



**POLITECNICO**  
**MILANO 1863**

# **Chemical modification of Sepiolite for Rubber Composites With Improved Mechanical Properties**

Daniele Locatelli

N. Pavlovic, V. Cipolletti, G. Peli, V. Barbera, L. Giannini, M. Galimberti

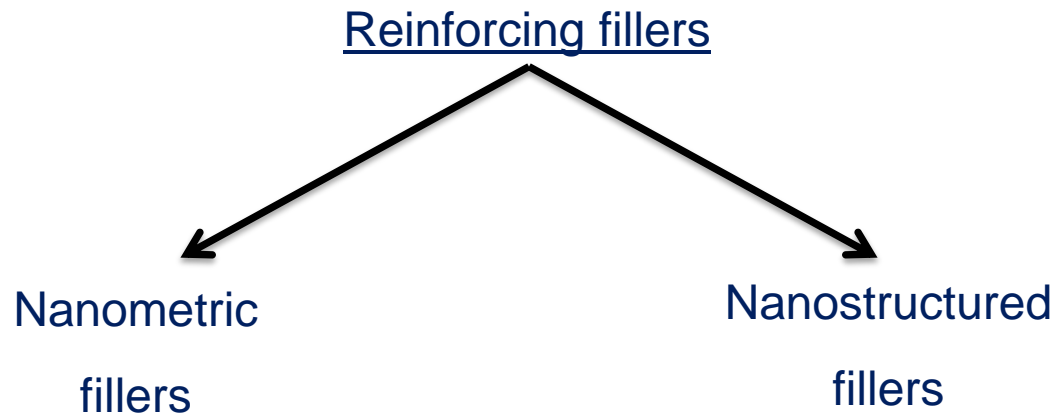
Warsaw, 26th – 28th November

*“Gum – elastic. There is probably no other inert substance the properties of which excite in the human mind an equal amount of curiosity, surprise and admiration.”*

[Charles Goodyear]



...However, elastomer composites would be almost useless without mechanical reinforcement



# Items of the presentation

1. Objectives
2. Prior art – high aspect ratio
3. Chemical modification of the surface of sepiolite
  - 3.1 TEOS +  $\text{NH}_4\text{OH}$
  - 3.2 TEOS/Silane +  $\text{NH}_4\text{OH}$
  - 3.3 Treatment with HCl
4. Final conclusions



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# Objectives

- To take advantage of nanometric high aspect ratio fillers for the mechanical reinforcement of rubbers
- To foster the chemical reactivity of sepiolite
- To obtain better dynamic-mechanical properties in rubber composites

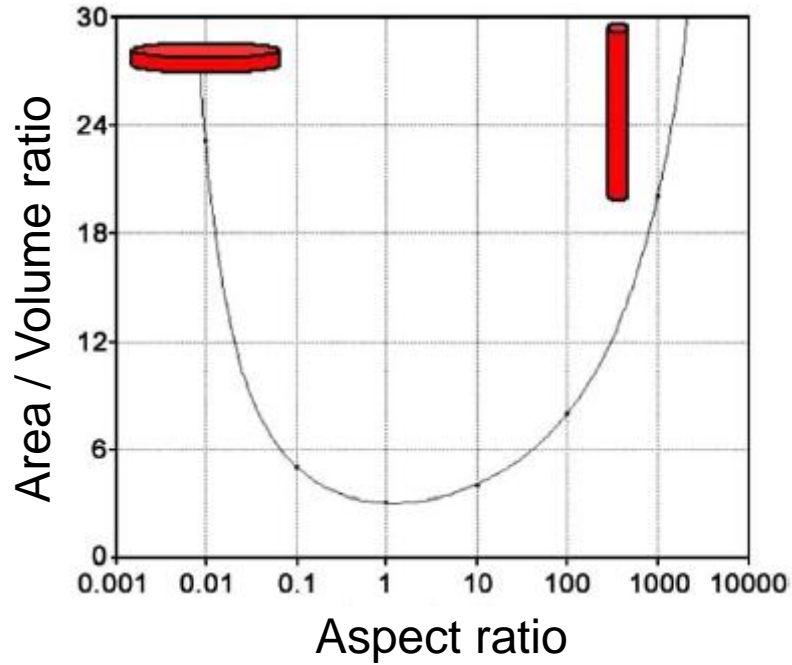


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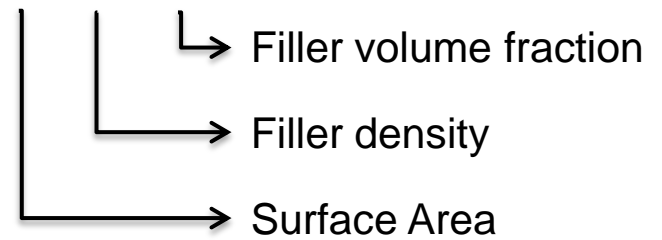
1. Objectives
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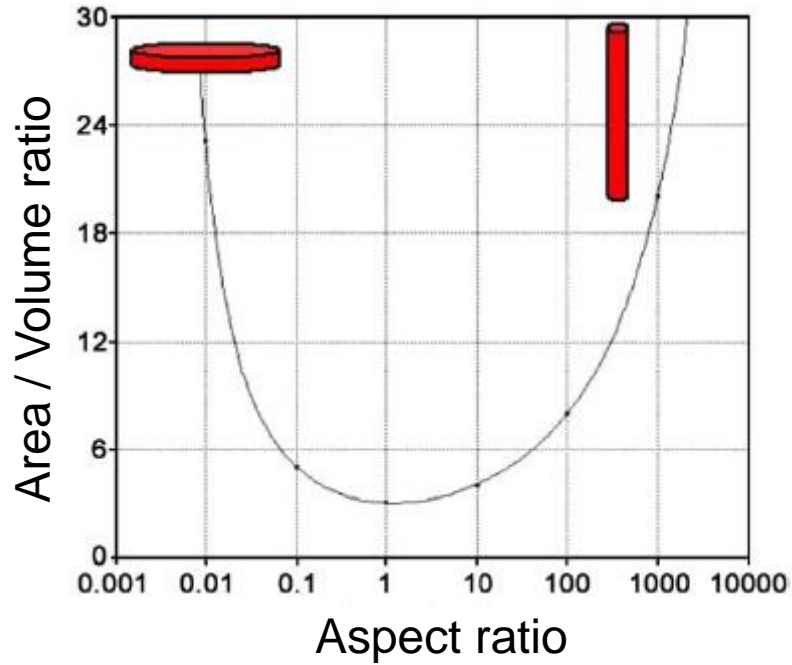
# High aspect ratio fillers – Dimensions and aspect ratio



$$\text{Interfacial Area (I.A.)} = S_a * \rho * \varphi$$



# High aspect ratio fillers – Dimensions and aspect ratio

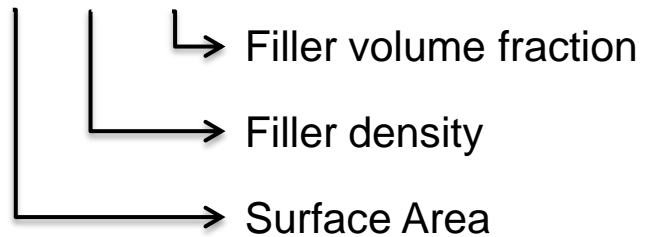


Higher I.A.

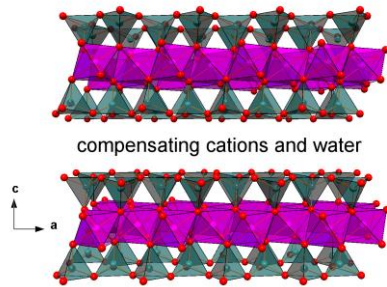


Higher surface of interaction  
between filler and polymer chain

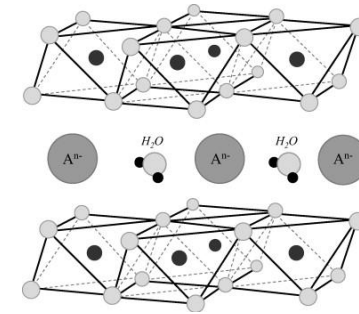
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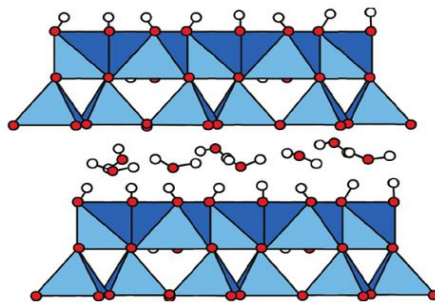
# High aspect ratio fillers – Nanometric fillers



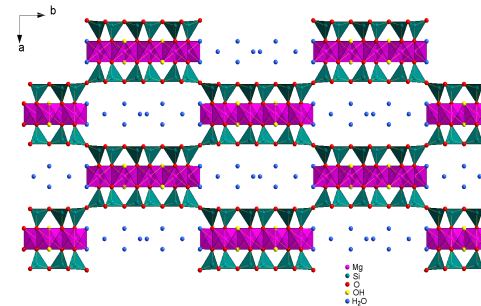
Montmorillonite



Hydrotalcite



Halloysite

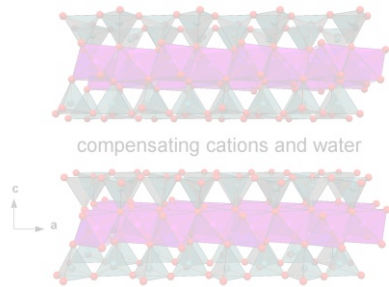


Sepiolite

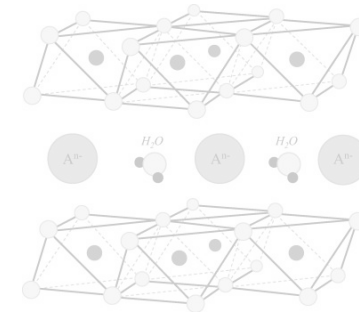
Primary particles have dimensions in the range of 1 to 100 nm

With high aspect ratio

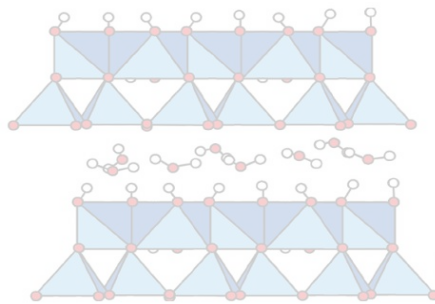
# Reinforcing fillers – Nanometric fillers



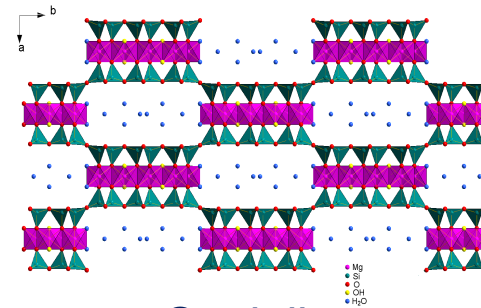
Montmorillonite



Hydrotalcite



Halloysite

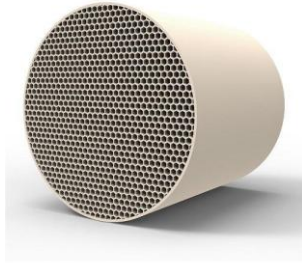


Sepiolite

Primary particles have dimensions in the range of 1 to 100 nm

With high aspect ratio

# A bio-filler: Sepiolite - Applications



Support for catalyst

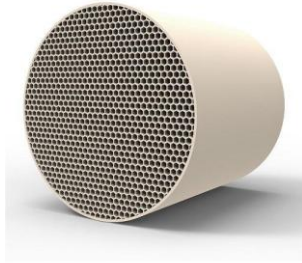


Oil adsorber



Repair monuments

# A bio-filler: Sepiolite - Applications



Support for catalyst



Oil adsorber



Repair monuments

What about new dynamic application?



