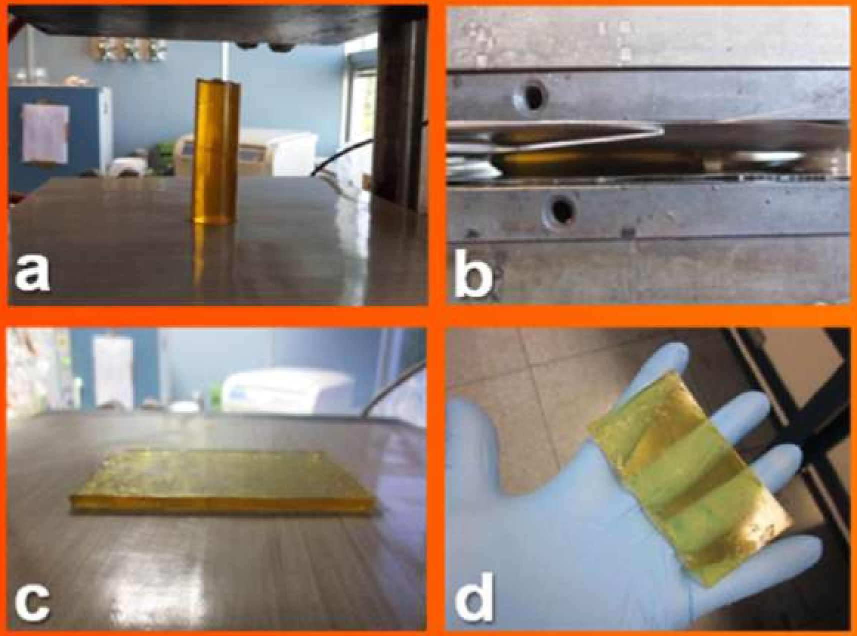


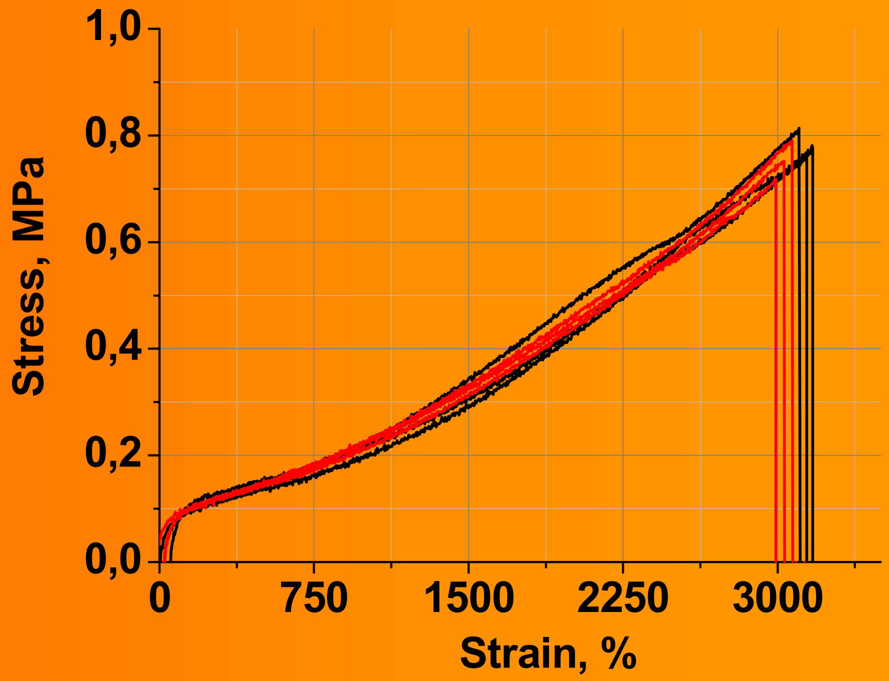


- 80% recovery in 2 hours
- Quantitative recovery in 24 hours

8. Self-healing poly(urea-urethane) (PUU) elastomer

Processability





These materials are recyclable!

R. Martin, A. Rekondo, A. Ruiz de Luzuriaga, G. Cabañero, H. J. Grande and I. Odriozola, *J. Mater. Chem. A*, **2014**, *2*, 5710–5715.

