

Final Workshop

**Mission Innovation Heating and Cooling –
Sorption Heat Pump Systems**

Taormina, 1st - 4th May 2023

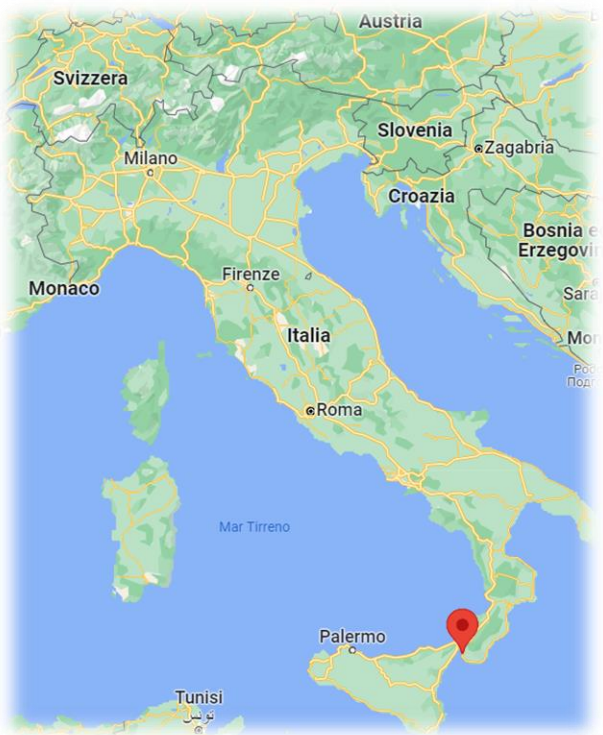
Research Activity Overview

***University Mediterranea
of Reggio Calabria***



Angela Malara
angela.malara@unirc.it

Location



Reggio Calabria



«The most beautiful km of Italy»



The city of the Strait



«Bronzi of Riace»



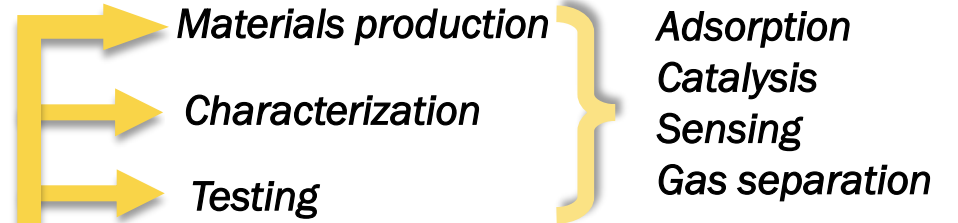
Bergamot

Mediterranea University of Reggio Calabria



DEPARTMENT OF CIVIL, ENERGY,
ENVIRONMENT AND MATERIAL
ENGINEERING

MATERIALS FOR
ENVIRONMENTAL AND
ENERGY SUSTAINABILITY
LABORATORY



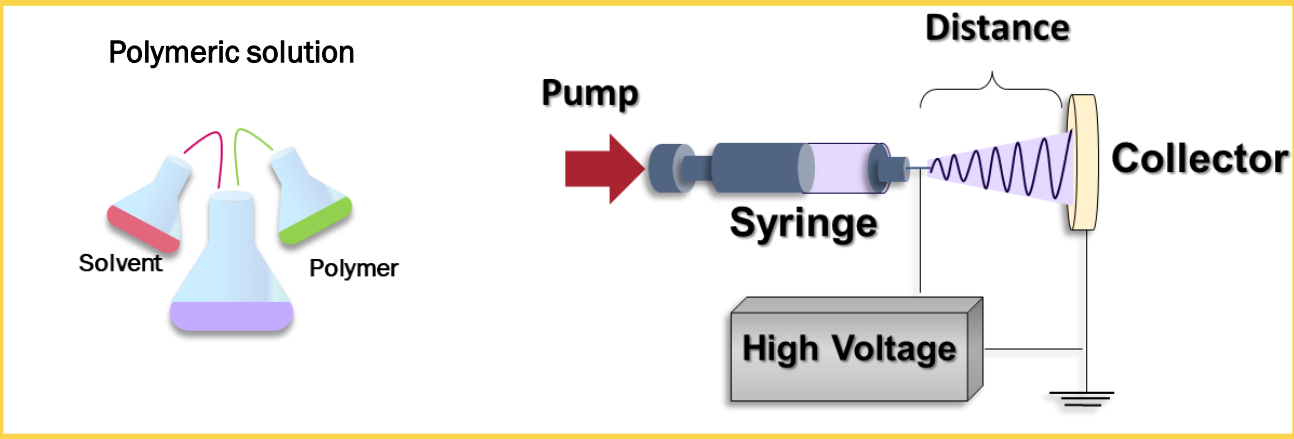
MATEES research group



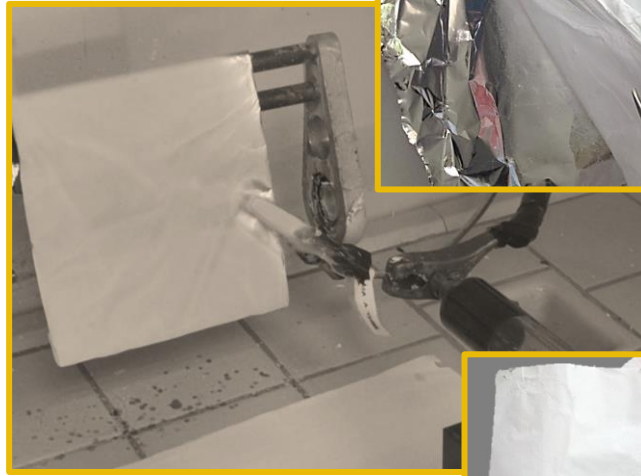
Electrospinning

Adsorption
Catalysis
Sensing
Gas separation

Production technique: ELECTROSPINNING



- ✓ The ElectroSpinning (ES) process is a fibre production method
- ✓ By means of an applied high voltage, a charged liquid jet is formed, elongated and deposited on the ground collector
- ✓ Simple and scalable preparation technique





Electrospinning of adsorption materials for heat transformation

“The real voyage of discovery consists not in seeking new landscapes, but in having new eyes.”