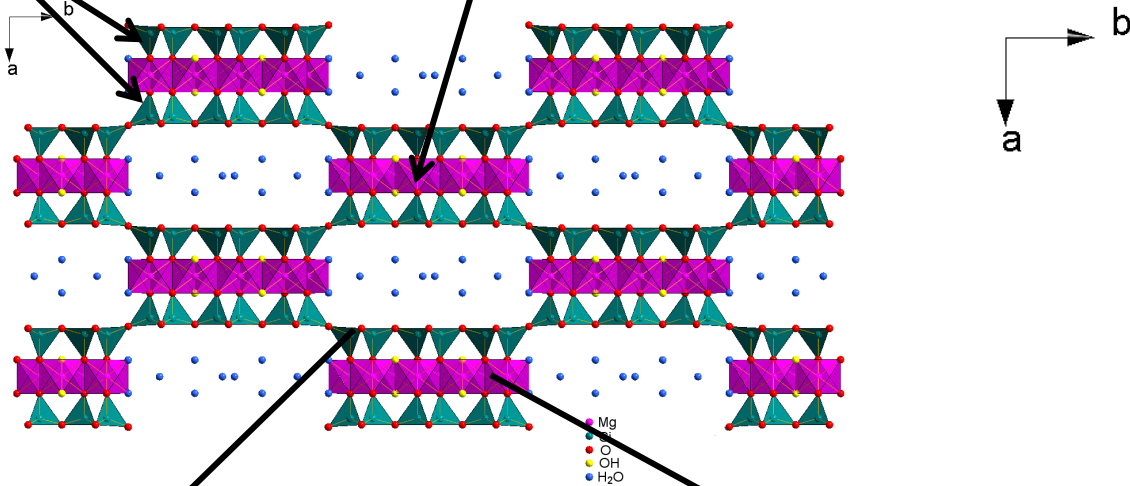
Reinforcement for tyre



# A bio-filler: Sepiolite – chemical structure

two-dimensional layers  
of tetrahedral  $\text{SiO}_4$  units

magnesium atoms,  
octahedrally coordinated



Fibers are typically 40-150 nm wide and 1-10  $\mu\text{m}$  long

the tetrahedral sheet is continuous

the octahedral sheet is discontinuous

Units connected with covalent bonds



Swelling or exfoliation is not possible

# A bio-filler: Sepiolite – Why?

σήπιον (sepion)  
+  
λίθος (lithos)



## Advantage

- naturally occurring
- easily available
- low cost
- high mechanical and thermal stability

## Disadvantage

- Low surface reactivity with polymer chain

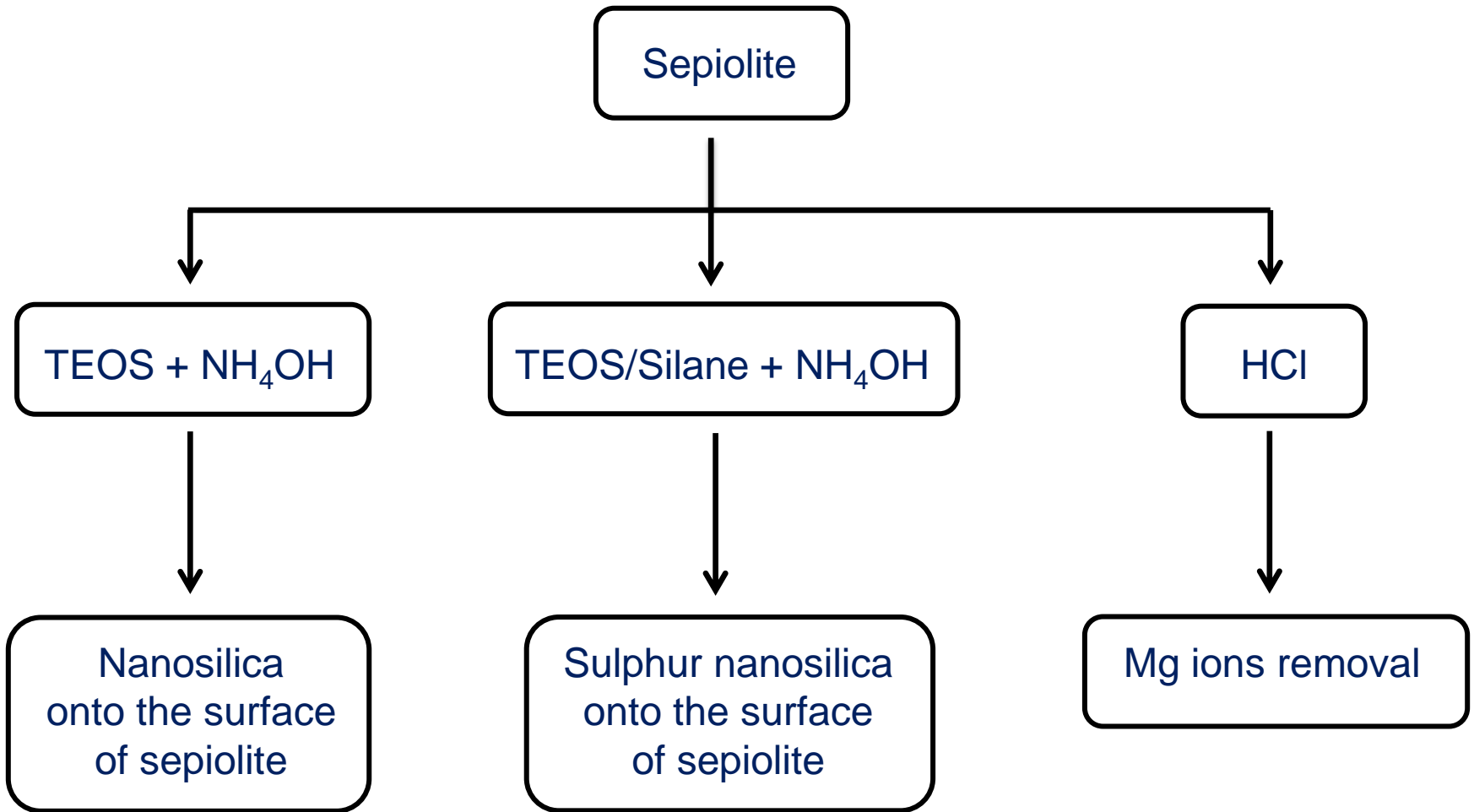


# Items of the presentation

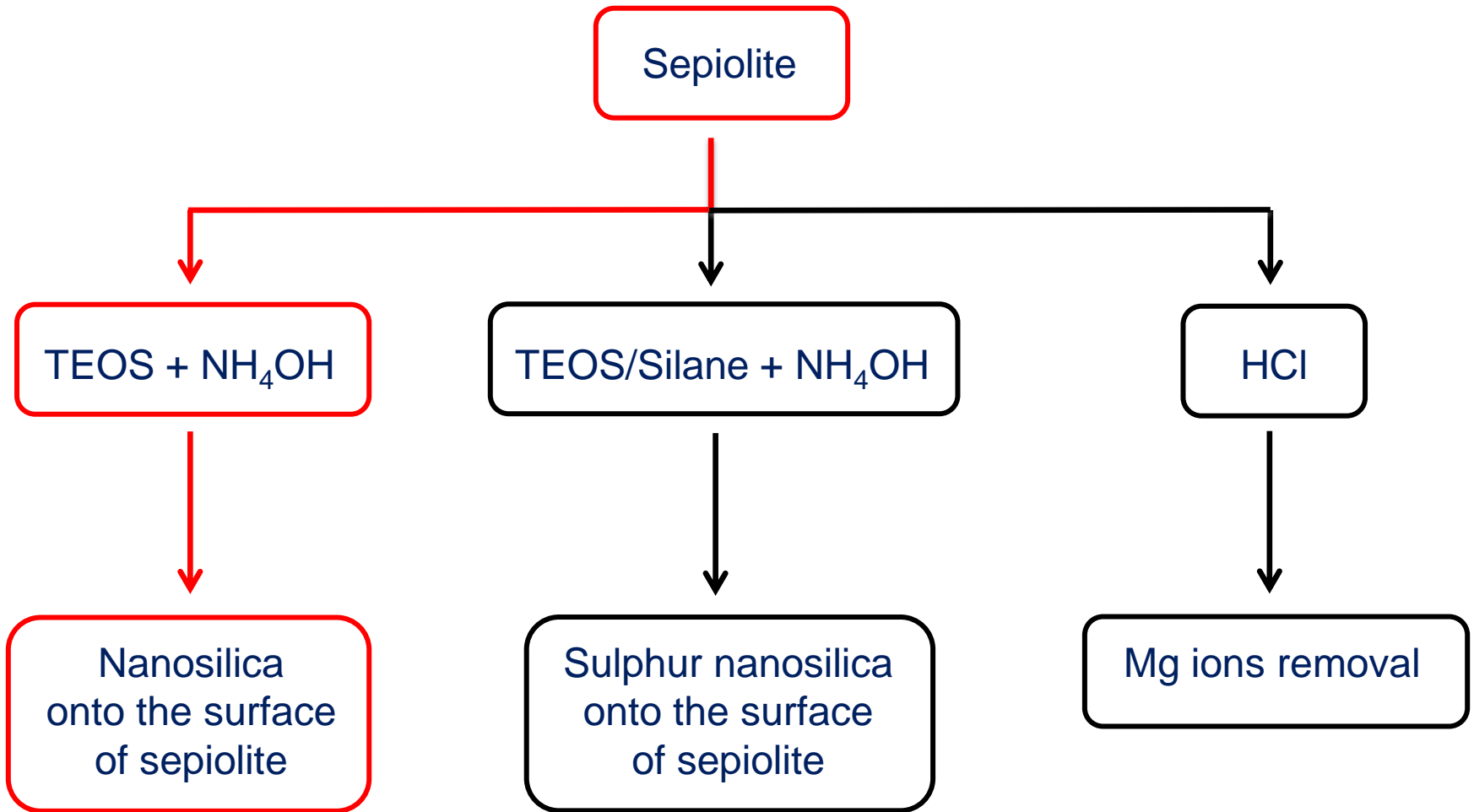
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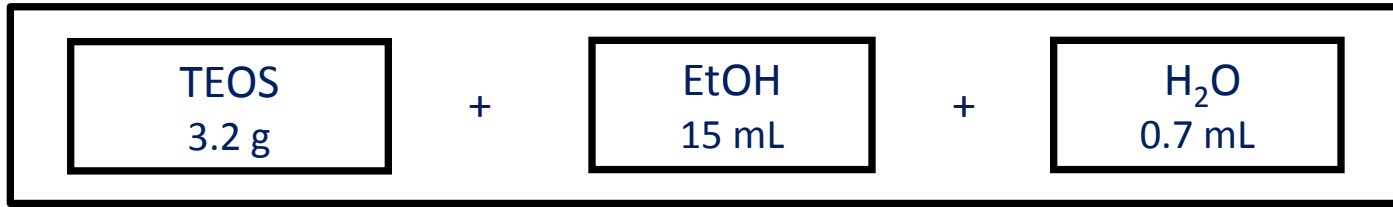
# How to foster the chemical reactivity of sepiolite?



