High dielectric constant elastomers for electromechanical applications

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and

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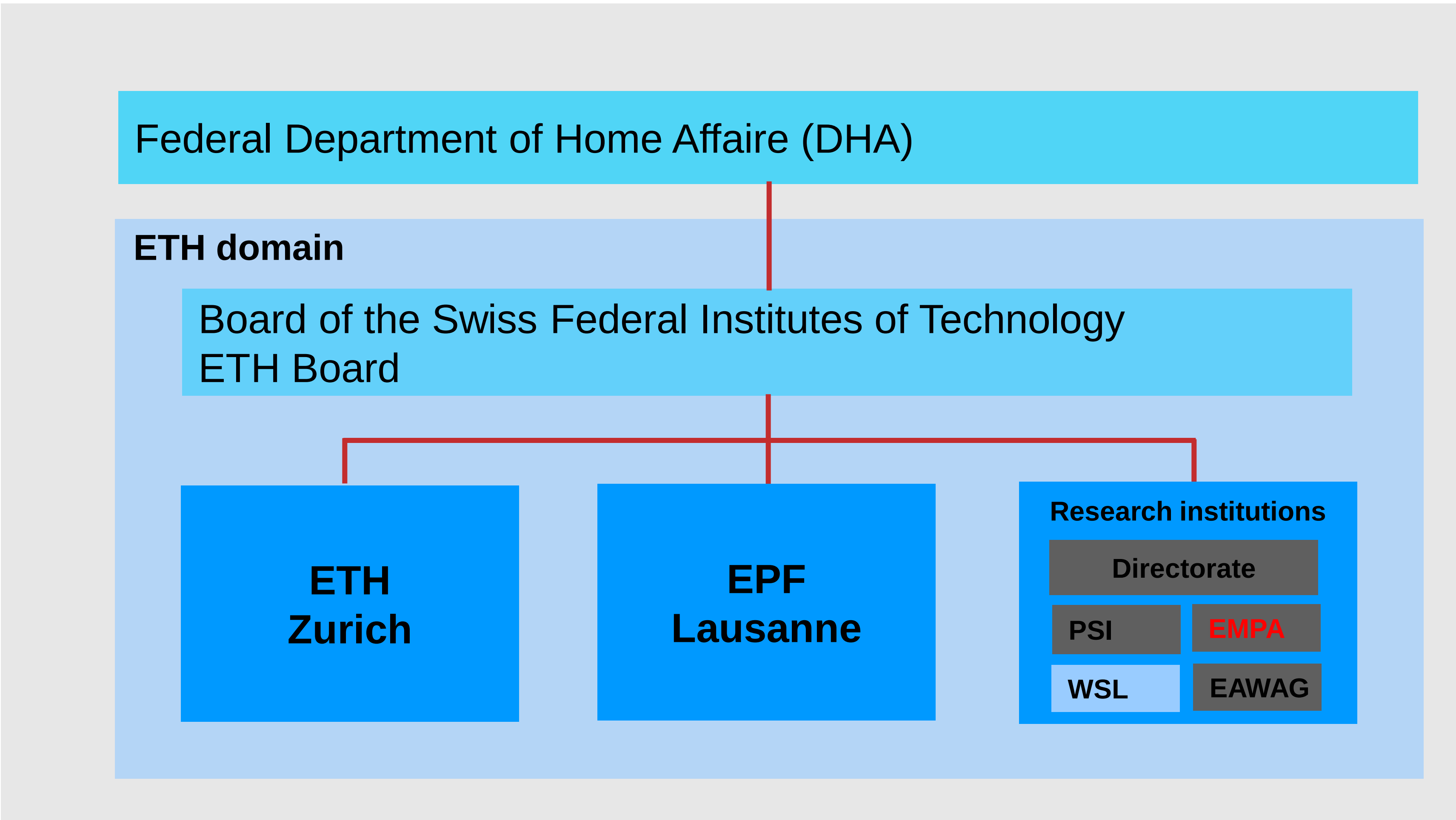
EPFL, Lausanne Switzerland

Empa part of the ETH Domain



Agenda

Strategies to increase the dielectric constant of elastomers while maintaining useful elastic properties and ensuring low electrical conductivity

A. Conductive nanoparticle composites

B. Silicones with dipole functionalities

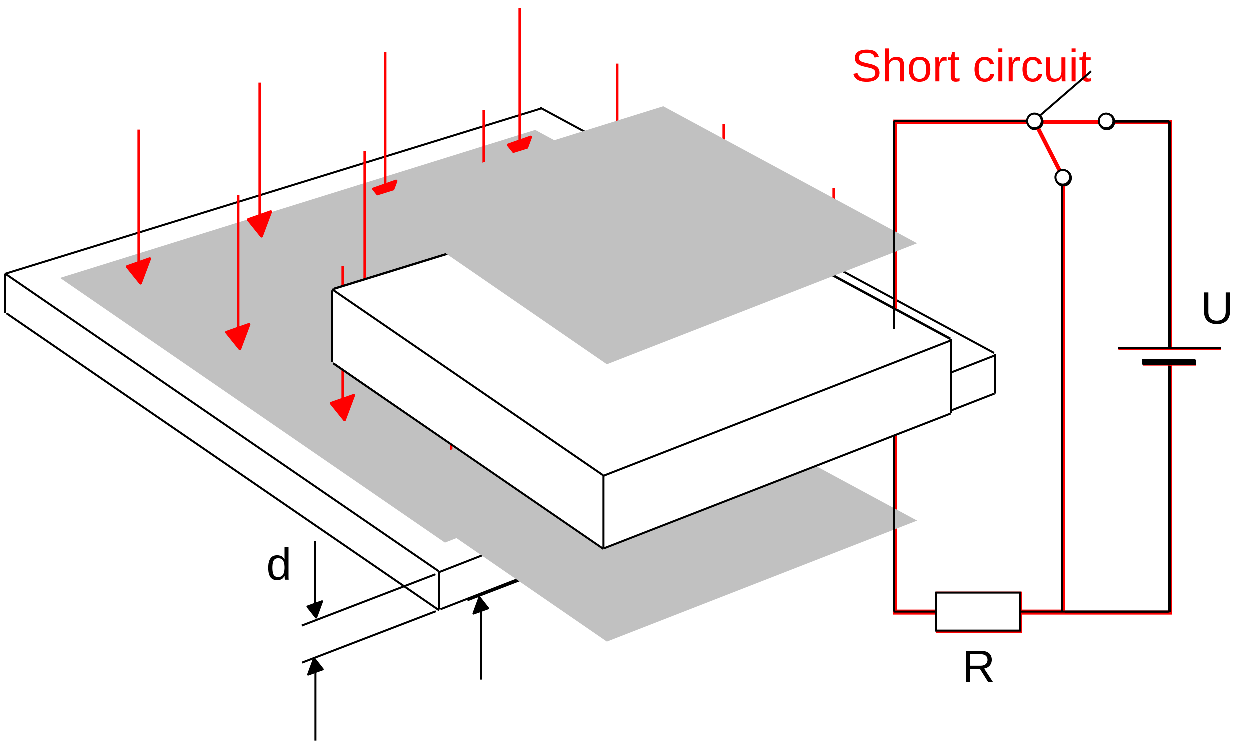
Working principle

$$s_z = \frac{p_{el}}{Y} = \frac{\varepsilon\varepsilon_0}{Y}\left(\frac{U}{z}\right)^2$$

p_{el} = electrostatic pressure
s_z = deformation in z direction
ε_0 = permittivity of vacuum
ε = relative permittivity
Y = compression modulus

optimize s_z

maximize ε
minimize Y and z



Polymer film

- Thin (10 - 100 μm)
- Elastic (small E-module)
- Incompressible
- Insulating
- High dielectric constant
- Breakdown resistant

Electrodes

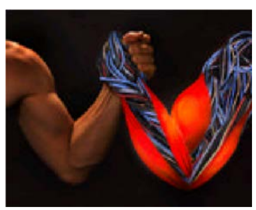
- Very thin (<1 μm)
- Flexible
- Conductive

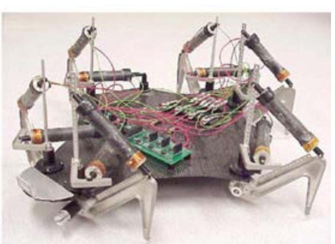
Current/Voltage source

- High voltage
- Small charging currents

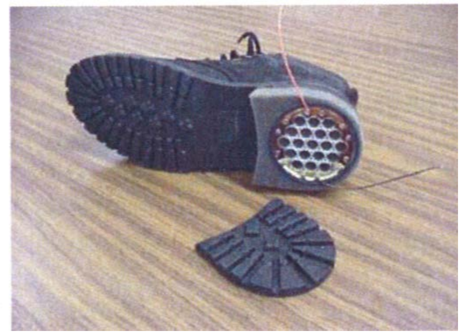
Applications for dielectric elastomer actuators

Actuators





Generators



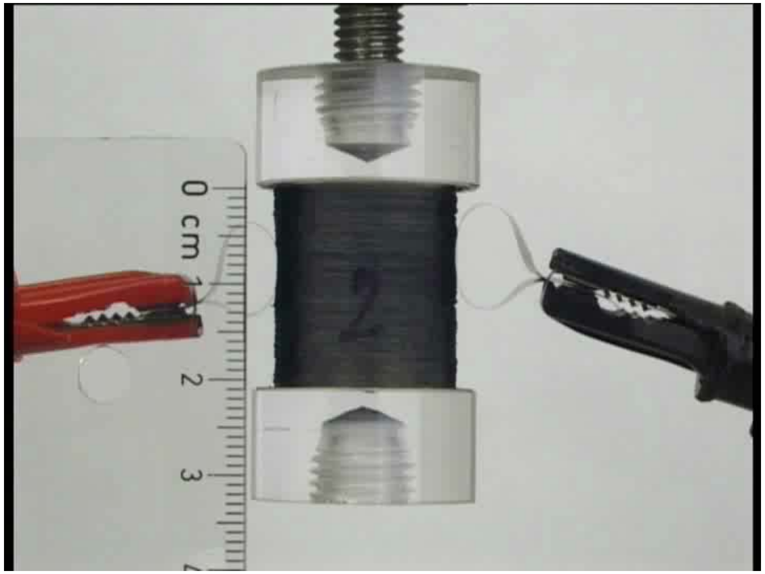
Sensors

Companies active in DEA include: Optotune, Artificial Muscle, Environmental Robots, Creganna-Micromuscle, Bayer materials science, CT Systems; Materials development: Bayer, Wacker

CTSystems

EMPA
Materials Science & Technology

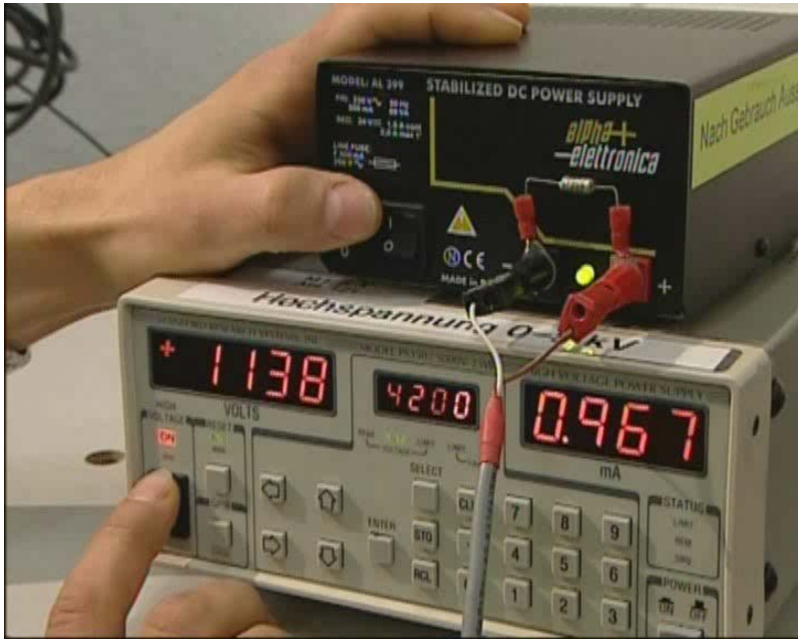
Compliant Transducer Systems



L = 21 mm
Ø = 20 mm
V = 4.2 kV
80 μm

courtesy Dr. G. Kovacs

G. Kovacs, L. Düring, S. Michel, G. Terrasi,
Sens. Actuators A, **2009**, *155*, 299



Numerical simulation of the effective permittivity of polymer-metal composites

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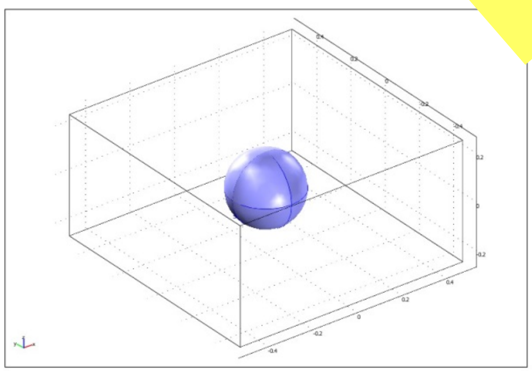
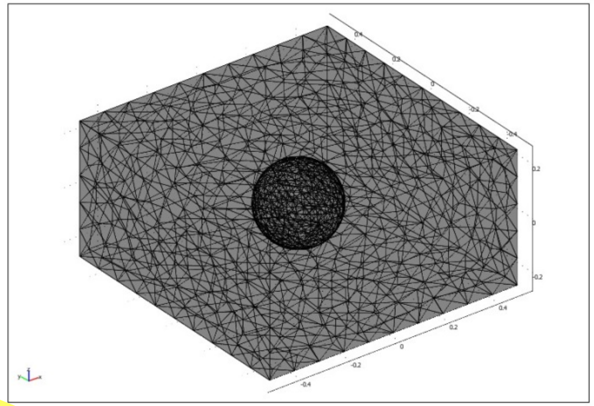
COMSOL - software

Specification of the boundary conditions (surface charge, potential, etc)



Mesh generation



Finite element method

Get linear system of equations →

solve using numerical methods

Determination of the effective permittivity of such a composite:

→ Plate capacitor

→ Specify the potential difference (U)

