Magnetically tuneable resistive composites

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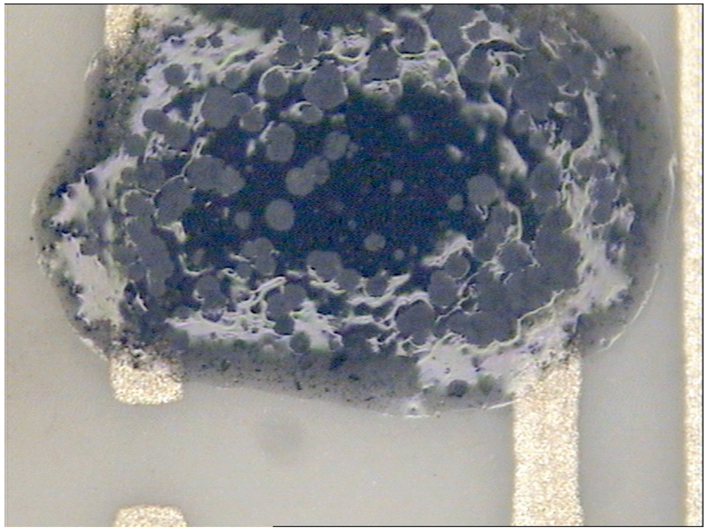
[1] EPFL – École Polytechnique Fédérale de Lausanne, Switzerland
[2] UBA - Universidad de Buenos Aires, Argentina



Outline

1. Introduction
2. Magnetic powders
3. Magnetically aligned elastomers
4. Thermoplastic compositions
5. Conclusion & outlook

Outline

1. **Introduction**

- **Our lab**
- **Conductor-insulator composites**

2. Magnetic powders

3. Magnetically aligned elastomers

4. Thermoplastic compositions

5. Conclusion & outlook

EPFL - Swiss Federal Institute of Technology

EPFL
École Polytechnique Fédérale de Lausanne

One of the two polytechnical schools in Switzerland

10’000	Population on the campus
6’000	Students
3’500	Collaborators
1’400	PhD. Students
250	Professors
550	MSFr budget / year
70	Companies on site
10	New start-ups / year

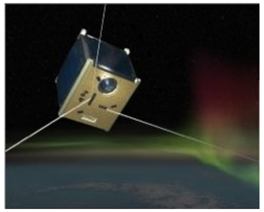
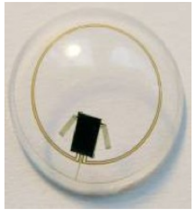
EPFL - Faculties - Engineering

- **SB:** School of basic sciences
  - Chemistry, mathematics and physics
- **SV:** School of life sciences
  - Genomics, neurosciences, …
- **ENAC:** School of civil + environmental engineering & architecture
  - Architecture, civil engineering, environmental sciences and technologies
- **I&C:** School of informatics and communications
  - Fundamental & applied computer science, communication systems
- **STI: School of engineering**
  - Electricity, materials, mechanical engineering, biomedical engineering, **microtechnology**

EPFL-STI - School of Engineering

- **IMX:** Institute of materials science & engineering
  - Metals, ceramic, polymers, composites, poweders, bio-/nanomaterials,…
- **IEL:** Institute of electrical engineering
  - Circuits & devices, power & energy, telecom, computers…
- **IGM:** Institute of mechanical engineering
  - Solid + fluid mechanics, heat + mass transfer, biomechanics, control…
- **IBI:** Institute of bioengineering
  - Biology, chemistry, biomaterials, … *(with school of life sciences)*
- **IMT: Institute of microengineering**
  - Microsystems, robotics, optics, production, …
  - Inherently multidisciplinary
- *+ several technology centres:*

http://imt.epfl.ch

IMT - Locations

The new IMT: 1 Institute on 2 Sites

Lausanne + Neuchâtel Campus

Distance: ~70 km or 45 min

Close collaborations

csem

Hes·so
Haute Ecole Spécialisée de Suisse occidentale

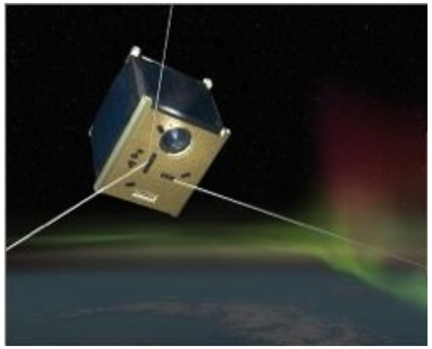
Industry

http://imt.epfl.ch

IMT - Highlights

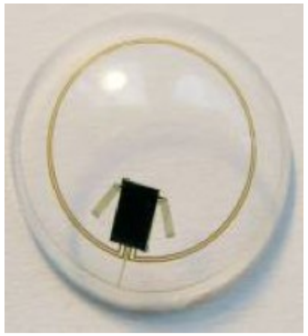

CMI - Centre of Micronanotechnology

- Technological platform dedicated to research in micro- and nanofabrication:
- Open to all researchers (academic & industry)



SwissCube

- Microsatellite for student education in space technologies & engineering
- Launched 23.9.2009



Disposable wireless eye pressure sensor

- Silicone contact lens with deposited strain gauge & antenna loop
- RFID-style power through antenna
- Integrated signal conditioning & wireless communication chip

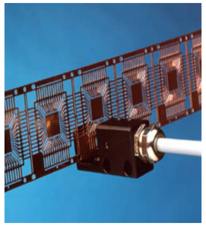
LPM - Lab. of microengineering for manufacturing

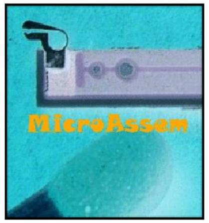
Laboratoire de Production Microtechnique

Vision & μ-Assembly

Director : Prof. J. Jacot

Group head : A. Dufaux

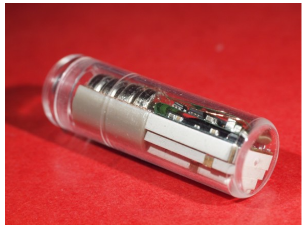




Product design

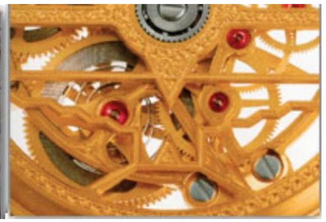
Director : Prof. P. Ryser

Group head : E. Meurville



Production strategy

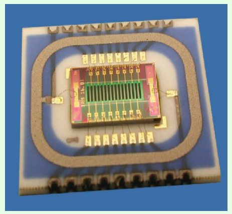
Director : Prof. M.-O. Hongler



Thick-film technology

Director : Prof. P. Ryser

Group head : Th. Maeder



Topics of LPM thick-film group @ EPFL

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

UNIVERSIDAD DE BUENOS AIRES · FACULTAD DE CIENCIAS EXACTAS Y NATURALES

Harsh Environments

Aerospace - Implantable systems
Chemistry – Nuclear - Reactive materials
High-temperature processes

Load sensors

Force / pressure sensing
Integration in packages
Structuration
Medecine / rehabilitation

