ESPCI PARIS | PSL

Thesis defense

Paris, 19 October, 2018

Soft dielectric materials for energy harvesting and sensing applications

Presented by

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ED 397

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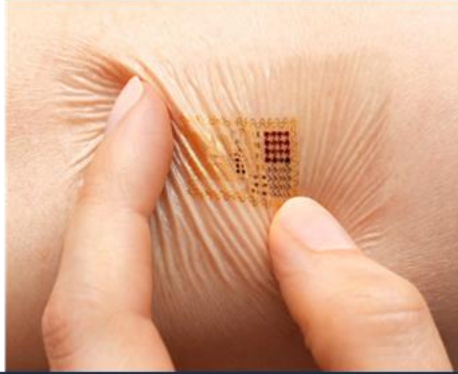
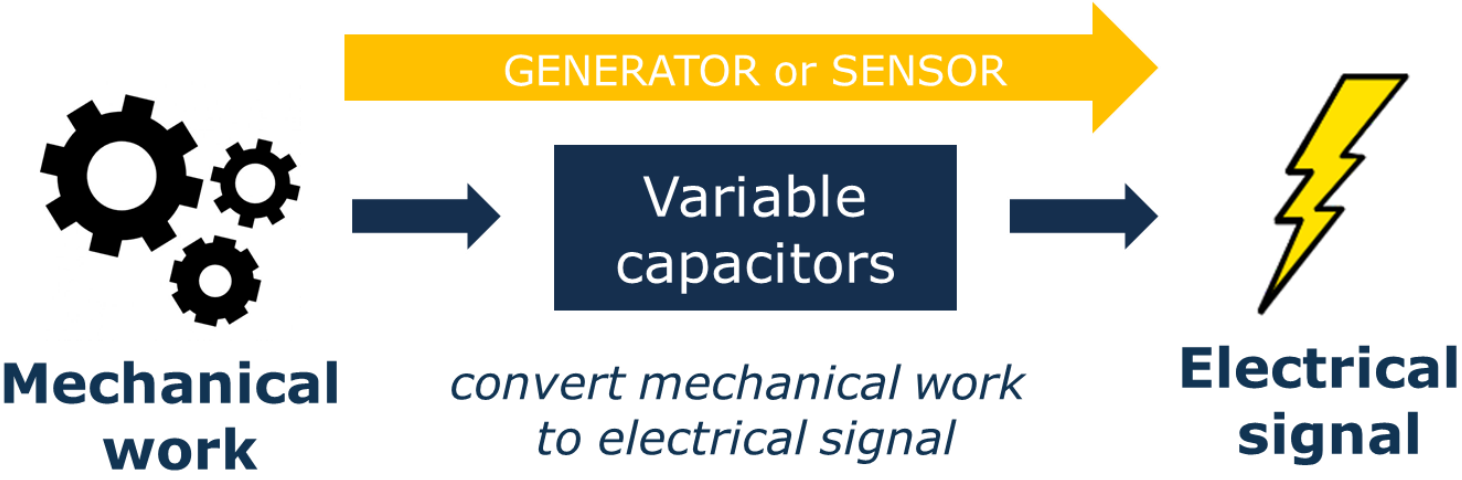
Towards flexible electronics

Human-machine interactions

Energy harvesting



Sensing

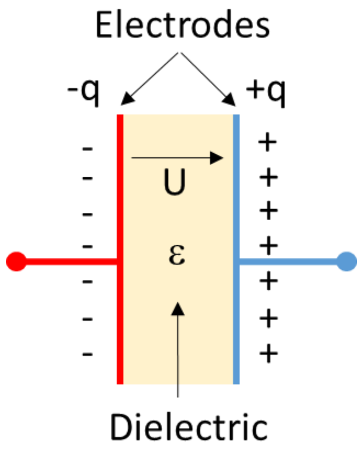


GENERATOR or SENSOR

Mechanical work → Variable capacitors → **Electrical signal**

convert mechanical work to electrical signal

How to make variable capacitors ?

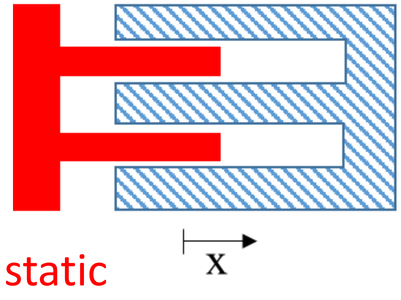


$$C = \frac{\varepsilon\varepsilon_0 S}{d}$$

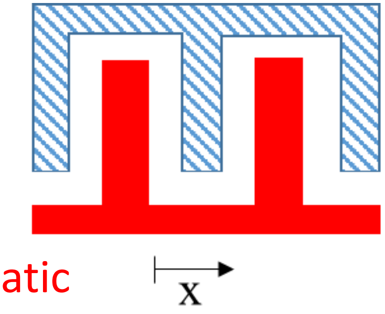
$$\Delta C$$

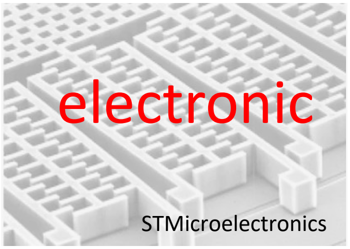
- Surface variation ΔS
- Distance variation Δd
- Permittivity variation $\Delta\varepsilon$

ΔS



Δd





➔ Rigid structure
➔ Low C (air)

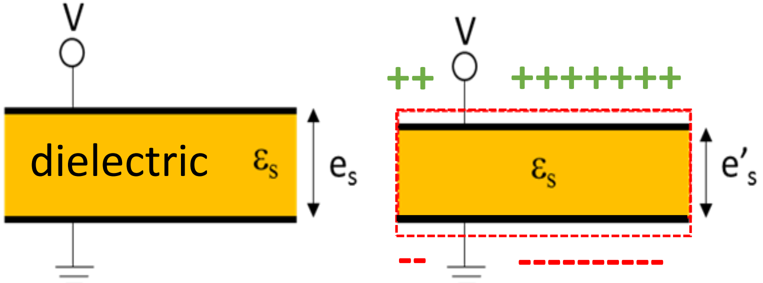
$\Delta\varepsilon$ Electrostrictive polymers

Electrostrictive polymers

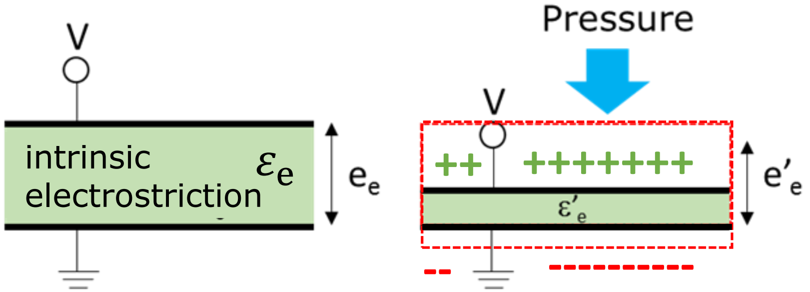
$$S = M^* E^2 \qquad M^* = M_{Maxwell} + M_{intrinsic} = M_{Maxwell} + \frac{\varepsilon_0 \Delta\varepsilon}{2\tau}$$

M*: apparent electrostrictive modulus ; **τ**: stress ; **ε**: dielectric permittivity ;

S: strain **; E:** Electric field

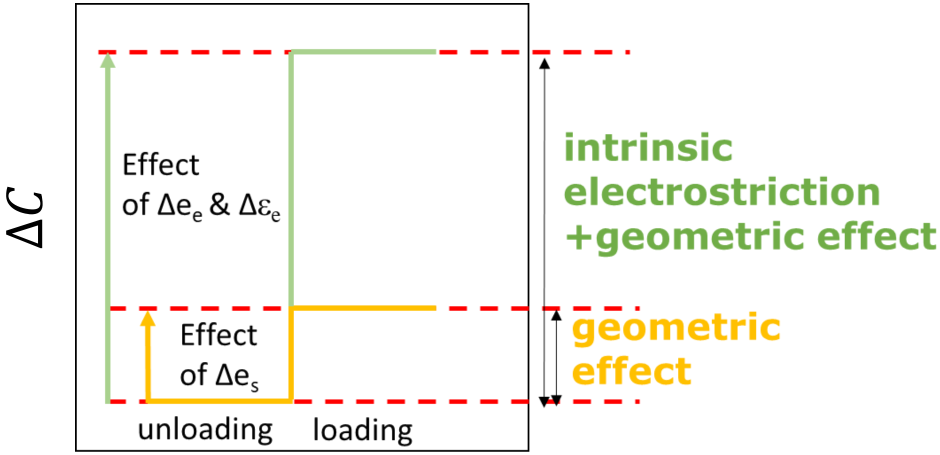


$$\varepsilon_{dielectric} \Rightarrow \varepsilon_{dielectric}$$



$$\varepsilon_{electro} \Rightarrow \varepsilon'_{electro}$$

High ΔC by material and geometrical effects

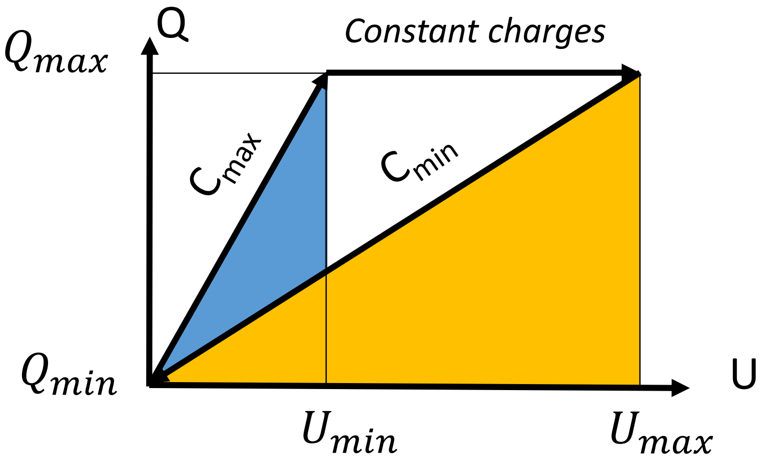


Interest in large capacitance variations with soft materials

- *Energy harvesting applications:* *mechanical energy* $\xrightarrow{\eta}$ *electrical energy*

$$E = \frac{1}{2} Q \times U$$

$$Q = C \times U$$

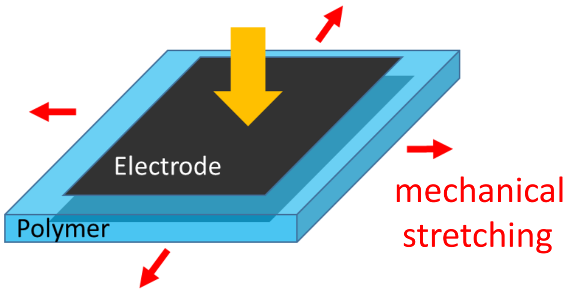


$$\Delta\ \text{Energy} = \frac{1}{2} U_{max} U_{min}\ \Delta C$$

Larges ΔC with low mechanical energy = high efficiency + high energy

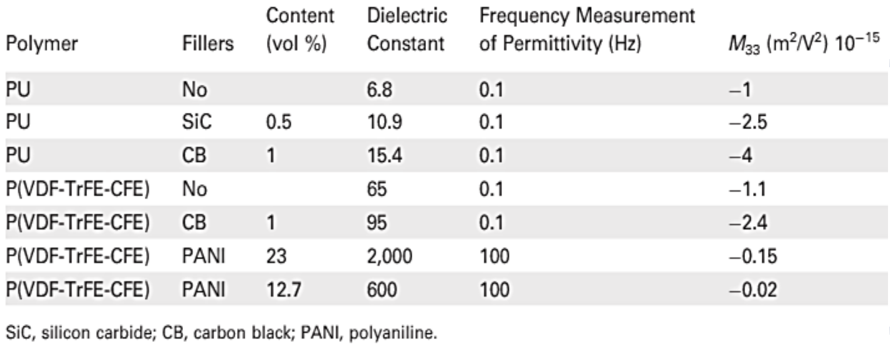
- *Sensing applications :* *capacitive sensors*

$$\text{Sensitivity} = \frac{\Delta C}{C_0 \times P}$$



Large ΔC with low mechanical pressure P = high sensitive sensor
High C : no amplification required

Electrostrictive polymers in energy harvesting



Polymer	Fillers	Content (vol %)	Dielectric Constant	Frequency Measurement of Permittivity (Hz)	M_{33} (m^2/V^2) 10^{-15}
PU	No		6.8	0.1	–1
PU	SiC	0.5	10.9	0.1	–2.5
PU	CB	1	15.4	0.1	–4
P(VDF-TrFE-CFE)	No		65	0.1	–1.1
P(VDF-TrFE-CFE)	CB	1	95	0.1	–2.4
P(VDF-TrFE-CFE)	PANI	23	2,000	100	–0.15
P(VDF-TrFE-CFE)	PANI	12.7	600	100	–0.02

SiC, silicon carbide; CB, carbon black; PANI, polyaniline.

