adolphe merkle institute
excellence in pure and applied nanoscience
UNIVERSITY OF FRIBOURG SWITZERLAND

VirginiaTech

Engineering smart nanocomposites for novel biomedical implants

E. Johan Foster

Adolphe Merkle Institute, Polymer Chemistry and Materials (CH)

And

Virginia Tech, Material Science and Engineering (USA)

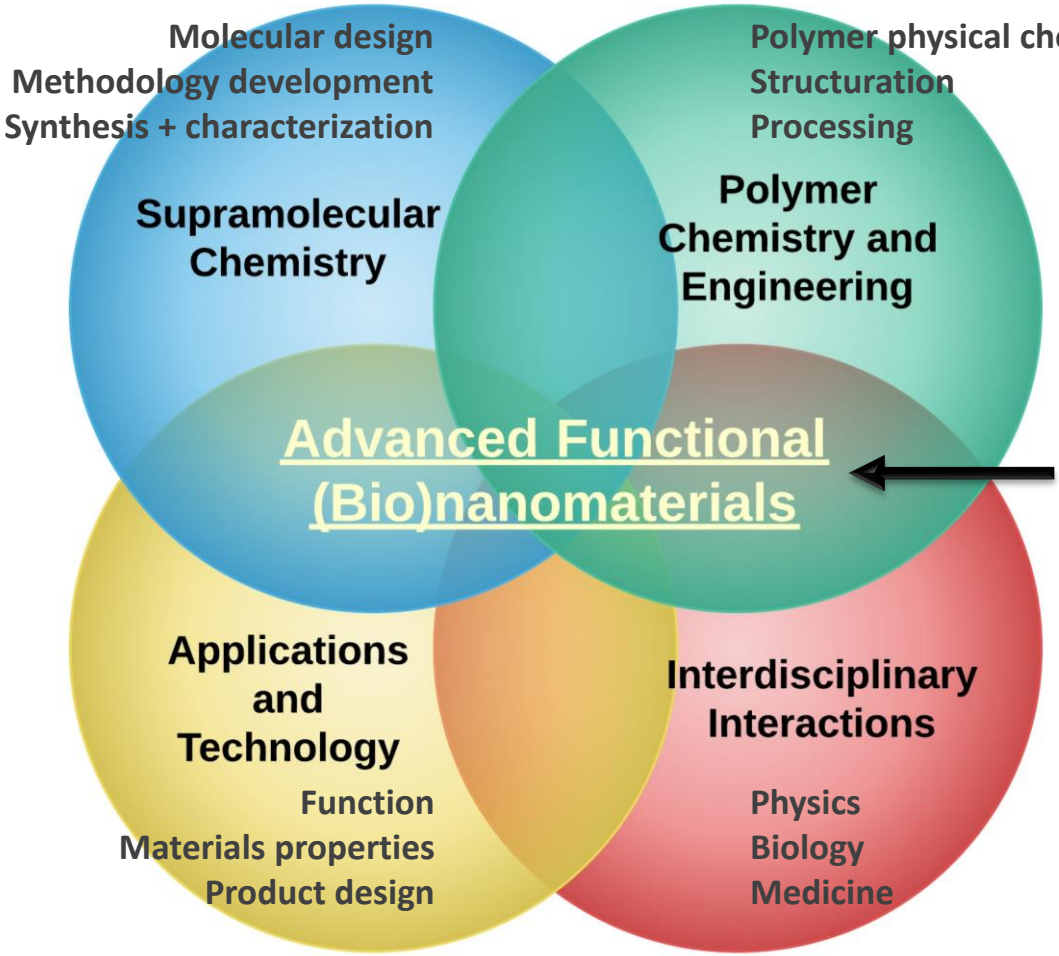
Meet and Match Event:
Surface Technologies for Medical Devices

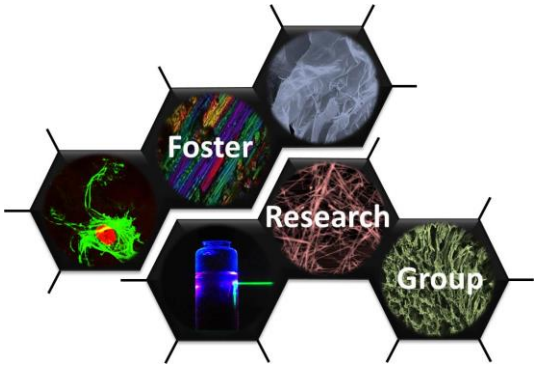
AMI – A New Research Institute in Fribourg, CH

First donnation by Adolphe Merkle 2006
Creation of Fribourg Center for Nanomaterials

Creation of Adolphe Merkle foundation 2007
Creation of Adolphe Merkle Institute 2008

The Foster Research Group





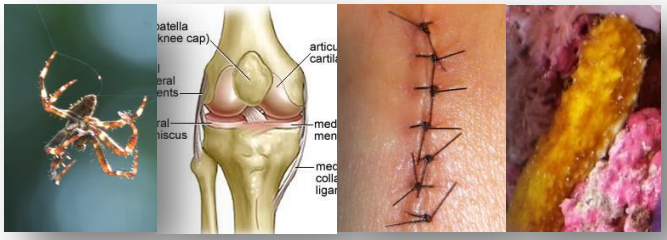
advanced functional (bio)nanomaterials through micro/nano-structuring, supramolecular, dynamic covalent and non-covalent interactions

Responsive ("Smart") Materials

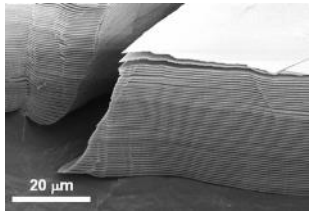
"Smart Materials" change their properties in response to an external stimulus in predictable and useful manner

