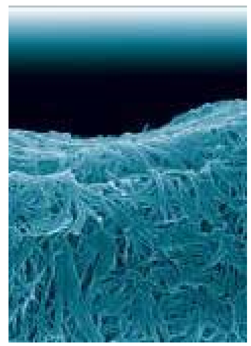
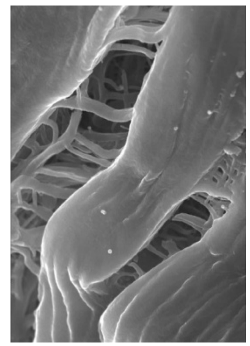
Mechanically Adaptive Polymer Nanocomposites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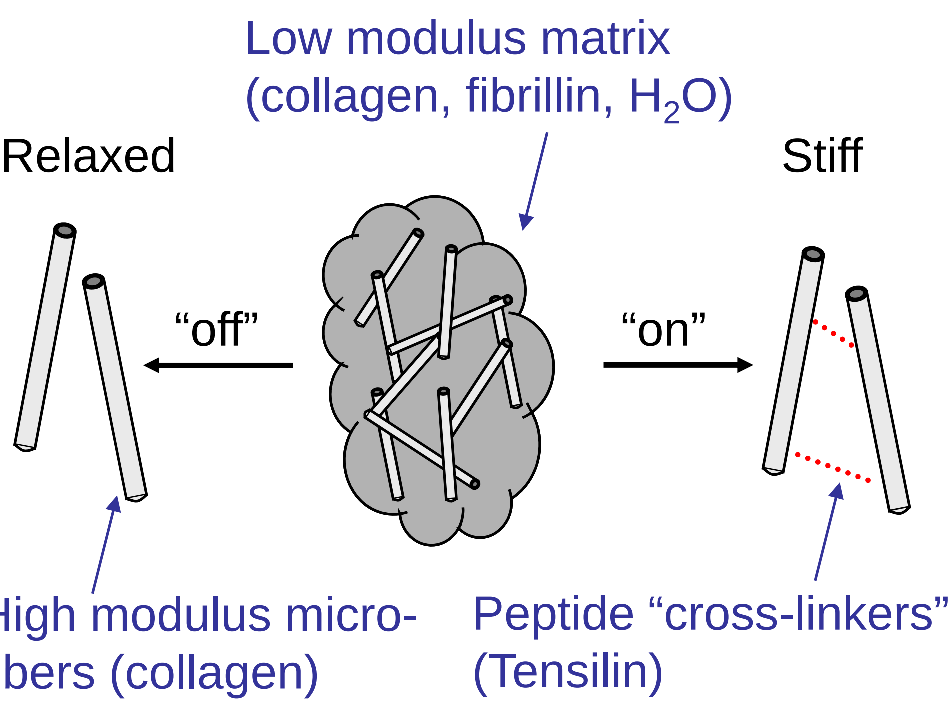
AM Foundation

Biomimetic Adaptive Materials

Deep dermis features mutable mechanical properties:

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



Switching through secretion of stiffening proteins (tensilin)

Effect is reversed through proteinases

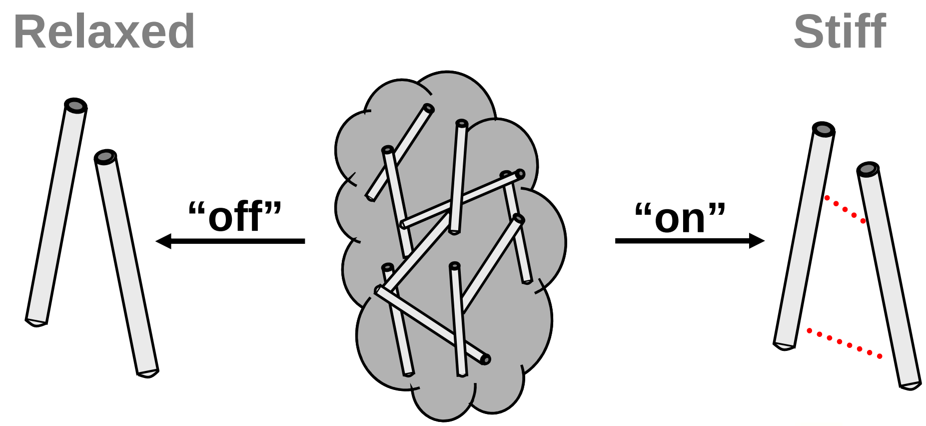
Can we create artificial materials that mimic design and response?

Szulgit, Shadwick *J. Exp. Biol.* **2000**. Trotter, Heuer et. *al. Biochem. Soc. Trans.* **2000**.
Weder, Rowan et al. *Science* **2008**, *319*, 1370.

Artificial Sea Cukes: Applications

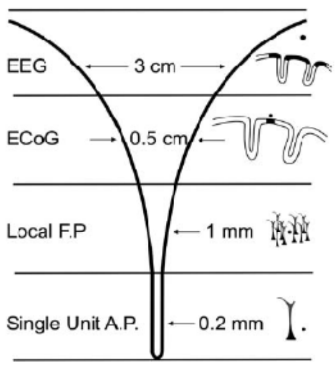
Stimuli

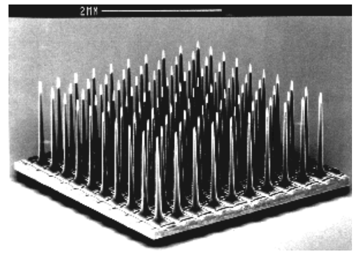
- Chemical
- Electrical
- Optical
- …



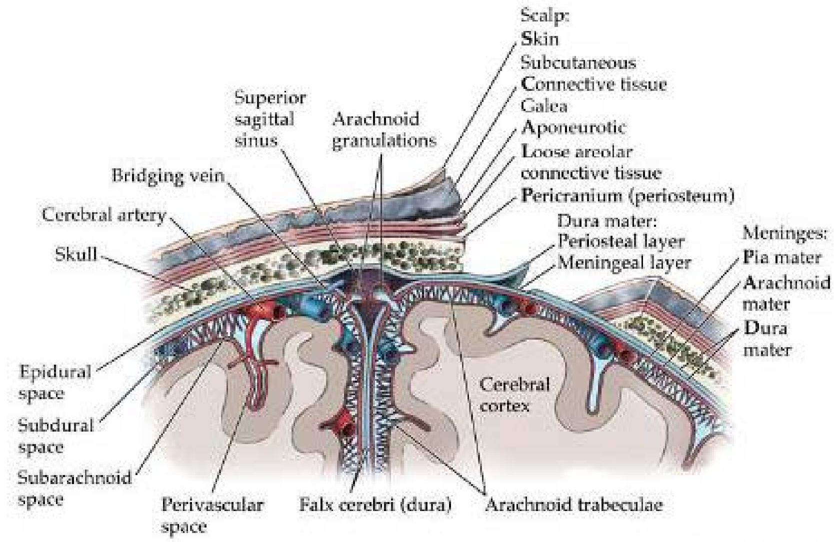
Applications

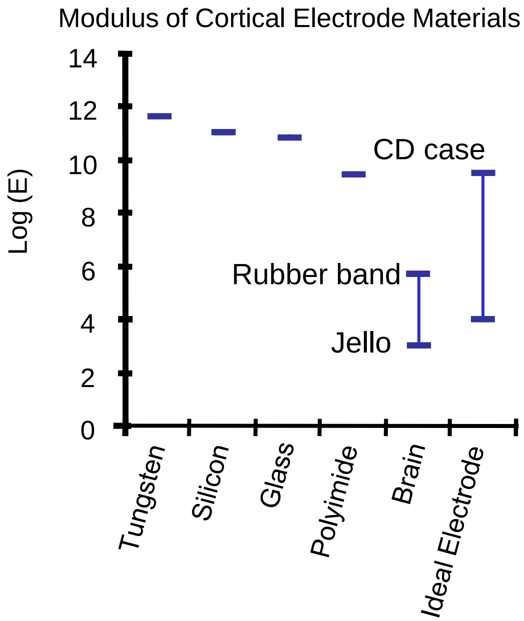
Cortical Interfacing





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





Lifetime of Probes / Tissue Response (Gliosis)

- Cellular Response to Implanted Material
- Mechanical Mismatch -> Leading Hypothesis for chronic failure
- 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

Ideal Adaptive Probe: Rigid for insertion, then soft
(Water responsive)

Improve the quality of life of patients that have sustained central nervous system disability:

Spinal cord injury, head trauma, stroke, Parkinson's disease...

Also: connect artificial organs (eye) to the brain

Kennedy et al. *IEEE Trans. Rehabil. Eng.* **2000**. Hochberg et al. *Nature* **2006**. Taylor et al. *Science* **2002**. Santhanam et. al. *Nature* **2006**. Nicolelis et al. Proc Natl Acad Sci USA, **2003**.

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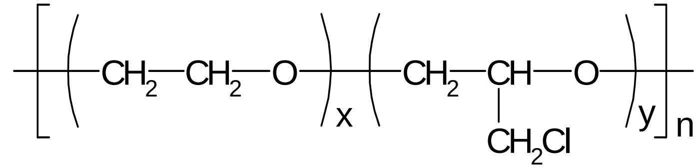
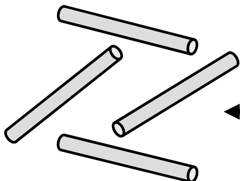
Reverse Engineering the Sea Cuke

Low modulus matrix (e.g. EO-EPI copolymer)

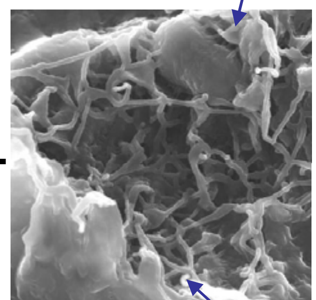


Young's Modulus *E*=0.3-3 MPa
Slightly water-swellable (25 % @ rt)
T_g = -37 ºC

Relaxed

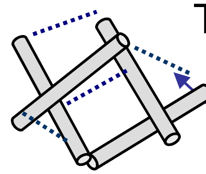


"off"



"on"

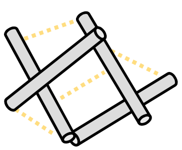
Stiff



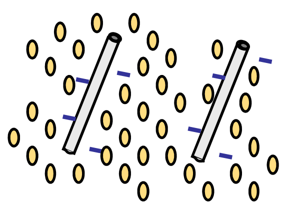
Turn off hydrogen bonding through competitive interactions with H_2O

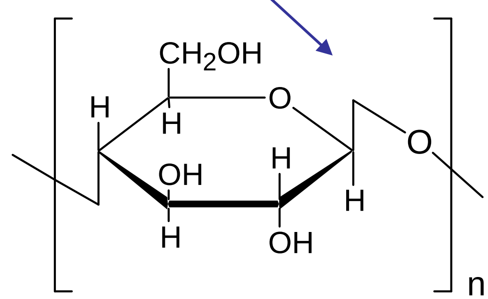
High-modulus nano-fibers (cellulose)