Technologies

LTCC
Thick-film

Fundamentals

Materials science
Processing
Theory + modelling

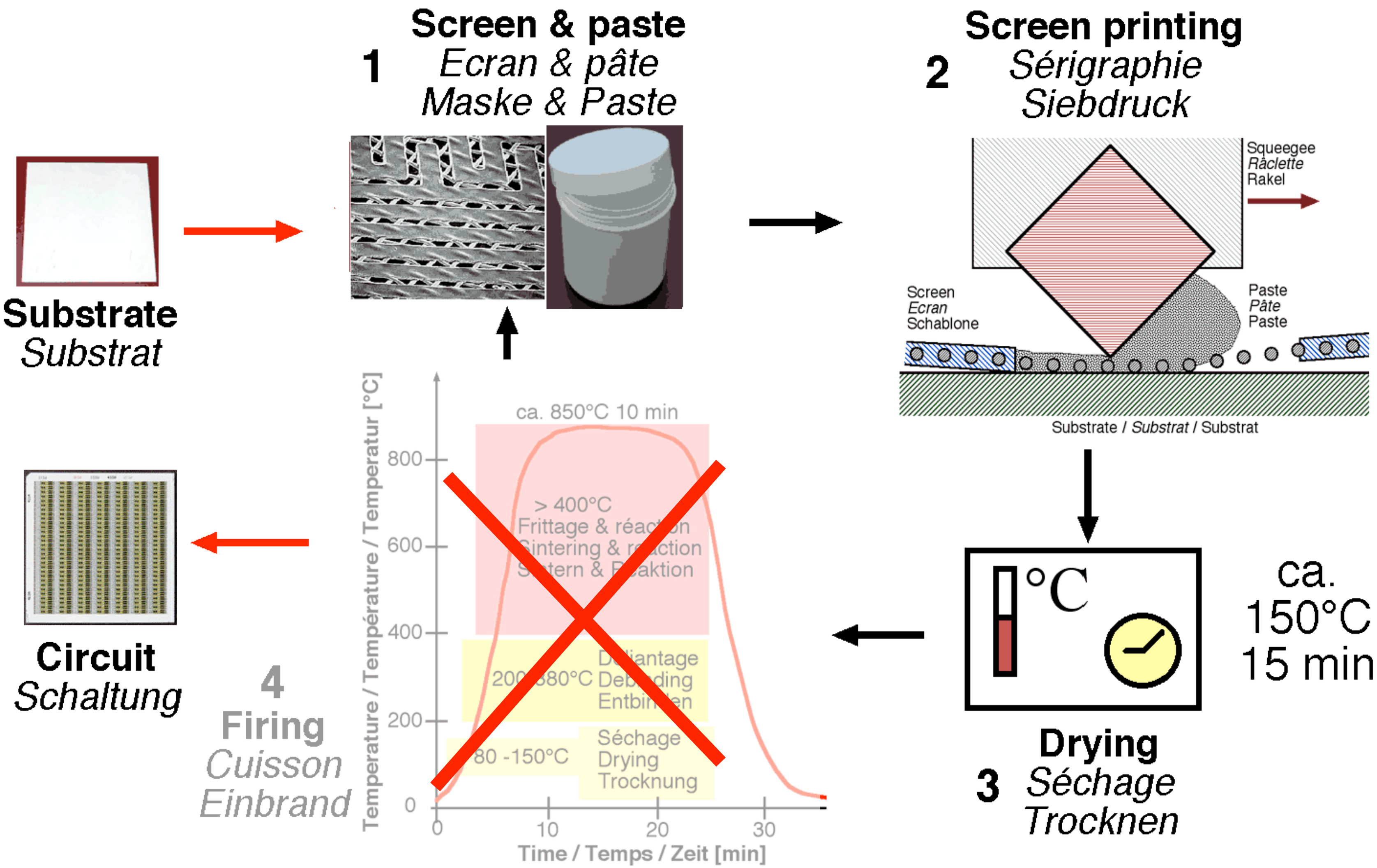
Ceramic microfluidics

Microreactors / calorimeters
Gas sensors
Fuel cells

Advanced Packaging

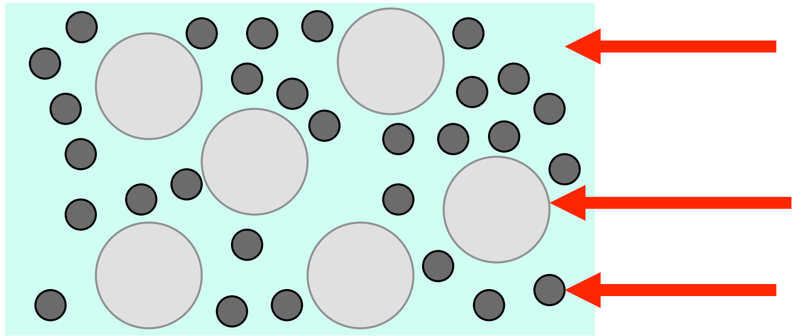
MEMS – Integrated functions
Hermetic – temperature control
Integrated sensors/actuators/fluidics
Structuration – sacrificial layers

Thick-film – polymer process flow



Insulator–conductor composite - paste

Classical (TF resistor)

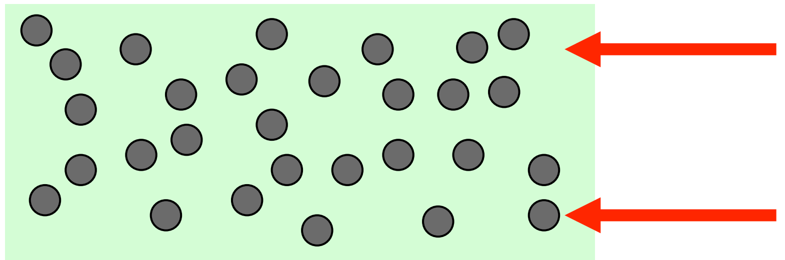


Organic vehicle (dissolved polymer)

Glass

Conducting oxide

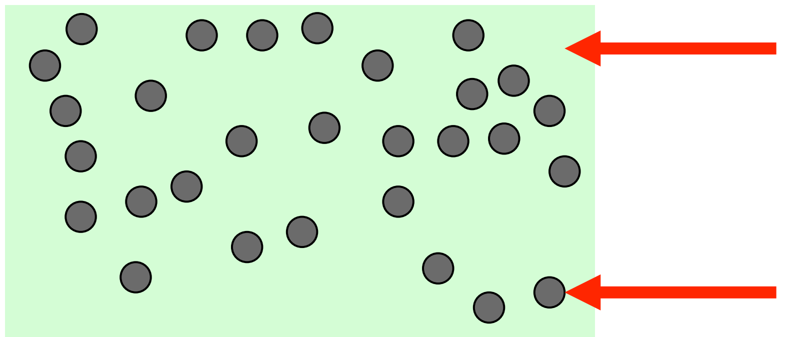
Thermoset resin



Precursor (epoxy, silicone, …) [solvent optional]

Conductor (typ. C)

Thermoplastic resin

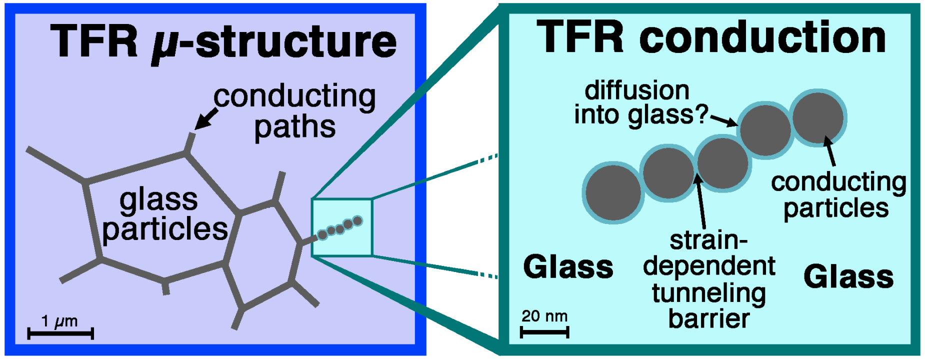


Dissolved polymer & additives [solvent needed]

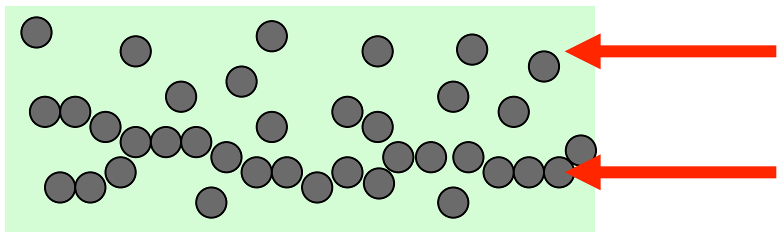
Conductor (typ. C)

Insulator–conductor composite - final

Classical (TF resistor)



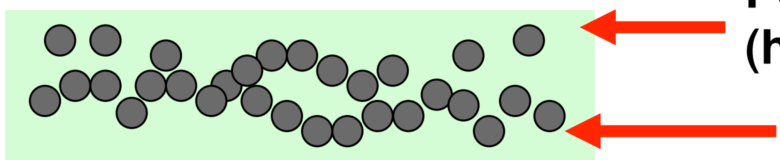
Thermoset resin



Polymerised resin (low shrinkage)

Conductor (percolation)

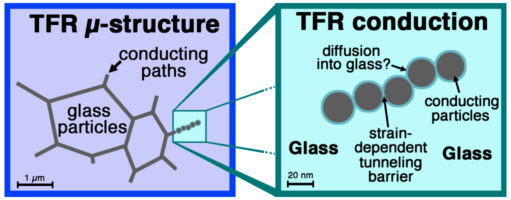
Thermoplastic resin



Polymer (high shrinkage)

Conductor (easy percolation)

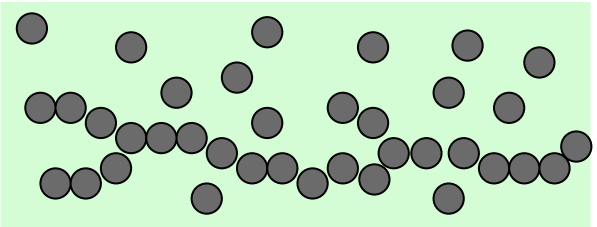
Insulator–conductor TF composites



Classical (TF resistor)

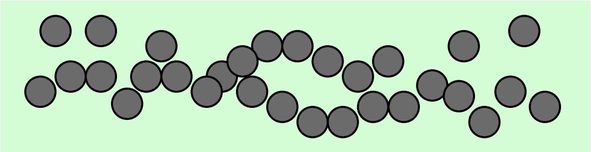
- Complete removal of original matrix
- Final insulating phase needed in formulation
  - Limited melting -> "segregation"

Thermoset resin



- Vehicle becomes matrix
- Low intrinsic shrinkage
  - Bulk materials possible
  - Shrinkage optionally enhanced by solvents

Thermoplastic resin in solvent



- Evaporation of >50% volume
- High intrinsic shrinkage
  - Percolation of conductor easy

Organic-matrix conductive composites

Thermoset resin vs. thermoplastic formulations

- Limited pot life for thermoset
- Solvent addition
  - Possible with both
  - Volume reduction
  - Affects particle arrangement in oven
  - Problematic for bulk samples
- Re-melting
  - Impossible for thermoset
  - **Low flow for simple thermoplastic (can be enhanced)**
- Conductive phase distribution
  - Organisation / segregation by affinities alone
  - **Can be forced, e.g. magnetic field on magnetic particles**

Outline

1. Introduction

2. **Magnetic powders**

- **Overview**
- **$CoFe_2O_4$ nanopowders**
- **$CoFe_2O_4$ microtubes**
- **Coating with conductor**