Temperature
Light
Magnetic field
Electrical field
Mechanical force
Chemicals …

Color
Transparency
Stiffness
Chemical properties
Small molecule release
Heal …

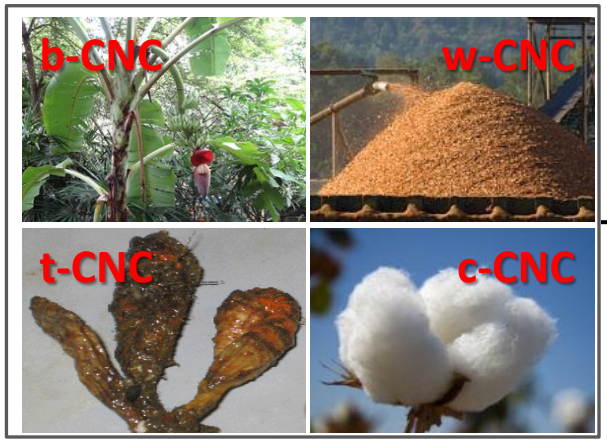


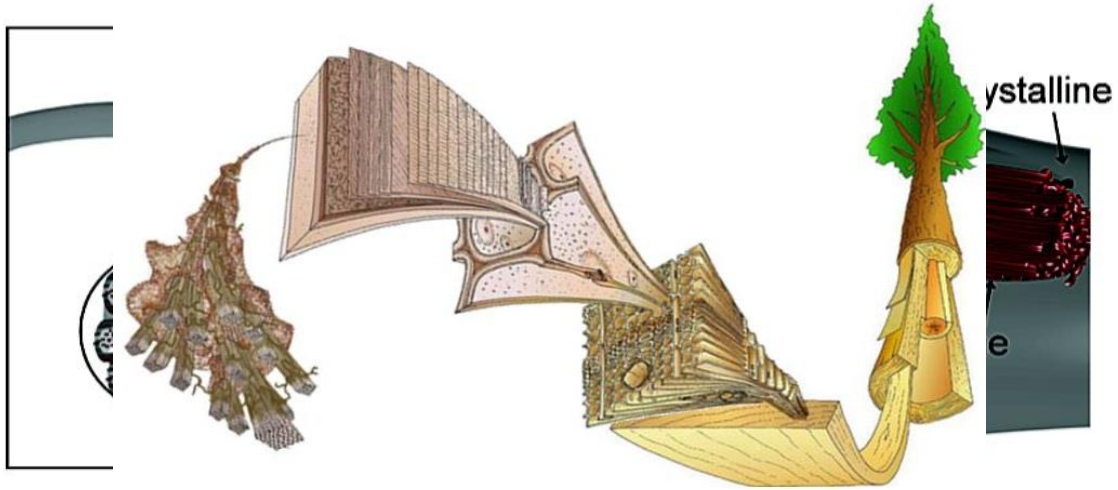
Inspiration From Nature



We also work on smart approaches to develop not-so-smart materials

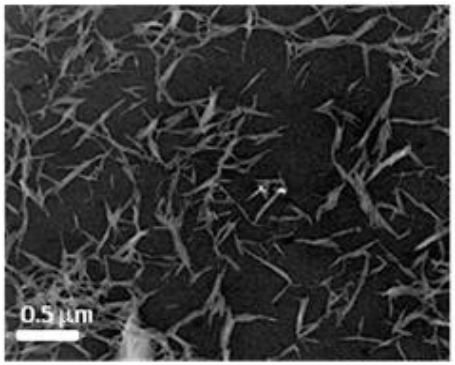
Nanofibers from Nature

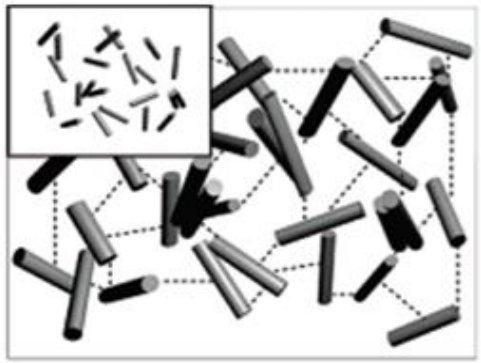


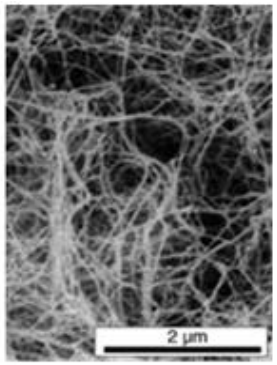


Strong acid hydrolysis + sonication

Enzymatic hydrolysis and shearing







CNC Cellulose Nanocrystals (or Cellulose Nanowhiskers)

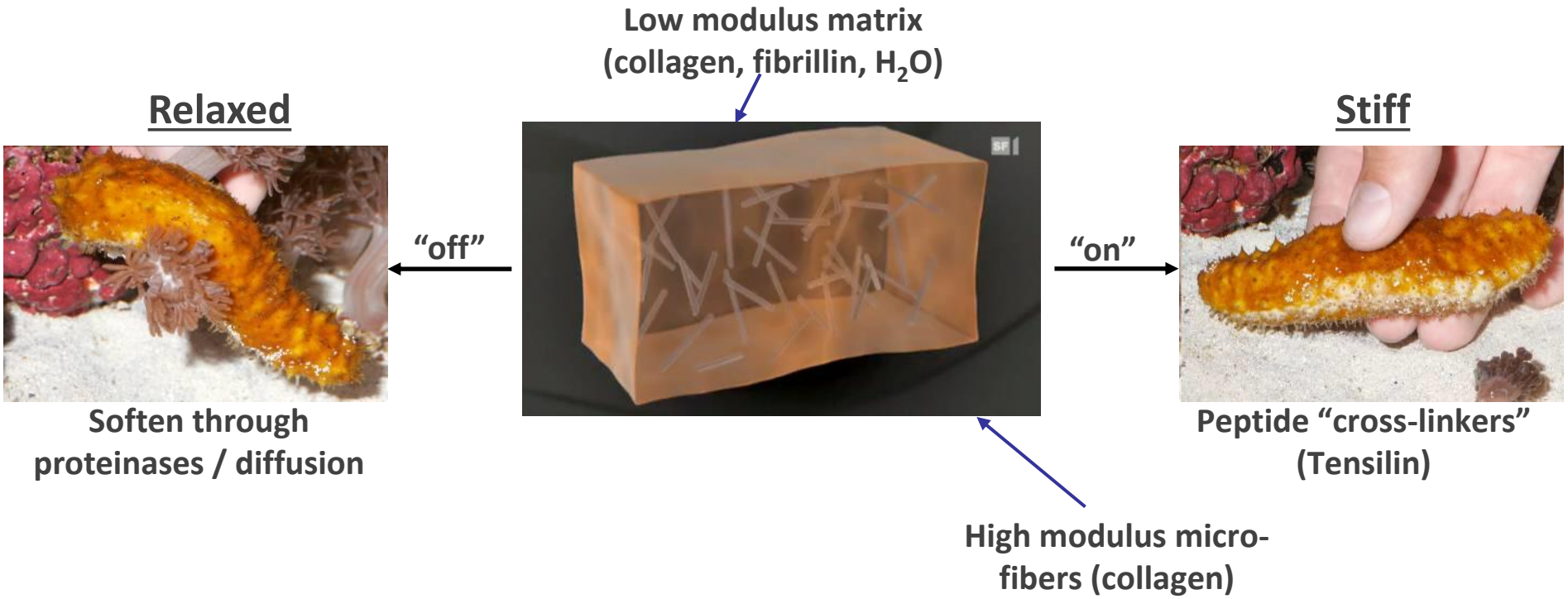
L = 100 – 2000 nm // d = 5 – 20 nm

MFC or NFC (Micro-/Nano-fibrilated Cellulose)

L = 10 – 100 µm // d = 15 – 100 nm

Assembled from: Paakko, M *et al. Biomacromolecules 2007, 8, (6), 1934-1941.* Paakko, M. *et al. Soft Matter 2008, 4, (12), 2492-2499.* Capadona, J. R. *et al. Biomacromolecules 2009, 10, (4), 712-716.*