Marcel Proust



 **SORPTION FRIENDS III**

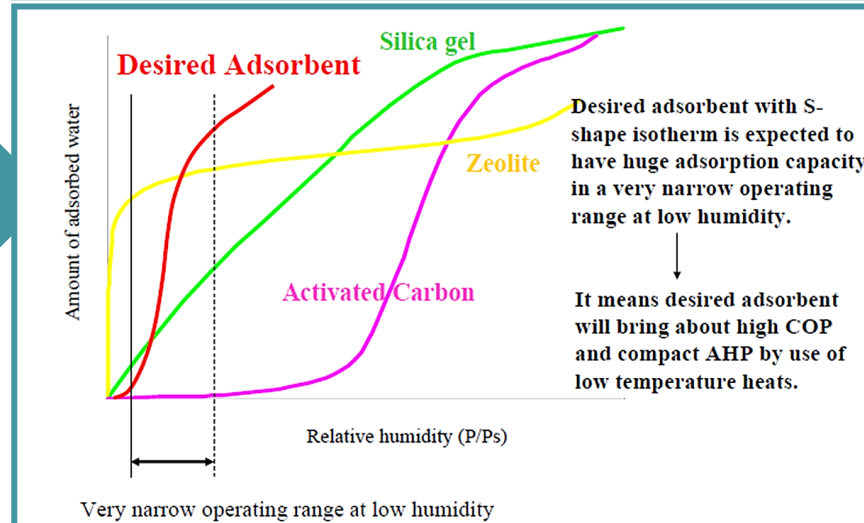


Adsorption materials for heat transformations

@ low temperatures ($T < 150\text{ }^{\circ}\text{C}$)
water vapor is the preferred fluid

THS	Working Pair (.../H ₂ O)	Applications
Adsorption	Silica gel	Solar cooling Heat pump Seasonal storage Long term storage
	Zeolites & zeotypes	
	Metal organic frameworks	
Chemical adsorption	MgSO ₄	
	CaCl ₂	
	SrBr ₂	

Adsorption isotherms



- Improvement of materials
- Efficient systems
- Low cost products



SORPTION FRIENDS III

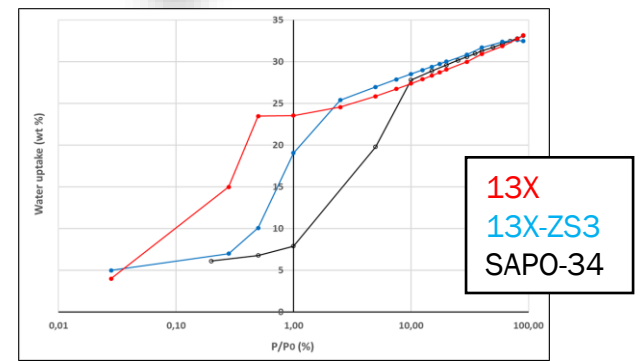
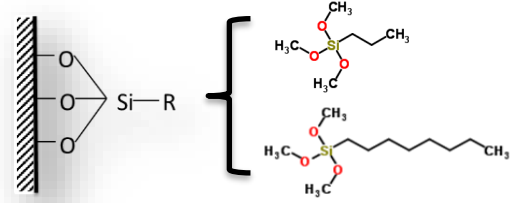


Adsorption materials for heat transformations



Modification of the electrostatic interaction by surface reactions

Zeolite 13X
Zeolite 4A



START

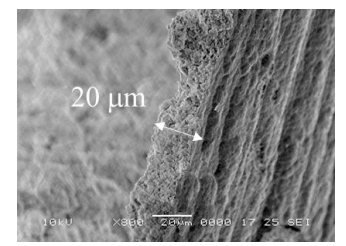
Materials

Systems

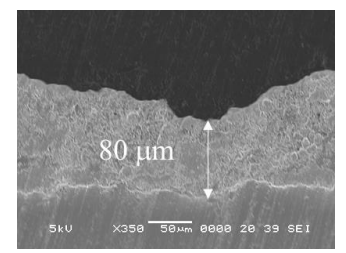
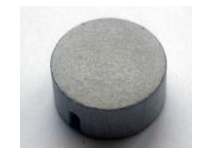


Direct synthesis on metals

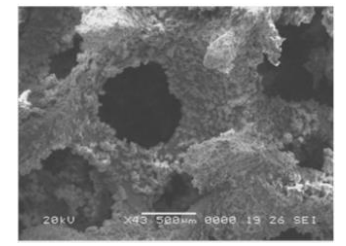
SAPO-34 on Al



NaY on Al

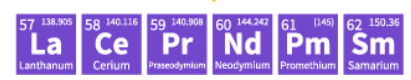


Zeolite on Al foams and C fibers

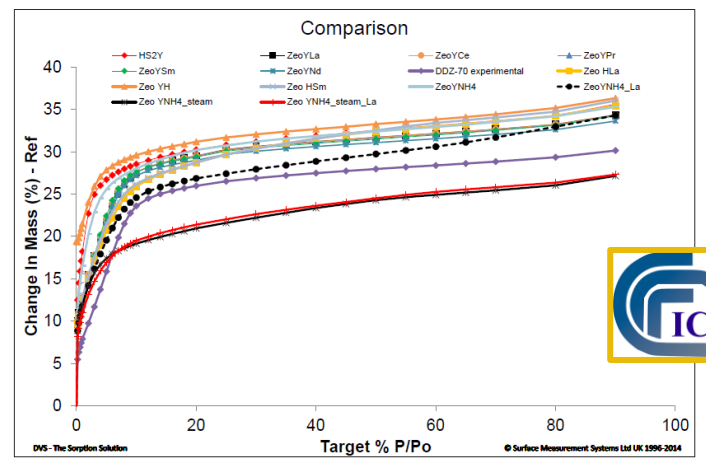


Modification of the electrostatic interaction by ions exchange

Na-Zeolite Y

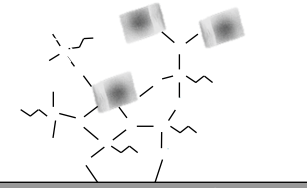
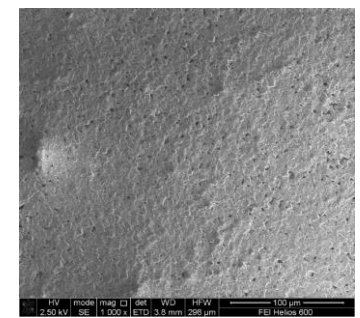


Rare earth elements



Binded coatings

SAPO-34 on Al

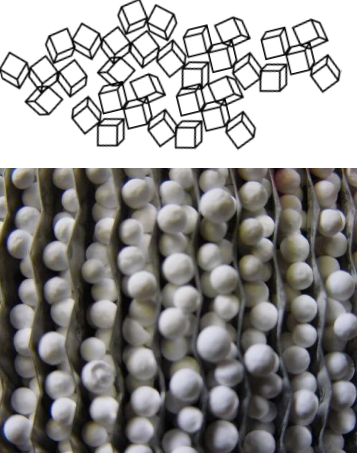


support surface



Innovative solution

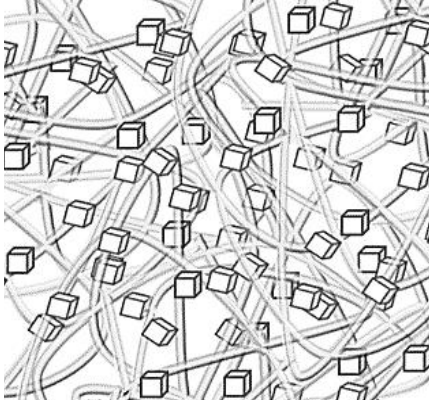
Grains
(Zeolite and Silica Gel)



- ✗ “Grains” fill the free space among fins of a heat exchanger
- ✗ Dusty system
- ✗ Scarce surface contact
- ✗ Heat and mass transfer problems