# How to foster the chemical reactivity of sepiolite?



# Sepiolite modified with TEOS



1h at 40°C  
under stirring

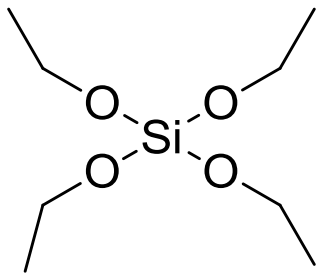
SEPIOLITE  
in EtOH, 65 mL

previous treatment  
with ultrasounds, 30 min

+ NH<sub>4</sub>OH (30% vol/vol aq sol.), 2 mL

1. 5h at 60°C under stirring  
2. filtering, washing

MODIFIED SEPIOLITE



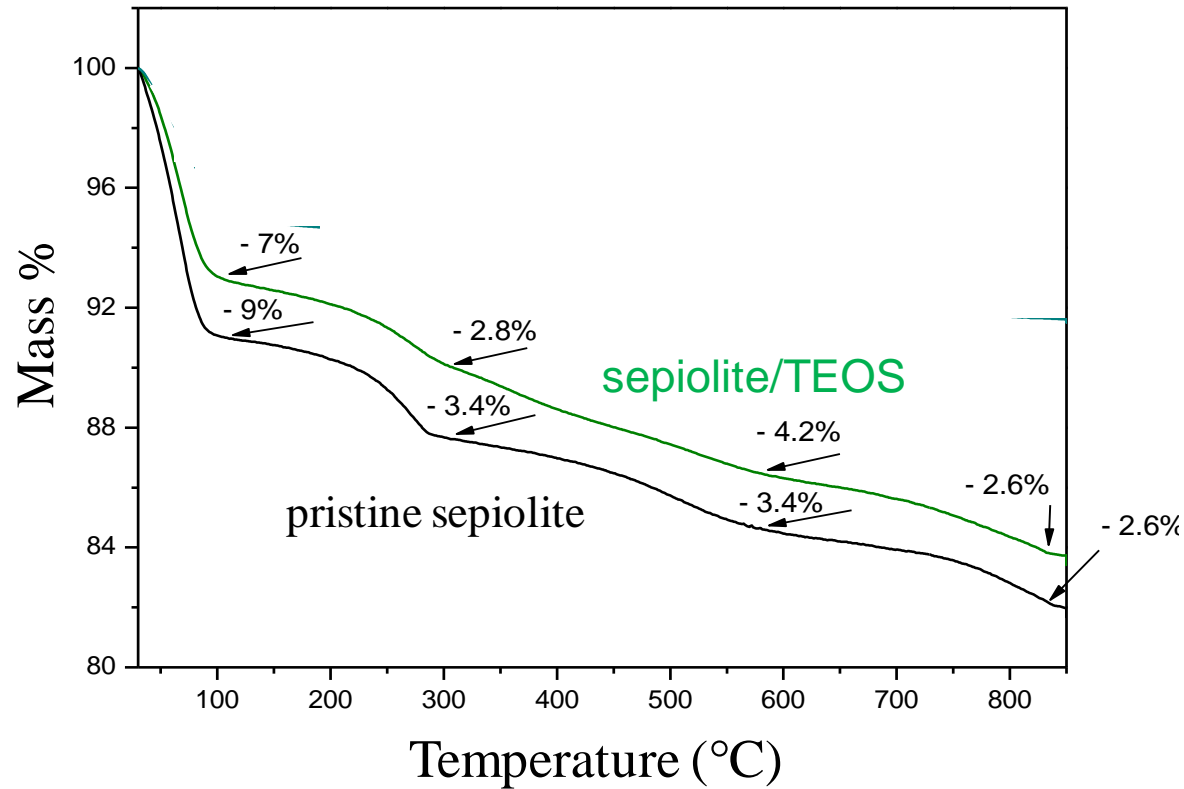
TEOS

IUPAC: tetraethyl orthosilicate



# Sepiolite modified with TEOS - TGA

## Thermogravimetric analysis



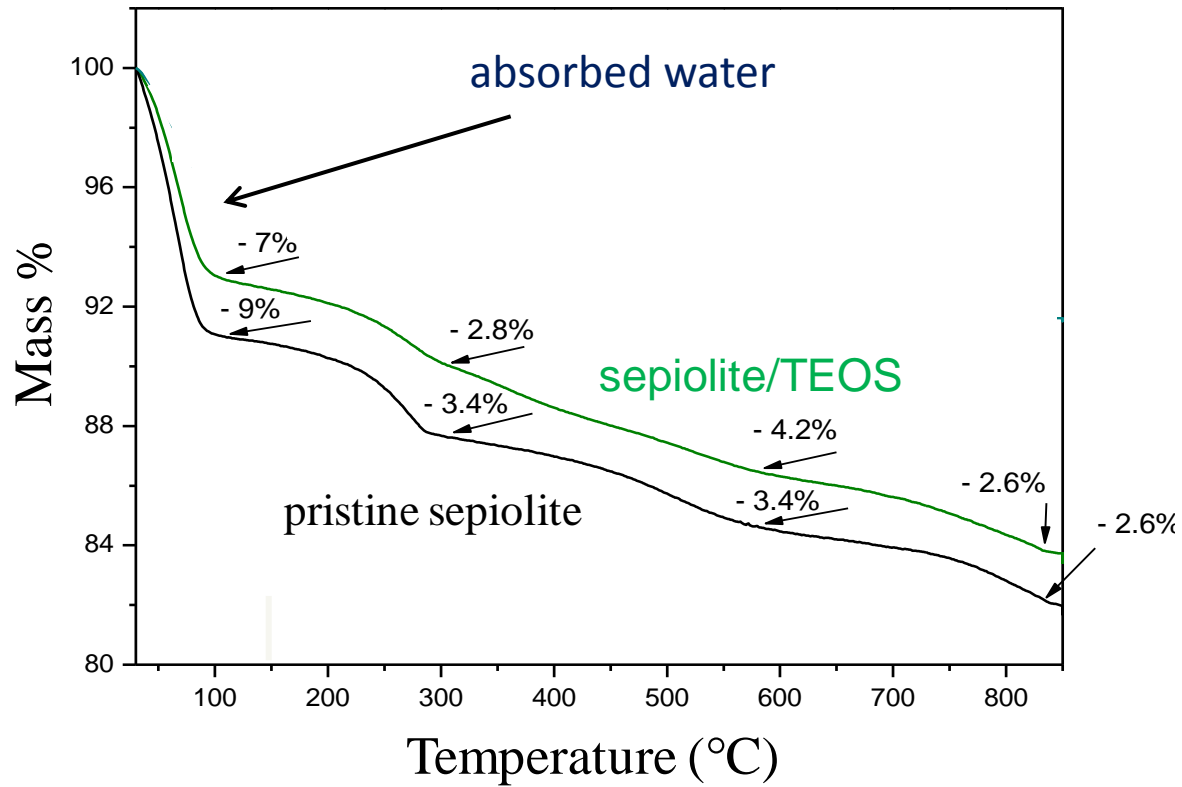
Nagata, H., Shimoda, S., & Sudo, T. *Clays & Clay Minerals*, **1974**.

Valentin, J.L., M.A. López-Manchado, A. Rodríguez, P. Posadas, L. Ibarraet, *Applied Clay Science*, **2007**, 36(4), 245-255



