NANOMETRIC HIGH ASPECT RATIO FILLERS AND CHEMICAL REACTIVITY WITH THE POLYMER MATRIX

Maurizio Galimberti[1]

Valeria Cipolletti,[2] Giulia Peli,[1] Vincenzina Barbera,[1] Andrea Bernardi,[1] Daniele Locatelli,[1] Luca Giannini[2]

[1]Politecnico di Milano [2]Pirelli Tyre

2018 International Elastomer Conference

194th Technical Meeting ACS Rubber Division

Louisville (KY) October 9 - 11, 2018

Objective of the research

To take advantage

of nanometric high aspect ratio fillers

for the mechanical reinforcement of rubbers.

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To take advantage

of nanometric high aspect ratio fillers

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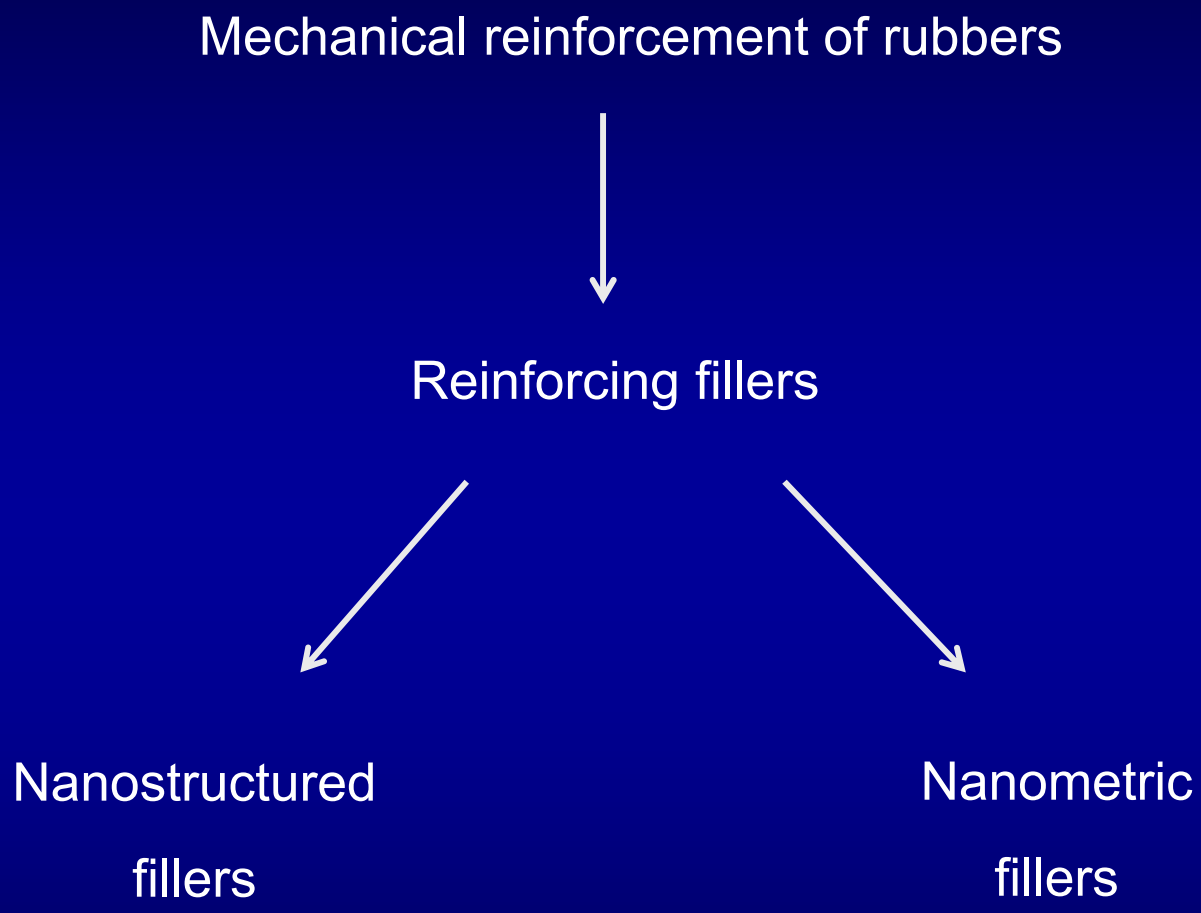
How?

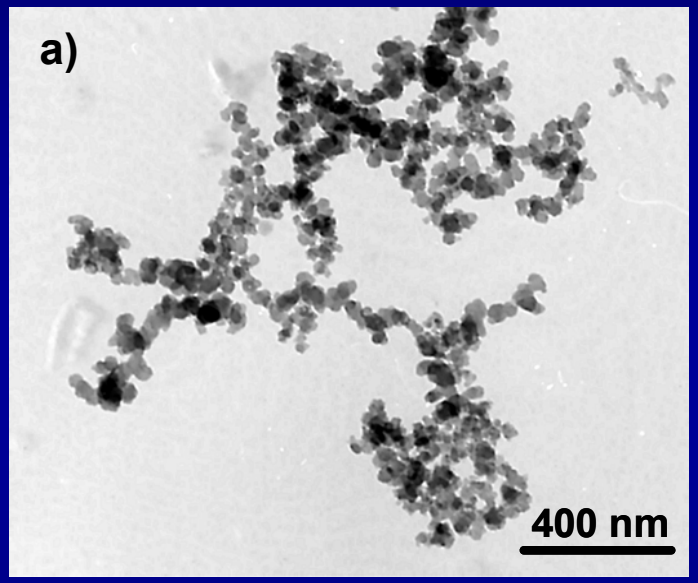
By fostering their chemical reactivity.

Mechanical reinforcement of rubbers

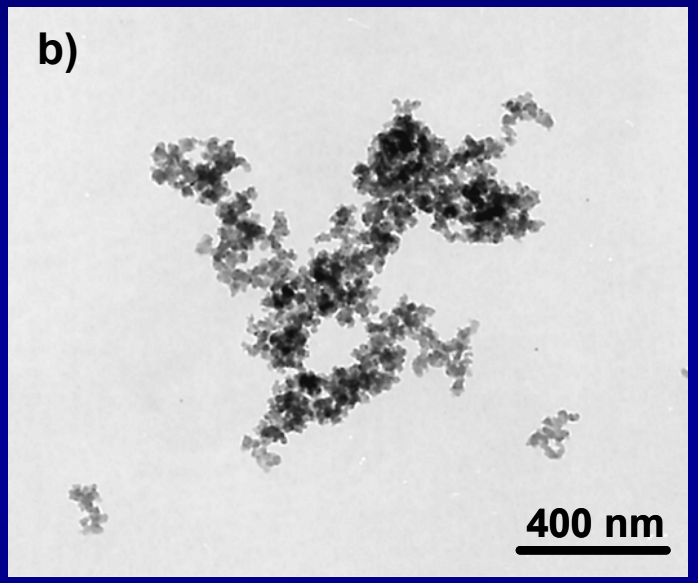


Reinforcing fillers - Nanostructured fillers

Carbon black

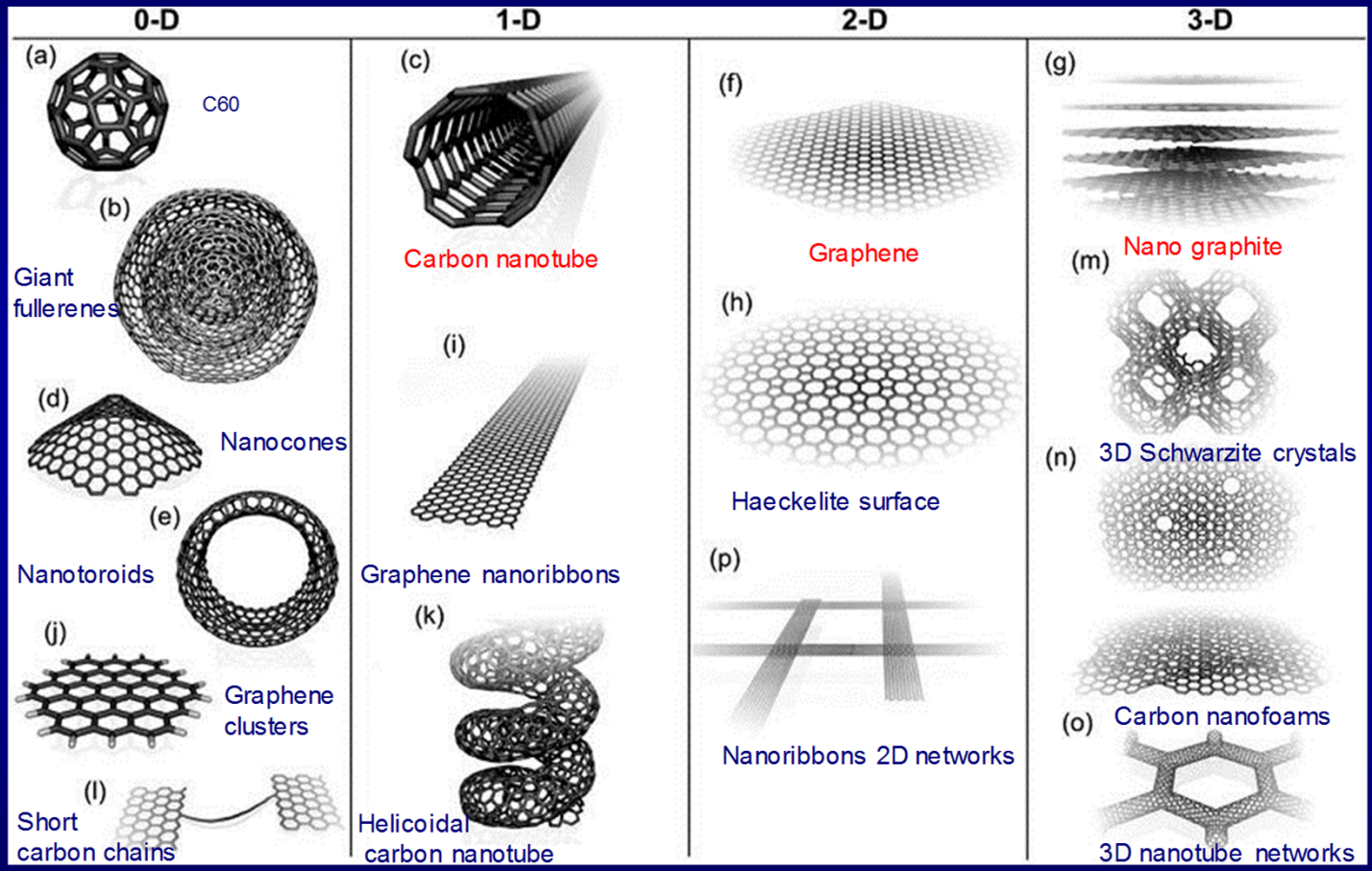


Silica



Reinforcing fillers - Nanometric fillers

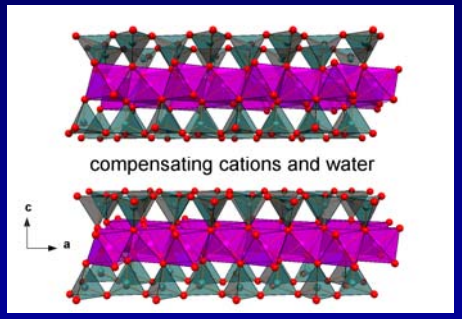
sp^2 carbon allotropes



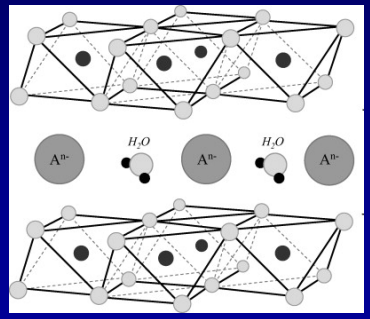
M. Terrones, et al. Nano Today 5 (4) (2010) 351-372.

