15 September 2025

Silica and silicates decorated with guanidinium groups: a potential platform for the generation of thermoresponsive solvent free nanofluids

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NanoMat@Lab

FUNCTIONAL MATERIALS

Roberto Scotti Barbara Di Credico Silvia Mostoni

Massimiliano D'Arienzo Roberto Nisticò Carmen Canevali

NanoMat@Lab aims at the synthesis and functional characterization of *inorganic pure and hybrid materials* for **energy saving and sustainability**

Research lines:

Inorganic Materials for

- Catalysis, photo and (photo)electro catalysis
- Rubber nanocomposites for tires
- Stimuli responsive applications

Collaboration with companies:

- ✔ Pirelli
- ✔ Fluorsid
- ✔ ENI
- ✔ Nuovo Pignone
- ✔ IVM chemicals
- ✔ Tecnovo and several others…

Our strategy

1 **Morphology control**

2 **Design of final objects with tailored structures and surfaces**

3 **Introduction in suitable matrices (organic or inorganic)**

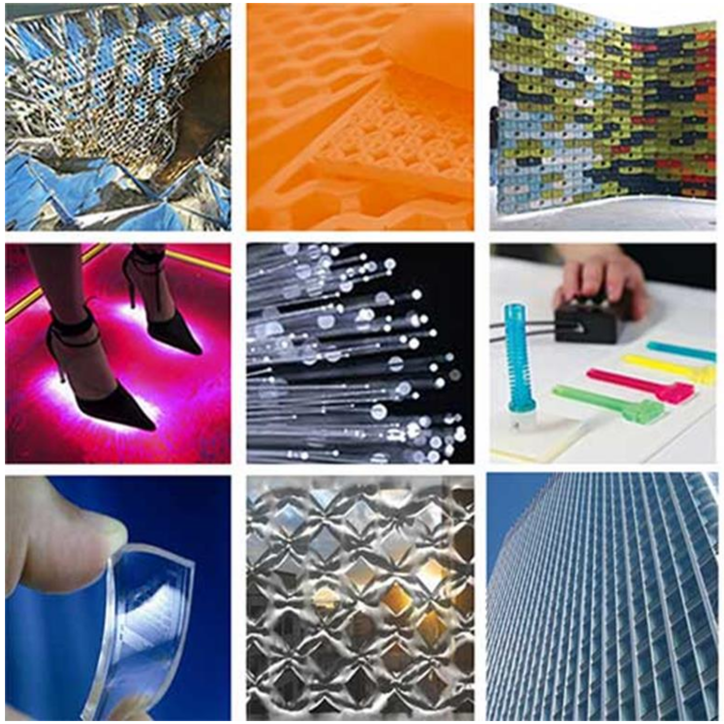
4 **Impart peculiar functional properties by engineering hybrid interfaces**

Stimuli-responsive nanocomposites

Stimuli-responsive materials

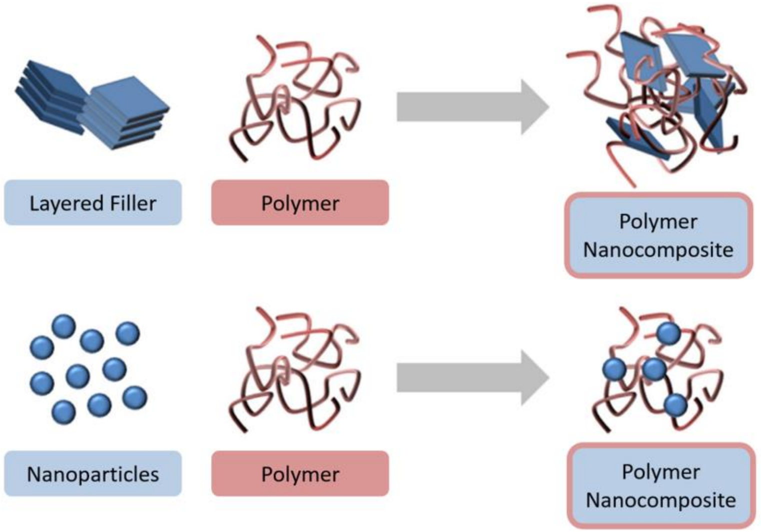
Advanced materials capable of responding to external or internal stimuli and environmental changes, triggering specific functions in response

- strain
- stress
- temperature
- chemicals
- pH
- electric and magnetic fields
- light

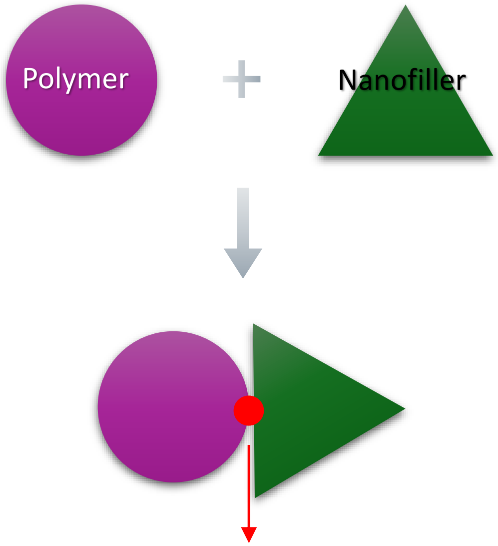


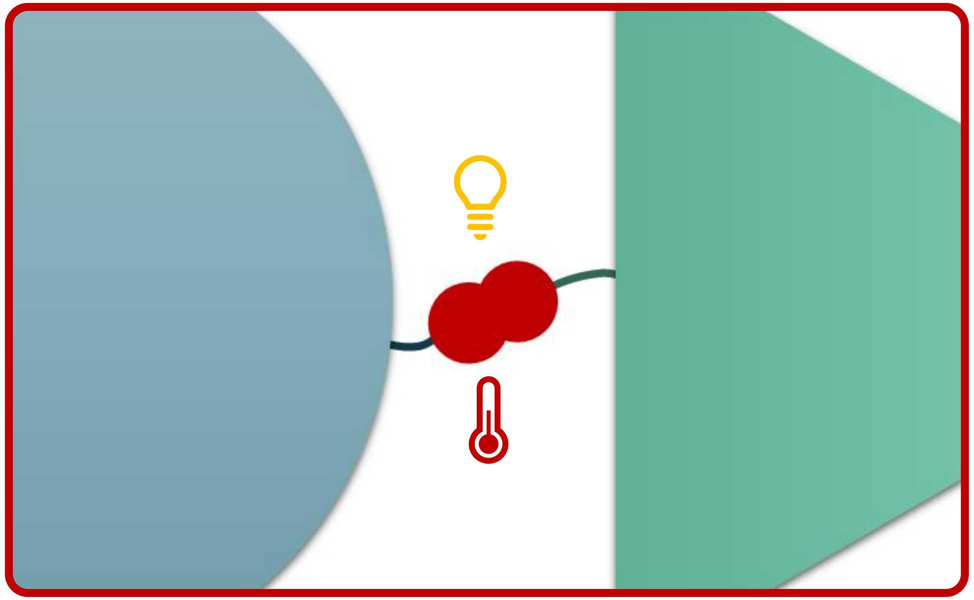
R. Busquets (Ed.), Emerging Nanotechnologies in Food Science, Elsevier, Boston (2017), pp. 119-147

Polymer nanocomposite



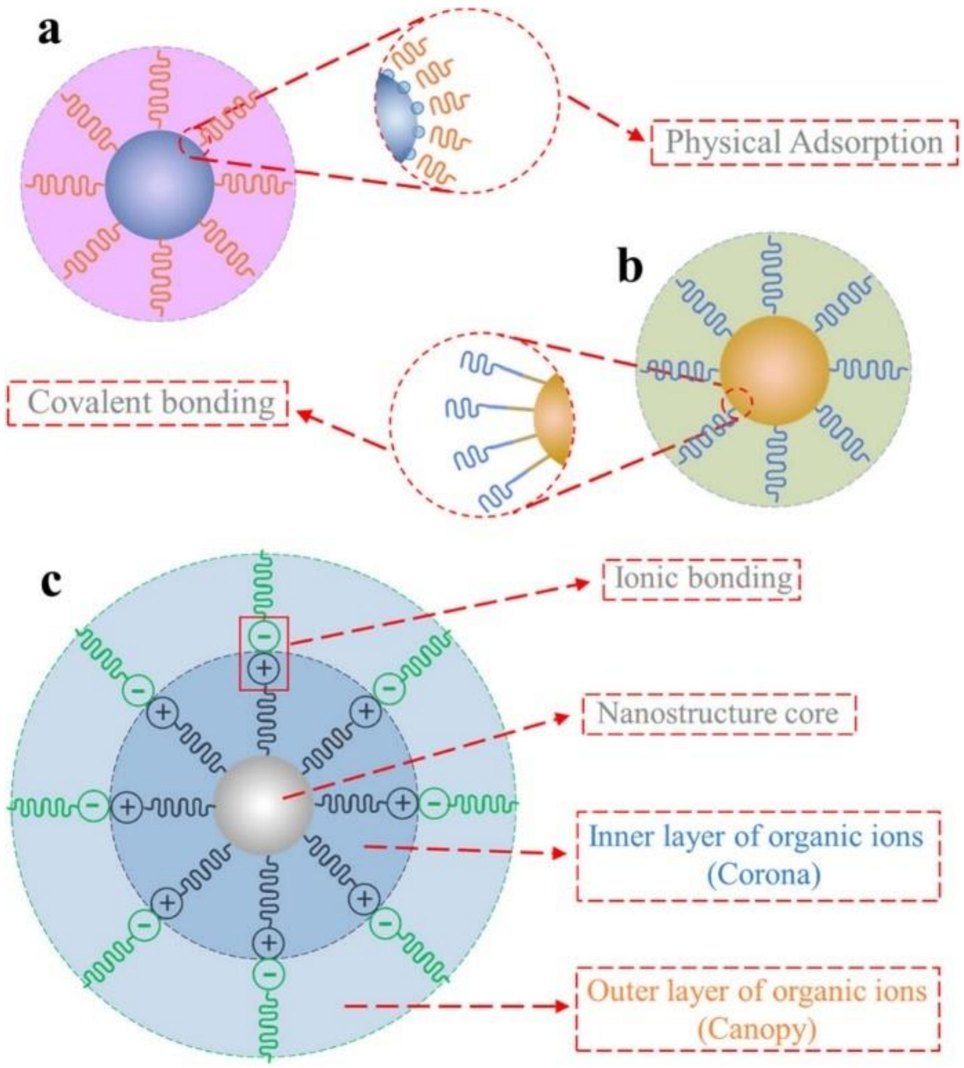
Combination of polymeric flexibility and easy processability with the robustness of inorganic components