Mechanically Adaptive Materials in Nature



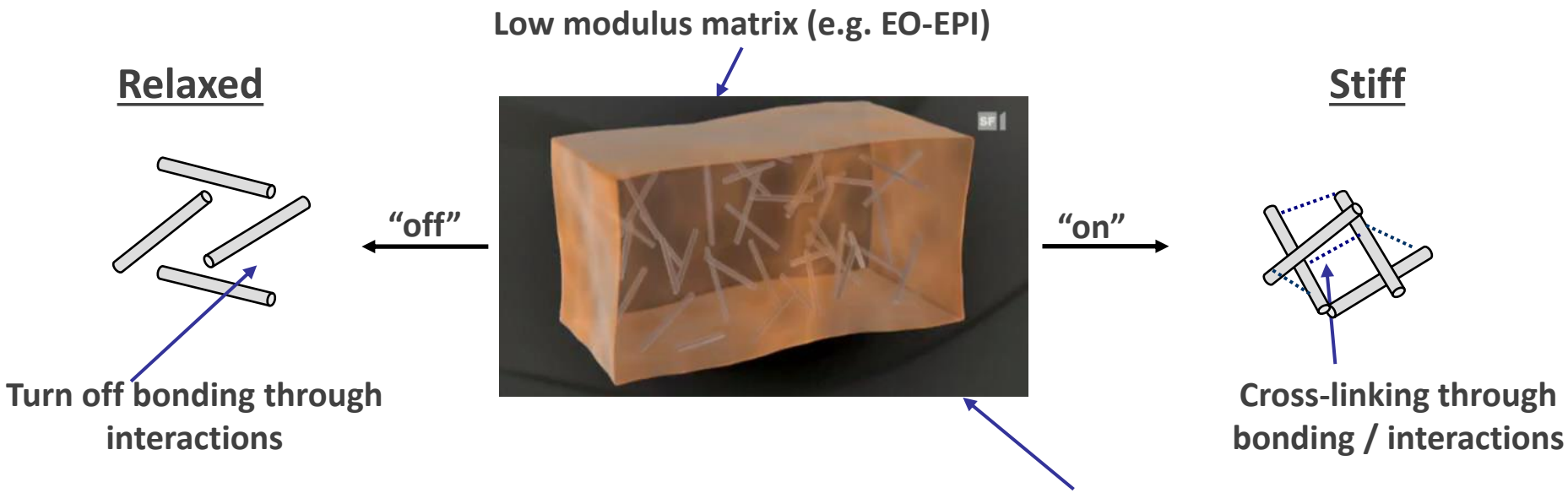
Deep dermis features mutable mechanical properties

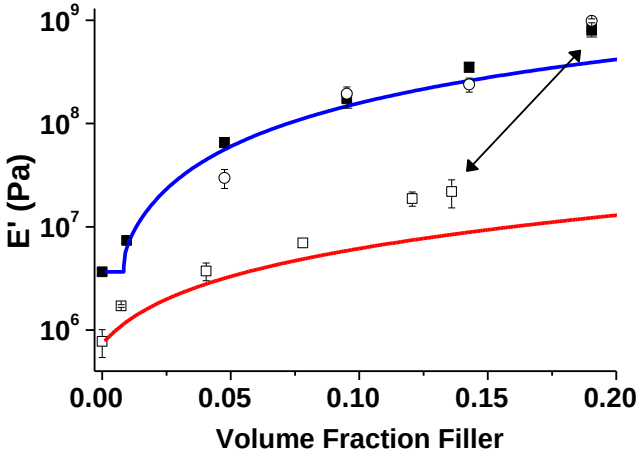
Animal can reversibly switch the modulus of its skin between 'soft' and 'rigid' within microseconds

***In vitro*: 5 to 50 MPa**

Szulgit, Shadwick J. Exp. Biol. 2000. Trotter, Heuer et. al. Biochem. Soc. Trans. 2000. *Macromolecules* **2011**, *44,* 6827. *Macromolecules* **2012**, *45,* 4707. *ACS Appl. Mat. Interf.* **2013,** *ASAP*, *ACS Appl. Mat. Interf.* **2013**, *5*, 1517. *European Patent application filed.*

Mechanically Adaptive Materials in the Lab

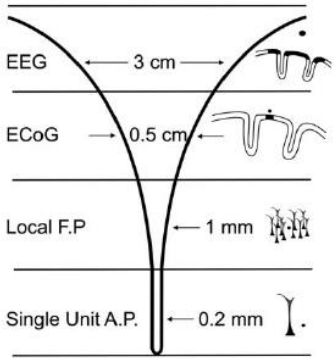


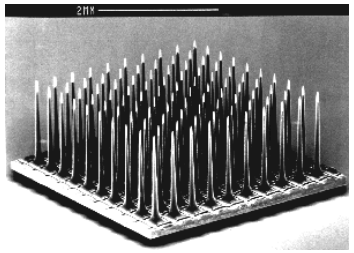


- Reinforcing soft polymers with a stiff filler
- **Exploiting covalent and non-covalent interactions**
- Reversible and irreversible reactions

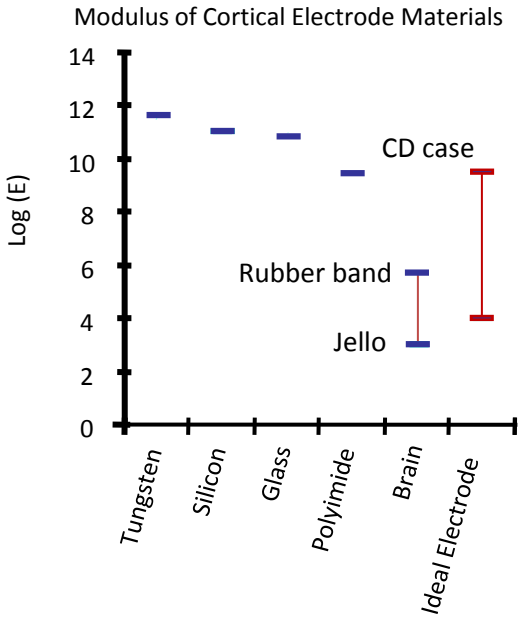
Macromolecules **2011**, *44*, 6827. *Macromolecules* **2012**, *45*, 4707. *ACS Appl. Mat. Interf.* **2013,** *ASAP*, *ACS Appl. Mat. Interf.* **2013**, *5*, 1517. *European Patent application filed.*

Cortical Interfacing





http://www.bioen.utah.edu/cni/projects/blindness.htm#overview



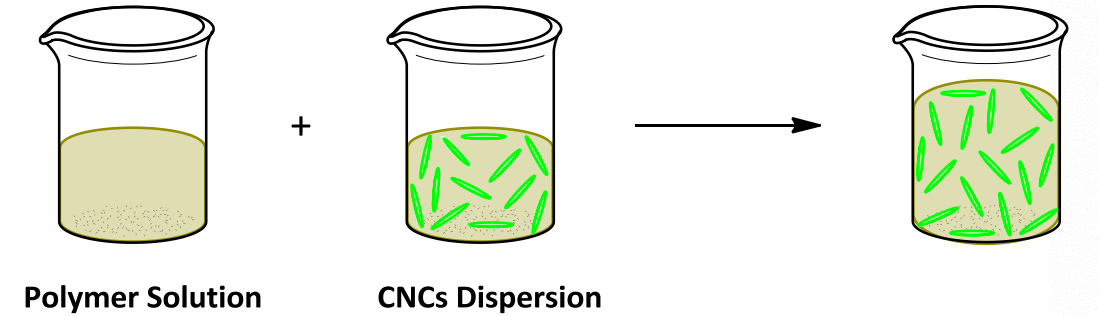
Lifetime of Probes / Tissue Response (Gliosis)