3. Magnetically aligned elastomers

4. Thermoplastic compositions

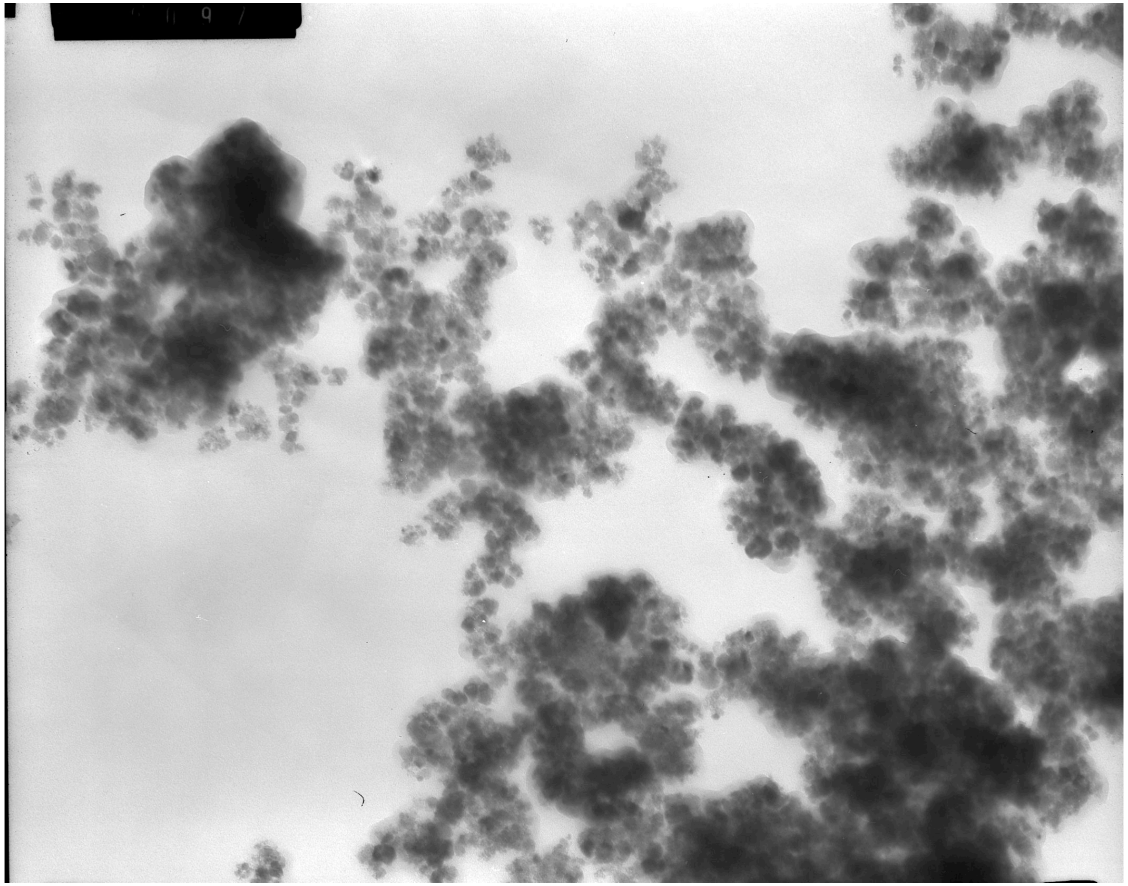
5. Conclusion & outlook

Soft magnetic powder types

- Magnetic metals (e.g. Fe, Co, Ni)
  - Strong magnetic response
- Magnetic oxides
  - Ferrites
    - Insulating, e.g. $CoFe_2O_4$, γ-Fe_2O_3…
    - Conducting, e.g. Fe_3O_4
    - Become superparamagnetic at nanoscale
  - Perovskites, e.g. $(La,Sr)MnO_3$
  - Other, e.g. CrO_2
- **All types**
  - Impart magnetism to polymer matrix
  - Degradation on surface (oxidation, hydroxides, …)
  - Usually disappointing conductivity
  - Can be protected, e.g. with Ag / Au coating

2010 Negri

Ferrites – $CoFe_2O_4$ nanopowders



TEM of nanopowder

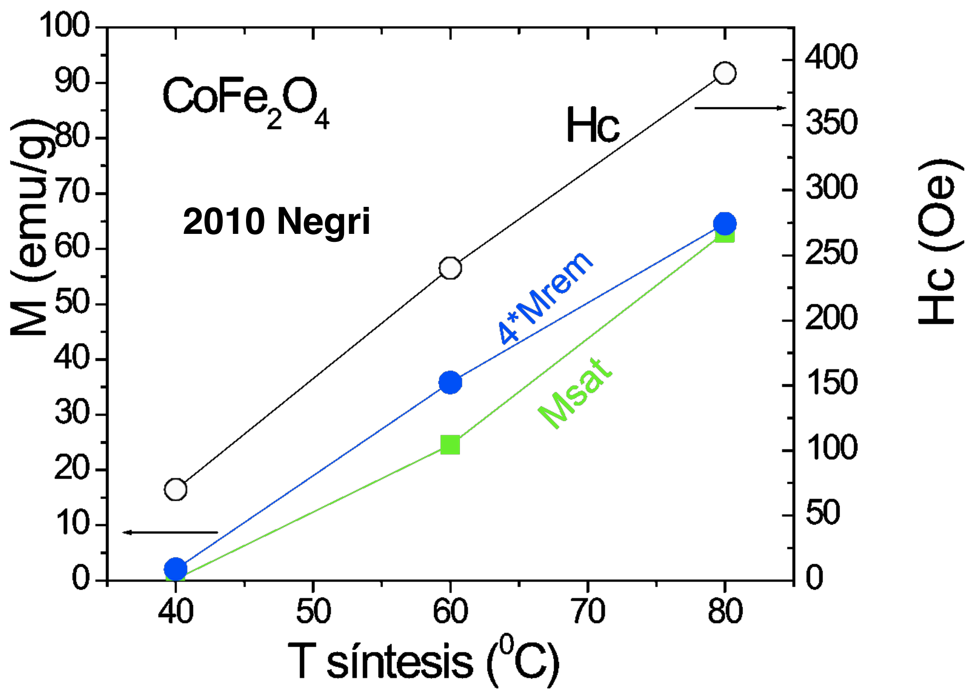
$CoFe_2O_4$ prepared at 25°C
Size ~2-3 nm