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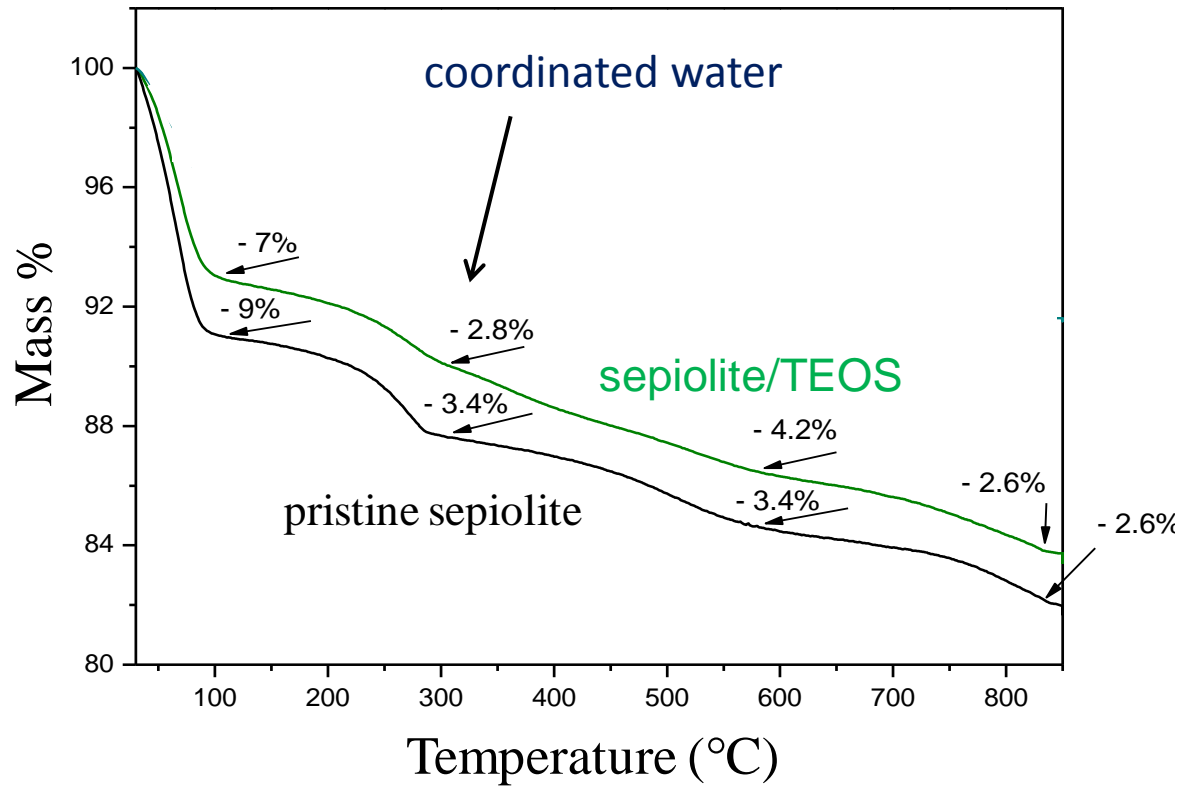
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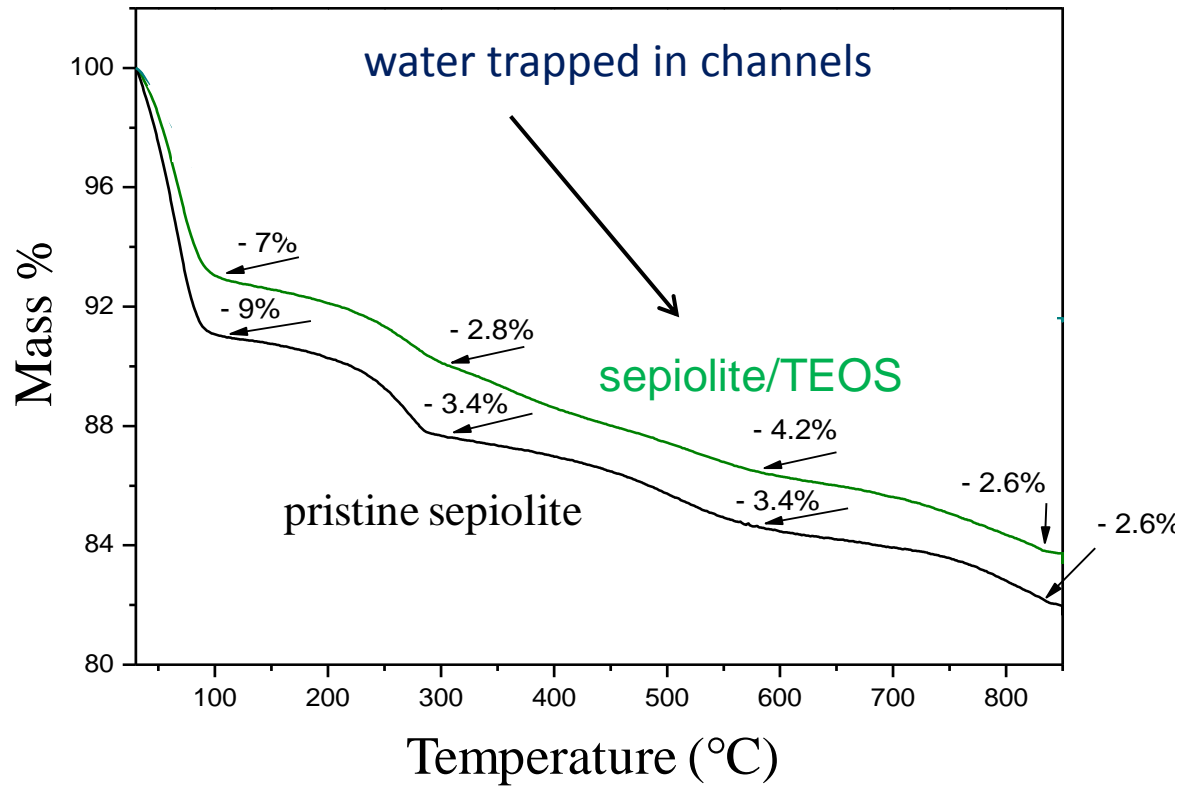
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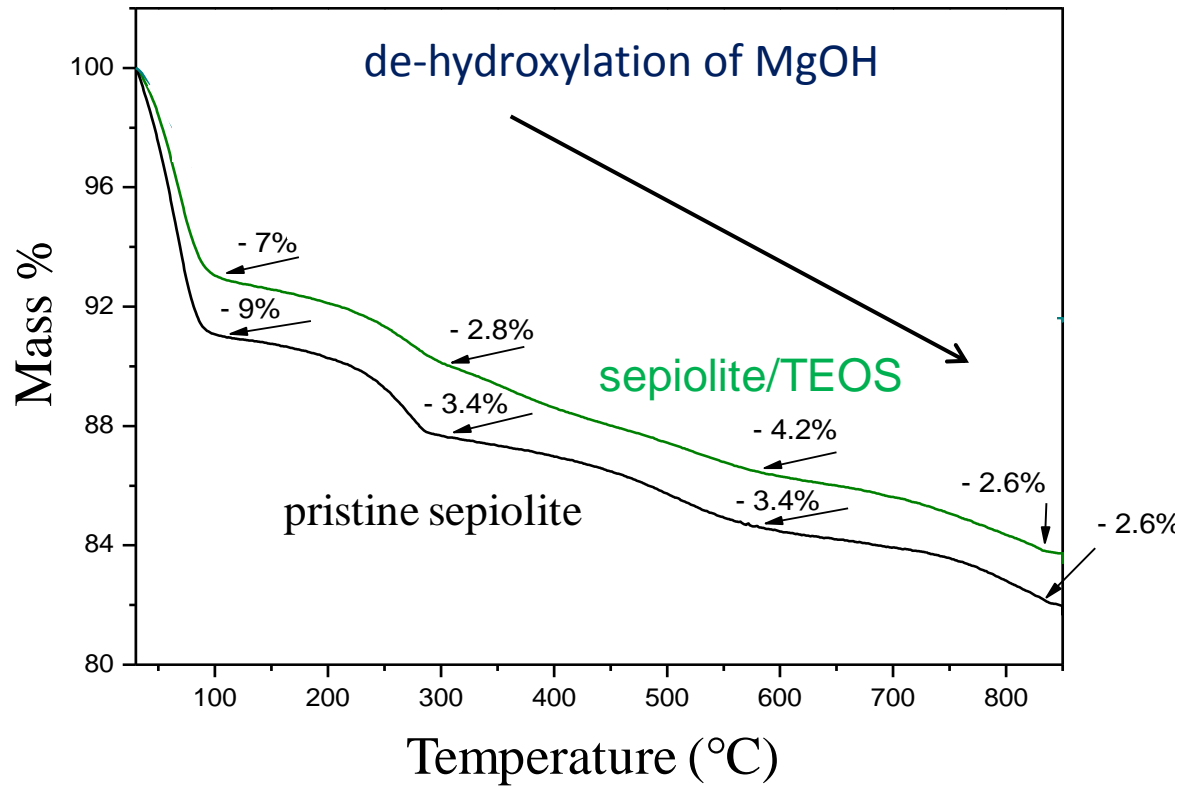
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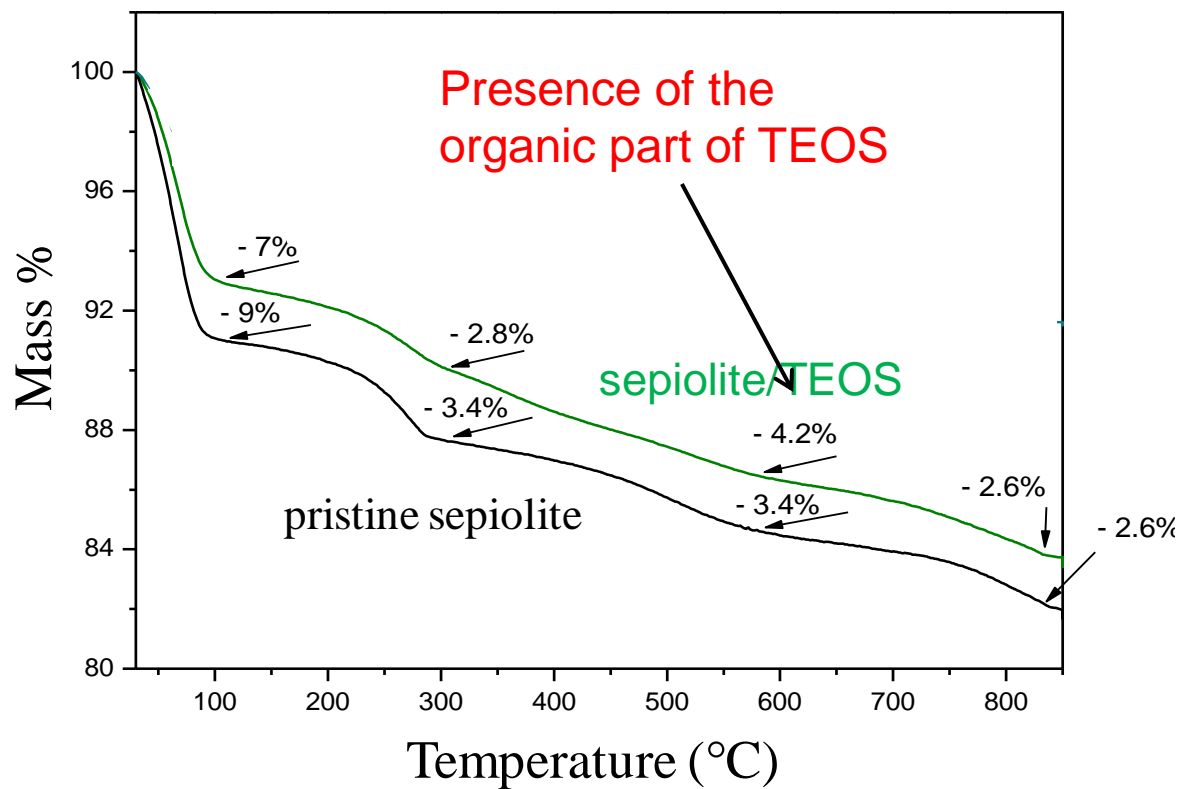
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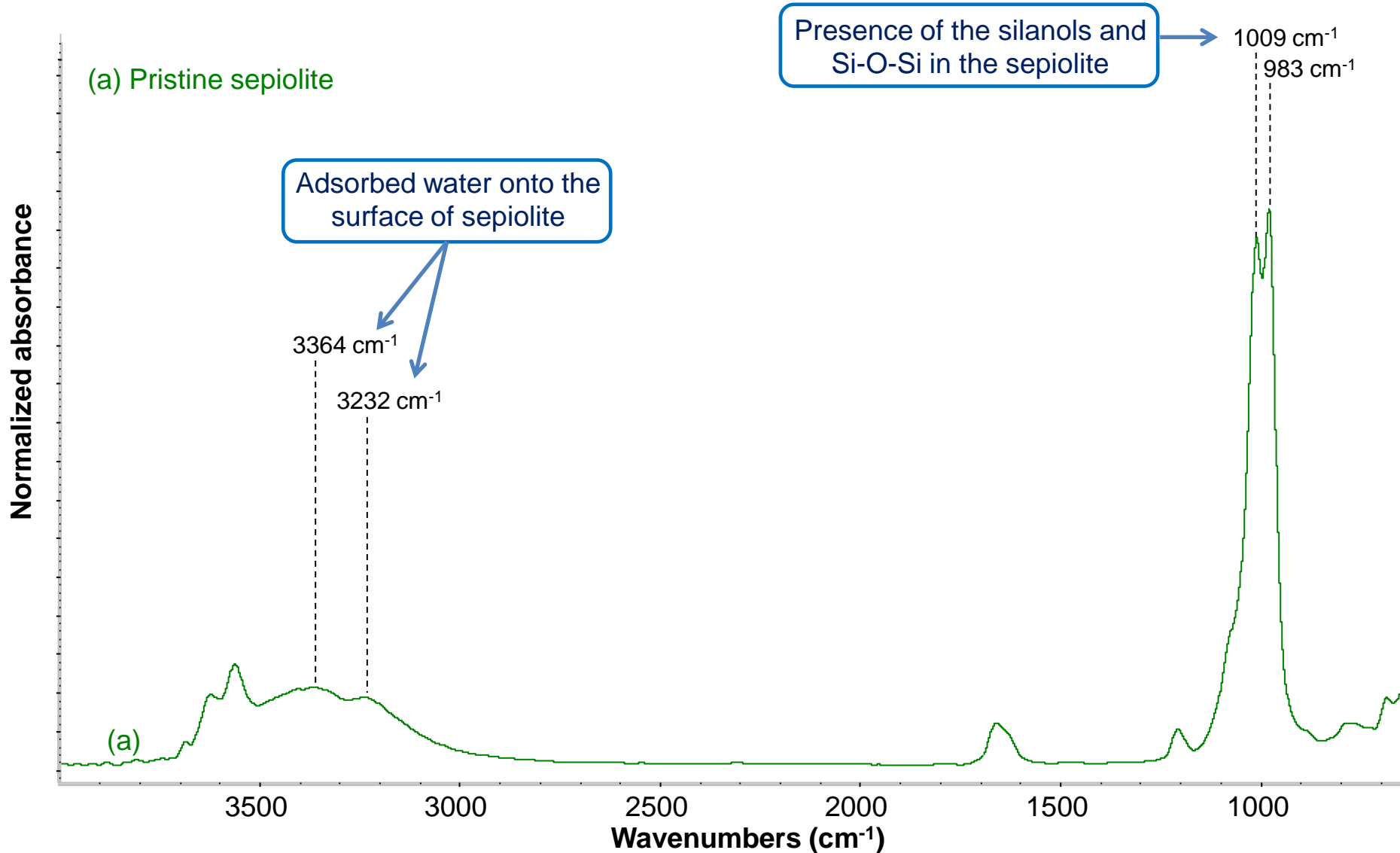


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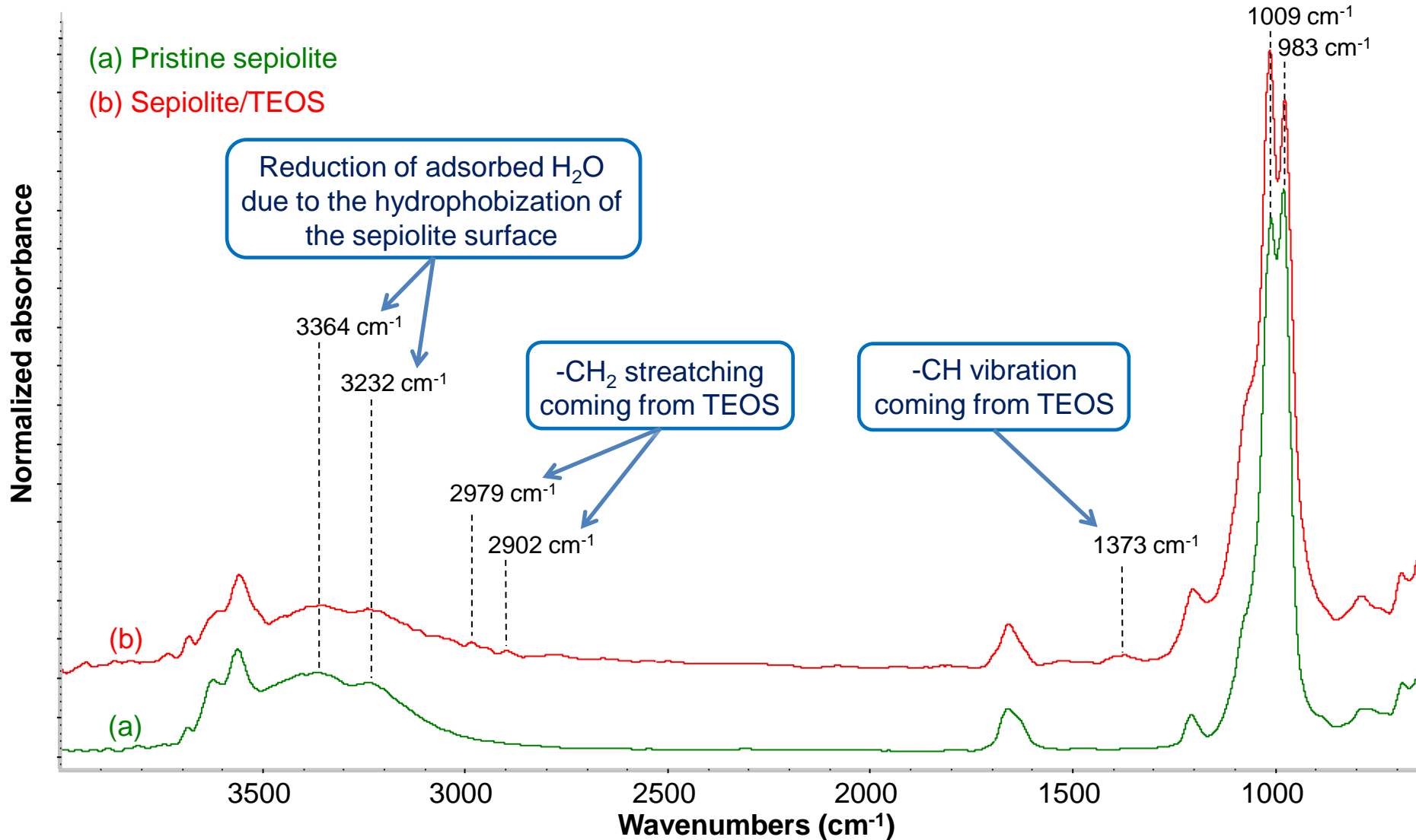
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# Pristine sepiolite – ATR analysis