→ Measure the accumulated charge on electrodes (Q)

$$\varepsilon_{eff} = \frac{1}{\varepsilon_0} \frac{d \cdot Q}{A \cdot U}$$

Validation of method

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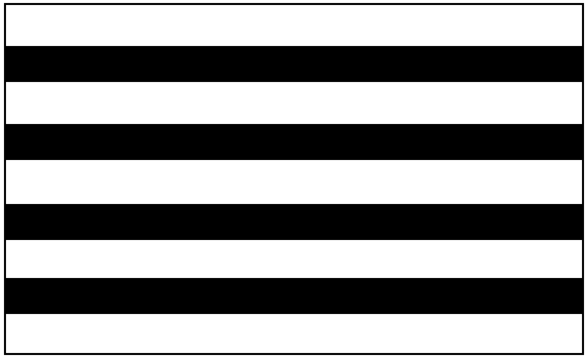
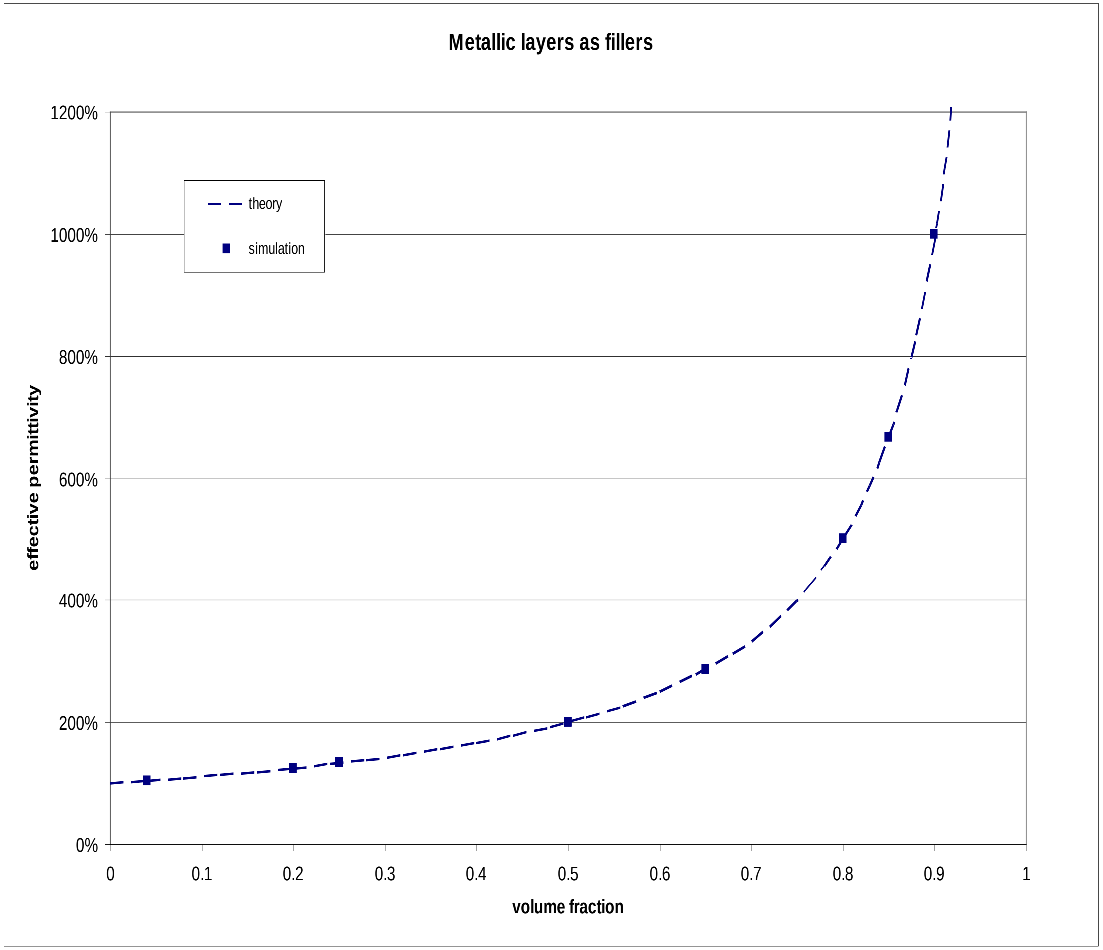
Metallic layers (zebra)



$$C_{zebra} = \frac{\varepsilon_0 \cdot A}{d \cdot (1 - f_{metal})}$$

$$\Rightarrow \varepsilon_{eff} = \frac{1}{(1 - f_{metal})}$$

P. Dahinden et al. internship, 2007

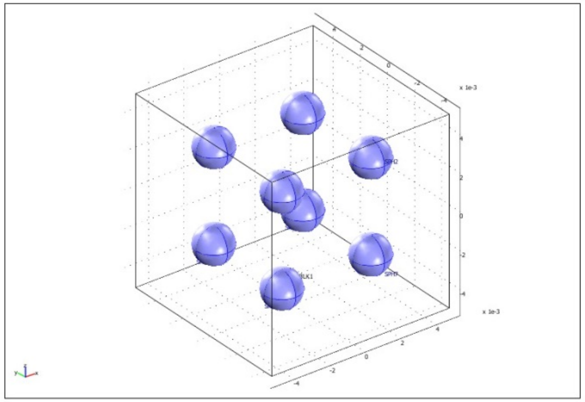


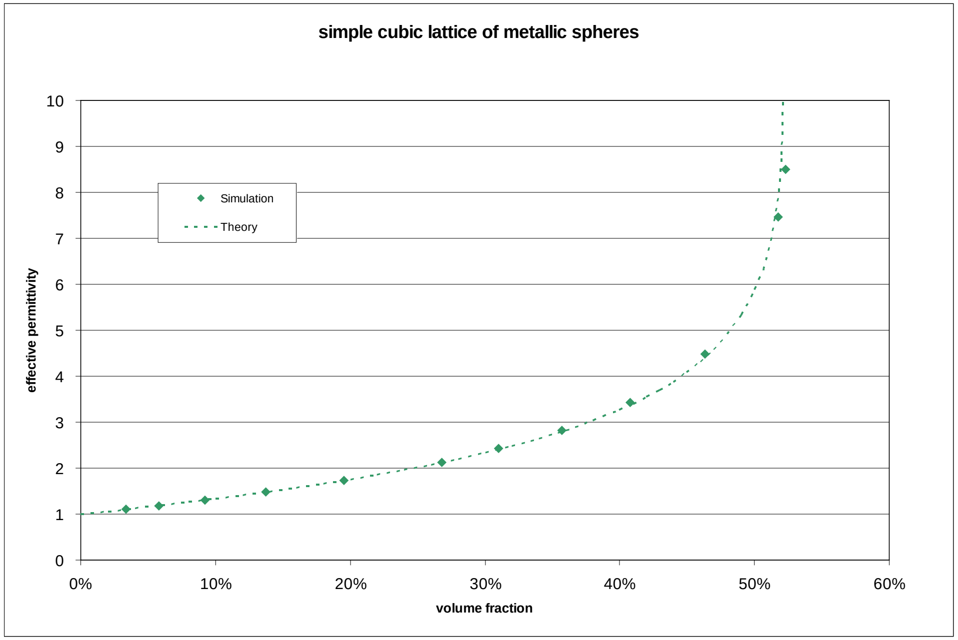
Simple cubic lattice

Metallic spheres in a simple-cubic lattice

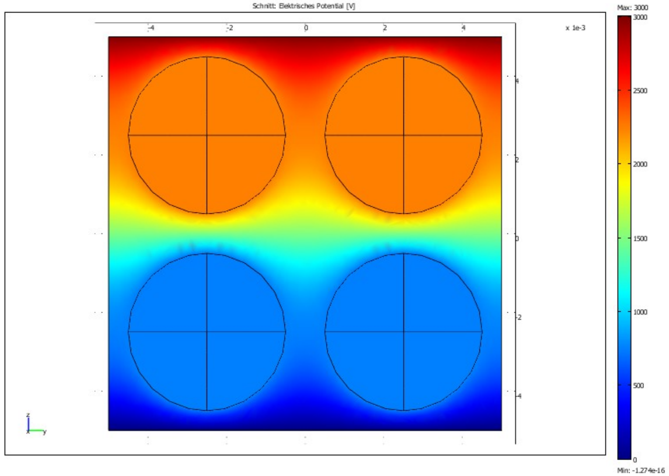
$$\frac{\varepsilon_{eff}}{\varepsilon_0} = -\frac{\pi}{2} \cdot \ln\left(\frac{\pi}{6} - f\right)$$

Mc Kenzie and Mc Phedran, 1977





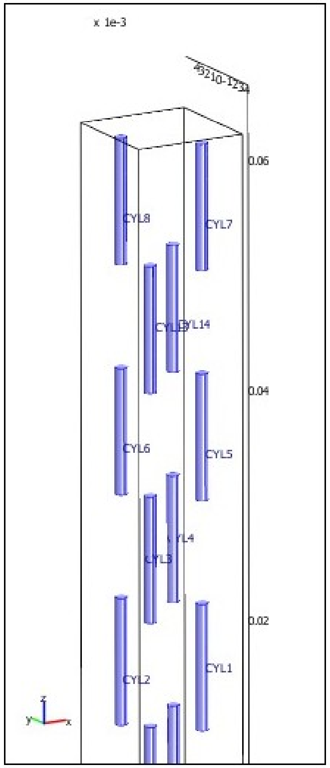
Electric potential

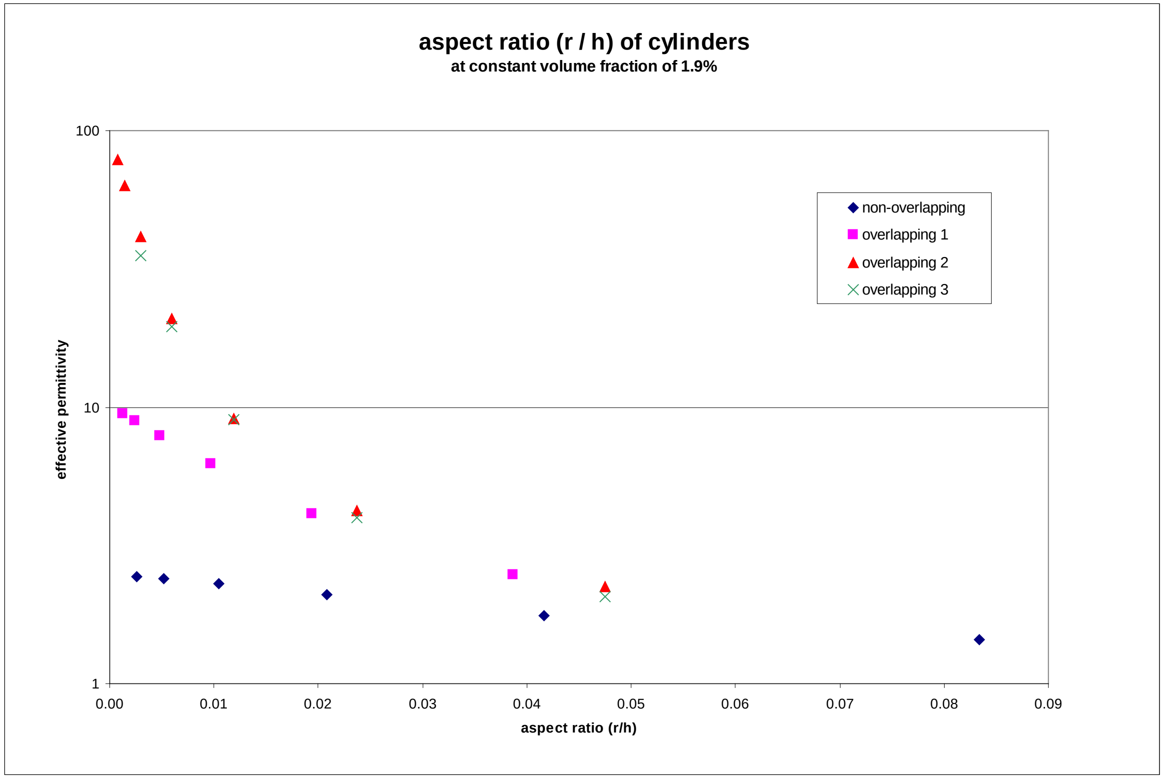


Cylinders: effect of aspect ratio

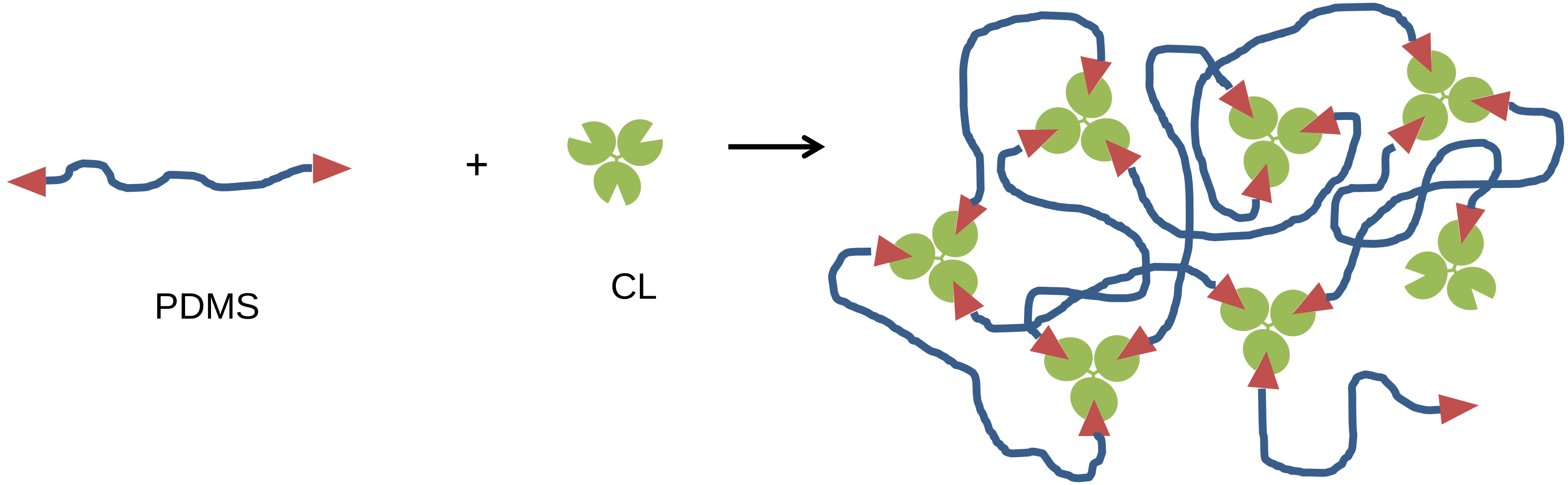
- Effect predicted and already applied to produce materials with ultra-high permittivity (e.g. MWNT)
- Simulation: increase the aspect ratio while keeping the volume fraction constant (@1.9%)

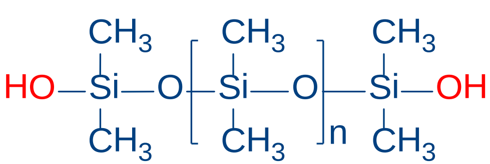
P. Dahinden, Master thesis, EPFL, 2009



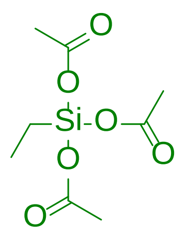


Synthesis of silicone elastomers

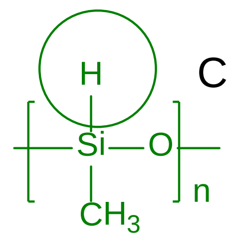




PDMS



CL
ETAS



Cross-linked film

CL
PMHS

0.1 < Y < 1.5 MPa

D. Opris, M. Molberg, C. Walder, Y. S. Ko, B. Fischer, F. A. Nüesch, *Adv. Funct. Mat.* **2011**, *21*, 3531-3539. Review: P. Brochu, Q. Pei, *Macromol. Rapid Commun.* **2010**, *31*, 10-36; C. Racles et al., Smart Mater. Struct. 22 (2013) 104004.