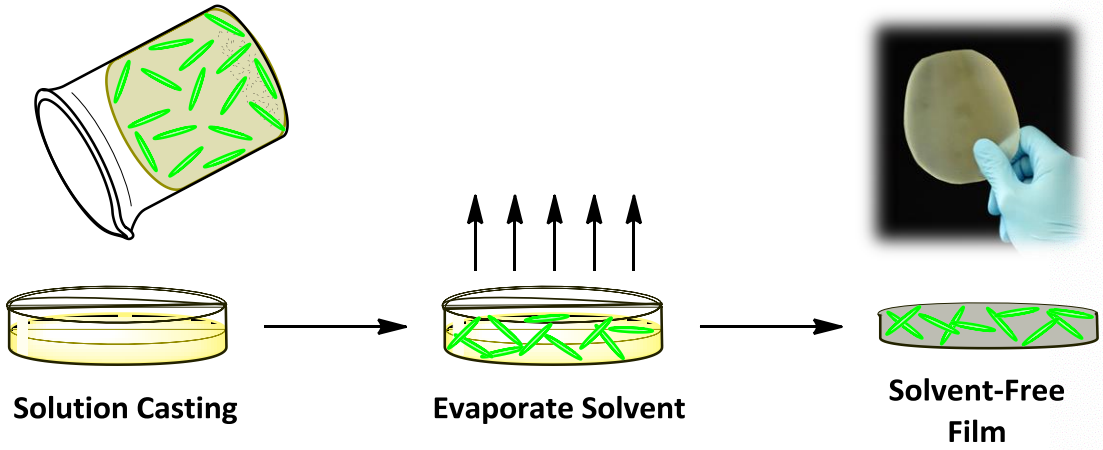
- Cellular Response to Implanted Material
- Mechanical Mismatch
- Micromotion

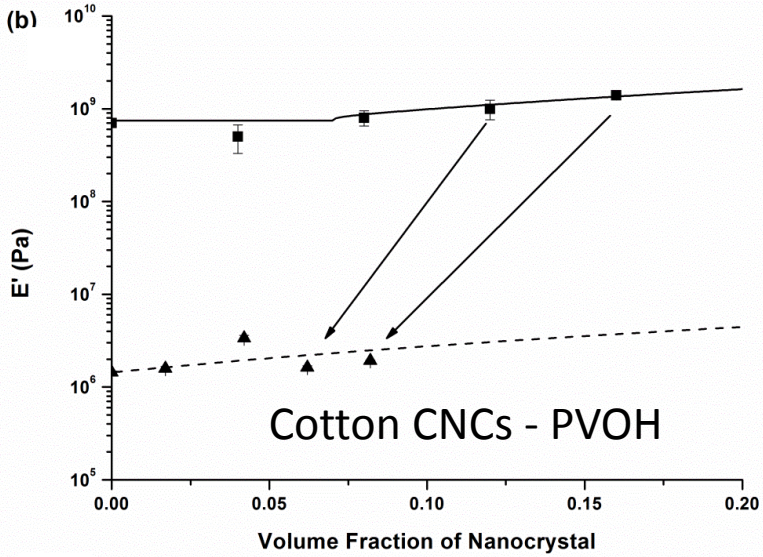
Mechanical Restrictions

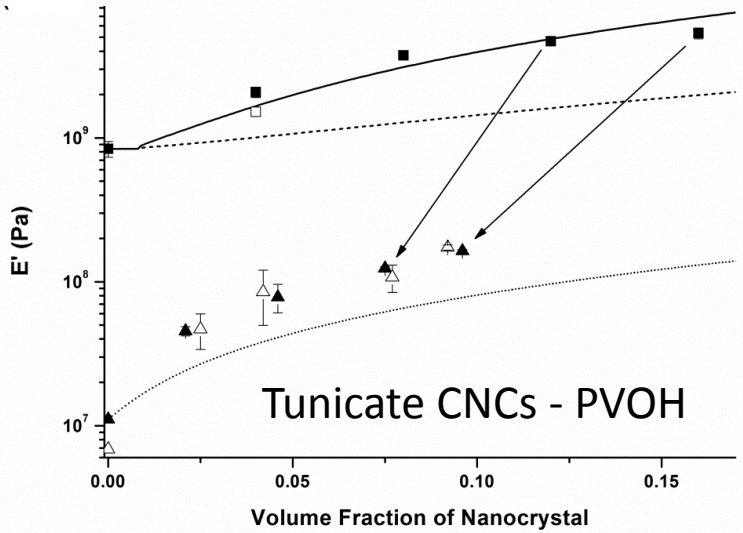
- Dura Mater (Stiffness *E* = 40 - 200 MPa)
- Pia Mater (*E*=40 MPa) -> Need stiff probe to insert
- Brain Stiffness: 6 – 600 KPa