Y(PU) ~ 40 MPa

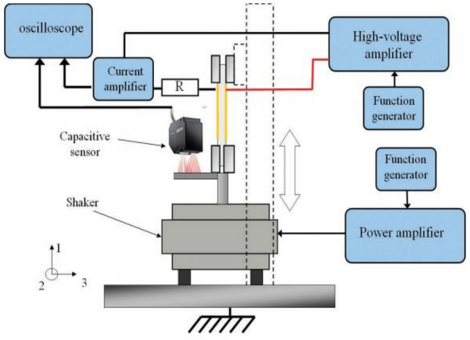
Y(PVDF) ~ GPa

High Young's Modulus

$M \sim 10^{-15}\ m^2/V^2$

$\varepsilon_r = 2\ 10^3$

M Lallart, *Journal of polymer science* (**2011**)



Sample	f(Hz)	ε_r (at f)	Y (Mpa)	Electric field (V/µm)	Power density (µW/cm3)
PU	100	4,4	40	10	8
PU 1%C	100	7,5	40	10	172
P(VDF-TrFE-CFE)	100	42,0	250	10	5840
P(VDF-TrFE-CFE)+1%C	100	74,0	250	10	8240

$$\frac{2\pi}{\varepsilon'}(M^*Y)^2\ J.m^{-1}V^{-2}cycle^{-1}$$

FOM

$1\ 10^{-11}$

$3\ 10^{-10}$

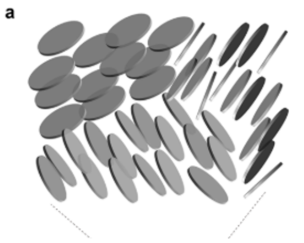
$1\ 10^{-8}$

$3\ 10^{-8}$

Power density ~ mW/cm³

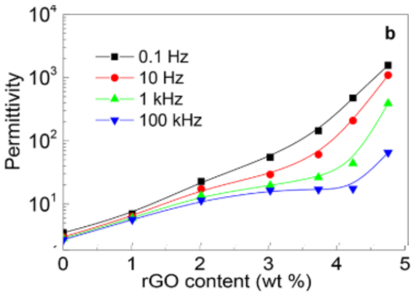
High electric field ~ 10 V/µm

M Lallart, *Journal of applied physics* (**2010**)

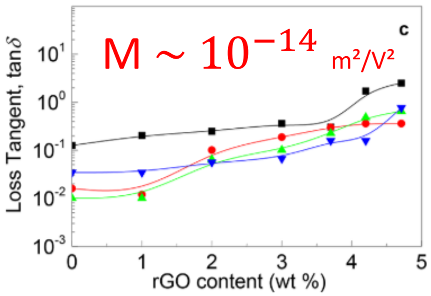


PDMS + nematic graphene oxide

Y(PDMS) ~MPa

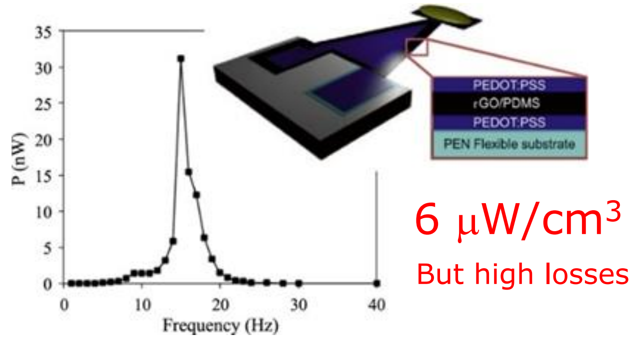


J Yuan, *ACS Nano* (**2018**)



$M \sim 10^{-14}$ m^2/V^2

High conductivity

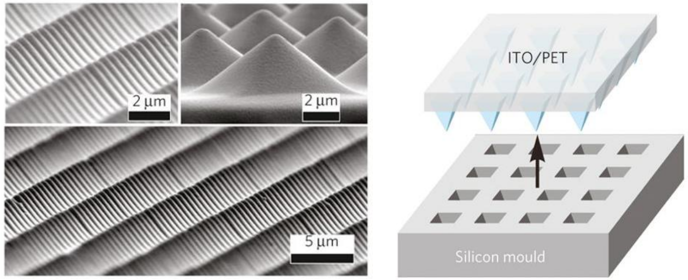


6 µW/cm³

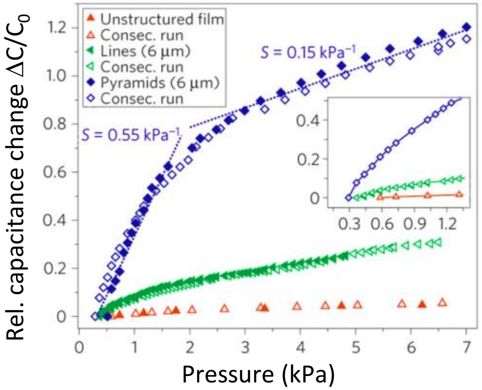
But high losses

H Nasser, *Nano Energy* (**2018**)

Current strategies for highly sensitive materials



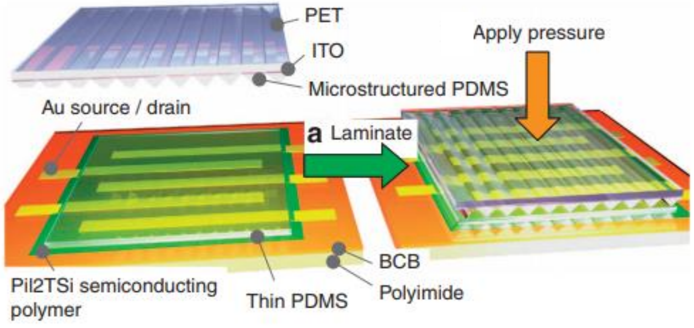
Bao et al. Nature Materials (**2010**)



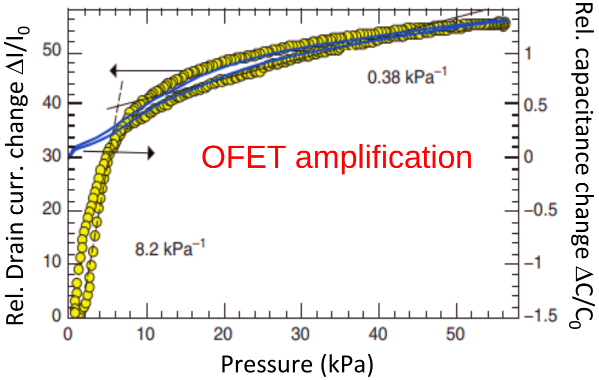
Surface microstructuration

➔ Touchy process

$$\frac{\Delta C}{PC_0} = 0.55\ kPa^{-1}$$



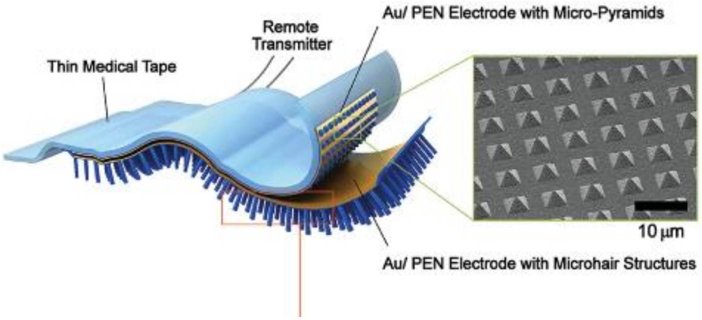
Bao et al. Nature Communications (**2013**)



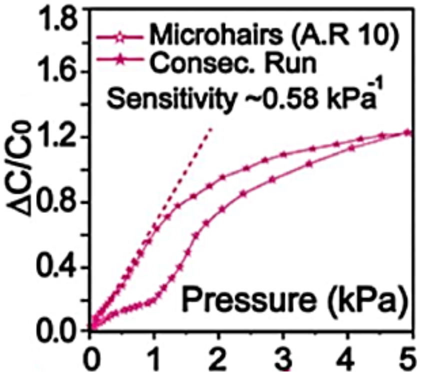
Signal amplification

➔ 120 V, Limited integration

$$\frac{\Delta I}{PI_0} = 8.20\ kPa^{-1}$$



Bao et al. Advanced Materials (**2014**)



Microhairs structure

➔ Limited reproductibility

$$\frac{\Delta C}{PC_0} = 0.58\ kPa^{-1}$$

Material by design

Challenges:

Electrical properties:

High permittivity, ε' *- low conductivity,* σ' *- Large electrostriction,* M

+ **Mechanical properties:**

Deformable - Low Young's modulus, Y

+ **Easy manufacturing:**

Green process - Large scale - Reliability

Our strategy

composites

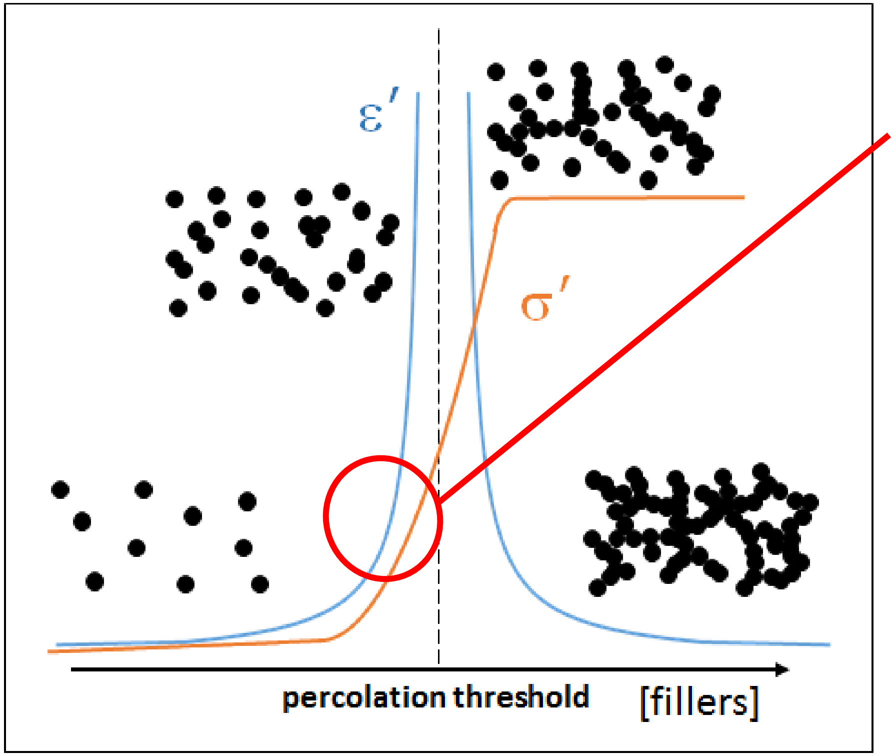
=

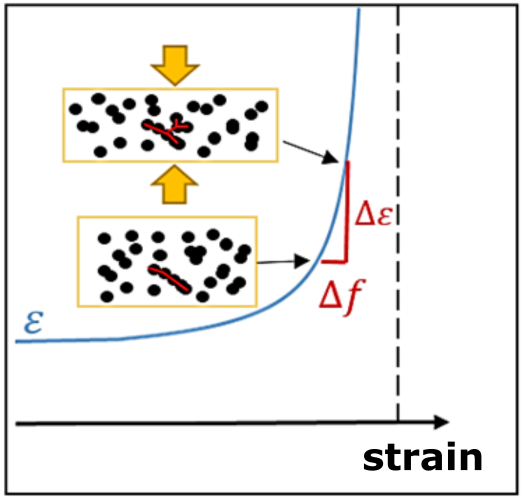
conductive fillers + porous elastomeric matrix

Our strategy

Interest in conductive fillers for high permittivity and electrostriction

- ↗ ε' by Maxwell-Wagner effect (interfacial polarization)
- ↗ **M** by local change in concentration under strain
- → σ' by beeing before the percolation





local change in concentration under strain

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

$$\sigma' = \sigma_{DC} + \omega\varepsilon''$$

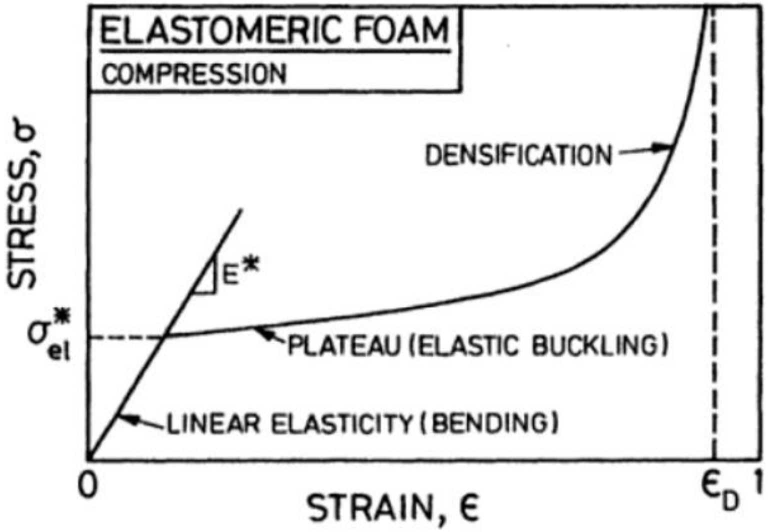
$$\tan\delta = \frac{\sigma'}{\omega\varepsilon'} \ll 1$$

$$M = \frac{\varepsilon_0 \Delta\varepsilon}{2\tau}$$

Alan Luna, Mickaël Pruvost et al., *Langmuir, 2017*

Our strategy

Interest in porous elastomeric matrix



Elastomeric foam

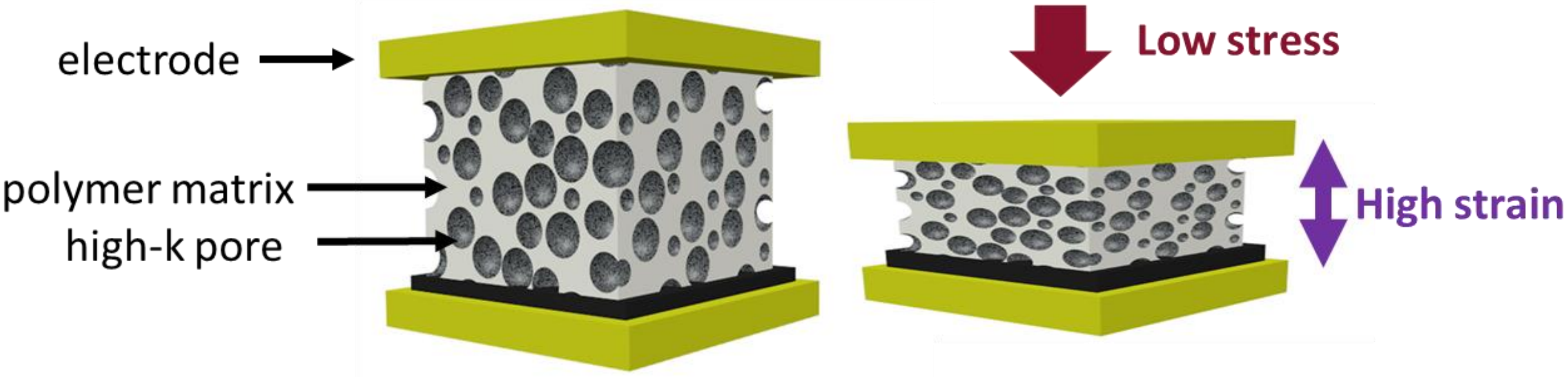
➔ porosity to highly deform the material at low stress

3 regimes :

- Linear elasticity (bending)
- Plateau (elastic buckling)
- Densification (bulk)

Michel Ashby, *Cellular Solid*, ***1988***

Ideal material



Contents:

Porous PDMS filled with carbon black:

➔Formulation path
➔Dielectric characterizations
➔Limits

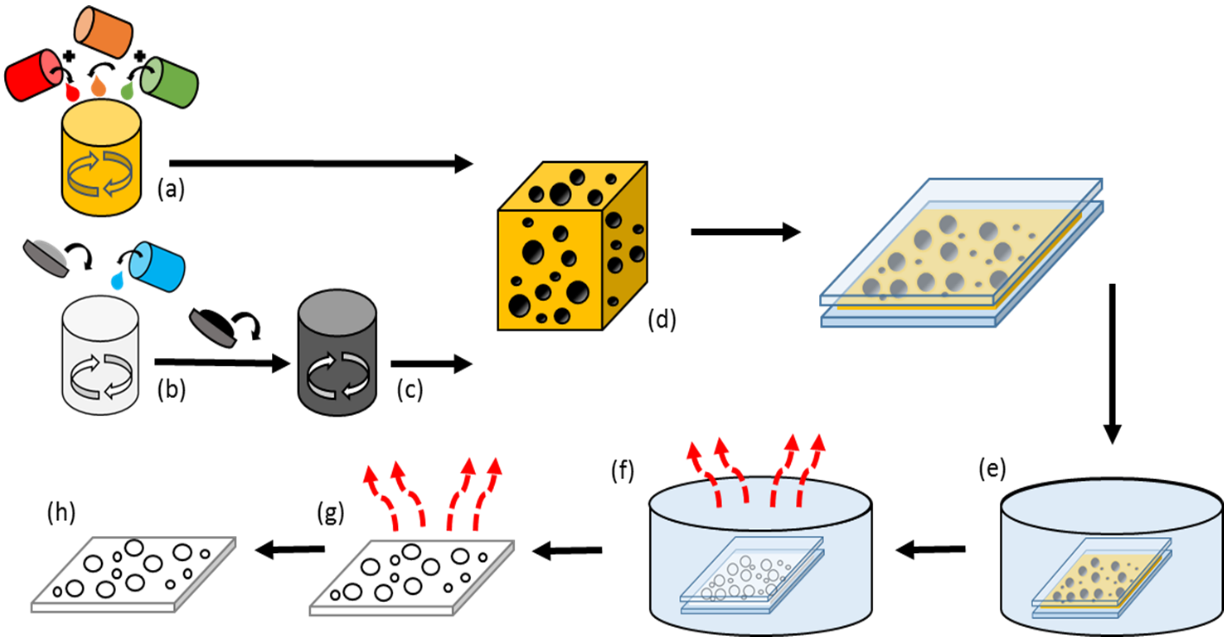
Bilayer composites:

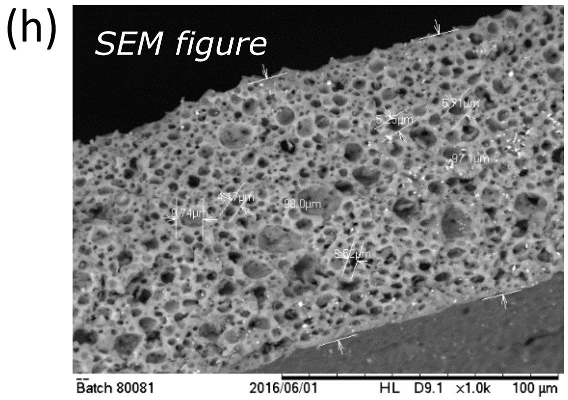
➔Theoretical model
➔Dielectric characterizations
➔Energy harvesting

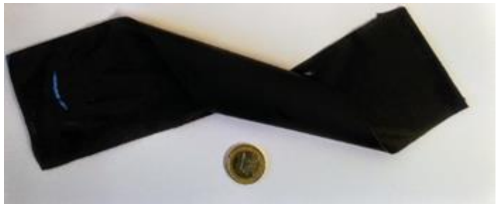
Applications:

➔Cantilever
➔Arterial pressure sensor

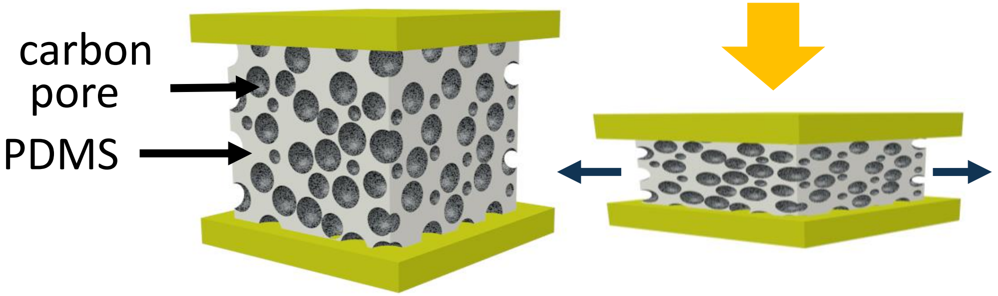
Formulation path: water in oil (W/O) emulsion







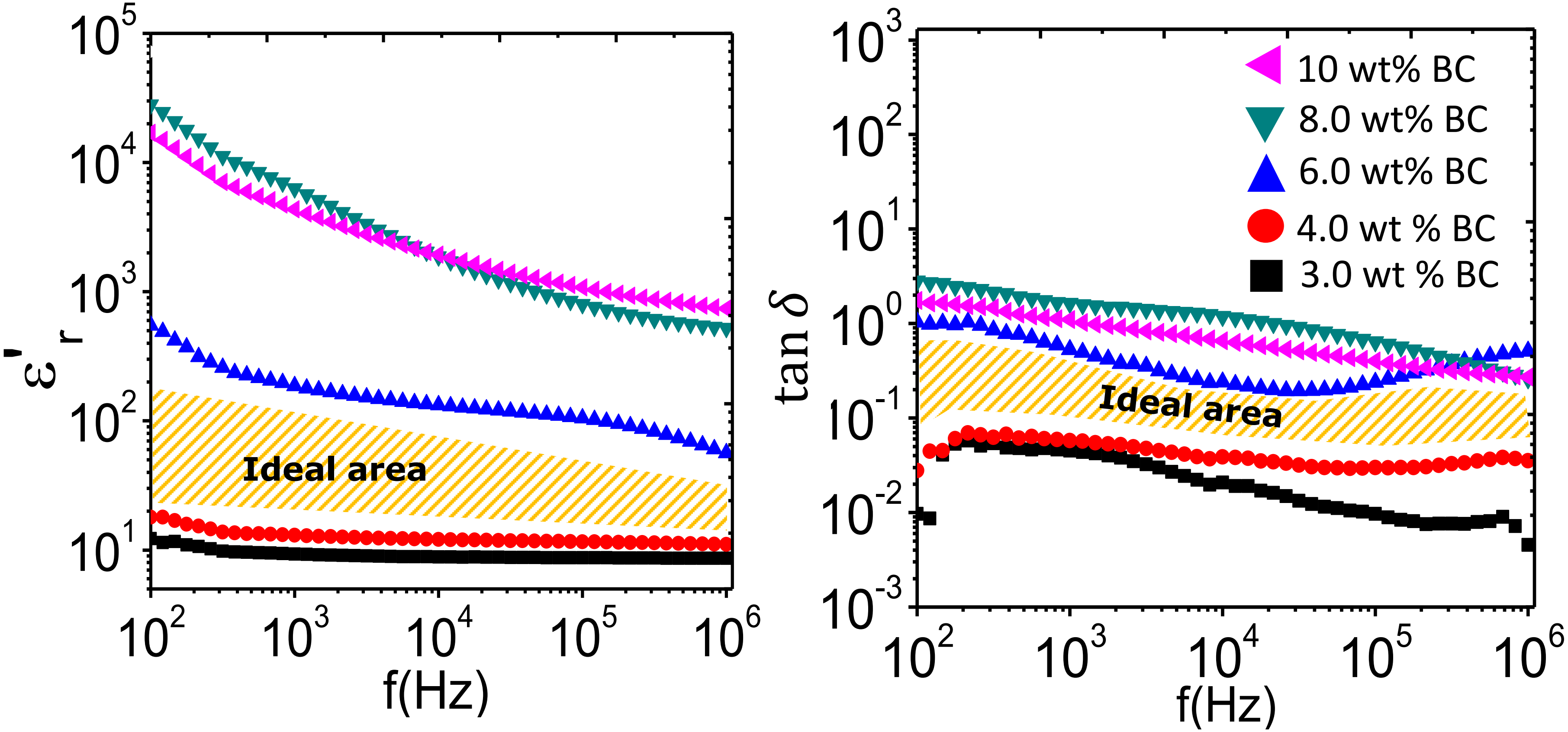
(a) Oil phase (70-40%)	(b)(c) Water phase (30-60%)
PDMS: 85 wt% Curing agent: 10 wt% Surfactant: 5 wt%	Black carbon: 3 – 8 wt% Arabic gum :5 wt% Water: adjusted wt%



DESIGN MATERIAL
- Isolated conductive pores
➔ No global conductive path
➔ Large fillers distribution
➔ Low Young's modulus

Dielectric response at rest vs frequency

water in oil emulsion (1:1 ratio)



ε_{PDMS} (100 Hz) ~ 2

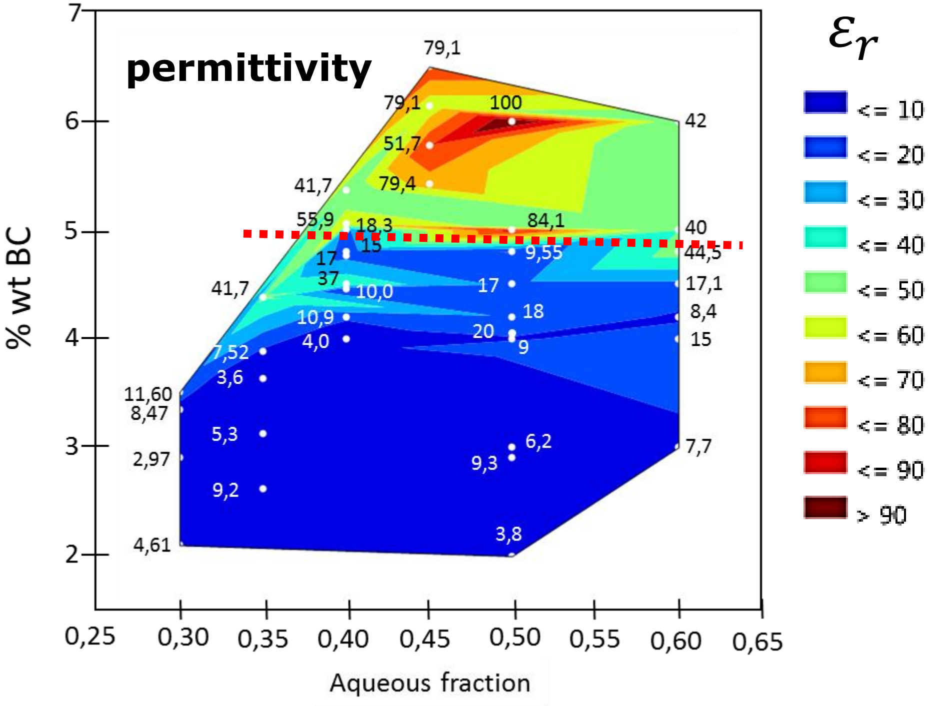
Ideal area
4 - 6 wt% CB

$\tan\delta : 0.01 - 1$
$\varepsilon_r : 20 - 500$
@ 100 Hz

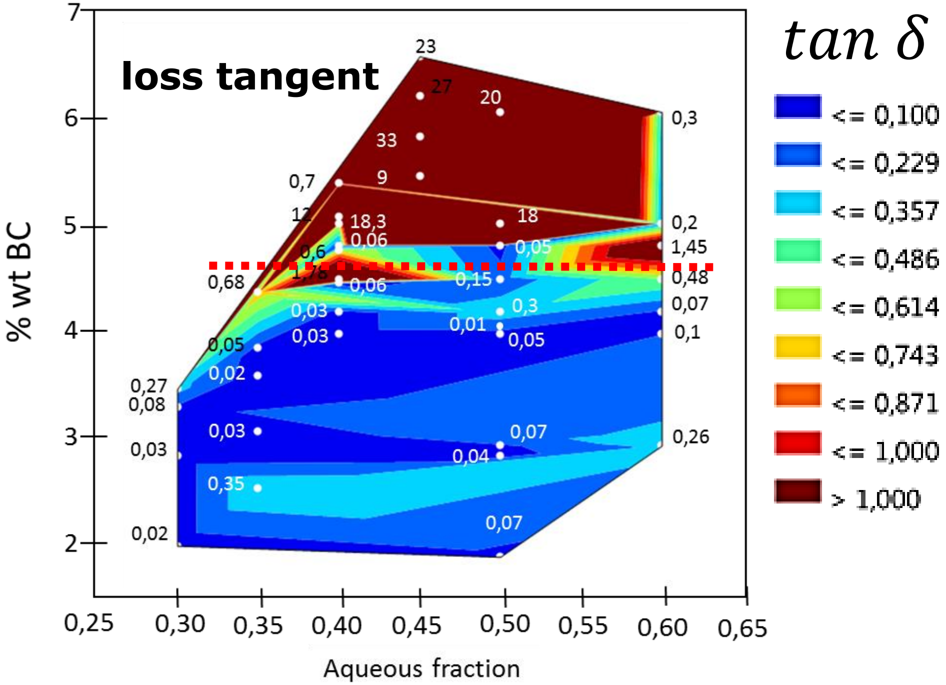
Influence of the formulation on dielectric properties

Carbon black ratio – aqueous fraction

@ 100 Hz



all-or-none ligne



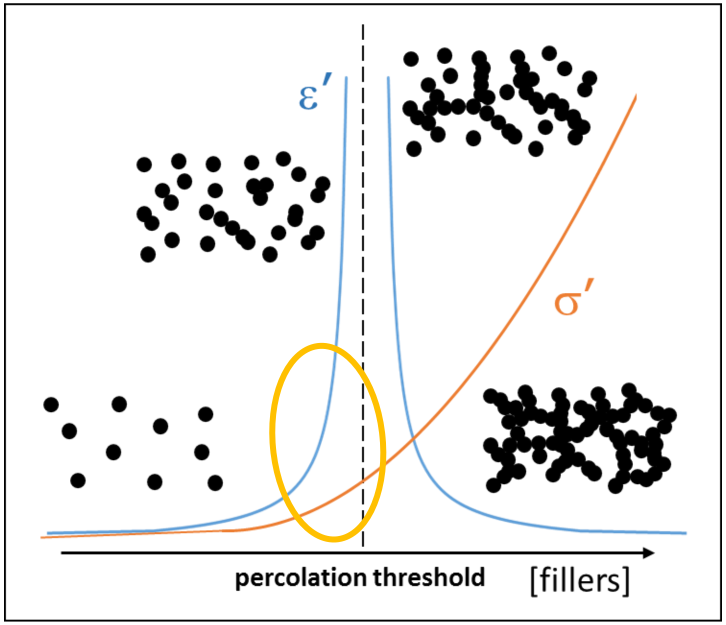
$\varepsilon_r \sim 30 - 40$ / $\tan\delta \sim 0.1$ - 0.2