Reinforcing fillers - Nanometric fillers

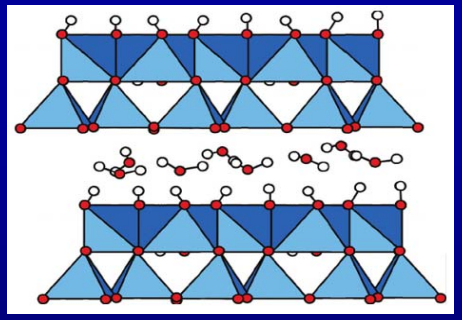
Inorganic Oxides and Hydroxides



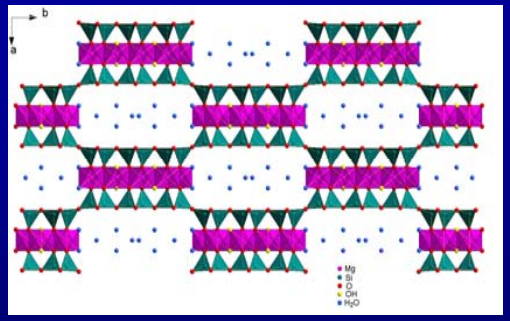
montmorillonite



hydrotalcite



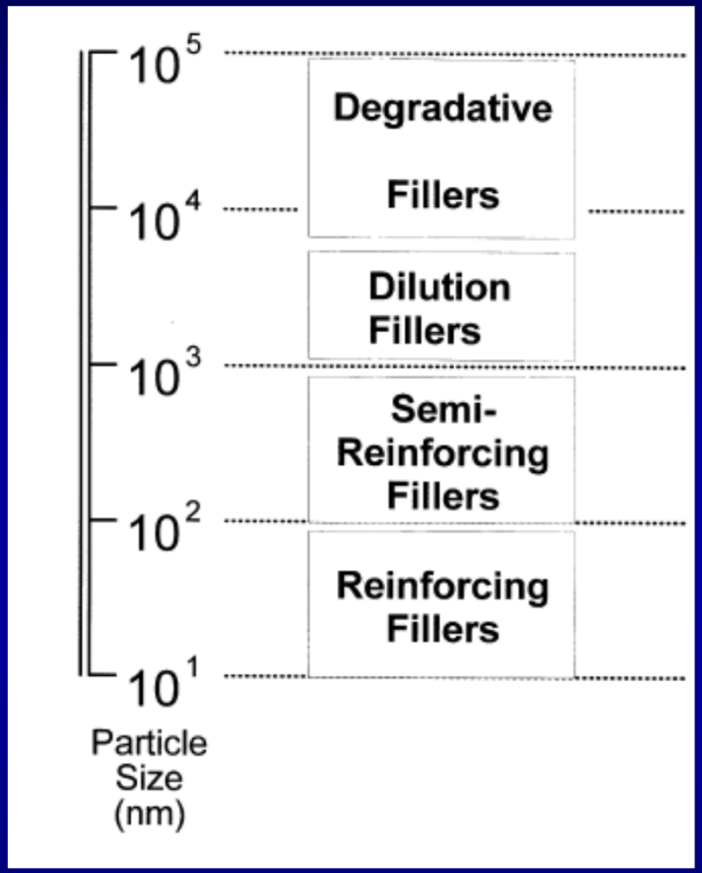
halloysite



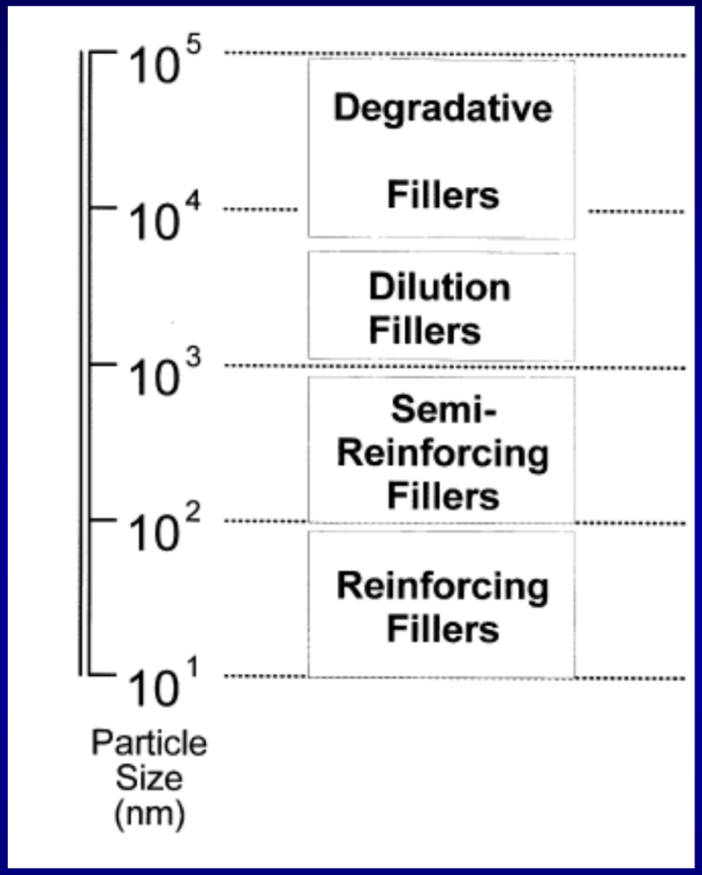
sepiolite

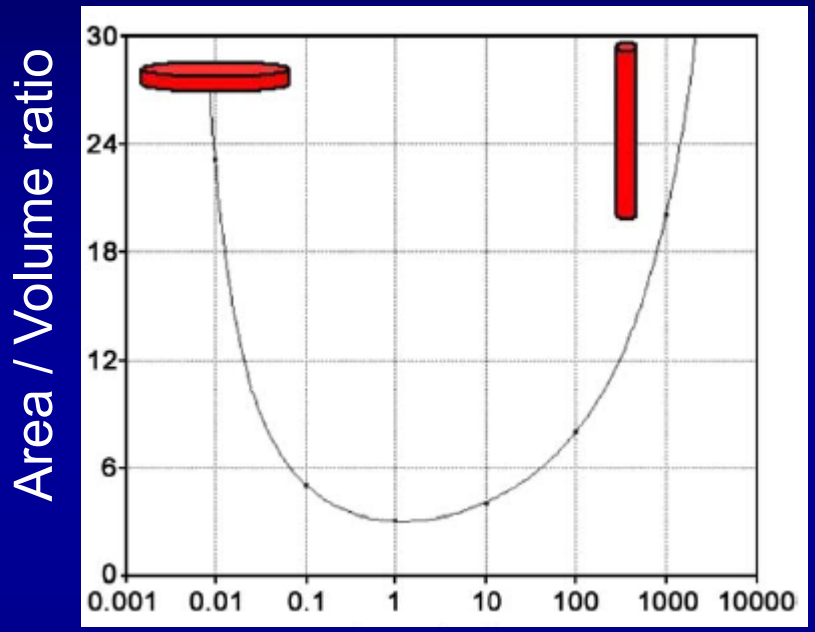
F. Bergaya, M. Jaber, J.F. Lambert, Natural and synthetic layered clays sepiolite, Chapter 1 in Rubber-Clay Nanocomposites. Galimberti, M. Ed, Wiley **2011**

Fillers - Classified by dimensions



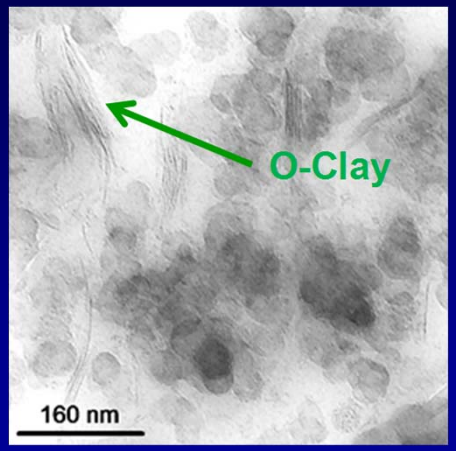
Fillers - Dimensions and aspect ratio

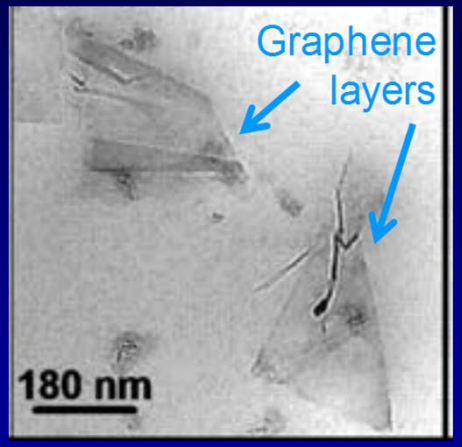


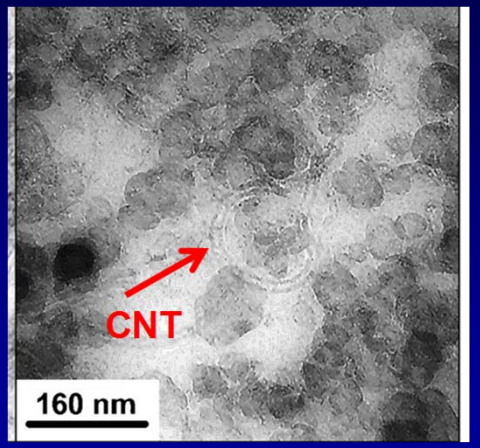


Interfacial area = surface area x density x volume fraction

Nanometric Fillers: large reinforcement







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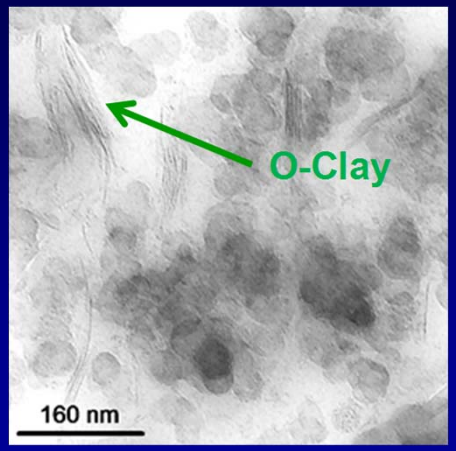
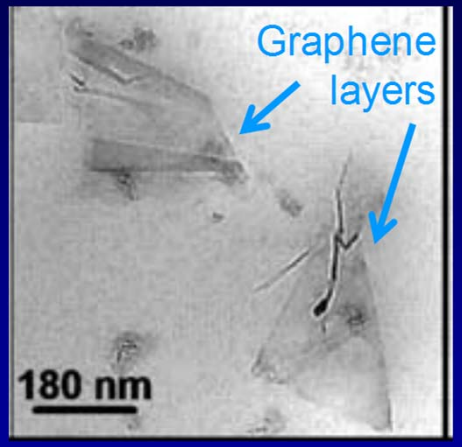
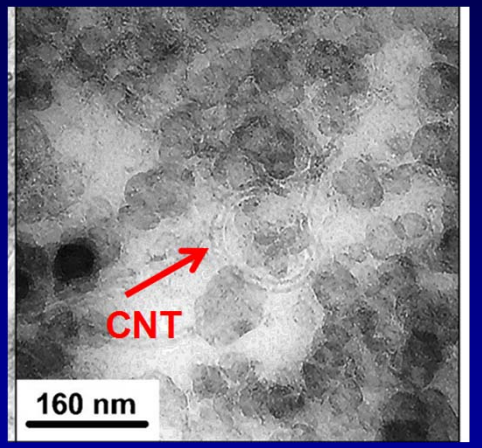
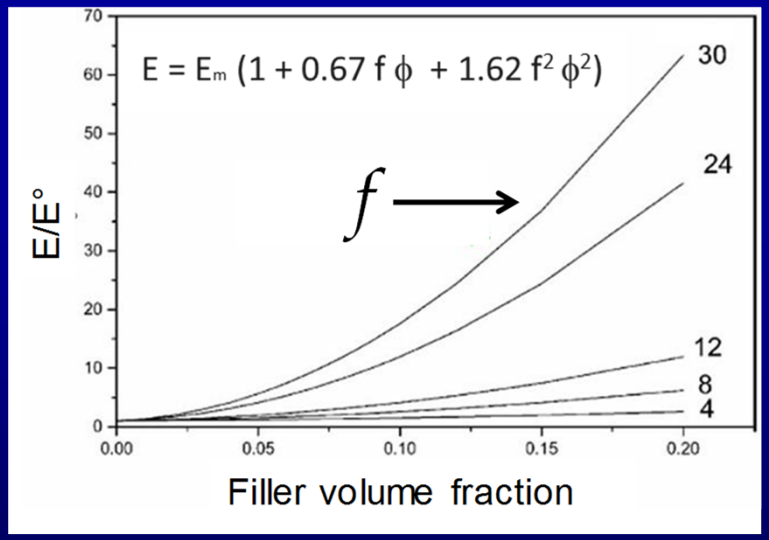
Galimberti M., V. Kumar, M. Coombs, V. Cipolletti, S. Agnelli, S. Pandini, L. Conzatti, RCT 87(2) (2014) 197-218

Nanometric Fillers: large reinforcement









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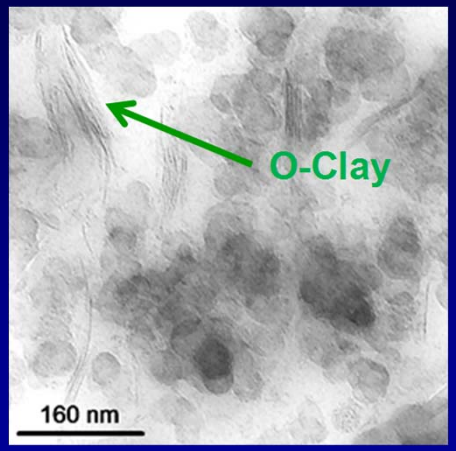