Adaptive-Nanocomposite Processing





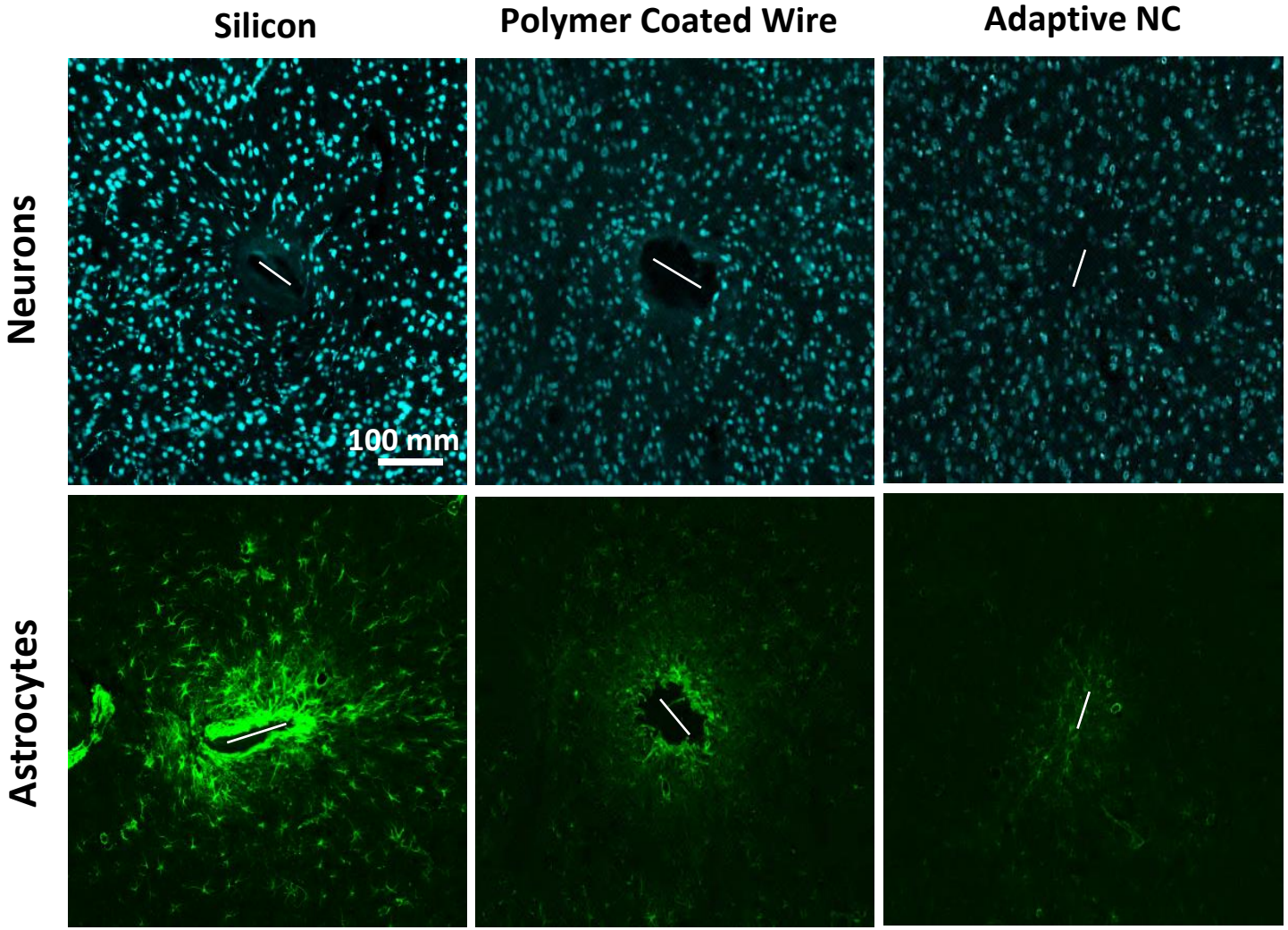




Mehdi Jorfi et al. ACS Applied Materials & Interfaces 2013 5 (4). 1517–1526

In Vivo Neuroinflammatory Response

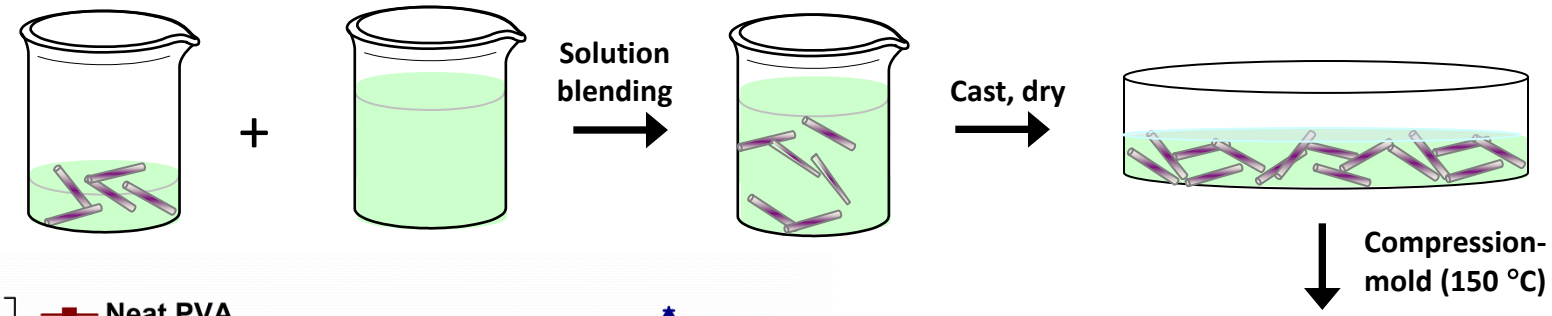
16 Week end point

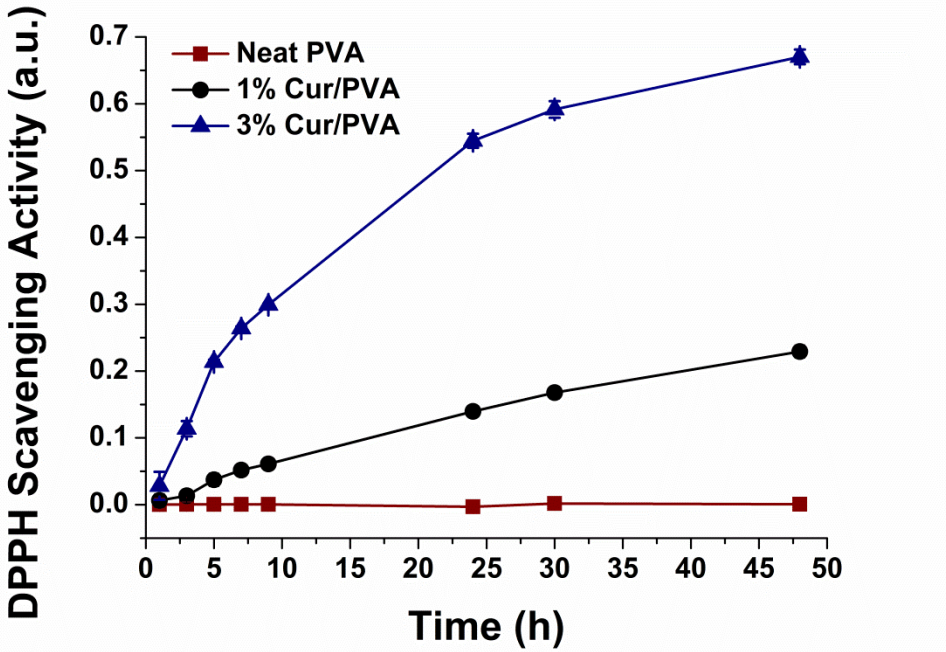


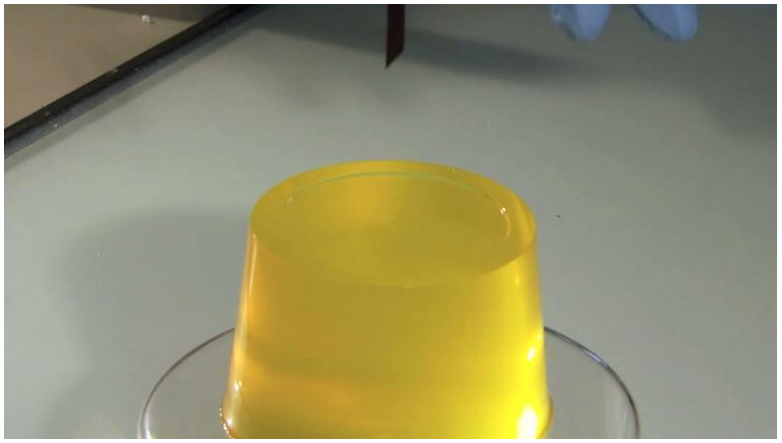
Mehdi Jorfi et al. ACS Applied Materials & Interfaces 2013 5 (4). 1517–1526

Drug Releasing, Mechanically Adaptive NCs

With t-CNCs and Curcumin or Resveratrol







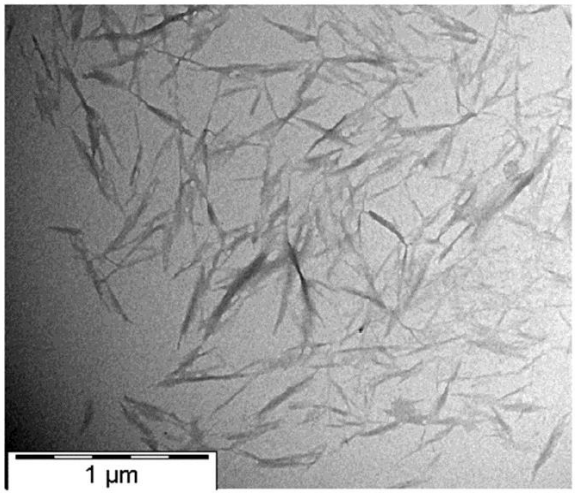
Supress acute inflammation by incorporation of anti-inflammatory drugs