Best compromises (permittivity versus conductivity) for self assembling material

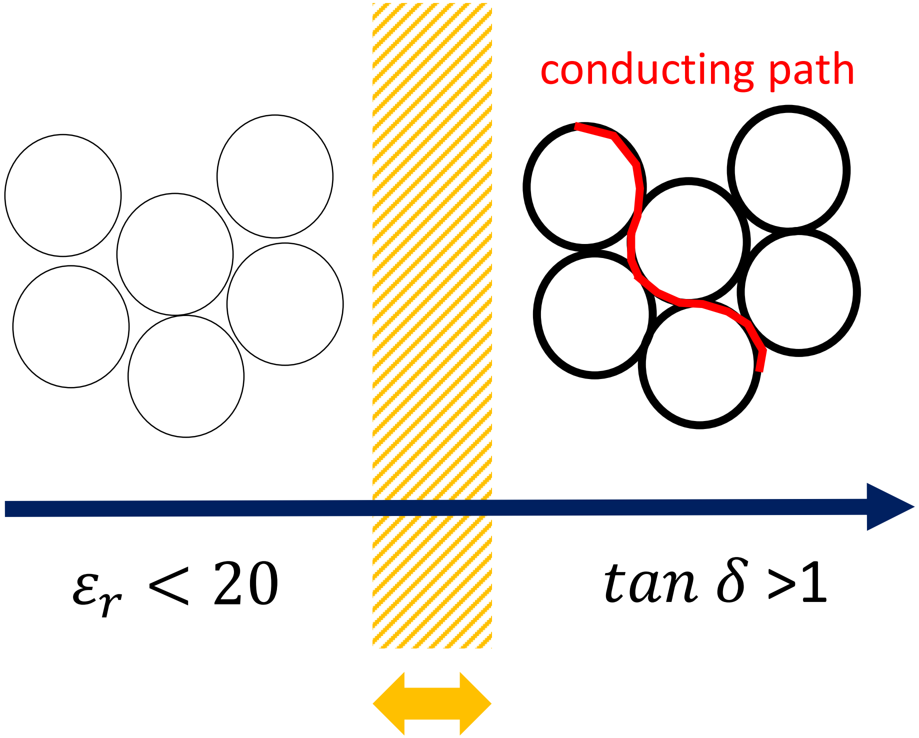
PVDF[1] : ε_r= 20, $\tan\delta$= 0.05

(1) Varma and Al, Express Polymer Letter, 2010

Limitations of W/O emulsion



- Limited increase
- Process dependant



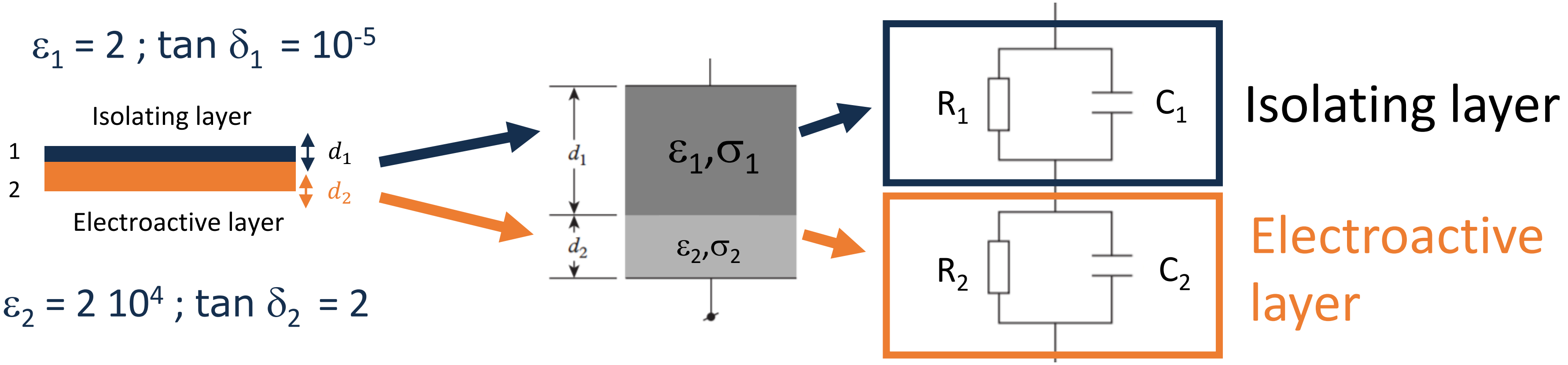
Narrow window

all-or-none behaviour

Bilayer composites

A way to remove conductivity

$\varepsilon_1 = 2$; $\tan \delta_1 = 10^{-5}$



Isolating layer

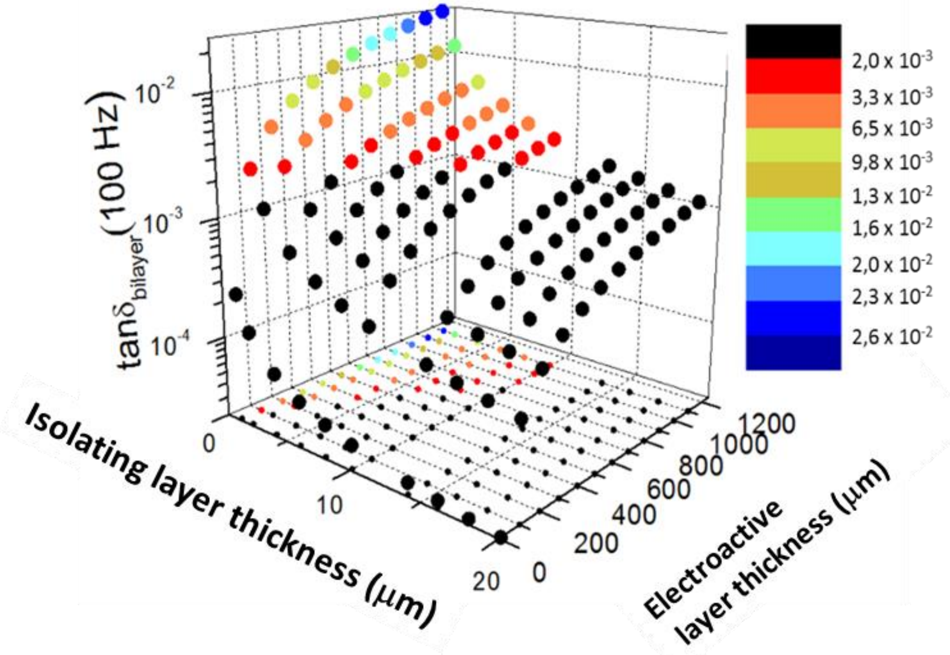
Electroactive layer

$\varepsilon_2 = 2\ 10^4$; $\tan \delta_2 = 2$

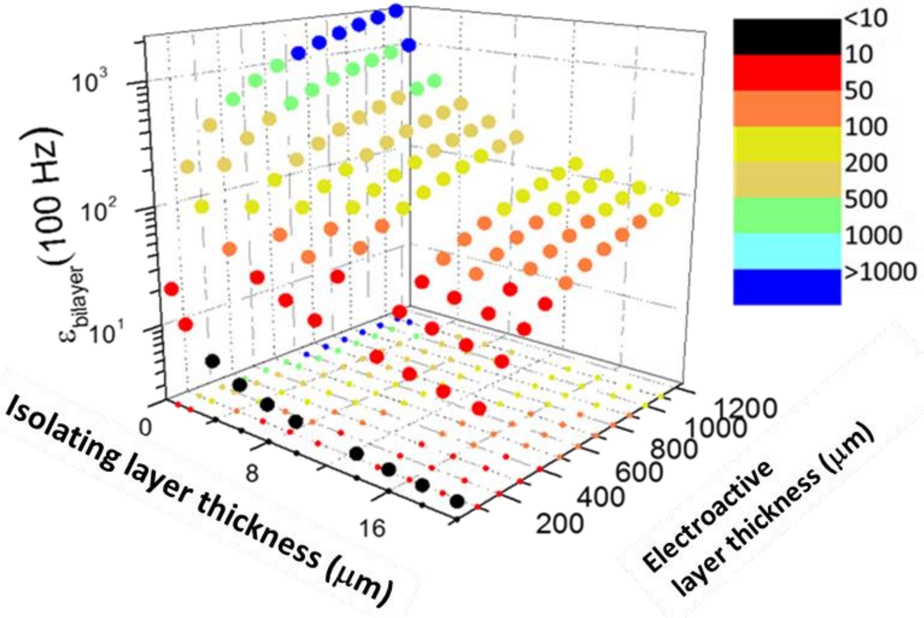
$\sigma_{bilayer} = f(\sigma_1, \sigma_2, d_1, d_2)$

$\varepsilon_{bilayer} = f(\varepsilon_1, \varepsilon_2, d_1, d_2)$

Loss tangent :

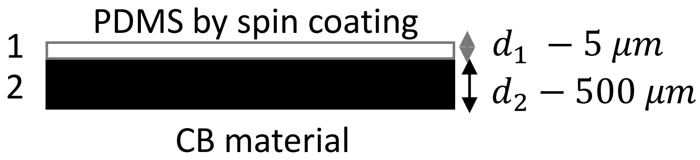


Permittivity :

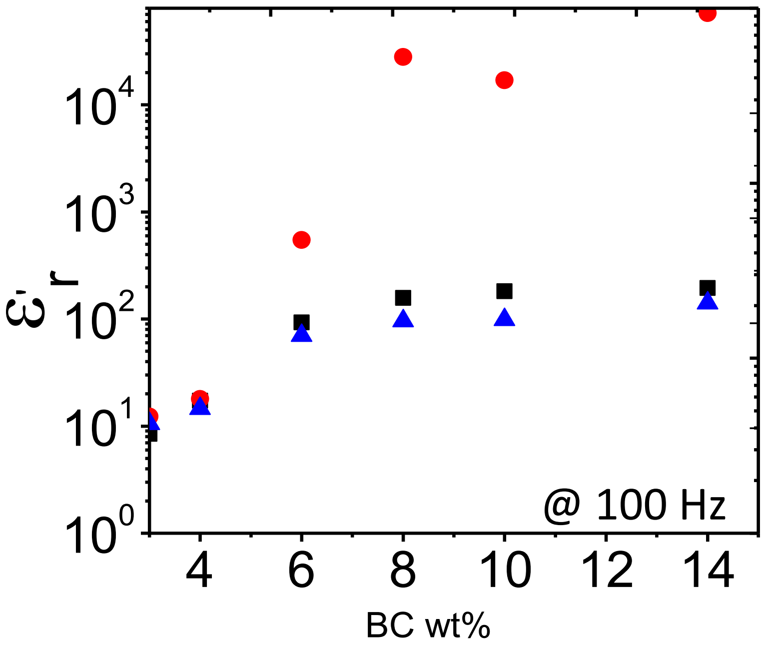


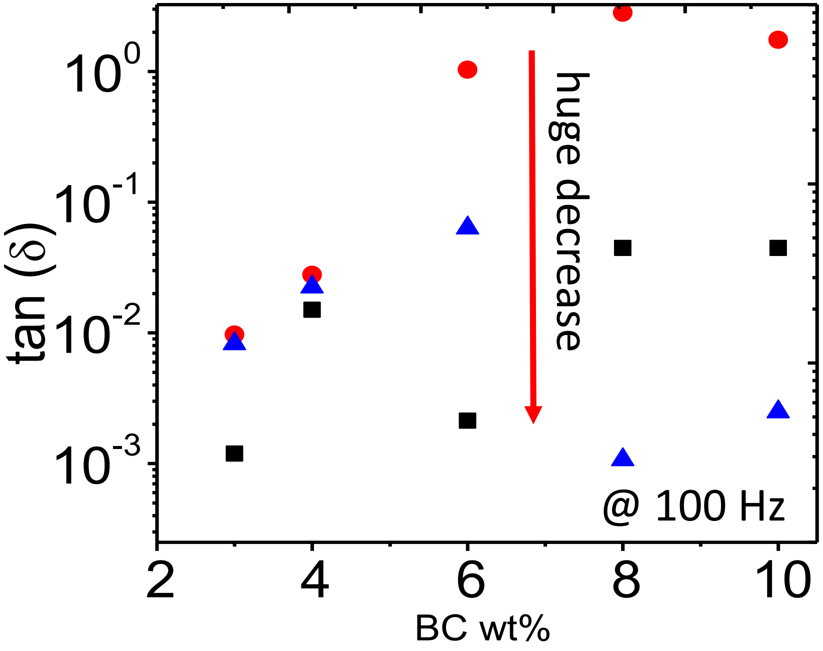
Dielectric responses at rest

Bilayer composites



■ bilayer material
● CB material
▲ theoretical predictions





Pure CB composite (10 wt%BC, 1:1)

$\varepsilon_{100\ \mathrm{Hz}} = 20\ 000$

$\mathrm{Tan}\ (\delta)_{100\ \mathrm{Hz}} = 1.5$

Isolating layer

Bilayer composite

$\varepsilon_{100\ \mathrm{Hz}} = 150$

$\mathrm{Tan}\ (\delta)_{100\ \mathrm{Hz}} = 0.05$

Mickaël Pruvost *et al. Multifunct. Mater*. 00 (2018)

Partial conclusion

new soft dielectric materials : composites PDMS/CB + isolating layer

Electrical properties:

$\varepsilon_{100\ \mathrm{Hz}} = 150$ and $\tan(\delta)_{100\ \mathrm{Hz}} = 0.05$

+ Mechanical properties:

$Y_{\mathrm{bulk}}\ (\mathrm{PDMS+CB}) \sim MPa$

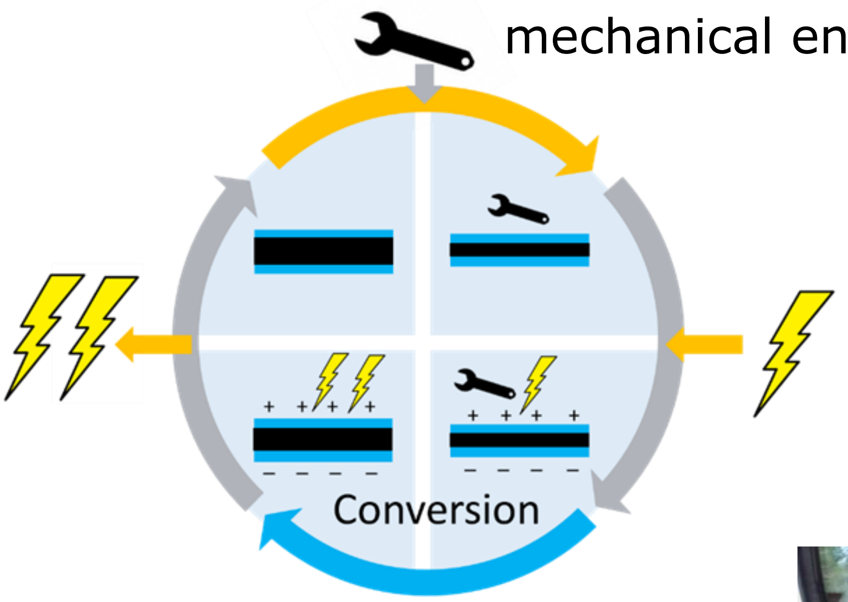
+ Easy manufacturing:

Emulsion path, no solvent, no reaction

Energy harvesting performances ?
What about their sensitivity to pressure ?