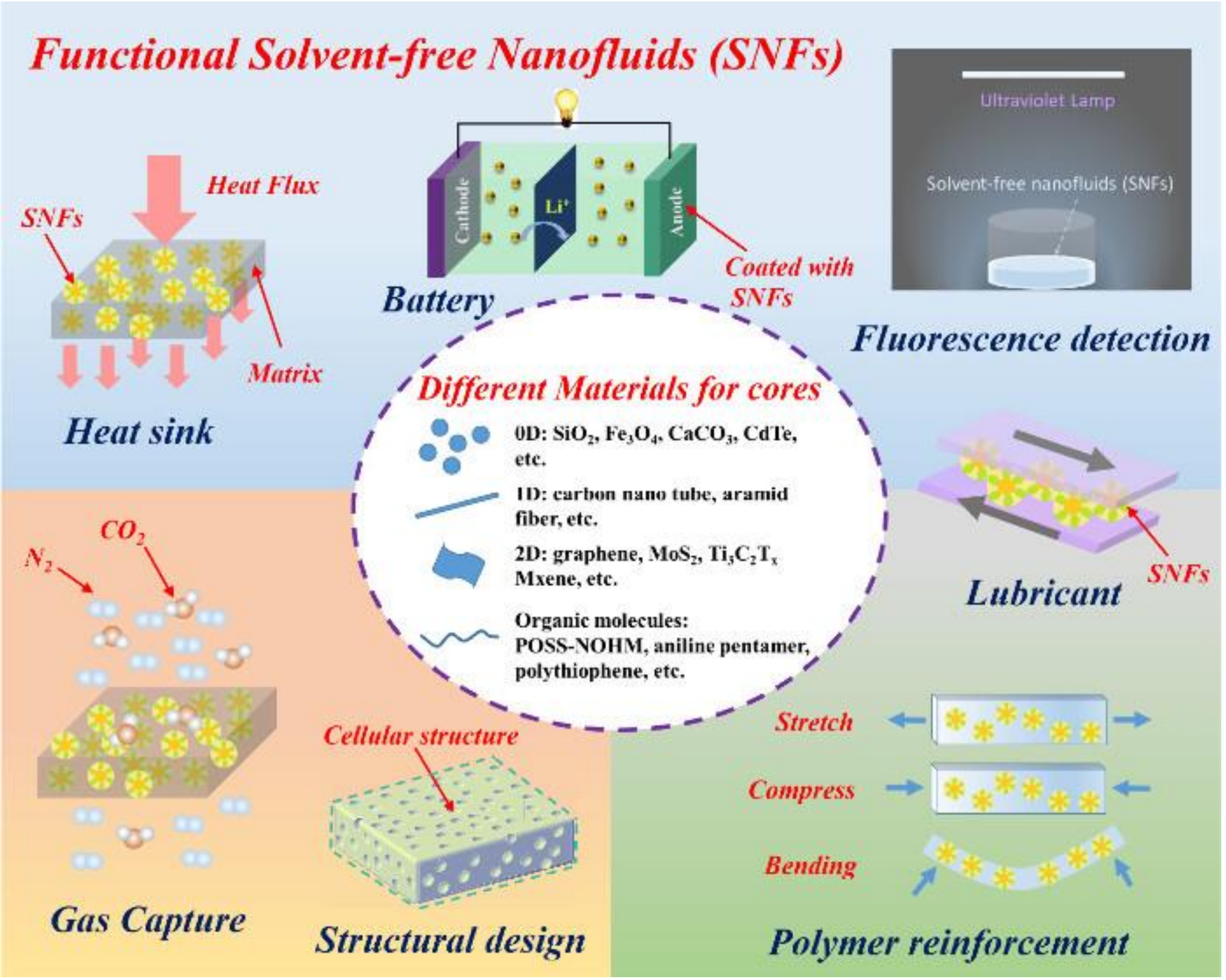




Generation of HYBRID INTERFACE through **sol-gel reactions** involving silanes

Stimuli-responsive Solvent-free Nanofluids (SNFs)

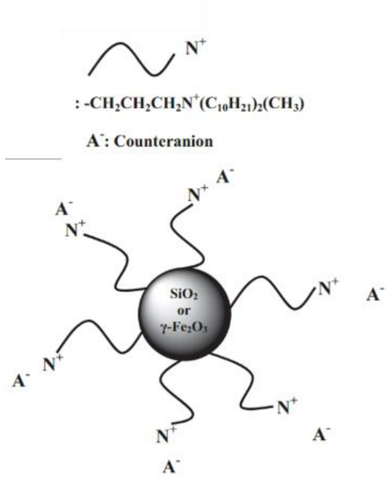


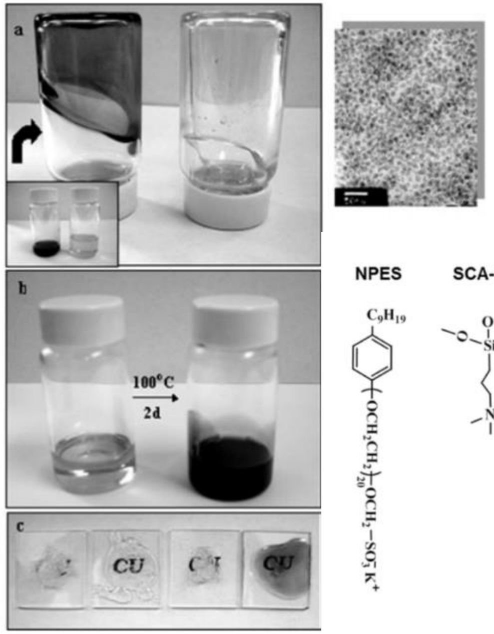


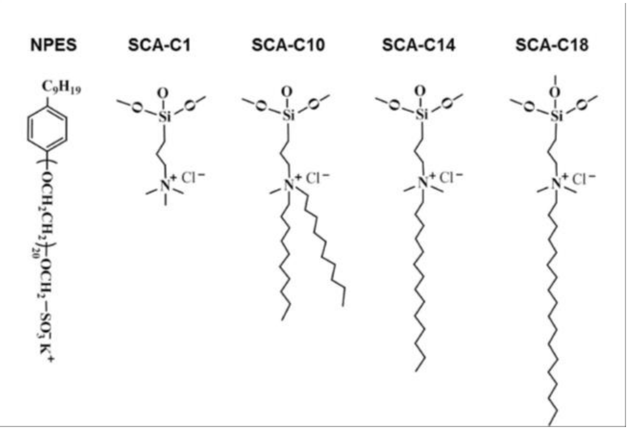
Liu, M. et al. *ACS Appl. Mater. Interfaces* **2024**, *16* (32), 41766–41787

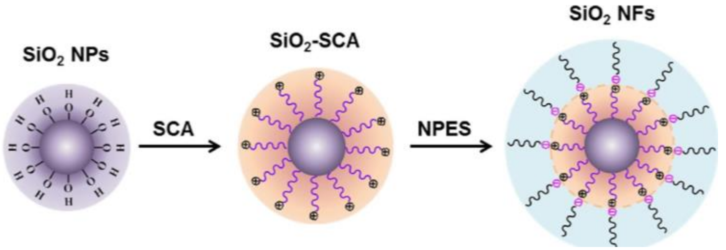
Zaibudeen, A. W. et al. *Colloids Surf. Physicochem. Eng. Asp*. **2017**, 518, 98–108