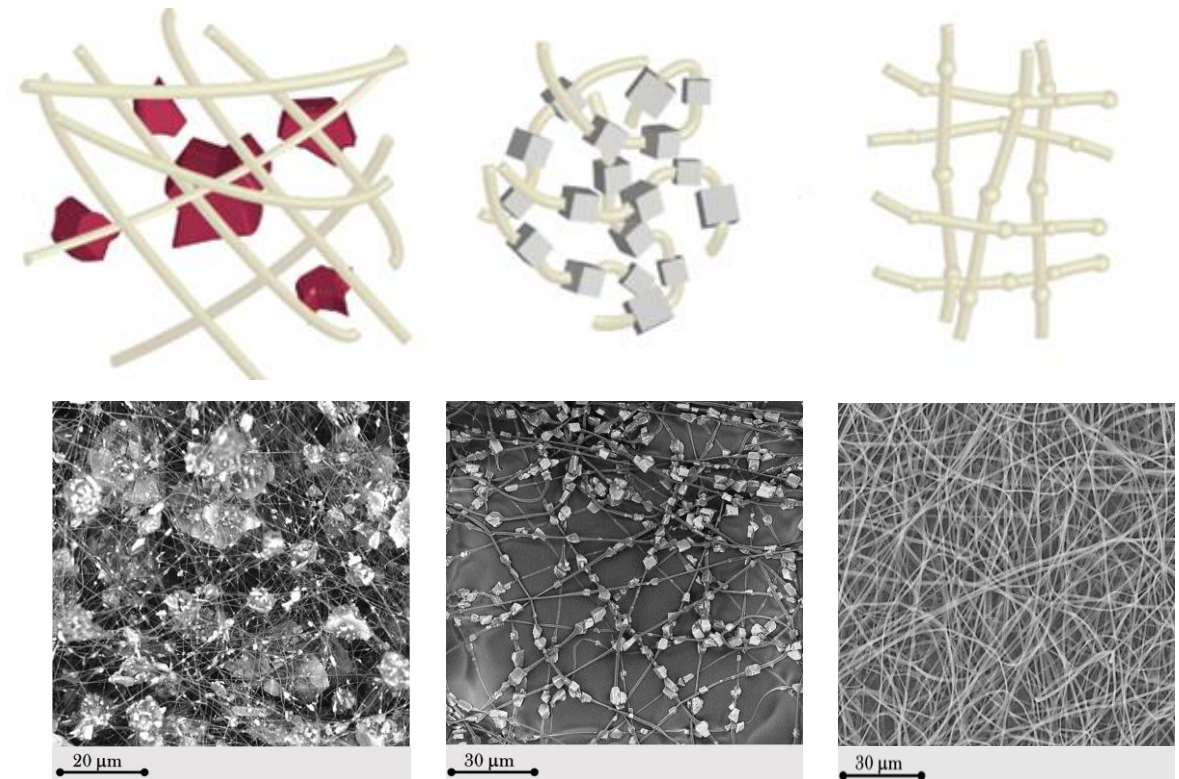
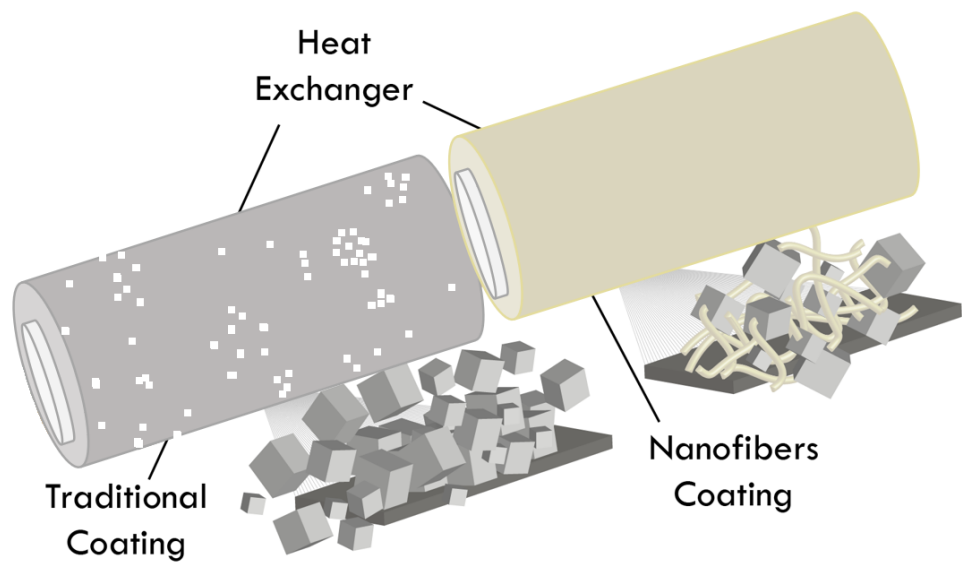


Grains embedded
in a matrix of polymeric fibers



- ✓ High surface area
- ✓ High permeability
- ✓ High mechanical stability
- ✓ Fits various geometries

Innovative solution



EP3543380 - 2018

Method for making the heat exchanger of a thermal adsorption machine and respective thermal machine

P.L. Antonucci, P. Frontera, L. Bonaccorsi and A. Malara

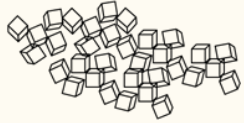



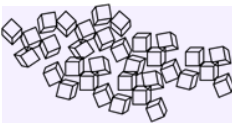

- ✓ Zeolite/silica gel powders embedded in the polymeric nanofibers
- ✓ High porous and high surface area composite materials
- ✓ No negative impact on the adsorption properties of zeolite/silica gel

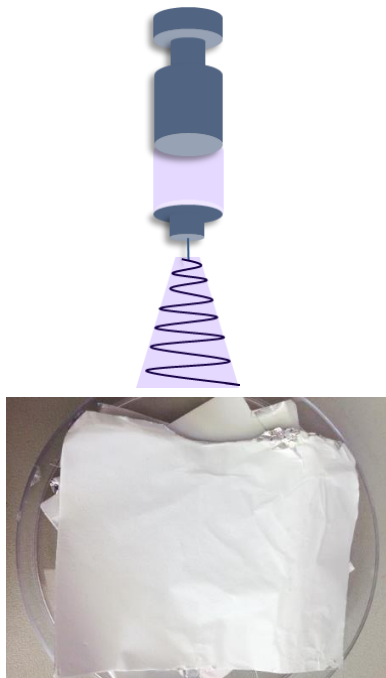
Fibrous adsorption materials for heat transformations

Polymer type

- PVP
- PAN
- PMMA
- PVA
- PEO
- PS

+

Additive type	Weight % (dry base)
 Zeolite SAPO-34	10-85 %
 Silica gel	10-80 %
 TEOS	5-24 %
 Hydrated salt CaCl₂	10-50 %
 +  Zeolite SAPO-34 + Hydrated salt CaCl₂	50+20 %



Electrospinning parameters

Syringe	10 ml
Needle (diameter)	0.7 mm
Distance	15 cm
Voltage	13.5 kV
Flow rate	1.2 ml/min