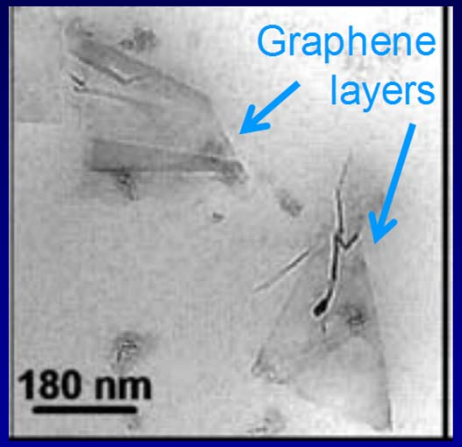

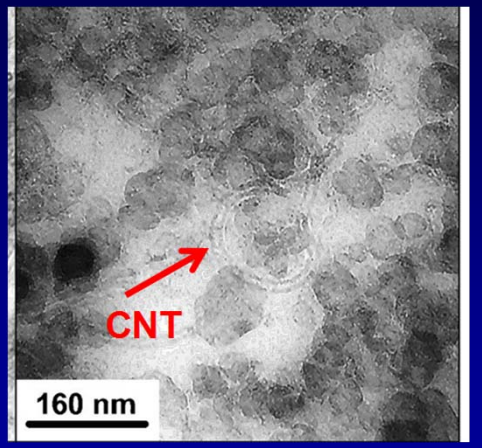

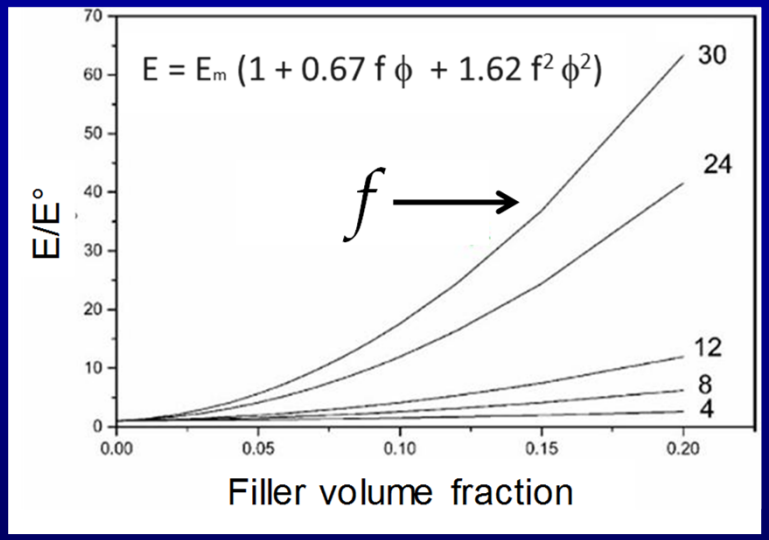

IR 100

ZnO 4, stearic acid 2,

sulfur 2, CBS 1

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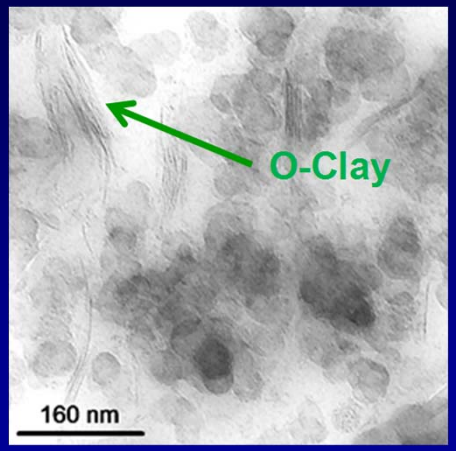

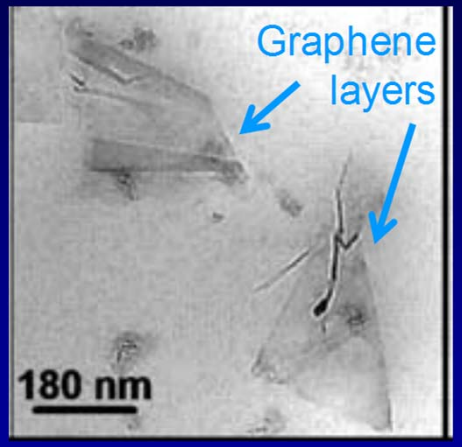

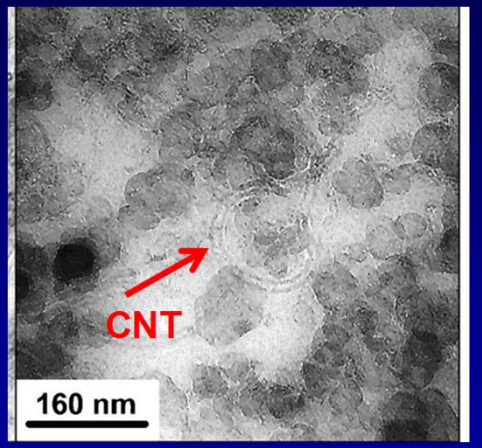

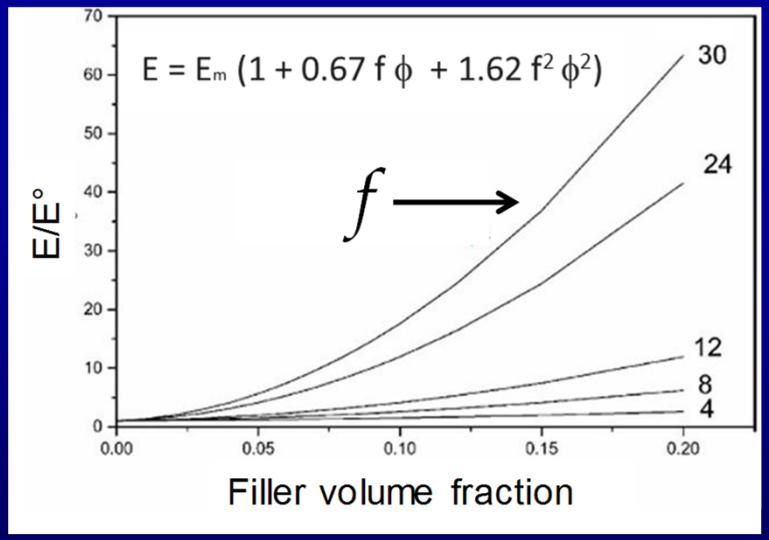

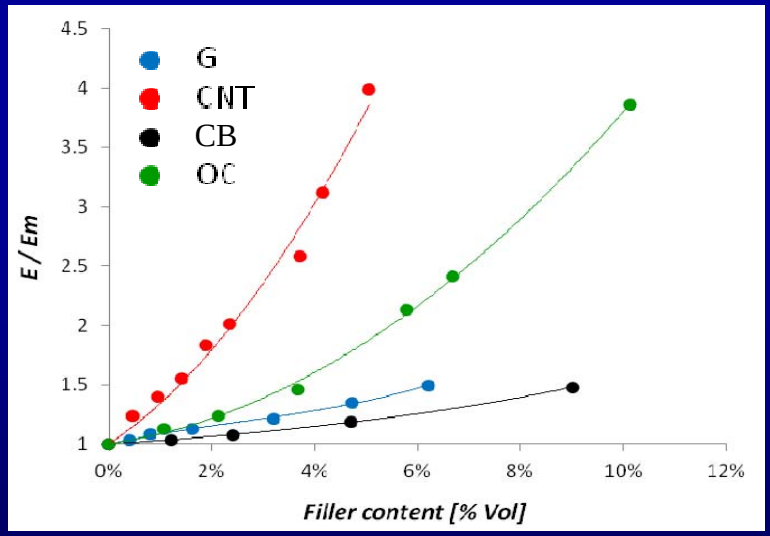

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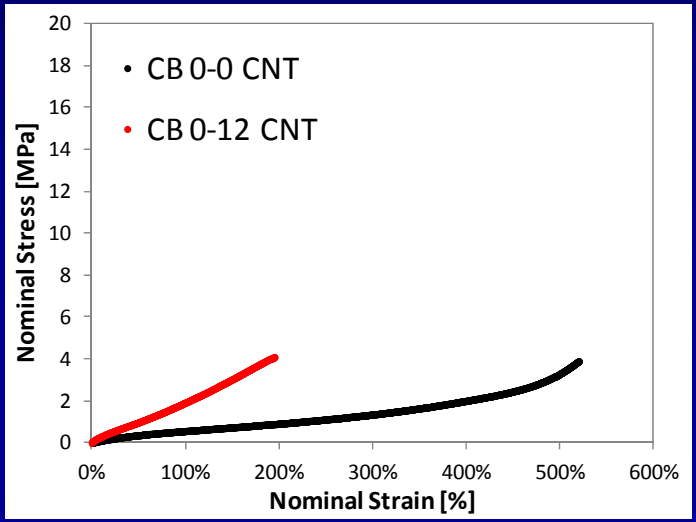
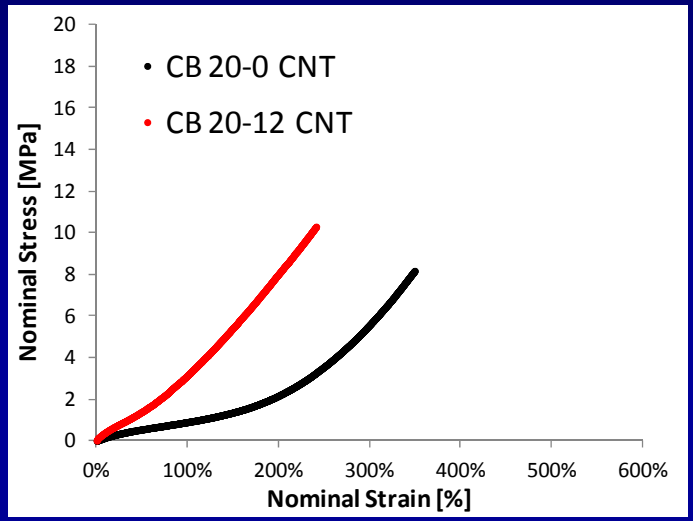
Nanometric high aspect ratio fillers: large reinforcement at low strain



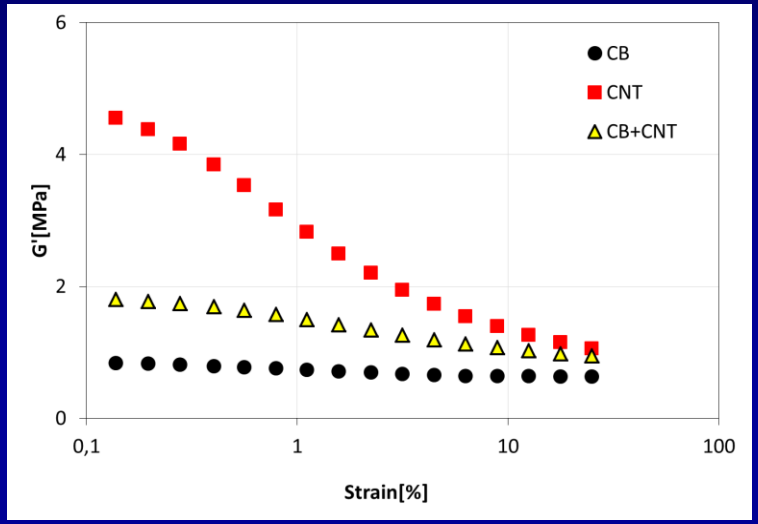


IR 100

Dicumyl peroxide 2

M. Galimberti, M. Coombs, V. Cipolletti, L. Giannini, T. Riccò, S. Pandini, L. Conzatti, M. Mauro, G. Guerra
"A comparative study of nano-fillers effects in rubber composites"
181th Technical Meeting of the Rubber Division of the American Chemical Society, Inc., San Antonio (TX) - April 22-25, 2012

Initial Modulus and Payne effect as a function of the total filler content



0.09 - 0.1
as total filler
volume fraction

Data from
shear stress tests,
@50°C

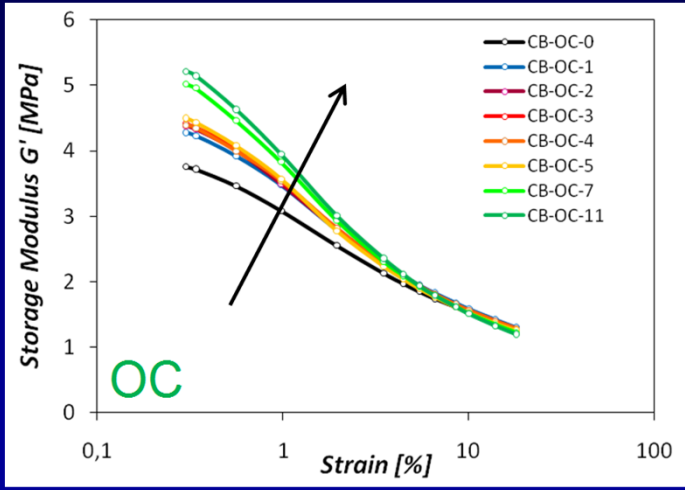
SBR 100

Dicumyl peroxide 2

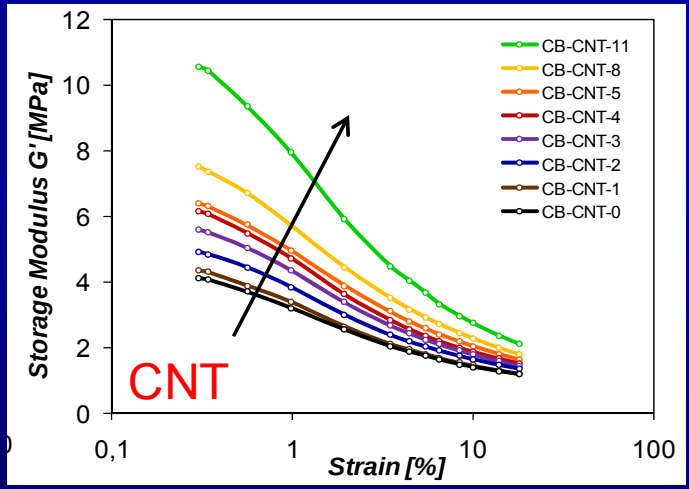
M. Galimberti, G. Infortuna, S. Guerra, V. Barbera, S. Agnelli, S. Pandini , eXPRESS Polymer Letters 2018, 12(3) 265–283