Cross-linking through hydrogen bonding



Turn off H-bonding

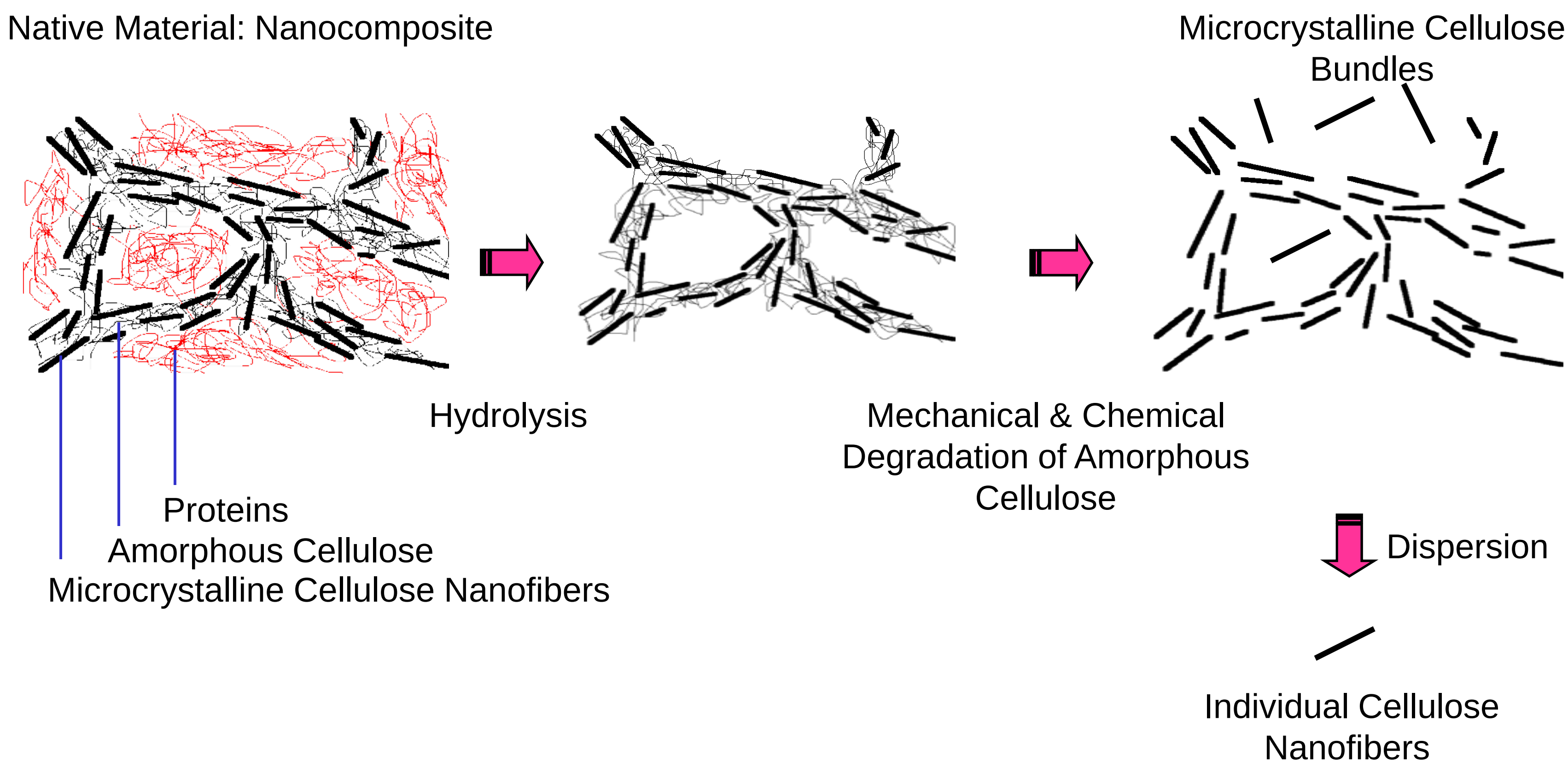




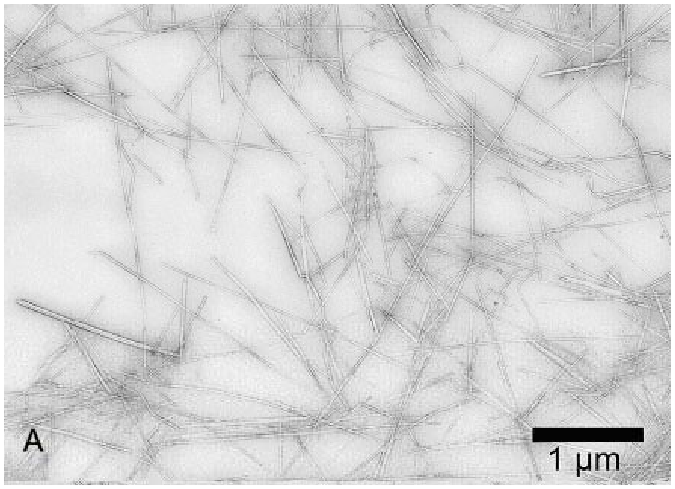
Capadona, van den Berg, Capadona, Rowan, Tyler, Weder *Nature Nanotech.* **2007**, *2*, 765.
Capadona, Shanmuganathan, Tyler, Rowan, Weder *Science* **2008**, *319*, 1370.
US Patent Applications filed.

Cellulose Nanofibers from Tunicates

Cellulose nanofibers ("whiskers") can be extracted from a variety of bio-sources including wood, cotton, wheat straw, animal tissue…

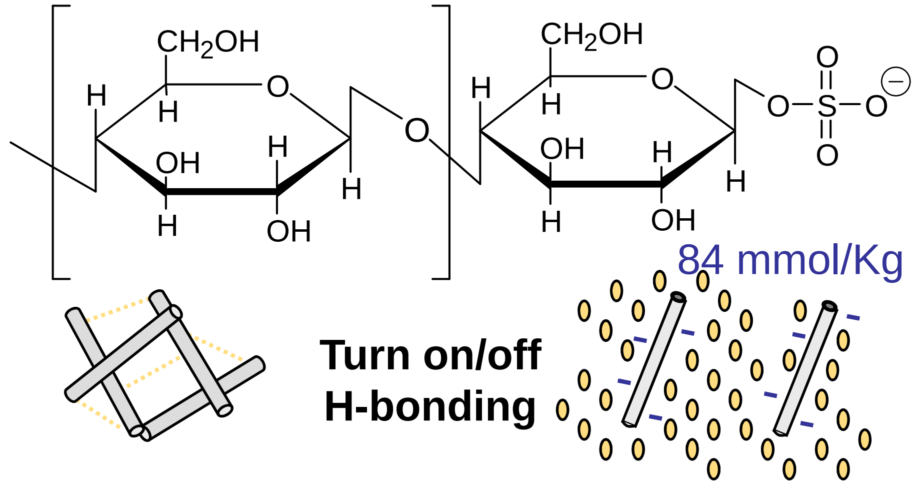


Properties of Tunicate Whiskers

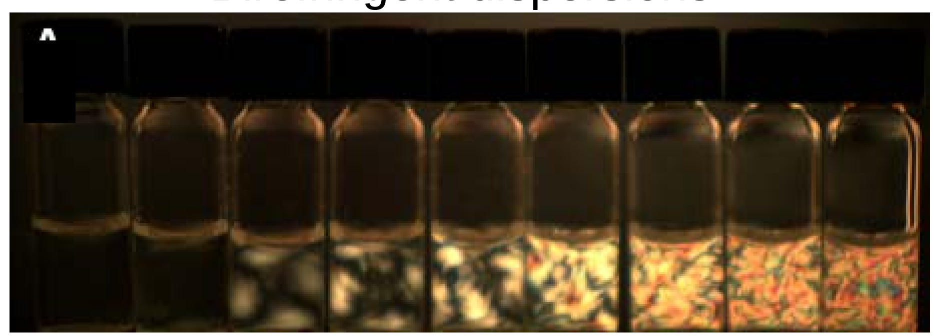


High aspect ratio (85)
l = 2.20 +/- 0.20 µm
d = 26.0 +/- 3.0 nm

High stiffness
Young's modulus ~120 – 150 GPa



Birefringent dispersions



0.1 0.5 1.0 2.0 3.0 4.0 5.0 6.0 7.0
mg/mL H_2O

Borsali *Macromol. Rapid Commun.* **2004**, *25*, 771. Eichhorn et al. *Biomacromolecules* **2005**, *6*, 1055. van den Berg, Capadona, Weder *Biomacromolecules* **2007**, *8*, 1353.

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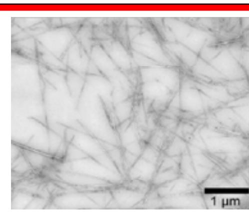
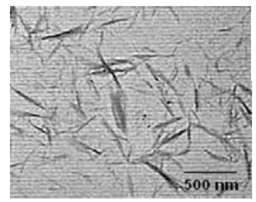
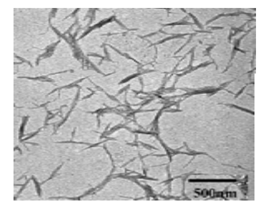
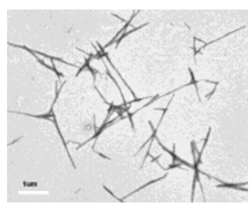
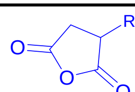
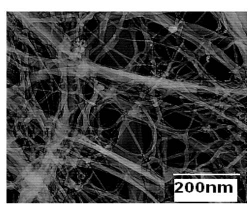
Other Whisker Types Employed

Source / Hydrolysis			
H_2SO_4 -OH $-SO_4^-$			
HCl -OH			
HCl, then ox. COOH -OH		Source • **Dimensions (length)** • **Availability** Isolation • **Surface Chemistry**	
H_2SO_4,  -O-alkyl $-SO_4^-$		*Biomacromolecules* **2007**, *8*, 1353. *Biomacromolecules* **2009**, *10*, 712.	

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Processing from 'New' Solvents

TWs can be 'conserved' by lyophilization

New solvents broaden processing options and range of accessible nanocomposites

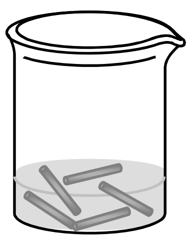
0.8 % TW dispersion in H_2O

Freeze dry

TW aerogel

Re-disperse

0.8 % TW dispersion in H_2O



Dispersions of freeze-dried, re-dispersed TWs (5 mg/mL)

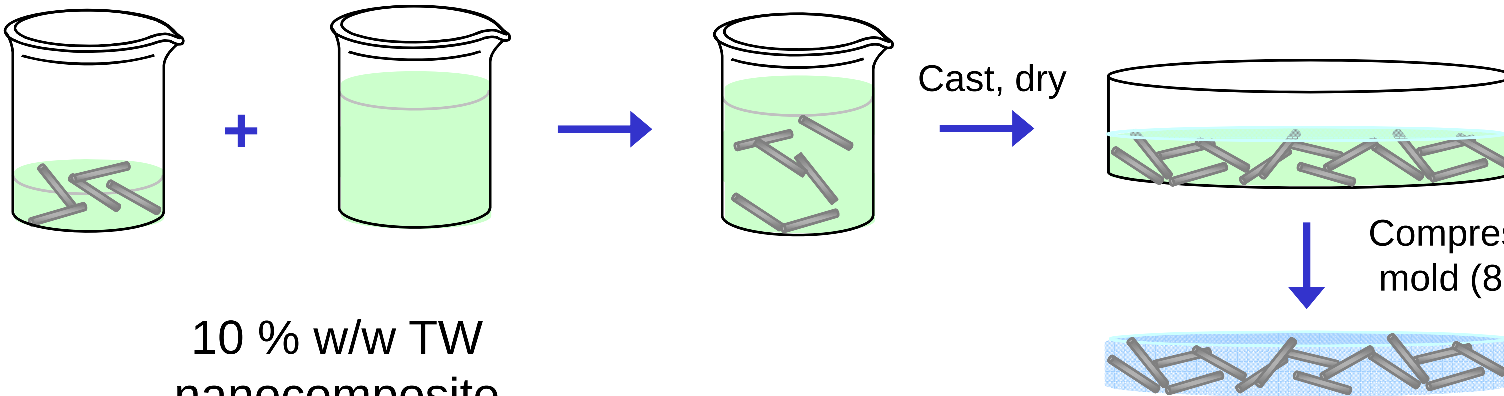
H_2O^* H_2O

*Not freeze-dried

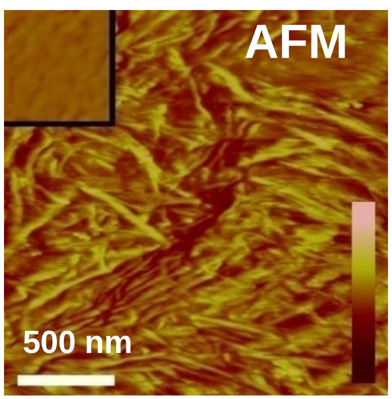
Turbak et al. US Patent 4378381 (**1983**). Dufresne et al. *Macromolecules* **2004**, *37*, 1386.
van den Berg, Capadona, Weder *Biomacromolecules* **2007**, *8*, 1353.
Gawryla, Schiraldi, Weder *J. Mater. Chem.* **2009**, *19*, 2118.