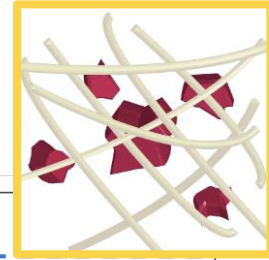
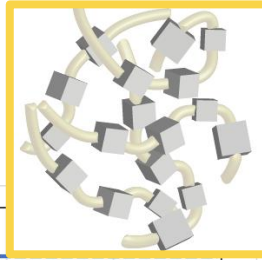
A. Malara et al., Materials 11(12) (2018) 2555
 A. Freni et al., Energy 187 (2019) 115971
 P. Frontera et al., Coatings 9(7) (2019) 443-454
 L. Bonaccorsi et al., Energies 13 (2020) 4299
 E. Bramanti et al., Materials Chemistry and Physics 287 (2022) 126248
 A. Malara et al., Heat Transfer Engineering, 43(19) (2022) 1652
 P. Frontera et al., Sustainability 15 (2023) 6567

Fibrous adsorption materials for heat transformations

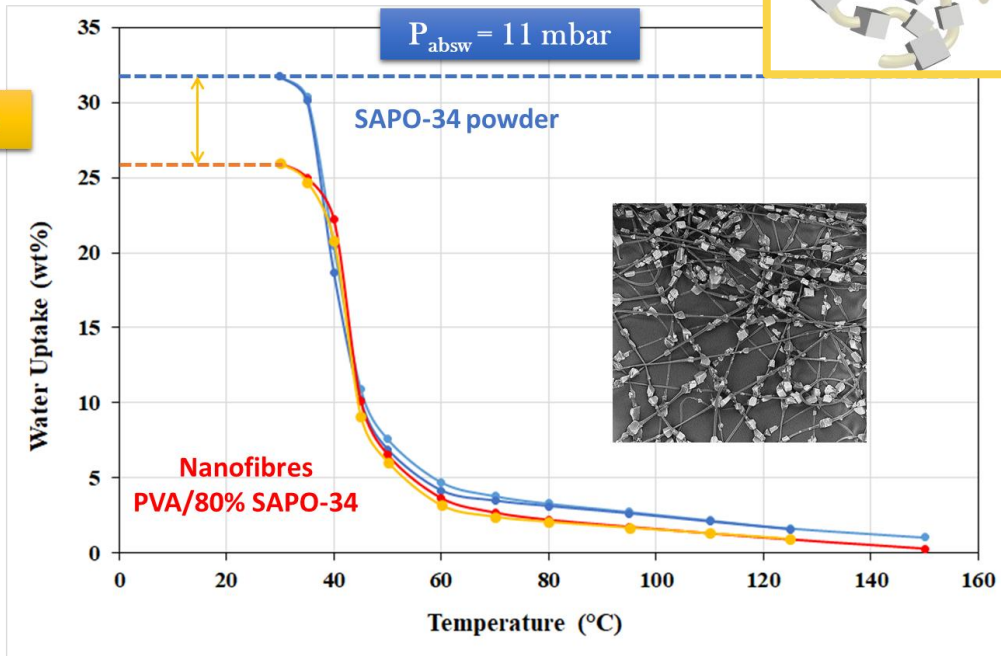
Water adsorption equilibrium curves

$P_{\text{absw}} = 11 \text{ mbar}$

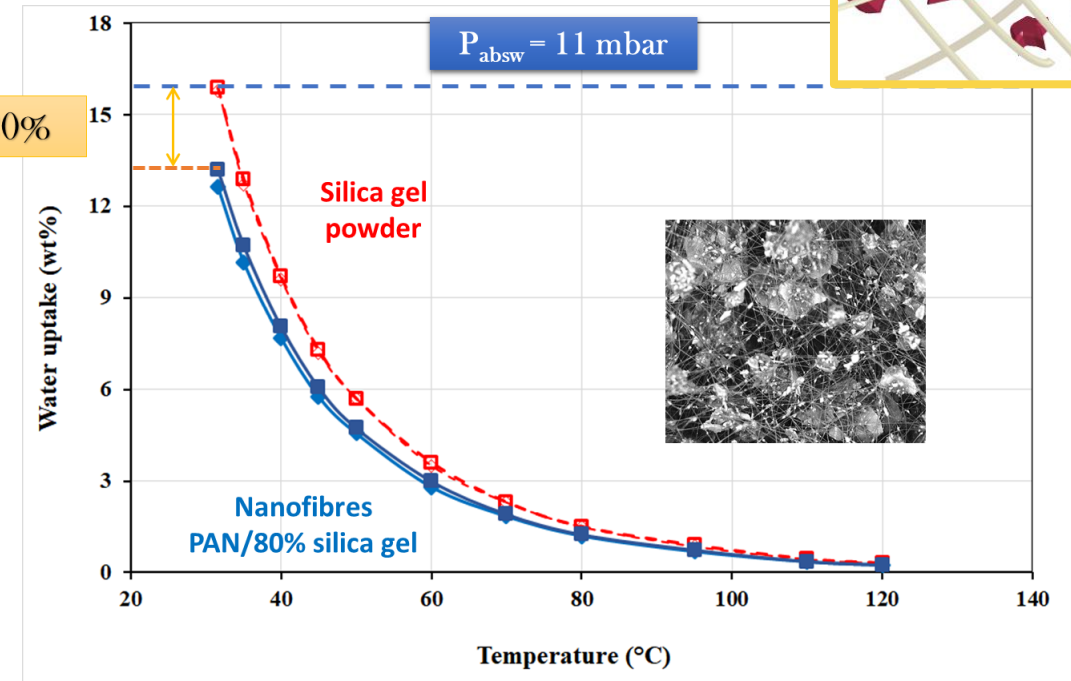