Crosslink density by swelling/extraction tests

$$\eta_{\text{swell}} = \frac{-\ln(1 - V_r) - V_r - \chi V_r^2}{2 V_s (V_r^{1/3} - 2 V_r / f)}$$

η_{swell}: crosslinking density
V_r: volume fraction of silicone rubber
V_s: molar volume of the solvent
χ: Flory solvent-polymer interaction parameter
f: functionality of crosslink

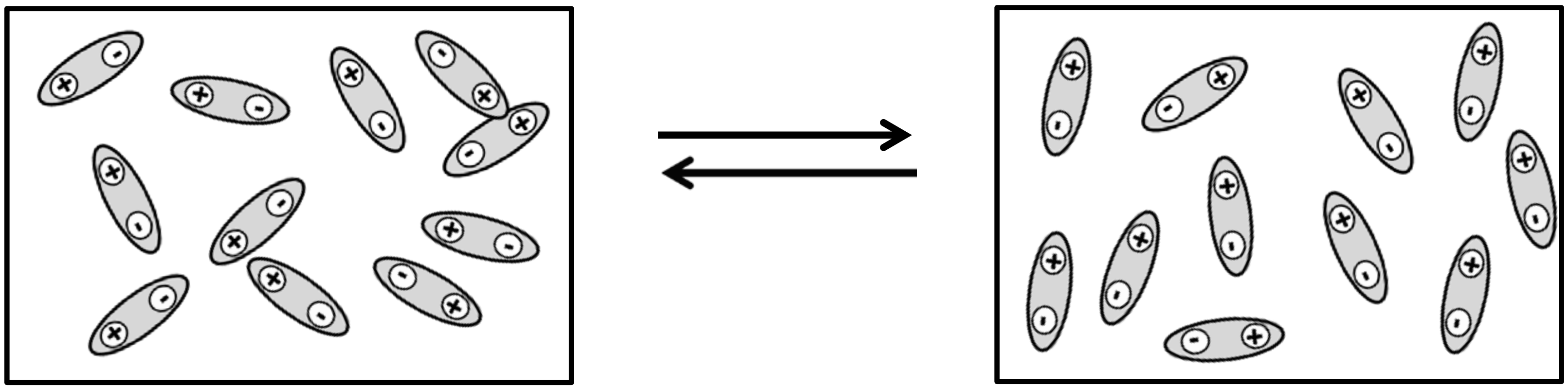
Sample	W_{ext} [%]	η [mole cm^{-3}]	M_c
A1	8.64	3.12×10^{-5}	16019
A2	5.59	5.55×10^{-5}	9007
A3	8.25	5.84×10^{-5}	8557
B1	9.93	6.9×10^{-5}	7248
B2	9.09	6.62×10^{-5}	7550
B3	4.23	9.55×10^{-5}	5235
C1	38.86	3.47×10^{-5}	14425
C2	45.99	2.24×10^{-5}	22328
C3	48.67	1.88×10^{-5}	26665

molecular weitght of PDMS: 140000g/mol

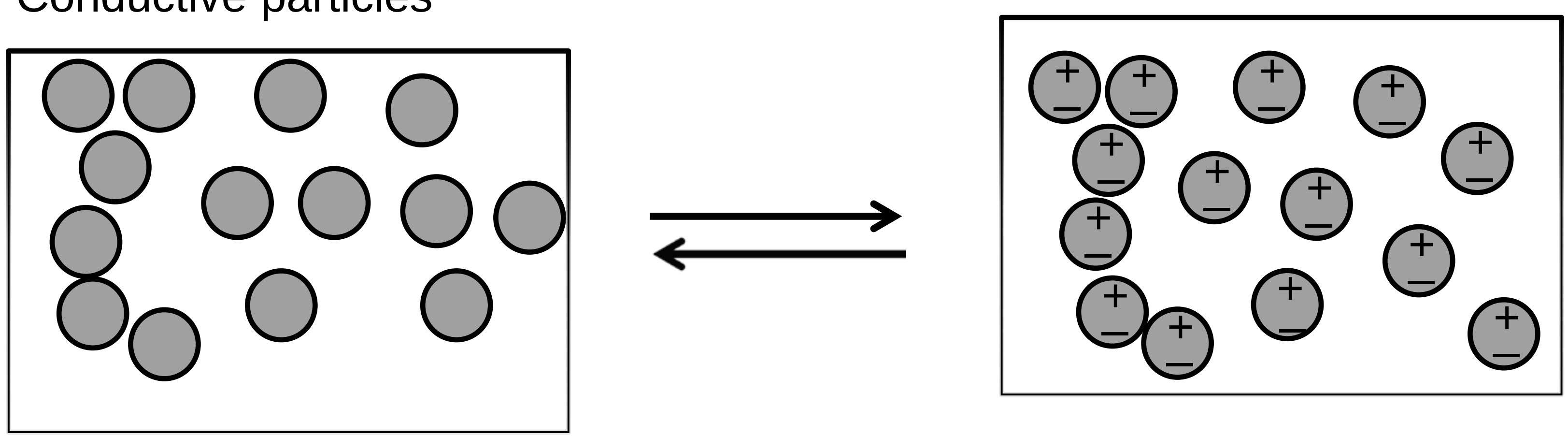
D. Opris, M. Molberg, C. Walder, Y. S. Ko, B. Fischer, F. A. Nüesch, *Adv. Funct. Mat.* **2011**

Approaches to increase the permittivity

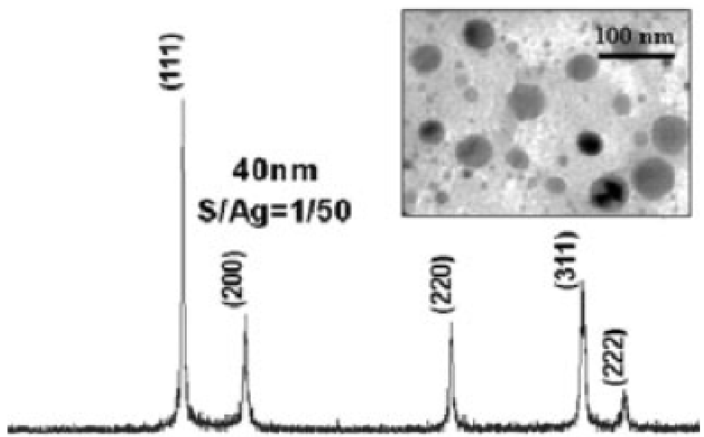
Dipoles

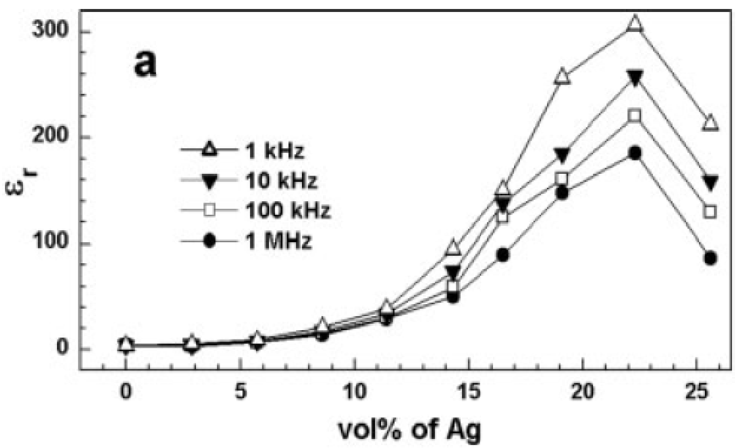


Conductive particles



AgNP (40 nm) in Epoxy

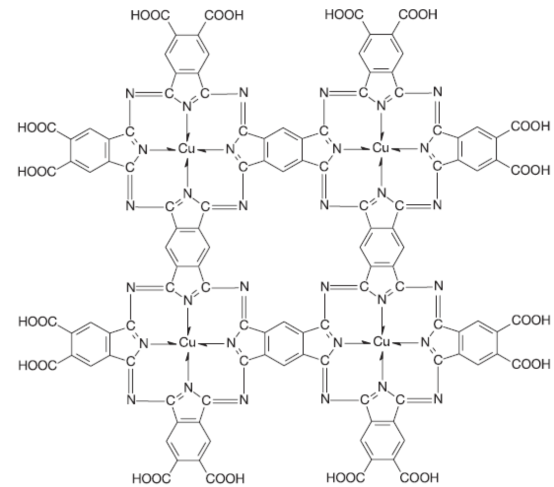


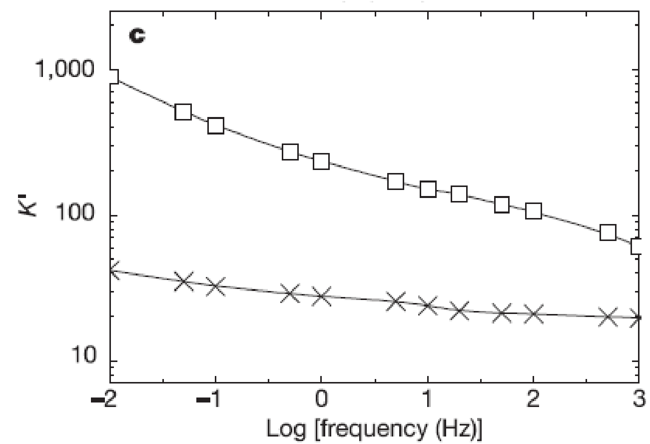


L

Lai et al., Adv. Mater., (2005), 17, 1777-1781

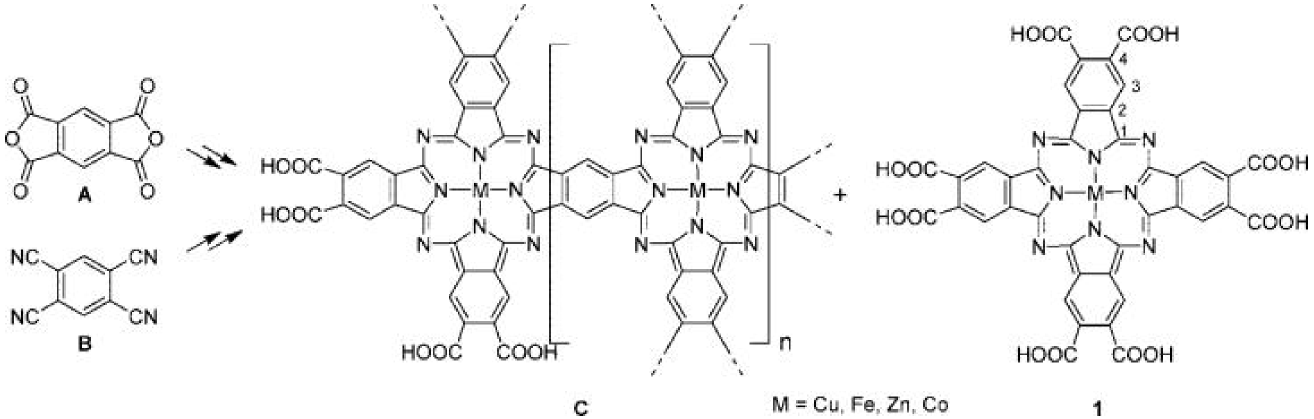
Carboxylated Cu-Phthalocyanine particles in 40% weight