# Sepiolite modified with TEOS – ATR analysis

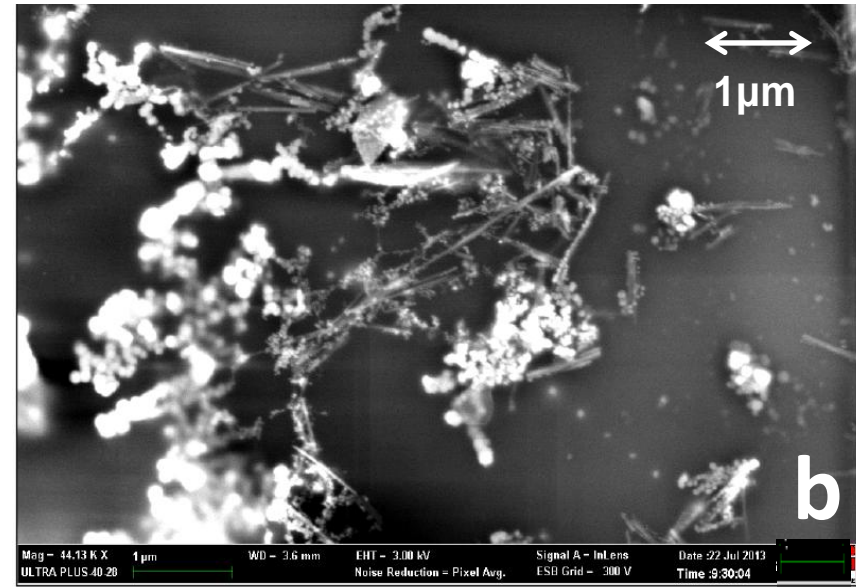
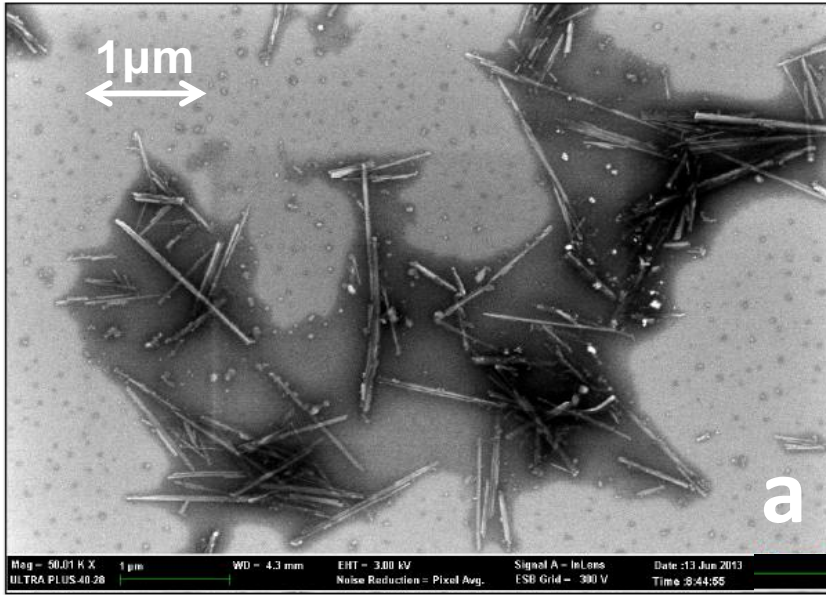


# Sepiolite modified with TEOS

## FESEM analysis

pristine sepiolite

sepiolite / TEOS



Fibrils of  
pristine sepiolite

silica nanoparticles  
on sepiolite fibrils



Treated sepiolite with TEOS  
with basic catalyst

- Rubber composites -



# NR based compounds with silica and sepiolite/TEOS

## Formulations

Ingredient	Filler(s) in the composite	
	Silica	Silica + sepiolite/TEOS
NR	100	100
Silica	45	35
Sepiolite/TEOS	0	10
Silane TESPT	3.6	3.6

Other ingredients: ZnO (3.6), Stearic acid (2), 6-PPD (2), Sulphur (2.8), TBBS (1.8)

# NR based compounds with silica and sepiolite/TEOS

## Dynamic mechanical properties

Property	Filler(s) in the composite	
	Silica	Silica + sepiolite/TEOS
G' (0.4%)	100	84,76
$\Delta G'$ (0.4%-35%)/G' (0.4%)	100	86,67
Tan Delta max	100	94,36

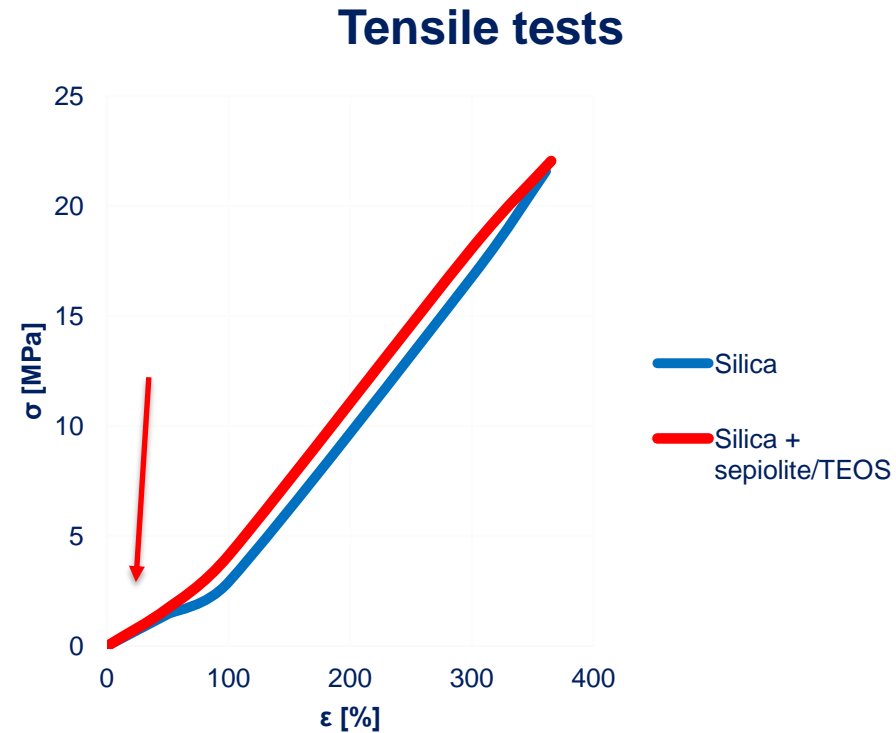
L. Giannini, M. Galimberti, V. Cipolletti, G. Peli WO 2016/174628 A1



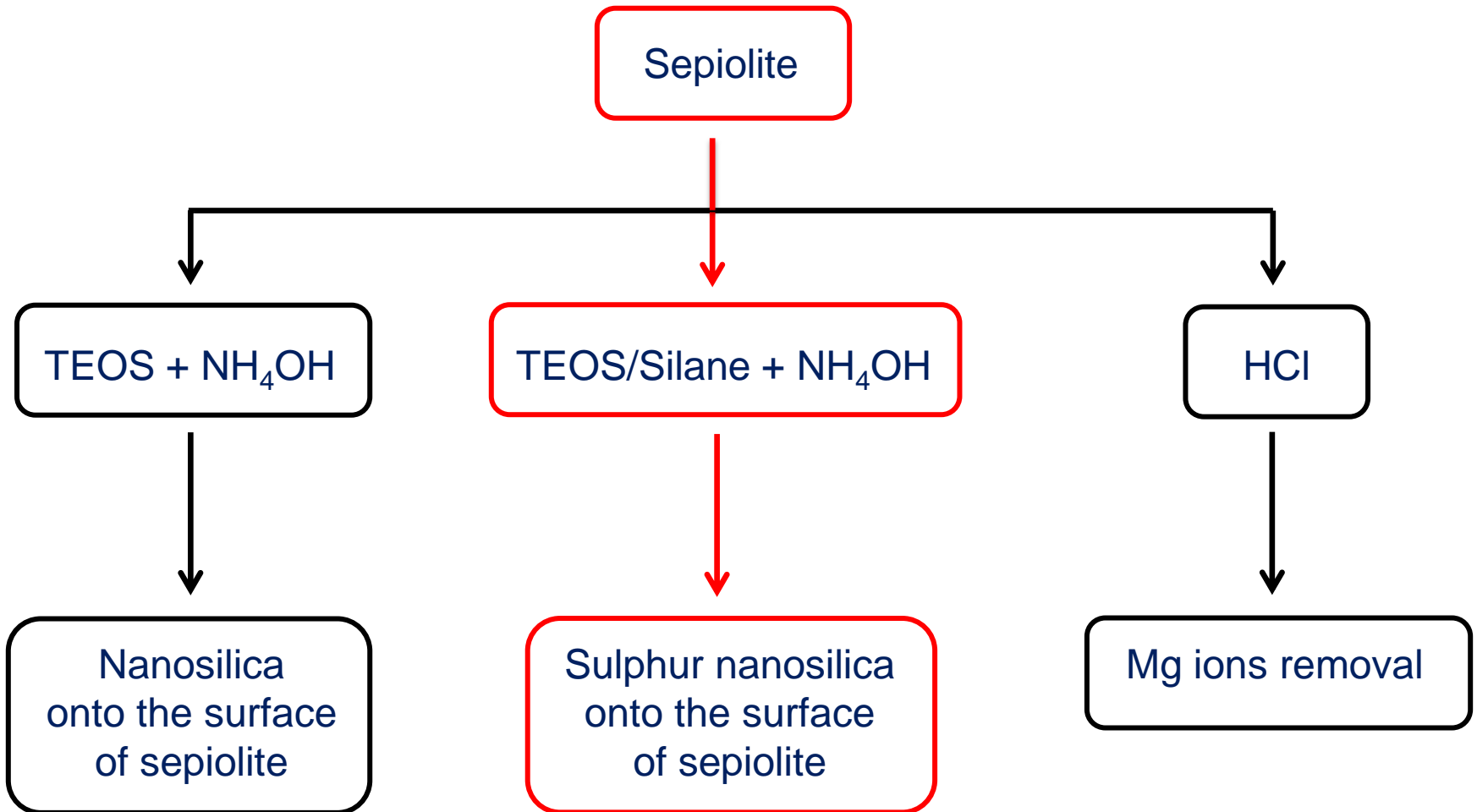
# NR based compounds with silica and sepiolite/TEOS

## Tensile tests

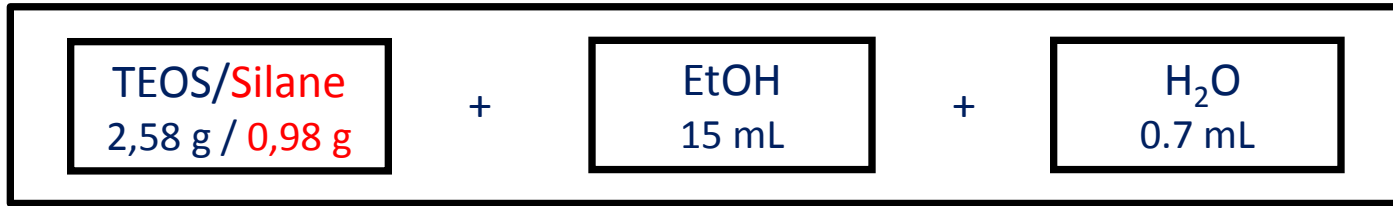
Property	Filler(s) in the composite	
	Silica	Silica + sepiolite/TEOS
$\sigma_{50}$ (MPa)	1.45	1.72
$\sigma_{100}$ (MPa)	2.91	4.12
$\sigma_{300}$ (MPa)	16.76	18.08
$\sigma_B$ (MPa)	21.57	22.04
$\epsilon_B$ (%)	361.05	365.07



# How to foster the chemical reactivity of sepiolite?



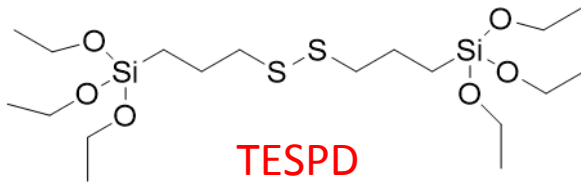
# Sepiolite modified with TEOS



1h at 40°C  
under stirring

SEPIOLITE  
in EtOH, 65 mL

previous treatment  
with ultrasounds, 30 min



+ NH<sub>4</sub>OH (30% in mass aq sol.), 2 mL

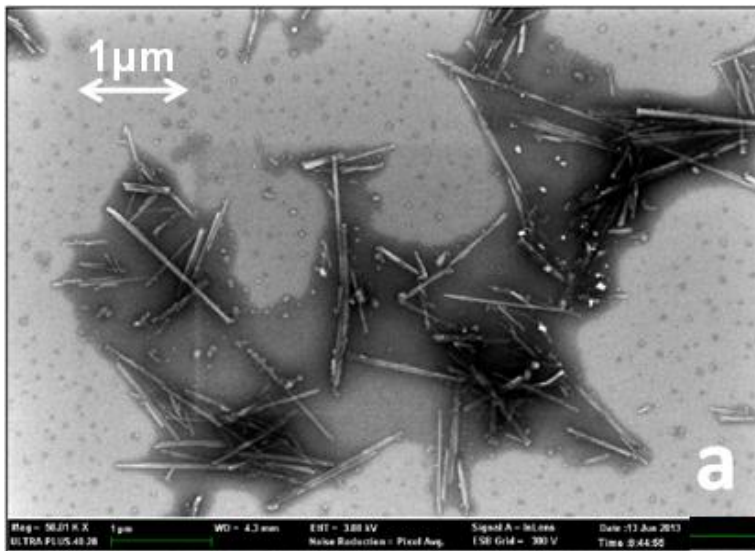
1. 5h at 60°C under stirring  
2. filtering, washing