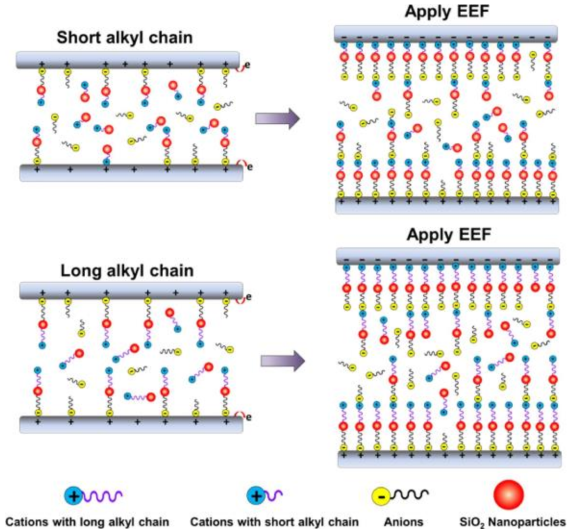
NPs with liquid-like behaviour







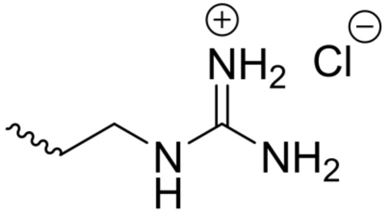




Bourlinos, A. B. et al. *Adv. Mater.* **2005**, *17* (2), 234–237

Guo, Y. et al. *Chemical Engineering Journal* **2020**, 383, 123202

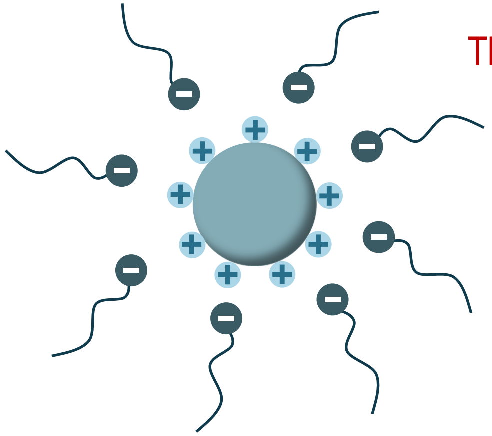
Peter Hesemann



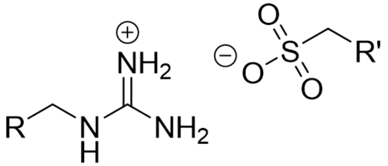
Guanidinium moiety

- Active unit for biological receptors
- Therapeutic application
- Ionic interaction with several anionic groups: carboxylate, sulfonate,…
- stability and specificity of these interactions make them valuable in areas like **drug delivery, sensor design**, and **catalysis**.

- ○ Synthesis of a **guanidinium alkoxysilane** (GuPTES)
- ○ Preparation of **guanidinium functionalized fillers**
- ○ Development of **SNFs by modification of guanidinium fillers with sulfo-PEG**

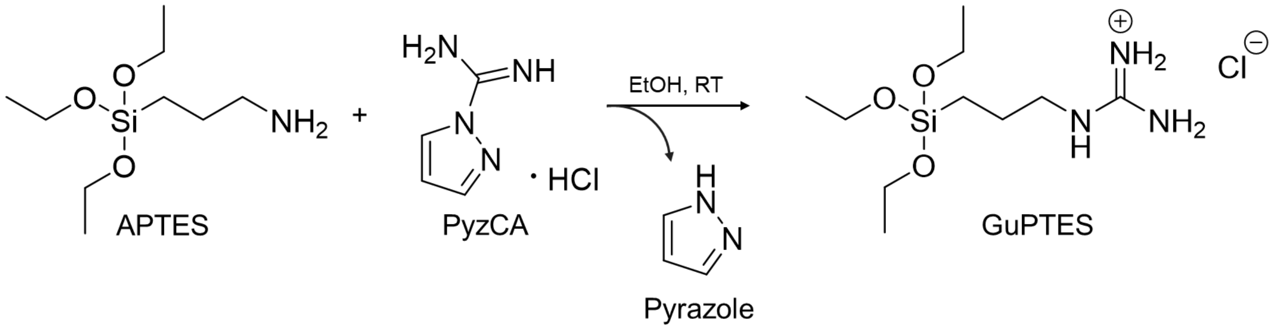


Thermoresponsive SFNs



Synthesis of guanidinium alkoxysilane

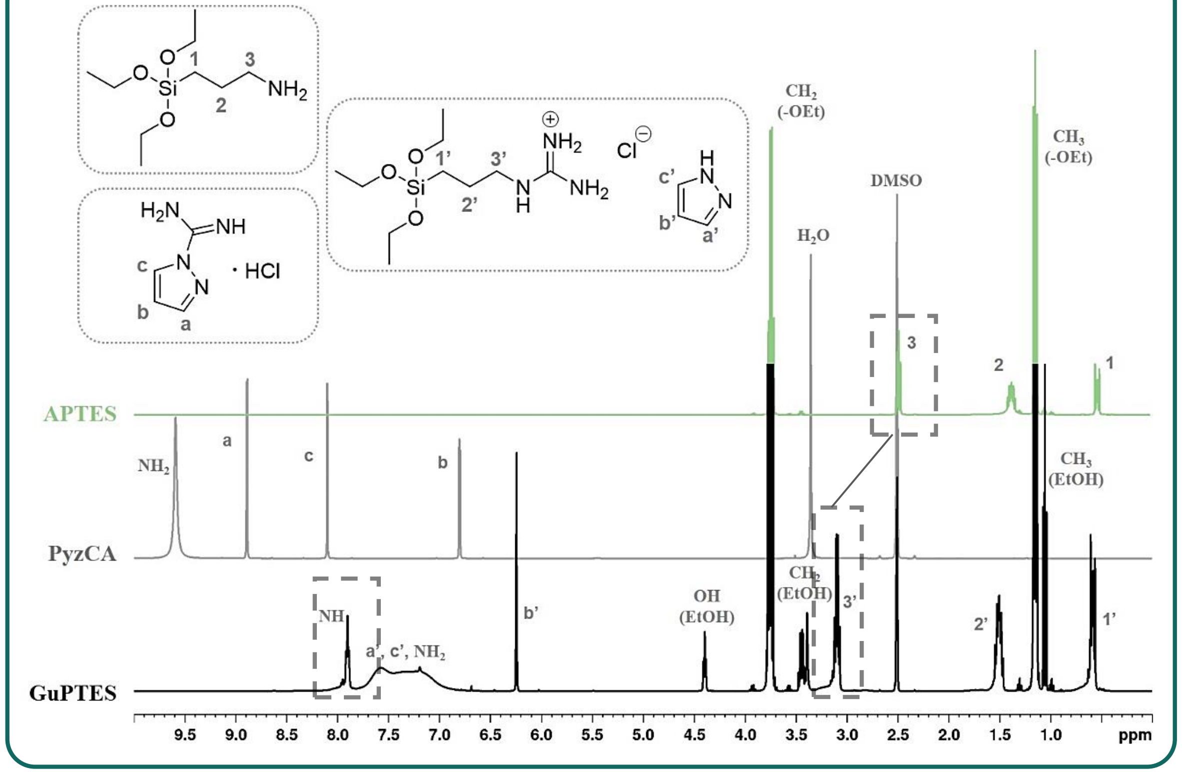
Sara Orsini



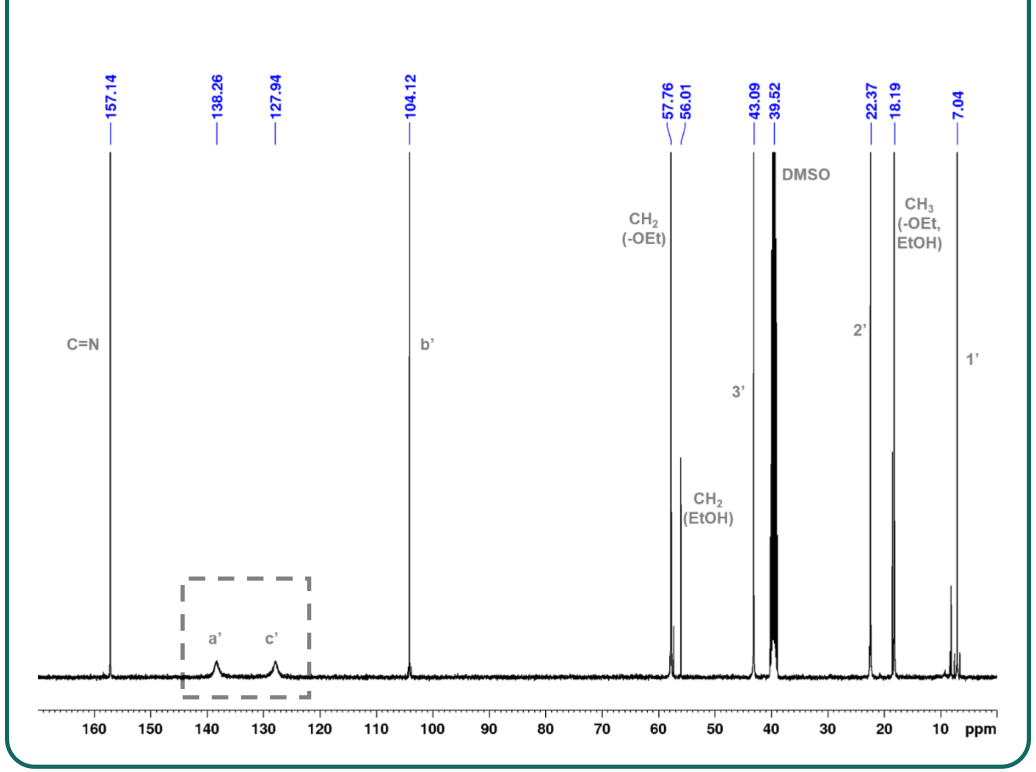
Liquid NMR spectroscopy confirms the formation of GuPTES:

- ^{1}H NMR: diagnostic peaks in the aromatic zone and H in 3'
- ^{13}C NMR: C=N e C-N

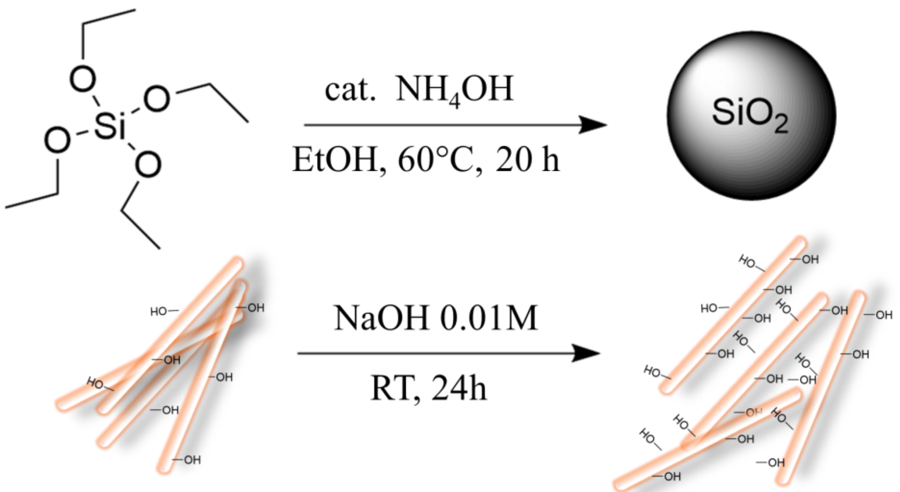
^{1}H NMR

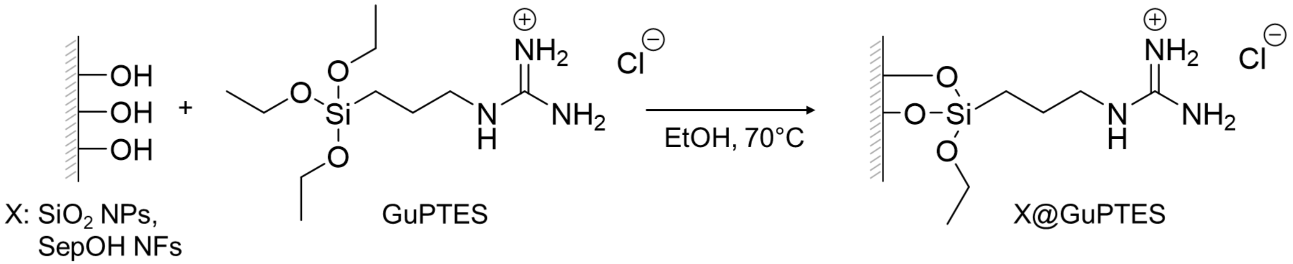


^{13}C NMR

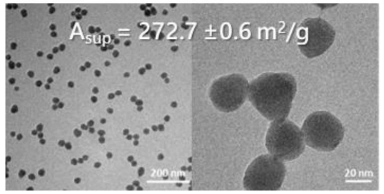


Preparation of guanidinium functionalized filler



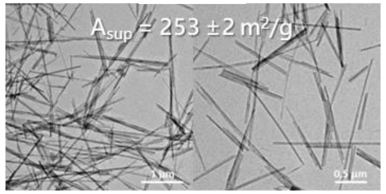


TEM



Stober SiO_2 NPs

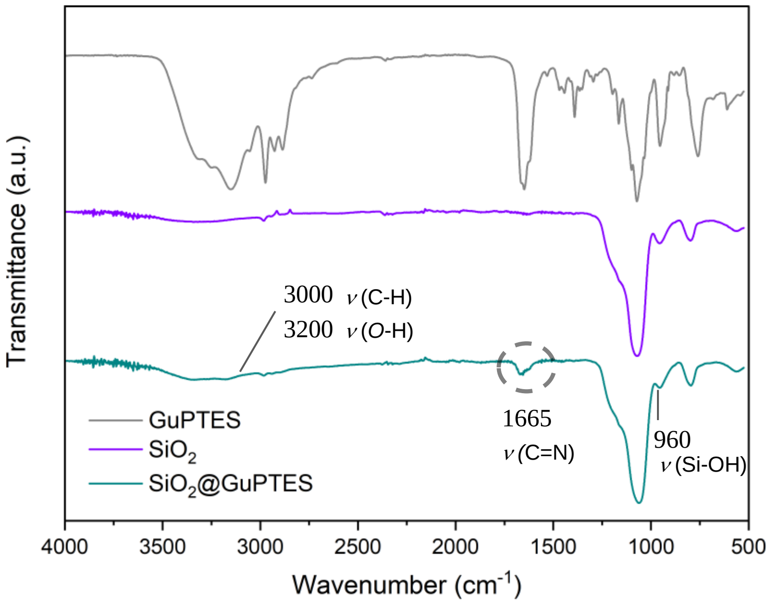
TEM

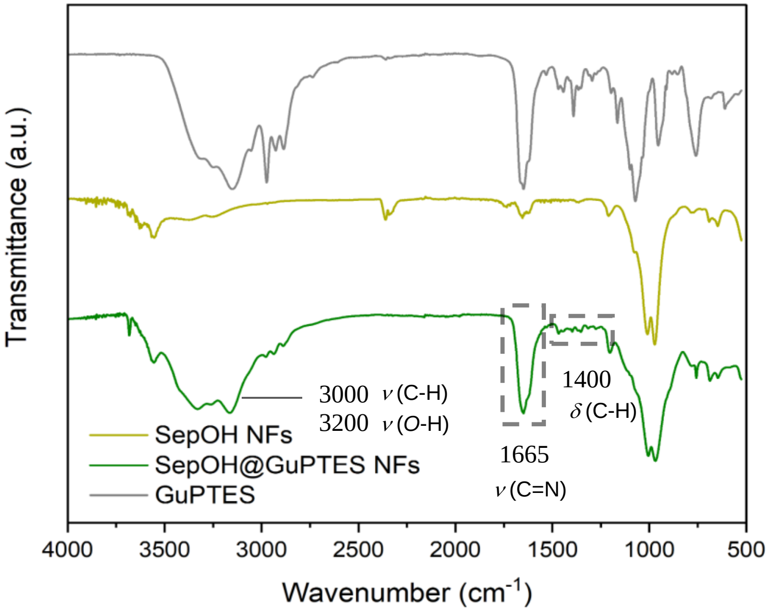


SepOH NFs

- C=N a 1665 cm^{-1}, decrease of Si-OH a 960 cm^{-1}
- Modification of peaks 3500-3000 cm^{-1}