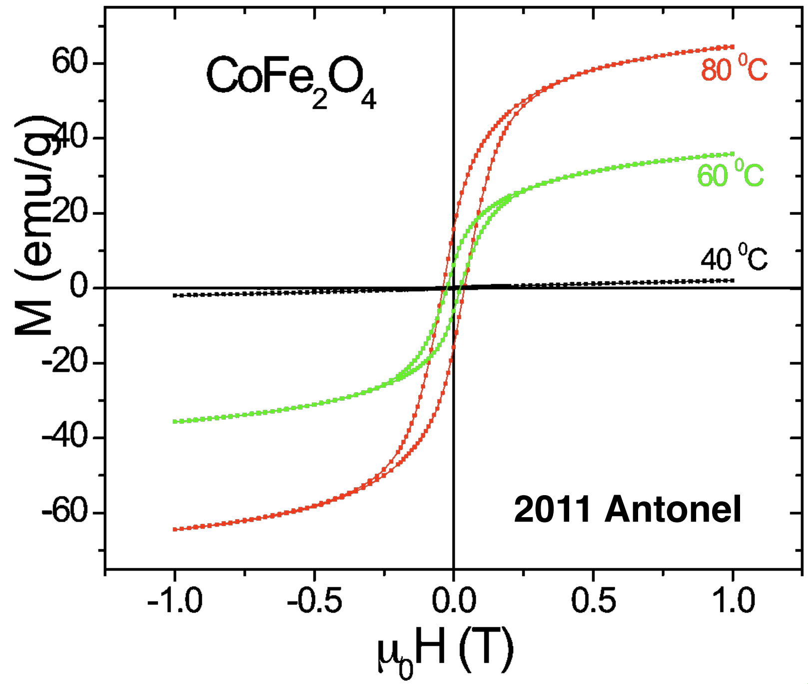
2010 Negri

Ferrites – $CoFe_2O_4$ nanopowders

Influence of the nanopowder preparation temperature

- $CoFe_2O_4$ prepared at 40°C, 60°C, 80°C
- Magnetic characterisation



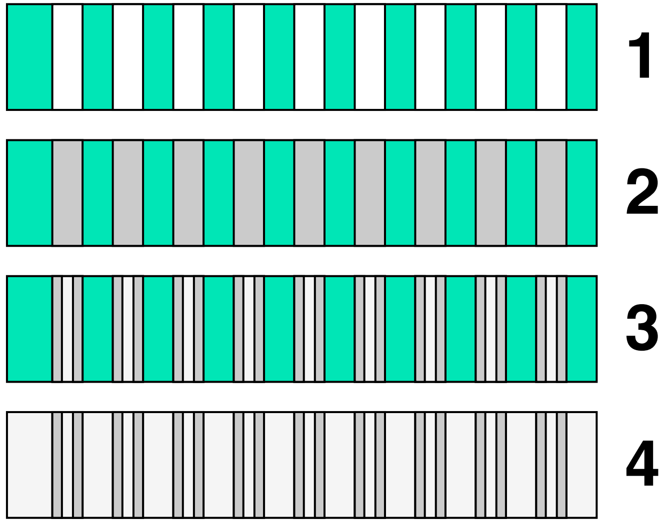


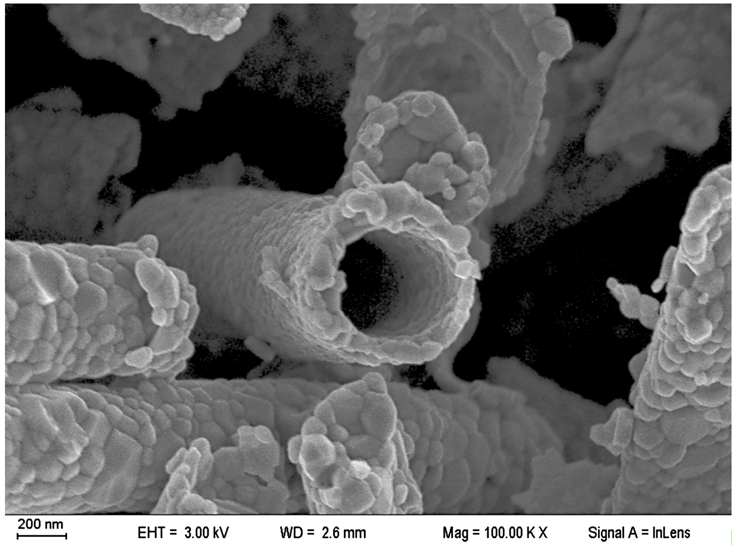
Ferrites – $CoFe_2O_4$ tubes

Fabrication of micro/nanotubes

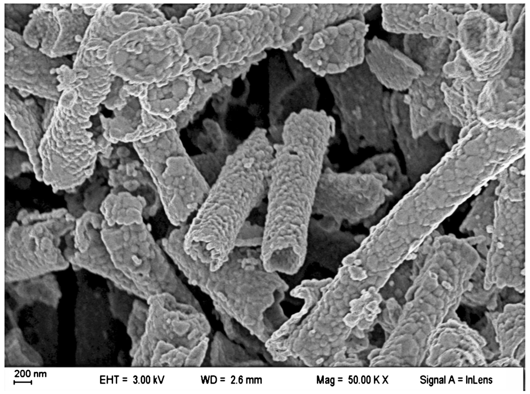
(G. Leyva, CNEA, Argentina)

1. **Select** polymer membrane with desired hole size (e.g. track-etch)
2. **Fill** with metal solution or suspension
3. **Dry**
   - Small holes : nanowires
   - Larger holes : nano/microtubes
4. **Fire** -> burnout of polymer & sintering of tubes



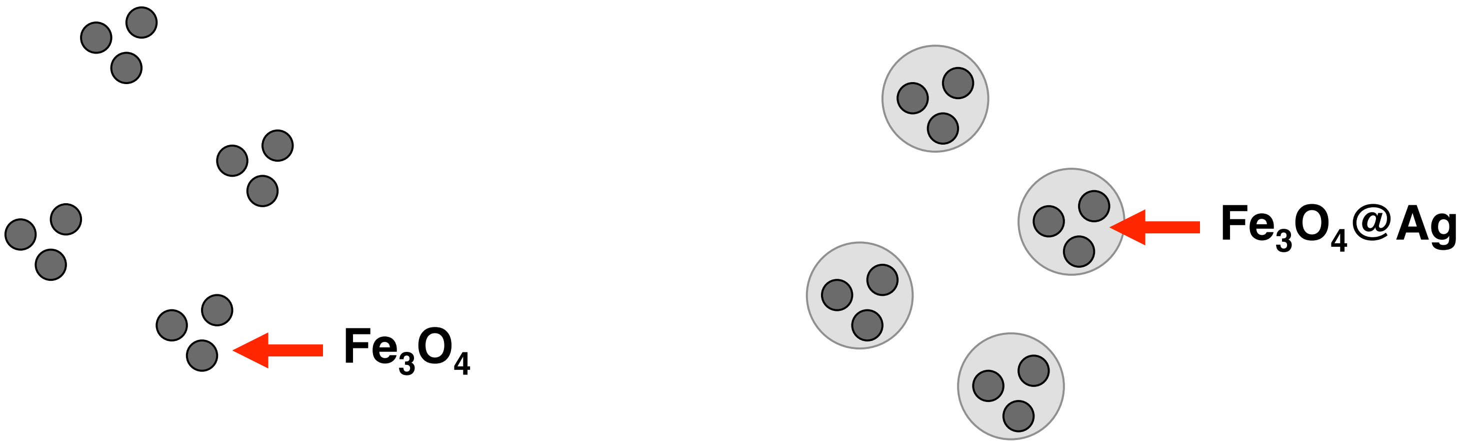


2010 Leyva



Coating with Ag conductor

- Chemical methods (classical)
- Agglomeration of particles
- Some drop in magnetic activity
- Compromise between activity & conductivity



Outline

1. Introduction
2. Magnetic powders
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- **Formulation**
- **Fabrication**
- **Mechanical properties**
- **Electrical properties**

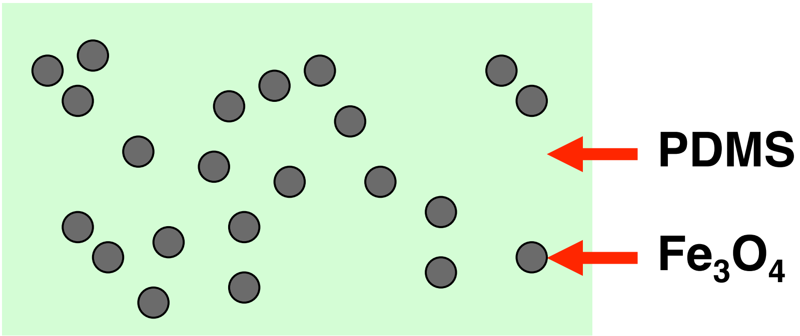
Formulation

Resin: silicone

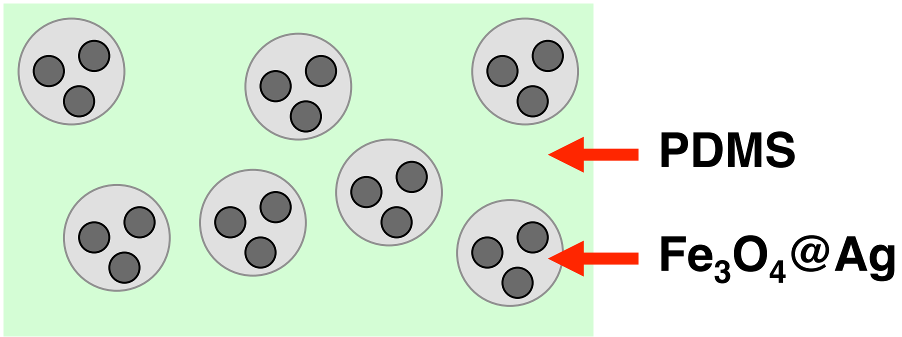
- PDMS = polydimethylsiloxane
- Sylgard 184
- Resin:hardener 10:1

Filler: ferrite

- Fe_3O_4, $CoFe_2O_4$, …
- Alone: non-conductive, for mechanical studies only
- +Ag: mechanical & electrical