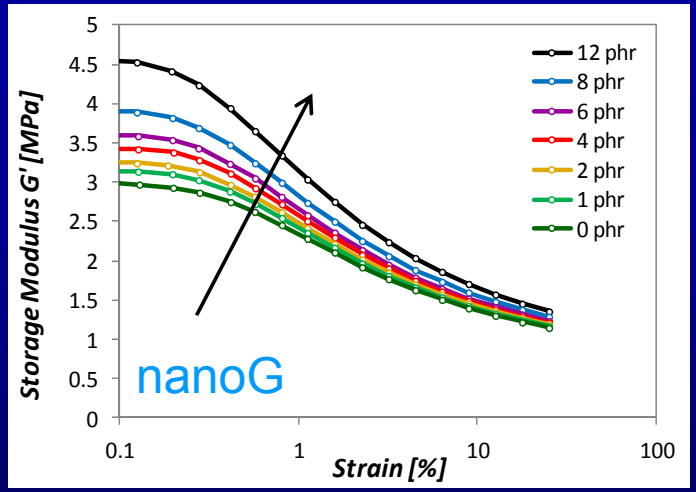
Nanometric Fillers: large Payne Effect

Data from
shear stress tests,
50°C



IR 100, CB 60,
TESPT 1 (with OC),
stearic acid 2, ZnO 4, 6PPD 2,
S 2, DCBS 1.8, PVI 0.5





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Qualitative interpretation of strain amplitude dependence of G'

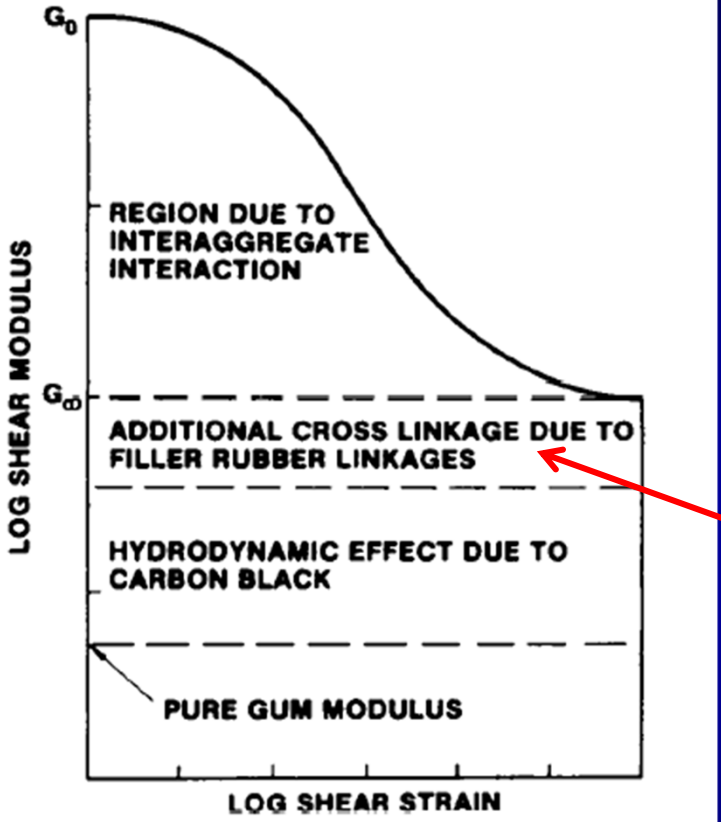


FIG. 12.—Qualitative interpretation of strain amplitude dependence of G' (after Payne[111]).

Medalia A.I., Rubber Chem Technol. 51, 437 (1978)

To foster the chemical reactivity

of high aspect ratio nanometric fillers

To foster the chemical reactivity

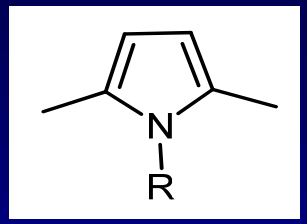
of high aspect ratio nanometric fillers

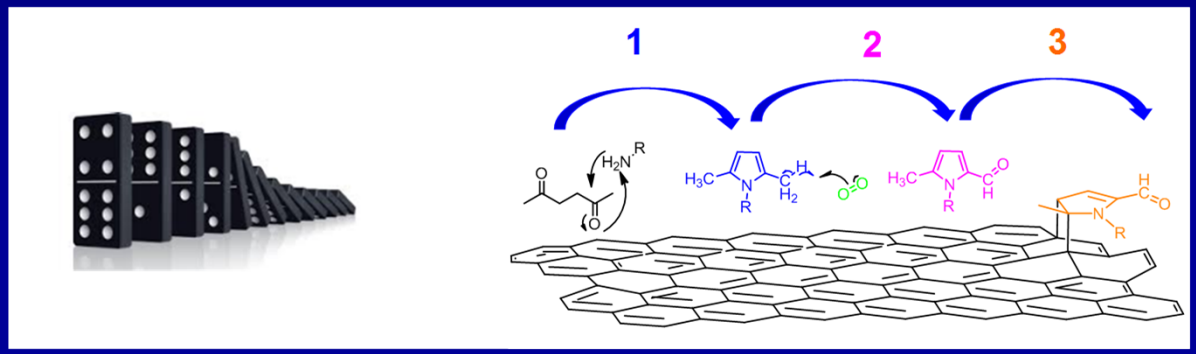
sp^2 carbon allotropes

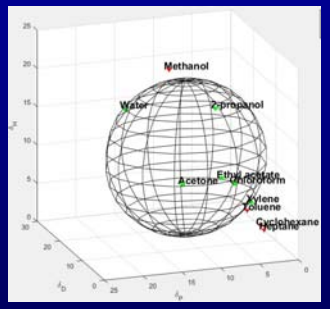
inorganic

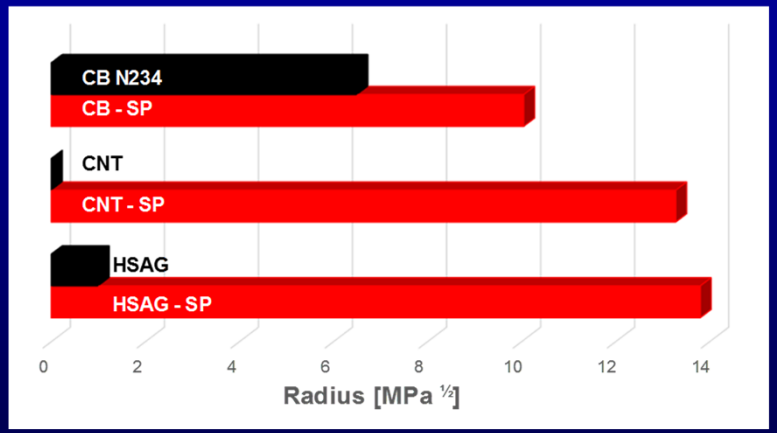
oxides and hydroxides

Functionalization of sp^2 carbon allotropes









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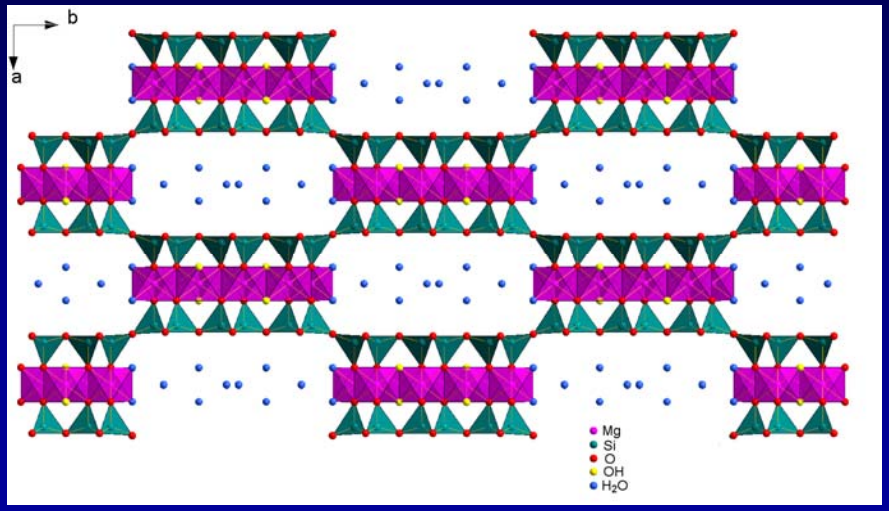
A bio-filler: Sepiolite

σήπιον (sepion)
+
λίθος (lithos)

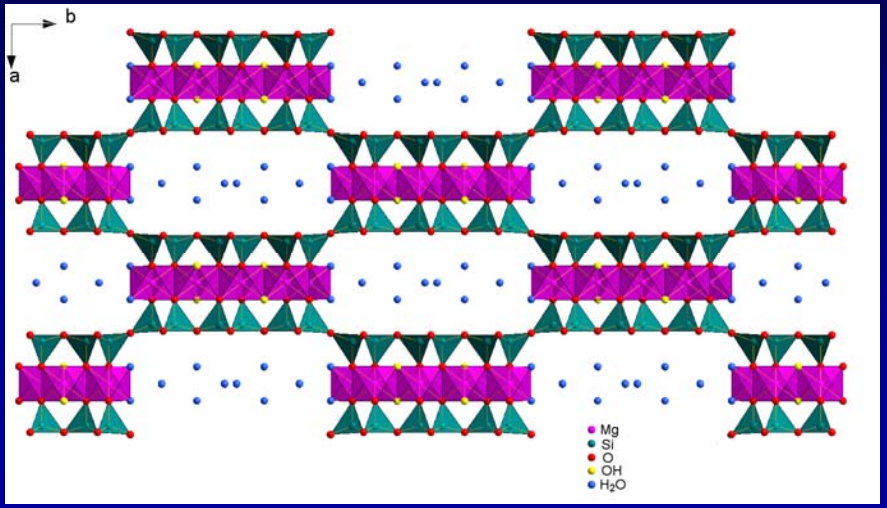


cuttlebone

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

Sepiolite

σήπιον (sepion)
+
λίθος (lithos)



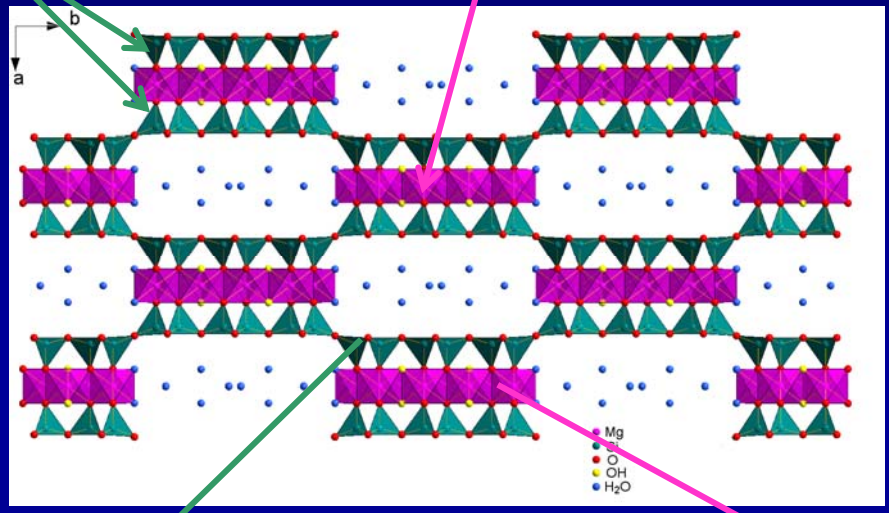
cuttlebone

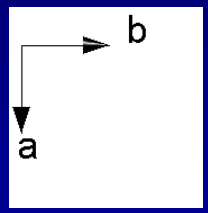
- naturally occurring, easily available, low cost
- high mechanical and thermal stability
- crystals are long, very thin, lath-like
- sepiolite is in laths or fibers,
  which form dense, spongy bundles
- fibers are typically 40–150 nm wide and 1–10 μm long

Sepiolite

two-dimensional layers of tetrahedral SiO_4 units

magnesium atoms, octahedrally coordinated



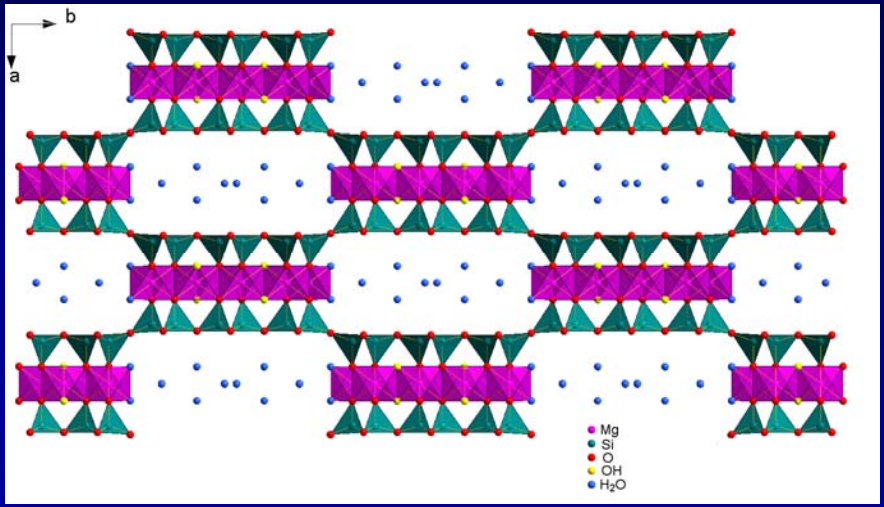


the tetrahedral sheet is continuous

the octahedral sheet is discontinuous

- the TOT units develop indefinitely along the c-axis
- channels are perpendicular to the plane of the slide

Sepiolite



Connections in the direction perpendicular to the layers: due, in part, to covalent bonds.