I generation of hybrid microfibers



$\Delta \text{wt} = 20\%$



$\Delta \text{wt} = 20\%$

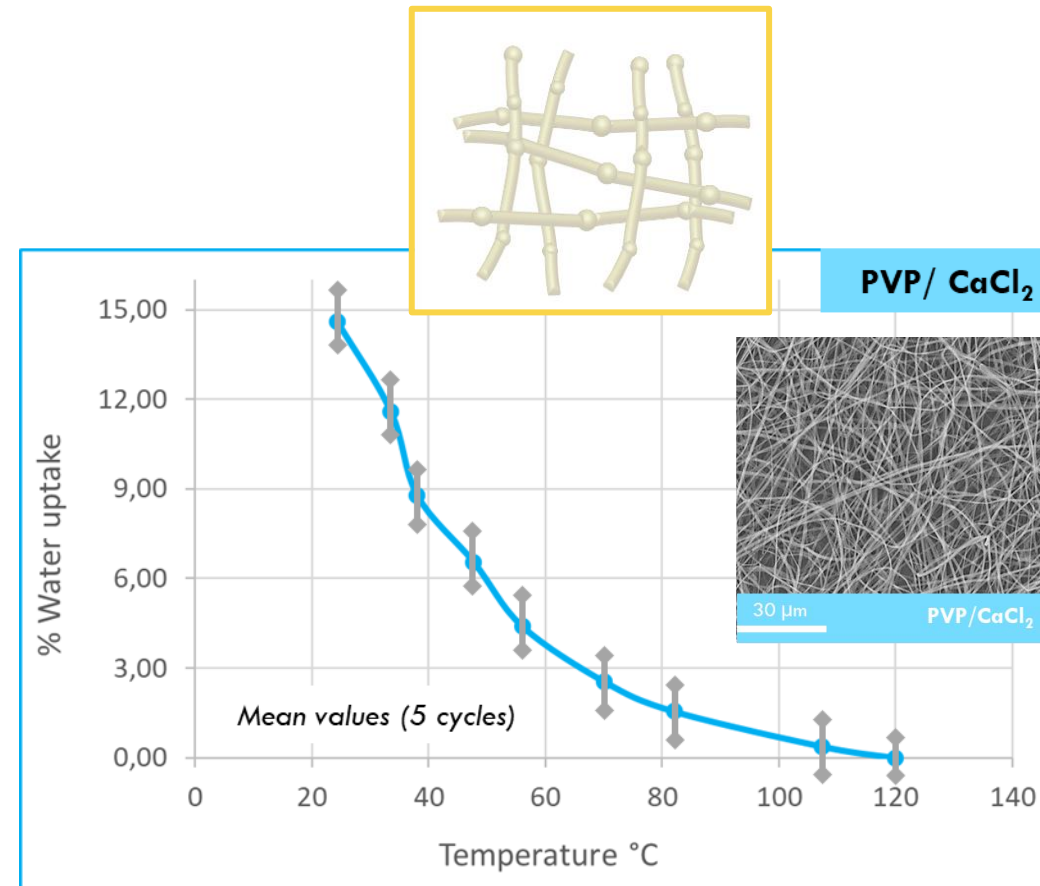
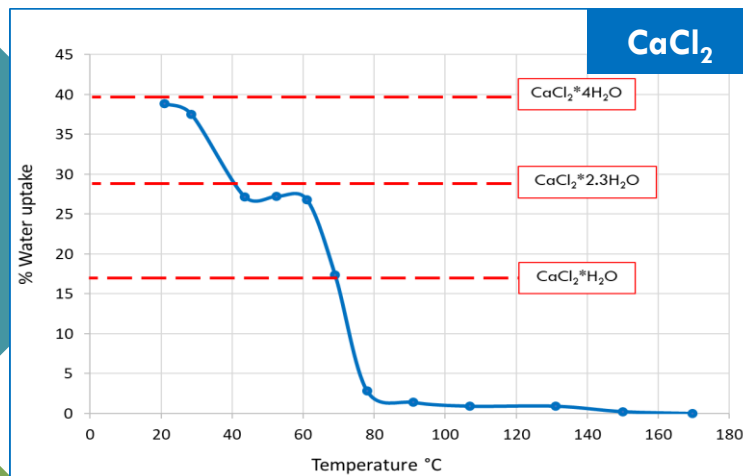
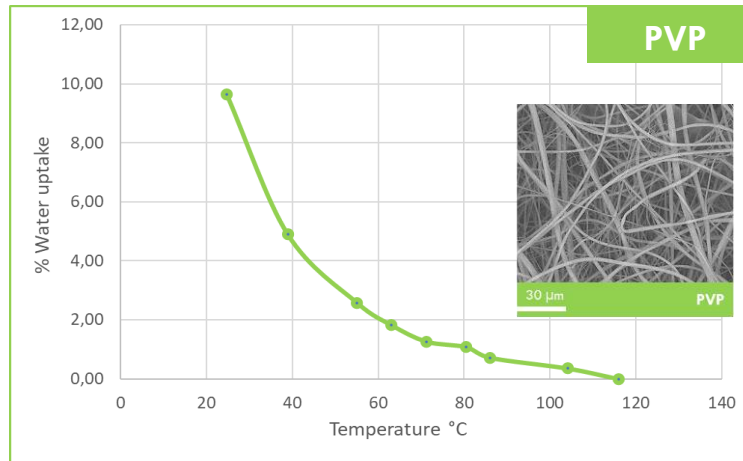


Fibrous adsorption materials for heat transformations

Water adsorption equilibrium curves

$P_{\text{absw}} = 11 \text{ mbar}$

II generation of hybrid microfibers



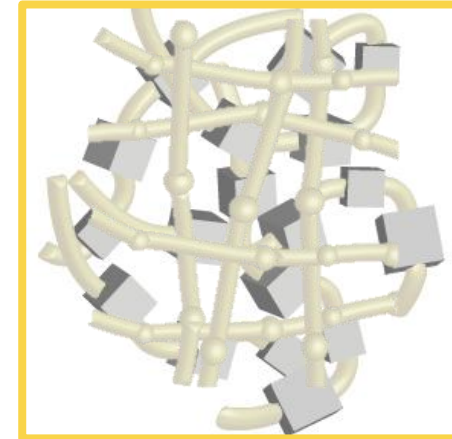
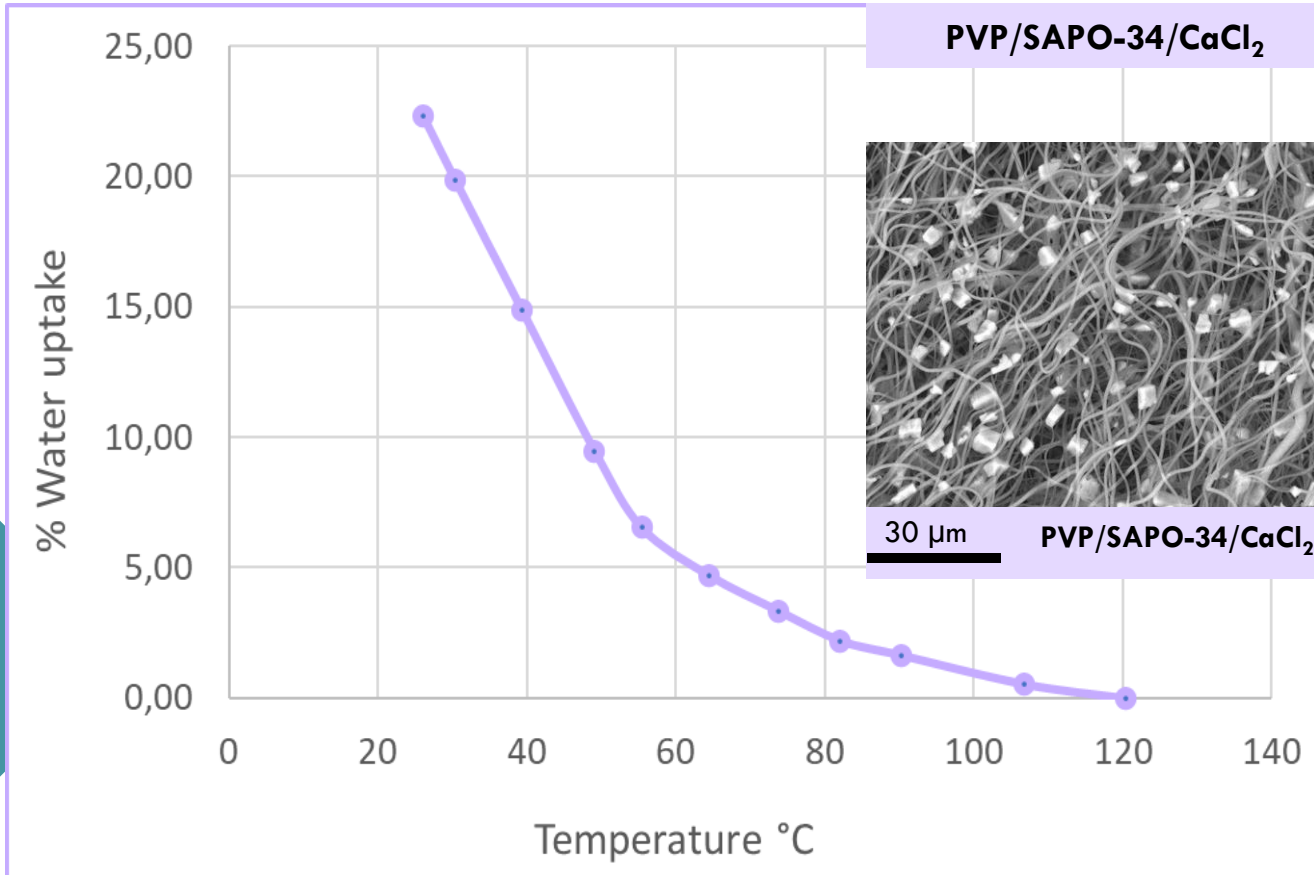
- ✓ Water uptake is proportional to PVP and CaCl₂ content
- ✓ CaCl₂ addition improves PVP microfibres adsorption with no evidence of properties degradation (5 cycles)
- ✓ No hysteresis phenomena have been observed