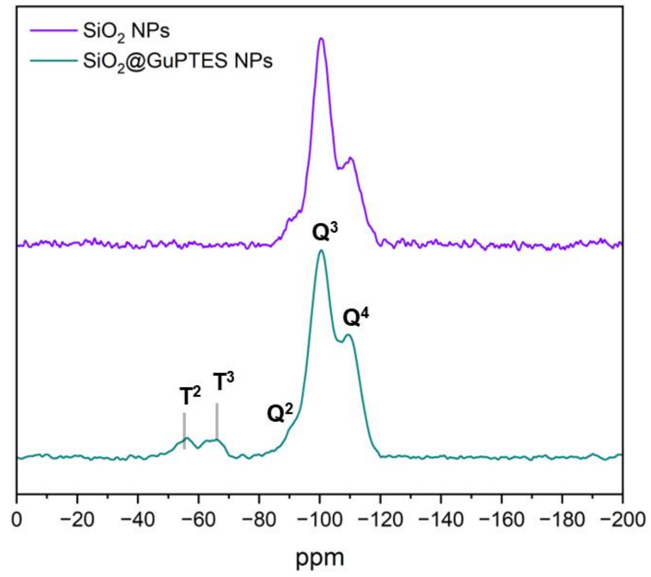
ATR FT-IR

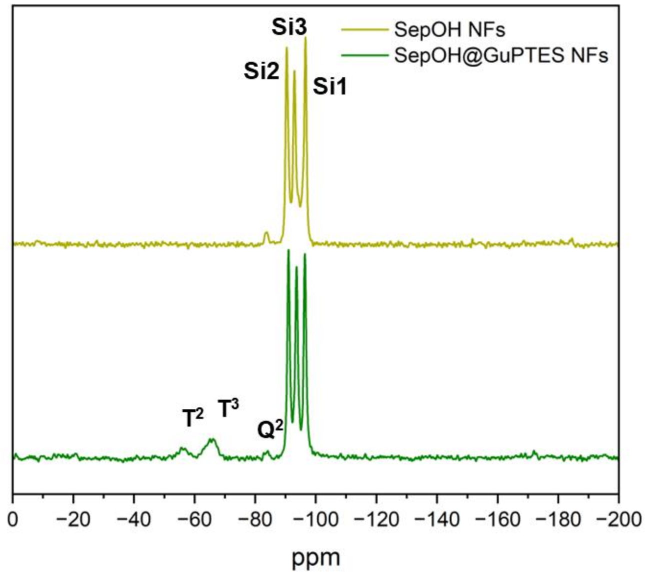


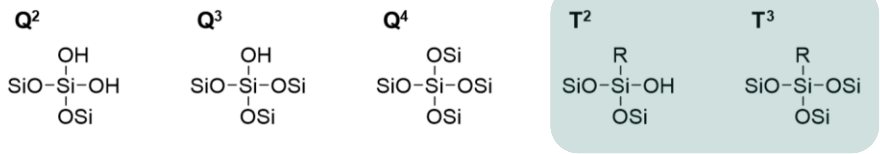


Characterization of guanidinium functionalized filler

^{29}Si CPMAS NMR

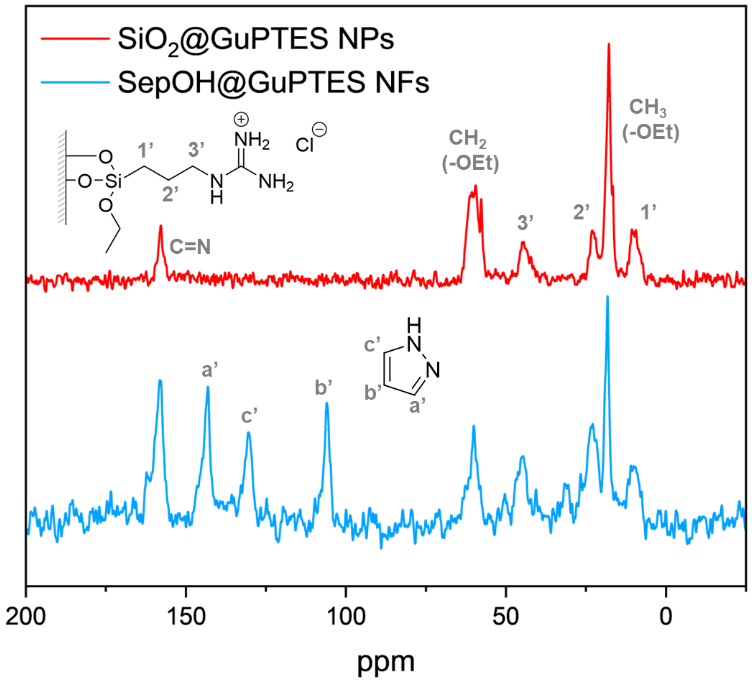






- Decrease of Q^3 / Q^4 ratio
- Peaks of T^2 e T^3 units of modified fillers

^{13}C CPMAS NMR



- Diagnostic peak of C=N
- Presence of EtOH traces
- Presence of pyrazole into the NFs

ζ-Potential

	Silice	Sepiolite
X	-19 ± 3 mV	-20 ± 5 mV
X@GuPTES	33 ± 4 mV	39 ± 7 mV

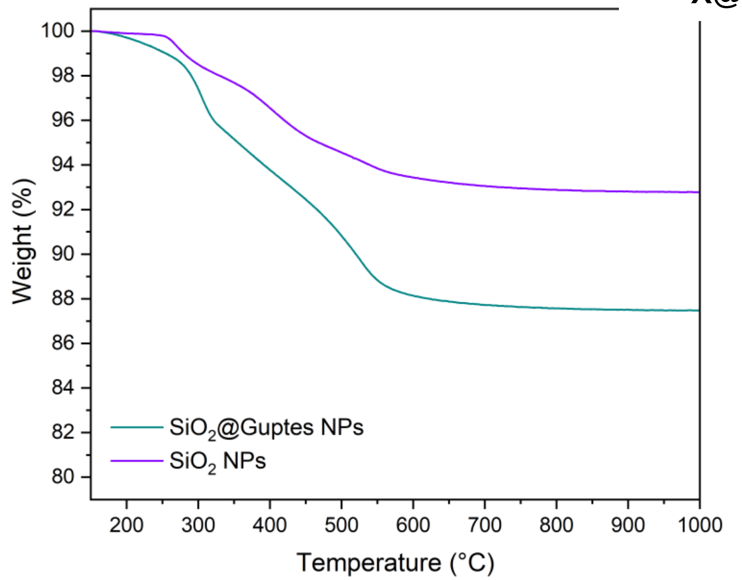
Guanidinium ion changes the ζ-Potential from negative to positive

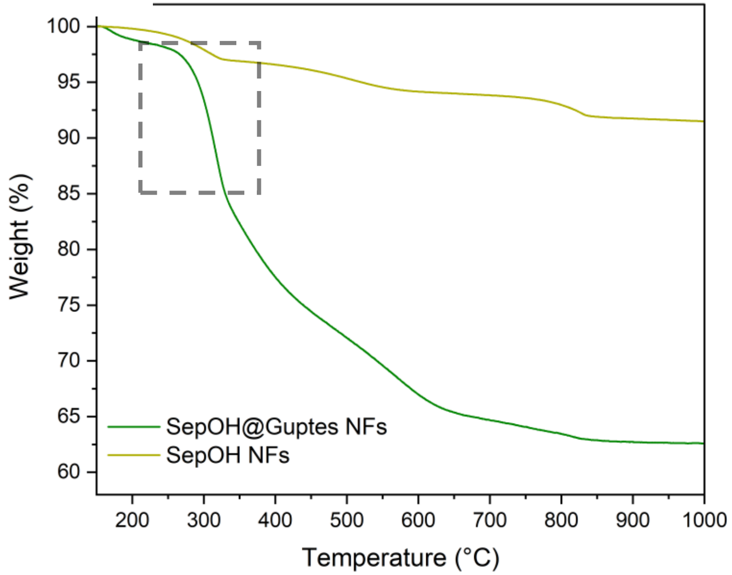
Sandra Diré
Emanuela Callone

UNIVERSITÀ DI TRENTO

Characterization of guanidinium functionalized filler

TGA of X@GuPTES





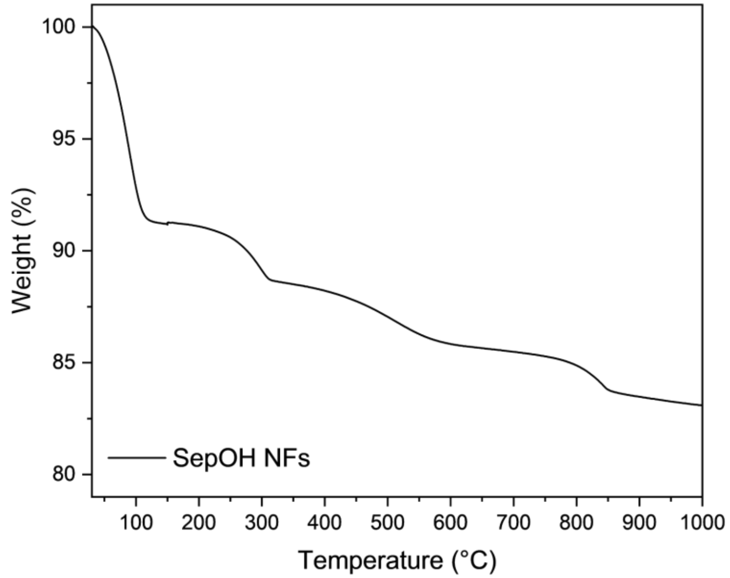
- the step observed for silica particles is in line with the typical functionalizations of previous projects
- the curve observed for sepiolite fibres shows a further step due to the loss of pyrazole

Degree of functionalization

$$\sigma = \frac{\mathrm{mol\,\%\,(Y)} \cdot N_A}{wt.\%_{(1000°C)st} \cdot A_{sup}(NPs)}$$

	σ (n. molecules/nm²)	
	TGA	CHNS
SiO_2@GuPTES NPs	1.28	1.67
SepOH@GuPTES NFs	5.74	12.87

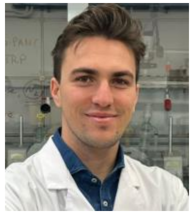
TGA of SepOH



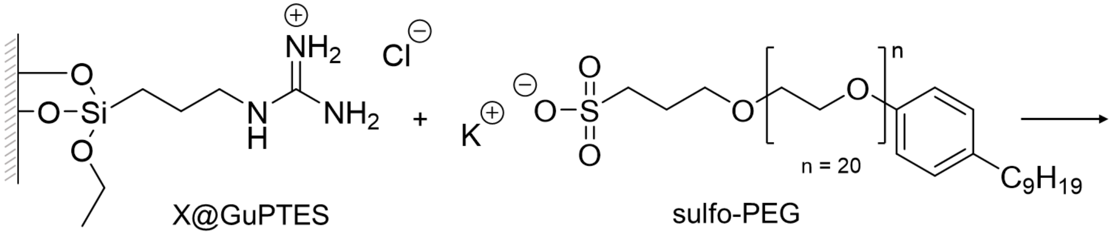
- the classic trend for sepiolite fibers has 4 steps of degradation, in which losses are related to zeolitic and coordinated water
- the overestimation of 12% (250-340 degrees) due to the pyrazole intercalated in the channels