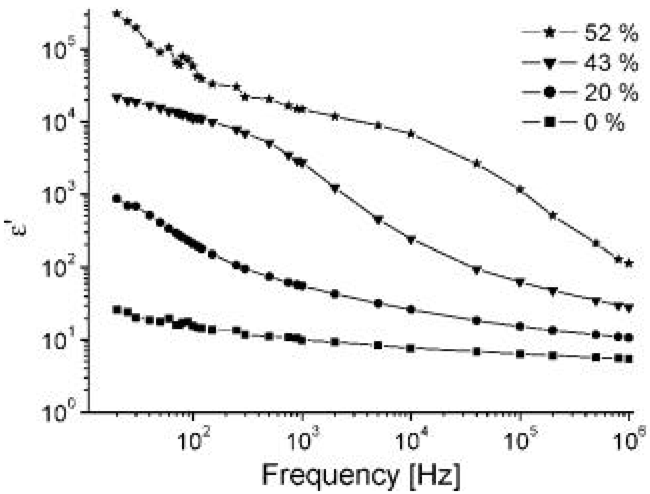


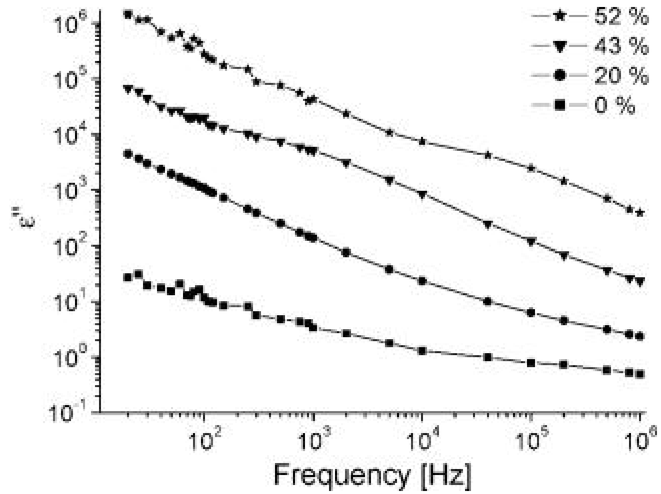


Q. M. Zhang et al., NATURE, 419 19 2002, p. 284

Synthesis carboxylated Cu-phthalocyanines







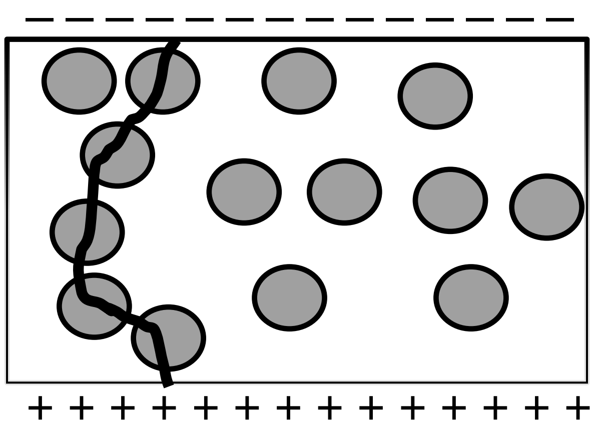
Real and imaginary permittivity at different degrees of relative humidity

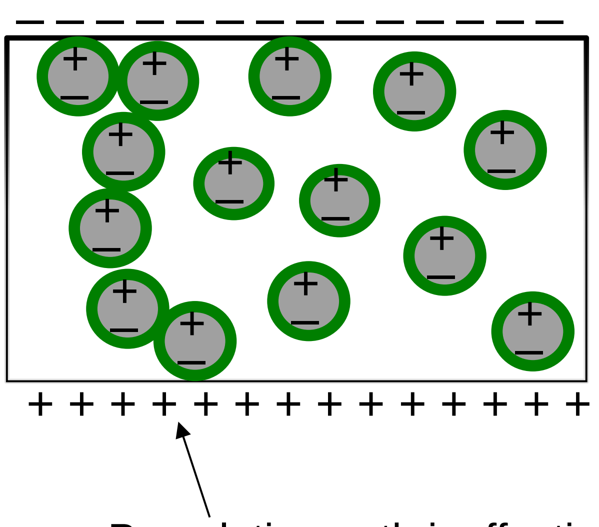
D. Opris et al., Chem. Mater. **2008,** *20,* 6889–6896

Siliconnes blended with metallic fillers

Conductive fillers: AgNPs

Studying ε as function of: particles size and shape
filler volume fraction
shell thickness





Percolation path ineffective

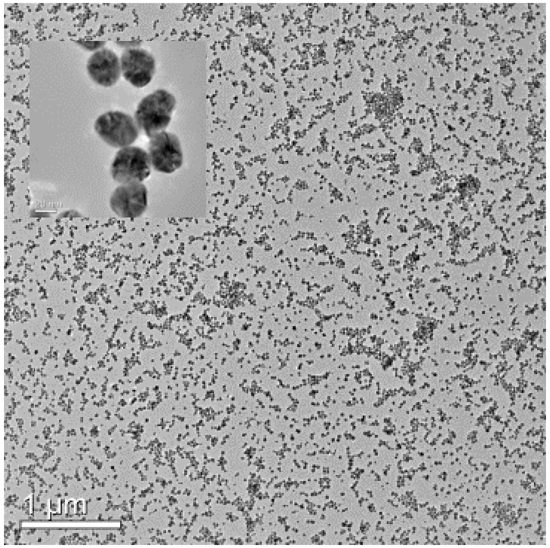
D. R. McKenzie, R. C. McPhedran, *Nature*, **1977**, *265*, 128.
M. Rycenga, C. M. Cobley, J. Zeng, W. Li, C. H. Moran, Q. Zhang, D. Qin, Y. Xia, *Chem. Rev.,* **2011**, *111*, 3669–3712.

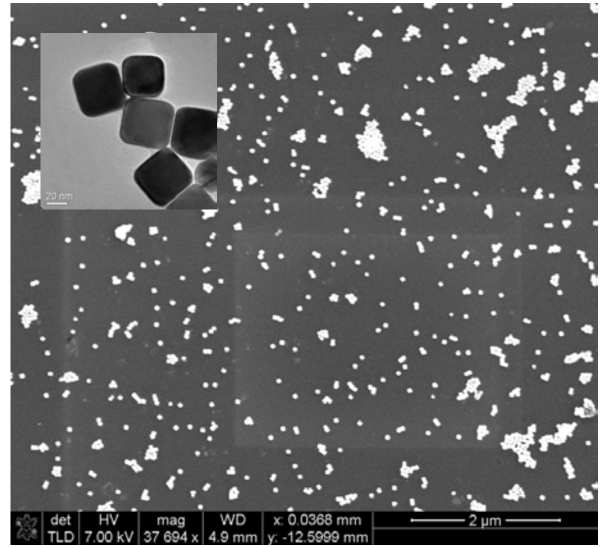
Synthesis of silver nanoparticles

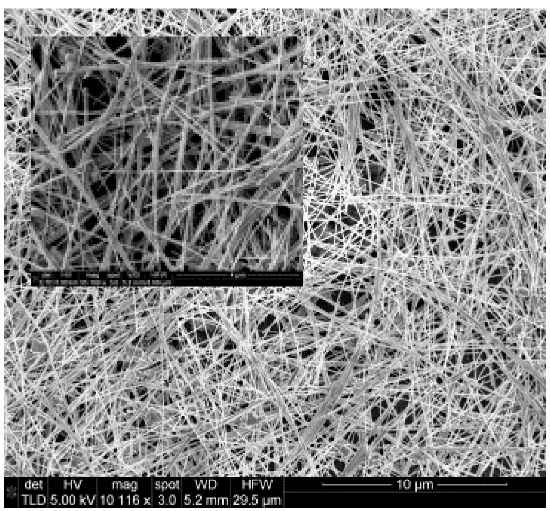
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

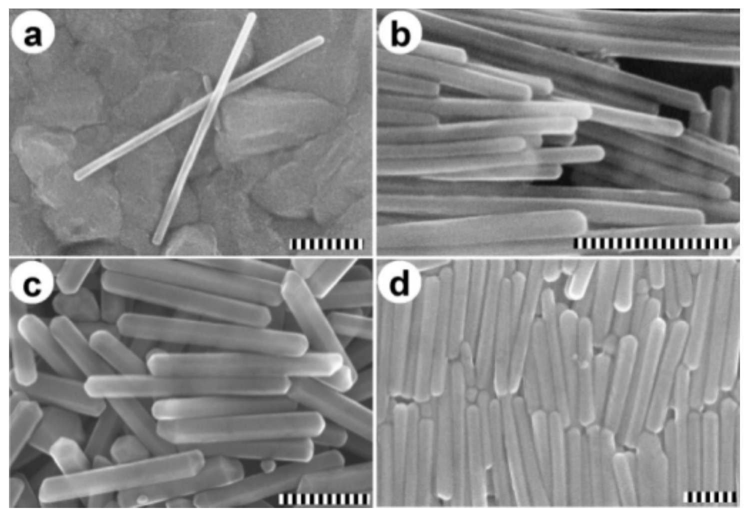
EMPA Materials Science & Technology

Collaboration with Prof. H. Hofmann, EPFL





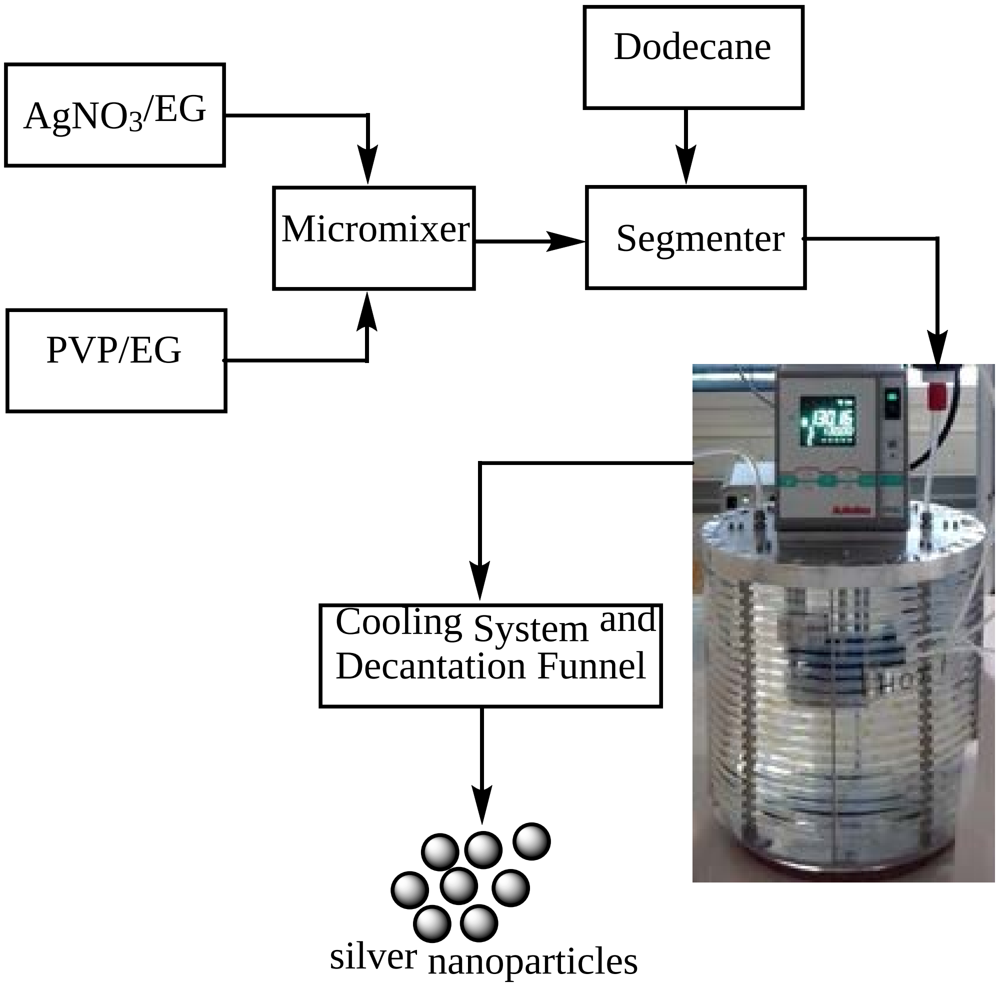


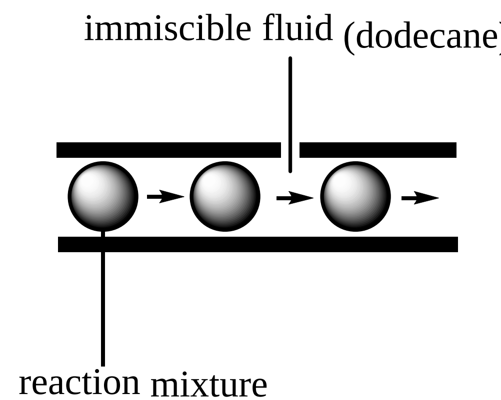


Particles: J. Zeng, X. Xia, M. Rycenga, P. Henneghan, Q. Li, Y. Xia, *Angew. Chem. Int. Ed.* **2011**, *50*, 244 –249.
Coating: W. Ströber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *26*, 62.