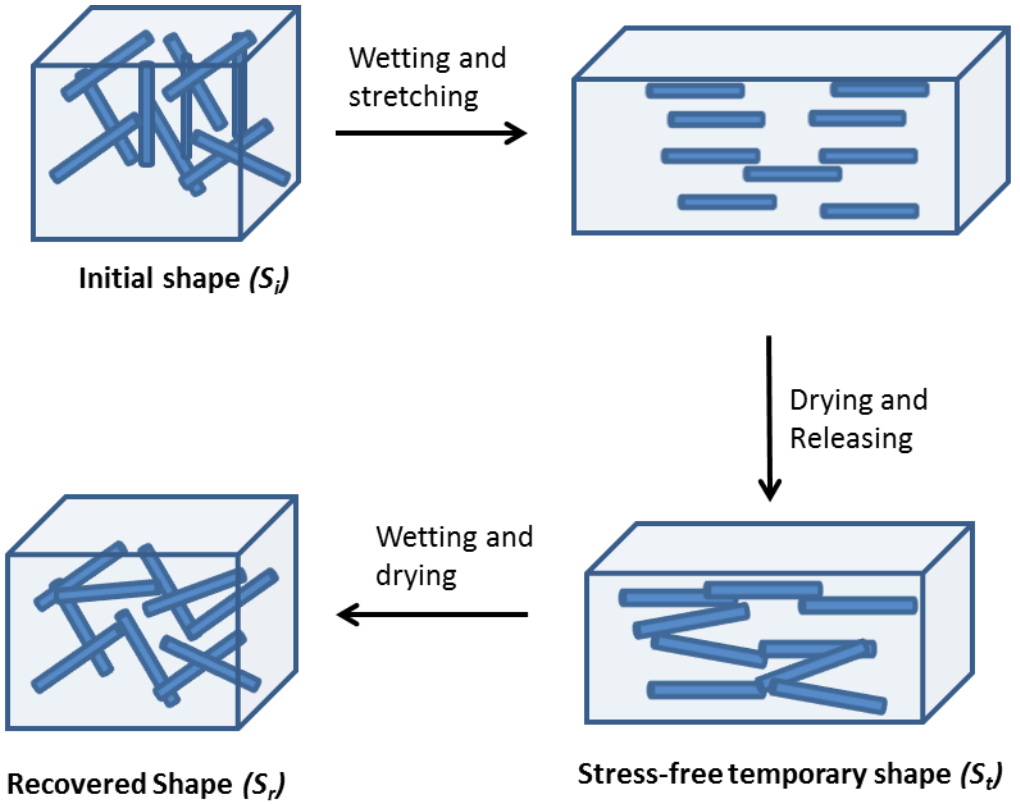
Jorfi, Potter, Householder, Foster, Weder, Capadona *Acta Biomaterialia. Accepted*

Water-Activated Shape-Memory Nanocomposites

Water Shape Memory Effect

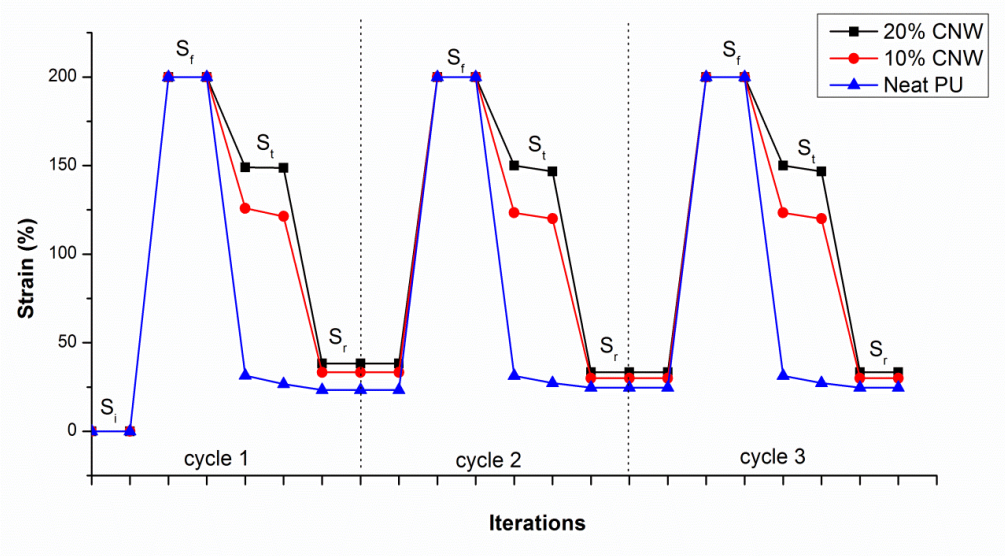
- Water disrupts hydrogen bonded percolating network
- Lower tensile strength upon wetting
- Temporary shape maintained by reestablished network
- Re-wetting allows return to original shape (with hysteresis)





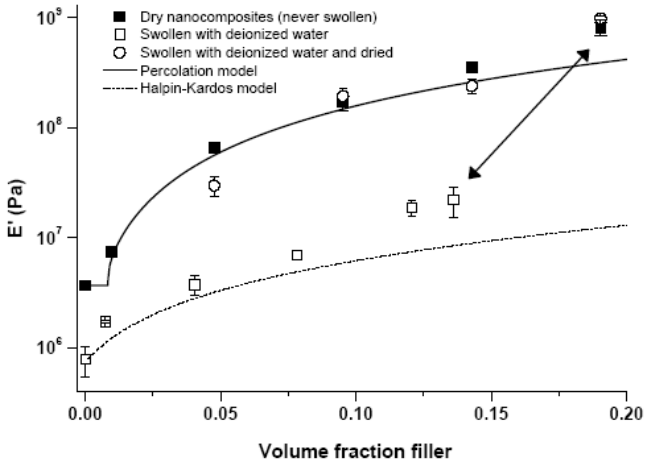
Bioinspired Mechanically Adaptive Polymer Nanocomposites with Water-Activated Shape-Memory Effect. Macromolecules 2011, 44, (17), 6827-6835.

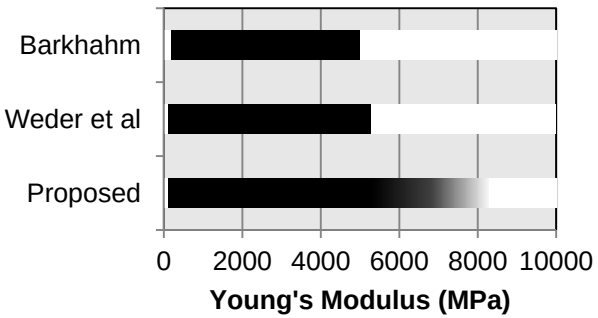
Water-Activated Shape-Memory Nanocomposites



Mechanically Adaptive Injection Needles

- Need to significantly increase the initial stiffness of mechanically adaptive materials; switching contrast must be lower; brittleness must be reduced
- Maximize whisker content; maximize whisker-matrix interactions; explore uniaxially oriented mechanically adaptive nanocomposite with anisotropic mechanical properties
- Mechanically adaptive nanocomposite needle with high initial stiffness



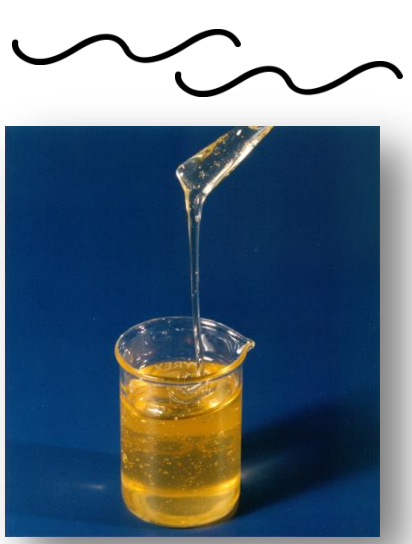


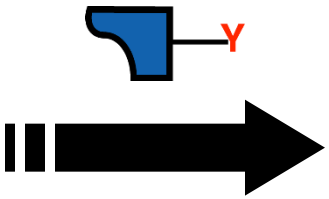
Mehdi Jorfi; E. Johan Foster et al. ACS Applied Materials & Interfaces 2013 5 (4). 1517–1526