Tartaglione G. et al. *Microporous and Mesoporous Materials* 107, (***2008***) 161–168

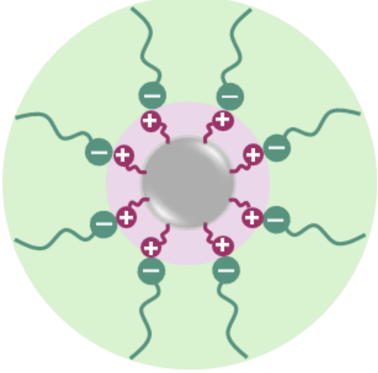
Preparation of Solvent Free Nanofluids (SFNs)



Davide Biancofiore

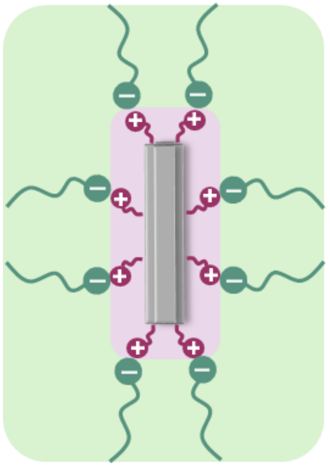


SiO$_2$@GuPTES

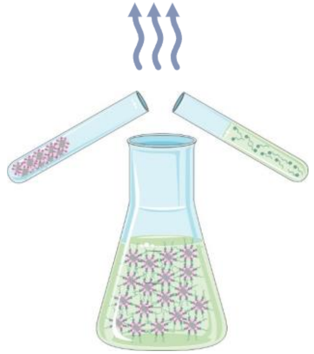


and

SepOH@GuPTES



X	Sample	Nominal filler loading	TGA filler loading
SiO$_2$@GuPTES	SiGu-sPEG_1	50 wt.%	57 wt.%
	SiGu-sPEG_2	33 wt.%	40 wt.%
	SiGu-sPEG_3	25 wt.%	15 wt.%
	SiGu-sPEG_5	17 wt.%	10 wt.%
SepOH@GuPTES	SepGu-sPEG_1	50 wt.%	45 wt.%
	SepGu-sPEG_2	33 wt.%	28 wt.%
	SepGu-sPEG_3	25 wt.%	21 wt.%
	SepGu-sPEG_5	17 wt.%	12 wt.%

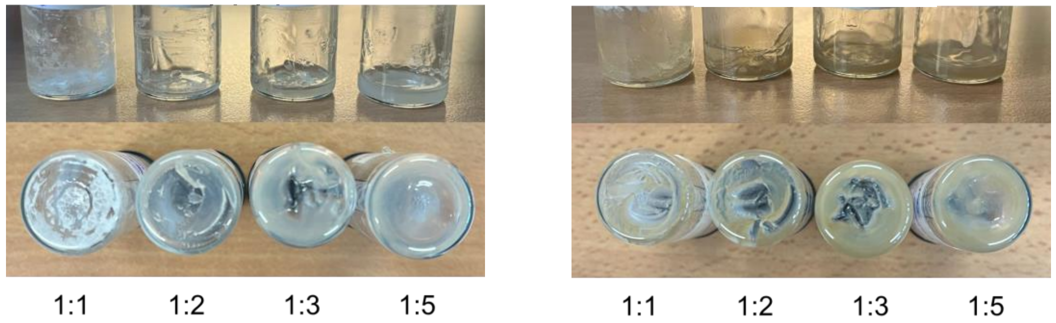


Solution mixing process

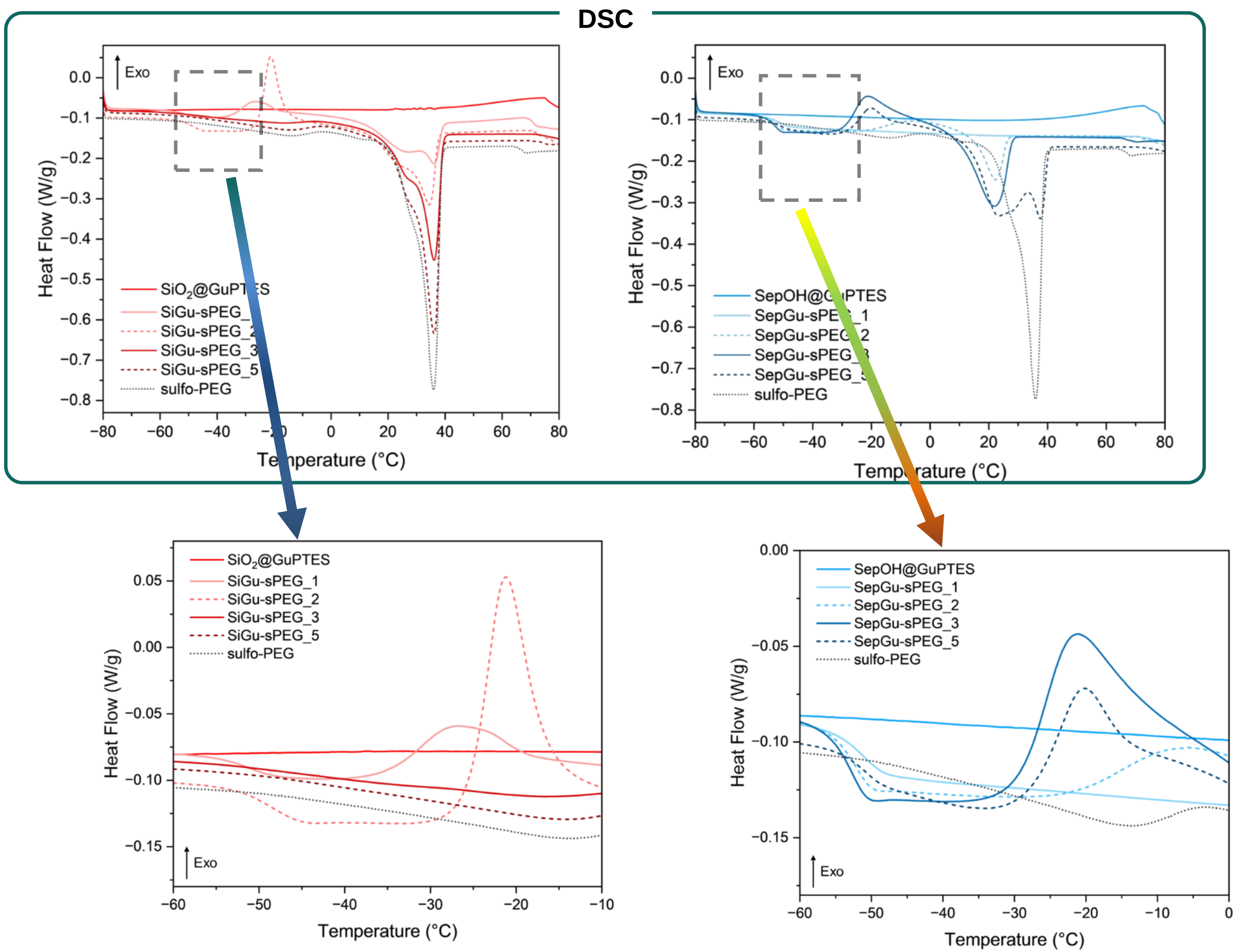
Removing solvent by slowly evaporation

SiO$_2$@GuPTES – sulfo-

SepOH@GuPTES – sulfo-PEG

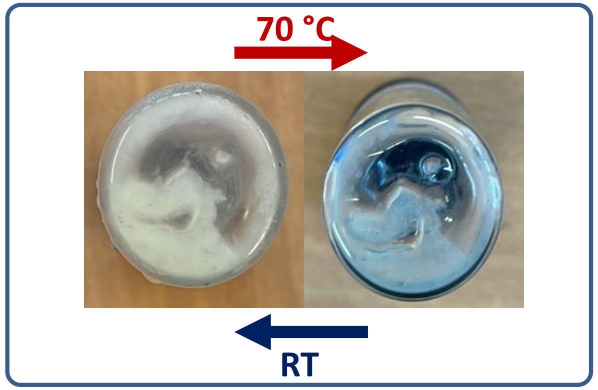


Thermal characterization of composites



- Presence of fillers alters the structure
- -20°C peak: **cooling crystallization** due to **alignment of polymer chains with fillers** during heating
- **“Bathtub” phenomenon**
- The phenomenon is more marked and observed at lower loadings in the presence of Sep NFs

Thermotropic phases that form at low T and the disappear at high T in a **reversible way: confinement**



macroscopic observation of the thermal response

Mauri, M. et al. *Polymers* **2018**, 10 (6), 655.