Fibrous adsorption materials for heat transformations

Water adsorption equilibrium curves

$P_{\text{absw}} = 11 \text{ mbar}$

III generation of hybrid microfibers



- ✓ Water uptake is proportional to PVP, SAPO-34, CaCl₂ content
- ✓ Zeolite addition increased adsorption performances significantly since zeolite porosity is not obstructed by the polymer/salt pair

UNDER INVESTIGATION

Fibrous adsorption materials for heat transformations

Characterization

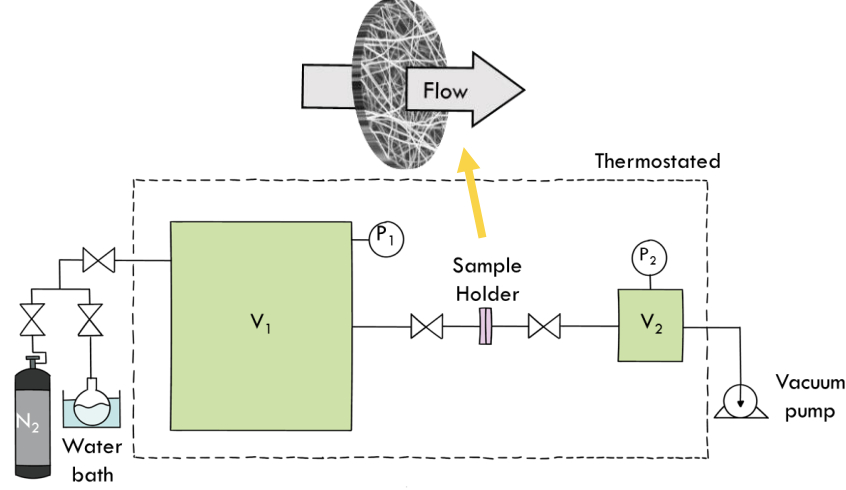


→ Vapor permeability

→ Thermal conductivity
(Guarded Hot Plate Method)

→ Mechanical properties

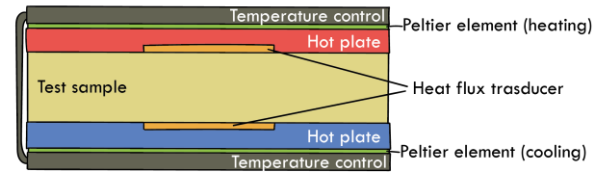
→ Durability



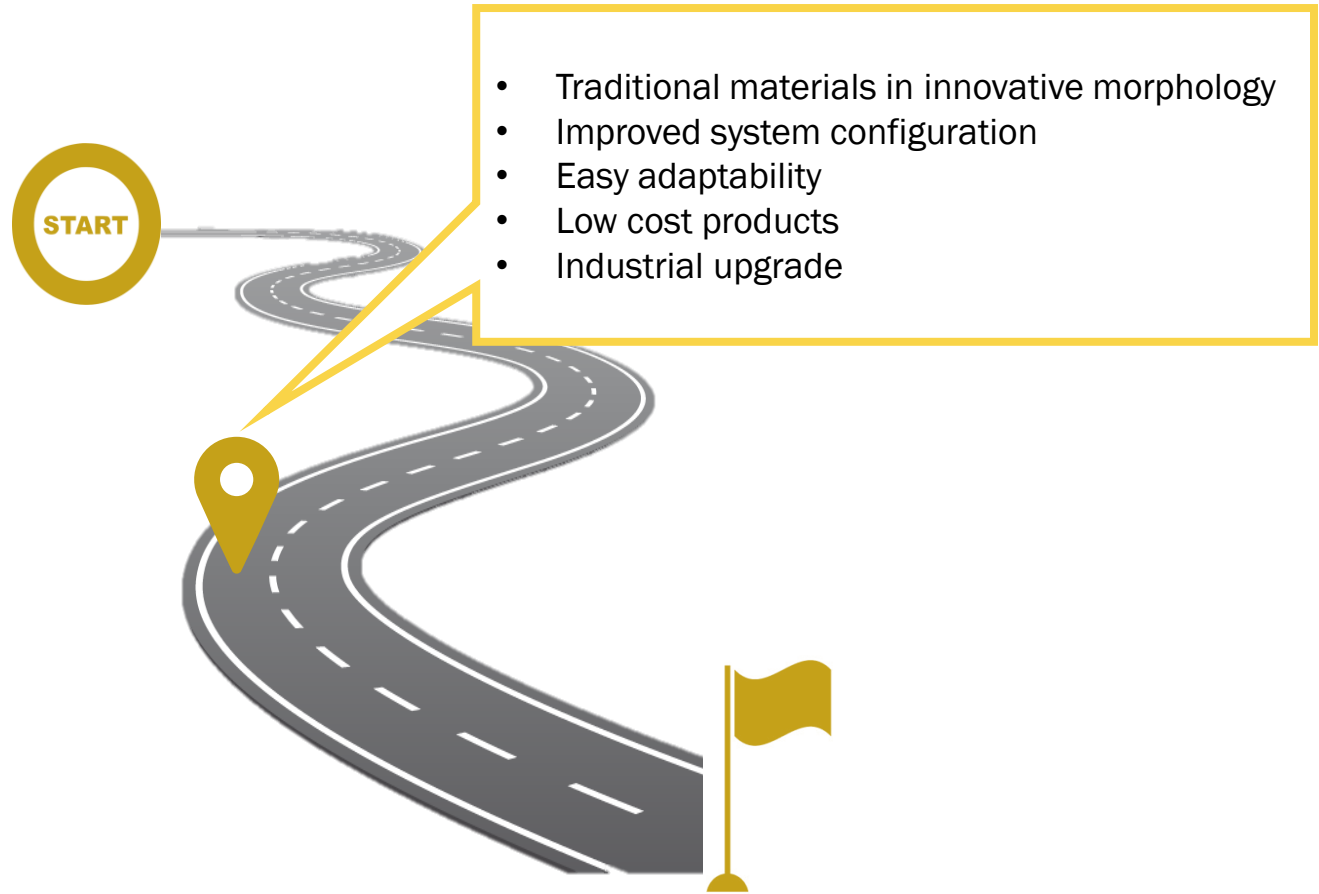
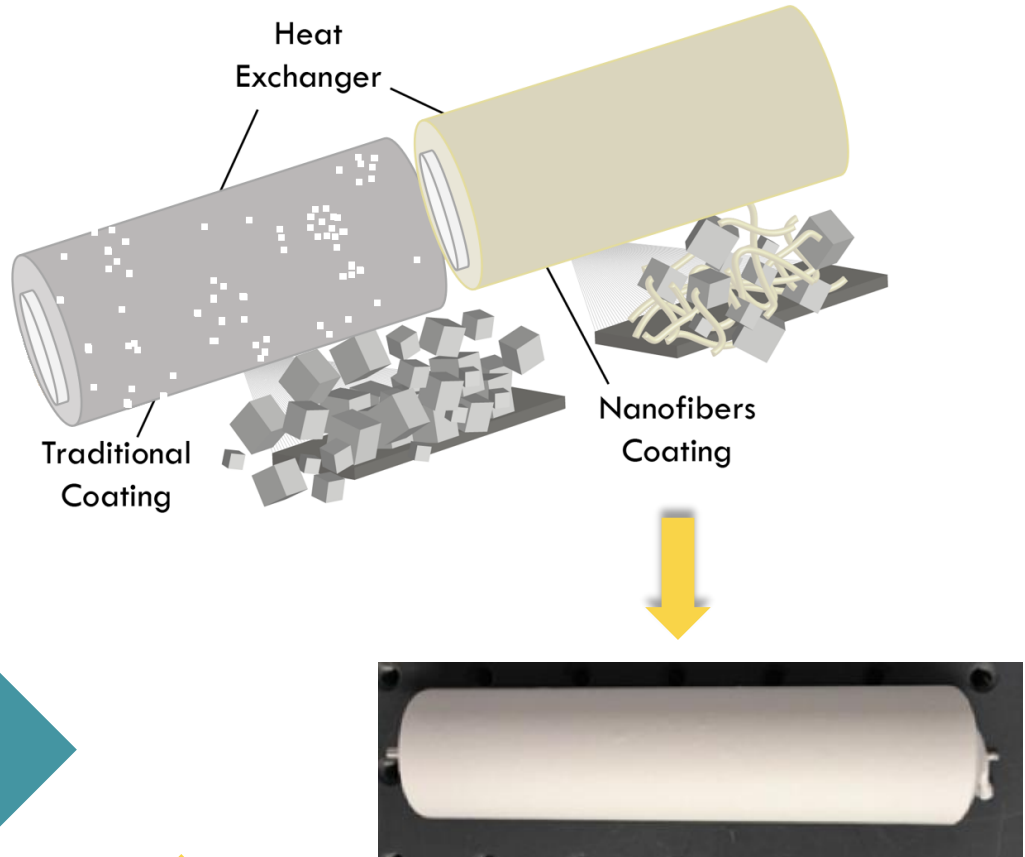
Darcy law