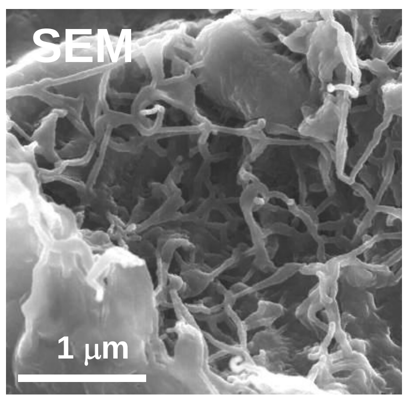
Processing from ‘New’ Solvents

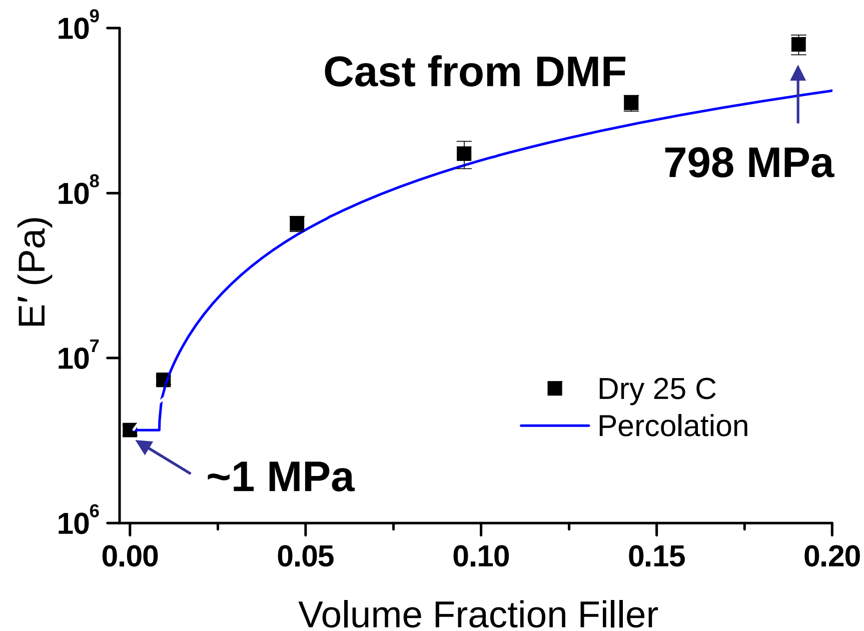
P(EO-EPI)/TW Nanocomposites by casting from a common solvent (DMF)



10 % w/w TW
nanocomposite







Data fit percolation model: strongly interacting 3-D nanofiber network

Capadona, Shanmuganathan, Tyler, Rowan, Weder *Science* **2008**, *319*, 1370.

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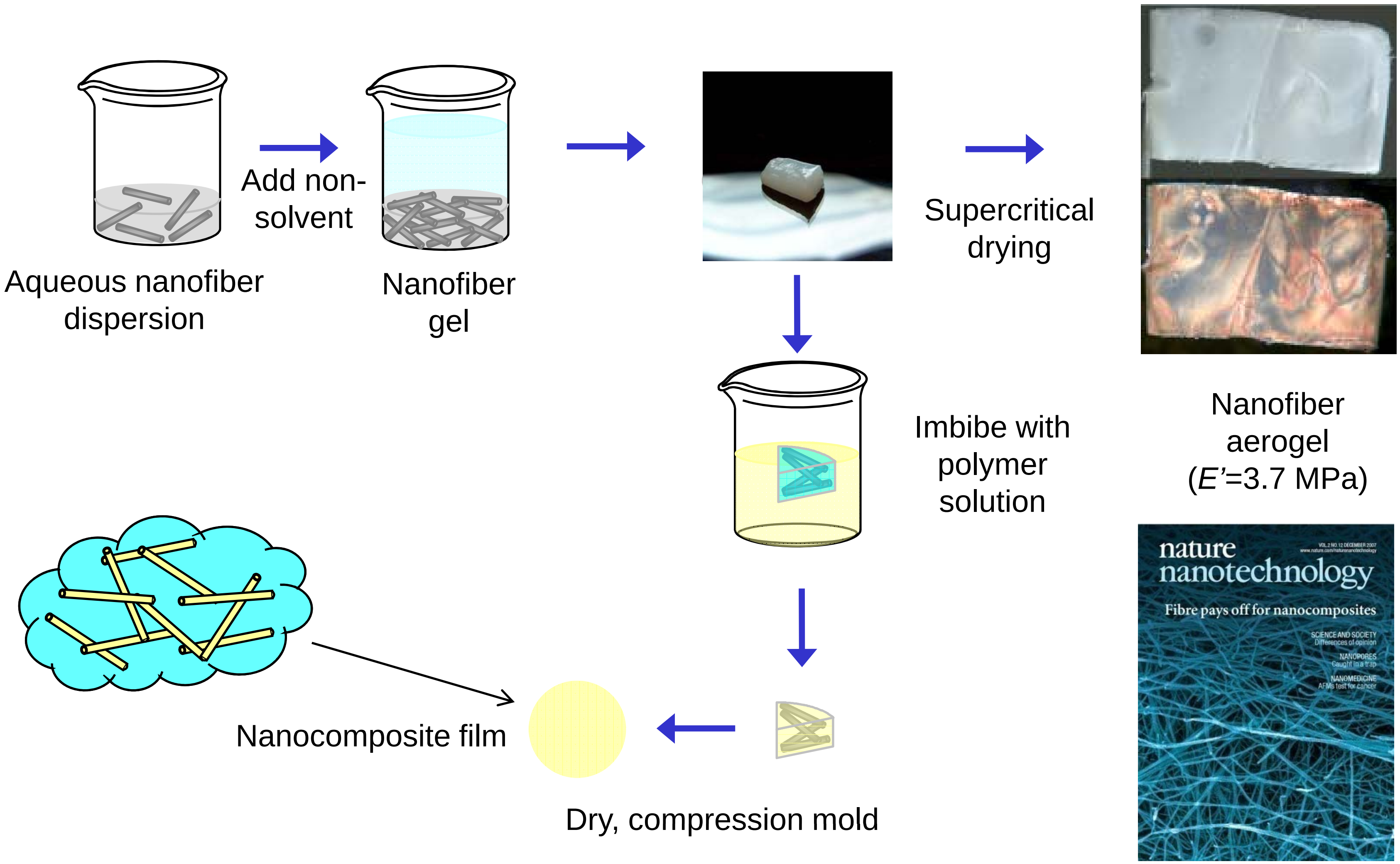
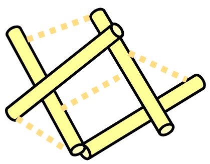
Processing with Template Approach



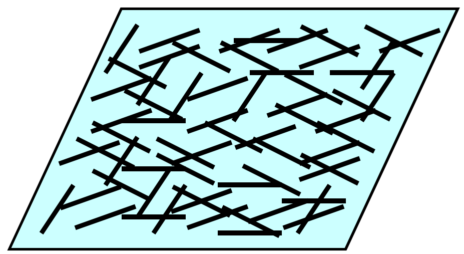
Capadona, van den Berg, Rowan, Tyler, Weder *Nature Nanotech.* **2007**, *2*, 765.
US Patent Application filed.

Models for Mechanical Properties

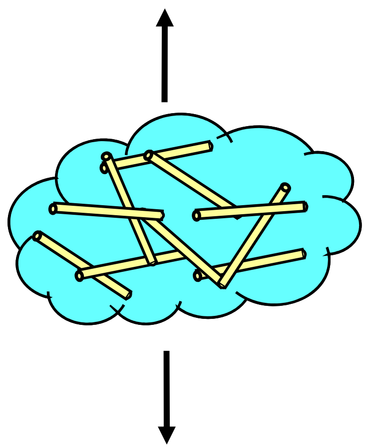
Percolation model



"percolation on"

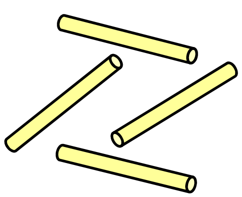


"complete interconnected network of fillers within the matrix"

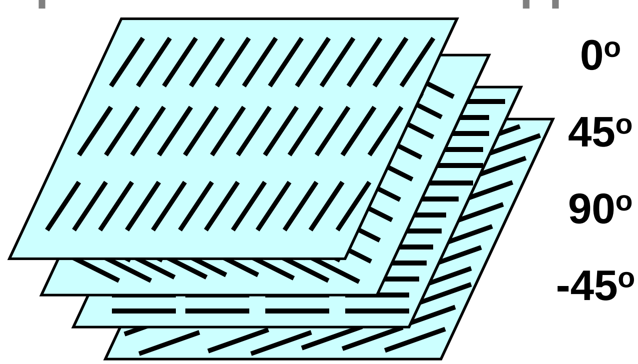


Takayanagi et al. J. Polym. Sci. **1964**, C5, 113. Ouali et al. *J. Plast. Rubber Comp. Process. Appl.* 1991, *16*, 55. Halpin, Kardos *J. Appl. Phys.* **1972**, *43*, 2235. Hajji et al. *Polym. Comp.* **1996**, *17*, 612. *Polymer Eng. Sci.* **1997**, *37*, 1732.

Halpin-Kardos / Halpin-Tsai: Mean field approach



"mean field / percolation off"



"fibers are smeared into the matrix to form a homogeneous continuum"

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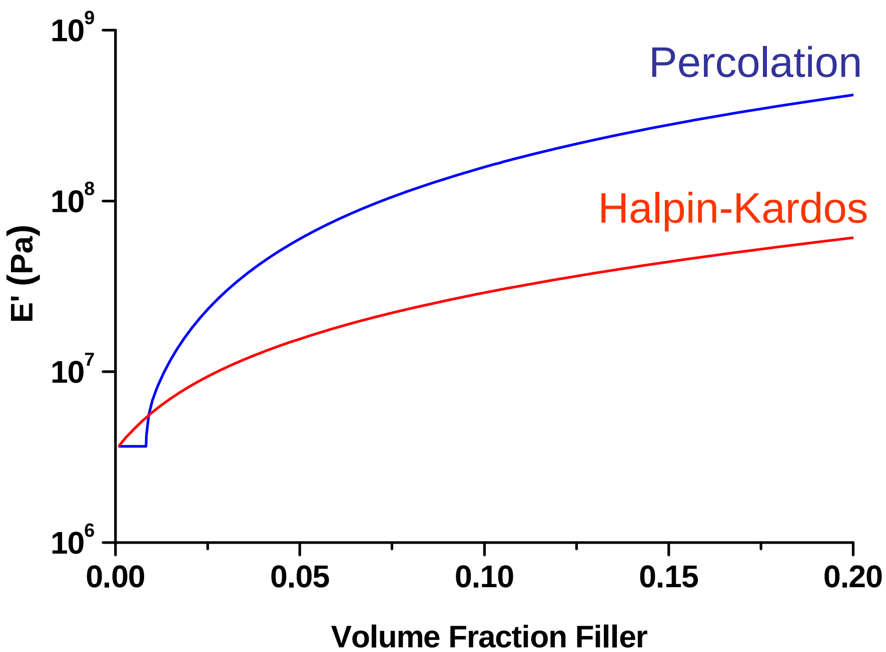
Models for Mechanical Properties



$$E' = \frac{(1 - 2\psi X_r)E_s E_r + (1 - X_r)\,\psi E_r^2}{(1 - X_r)E_r + (X_r - \psi)E_s}$$

$$\psi = X_r \left(\frac{X_r - X_c}{1 - X_c}\right)^{0.4}$$

All components can be experimentally determined:

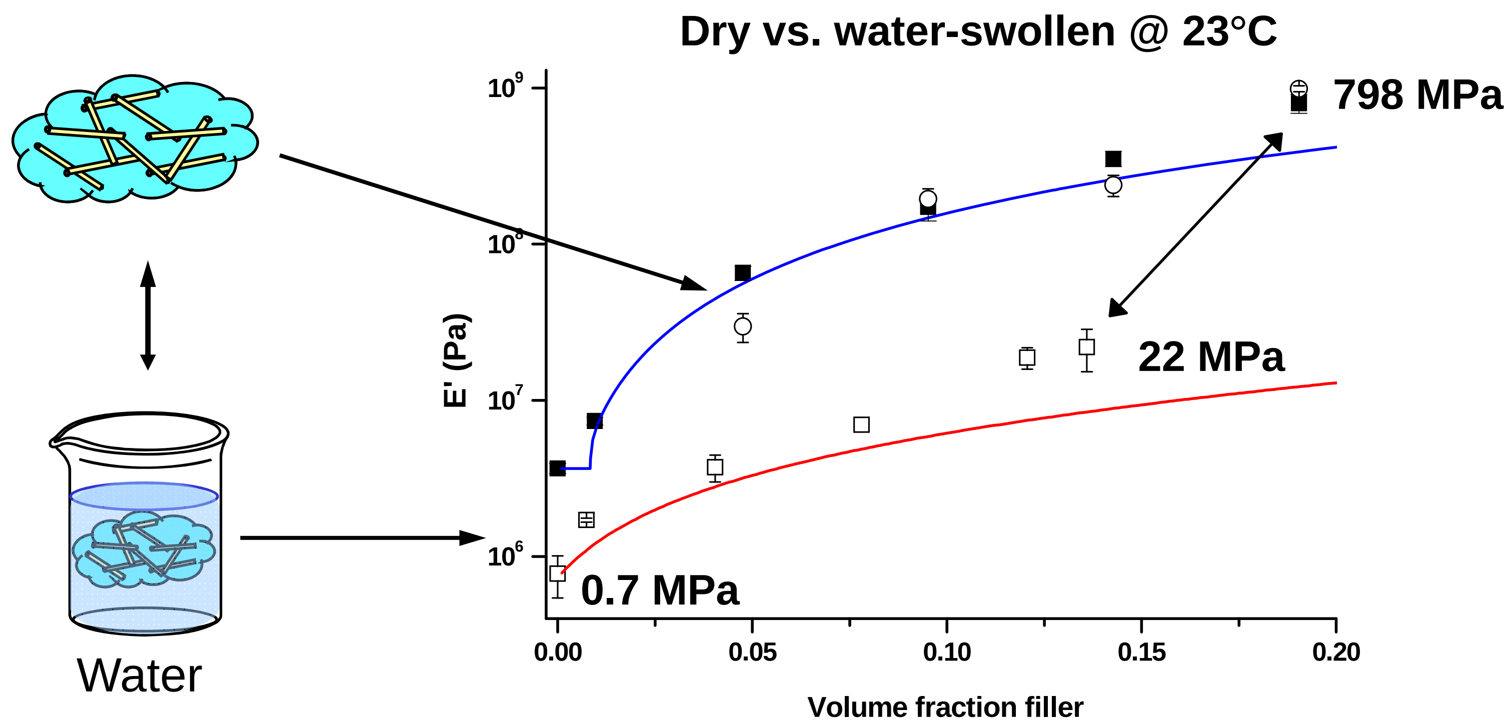
E' = Tensile storage modulus of composite
E'_s = Tensile storage modulus of soft phase
E'_r = Tensile modulus rigid phase (3.9 GPa)
X_r = volume fraction of rigid phase
X_c = critical volume fraction f. percolation
X_c = 0.7/*f*, *f* = aspect ratio *L*/*d* = 84

E' = 2*G'*(*n* + 1), *n* = Poisson's ratio = 0.3
G' = Shear storage modulus of composite

Tensile storage modulus *E'* of nanocomposite strongly depends on nanofiber concentration and connectivity between nanofibers

Takayanagi et al. *J. Polym. Sci.* **1964**, *C5*, 113.
Haji et al. *Polym. Comp.* **1996**, *17*, 612.

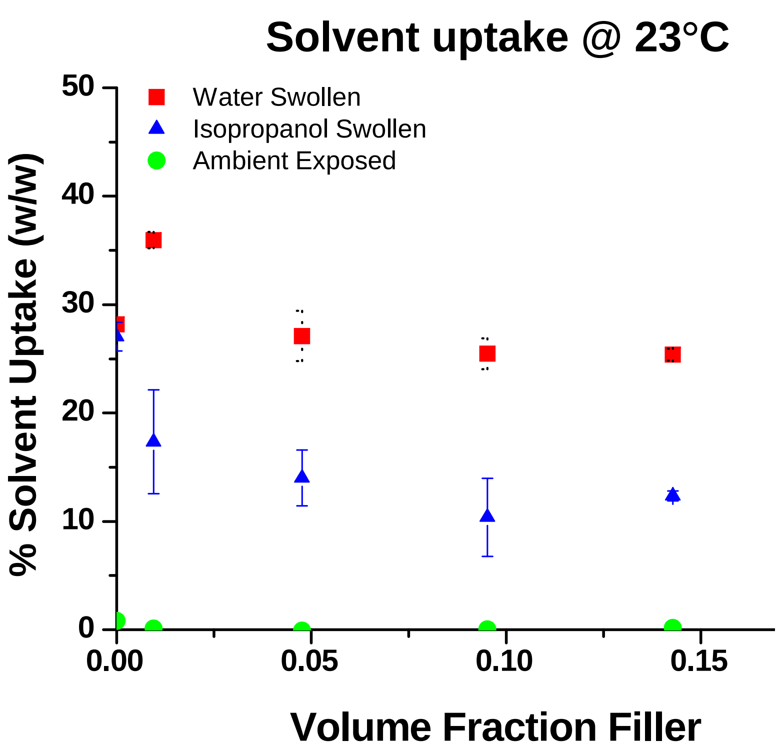
Chemo-Mechanical Response of P(EO-EPI)/TW Nanocomposites

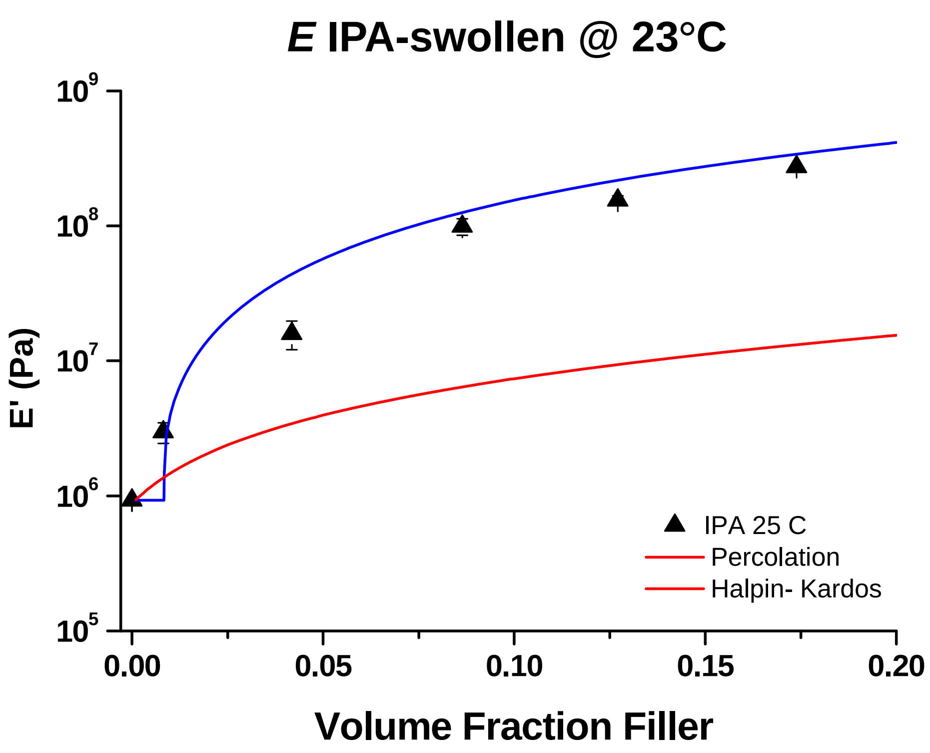


- Stiffness decreases dramatically (40x) upon swelling with water or ACSF
- "On" moduli match Percolation Model, "Off" moduli approach Halpin-Kardos Model, Effect is fully reversible (supports proposed mechanism)
- Materials do mimic structure and properties of sea cucumber dermis

Capadona, Shanmuganathan, Tyler, Rowan, Weder *Science* **2008**, *319*, 1370.

Chemo-Mechanical Response of P(EO-EPI)/TW Nanocomposites

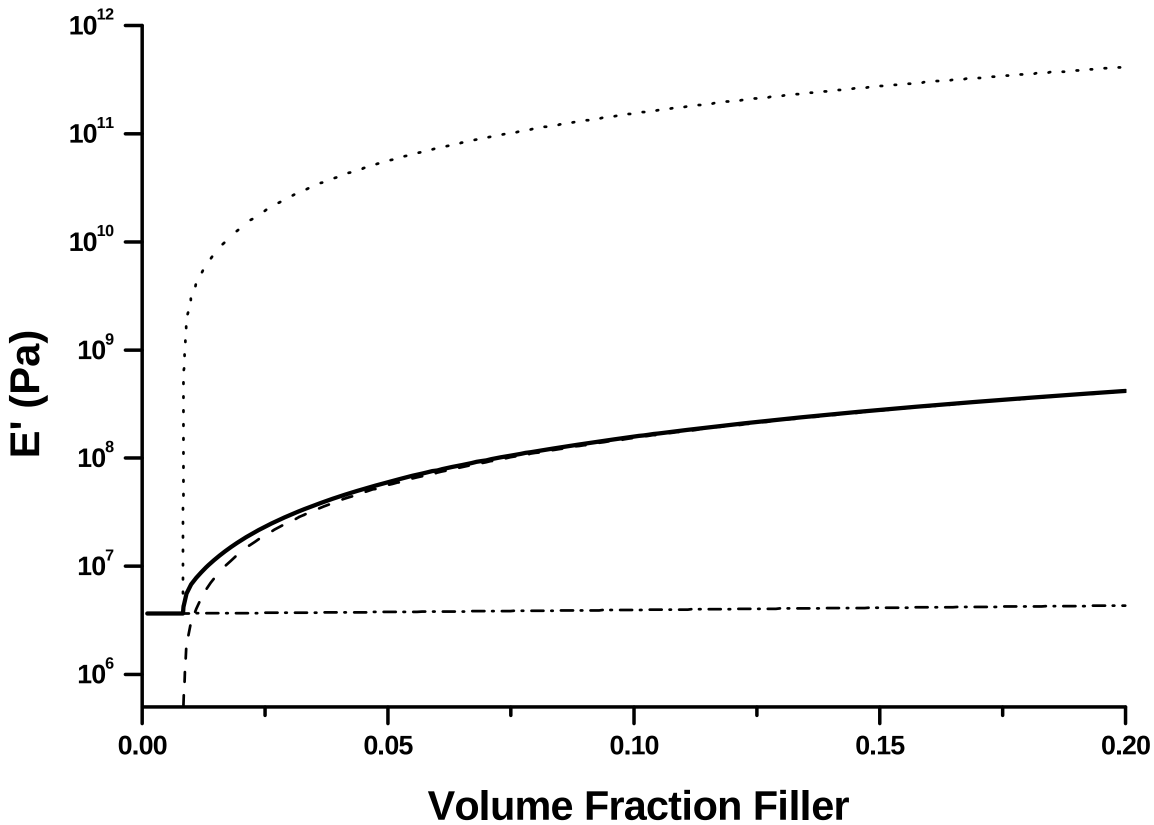




Modest swelling in H_2O (~26%) and isopropanol (14%)

No switching upon swelling with IPA (does not disperse whiskers)
-> Demonstrates selectivity

Chemo-Mechanical Response of P(EO-EPI)/TW Nanocomposites



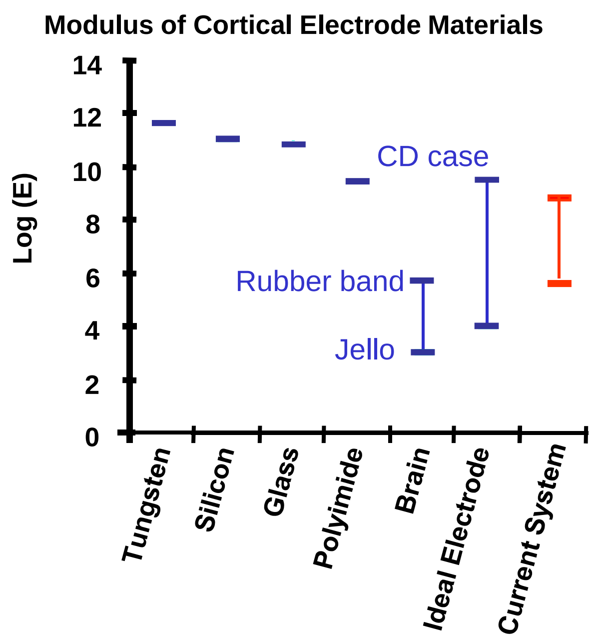
— Percolation model with data for vacuum-dried nanocomposites

--- Percolation model with $E'_s = 0$ (assuming 'total plasticization')