Time Domain NMR

In collaboration with Prof. Simonutti e Dr. Mauri

- Two-component pattern: difference in the mobile proton populations

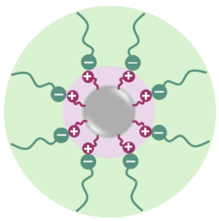
$$y = A\ exp^{-\frac{x^2}{D}} + B\ exp^{-\frac{x}{T_2 b}}$$

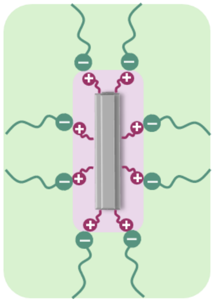
- Relaxation times as the exponential decay constant obtained by interpolation of a two-component exponential function

- Increasing filler loading, relaxation time decreases: **structural constrains**

SepOH@GuPTES

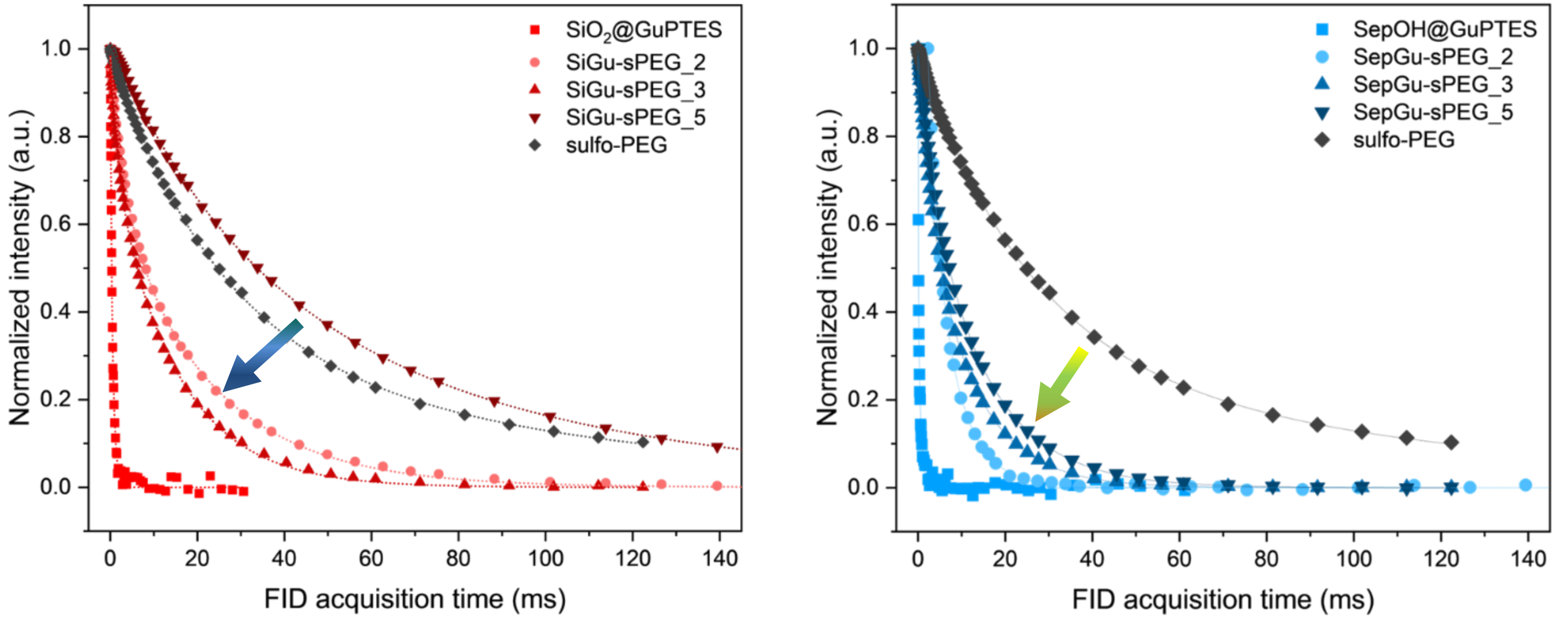
SiO_2@GuPTES





Besghini D. et al. *Macromolecules* **2023**, 56 (12), 4694–4704.

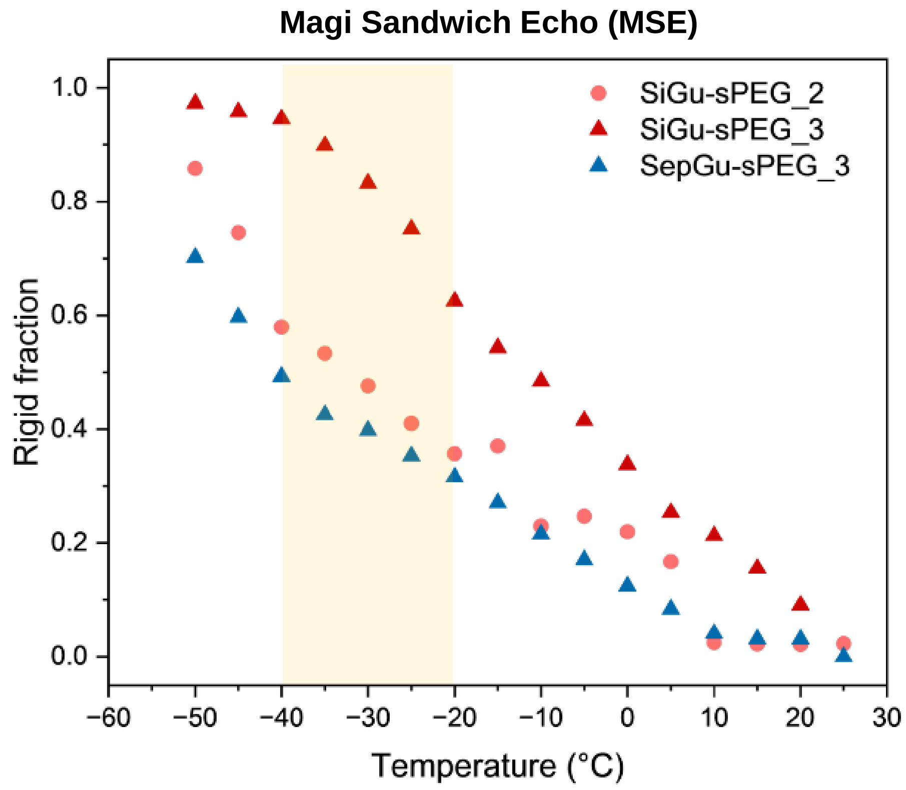
^{1}H TD-NMR



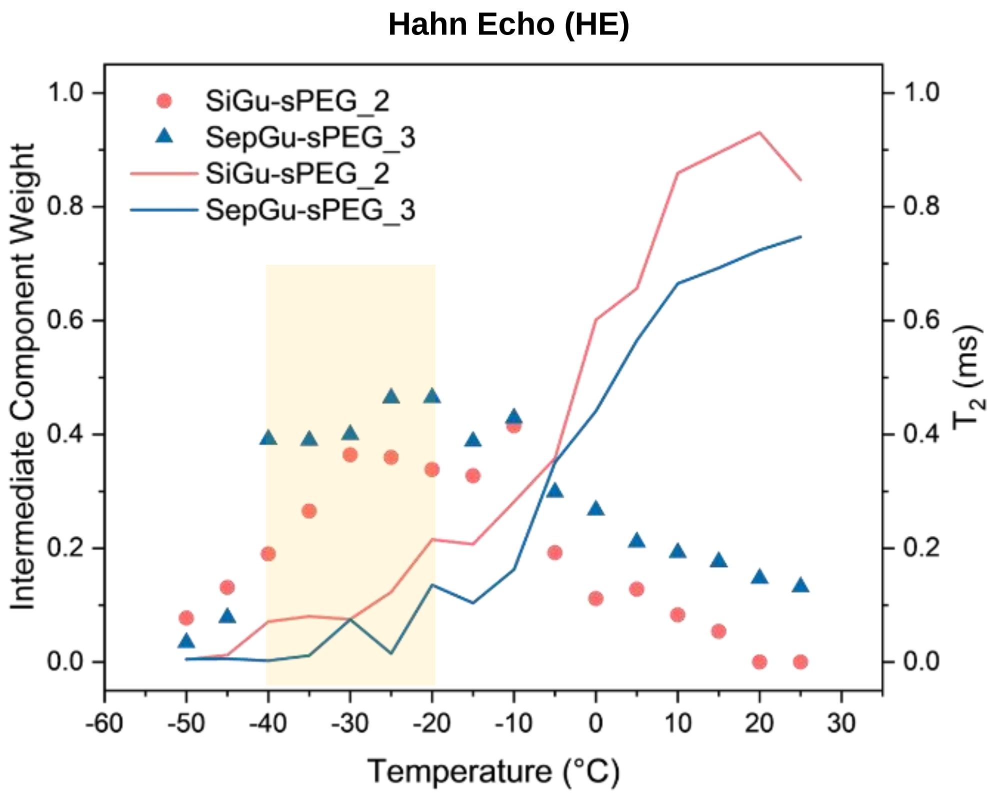
Sample	T_{2a}	T_{2b}
SiO_2@GuPTES	0.17	0.64
SiGu-sPEG_2	3.50	22.33
SiGu-sPEG_3	1.82	14.8
SiGu-sPEG_5	30	78
sulfo-PEG	24.85	101

Sample	T_{2a}	T_{2b}
SepOH@GuPTES	0.046	0.60
SepGu-sPEG_2	2.4	6.5
SepGu-sPEG_3	3.0	11.3
SepGu-sPEG_5	3.9	14.0
sulfo-PEG	24.8	101