Segmental flow tubular reactor synthesis

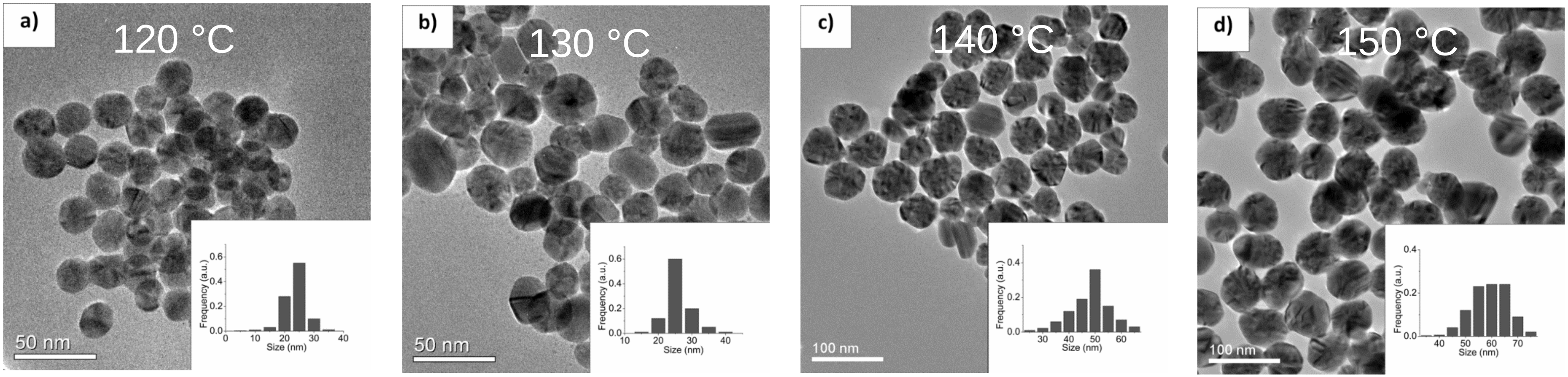
Collaboration: Dr. A. Testion, PSI, Prof. H. Hofmann, EPFL

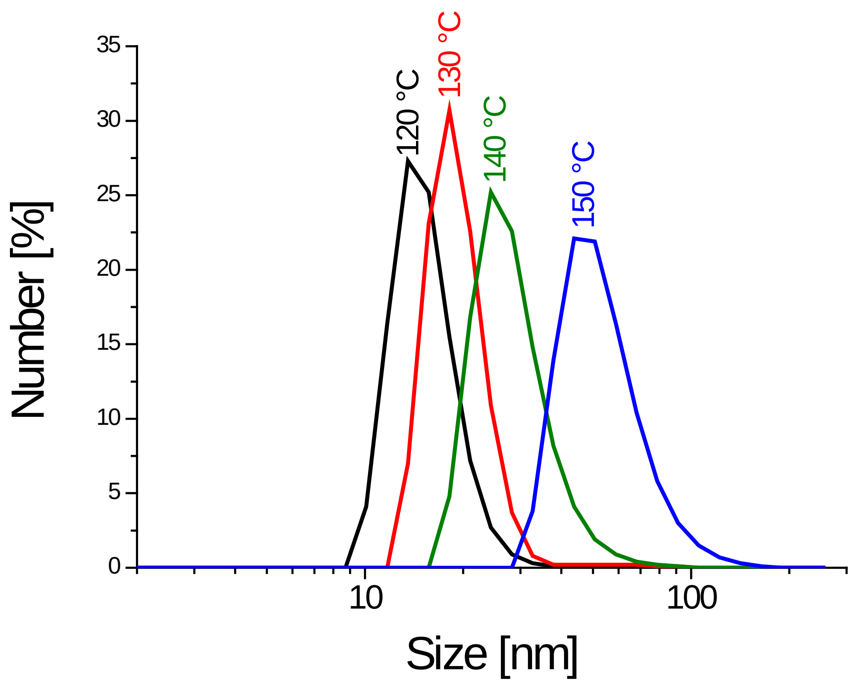


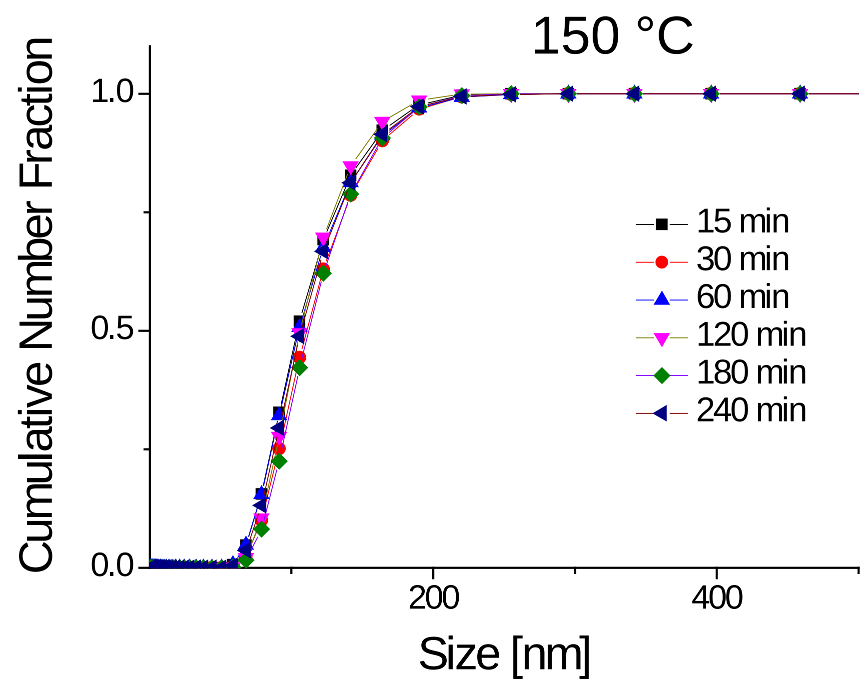


2.3 g Ag nanoparticles /h

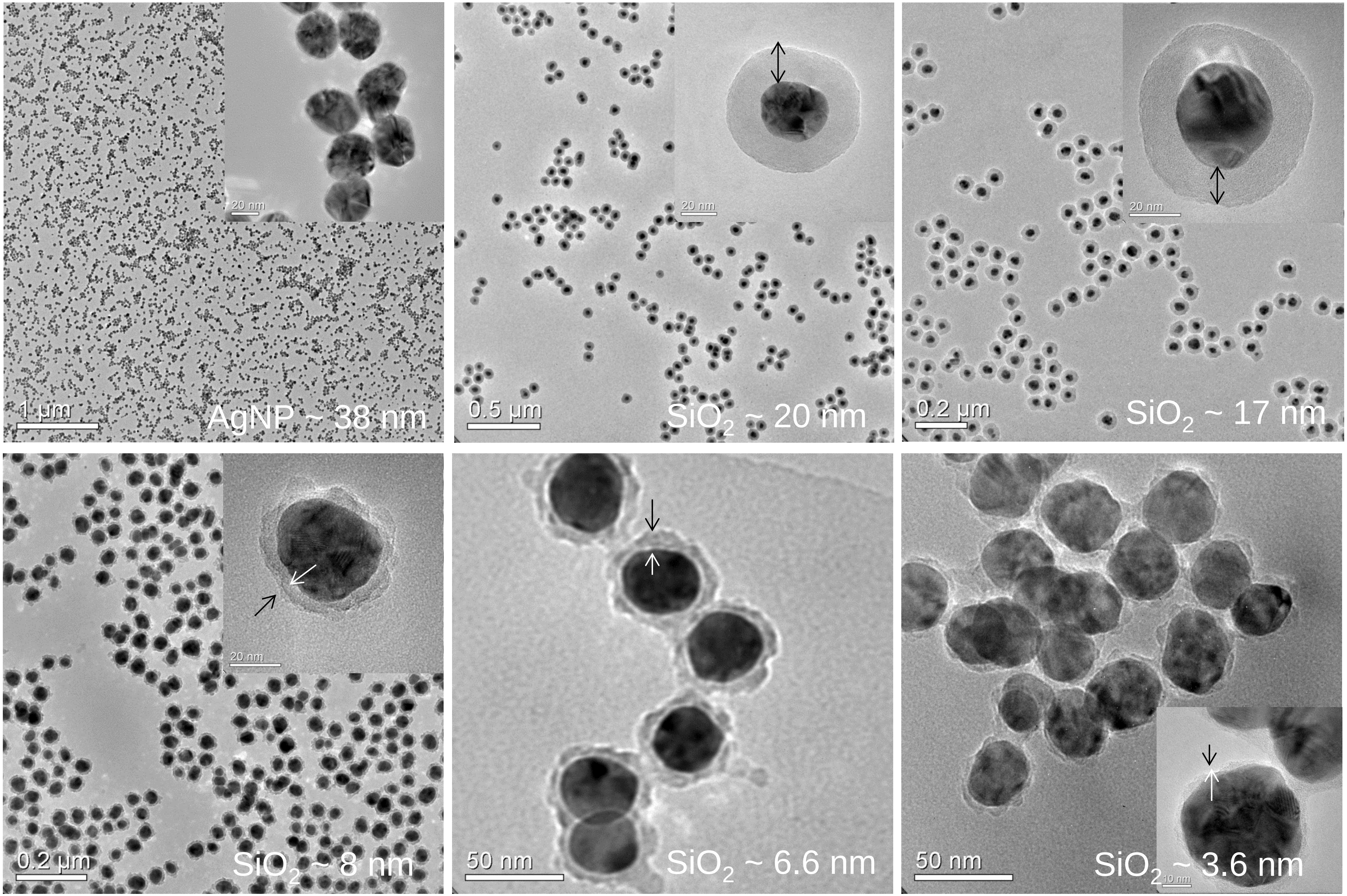
J. E. Q. Quinsaat, A. Testion, S. Pin, T. Hutwelker, F. A. Nüesch, P. Bowen, H. Hofmann, C. Ludwig, D. M. Opris, *J. Phys. Chem.* **2014**, 118, 11093−11103.


a)
120 °C
50 nm
b)
130 °C
50 nm
c)
140 °C
100 nm
d)
150 °C
100 nm
Frequency (a.u.)
Size (nm)


120 °C
130 °C
140 °C
150 °C
Number [%]
Size [nm]
0
5
10
15
20
25
30
35
10
100


150 °C
Cumulative Number Fraction
Size [nm]
0.0
0.5
1.0
200
400
15 min
30 min
60 min
120 min
180 min
240 min

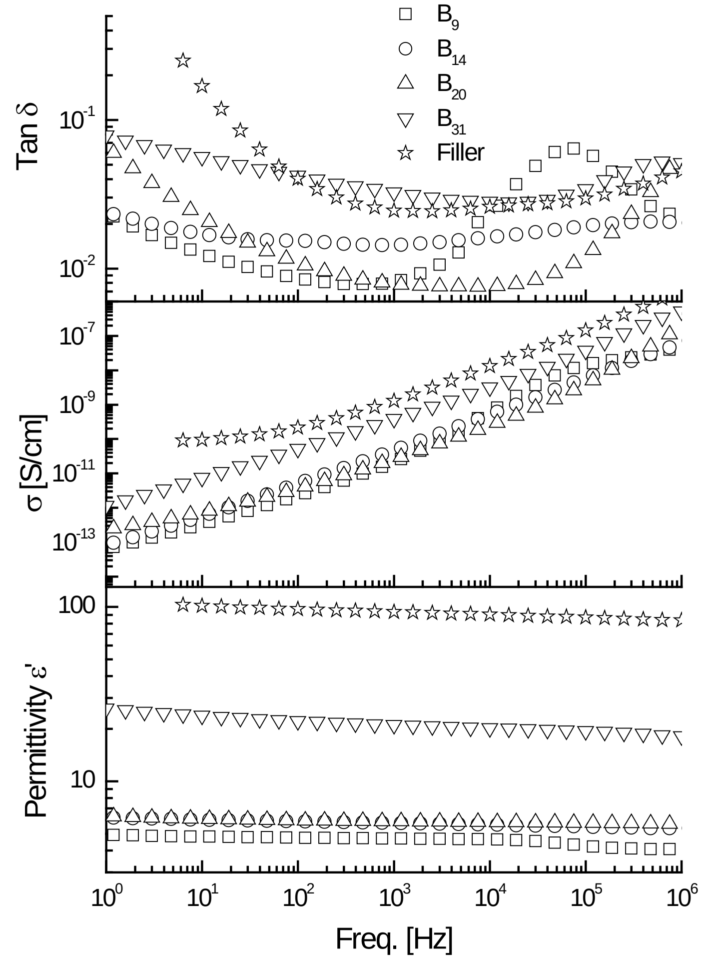
SiO$_2$@AgNPs



1 µm
20 nm
AgNP ~ 38 nm
0.5 µm
20 nm
SiO2 ~ 20 nm
0.2 µm
20 nm
SiO2 ~ 17 nm
0.2 µm
20 nm
SiO2 ~ 8 nm
50 nm
SiO2 ~ 6.6 nm
50 nm
10 nm
SiO2 ~ 3.6 nm

Coming close to percolation

Sample	vol% Ag	ρ [g/cm³]	ε'	tan δ	E_b [V/mm][b]	E_b [V/mm][c]
B_{31}	31	4.76	21	0.0300	-	1.3
$^{stiff}B_{20}$	20	3.05	6.8	0.0142	19.0	5.8
B_{20}	20	3.05	5.9	0.0078	13.4	5.9
B_{14}	14	2.46	5.7	0.0144	21.4	12.3
B_9	9	1.83	4.7	0.0083	23.1	29.4

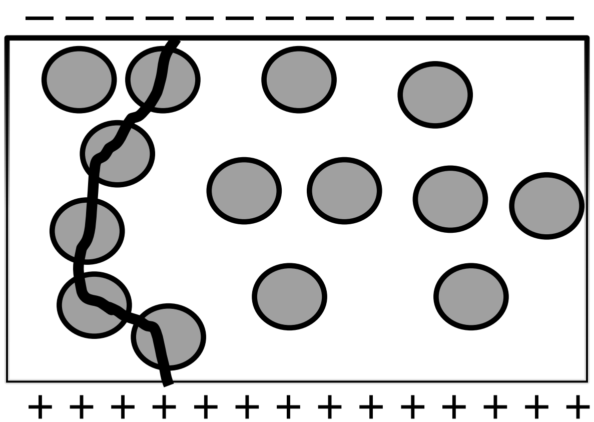


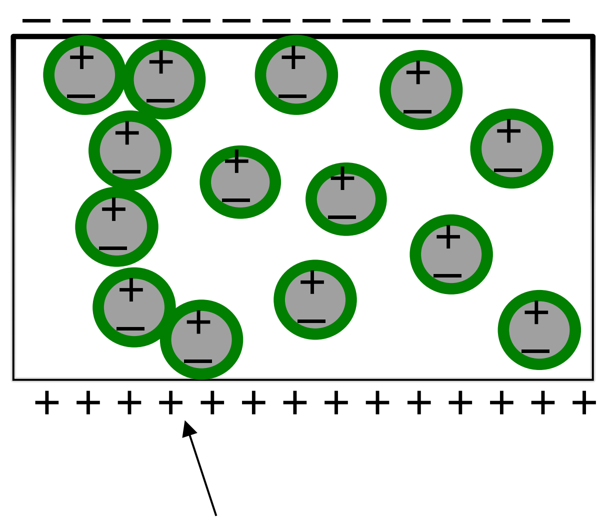
J. E. Q. Quinsaat et al., J.Mater.Chem.A ,**2015**, 3, 14675–14685

Siliconesblended with organic conductive fillers

Conductive fillers: polyaniline

Studying ε as function of: particle size and shape
filler volume fraction
shell thickness