··· Percolation model with E'_r increased 1000-fold

-·· Percolation model with E'_r decreased 1000-fold

Properties of 1st Generation Materials

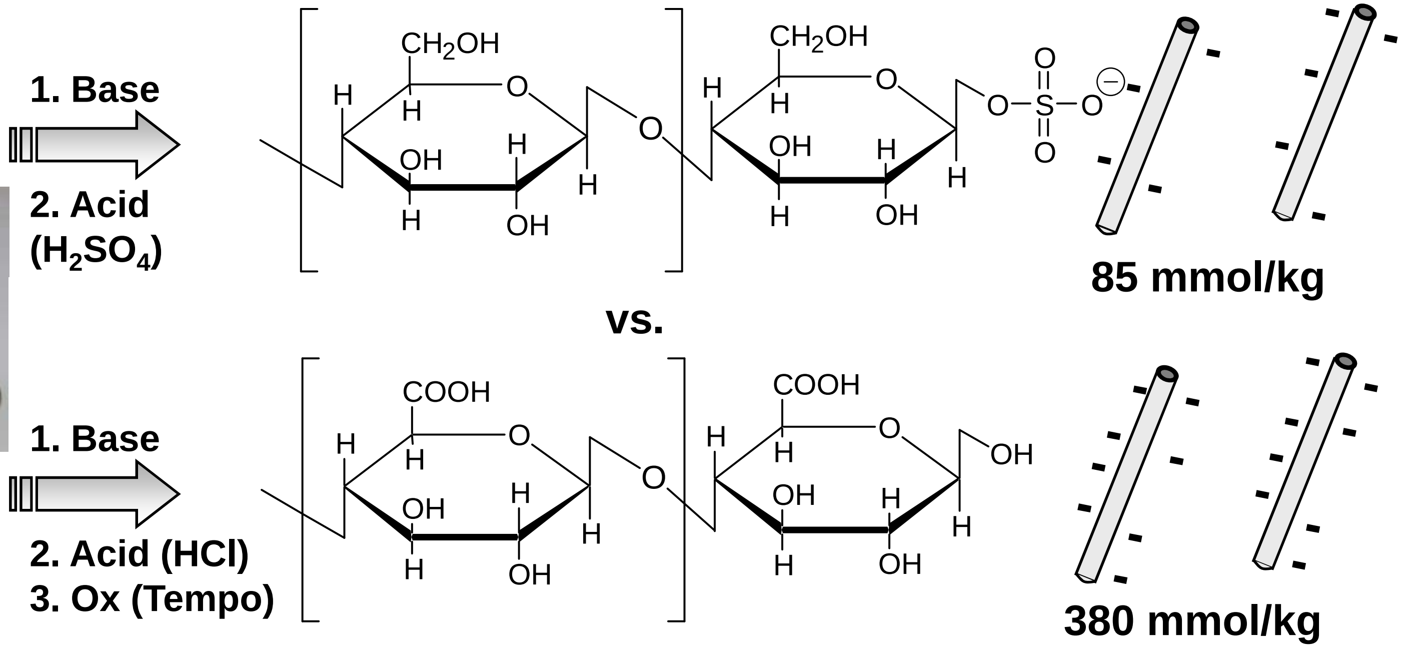


Overall goal: switching of 4-6 orders of magnitude; 5 GPa to < 1 MPa

Demonstrated: 2.5 orders of magnitude; 800 MPa to 22 Mpa

Need to further increase mechanical contrast

Soften the "Off" State



Soften "off" state through higher charge density on the whiskers

Capadona, Shanmuganathan, Rowan, Weder *unpublished*.

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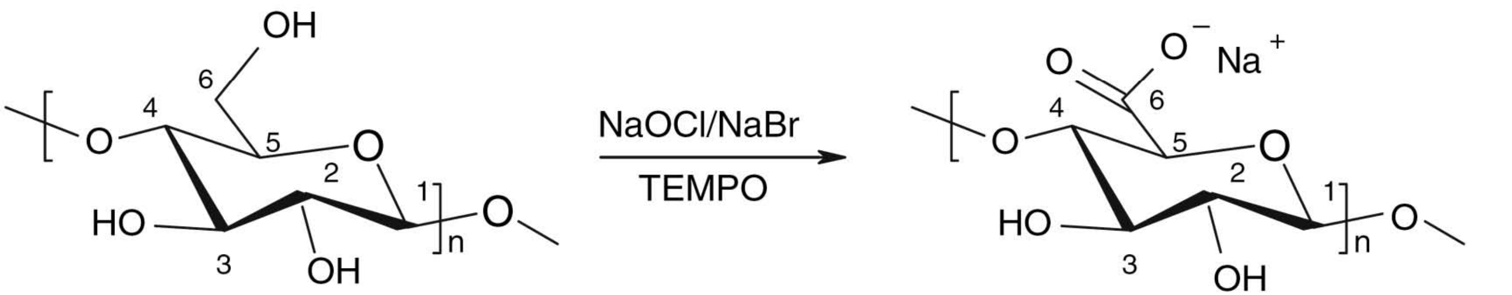
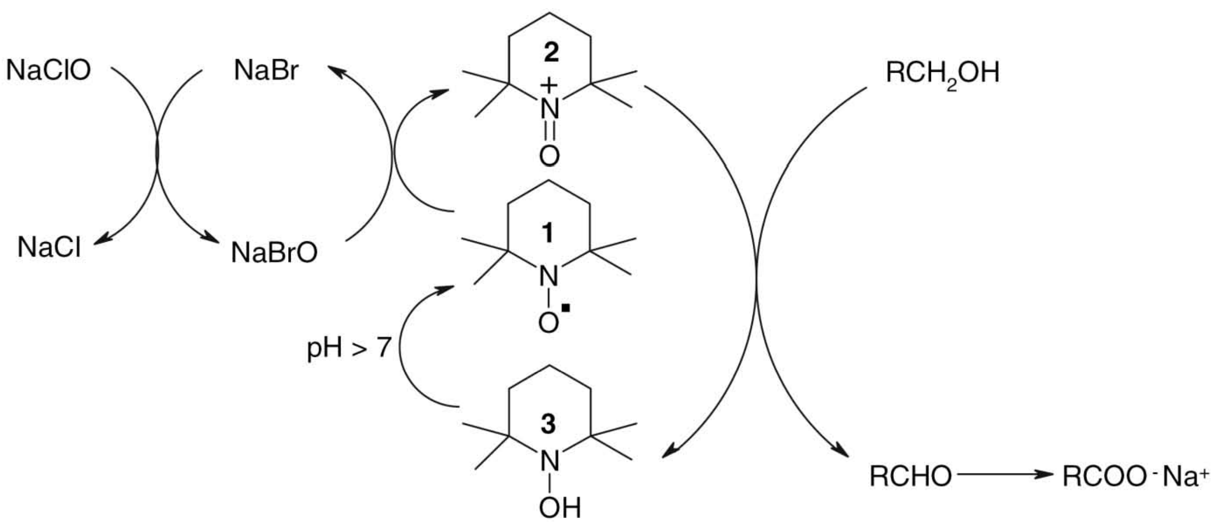
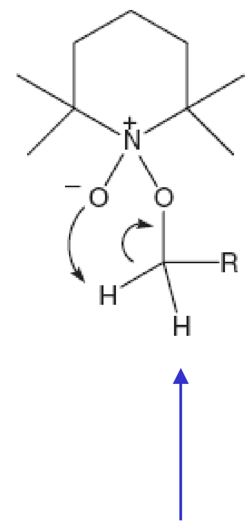
Soften the “Off” State

TEMPO-mediated oxidation allows for selective carboxylation







TEMPO: 2,2,6,6-tetramethyl-l-piperidinyloxy

sterically confined cyclic elimination
prefers less hindered primary alcohols

De Nooy, Besemer, van Bekkum *Carbohydr. Res.* **1995**, *269*, 89.

Soften the "Off" State

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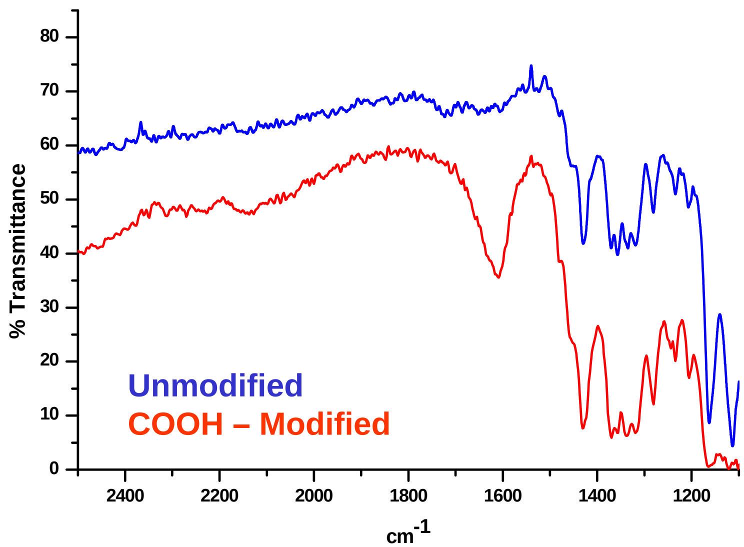
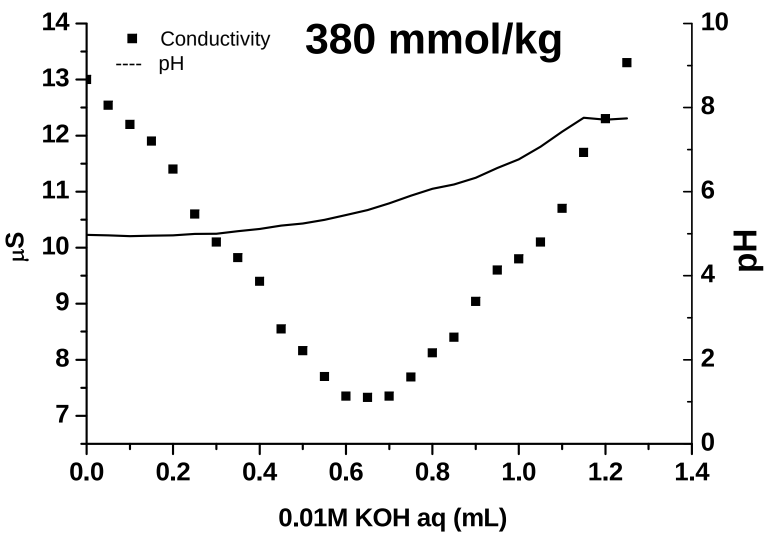
FTIR



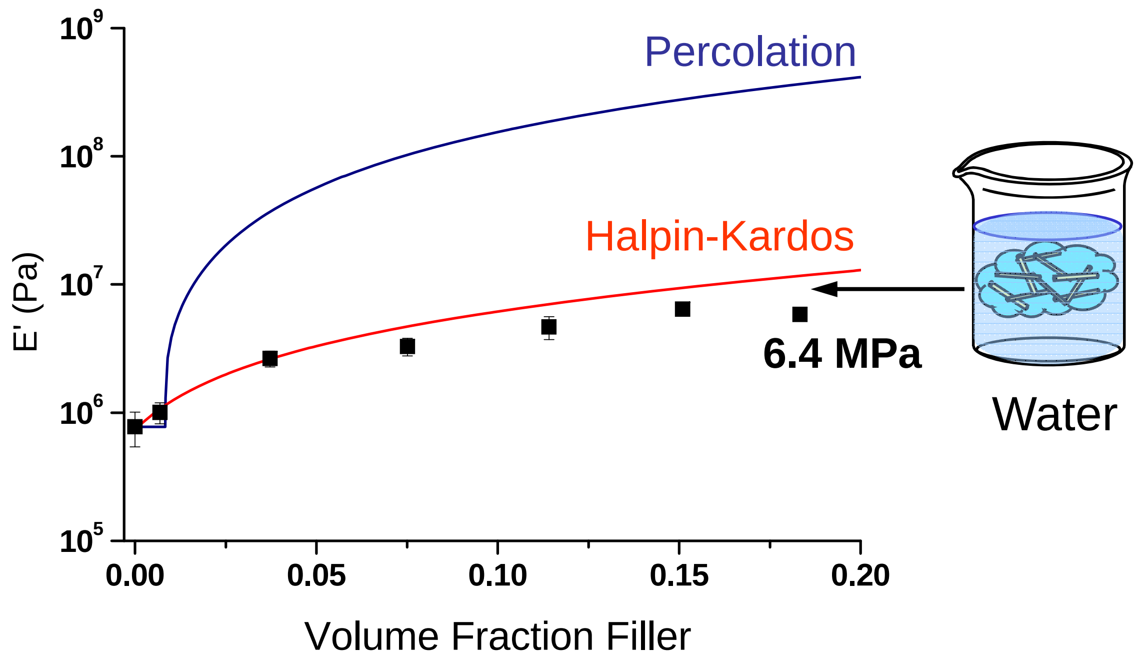
Carboxylate Density



Capadona, Shanmuganathan, Rowan, Weder *unpublished*.