↓

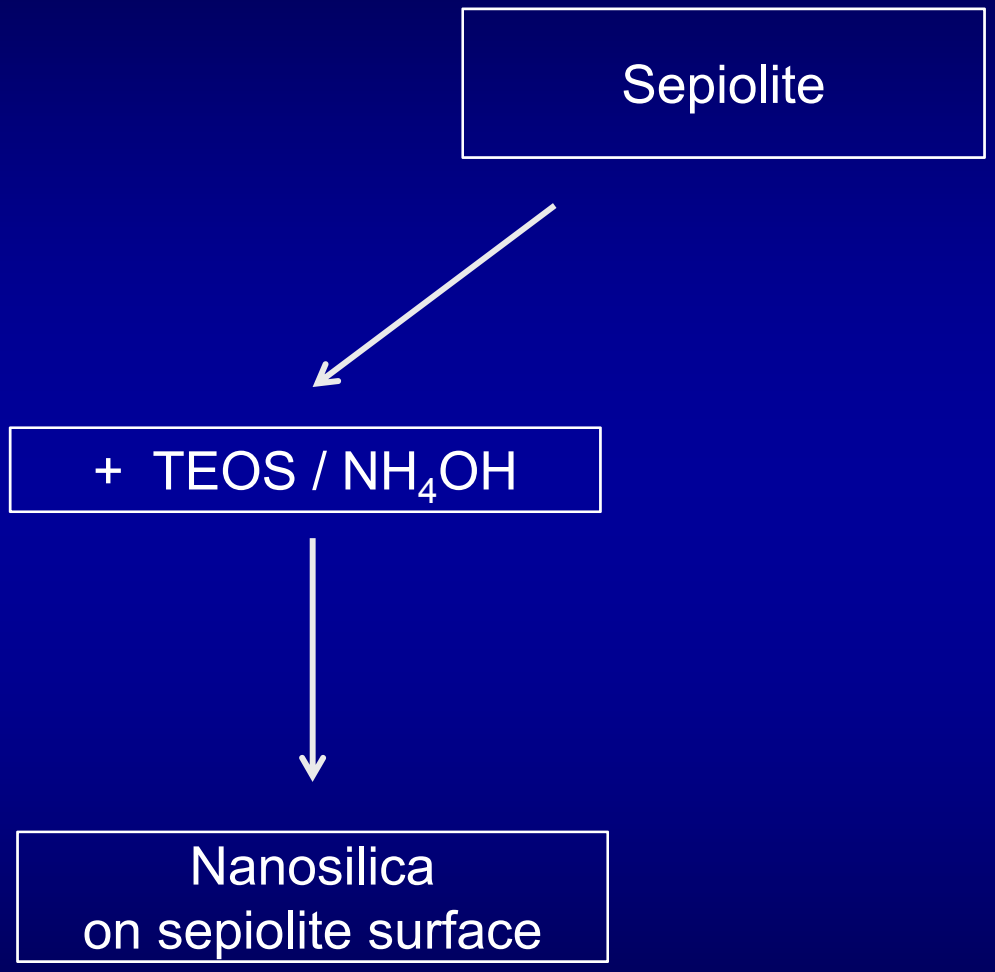
Sepiolite and the minerals of this group cannot swell or exfoliate!

Sepiolite

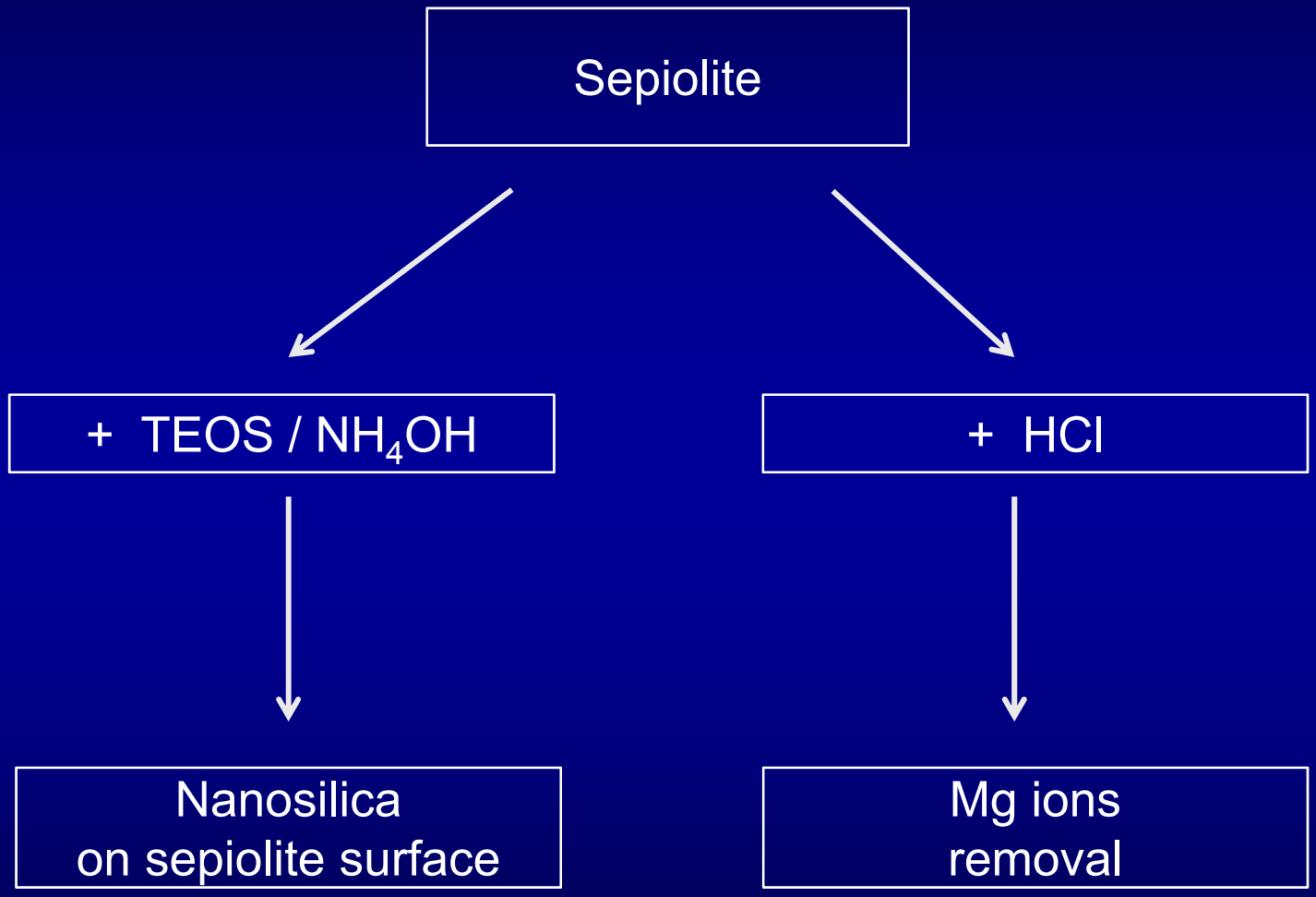
max length = 2 µm

How to foster the chemical reactivity of sepiolite?

How to foster the chemical reactivity of sepiolite?

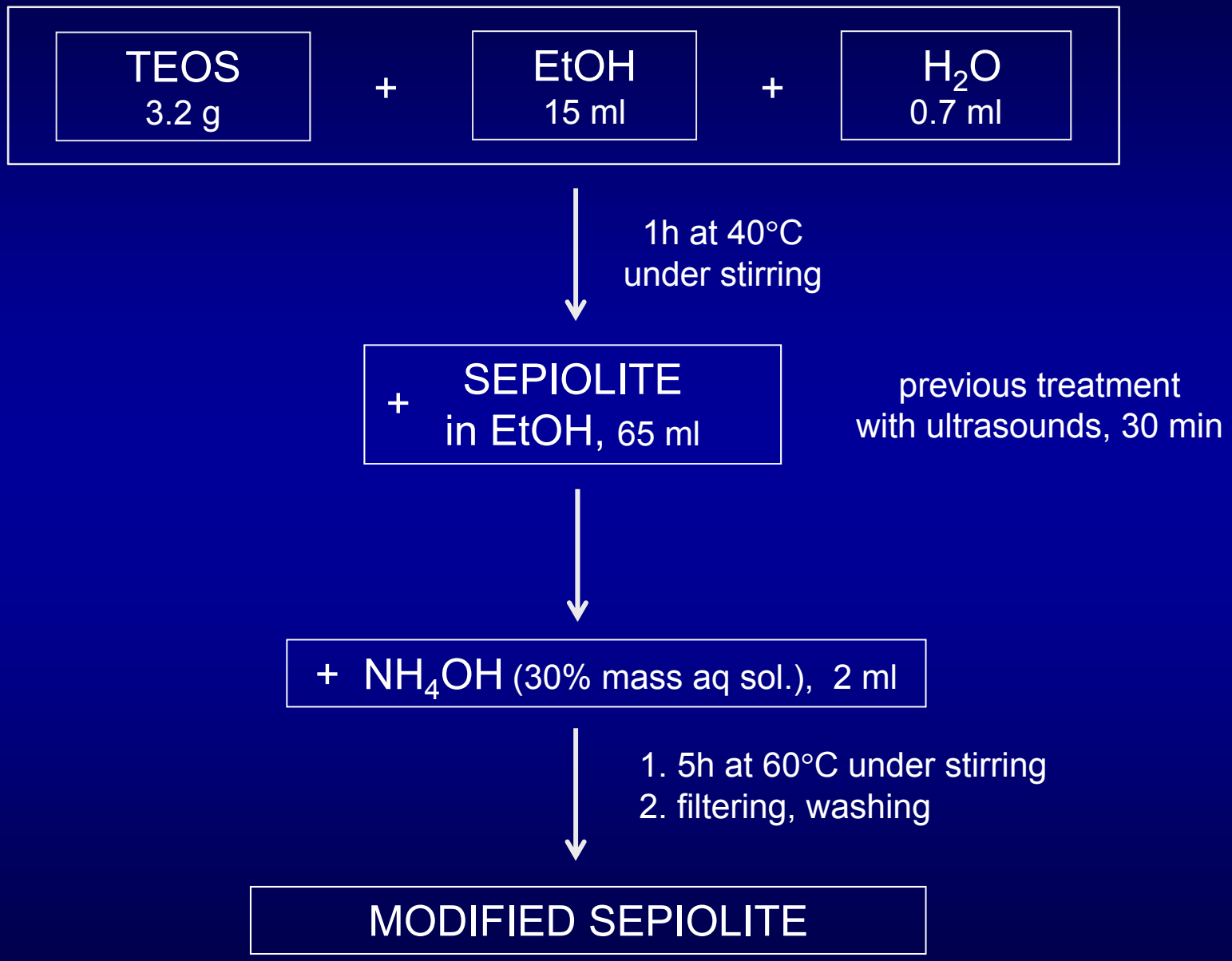


How to foster the chemical reactivity of sepiolite?