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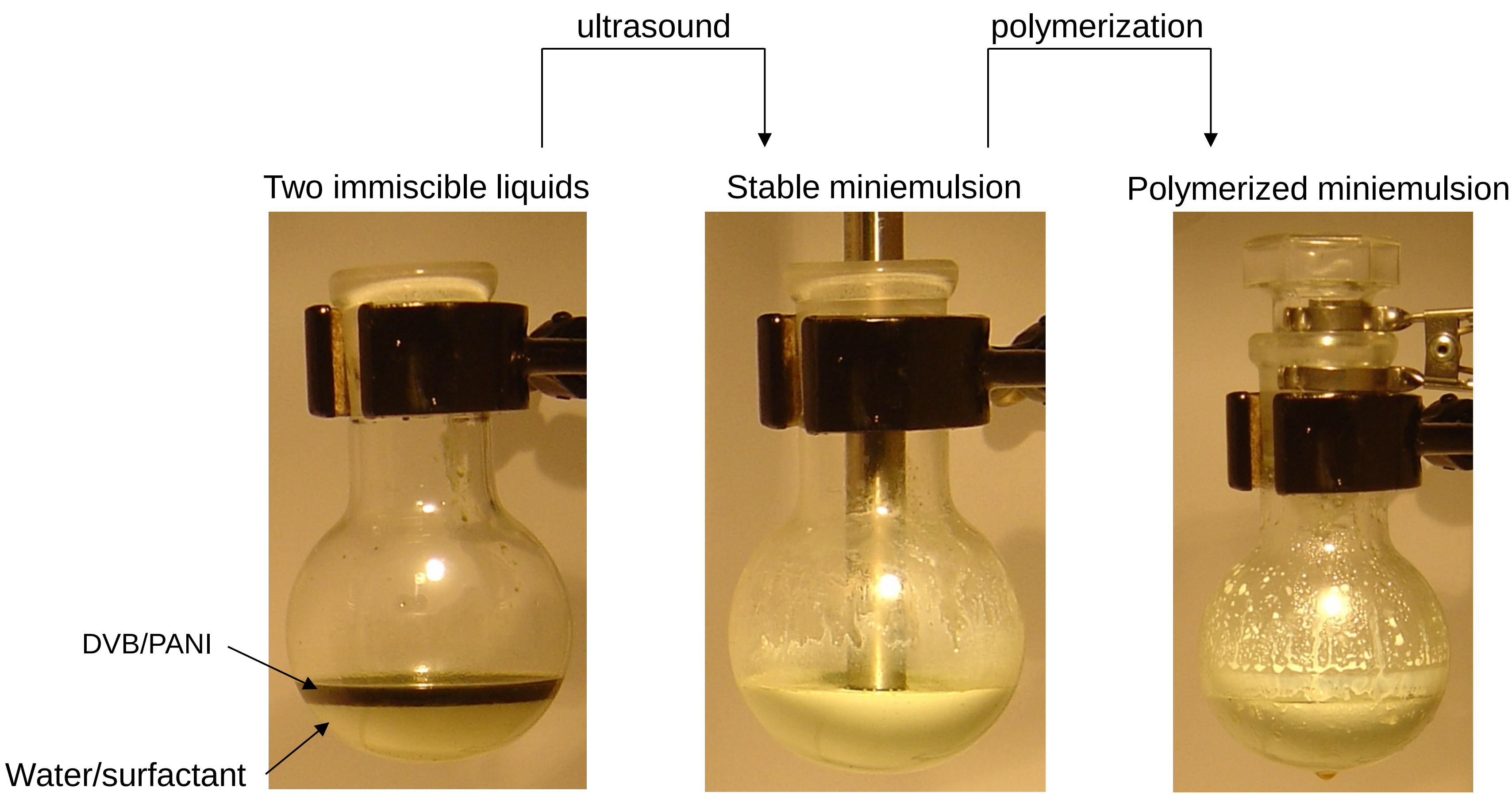
M. Rycenga, C. M. Cobley, J. Zeng, W. Li, C. H. Moran, Q. Zhang, D. Qin, Y. Xia, *Chem. Rev.,* **2011**, *111*, 3669–3712.

Miniemulsion polymerization



Monomer: divinyl benzene

M. Molberg, D. Crespy, P. Raupper, F. Nüesch, J.-A. Manson, C. Löwe, D. M. Opris, *Adv. Funct. Mater.* **2010**, *20*, 3280–3291.

PDVB@PANI in PDMS

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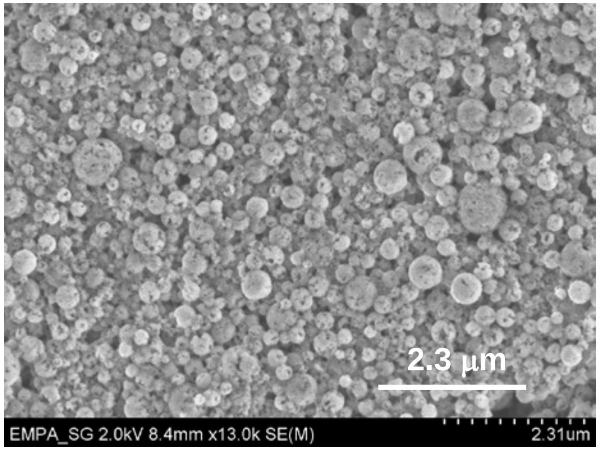

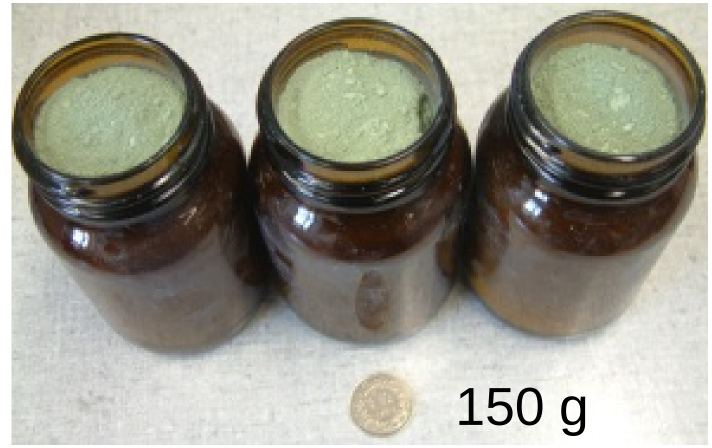

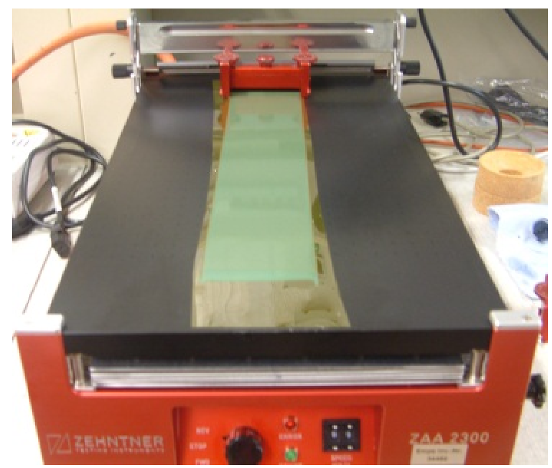

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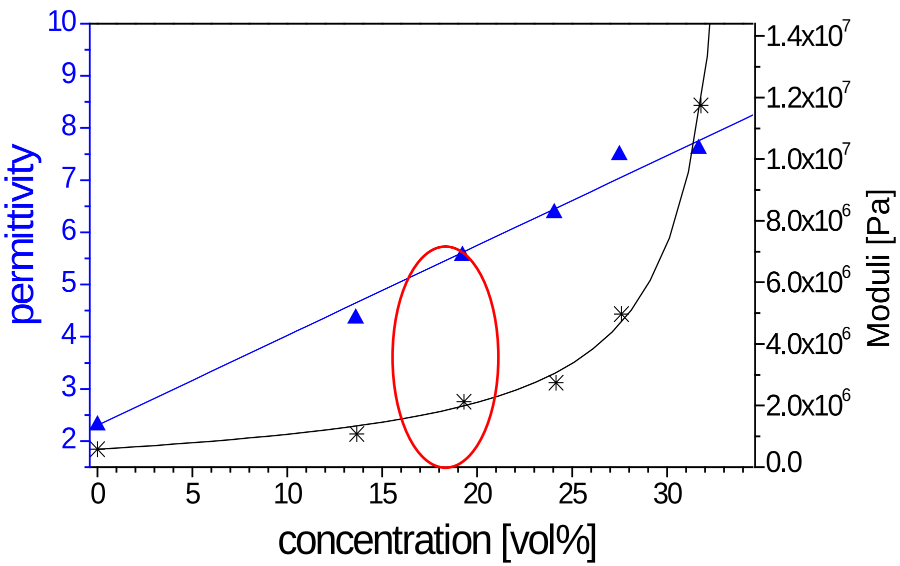
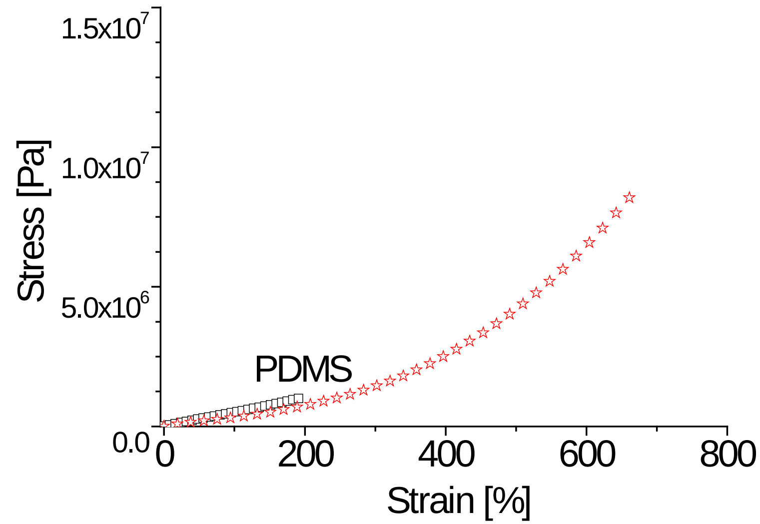
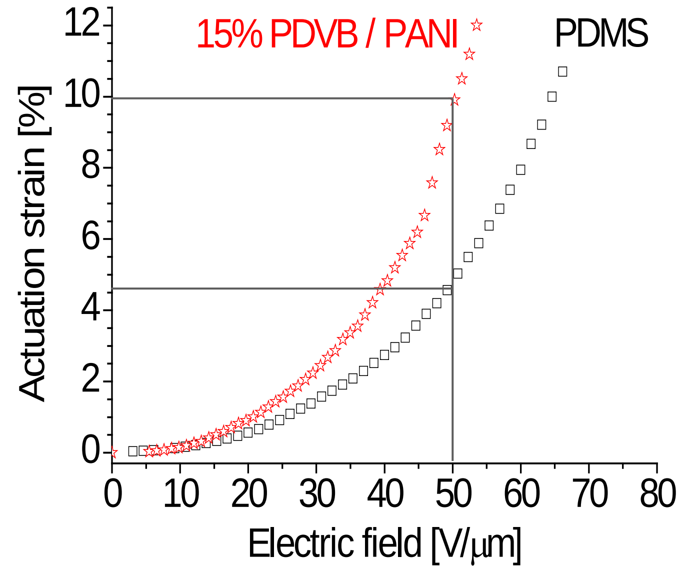
PDVB@PANI in PDMS



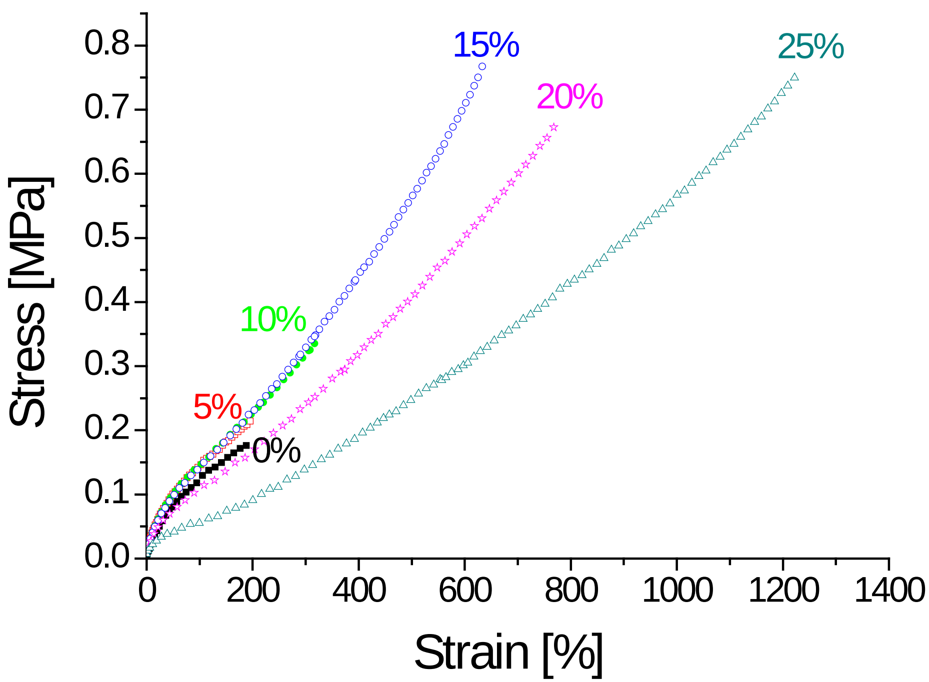


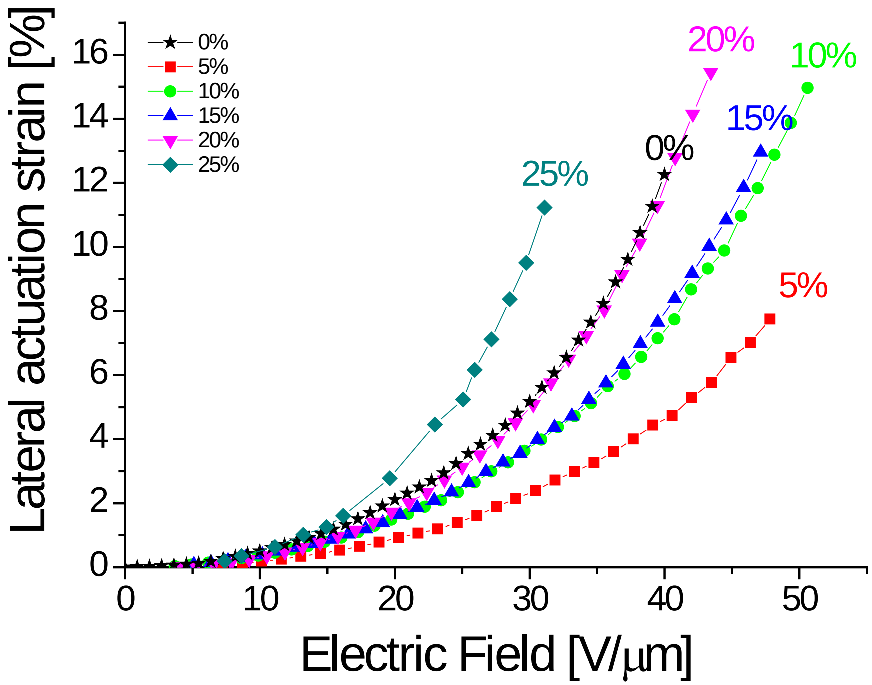


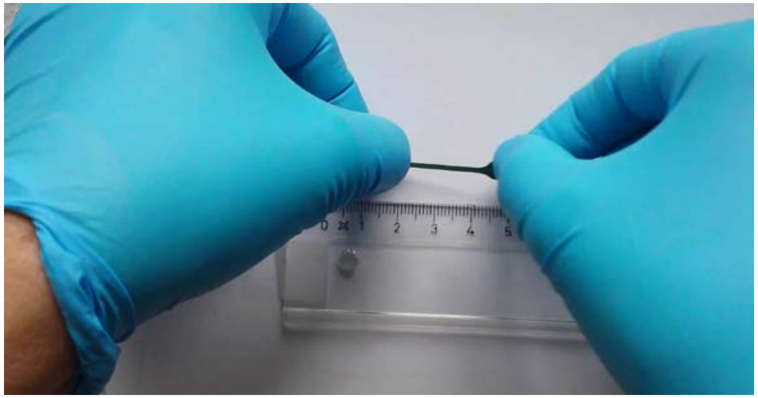
	ε	Y (kPa)	Strain (50V/µm)	Breakdown (V/µm)	ε/Y
PDMS	2.3	570	4.8 %	66.2	3.97
Composite	3.3	532	10 %	53.6 V/µm	6.2