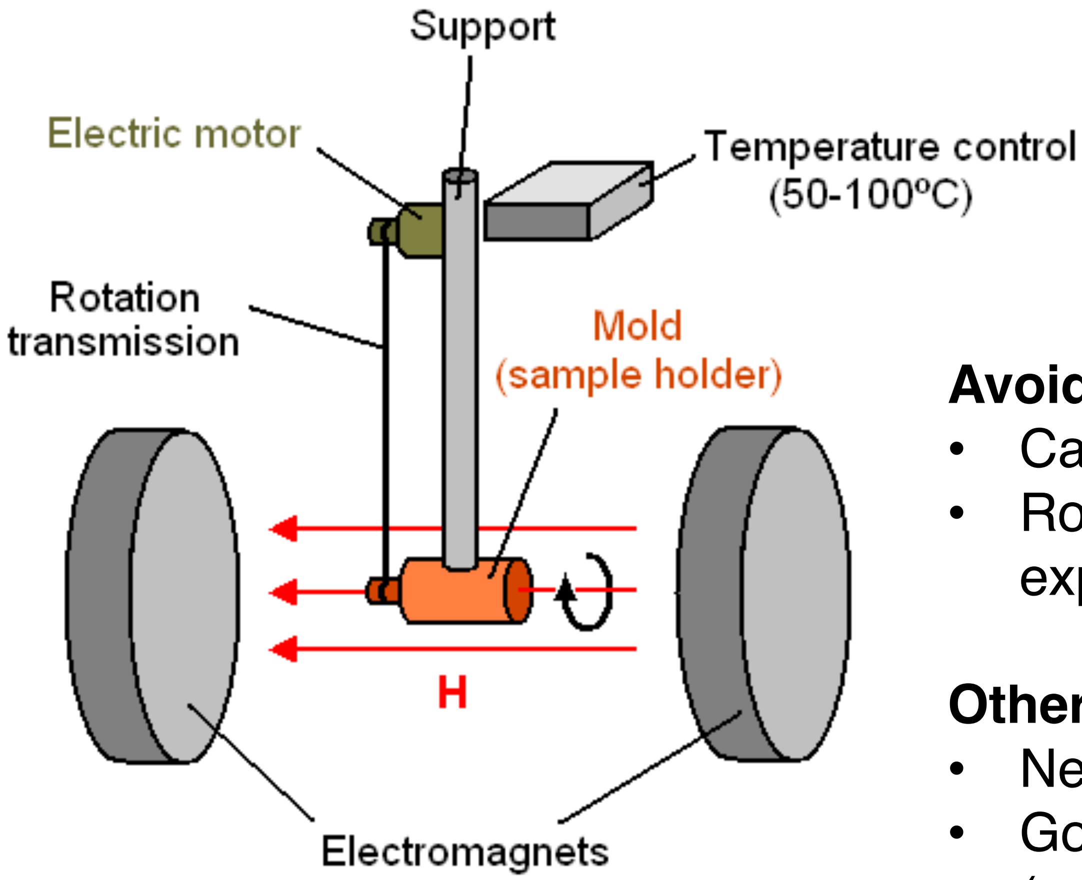


For mechanical investigations only



For mechanical & electrical investigations

Fabrication of bulk composites



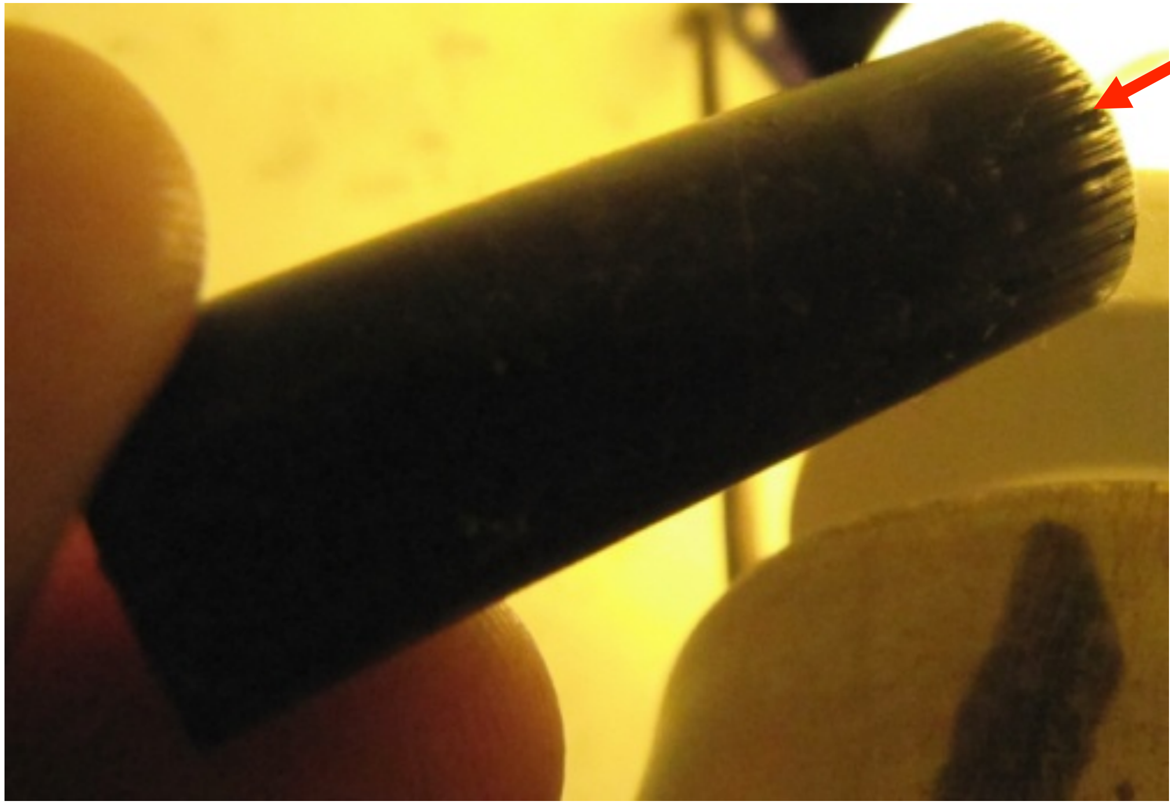
2011 Mietta

Sedimentation risk
- Low initial viscosity (further lowered by heating)
- Large density difference

Avoid sedimentation
- Cancel out gravity
- Rotate sample so that average experienced gravity is zero

Other issues
- Need large & strong magnets
- Good temperature control difficult (rotating sample & little space)
- In-situ observation difficult

Samples after hardening under field

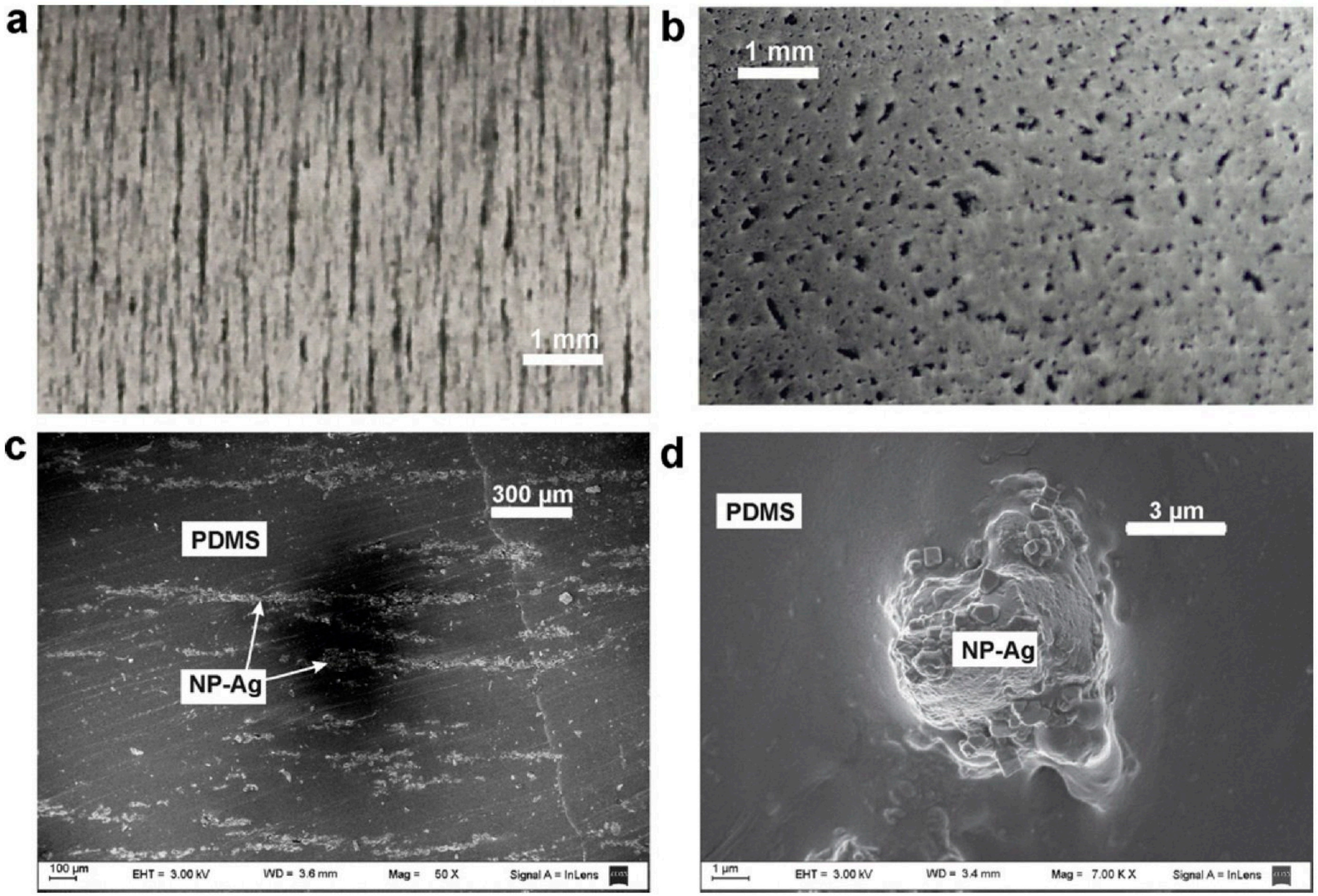


Lines are clearly seen!