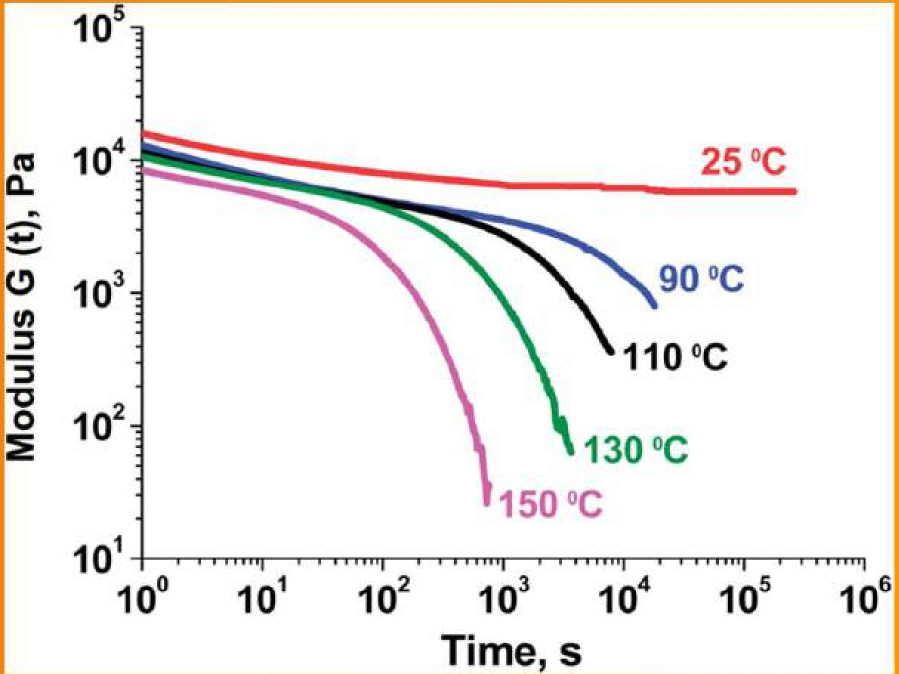
8. Self-healing poly(urea-urethane) (PUU) elastomer

Stress relaxation experiments

- ✓ At 150 C the sample needed about 4 minutes to relax until 10% of its initial modulus value (G).
- ✓ At 130 and 110 C, the same relaxation process needed about 15 minutes and 1 hour, respectively.
- ✓ At temperatures below 100 C this relaxation process appeared to take much longer, needing 4 hours at 90 C.
- ✓ At room temperature the PUU elastomer showed very low relaxation after 3 days of experiment.

Two main conclusions:

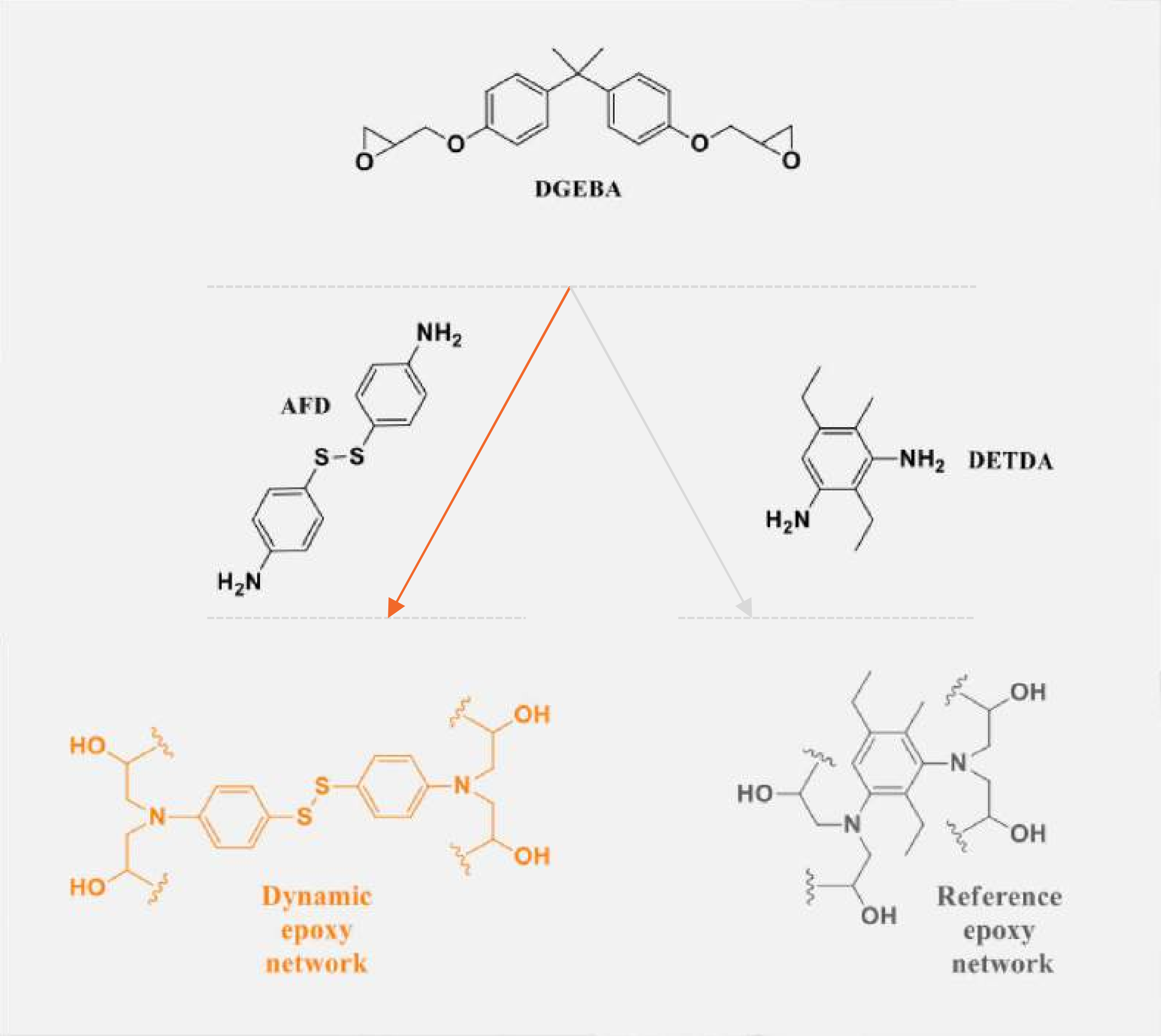
- This PUU did not relax easily at room temperature, although having aromatic disulfide bridges that are able to undergo exchange at such a temperature.
- Another interaction exist which was eliminated above 100 C. It was attributed to the quadruple H-bonding of the urea groups and would be mainly responsible for preventing flow or relaxation at room temperature.



Stress relaxation plots as a function of time recorded at room temperature (red), 90ºC (blue), 110ºC (black), 130ºC (green) and 150ºC (purple) for an applied strain of 10%.

R. Martin, A. Rekondo, A. Ruiz de Luzuriaga, G. Cabañero, H. J. Grande and I. Odriozola, *J. Mater. Chem. A*, **2014**, *2*, 5710–5715.

9. Epoxy vitrimers based on aromatic disulfide



	Reference network	Dynamic network
Tg (DSC) [ºC]	127	**130**
Tg (DMA) [ºC]	130	**130**
Td [ºC]	350	**300**
E´(25ºC) [GPa]	2,5	**2,6**
E´(150ºC) [MPa]	20	**20**
Stress [MPa]	81	**88**
Strain [%]	7,3	**7,1**

Comparable thermal and mechanical properties using our dynamic hardener instead of a conventional hardener.

10. Dynamic fibre reinforced composites based on aromatic disulfide

3R Composites

- Lecture 3: Manufacturing processes of 3R Composite Materials: Virginie Boucher
- Lecture 4: Revalorization routes of 3R-CAN composites materials: Alaitz Rekondo

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Circular Bio-based Europe
Joint Undertaking

Bio-based Industries Consortium

Funded by the European Union

The project is supported by the Circular Bio-based Europe Joint Undertaking and its members. Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or CBE JU. Neither the European Union nor the granting authority can be held responsible for them.

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