$$k = u\mu \frac{dP}{dx}$$

- k Permeability
- μ Fluid viscosity
- u Fluid velocity
- dP Pressure drop
- dx Thickness



Conclusions



Final Workshop
Mission Innovation Heating and Cooling –
Sorption Heat Pump Systems

Taormina, 1st - 4th May 2023



*Thank you
for your
kind attention*

Research **view**

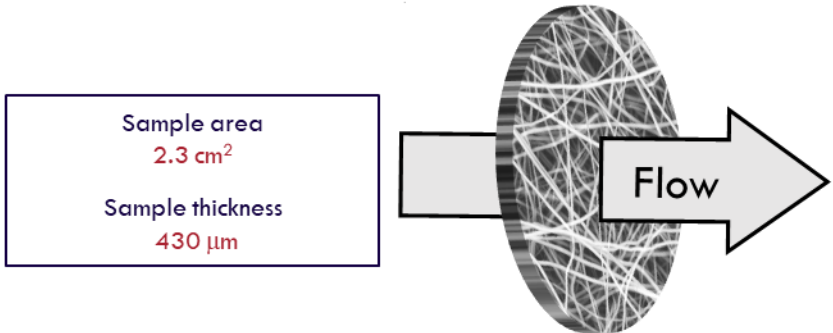
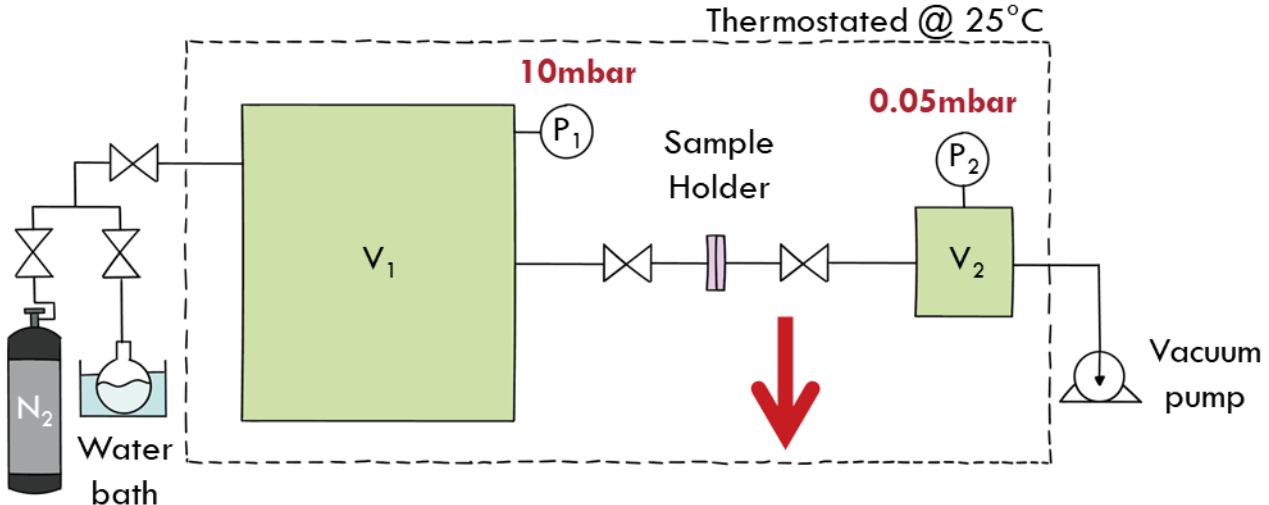
***University Mediterranea
of Reggio Calabria***



Angela Malara
angela.malara@unirc.it

Permeability measurement

Permeability @10mbar



Darcy law

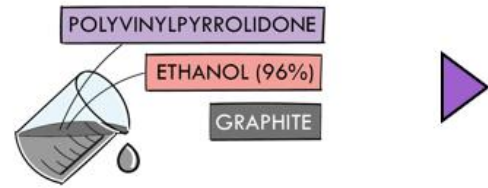
$$k = u\mu \frac{dP}{dx}$$

- k Permeability
- μ Fluid viscosity
- u Fluid velocity
- dP Pressure drop
- dx Thickness