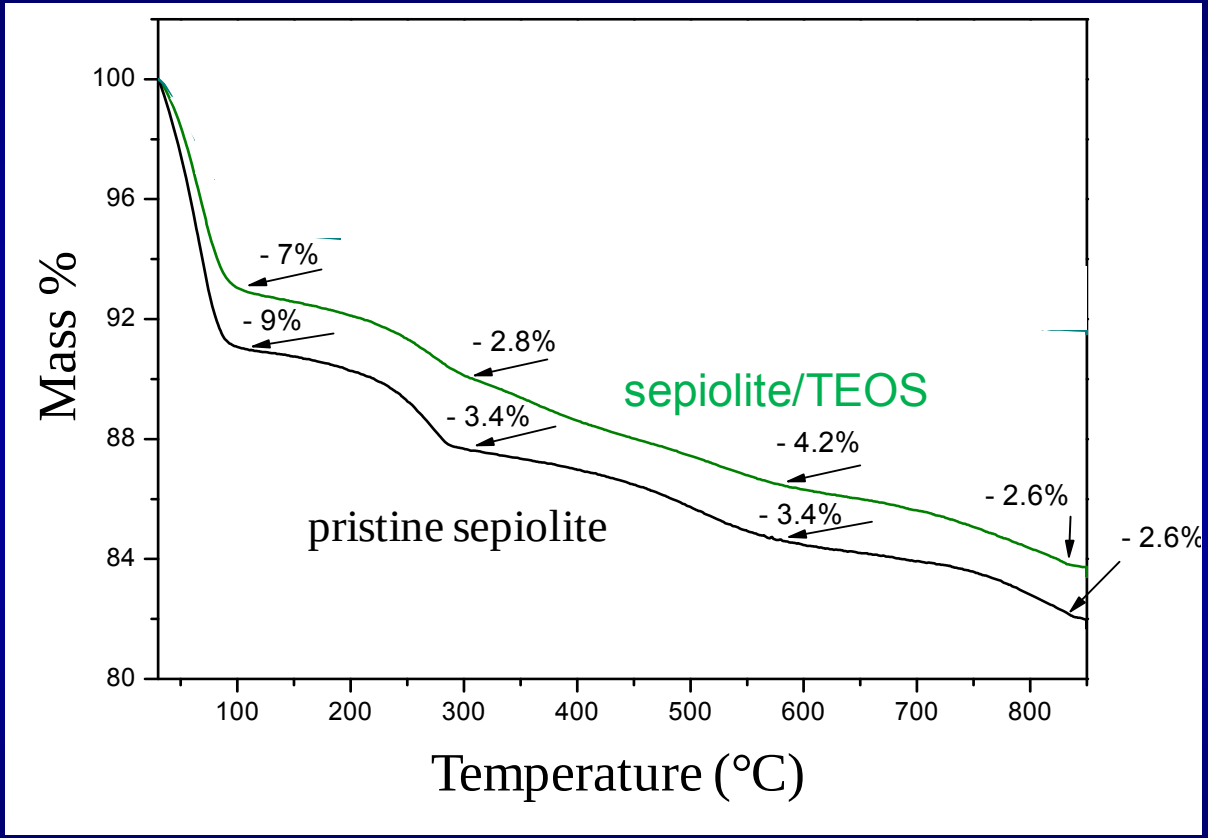
Treatment of sepiolite with TEOS

Treatment of sepiolite with TEOS



Sepiolite modified with TEOS

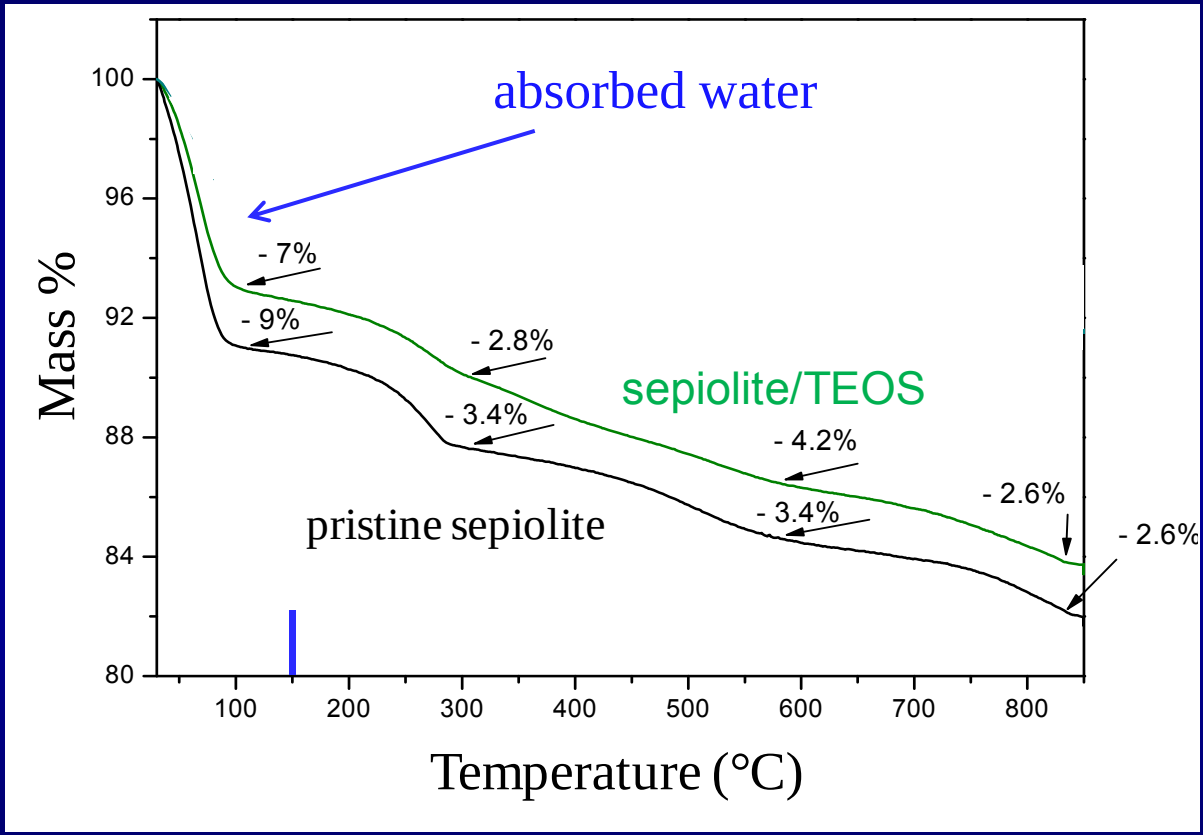
Thermogravimetric analysis



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

Sepiolite modified with TEOS

Thermogravimetric analysis



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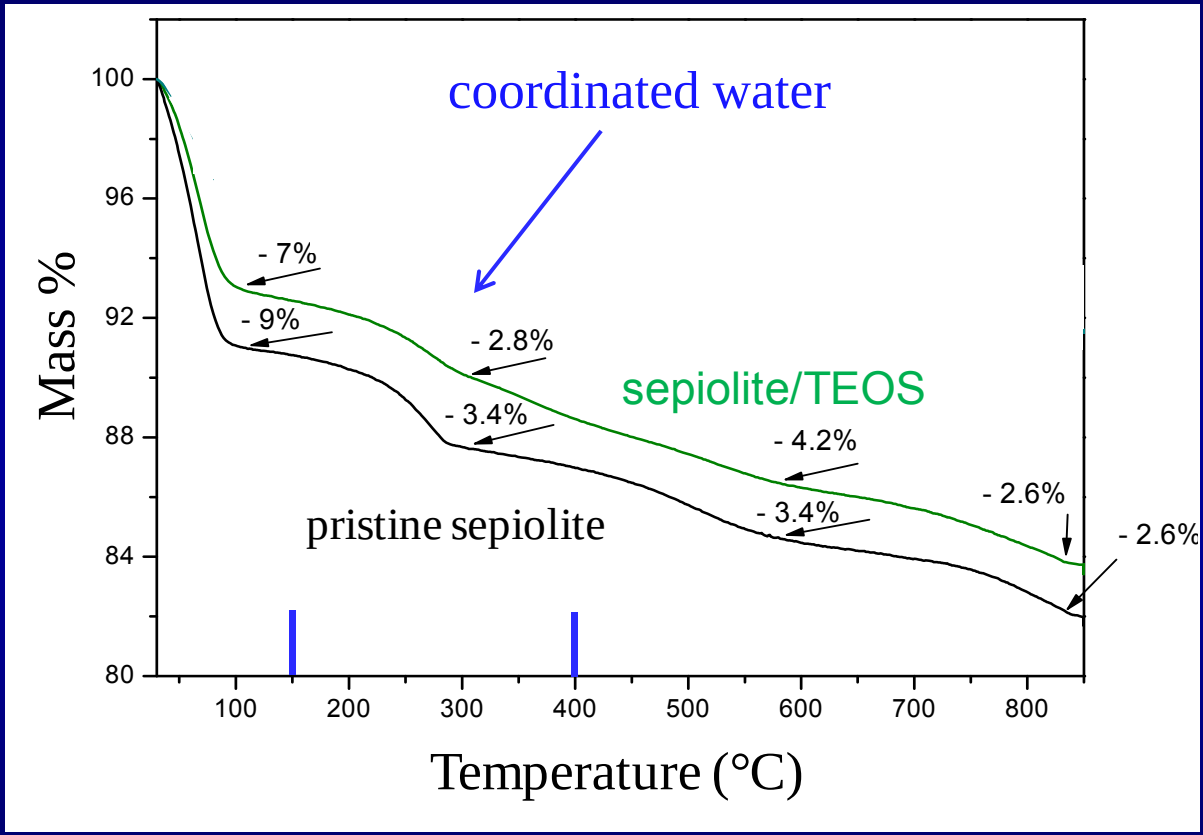
Sepiolite modified with TEOS

Thermogravimetric analysis



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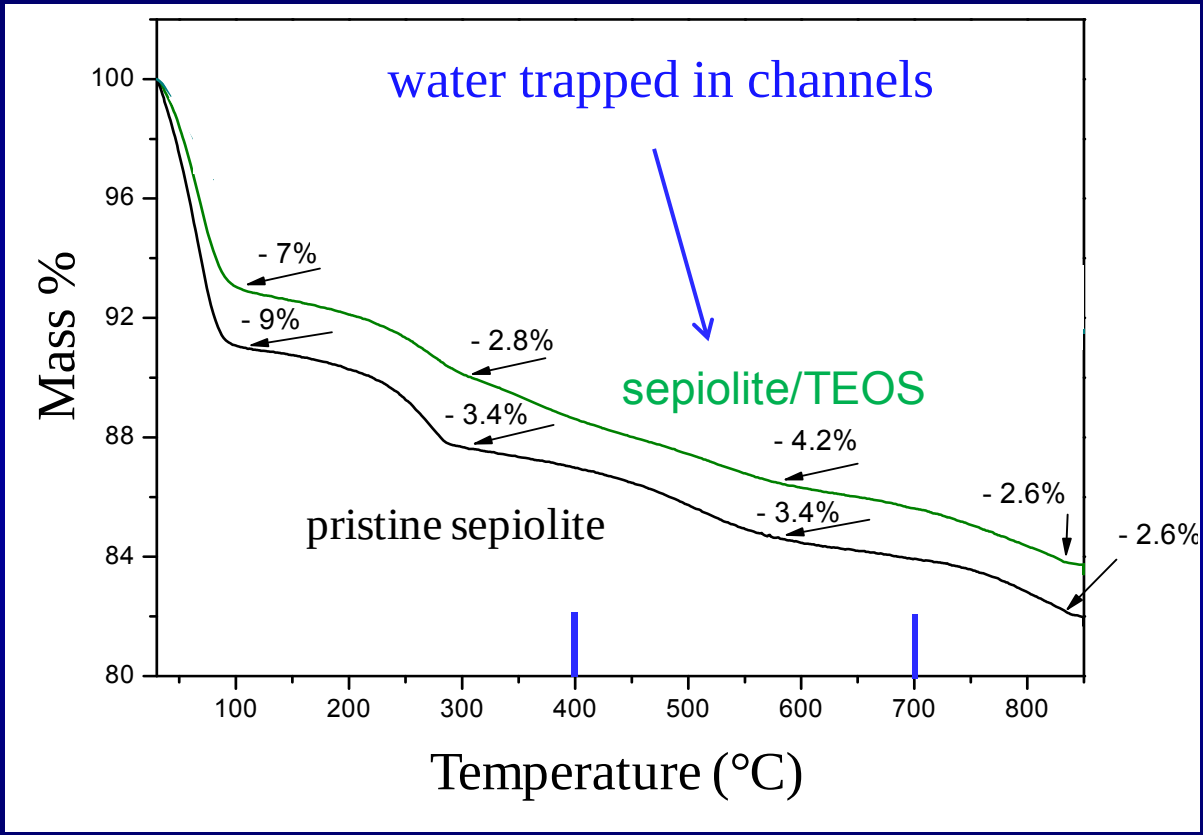
Sepiolite modified with TEOS