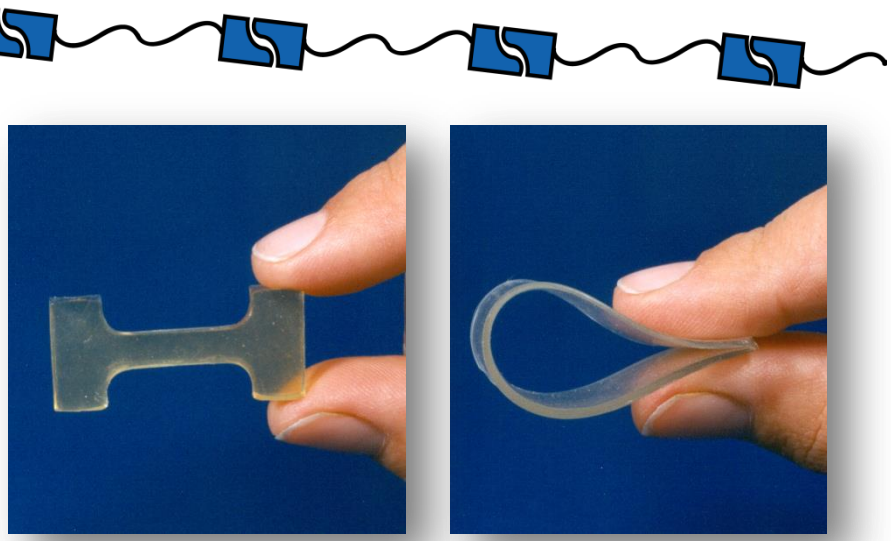
Polymer nanocomposite having switchable mechanical properties. European Patent Application Filed 2012. Patent/Application Number 61/700,995

Medical injection device. European Patent Application Filed 2012. Patent/Application Number 61/701,000

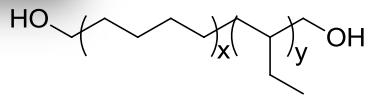
Supramolecular Functionality





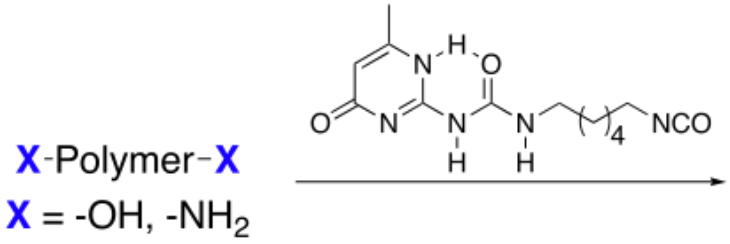


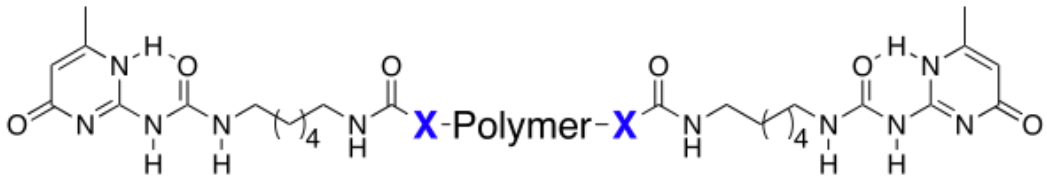
Kraton (Shell)



end-functionalized polymer

Synthesis of a simple synthon out of commercially available unit:

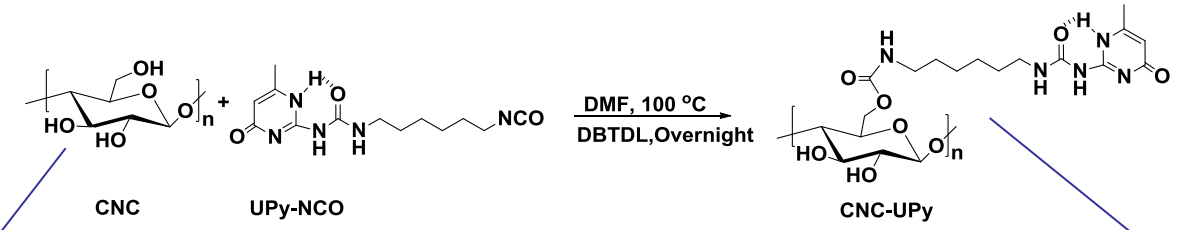


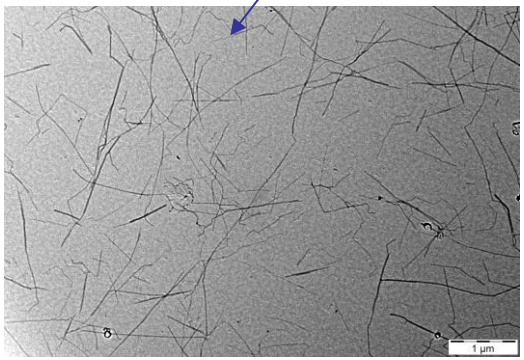


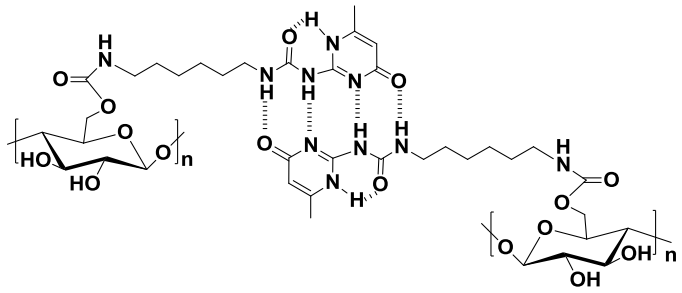
Makes a nice material, but it is soft!

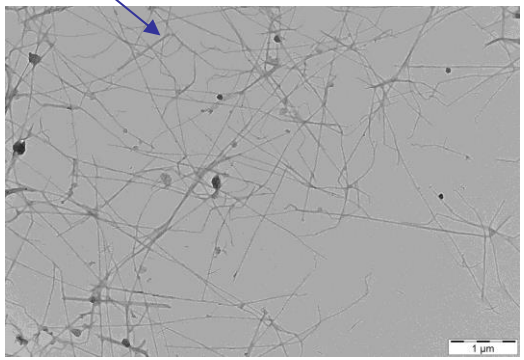
R.P. Sijbesma et. al.