- ✓ N₂ flow and water vapour
- ✓ High permeability to gas and water vapor in the analyzed conditions

Sample	k (m ²)	
	N ₂	H ₂ O vapour
PVP	1,05E-13	1,58E-14
PVP/CaCl ₂	1,11E-13	1,02E-14
PVP/SAPO34/CaCl ₂	3,30E-13	9,64E-15

Thermal conductivity measurement



2.1. Preparation of solutions

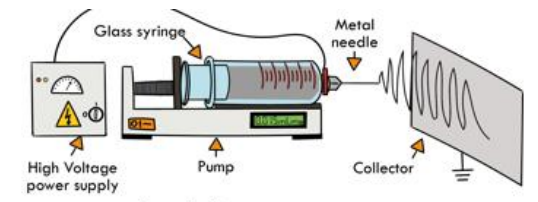
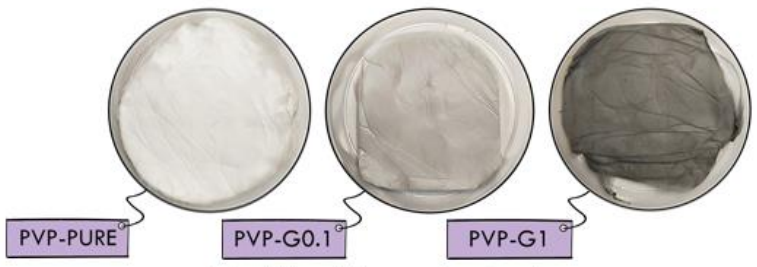


Figure 1. Electrospinning setup

2.2. Production by Electrospinning process



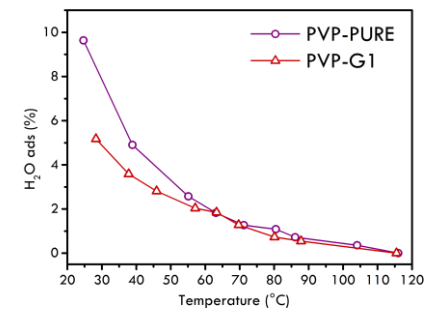
2.3. Microfibers obtained

Table 1. Parameters of solution

SAMPLE	PVP/EtOH (w/w%)	PVP/GRAPHITE (w/w%)
PVP-PURE	16.7/83.3	-
PVP-G0.1	12.5/87.5	91.0/9.0
PVP-G1	12.5/87.5	50.0/50.0

According to the results of measurements on thermal conductivity, the incorporation of graphite flakes resulted in an improvement in the fibers' capacity to transfer heat. In addition, the presence of graphite has led to an increase in the permeability of the fibers as well as a decrease in the adsorption capacity that is proportionate to the graphite concentration.

Water vapour adsorption



Permeability

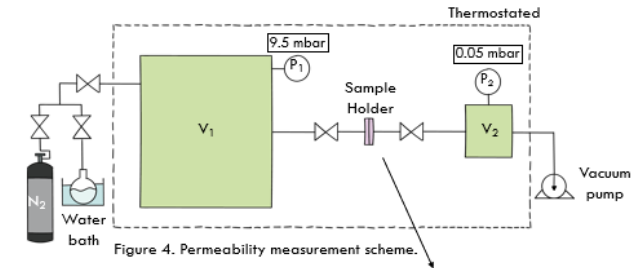
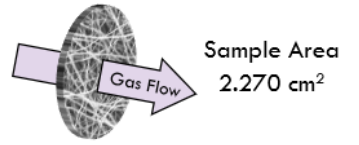


Figure 4. Permeability measurement scheme.

Table 2. Results of permeability test

SAMPLE	k [N ₂] (m ²)	k [H ₂ O] (m ²)
PVP-PURE	1,05 E-13	1,58 E-14
PVP-G0.1	1,10 E-13	1,62 E-14
PVP-G1	1,42 E-13	1,76 E-14



Thermal conductivity

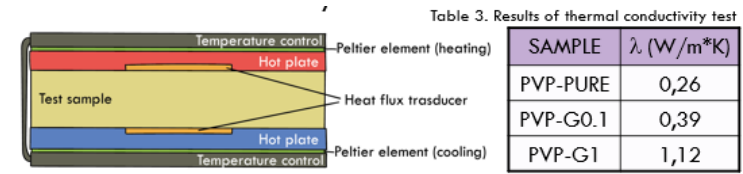
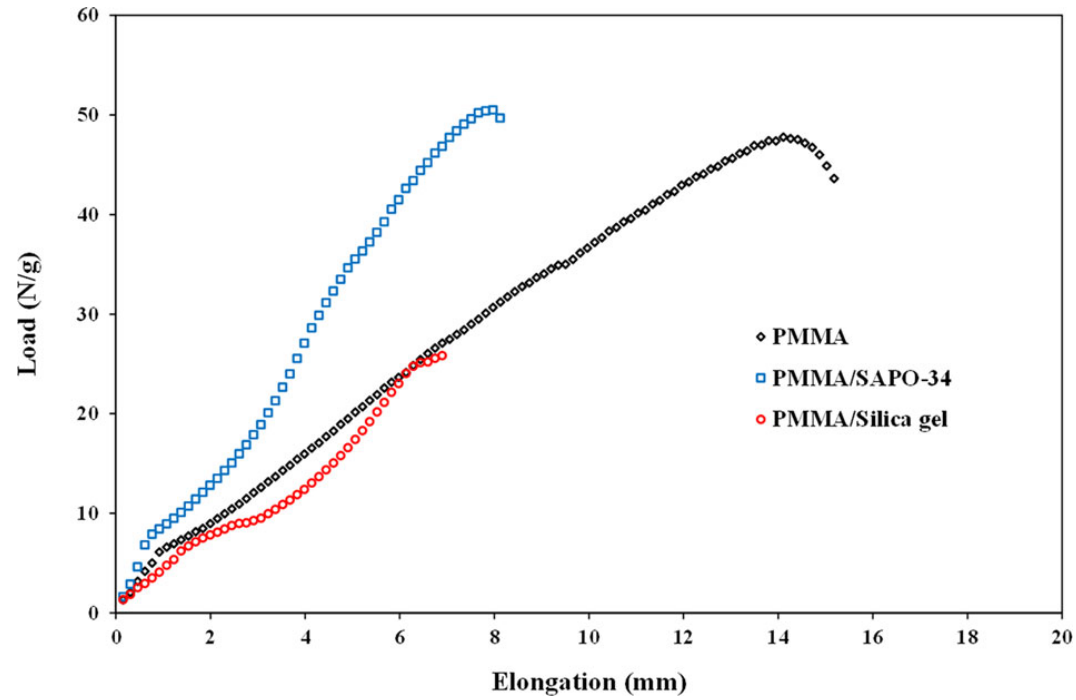


Table 3. Results of thermal conductivity test

SAMPLE	λ (W/m²K)
PVP-PURE	0,26
PVP-G0.1	0,39
PVP-G1	1,12

Mechanical properties



The addition of SAPO-34 particles in PMMA acted like a strengthening additive for the polymeric matrix improving the coatings/textiles mechanical properties. On the opposite, the silica gel addition was detrimental to the mechanical response.