Thermogravimetric analysis



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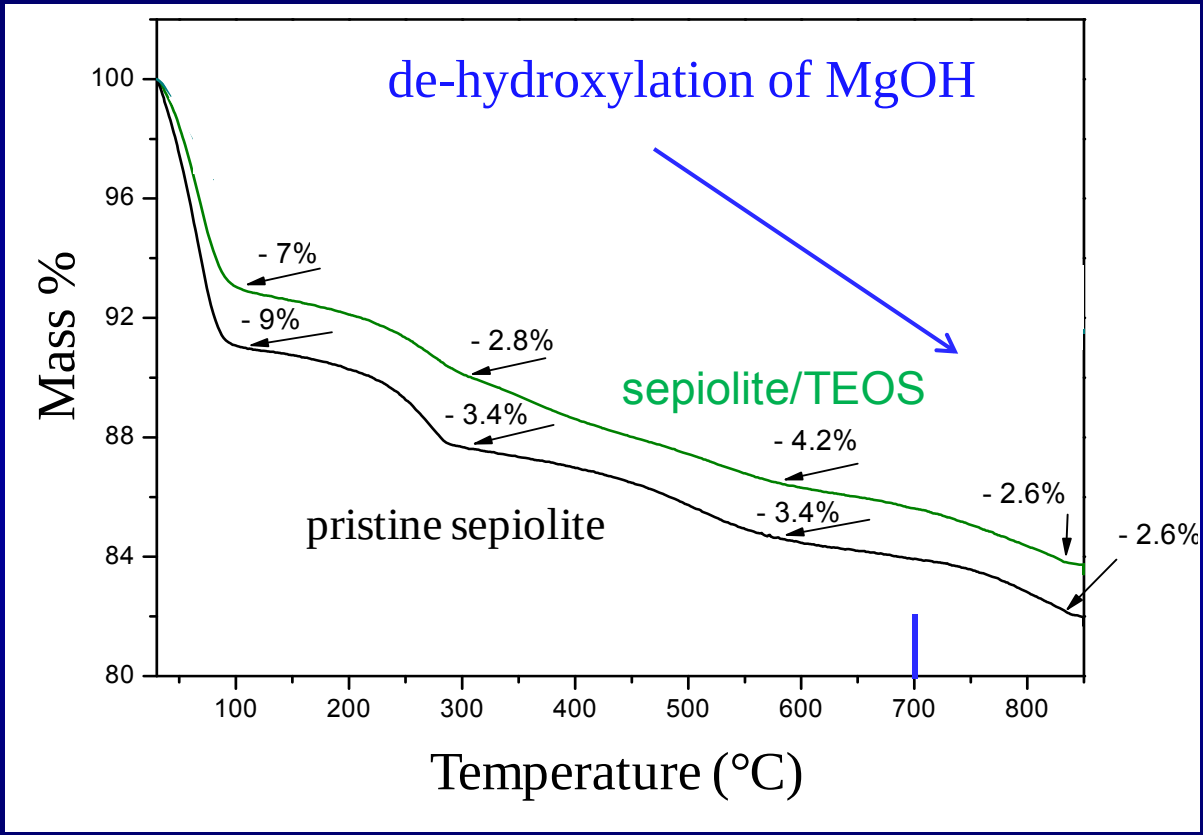
Sepiolite modified with TEOS

Thermogravimetric analysis



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

Sepiolite modified with TEOS

Thermogravimetric analysis

	Mass losses in different T (°C) ranges				Residue
	T < 150	150 < T < 400	400 < T < 700	700 < T < 850	T > 850°C
Pristine Sepiolite	9.0	3.4	3.4	2.6	82.0
Sepiolite / TEOS	7.0	2.8	4.2	2.6	83.8

Sepiolite / TEOS

Lower mass loss in 150 < T < 400

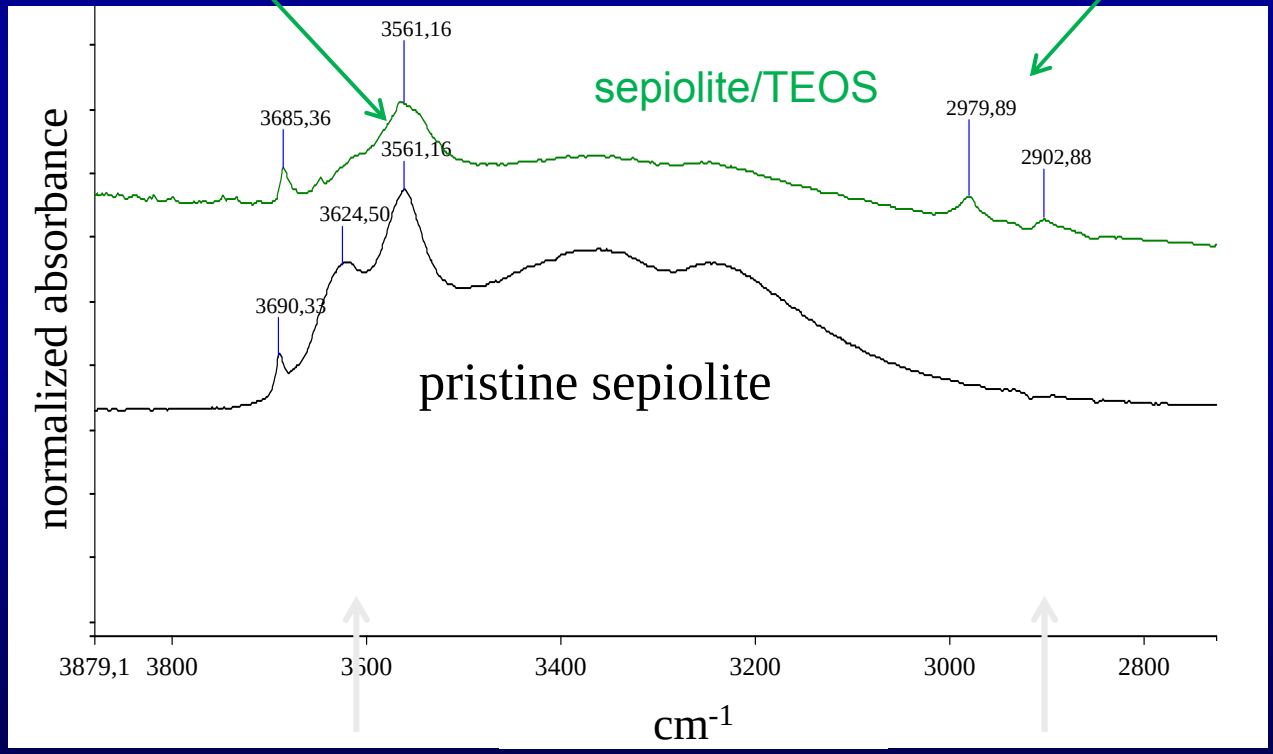
Larger mass loss in the range 400 < T < 700

Sepiolite modified with TEOS

ATR-IR analysis

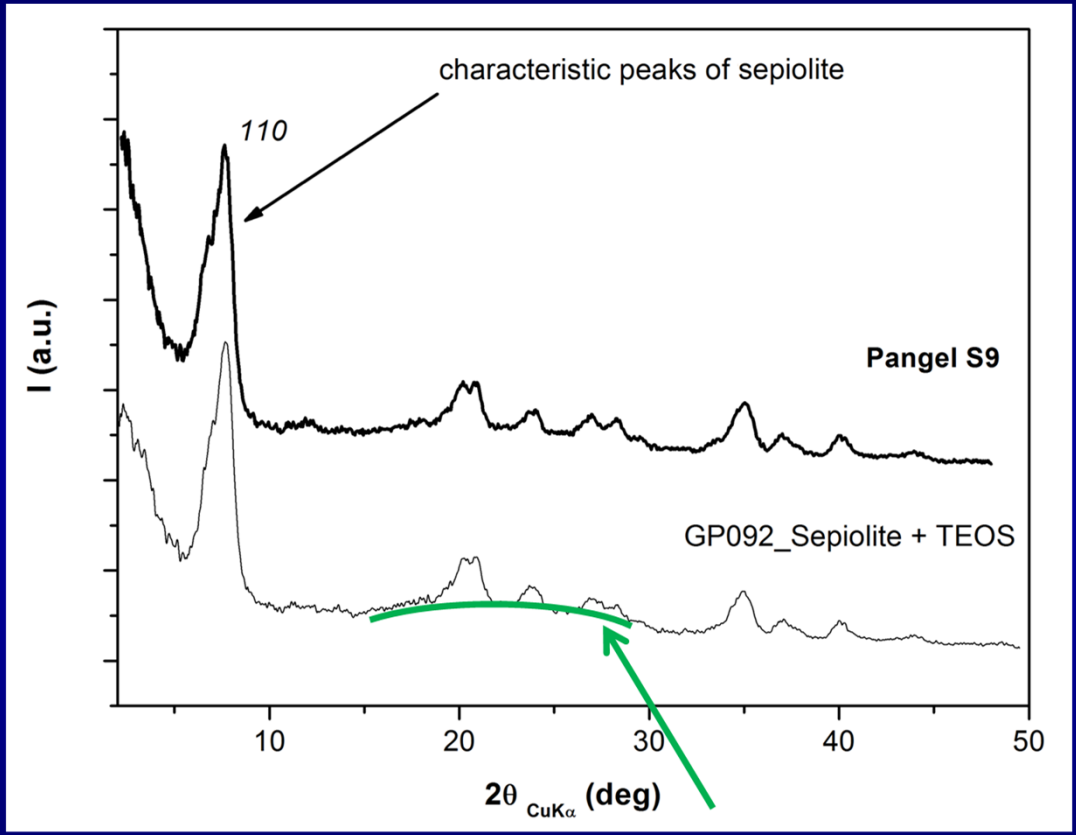
reduction of the intensity of the peak
due to H_2O coordinated
to the octahedral layers of sepiolite

stretching of $-CH_2$
coming from TEOS



Sepiolite modified with TEOS

WAXD analysis



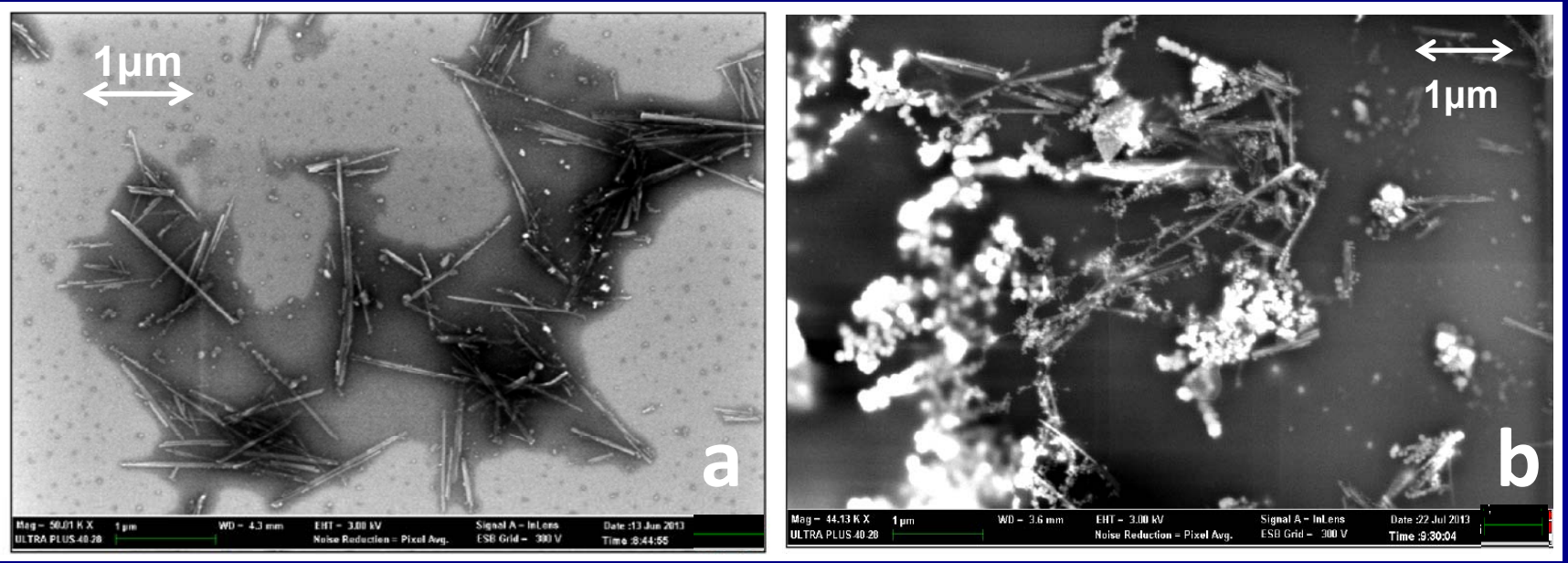
halo attributed to amorphous silica

Sepiolite modified with TEOS (Sepiolite/TEOS)

FESEM analysis

pristine sepiolite

sepiolite / TEOS



typical fibrillar shape of pristine sepiolite

silica nanoparticles on sepiolite fibrils

NR based compounds with silica and sepiolite/TEOS

Formulations
(phr)

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

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NR based compounds with silica and sepiolite/TEOS

Strain sweep tests

	Filler(s) in the composite	
Property	Silica	Silica + sepiolite/TEOS
G' (0.4%)	1.51	1.28
ΔG' (0.4%-35%)/G' (0.4%)	0.30	0.26
Tan Delta max	0.071	0.067

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NR based compounds with silica and sepiolite/TEOS

Tensile tests

Property	Filler(s) in the composite	
	Silica	Silica + sepiolite/TEOS
σ_{50} (MPa)	1.45	1.72
σ_{100} (MPa)	2.91	4.12
σ_{300} (MPa)	16.76	18.08
σ_B (MPa)	21.57	22.04
ε_B (%)	361.05	365.07