Soften the “Off” State

Off-state modulus of P(EO-EPI)/carboxy-TW nanocomposites is lowered



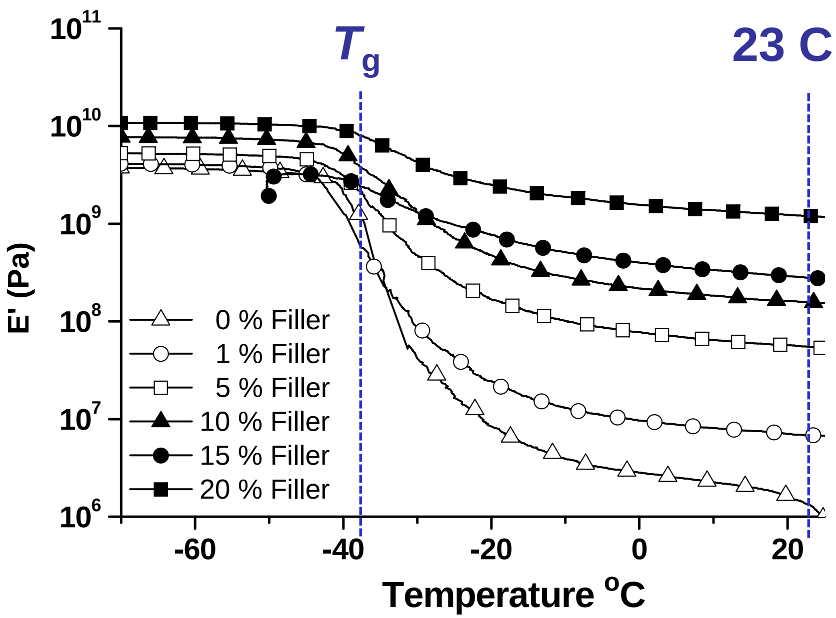
Soften “off” state through higher charge density on the whiskers

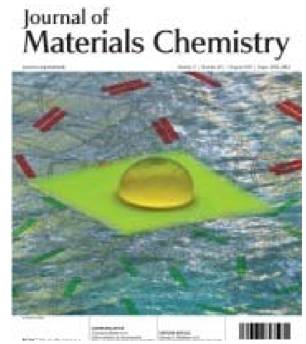
Data suggest complete dissociation of the whisker – whisker interactions

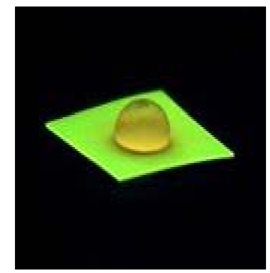
Capadona, Shanmuganathan, Rowan, Weder *unpublished*.

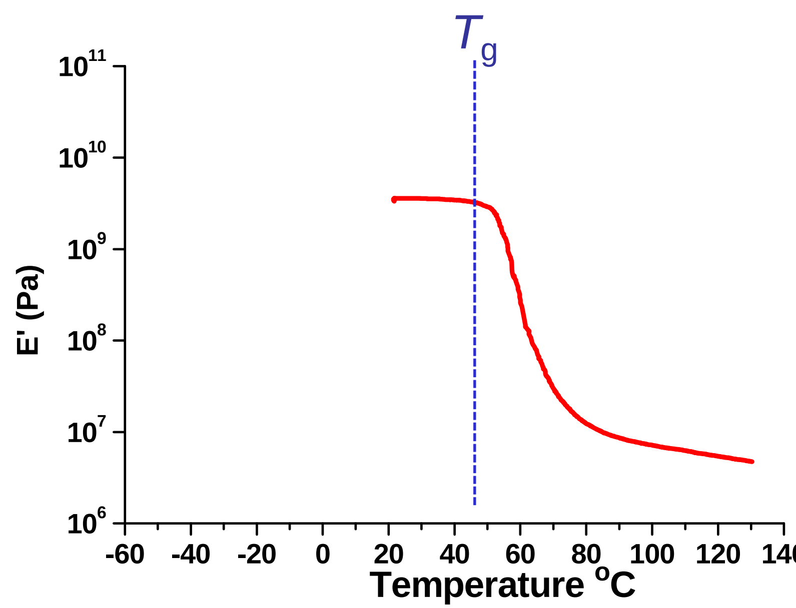
Stiffen the “On” State

DMTA traces of dry TW/P(EO-EPI) nanocomposites







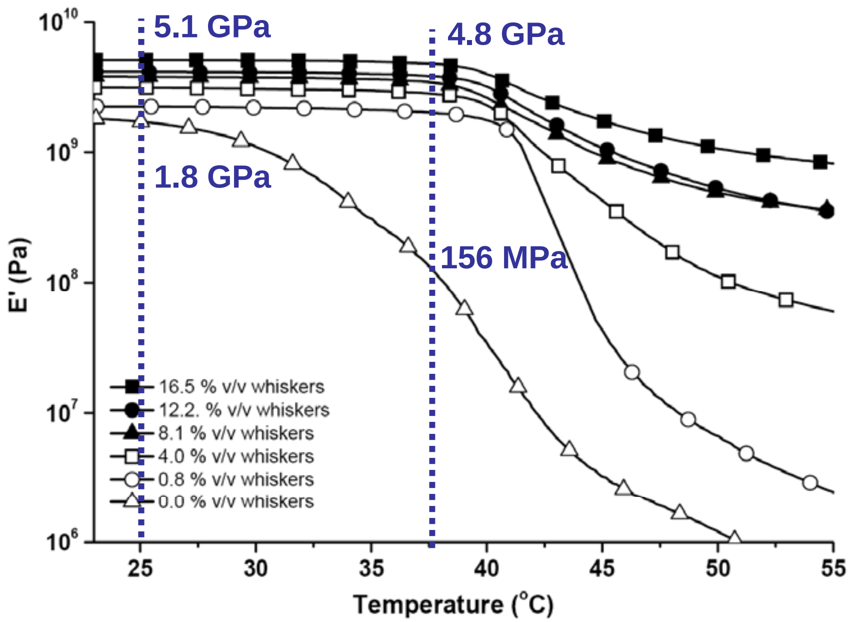


Exploit thermal transition!

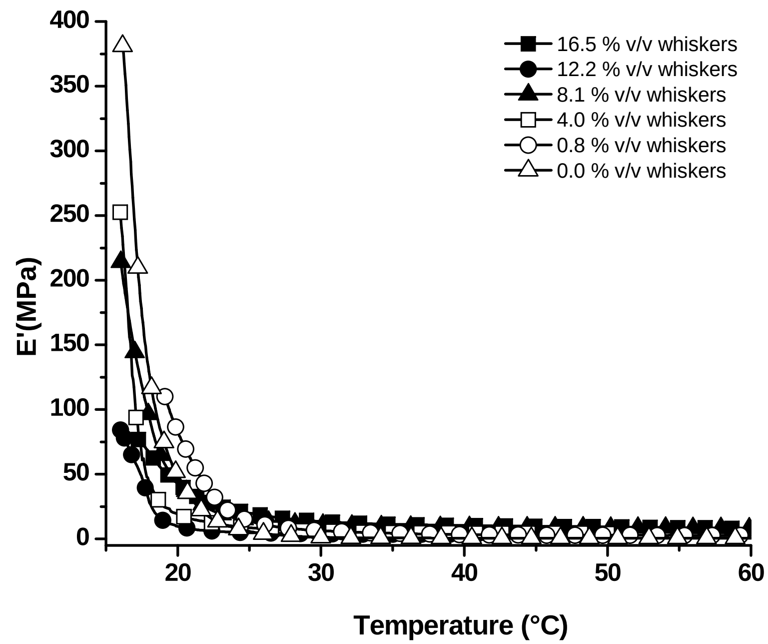
Weder et al. *US 7,223,988* (**2007**). *J. Mater. Chem.* **2007**, *17*, 2989. *Science* **2008**, *319*, 1370. *Progr. Polym. Sci.* **2009**, In Press.

TW/PVAc Nanocomposites

Dry Nanocomposites



ACSF Swollen Nanocomposites



Use PVAc as matrix: T_g ~42°C; minimal aqueous swelling (4.5%)

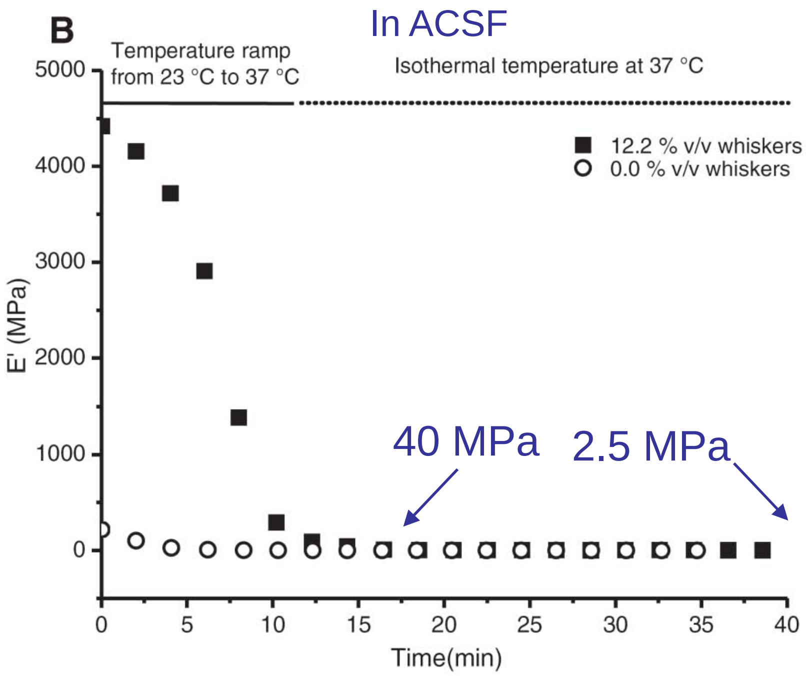
Softening temperature increases above physiological temperature

Exposure to water plasticizes nanocomposites, drops T_g and switches TW-TW interactions off: Rapid mechanical switching from GPa to MPa range

Capadona, Shanmuganathan, Tyler, Rowan, Weder *Science* **2008**, *319*, 1370.

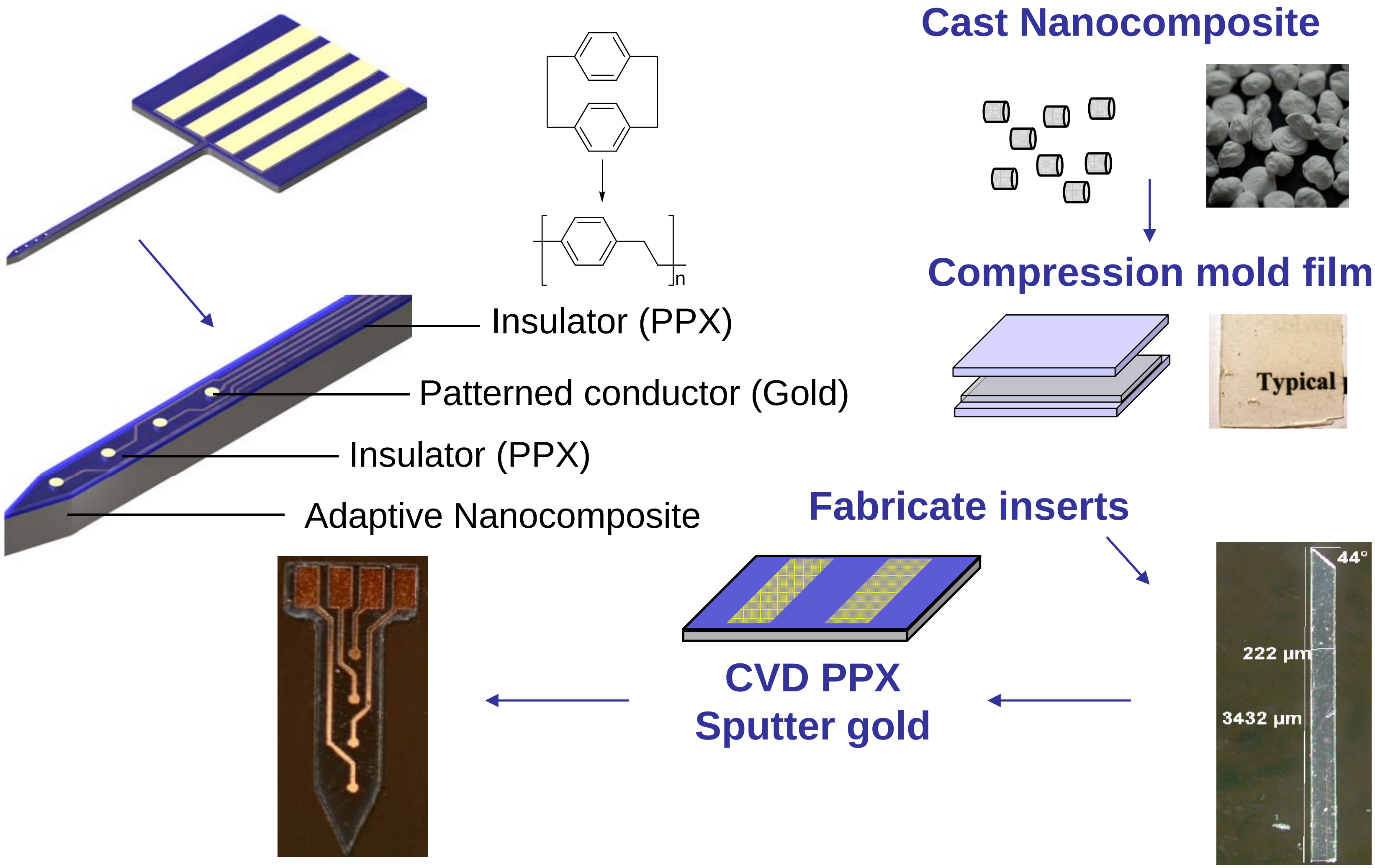
Switching Under Physiol. Cond.