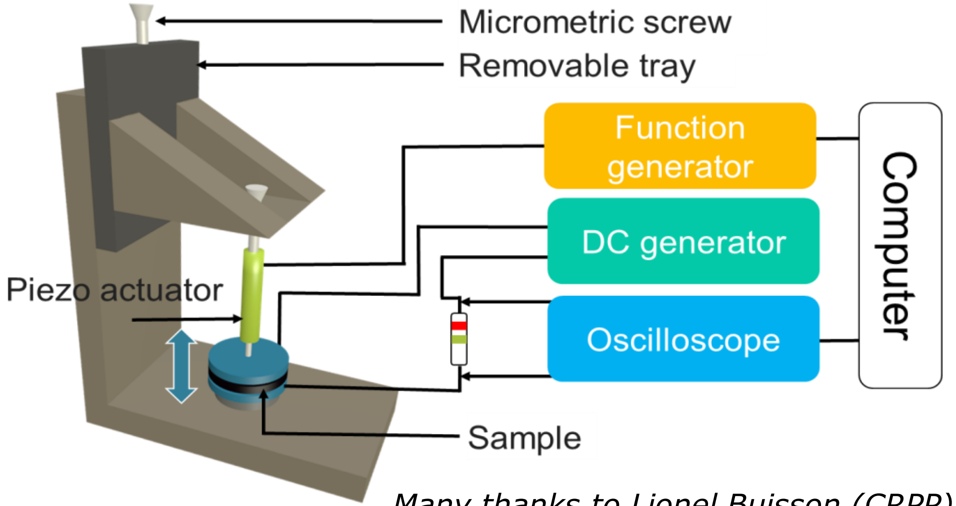
↳ Electrostriction

Experimental setup for energy harvesting estimation


mechanical energy

energy harvested

dielectric material
⇒ passive material
polarization required


Micrometric screw

Removable tray

Function generator

DC generator

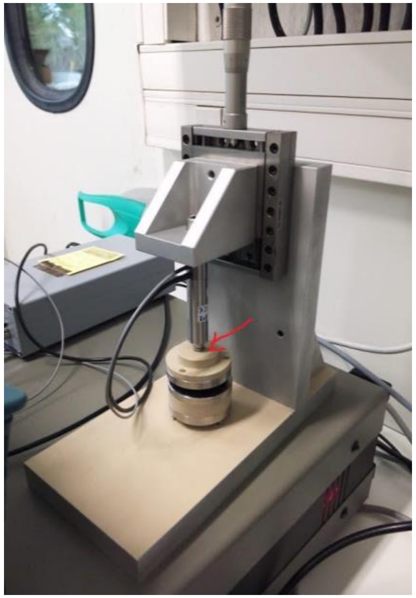
Oscilloscope

Computer

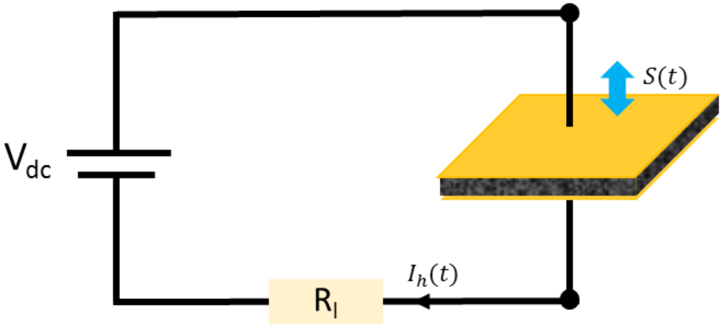
Piezo actuator

Sample

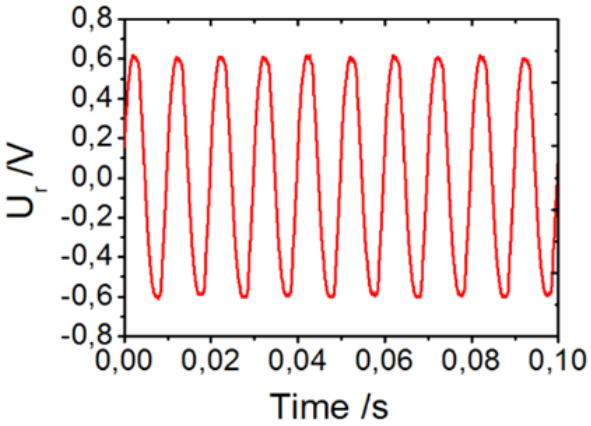
Many thanks to Lionel Buisson (CRPP)



Current modelling



Electrical signal at R_{load}



$$I_h(t) = -\frac{AR_l\varepsilon\varepsilon_0}{d}\frac{\partial I_h(t)}{\partial t} + 2\,A\,M_{33}^*\,Y\,E_{dc}\frac{\partial S(t)}{\partial t}$$

Electromechanical model

M Lallart, *Journal of applied physics* (**2010**)

Resolution with sinus strain and load resistance

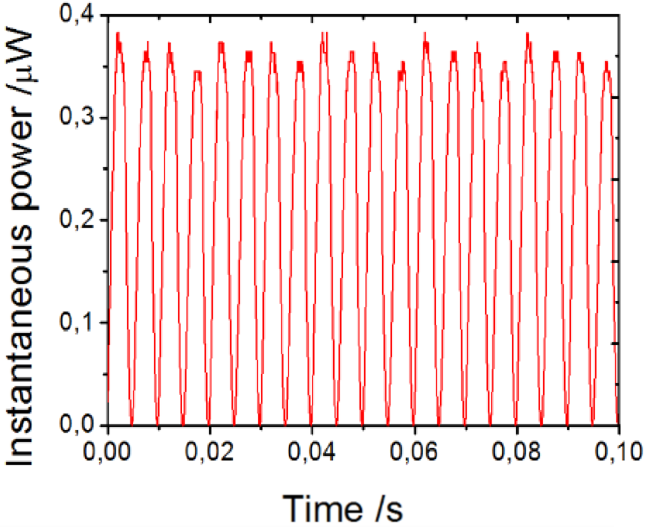
$$I_{h,max} = \frac{2\,M_{33}^*YE_{dc}\omega AS}{1+\left(\frac{\omega AR_l\varepsilon\varepsilon_0}{d}\right)^2}\left(\frac{\omega AR_l\varepsilon\varepsilon_0}{d}\,sin\left(\arctan\left(\frac{\omega AR_l\varepsilon\varepsilon_0}{d}\right)\right) + cos(\arctan\left(\frac{\omega AR_l\varepsilon\varepsilon_0}{d}\right))\right)$$

All the parameters are known, exepted M_{33}^* ➔ $I_{h,max}=f(E_{dc})$

	% CB	Ybulk (MPa)	M_{33}^* (m².V⁻²)
1:1 W/O ratio	8.0	1,40	$1{,}07\cdot10^{-15}$
	10.0	1,61	$8{,}46\cdot10^{-15}$

Mickaël Pruvost, Wilbert J. Smit, Cécile Monteux, Philippe Poulin, Annie Colin. Microporous electrostrictive materials for vibrational energy harvesting. *Multifunct. Mater*. 00 (**2018**)

Harvested power and its optimization

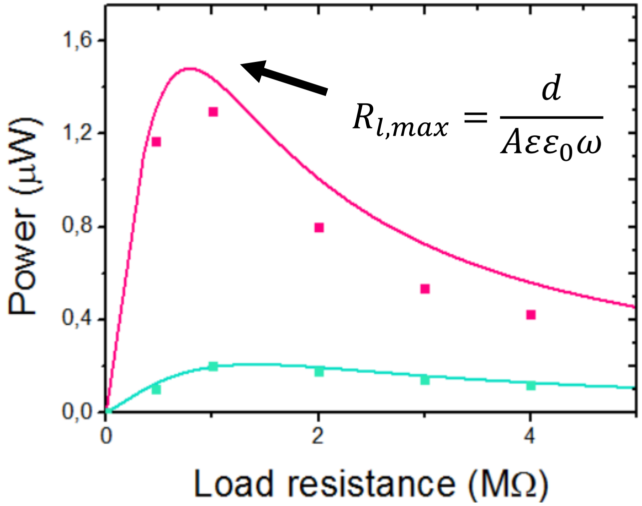


$$\bar{P} = \frac{R_l}{T}\int_0^T \mathrm{d}t\ \ I_h{}^2(t)$$

T : period of time
I_h: harvested current
R_l: load resistance

experimental measurements

$$\bar{P} = \frac{R_l}{2}\,\frac{(2\,M_{33}^{*}Y\boldsymbol{E_{dc}}\omega A S)^2}{1+\left(\frac{R_l\varepsilon\varepsilon_0\omega A}{d}\right)^2}$$



$$R_{l,max} = \frac{d}{A\varepsilon\varepsilon_0\omega}$$

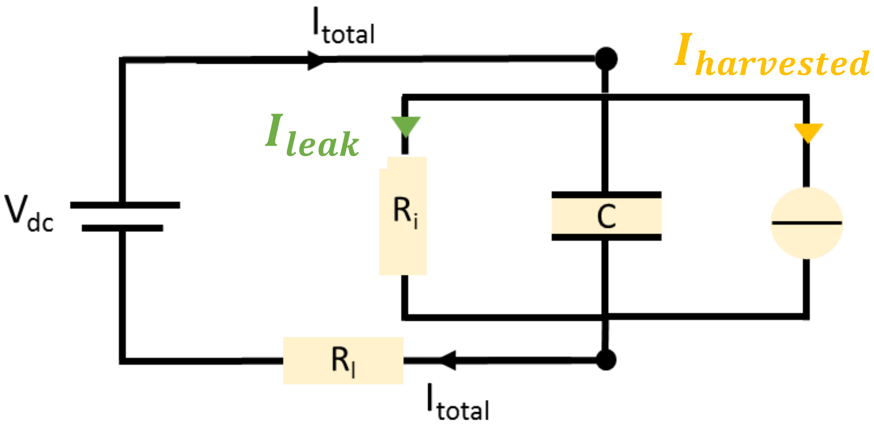
🟥 10 wt% CB
🟩 8 wt% CB

$$P(10\ wt\%) = 1.3\ \mu w$$

Raw power density
1.6 µw/cm^3

Which electrical efficiency ?

Electrical losses and electrical efficiency



$$I_{leak} = \frac{V_{dc}}{R_{i(DC)} + R_l} \qquad R_{i(DC)} = \frac{d}{\sigma_{DC} A}$$

I_{leak} direct leak current (DC)

Depends on materials DC conductivity (no mechanical excitation)

$$P_{\text{loss}} = \frac{V_{dc}^2}{R_{i(DC)} + R_l} \approx \frac{V_{dc}^2}{R_{i(DC)}} \qquad R_i \gg R_l$$

$$electrical\ gain = \frac{P_{harvested}}{P_{\text{loss}}}$$

% CB	Harvested power (µW)	Power loss (µW)	Net power production (µW)	Electrical gain factor
8.00	0.20	0.12	0.08	1.74
10.0	1.3	1.0	0.3	1.31

0.4 µW.cm^{-3}

Net power density production

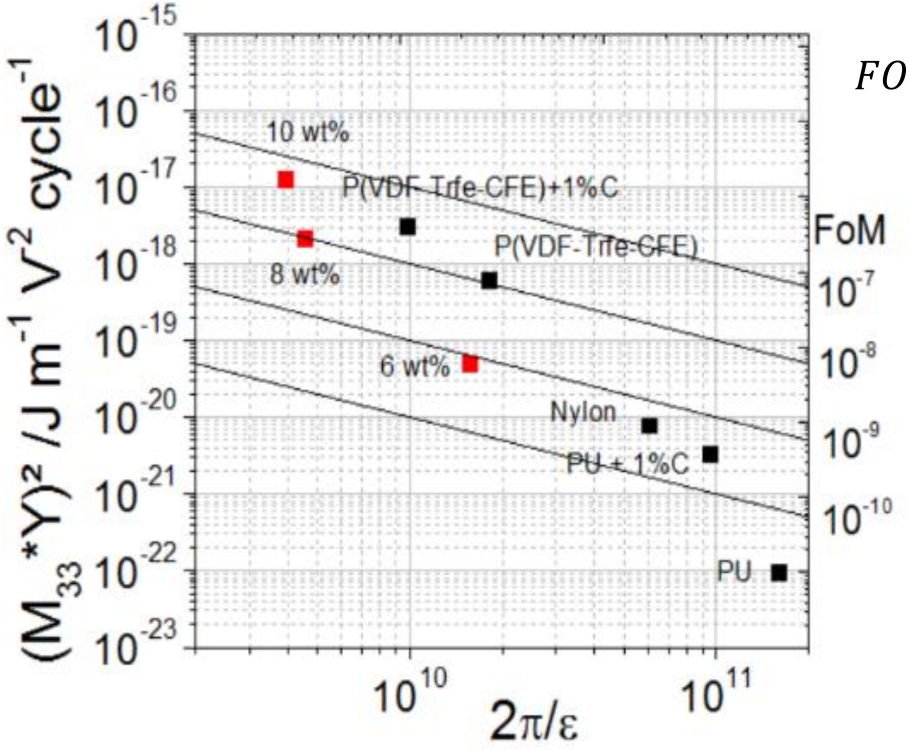
But only 0.04 V/µm

Comparison of energy harvesting capacities between materials

The power harvestable depends on
- **external parameters** : materials surface, thickness, polarization voltage, frequence, strain
- **intern parameters :** Young’s modulus, permittivity, electrostrictive modulus

$$FOM = \left(\frac{2\pi}{\varepsilon\prime}\right)(M^{*}Y)^{2} \quad (J.m^{-1}V^{-2}cycle^{-1})$$

M Lallart, *Journal of applied physics* (**2010**)



$$FOM(\,(P(VDF - Trfe - CFE) + 1\%\,C) = 3 \times 10^{-8}$$

× 3

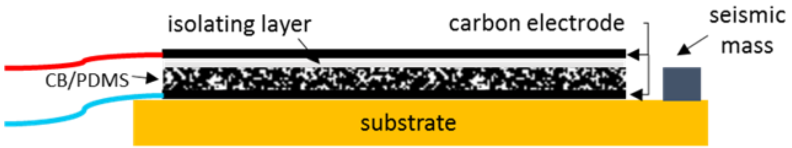
$$\boldsymbol{FOM(10\,\%\,CB) = 10^{-7}}$$

$J.m^{-1}V^{-2}cycle^{-1}$

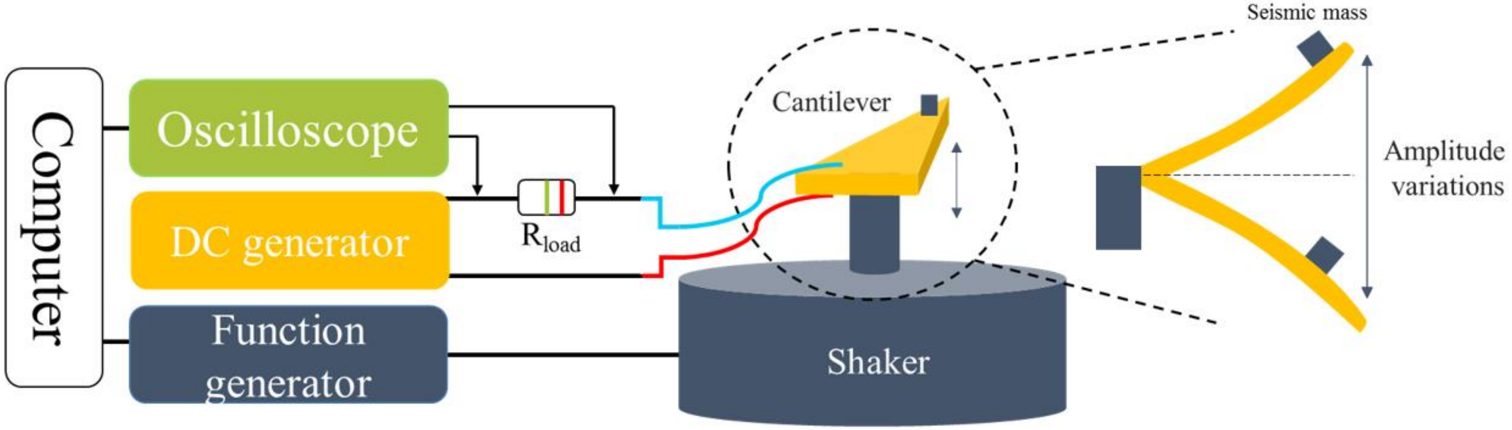
low cost dielectric materials with:
- a less toxic process
- a better integration (Y~ MPa)
- higher performances (M, ε, σ)