MODIFIED SEPIOLITE

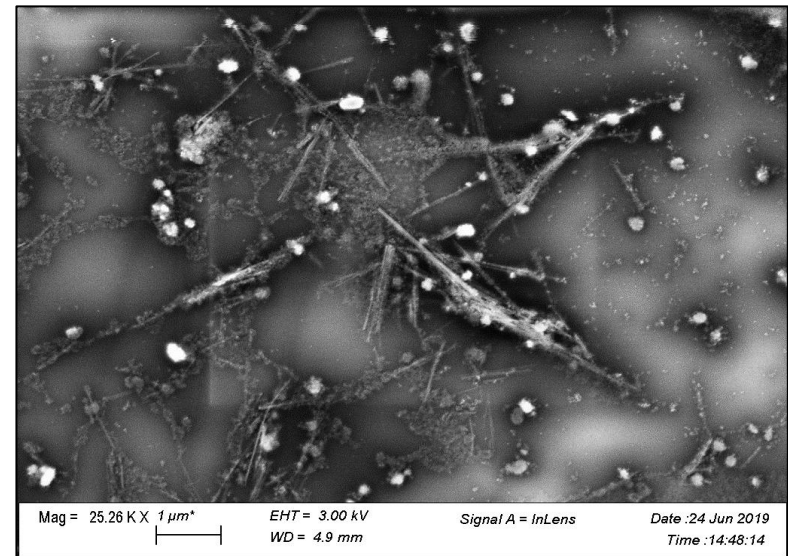


# Characterization – Elemental analysis and FESEM

	C (% wt)	S (% wt)
Sepiolite	0	0
Sepiolite/TEOS/TESPD	3,39	<b>0,56</b>
Sepiolite/TESPD	5,45	<b>2,89</b>

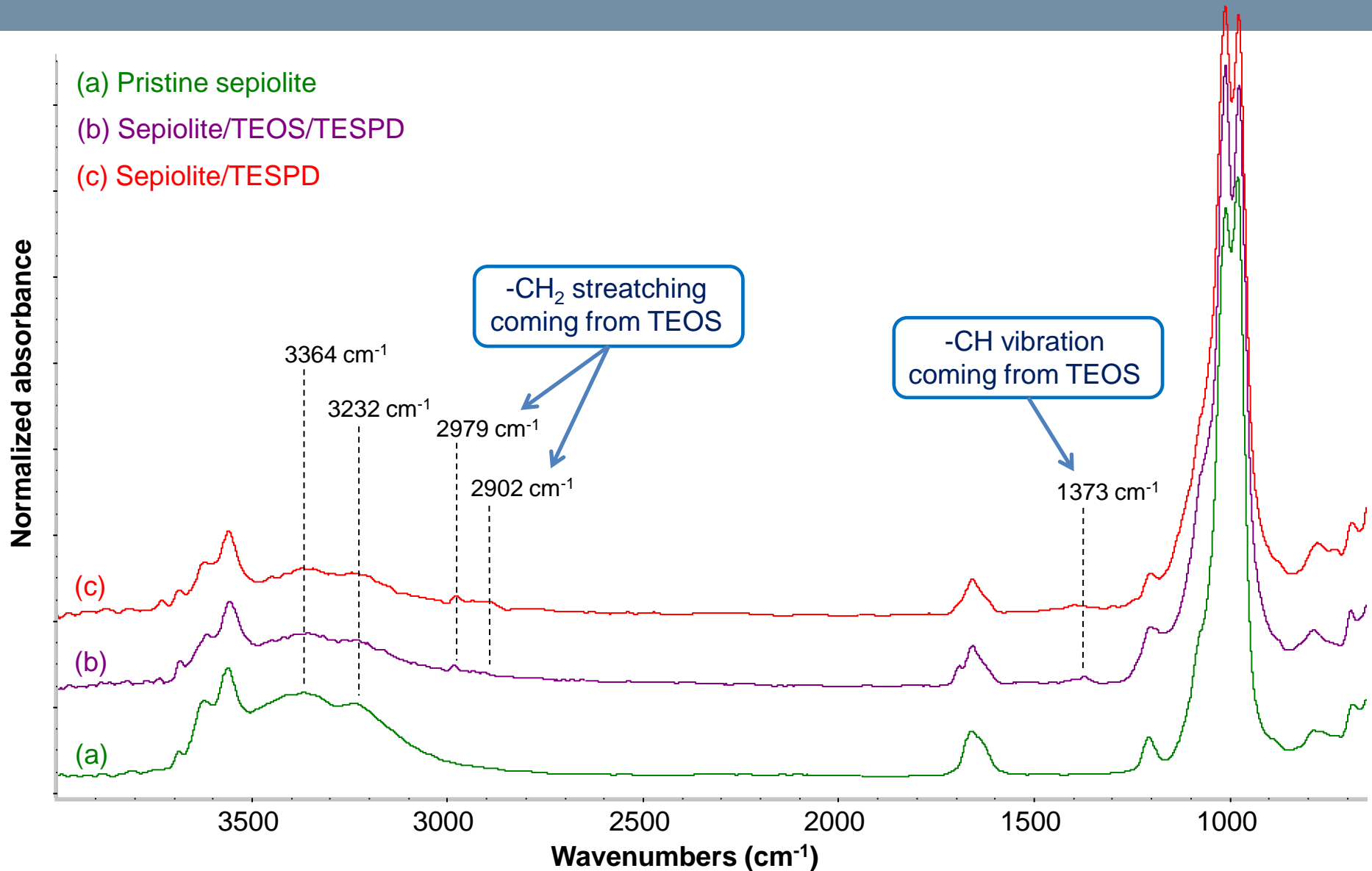


Pristine sepiolite

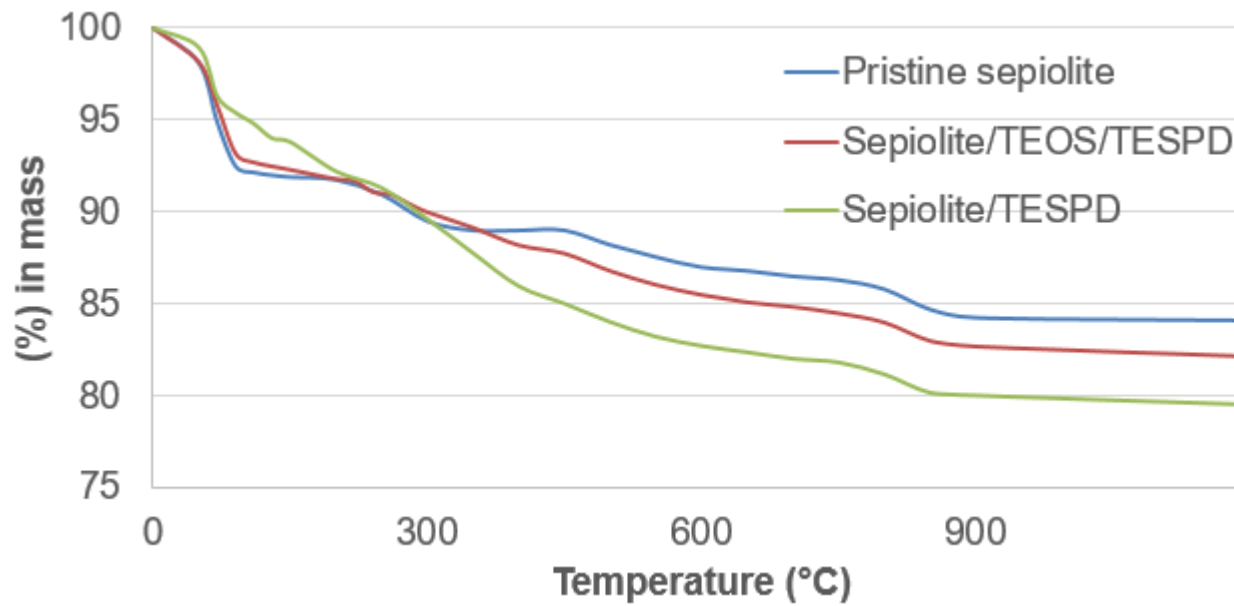


Sulphur-based silica nanoparticles  
onto sepiolite fibrils

# Sepiolite modified with TEOS/TESPD



	Mass loss [%] T < 150 °C	Mass loss [%] 150 ° < T < 450 °C	Mass loss [%] 450 ° < T < 750 °C	Mass loss [%] T > 750 °C
Pristine sepiolite	8,1	3,3	2,7	2,0
Sepiolite/TEOS/TESPD	6,2	6,2	3,3	2,1
Sepiolite/TESPD	5,6	8,2	4,4	2,3



Treated sepiolite with TEOS/TESPD  
with basic catalyst

- Rubber composites -



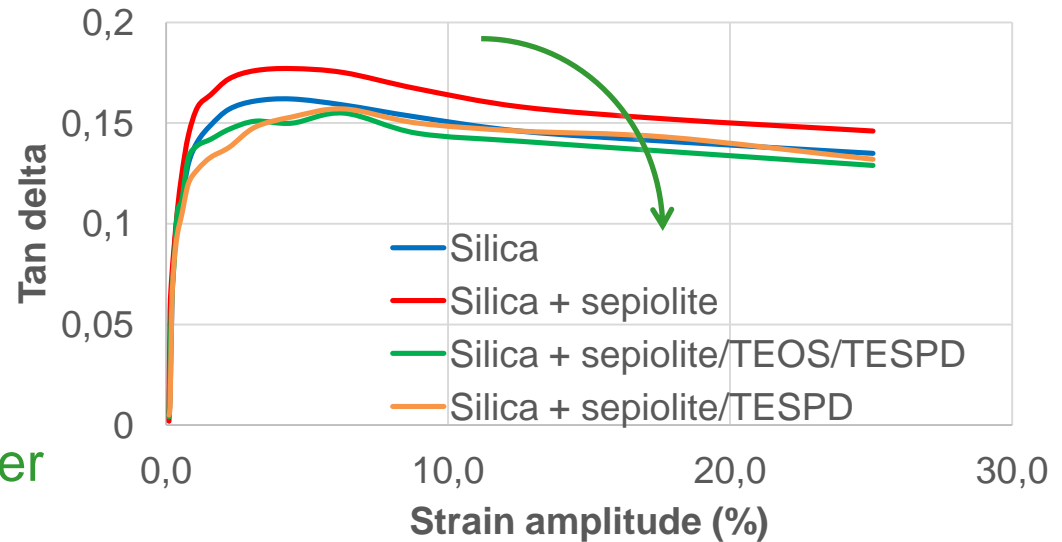
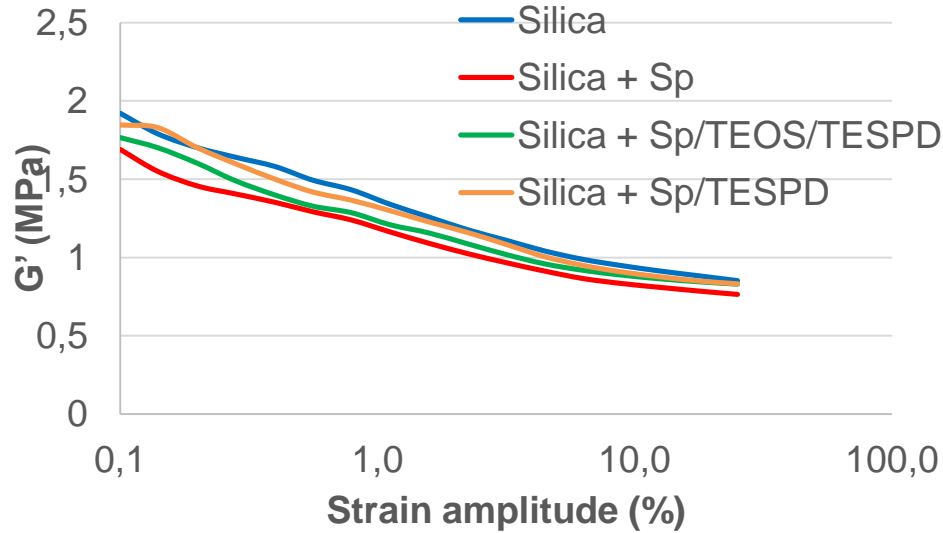
# Sepiolite modified with TEOS/TESPD – Recipe