Time Domain NMR: rigid fraction vs T



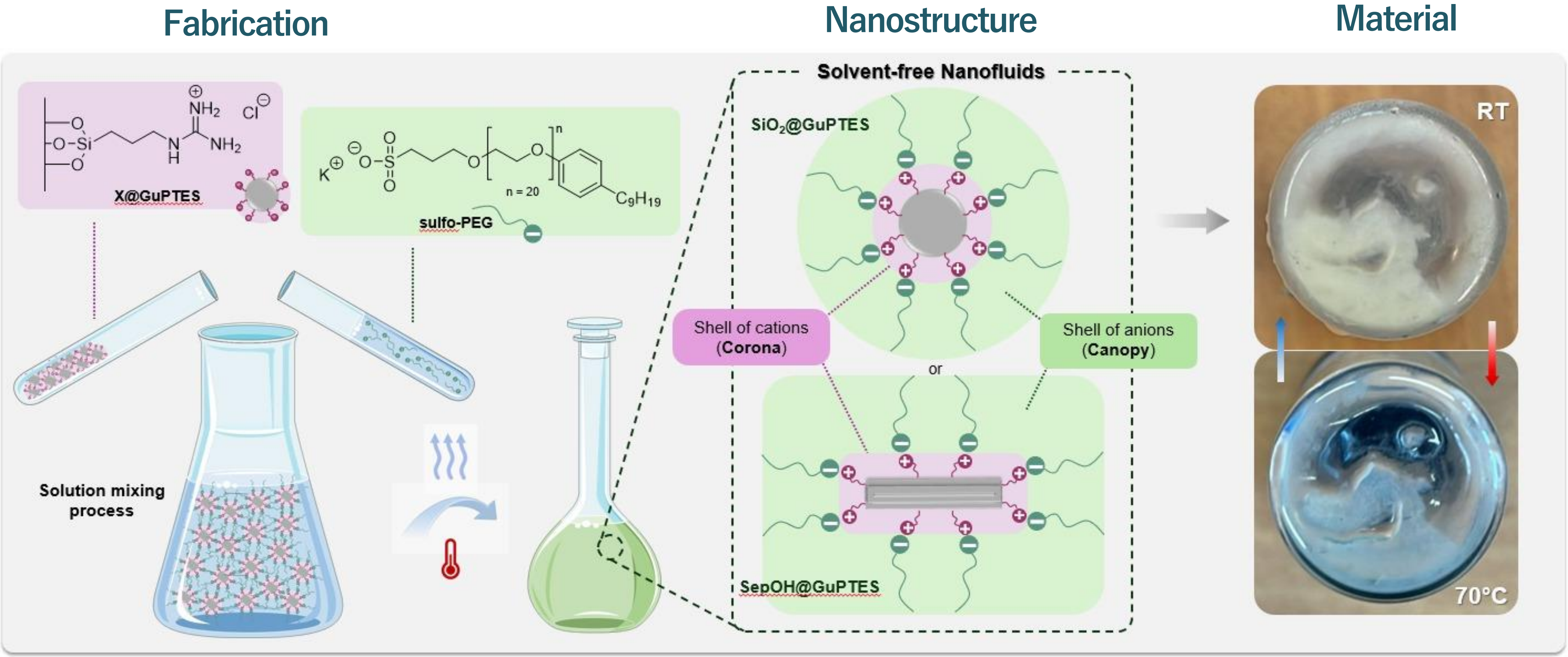
- Presence of concavity for the samples with “bathtub”: **change in polymer chains mobility due to costraints induced by the filler**
- Visible for samples with SepOH at a lower loading (25 wt. %)



- Comparison of trends shows **increased mobility of silica-containing composites suggesting nanofluid behaviour**
- Change in local dynamics along with temperature variation: **thermotropic and thermoregulable nanoconfined domains**

Da Cruz C. et al *J. Phys. Chem. B* **2005**, *109* (30), 14292–14299

Conclusions and Perspectives



- Attempts to remove pyrazole by reaction with zinc acetate
- SAXS to evaluate the structural evolution as a function of temperature
- Study of rheological and tribological properties for application as smart lubricants

Thank you!

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If you want to go fast, go alone; but if you want to go far, go together

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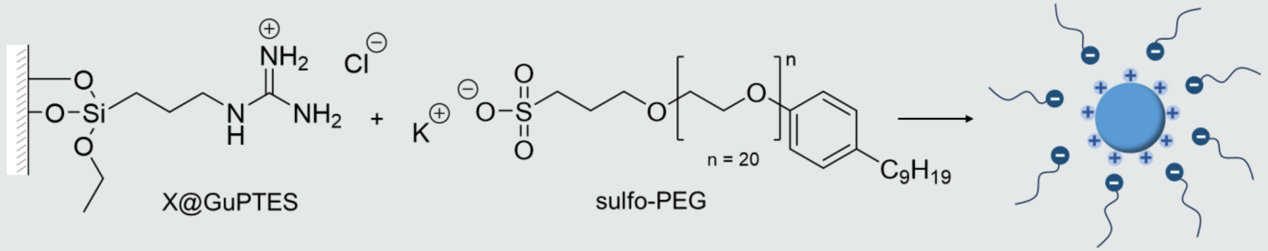
Back-up slides

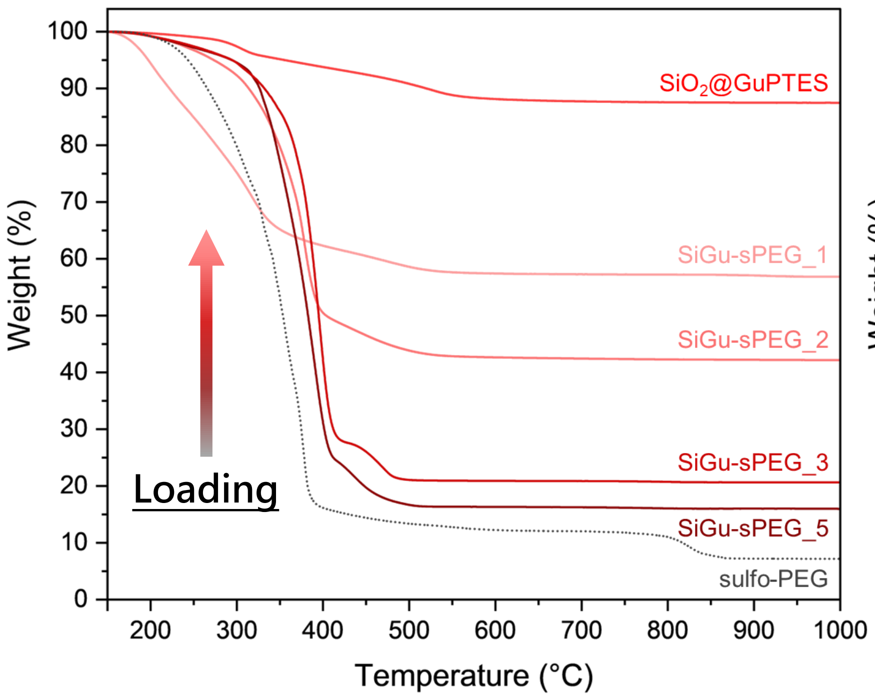
PREPARATION OF THERMO-RESPONSIVE SNFs

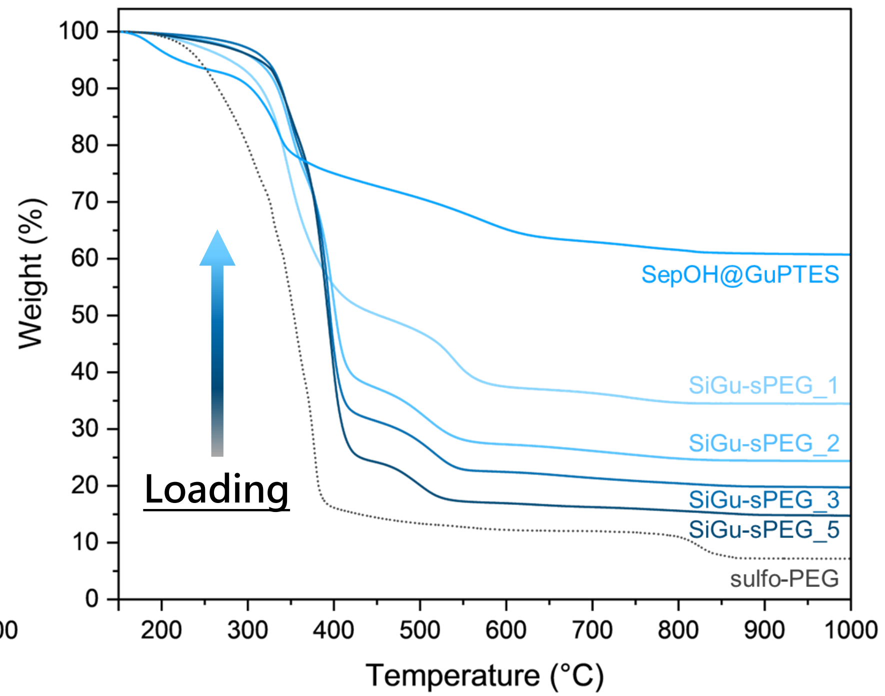
Modification of guanidinium fillers with sulfo-PEG



- Decomposition temperature of SNFs increases by approximately 40°C compared to sulfo-PEG
- Nominal loading values correspond closely to the TGA calculated values

TGA





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