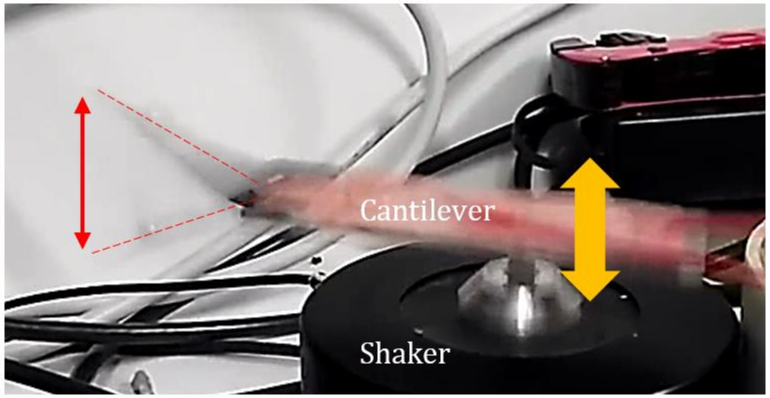
Material integration

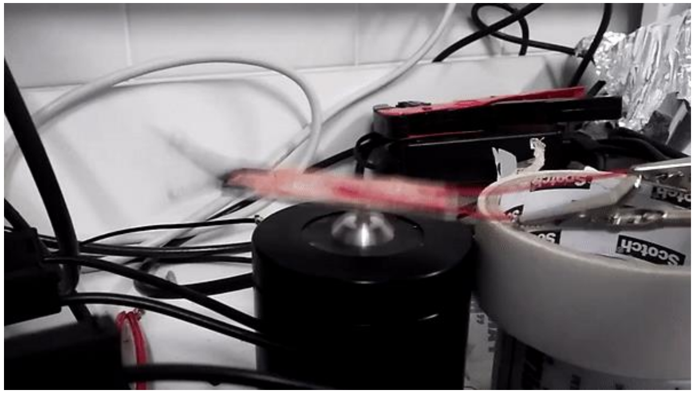
cantilever application



10 CB% material + PET
90 μm/2.5 μm

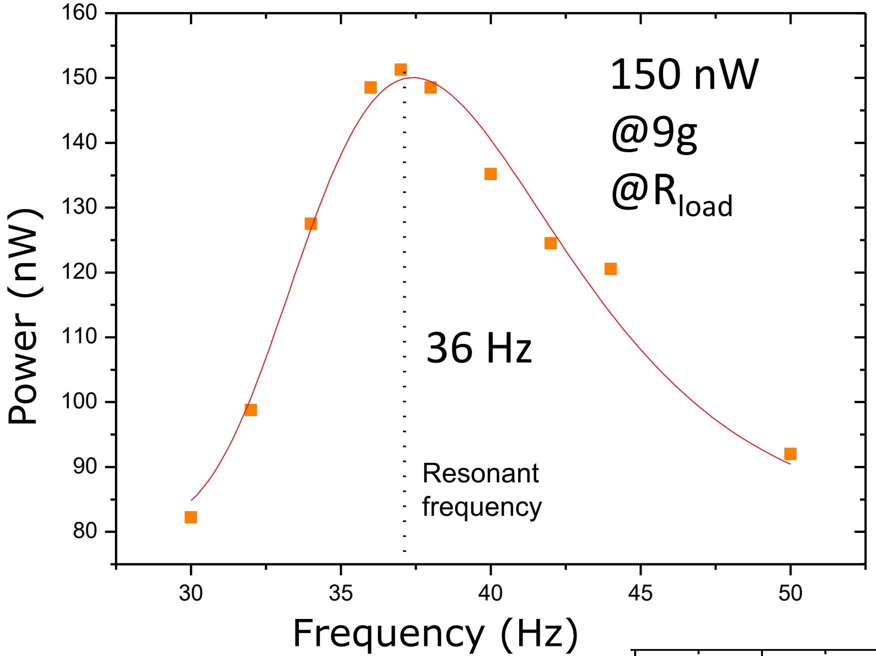


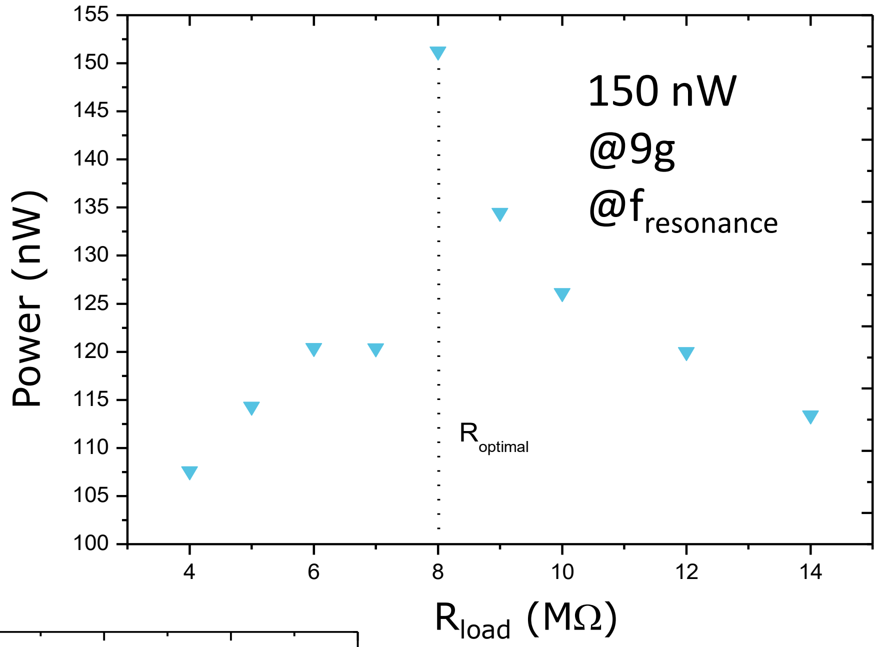


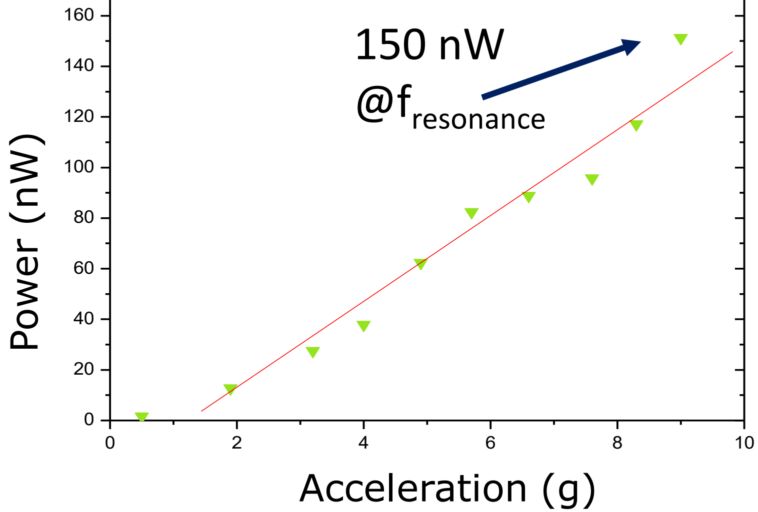


Cantilever performances

Without seismic mass

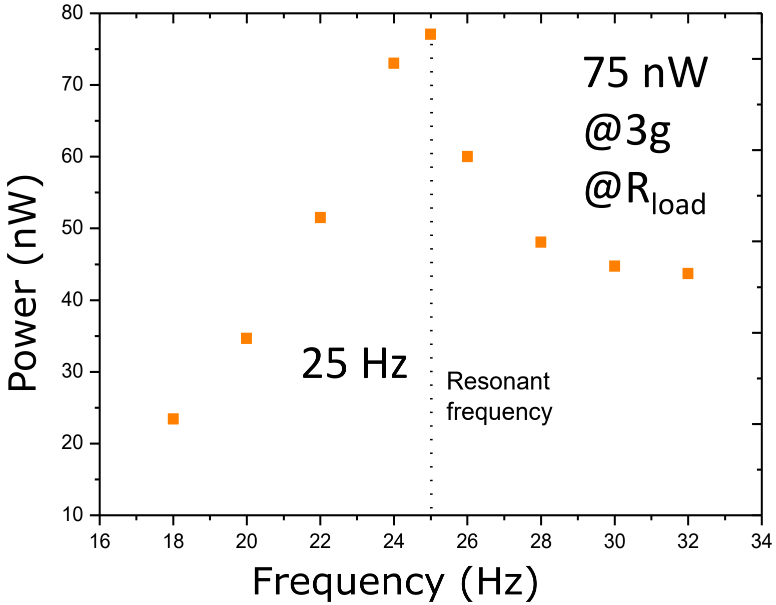


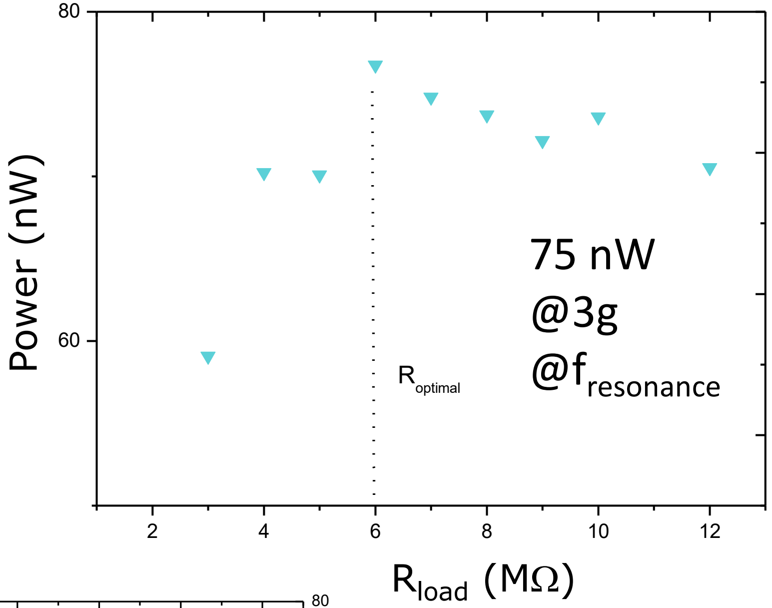


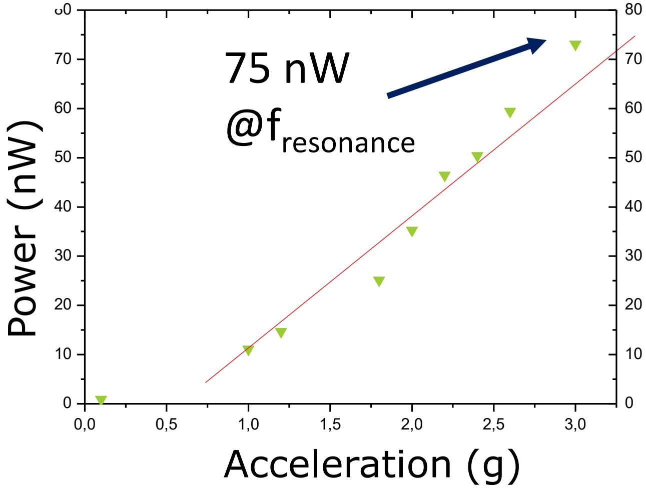


Cantilever performances

With seismic mass (0,35 g)







Harvested power and order of magnitudes

% CB	a (g)	Harvested power (nW)	Power loss (nW)	Net power production (nW)	Electrical gain factor
10,0	3	75	1.4	73.6	53
10.0	2	35	1.4	33,6	25
10.0	1	10	1.4	**8,6**	7

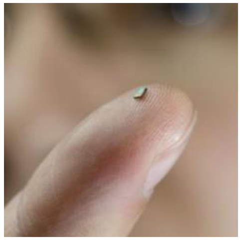
1g at the resonant frequency of 25 Hz recovered a power density of

0.12 μW/cm^3

Machine tool : 1g, f_{peak}=70 Hz
Car engine compartment : 1 g, f_{peak}=200 Hz

(A Hajati's Thesis, MIT, **2011**)

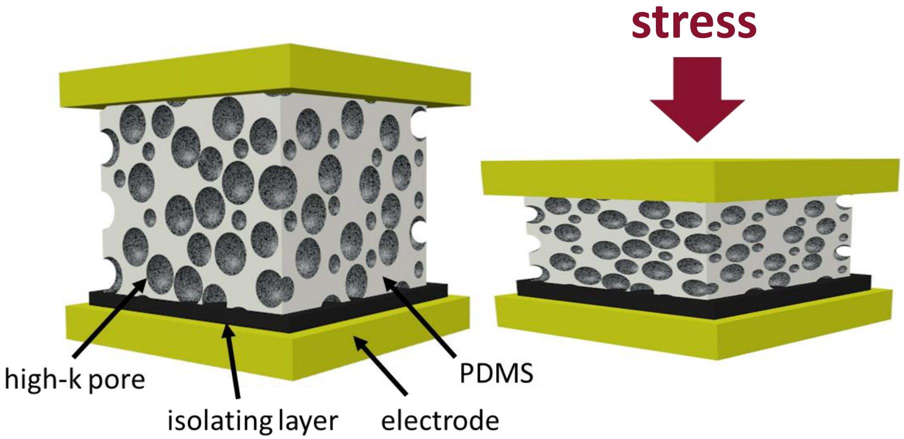
Temperature sensor
3 nW (iMac 30 W)
0.20 mm²



(Hao Gao et Al., IEEE Journal of Solid-State Circuits, **2016**)