2011 Mietta

Samples after hardening under field

Lateral cut parallel to chains | **Longitudinal cut across chains** | **2013 Mietta**

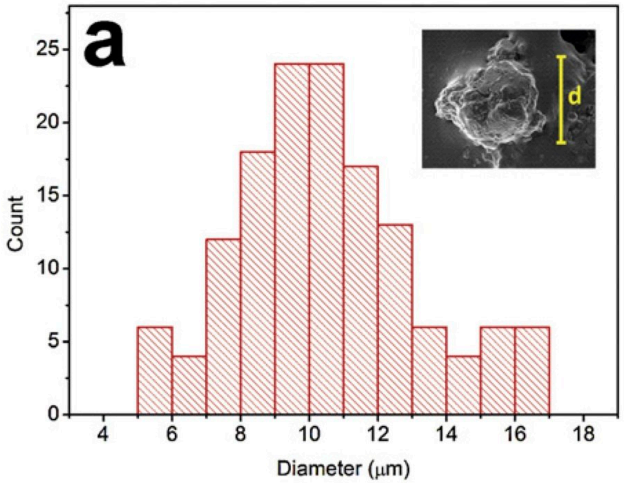


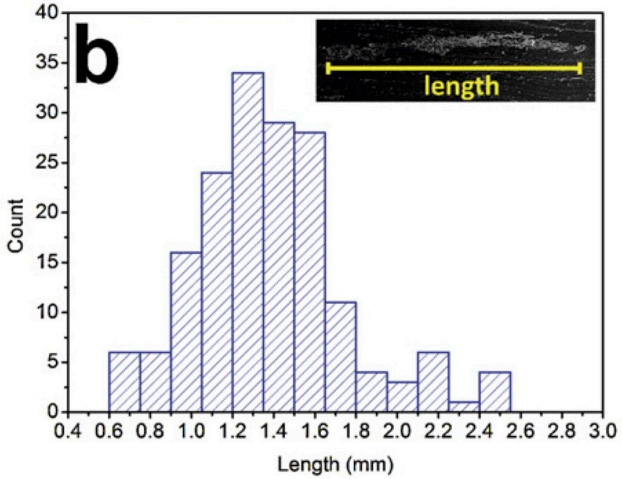
Optical

SEM

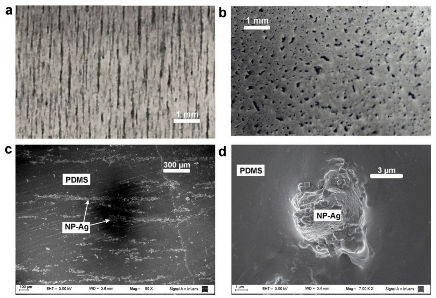
Samples after hardening under field

- Very strong geometric anisotropy





2013 Mietta

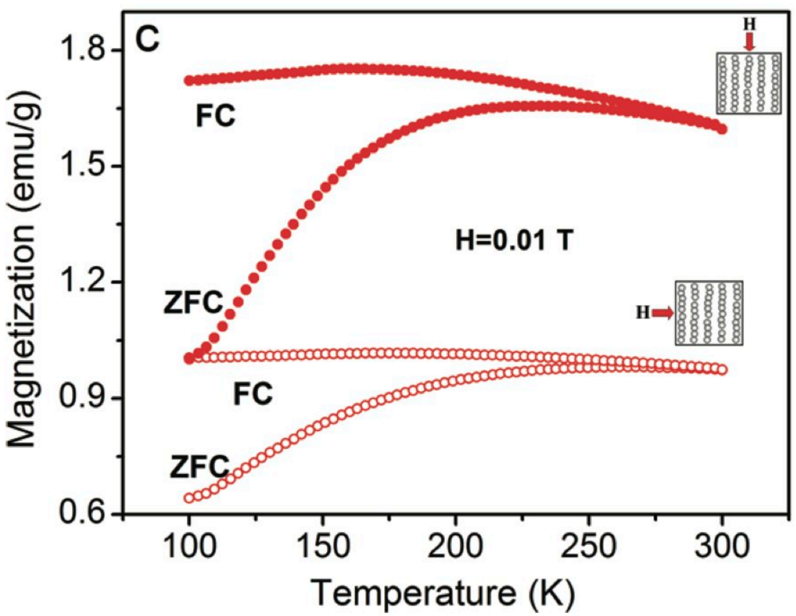


2013 Mietta

Magnetic studies

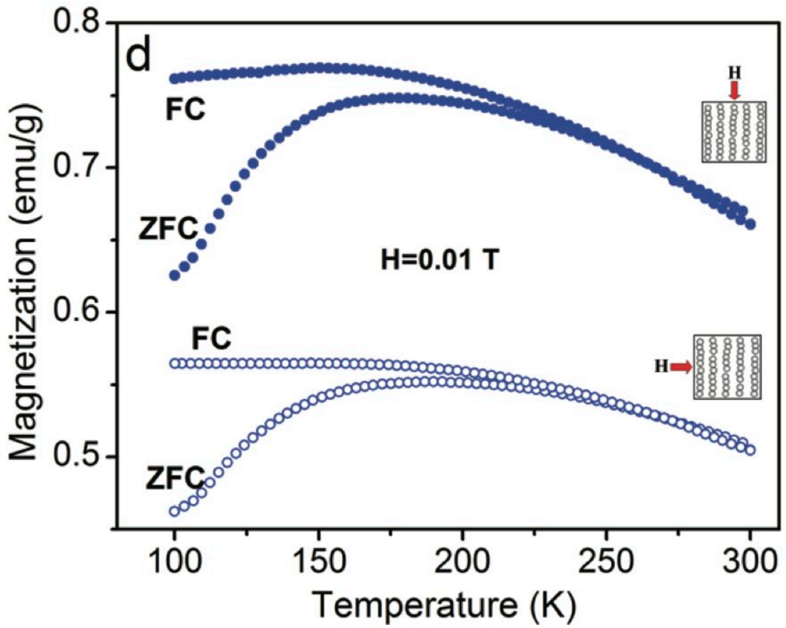
- High magnetic anisotropy due to alignment of magnetic filler
- Similar response for Fe_3O_4 & Fe_3O_4@Ag fillers (expected)