D. M. Opris, M. Molberg, C. Walder, Y. S. Ko, B. Fischer, F. A. Nüesch, *Adv. Funct. Mater.* **2011**, *21*, 3531-3539; M. Molberg, D. Crespy, P. Rupper, F. Nüesch, J.-A. E. Månson, C. Löwe, D. M. Opris, *Adv. Funct. Mater.* **2010**, *20*, 3280-3291.

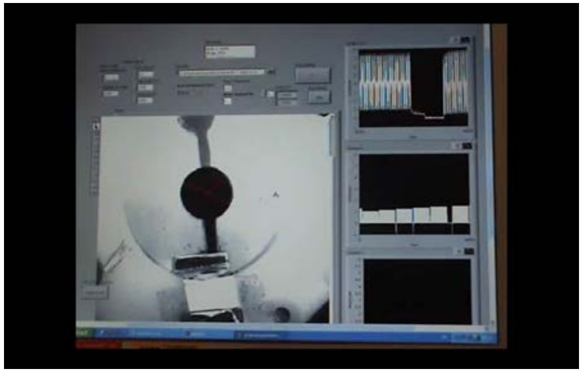
PDVB@PANI in PDMS





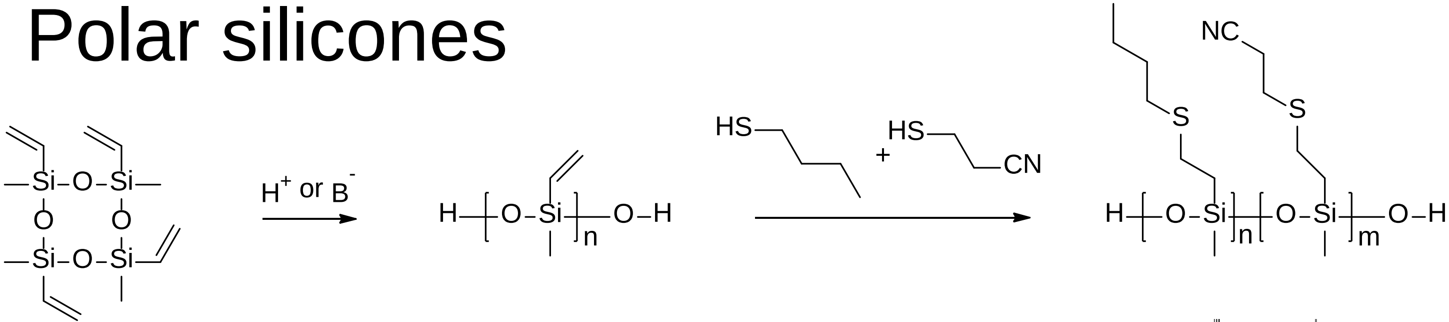


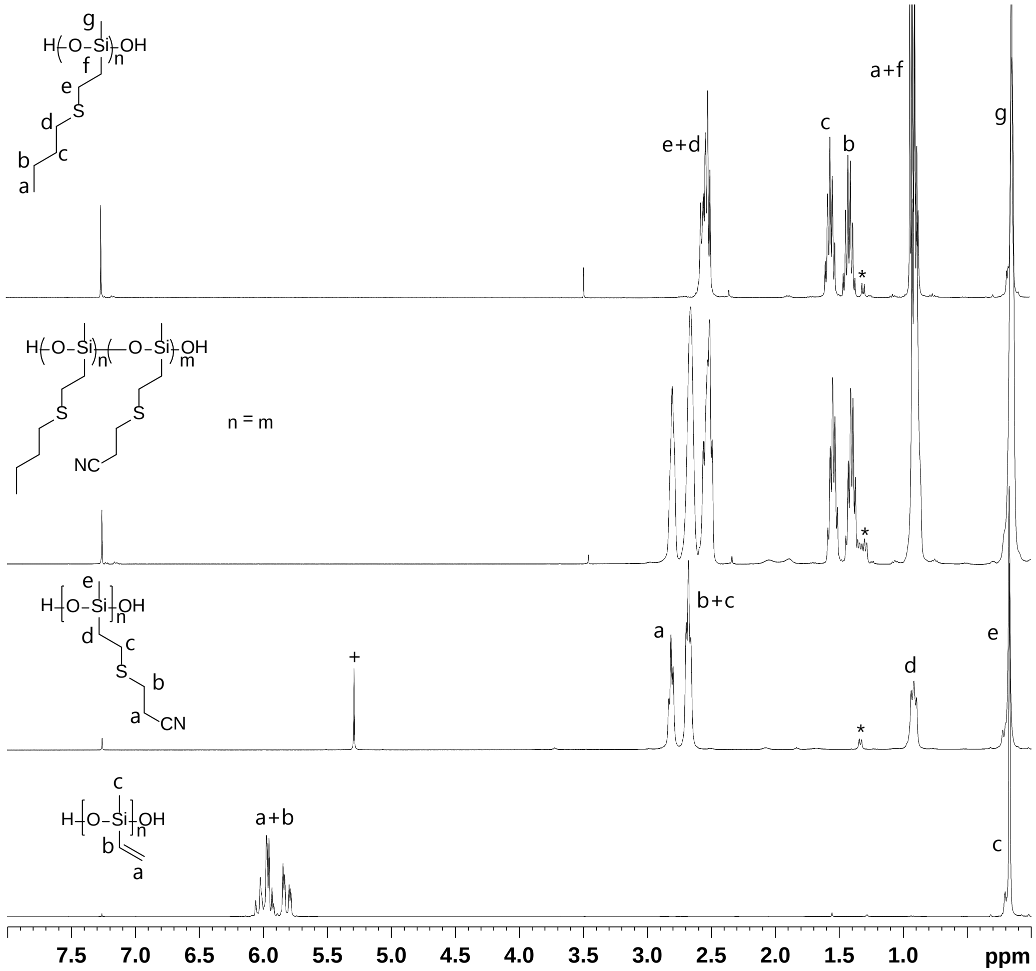
D_{20} at 5 Hz and 3300 V (42.8 V/µm)



D. M. Opris, M. Molberg, C. Walder, Y. S. Ko, B. Fischer, F. A. Nüesch, *Adv. Funct. Mater.* **2011**, *21*, 3531.

Polar silicones





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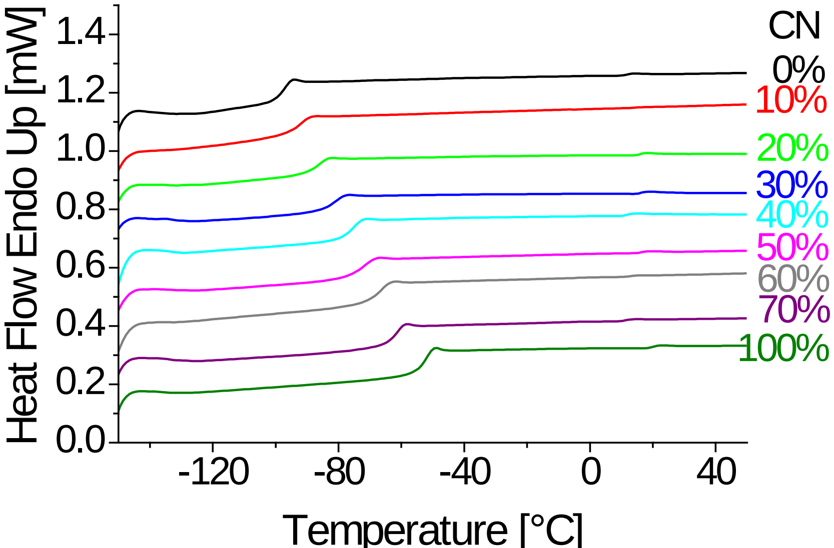
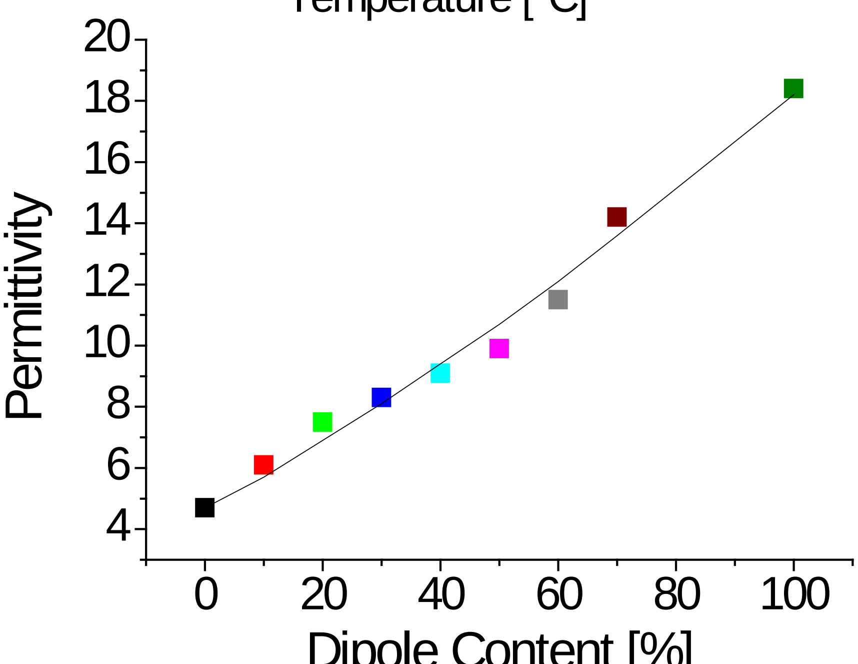
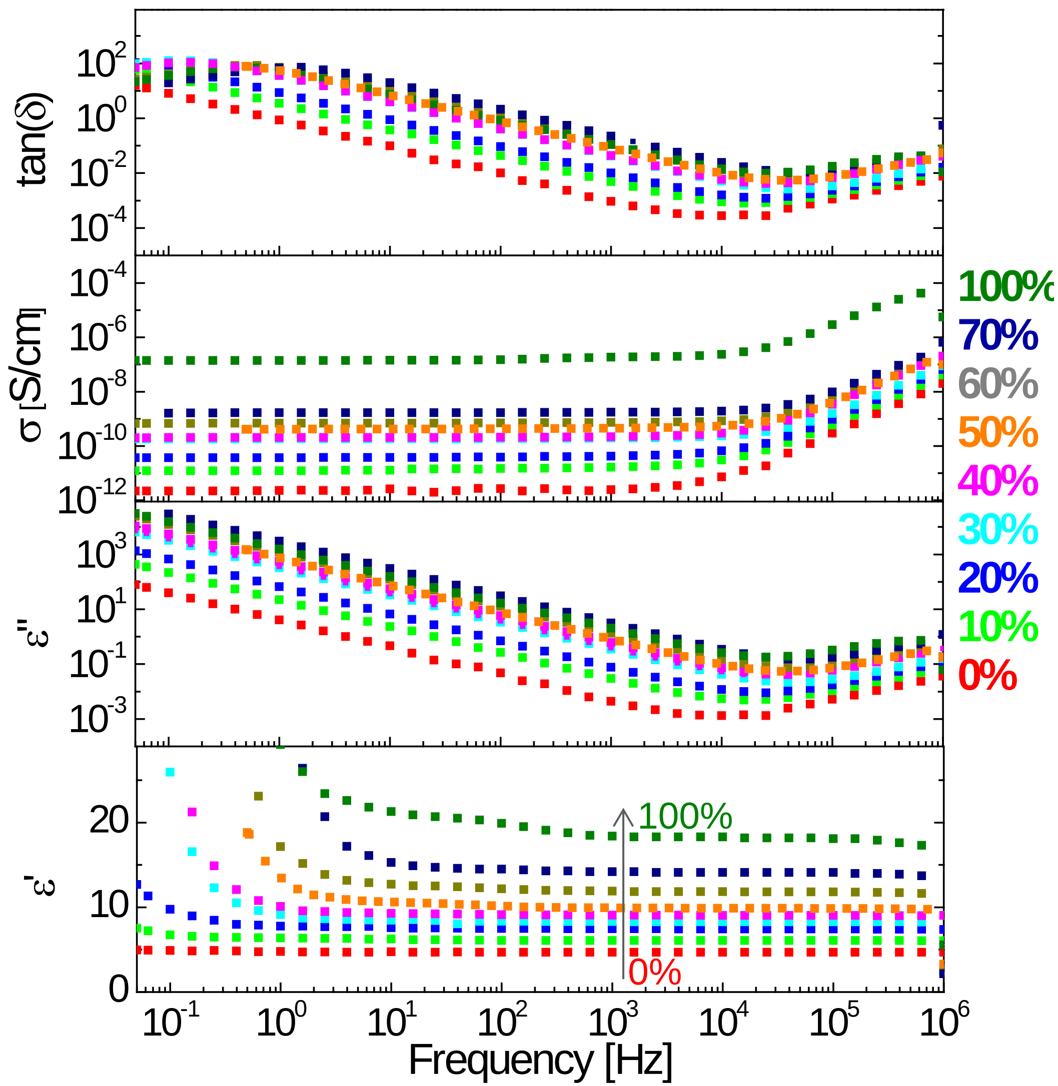
D.M. Opris, Empa