Partial conclusion 2

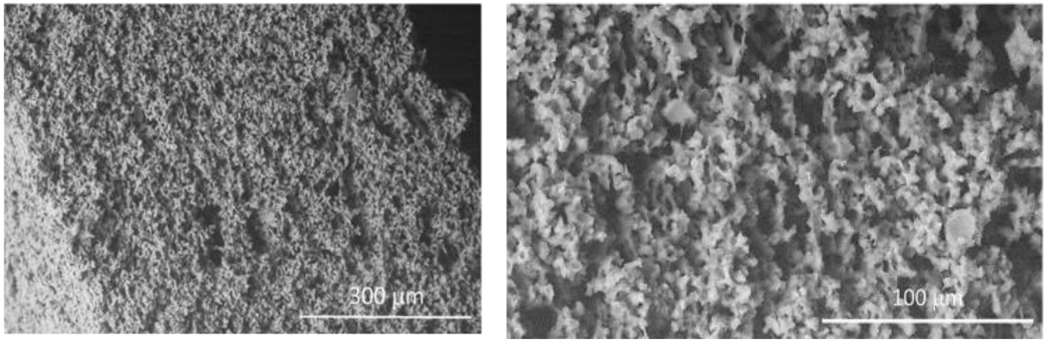
For energy harvesting applications ➔ « infinite » stress source



$$Y_{bulk} \sim MPa$$

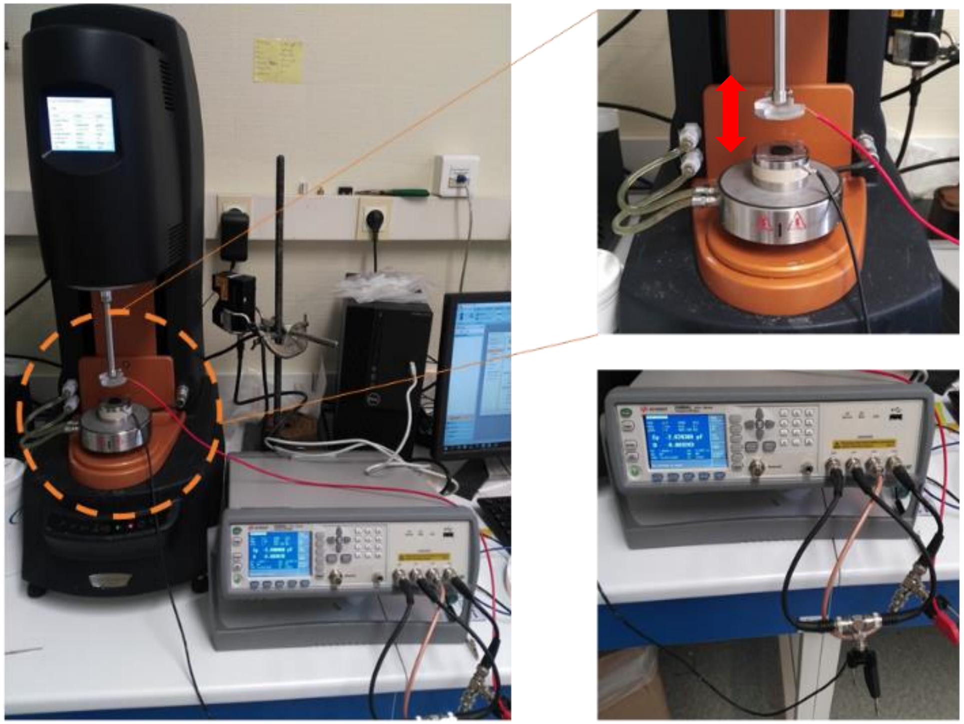
$$\text{Sensitivity} = \frac{\Delta C}{C_0 \times P}$$

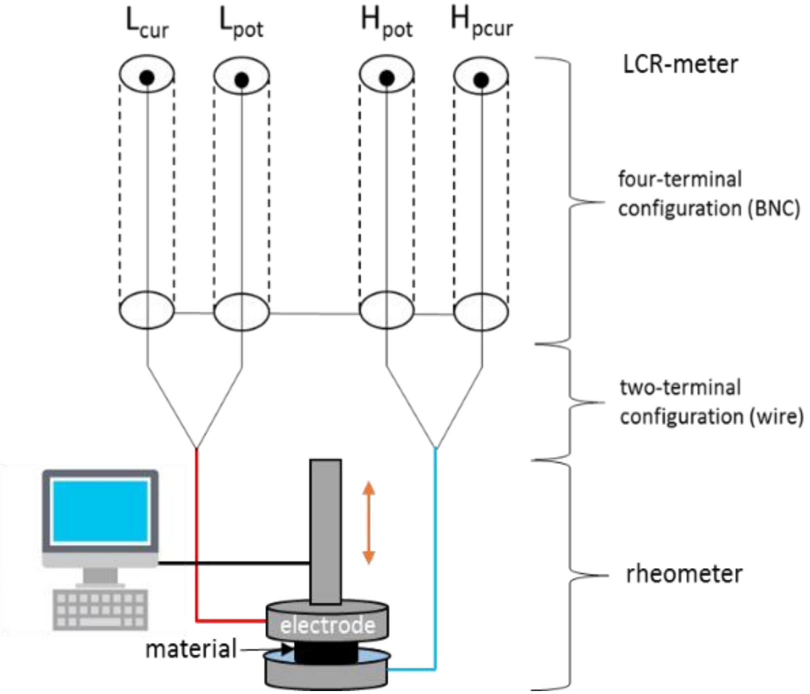
For sensing applications ➔ high strain with low stress is required



Porous PDMS’ (**80 wt% dispersed phase**) filled with carbon black (10 wt%) + isolating layer

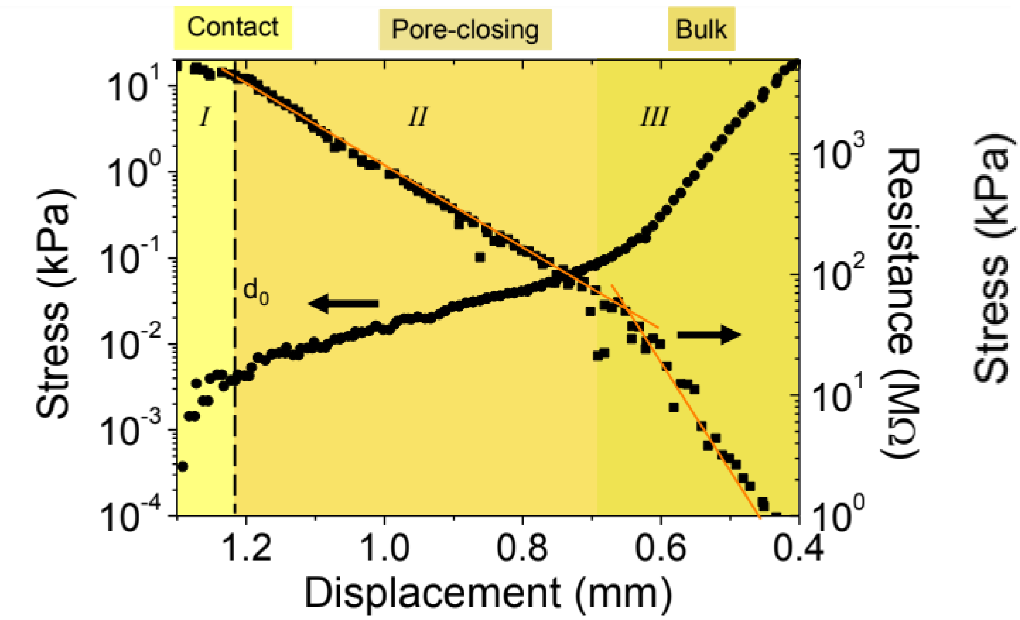
Experimental setup for mechanical and pressure sensing measurements

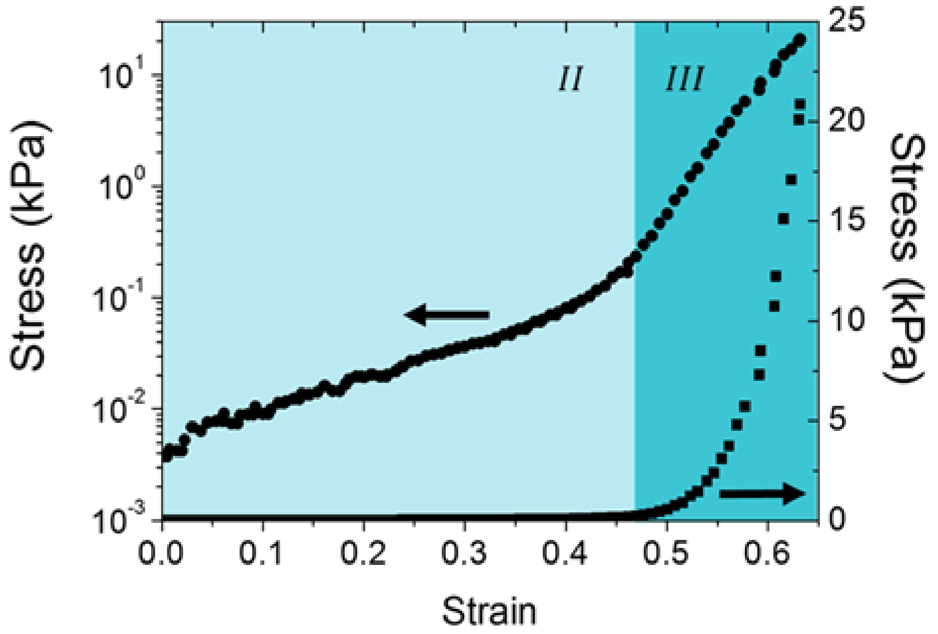


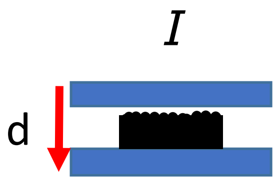


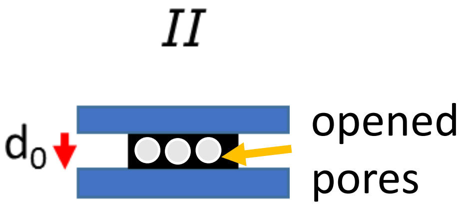
- rheometer used as mechanized *z*-axis stage and force gauge
- linear loading–unloading cycles
- ε, σ are measured at 1 kHz with a bias of 1 V (LCR-meter)

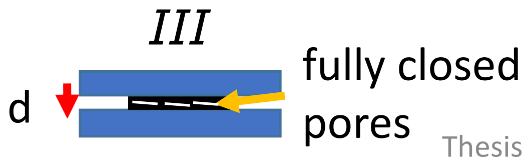
Mechanical studies









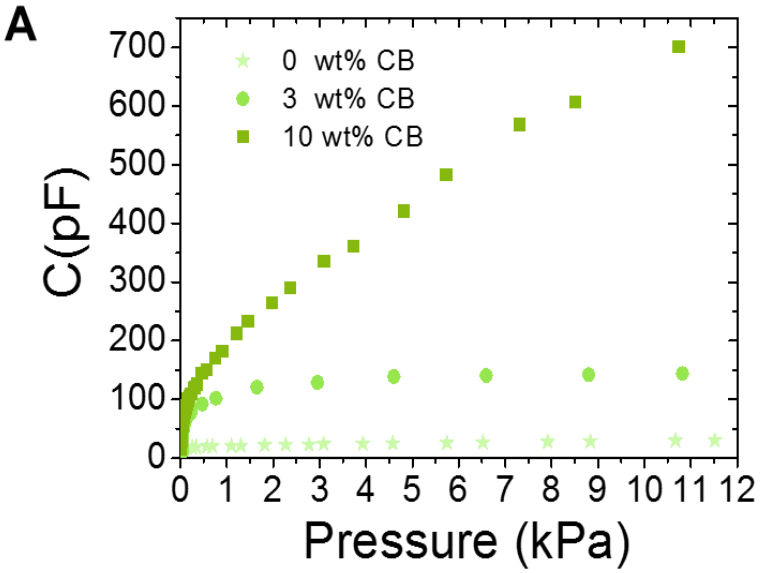


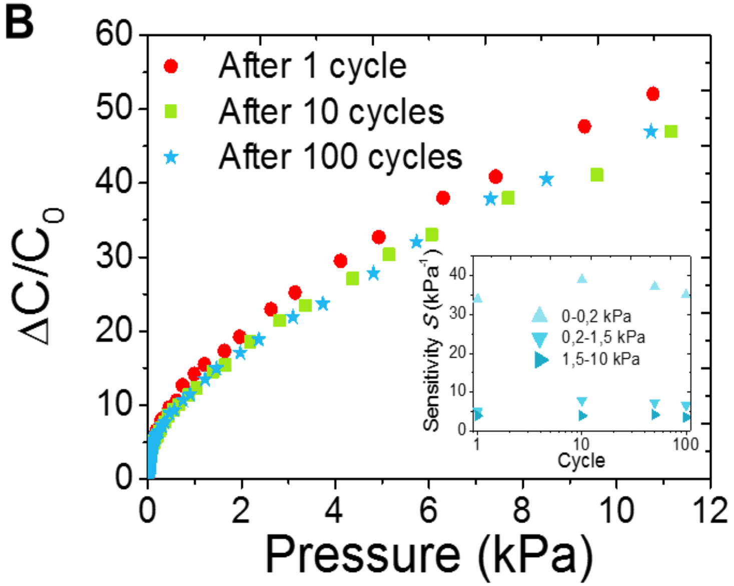
I : Contact

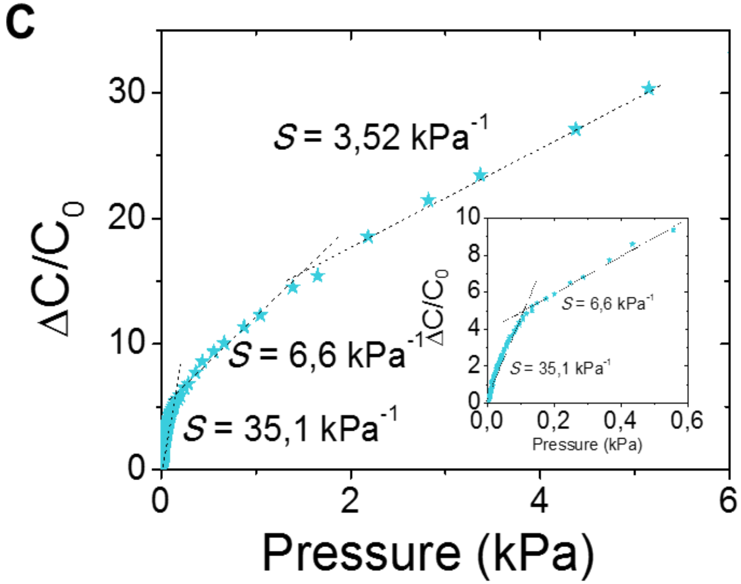
II : Plateau (elastic buckling)

III : Increase (densification)