Ingredients	Filler in the composite			
	Silica	Silica + Sp	Silica + Sp/TEOS/TESPD	Silica + Sp/TEOS
Natural rubber	100	100	100	100
Silica	45	35	35	35
Sepiolite	0	11,5	0	0
Sepiolite/TEOS/TESPD	0	0	11,5	0
Sepiolite/TESPD	0	0	0	11,5
TESPT	3,6	3,6	3,6	3,6
Sulphur	2	2	2	2

\*Addition in all composites: stearic acid (2); ZnO (3,6); 6PPD (2); TBBS (1,8)



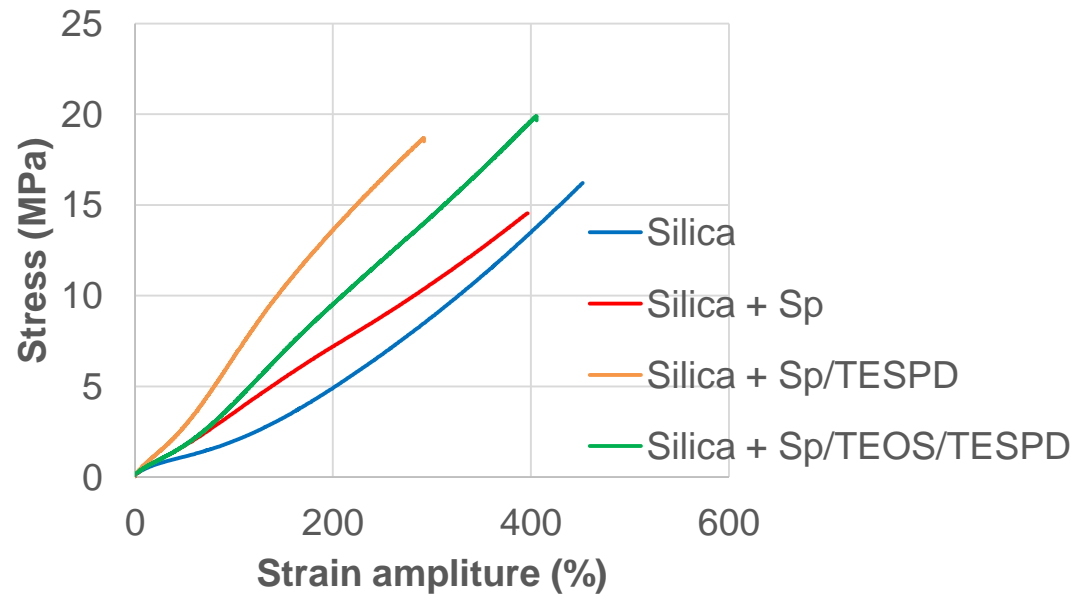
# Sepiolite modified with TEOS/TESPD



➤ Tan delta: the lower, the better



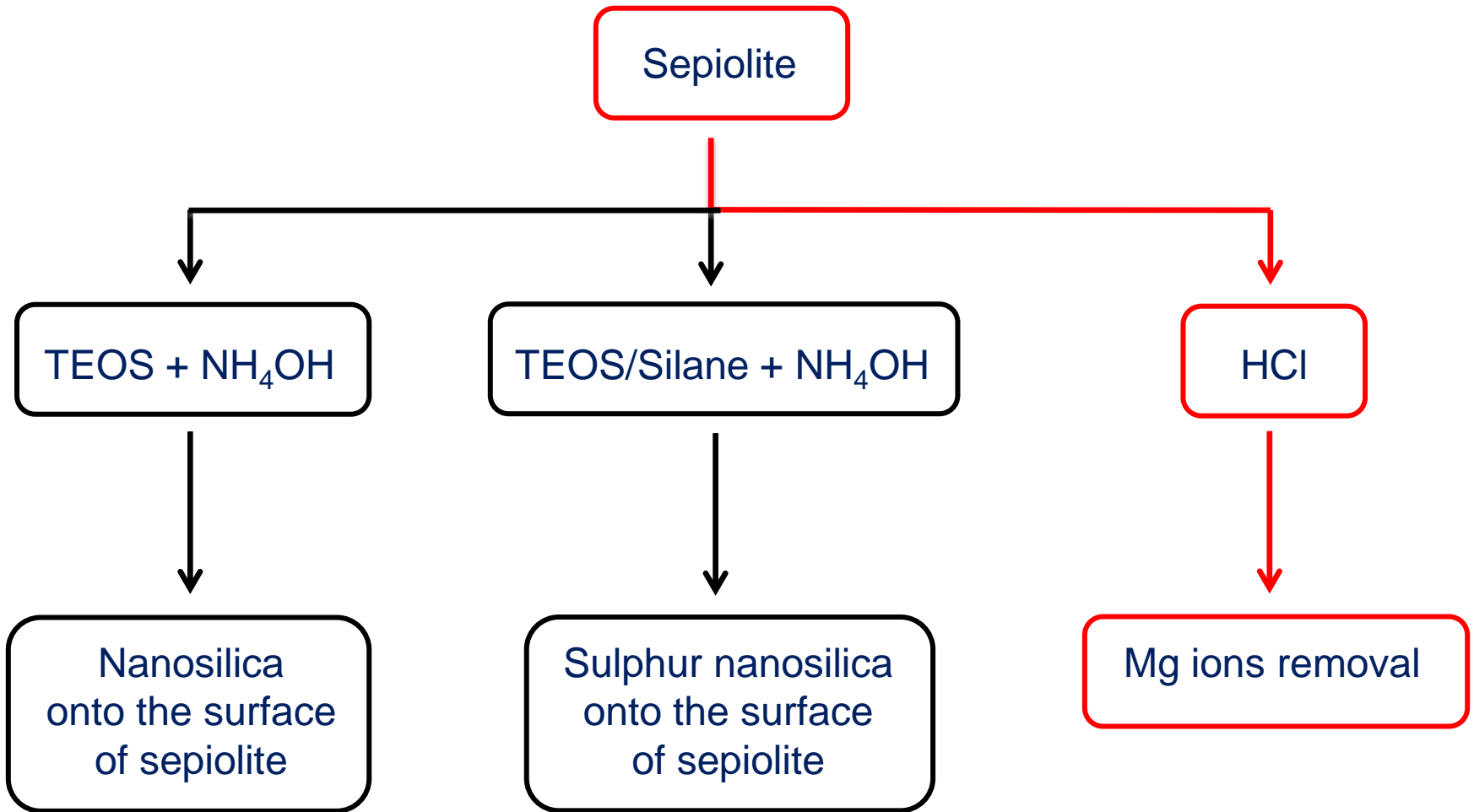
# Sepiolite modified with TEOS/TESPD – stress vs strain



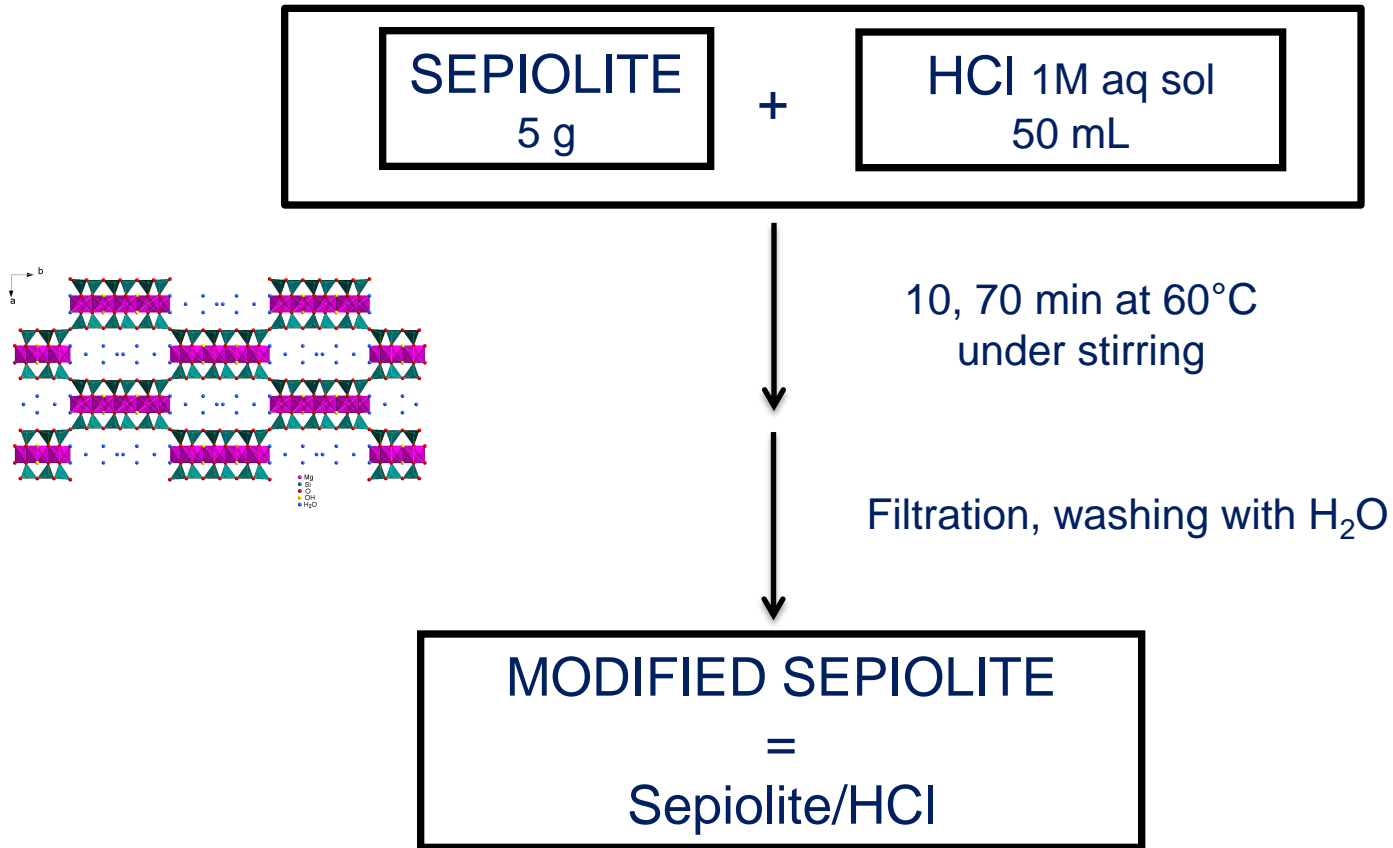
	Silica	Silica + sepiolite/TEOS/TESPD	Silica + sepiolite/TESPD
$\sigma_{50}$	1,45	1,76	2,81
$\sigma_{100}$	2,91	4,09	6,66
$\sigma_{300}$	16,76	14,38	-
$\sigma_B$	21,57	19,65	18,51
$\epsilon_B$	361,05	405,96	291,98



# How to foster the chemical reactivity of sepiolite?



# Treatment of sepiolite with HCl

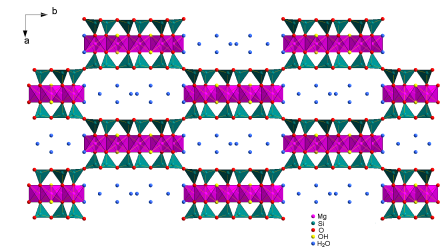


# Treatment of sepiolite with HCl

## Extracted Magnesium

Treatment time (min)	Extracted Mg <sup>a</sup>			Residual Mg
	mmol/(g of sepiolite)	%		%
10	2.1	34.0		66.0
70	5.1	82.0		18.0