Thermal and mechanical properties of polar silicones

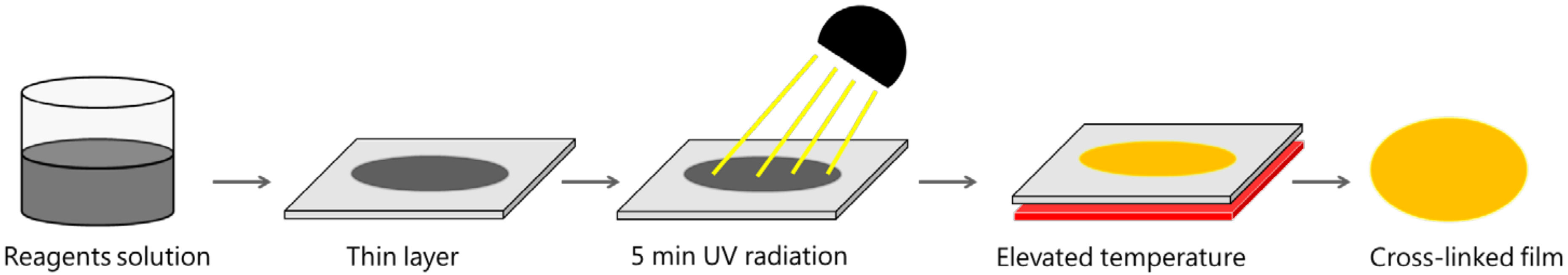


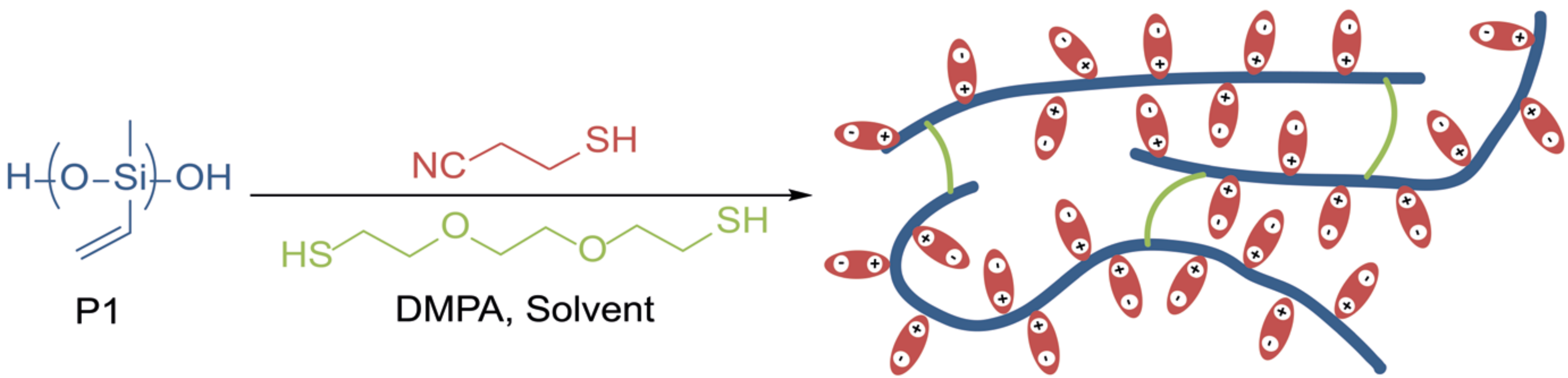




S. J. Dünki, M. Tress, F. Kremer, S. Y. Ko, F. A. Nüesch, C.-D. Varganici, C. Racles, D. M. Opris, RSC Adv., **2015**, 5, 50054

Cross-linking via side-groups





S. J. Dünki, Y. S. Ko, F. A. Nüesch, D. M. Opris, Adv. Funct. Mater. **2015**, 25, 2467–2475
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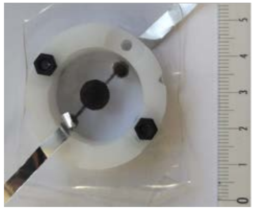
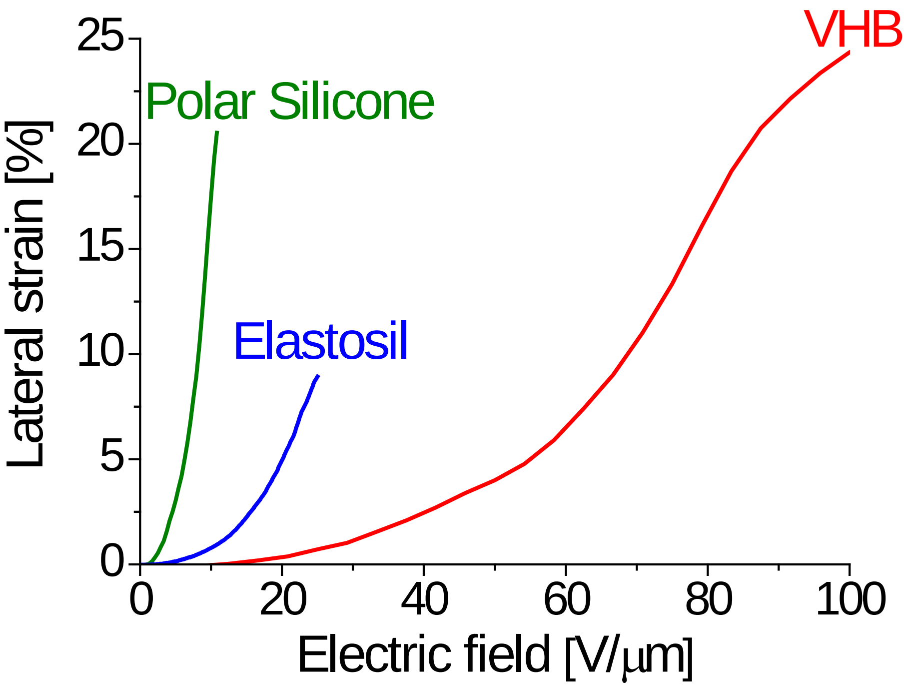
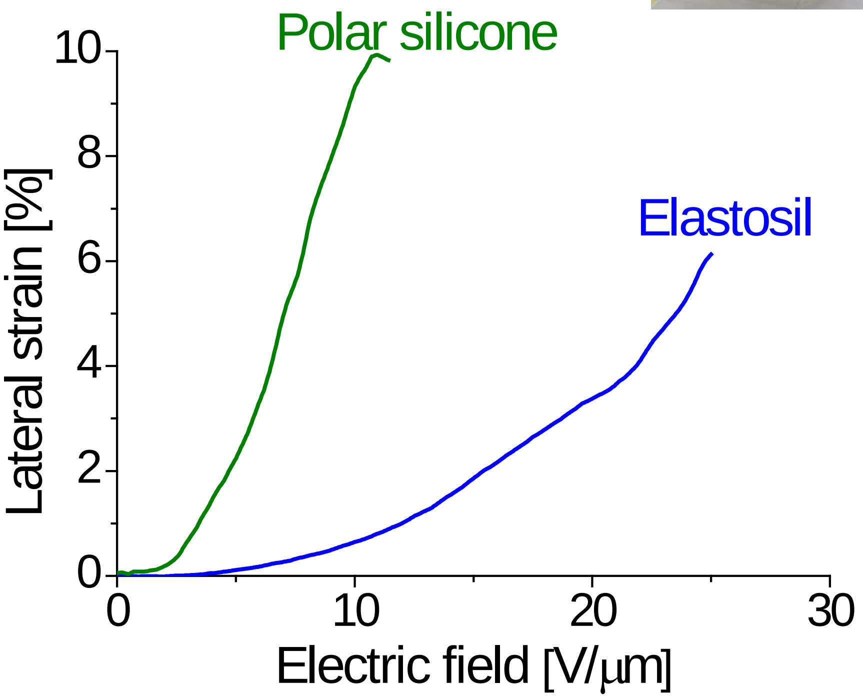
Electromechanical performance

~30% prestrain for polar silicone
~30% prestrain for Elastosil
~300% prestrain for VHB

0% prestrain





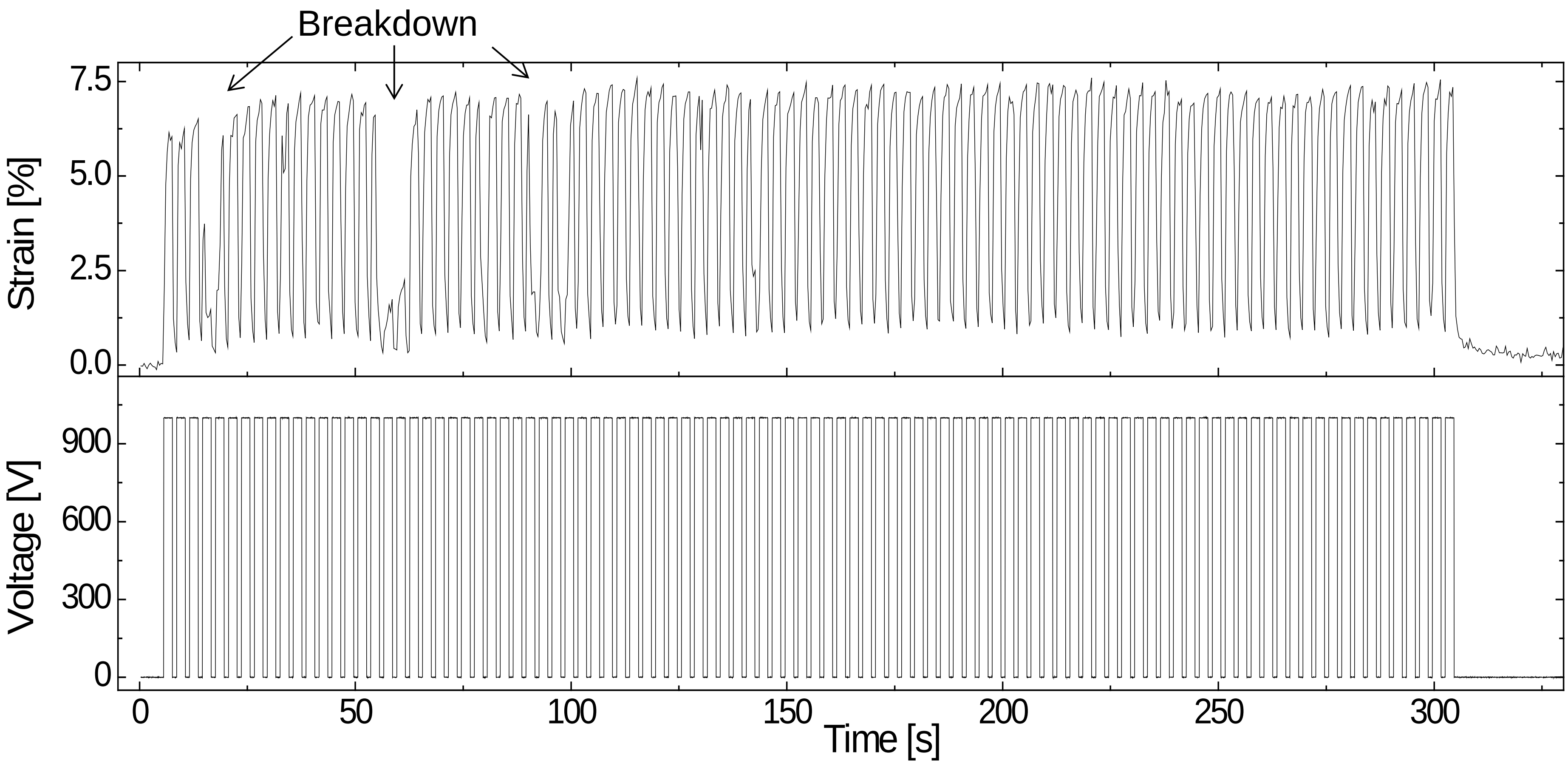


	10.8 V/µm
Polar silicone	20.5% strain
Elastosil	0.9% strain
VHB	0% strain

	10 V/µm
Polar silicone	10% strain
Elastosil	0.6% strain

S. Dünki, Y. S. Ko, F. A. Nüesch, D. M. Opris, *Adv. Funct. Mater*, **25** (16), 2467-2475, 2015.

Self-repairing properties



100 cycles, 0.33 Hz, 8.3 V/μm

H. Stoyanov, P. Brochu, X. Niu, C. Lai, S. Yun, Q. Pei, *RSC Adv.* **2013**, *3*, 2272-2278; W. Yuan, H. Li, P. Brochu, X. Niu, Q. Pei, *Intern. J. Smart Nano Mater.* **2010**, *1*, 40-52; W. Yuan, L. Hu, Z. Yu, T. Lam, J. Biggs, S. M. Ha, D. Xi, B. Chen, M. K. Senesky, G. Grüner, Q. Pei, *Adv. Mater*. **2008**, *20*, 621-625; S. Hunt, T. G. McKay, I. A. Anderson, *Appl. Phys. Lett.* **2014**, *104*, 113701.

Conclusions

- Electric permittivity can be increased by filler particles at the expense of decreased breakdown field
- Elasticity and softness can be maintained even at high loadings (30%)
- Strain at break is increased by the fillers
- Dipole functionalization allows to achieve polymers with $\varepsilon > 18$
- Glass transition temperture still below - 50°C
- Actuation threshold for polar silicone elastomers well below 10 V/μm

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