2012 Mietta



PDMS + Fe_3O_4

2012 Mietta

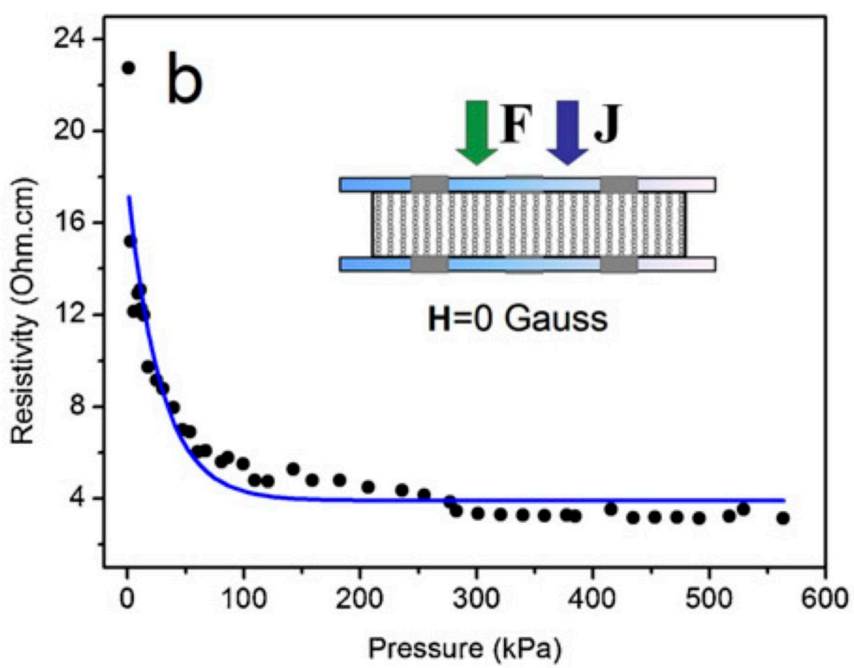


PDMS + Fe_3O_4@Ag

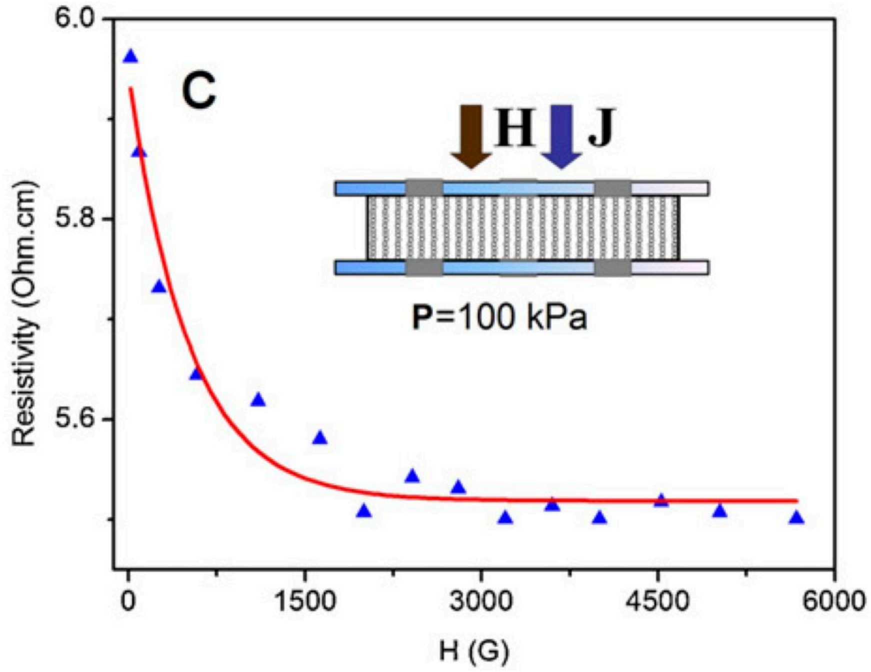
Piezo- & magnetoresistivity

- The samples are both strongly piezo- & magnetoresisitve

2013 Mietta



2013 Mietta

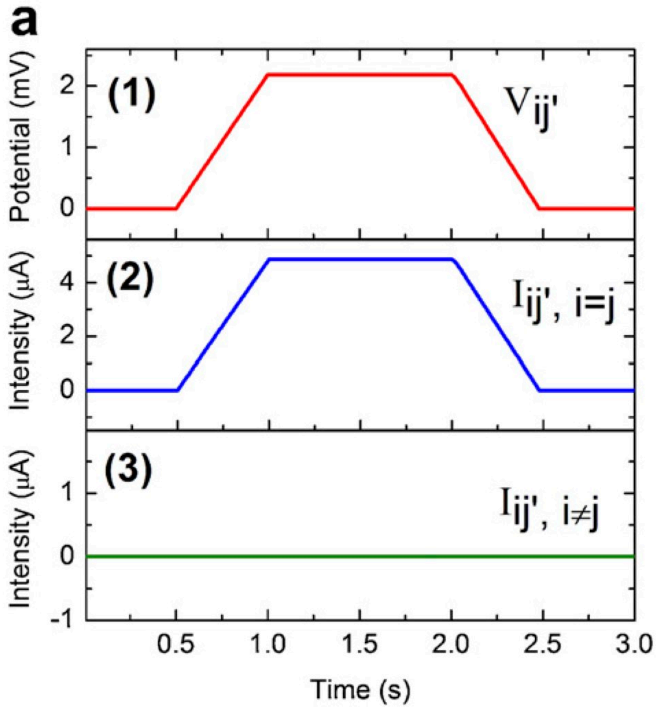


Piezoresistive effect

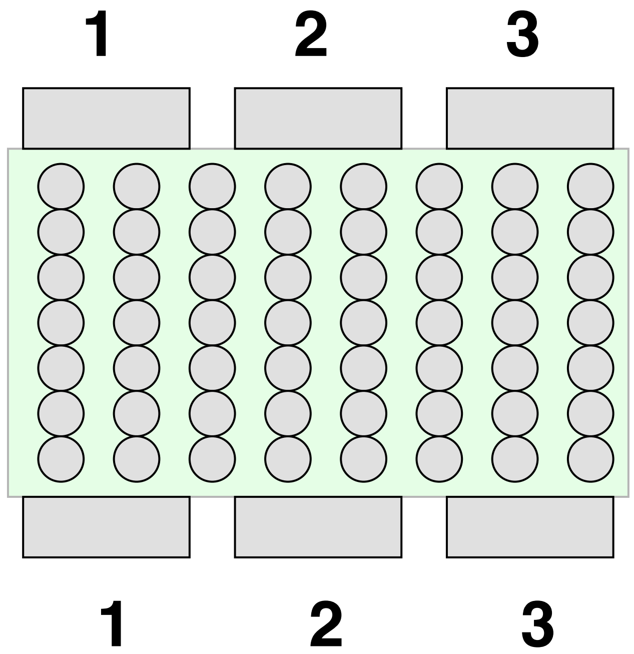
Magnetoresistive effect

1D conduction

- Facing electrodes : conduction seen
- Misaligned electrodes : no conduction
- **Perfect 1D conductor!**



2013 Mietta



Outline

1. Introduction
2. Magnetic powders
3. Magnetically aligned elastomers
4. **Thermoplastic compositions**
5. Conclusion & outlook

- **Formulation**
- **Processing**
- **Preliminary results**

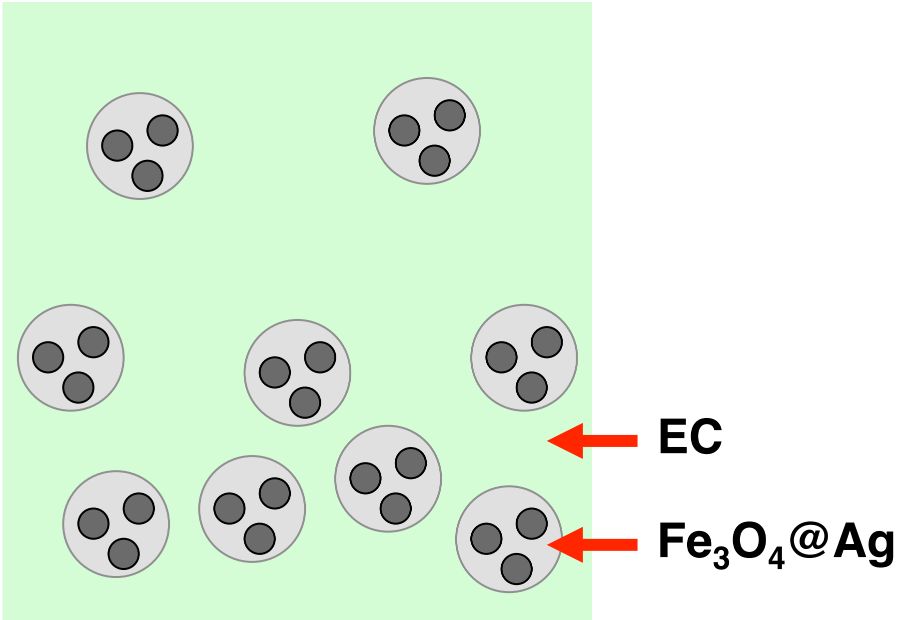
Formulation

Resin: thermoplastic + wax

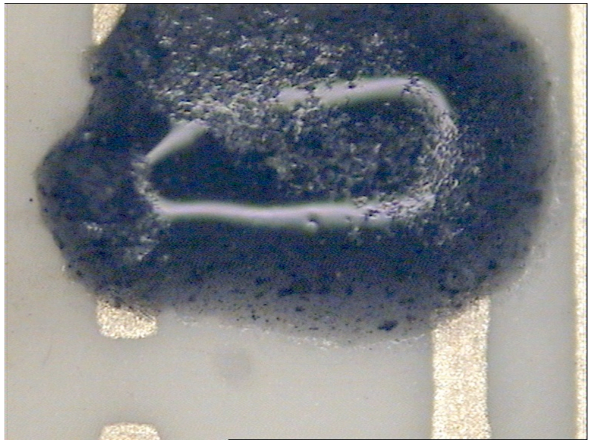
- Ethylcellulose EC resin
- Cetanol / octadecanol wax
- (Different solvents before drying)
- **Hot-melt composition**
  - EC : T_g ~150°C
  - Melting alone: degradation
  - & wax: melting at <100°C, low viscosity