<sup>a</sup> determined through titration

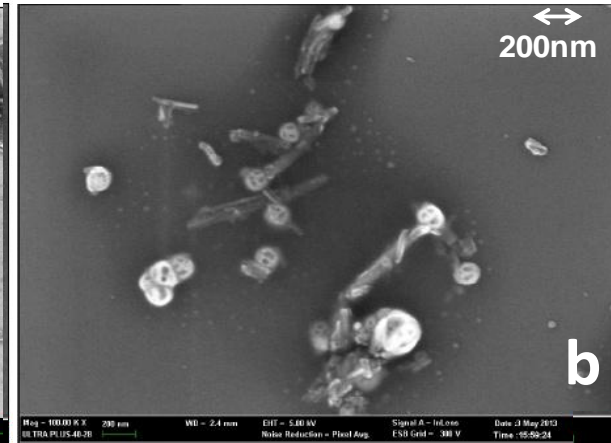
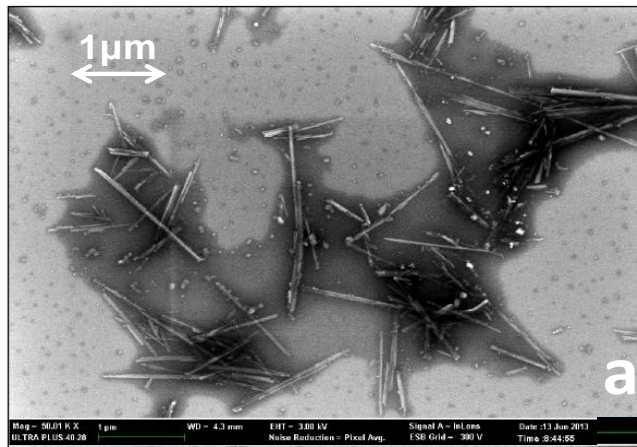


# Treatment of sepiolite with HCl

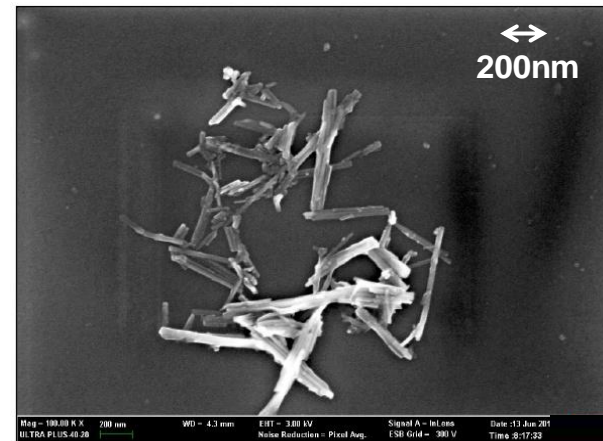
## FESEM analysis

pristine sepiolite

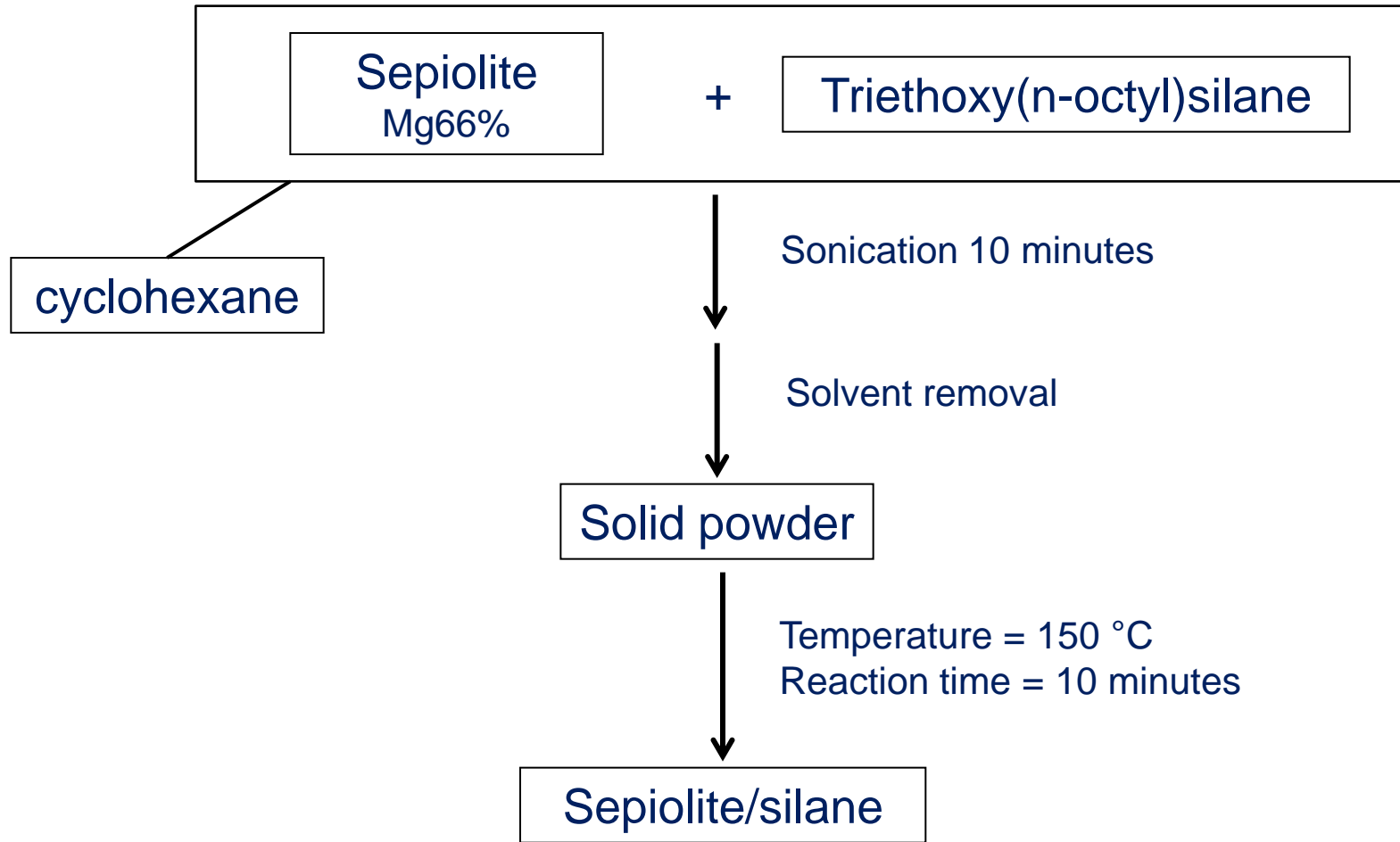
sepiolite / HCl - Mg 18%



sepiolite / HCl - Mg 66%



# Sepiolite/HCl – Silanization with triethoxy(n-octyl)silane



# Sepiolite/HCl – Silanization with triethoxy(n-octyl)silane

Silicate	Silane in the final adduct (mass%)
Silica	4.1
Pristine sepiolite	3.5
Sepiolite/HCl. Mg 66%	4.0

Higher affinity to interact with silane molecule



Treated sepiolite with HCl

- Rubber composites -



# NR based compounds with silica and sepiolite/HCl (Mg 80%)

Ingredient	Filler in the composite		
	Silica	Silica + Sepiolite	Silica + Sepiolite/HCl (Mg 80%)
IR	40	40	40
BR (Nd)	60	60	60
CB N550	25	25	25
Silica Zeosil 1115	30	20	20
Sepiolite	0	7	7
Sepiolite/HCl Mg80%	0	0	7
Silane TESPT	5.0	5.0	5.0

L. Giannini, L. Tadiello, T. Hanel, M. Galimberti, V. Cipolletti, G. Peli, F. Morazzoni, R. Scotti, B. Di Credico WO 2016/174629A1



# NR based compounds with silica and sepiolite/HCl (Mg 80%)

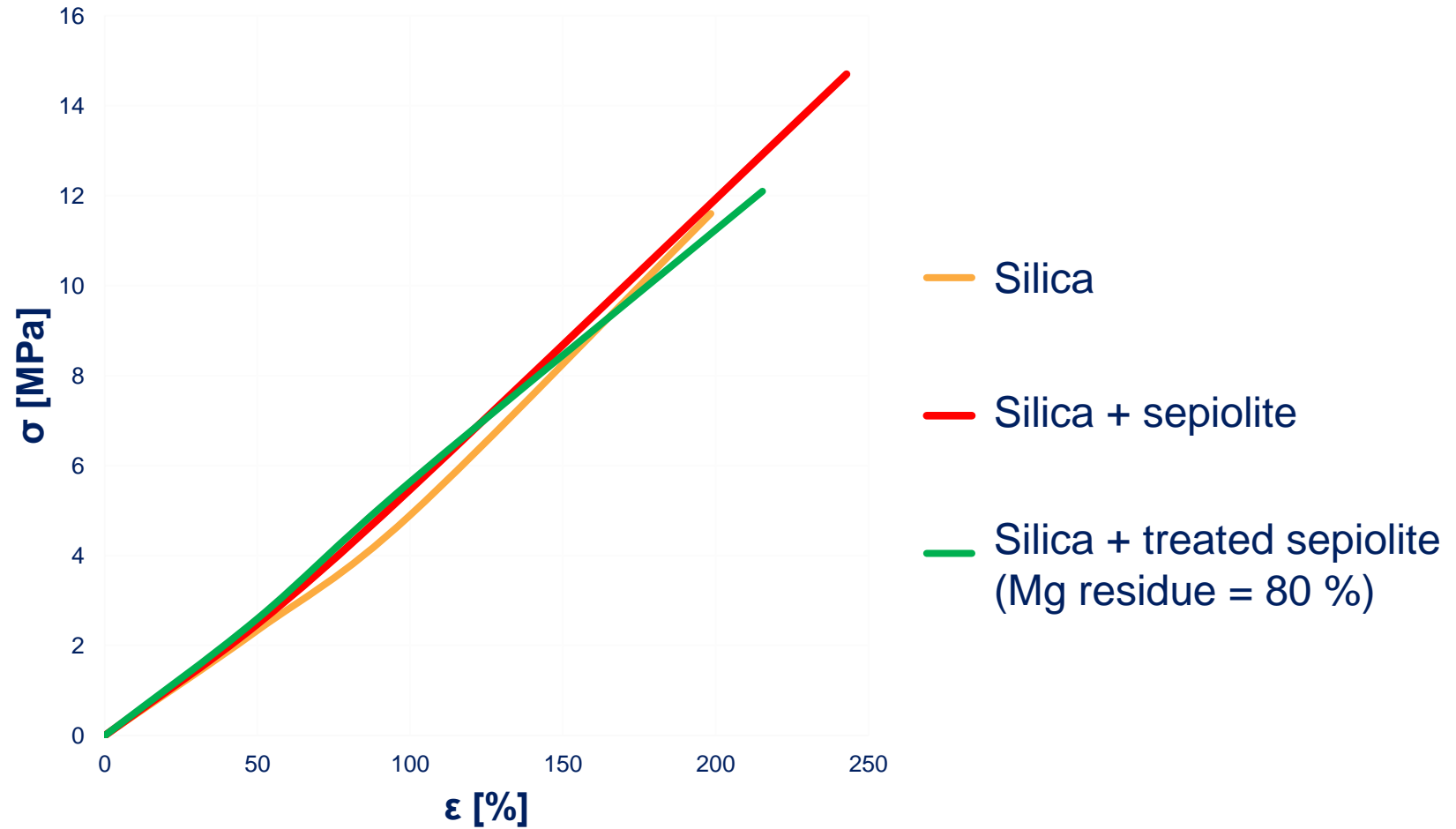
Property	Filler in the composite		
	Silica	Silica + Sepiolite	Silica + Sepiolite/HCl (Mg 80%)
E' (23°C) 100 Hz	100	103	113
E' (70°C) 100 Hz	100	102	113
Tan Delta (23°C) 100 Hz	100	107	87
Tan Delta (23°C) 100 Hz	100	106	85

➤ Tan delta: the lower, the better



# NR based compounds with silica and sepiolite/HCl (Mg 80%)

## Tensile tests



# Items of the presentation

1. Objectives
2. Prior art – high aspect ratio
3. Chemical modification of the surface of sepiolite
  - 3.1 TEOS +  $\text{NH}_4\text{OH}$
  - 3.2 TEOS/Silane +  $\text{NH}_4\text{OH}$
  - 3.3 Treatment with HCl
4. **Final conclusions**



# Final conclusions

- The **chemical modification of sepiolite** was achieved preserving the fibrillar structure
- Three different **easy methods** were used to **modify the reactivity of the sepiolite surface**
- Acid treatment revealed **larger reactivity with a silane**
- The **best compromise** between dynamic-mechanical properties and tensile test was achieved with modified sepiolite

# From basic research to commercial development

The new P ZERO™ VELO: SmartNet Silica™ at work



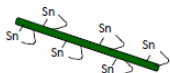
CORIMAV



Joint Labs

POLITECNICO  
MILANO 1863

SmartNet Silica™



elongated  
primary particle shape  
as "new Nanofillers"



surface chemistry of  
precipitated Silica  
«best in class for Hysteresis»

Tailoring new fillers by control of particle shape and surface - L. Giannini - Copyright Pirelli 2018

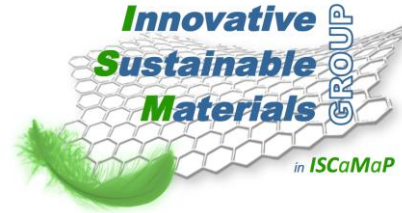


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