Reversible Crosslinking

*a potent paradigm for designer materials*

Wouter G. Ellenbroek & Kees Storm

Eindhoven University of Technology
Department of Applied Physics
&
Institute for Complex Molecular Systems

**Project**
Harnessing Reversible Crosslinks for Toughness of Gels

**Research Line**
Reversible Crosslinks as a powerful motif in high tech materials
Who are we?

Wouter Ellenbroek

Kees Storm

Costantino Creton (ESPCI)

Other members of group TPS
Theory of Polymers and Soft Matter

Paul van der Schoot

Alexey Lyulin
Dynamic structures in nature: remodeling

http://treewright.blogspot.nl/2010/04/reaction-wood.html

https://www.youtube.com/watch?v=atalIS1Zuf8
Dynamic structures in synthetics: vitrimers

Vitrimers
As stable as thermosets
As malleable as thermoplasts

http://www.univ-psl.fr/default/EN/all/psl_en/the_vitrimer.htm
Dynamic structures in synthetics: self-healing


https://youtu.be/F0ltKCH24ck?t=27s
Outline

• Crosslink dynamics $\iff$ mechanical properties
• Recent experimental advances
• Our research questions
• Our modeling approach
• 3TU perspective
Strong and weak crosslinks

Reversible Crosslink: Any crosslink that can reform by itself after damage

Sun et al., Nat. Mater. 12 932 (2013)
Lifetime vs. Strength of Crosslinks

- **binding energy**
  - weak: << thermal energy
  - intermediate: ~ thermal energy
  - strong: >> thermal energy

- **lifetime**
  - weak: very short
  - intermediate: relevant to timescale of deformations
  - strong: “infinite”

- **mechanics**
  - weak
  - intermediate: interesting
  - strong: as a permanent bond
intermediate-strength reversible crosslinks are most interesting for the mechanics
Gels with added reversible linkers

Stress and strain for various linkers

**Fast linkers**
- no linear effect
- some toughening

**Slow linkers**
- no linear effect
- large toughening

**Very slow linkers**
- higher modulus
- more brittle

Stress and strain for various linkers

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The “slow” (intermediate) linkers increase the strain-at-break and the toughness.

Questions

1. How does the toughening work?

2. Why is the linear modulus unaffected while toughening is induced at larger strains?

3. How can we maximize the toughening effect?
Ideas: Rebinding and cooperativity

Relaxed

Under tension

green
reversible crosslinker
black
permanent crosslinker

pull

pull
Ideas: Clusters of Linkers

- cluster of reversible linkers
- cluster of reversible linkers around permanent linker
### Multiscale approach

**Step 1**
*understand dynamics of clusters of linkers*

- **Coarse grained MD**
  - include permanent and reversible linkers
  - vary composition
  - vary lifetime of reversible linkers
  - find strain-rate dependent stress-strain curves

**Step 2**
effective description of linker clusters for network study

- **Hybrid Langevin / MC model**
  - add linker clusters
  - study strain-rate dependent mechanics

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Pull cluster of reversible linkers around permanent linker
Reversible linkers in model collagen

Movie by Cyril Vrusch (Ph.D. student)
Design optimization

Goals
- Identify high-potential material designs
- Other targets than strain-at-break or toughness?

Additional experiments to verify numerically obtained ideas?

Collaborations towards new applications?
within the context of this project

Eindhoven
  Macromolecular and Organic Chemistry
Delft
  Advanced Soft Matter Group (Chem.E)
  Engineering Thermodynamics Group (3ME)
Twente
  Materials science and Technology of Polymers

other topics?
Activities within TPS

buckling of growing filaments (with Remy Kusters, L. Mahadevan)

cross-hatched ordering of collagen fibers (with Cyril Vrusch, Carlijn Bouten)

Function and soft mechanics of biomaterials

Kees Storm
Activities within TPS

Paul van der Schoot


Jamali et al. PRE 91 (2015), 042507

Self-assembly of soft and biomaterials

composites

percolation

biopolymers

colloids

liquid crystals

viruses

Technische Universiteit Eindhoven
University of Technology
Activities within TPS

Focus on Nanocomposites
CNT, graphene – polyimide
carbon black – rubber
silica – rubber
modified cellulose - PLA
silica - Nafion
fullerene - P3HT
CNT – vitrimer epoxy
....

Multiscale simulation of polymer dynamics

Formation of P3HT/PCBM solar cells
Activities within TPS

Responsive soft matter

disordered networks and composites on the verge of losing rigidity

Simple building blocks for unusual self-assembling structures
In short...

How and why do intermediate-strength reversible crosslinks toughen gels?

Kees Storm

Costantino Creton (ESPCI)

Cyril Vrusch
Rint Sijbesma

FOM

TU/e
Technische Universiteit Eindhoven
University of Technology

NWO
Netherlands Organisation for Scientific Research

3TU.Federatie