Supramolecular Photoactive Cellulose Nanocrystals









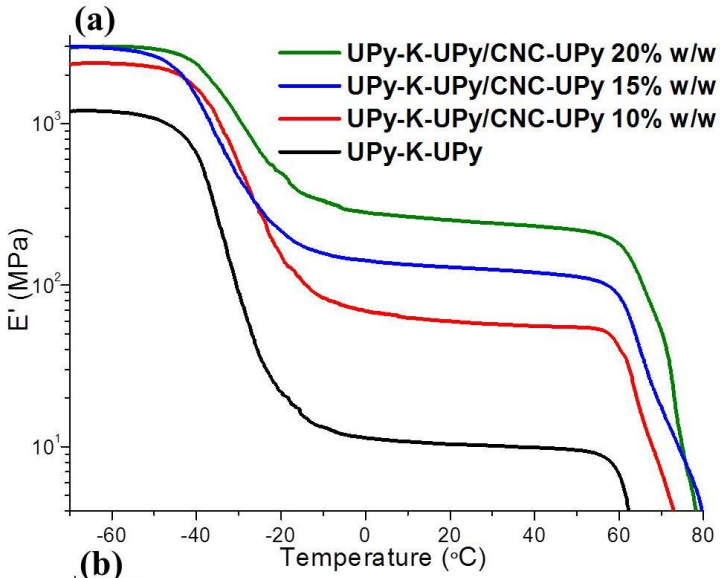
Neat CNC | UPy-CNC

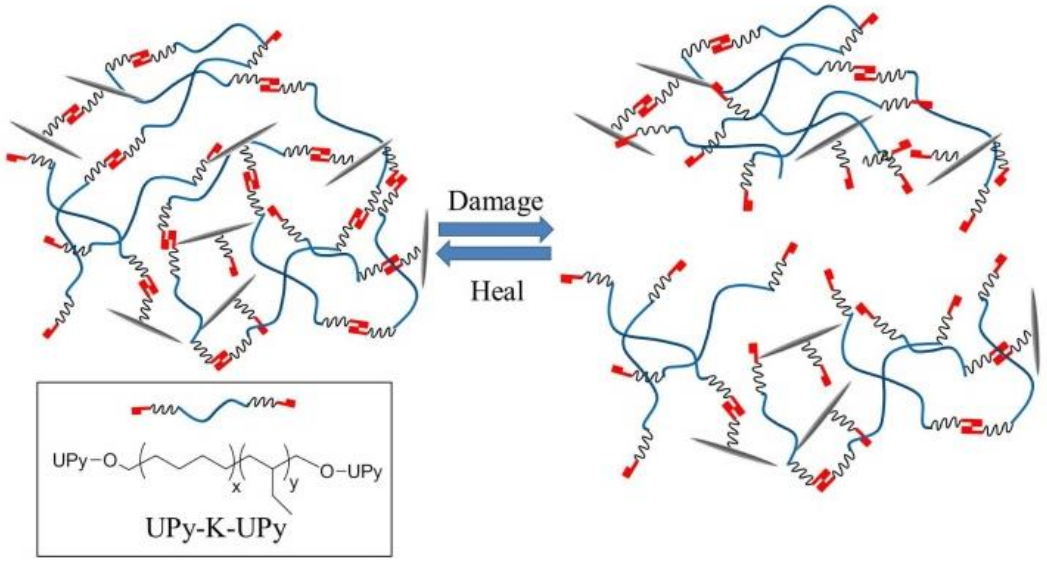
Neat CNC | UPy-CNC

- Modification of polymers (PVAc, kraton, PEG), to look at matrix-filler interactions
- Exploiting light (non-diffusive) to change hydrogen bonding character within the nanocomposite
- Using heat and chemical (eg. acid) for 'slow' diffusive mechanical change

Light-Healable Supramolecular Nanocomposites Based on Modified Cellulose Nanocrystals. ACS Macro Letters 2013 2(3) pp 236–240

A `Better` Supramolecular System



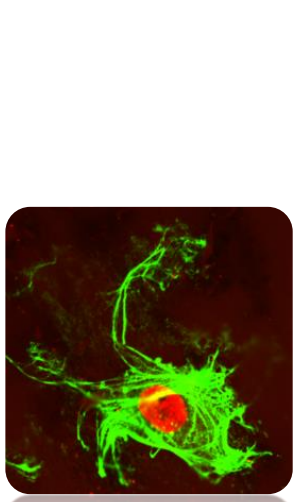


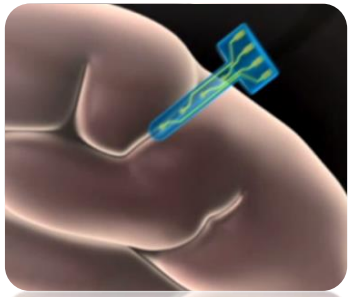
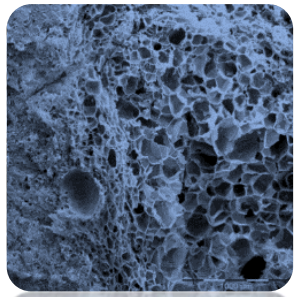
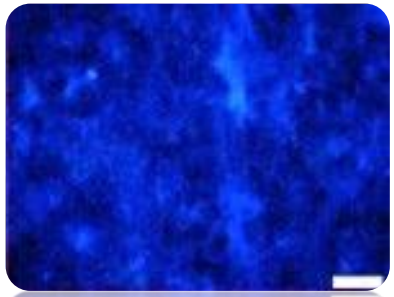
Most Cited Article in ACS Macro Letters in 2013

Light-Healable Supramolecular Nanocomposites Based on Modified Cellulose Nanocrystals. ACS Macro Letters 2013 2(3) pp 236–240

General Conclusions

- **Smart design can provide the next generation of materials. Moderating non-covalent and covalent interactions between small molecules, particles, telechelic building blocks, or combinations thereof by external stimuli, is a powerful and simple approach to create useful new materials with adaptive properties**
- **CNC provide a fantastic opportunity to reinforce and add smart aspects to polymeric systems**
- **Synthetic protocols have been developed to process a wide variety of smart and 'dumb' materials for a variety of potential medical and industrial applications**



Acknowledgements

Current Group Members

- **Mahesh Biyani (IN)**
- **Mehdi Jorfi (IR)**
- **Tobias Kuhnt (DE)**
- **Silvana Mueller (CH)**
- **Sandra Camarero Espinosa (ES)**
- Bastien Schyrr (CH)
- **Janak Sapkota (NP)**
- Apiradee (May) Nicharat (TH)
- Jens Natterodt (DE)
- Anuja Shirole (IN)
- Jeremie Loup (CH)

Past Group Members

- Odin Achorn (US)
- Christian Heinzmann (DE)
- David Thevenaz (CH)
- Marcus Forand (US)
- **Dr. Pratheep Annamalai (IN)**
- **Dr. Sandeep Kumar (IN)**
- Agueda Sonseca Olalla (ES)
- Ainara Saralegui Otamendi (ES)
- **Dr. Matthew Roberts (US)**

Collaborators (some of them at least)

- Stephen Eichhorn, Exeter, UK
- Stuart Rowan, CWRU, US
- Robert Moon, Purdue U, US
- Jeffrey Capadona, VA Med, US
- Jeffrey Gilman, NIST, US
- Pitt Supaphol, Chulalongkorn U. TH
- Martin Clift and Barbara Rothen, AMI, CH
- Bettina Steinmann, 3D Systems, CH & US
- Andreas Greiner, U. Marburg, DE
- Helmut Coelfen, U. Konstanz, DE
- Jin Montclare - Polytech Inst. New York, US
- Erik Berda, UNH, US
- Marco Giacinti Baschetti, U Bologna, IT
- Brett Helms, Molecular Foundry, US
- Julien Bras, Grenoble, FR
- Dylan Boday, IBM, US

Réseau nanotechnologies
Nanotechnologie Netzwerk

Firmenich

FNSNF
Fonds national suisse
Schweizerischer Nationalfonds
Fondo nazionale svizzero
Swiss National Science Foundation

FINANCÉ PAR ANR

FRESENIUS KABI

3D SYSTEMS