Properties of 12 % v/v PVAc/TW Nanocomposites



Capadona, Shanmuganathan, Tyler, Rowan, Weder *Science* **2008**, *319*, 1370.
Shanmuganathan, Capadona, Rowan, Weder *Progr. Polym. Sci.* **2009**, *in press*.
Shanmuganathan, Capadona, Rowan, Weder *J. Mater. Chem.* **2009**, *in press*.

First Cortical Electrodes



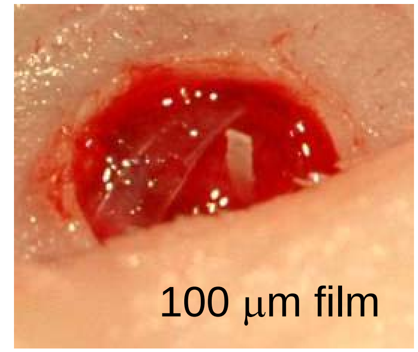
Hess, A.; Dunning, J.; Harris, J.; Capadona, J.R.; Shanmuganathan, K.; Rowan, S.; Weder, C.; Tyler, D.; Zorman, C.A. *IEEE Proceedings, Transducers* **2009**, in press.

Animal Model for Glia Scar Formation

Cut through soft tissue and expose skull

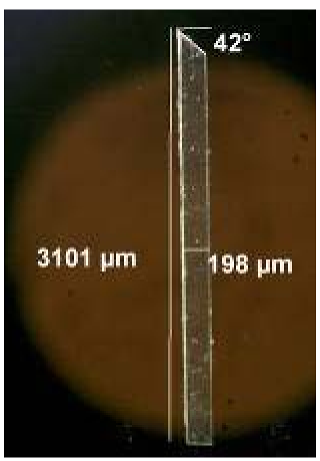
Drill through skull to expose cortical tissue

Insert probes into the cortical tissue

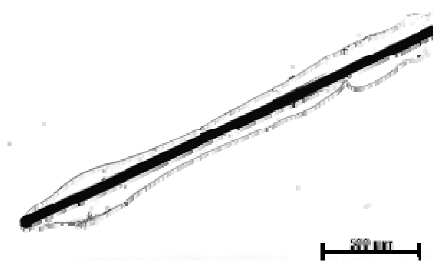


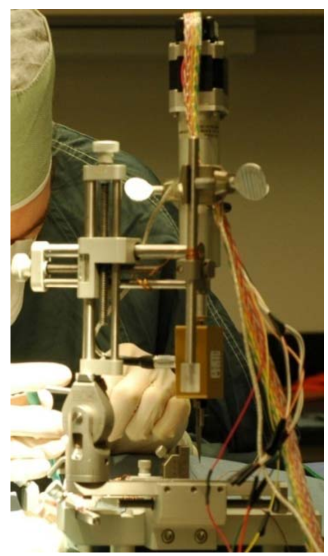
Dissolve glucose with saline, seal hole.

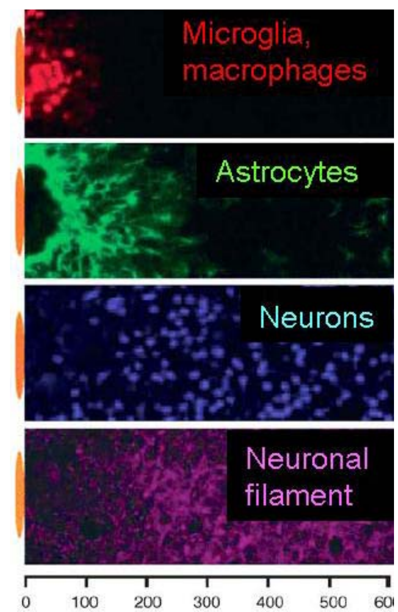
NC = 12.2% v/v TW in PVAc



Wire = 300 μm Tungsten dip coated with PVAc



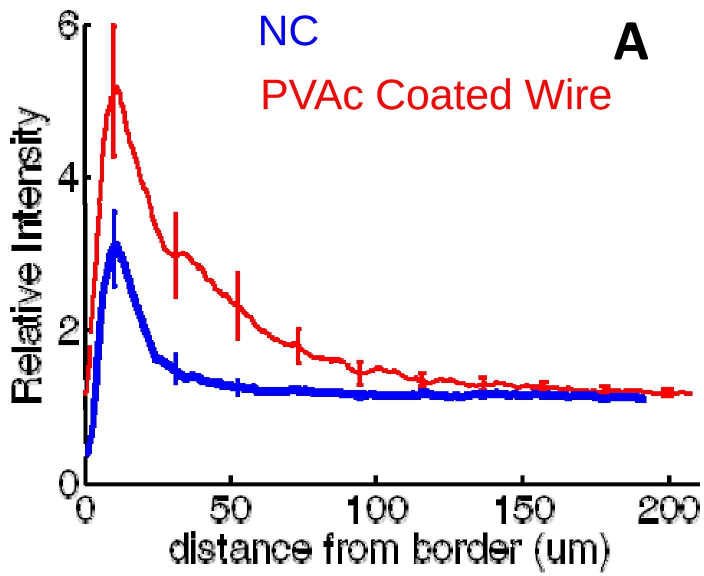




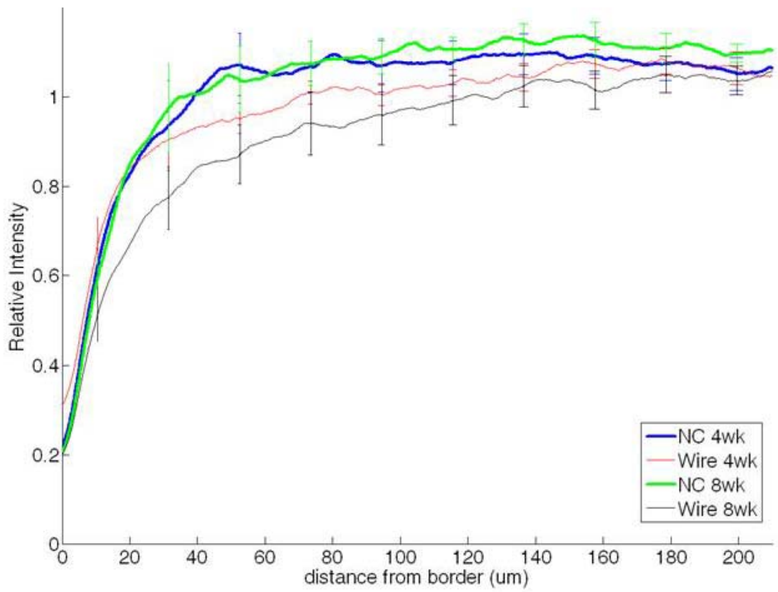
Biran et al. *Exp. Neurol.* **2005**

Chronic Implantation - Histology

Activated Microglia / Macrophages (ED1)



Neuronal Nuclei (NueN)



Stability of the neural tissue – device interface from 4 to 8 weeks

Adaptive nanocomposites cause less inflammation and support a more stable neural integration.

Harris, J.; Capadona, J.R.; Shanmuganathan, K.; Rowan, S.; Weder, C.; Zorman, C.A .; Tyler, D. unpublished

Electrophysiology: Single Unit Activity Recording in Cockroaches

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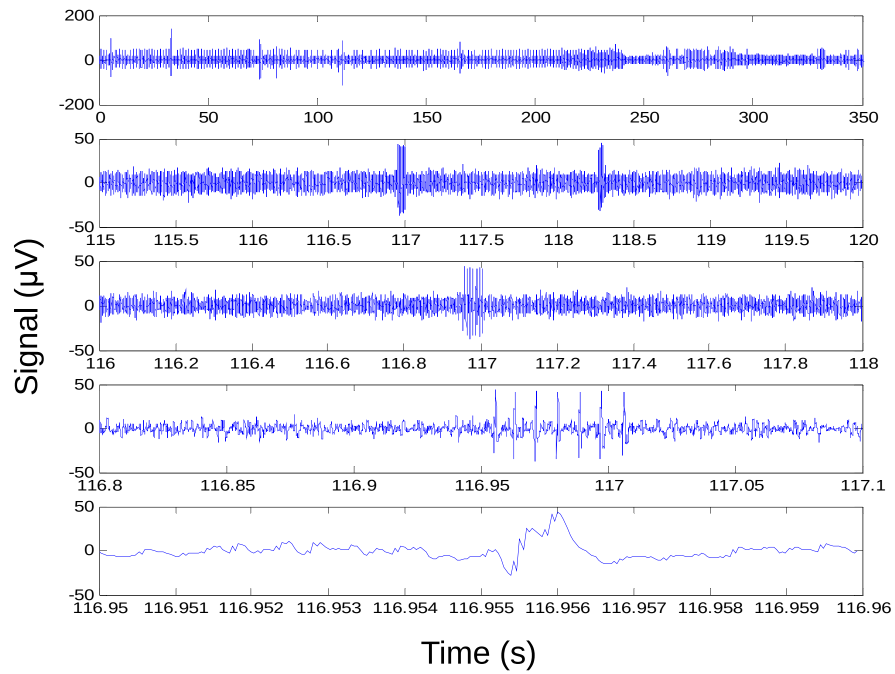
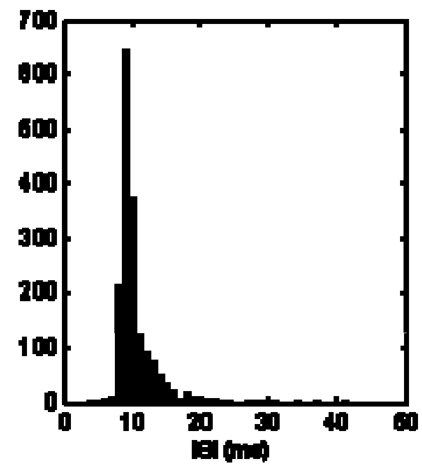
12 % v/v PVAc/TW Nanocomposites

Waveforms, sampled at 24.4 kHz



Interspike Interval Histogram



1880 spikes with all intervals above 3 ms

Hess, A.; Dunning, J.; Harris, J.; Capadona, J.R.; Shanmuganathan, K.; Rowan, S.; Weder, C.; Tyler, D.; Zorman, C.A. *IEEE Proceedings, Transducers* **2009**, in press.