Capacitance studies



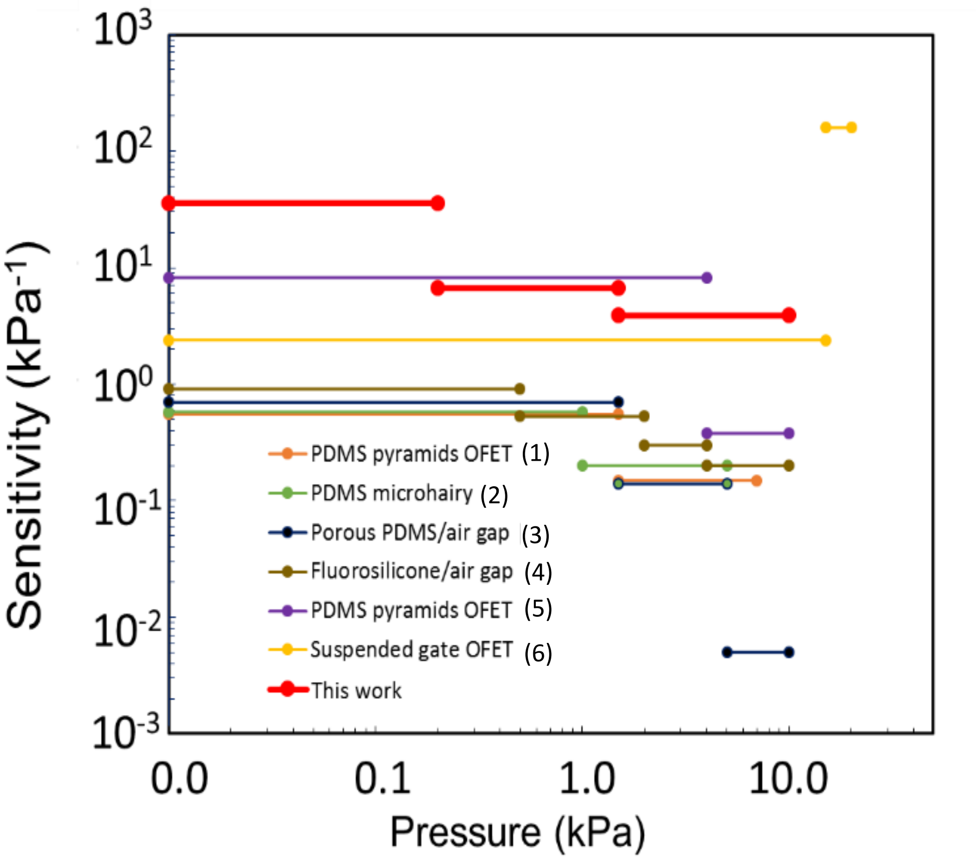


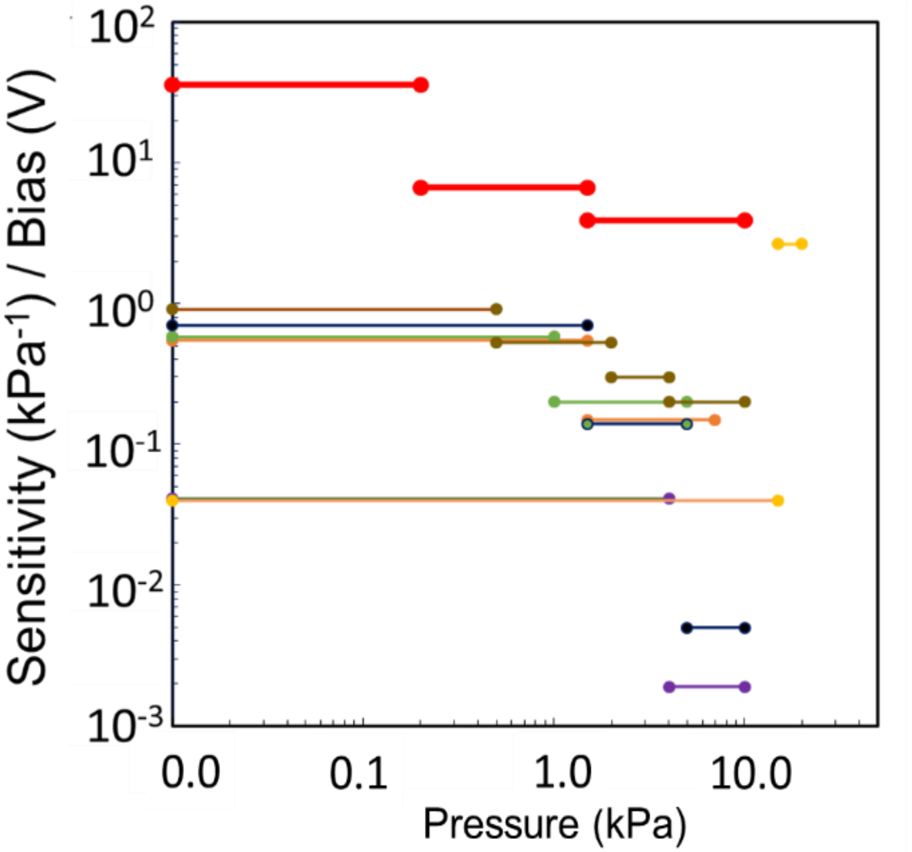


S=35.1 kPa^{-1} } elastic buckling

S=6.6 kPa^{-1}
S=3.52kPa-1 } densification

Sensitivities reported in litterature

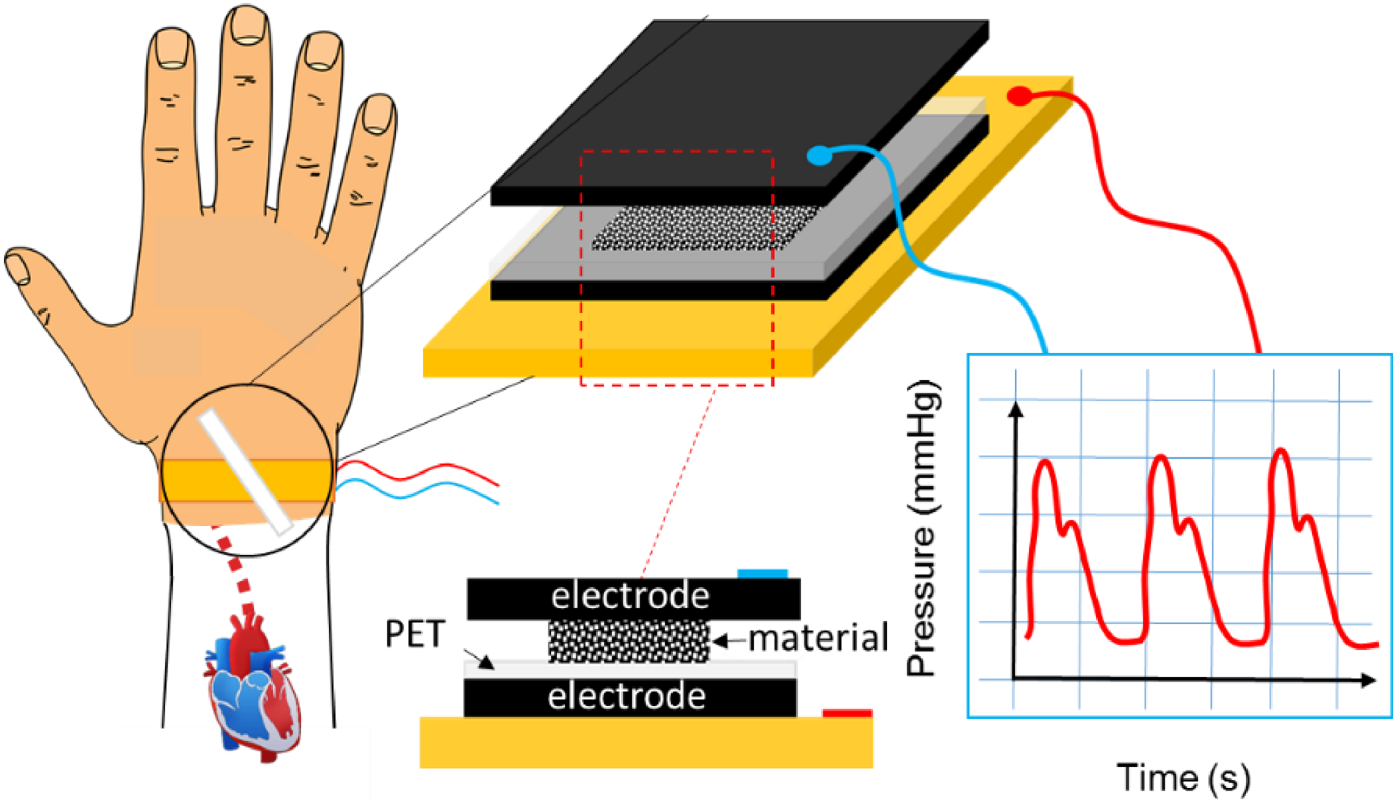




(1) Z. Bao, Nature Materials. 9 (2010)
(2) Z. Bao, Advanced Materials. 27 (2015)
(3) Z. Bao, Advanced Materials. 26 (2014)
(4) L. Beccai, Advanced Materials. 26 (2014)
(5) Z. Bao, Nature Communications. 4 (2013)
(6) D. Zhu, Nature Communications. 6 (2015)

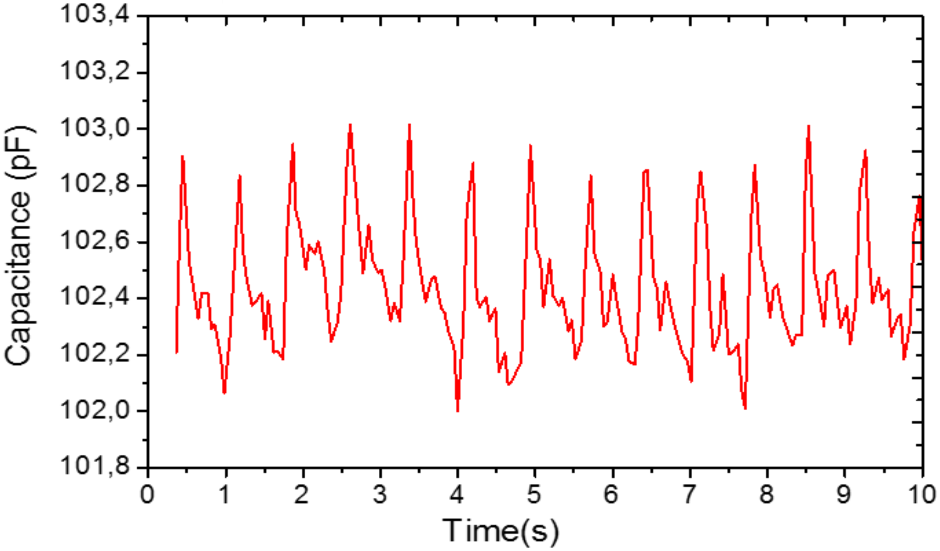
Our work is far above the lattest reported results

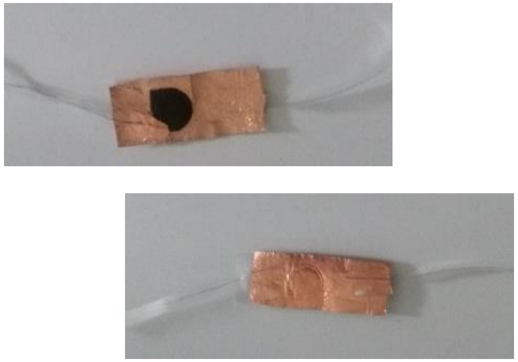
Prototype of blood pressure sensor

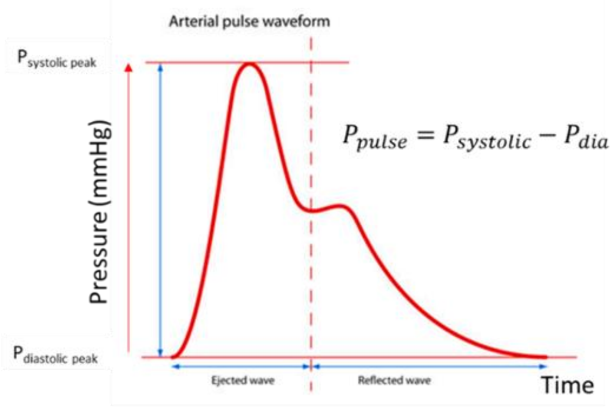


Patterns : **Pruvost** *et al + Solvay* PCT/EP2018/050002 ; PCT/EP2018/050003 ; PCT/EP2018/059956 ; PCT/EP2018/059957

Blood pressure record







Towards an **ambulatory** device for measuring blood pressure

Conclusion

- We succeeded in developping, by design, **new soft dielectric** composites based on a porous polymer matrix filled with carbon black

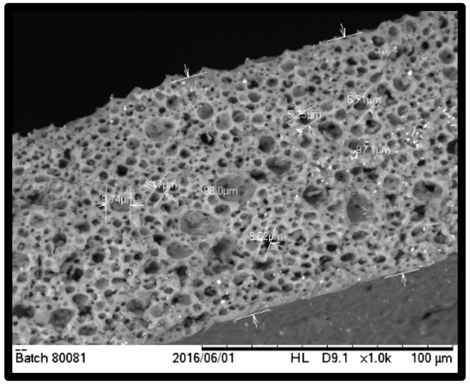
- The **bilayer strategy** allowed us to limit the dielectric losses and enlarged the formulation window

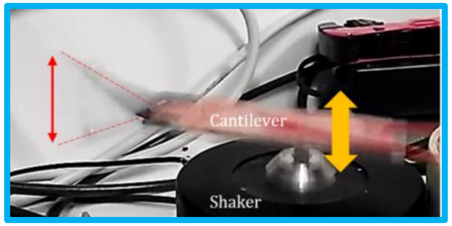
- We highly enhanced the Figure of Merit for vibrational energy harvesting purposes

- We sucessfully integrated the materials into a cantilever structure with an harvested power density of **0.12 μW/cm^3** at 1g

- We greatly improved the sensitivity (**S=35.1 kPa^{-1}**) to pressure sensor without any amplification or surface microstructuration

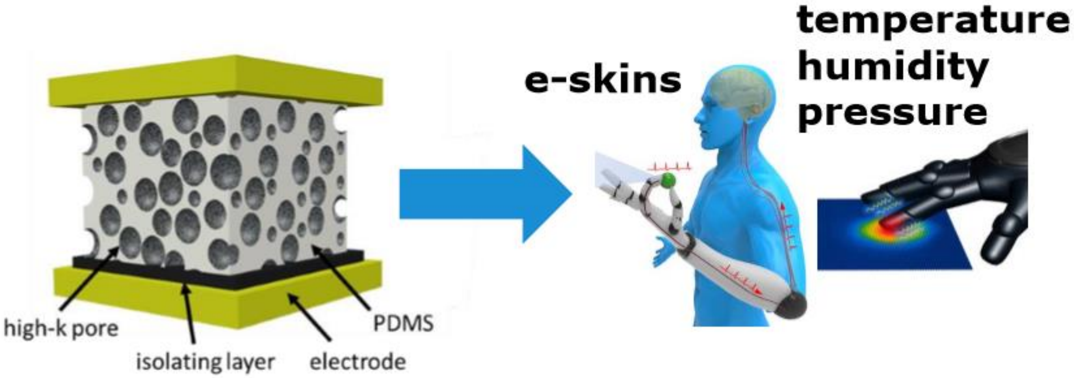
- The integration of our materials into **blood pressure sensors** is prooved





Outlooks

- change in polymer chemistry (PDMS bottlebrush)
- development of multifunctional wearable sensors (temperature, humidity, etc.)
- integration into flexible e-skins (robotic)
- technological implementation via valorization project of the heart pressure sensors



Thank you for your attention