Filler: coated ferrites

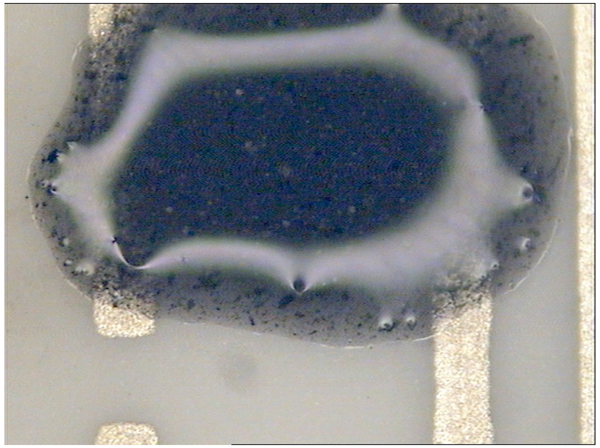
- Fe_3O_4@Ag
- $CoFe_2O_4$@Ag



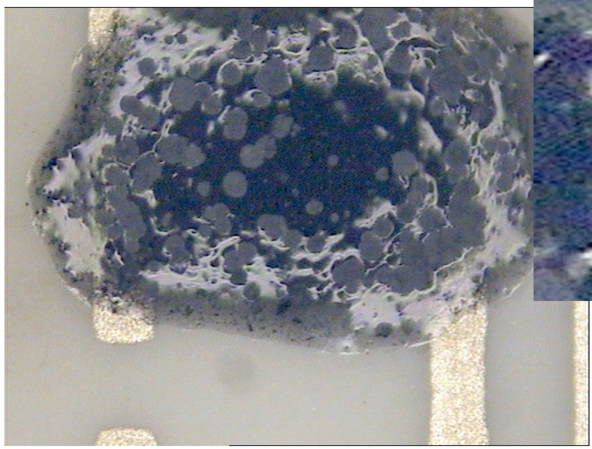
Processing – drying & (re)melting



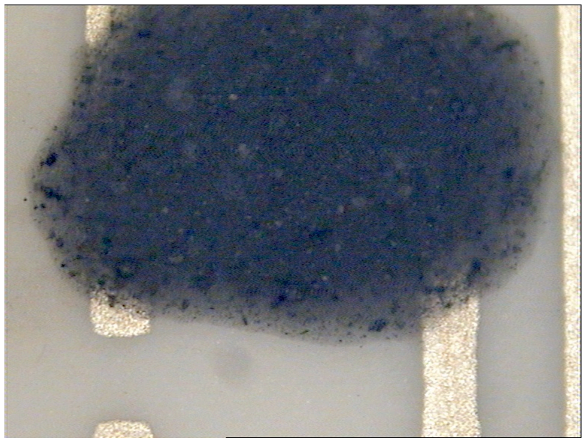
1) Wet, cold



2) Drying -> molten, hot

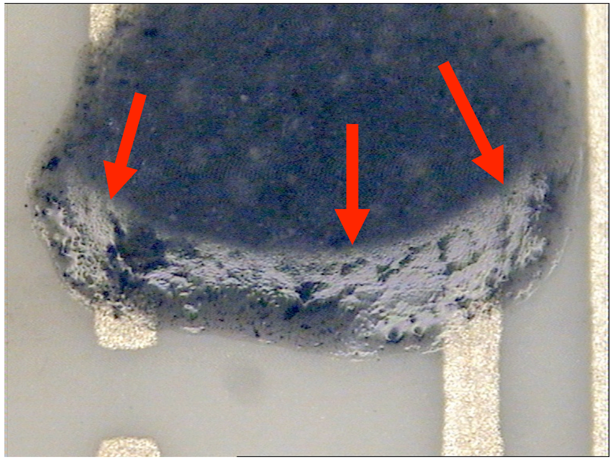


3) Crystallisation, cooling

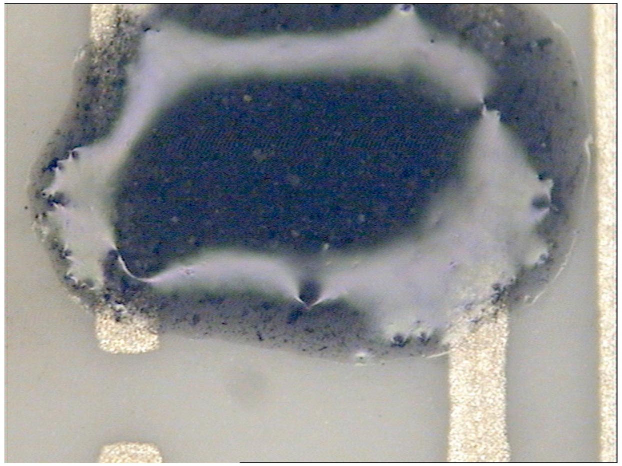


4) Crystallised, cold

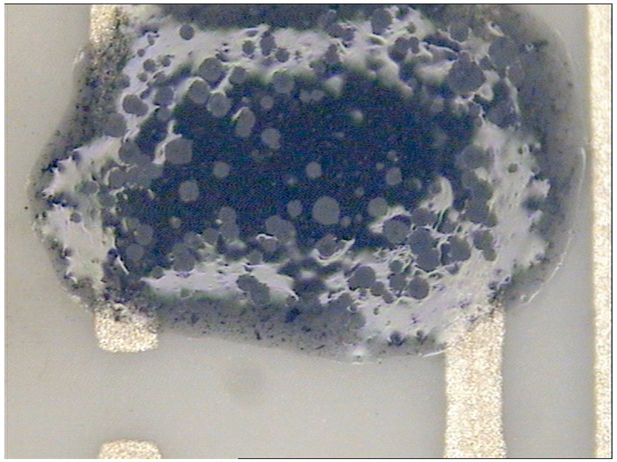
Processing – drying & (re)melting



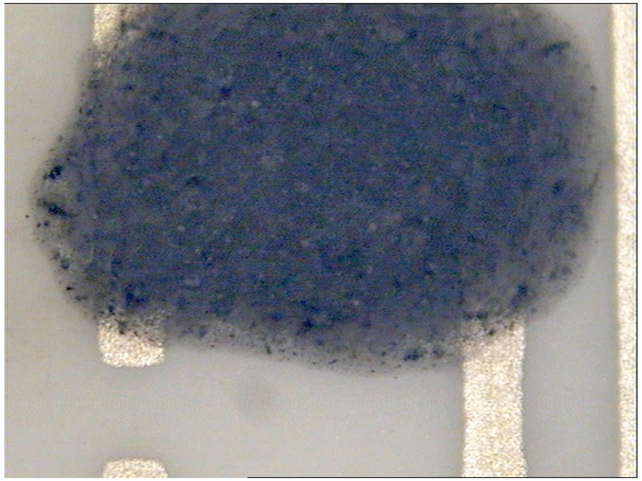
5) Remelting



6) Molten, hot



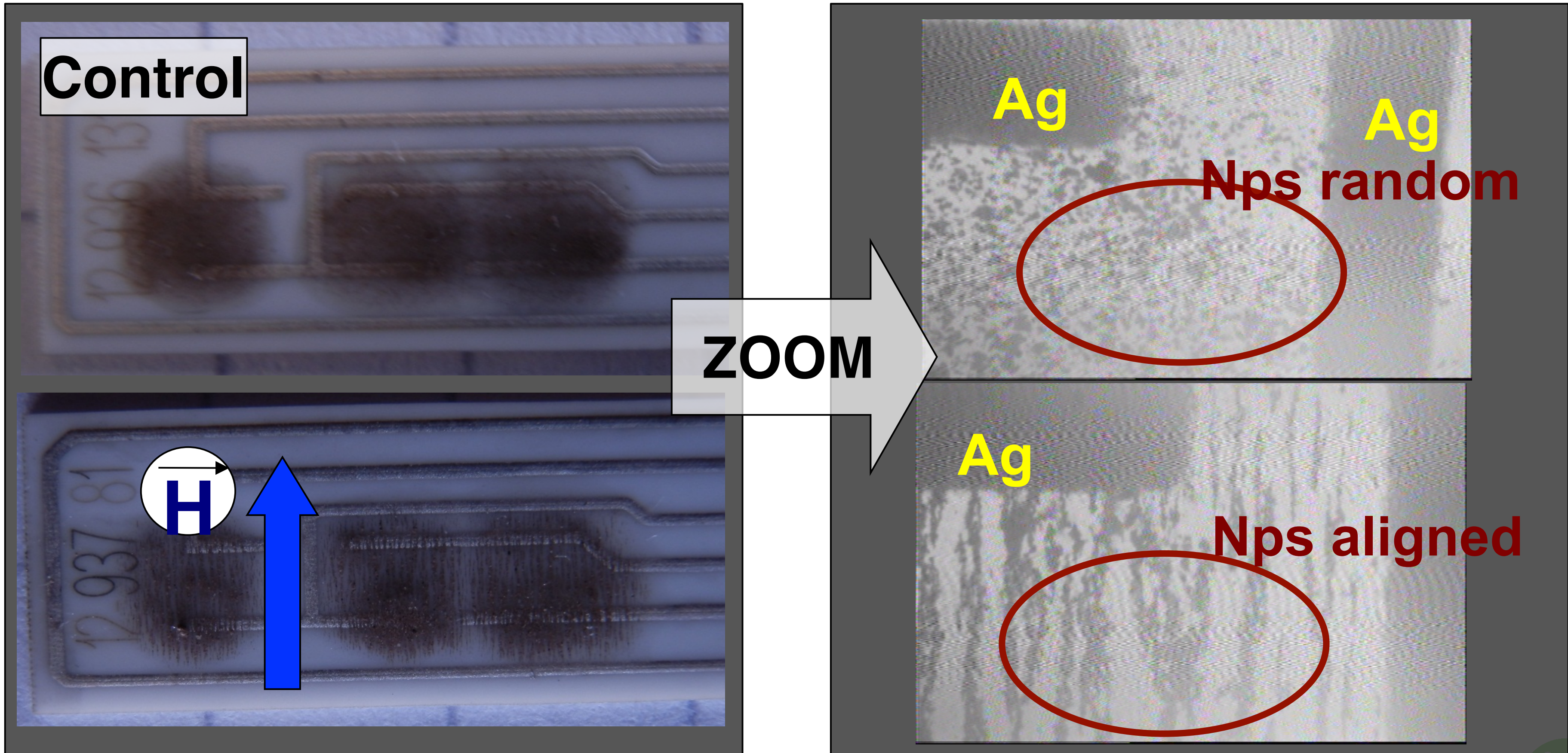
7) Crystallisation, cooling



8) Crystallised, cold

Preliminary results

- Magnetic alignment achieved
- Can be changed (remelting)
- Conductivity not achieved yet at low volume fractions <15%



Conclusions & outlook

Achievements

- Magnetic particle alignment in PDMS & thermoplastic hot-melt EC+wax matrices
- 1D conduction
- Anisotropic mechanical response
- Anisotropic piezo- & magnetoresistivity

Outlook / issues

- Characterise EC+wax behaviour
- Achieve conduction & its "magnetic reprogramming" in thermoplastic hot-melt matrix

Questions?

Thank you for your attention!

References

- **2010 Leyva.** Leyva-AG, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica (CNEA) Buenos Aires (AR), private communication, 2010.
- **2010 Negri**. Negri-M, Universidad de Buenos Aires (AR), "Magnetic and conducting elastic composites", Presentation held at EPFL-LPM (CH), 30.4.2010, 2010.
- **2011 Antonel**. Antonel-PS Guillermo-J Perez-OE Butera-A Leyva-AG Negri-RM, "Magnetic and elastic properties of $CoFe_2O_4$-polydimethylsiloxane magnetically oriented elastomer nanocomposites", Journal of Applied Physics 110 (4), 043920, 2011.
- **2011 Mietta.** Mietta-JL Ruiz-MM Antonel-PS Pérez-O Butera-A Jorge-G Maeder-T Negri-RM Leyva-AG, "Magnetoresistencia y elasticidad anisotrópica en elastómeros formados por cadenas de nanopartículas y nanotubos orientadas magnéticamente [magnetoresistance and anisotropic elasticity in elastomers formed by chains of magnetically oriented nanoparticles and nanotubes]", Presentation, Sólidos meeting, San Miguel de Tucumán (AR), 2011.
- **2012 Mietta**. Mietta-JL Ruiz-M Antonel-PS Perez-OE Butera-A Jorge-G Negri-RM, "Anisotropic magnetoresistance and piezoresistivity in structured Fe_3O_4-silver coated-PDMS elastomers at room temperature", Langmuir 28 (17), 6985–6996, 2012.
- **2013 Mietta**. Mietta-JL Jorge-G Perez-OE Maeder-T Negri-RM, "Superparamagnetic anisotropic elastomer connectors exhibiting reversible magneto-piezoresistivity", Sensors and Actuators A 192, 34–41, 2013.