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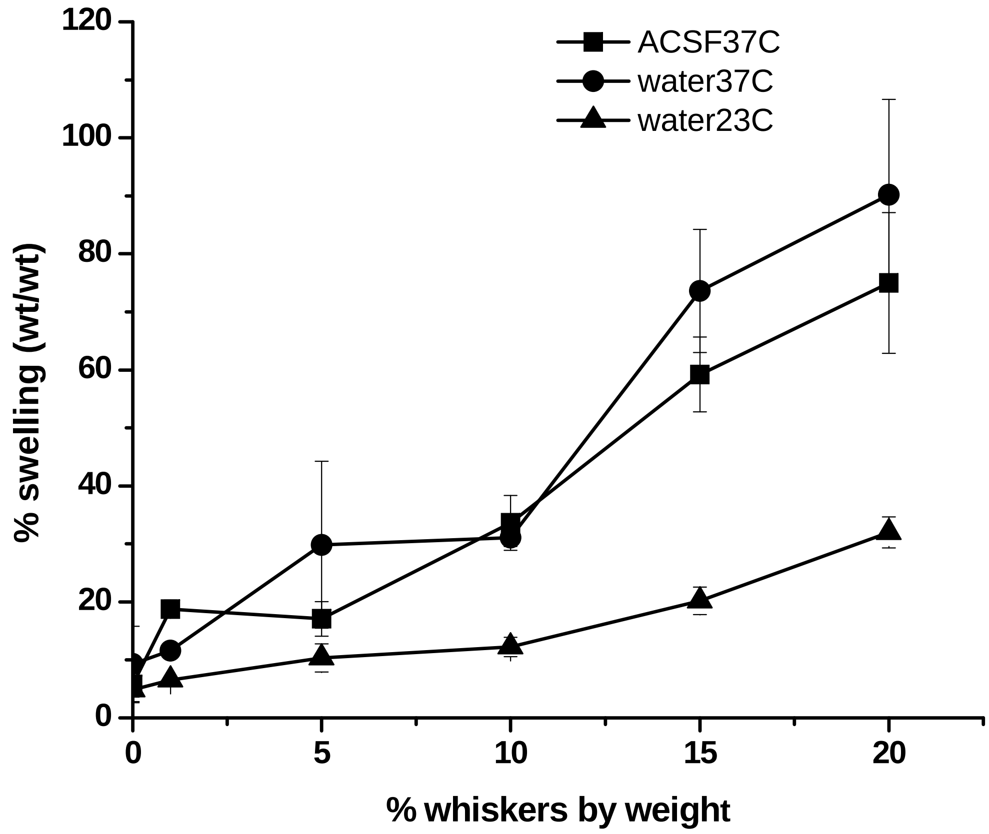
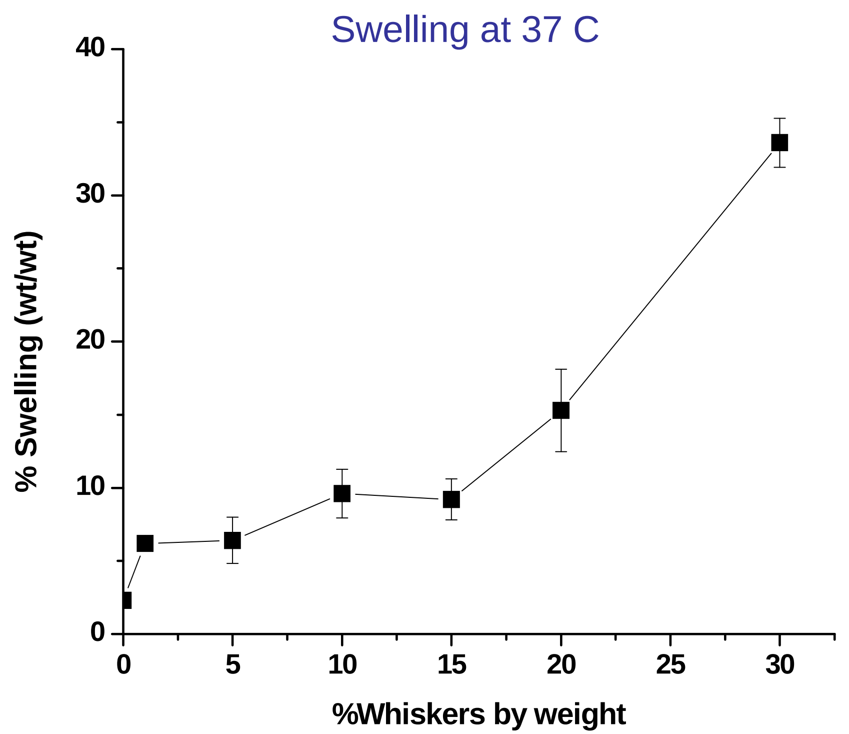
Next Goals: Reduce Aqueous Swelling

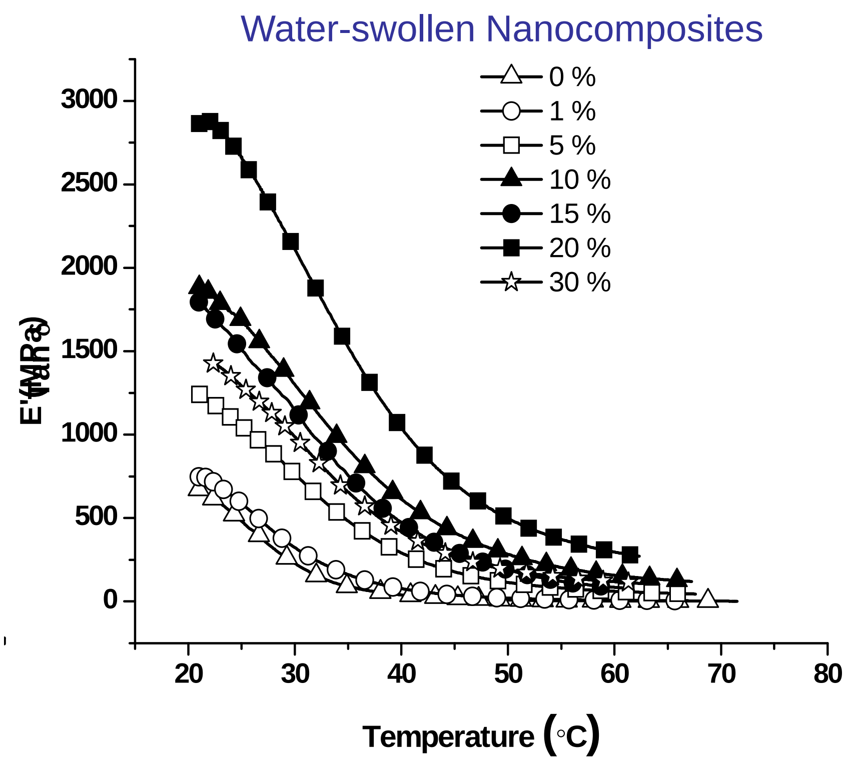
PVAc/TW nanocomposites swell significantly under physiological conditions



Capadona, Shanmuganathan, Tyler, Rowan, Weder *Science* **2008**, *319*, 1370.
Shanmuganathan, Capadona, Rowan, Weder *Progr. Polym. Sci.* **2009**, *in press*.
Shanmuganathan, Capadona, Rowan, Weder *J. Mater. Chem.* **2009**, *in press*.

PBMA as Hydrophobic Matrix: Reduced Swelling and Mech. Contrast





Use PBMA as matrix: T_g ~70°C; minimal aqueous swelling (1%)

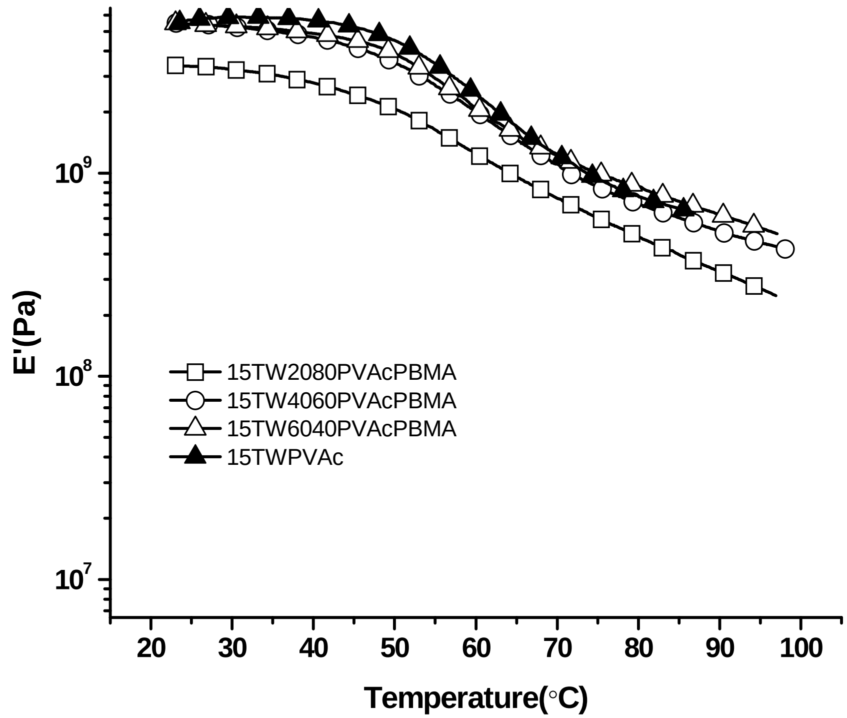
Swelling reduced compared to PVAc

Limited plasticization -> "Off" state not reached at 37°C

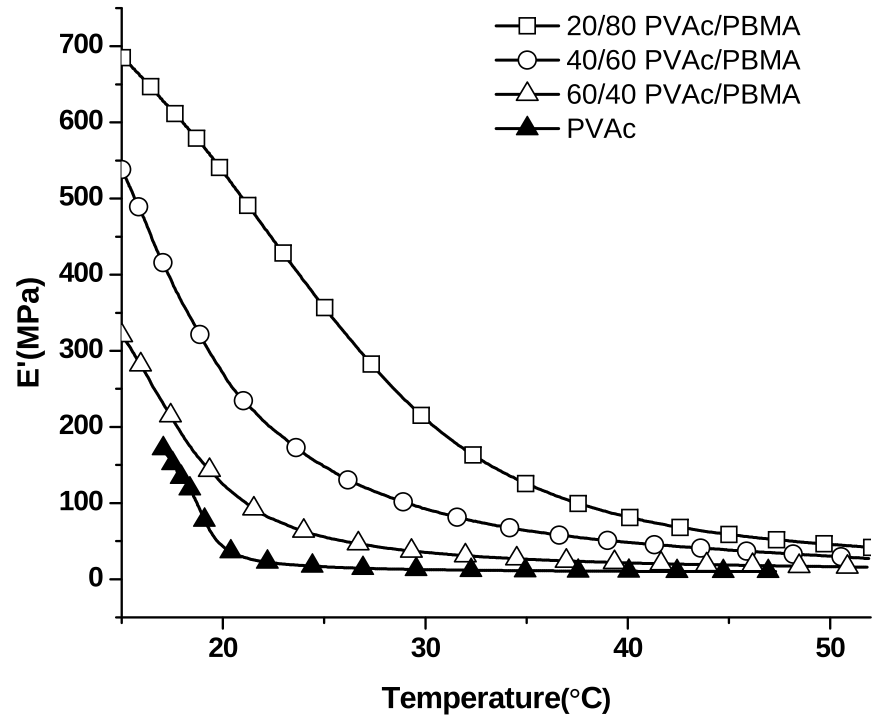
Shanmuganathan, Capadona, Rowan, Weder Submitted.

PBMA/PVAc Blends (Almost) a Winning Team

Dry Nanocomposites (15 % TW)



Water-swollen Nanocomposites (15 % TW)

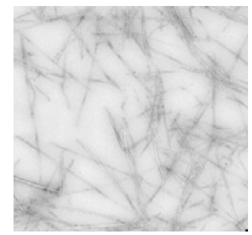


Use PBMA/PVAc blends as matrix

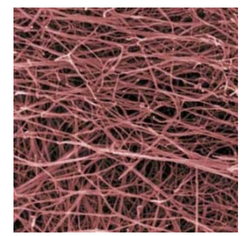
Shanmuganathan, Capadona, Rowan, Weder Submitted.

Conclusions

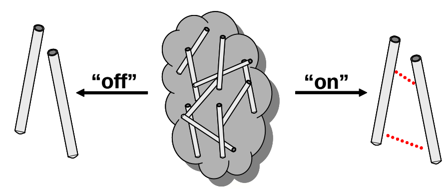
- Nature is an extraordinary source of inspiration for the design of functional materials



- Cellulose whiskers from renewable sources are an attractive component for artificial nanocomposites
- Cellulose - and other - nanofibers can readily be processed by *exploiting* non-covalent interactions



- Control over nanostructure is key to create materials with ultimate properties
- Copying the sea cucumber's cool trick has allowed for the creation of a new family of dynamic adaptive materials



- Dynamic adaptive polymers appear to be useful for cortical electrodes and other applications

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Dr. Markus Geuss
Dr. Lorraine Hsu
Dr. Liming Tang
Dr. Otto van den Berg (now Arcelor M.)

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