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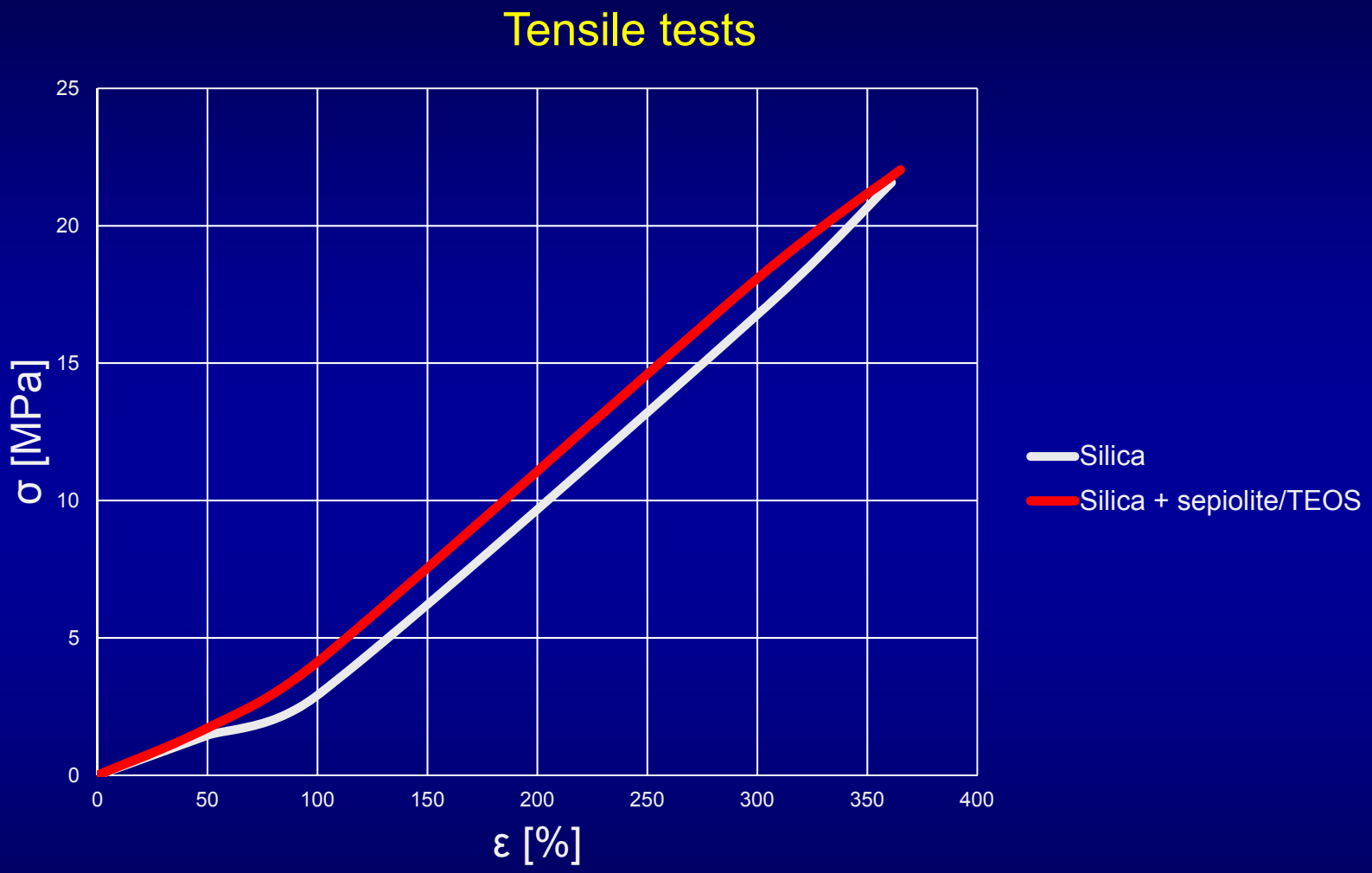
NR based compounds with silica and sepiolite/TEOS



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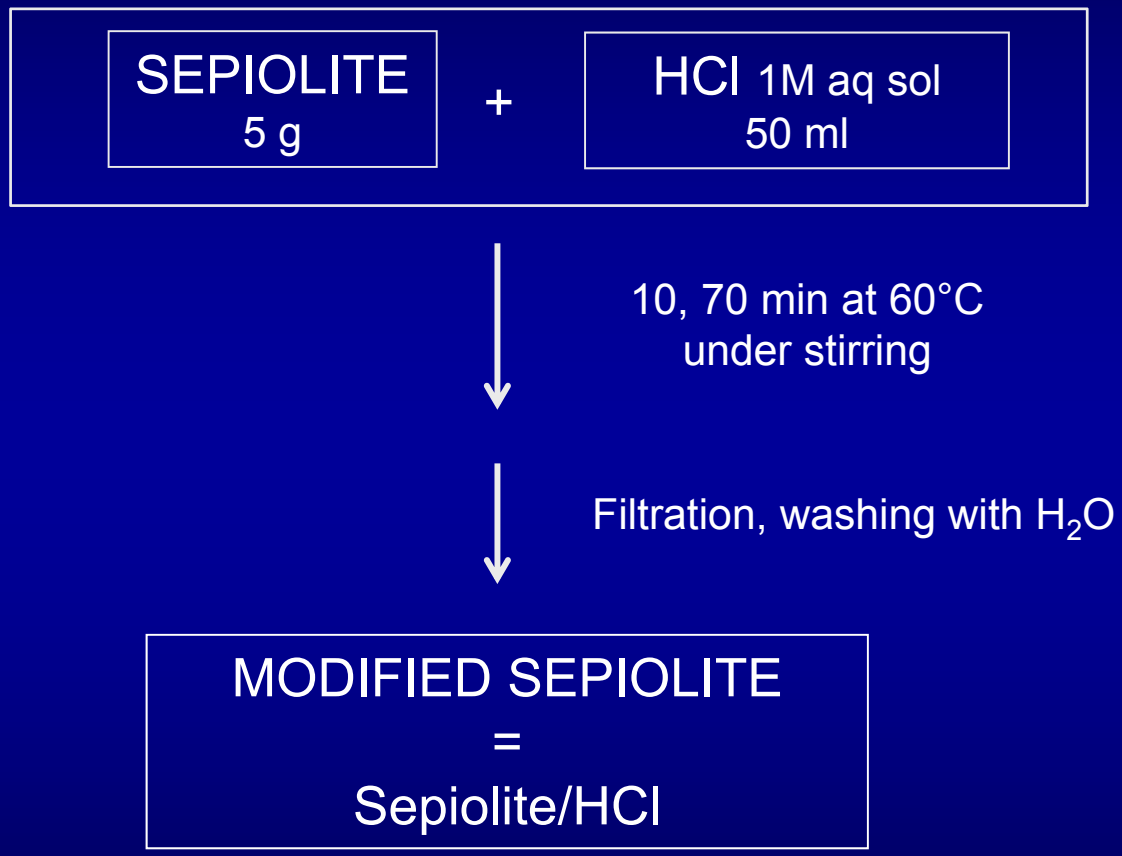
Treatment of sepiolite with Acid

Treatment of sepiolite with acid



Sepiolite treated with HCl

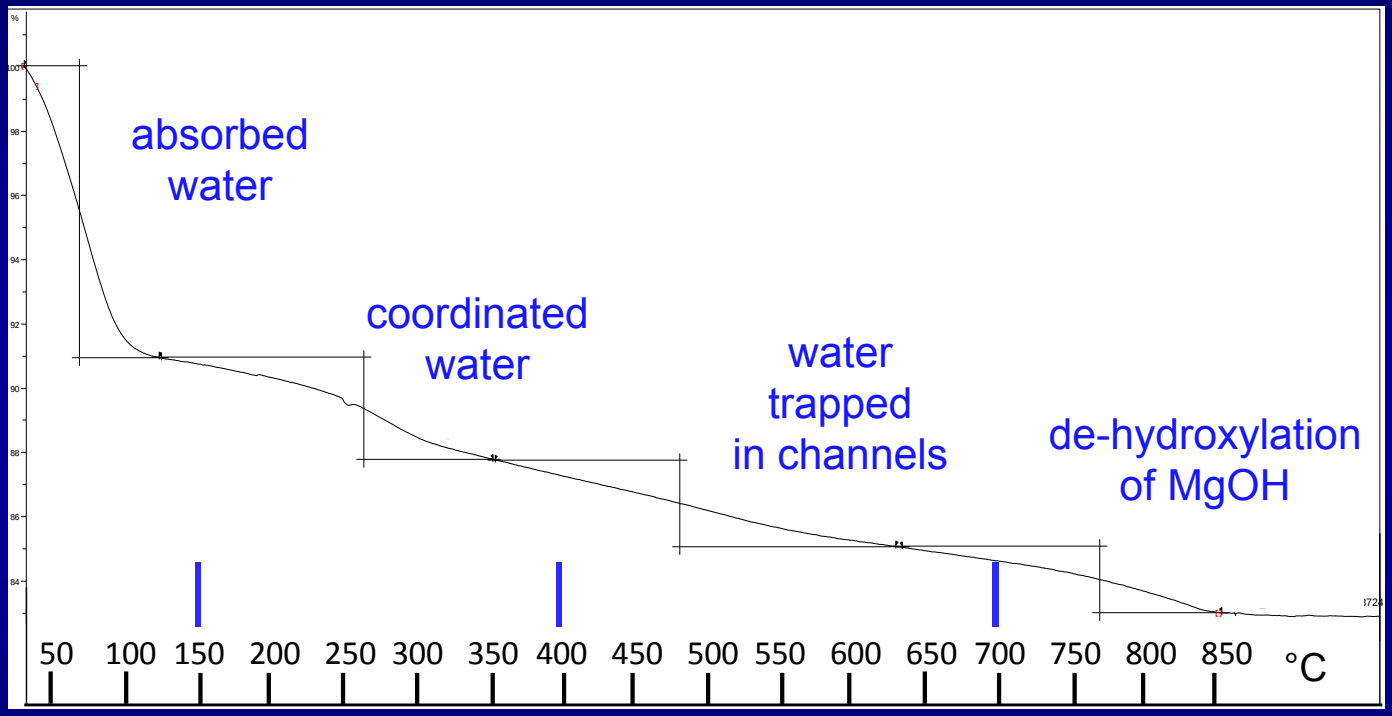
Extracted Magnesium

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

[a] determined through titration

Sepiolite treated with HCl - Residual Mg: 66%

Thermogravimetric analysis



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Sepiolite treated with HCl

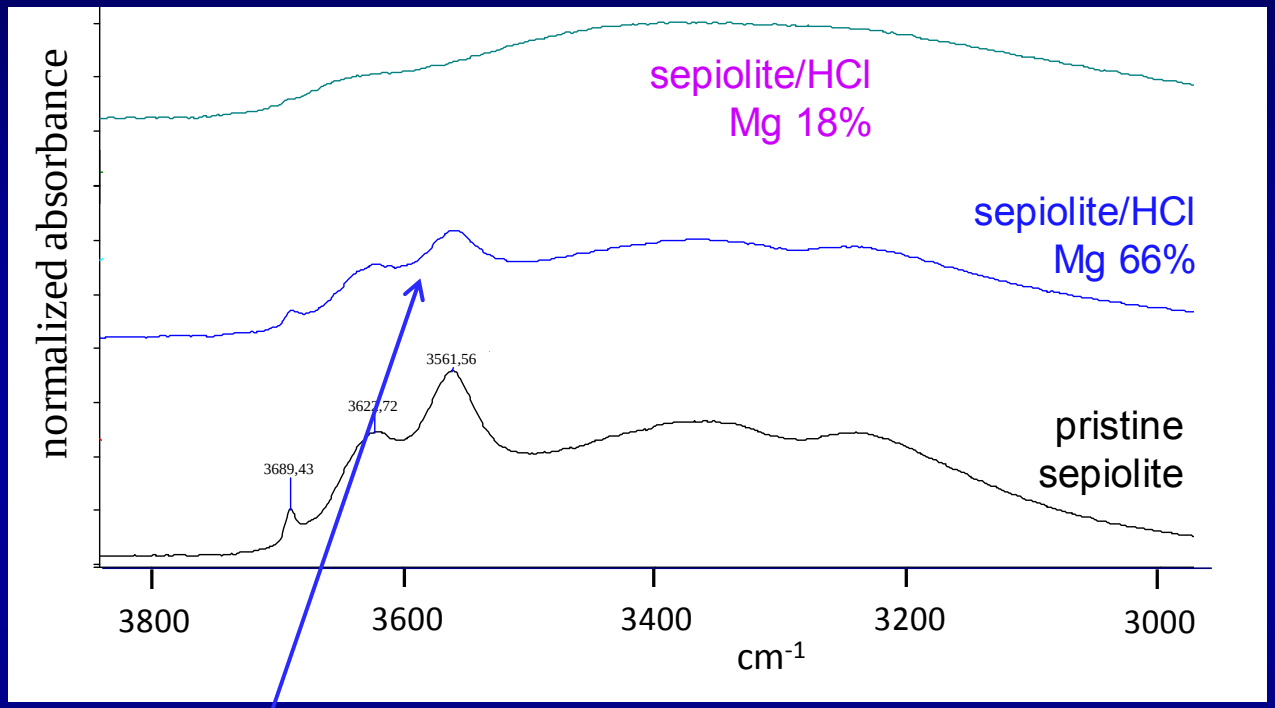
Thermogravimetric analysis

	Mass losses in different T (°C) ranges				Residue
	T < 150	150 < T < 400	400 < T < 700	700 < T < 850	T > 850°C
Pristine Sepiolite	9.0	3.3	3.3	2.3	82.1
Sepiolite / HCl Mg 66%[a]	9.0	3.2	2.7	2.0	83.1
Sepiolite / HCl Mg 18%[a]	7.2	=	=	4.5	88.3

[a]residual Mg

Sepiolite treated with HCl

ATR-IR analysis

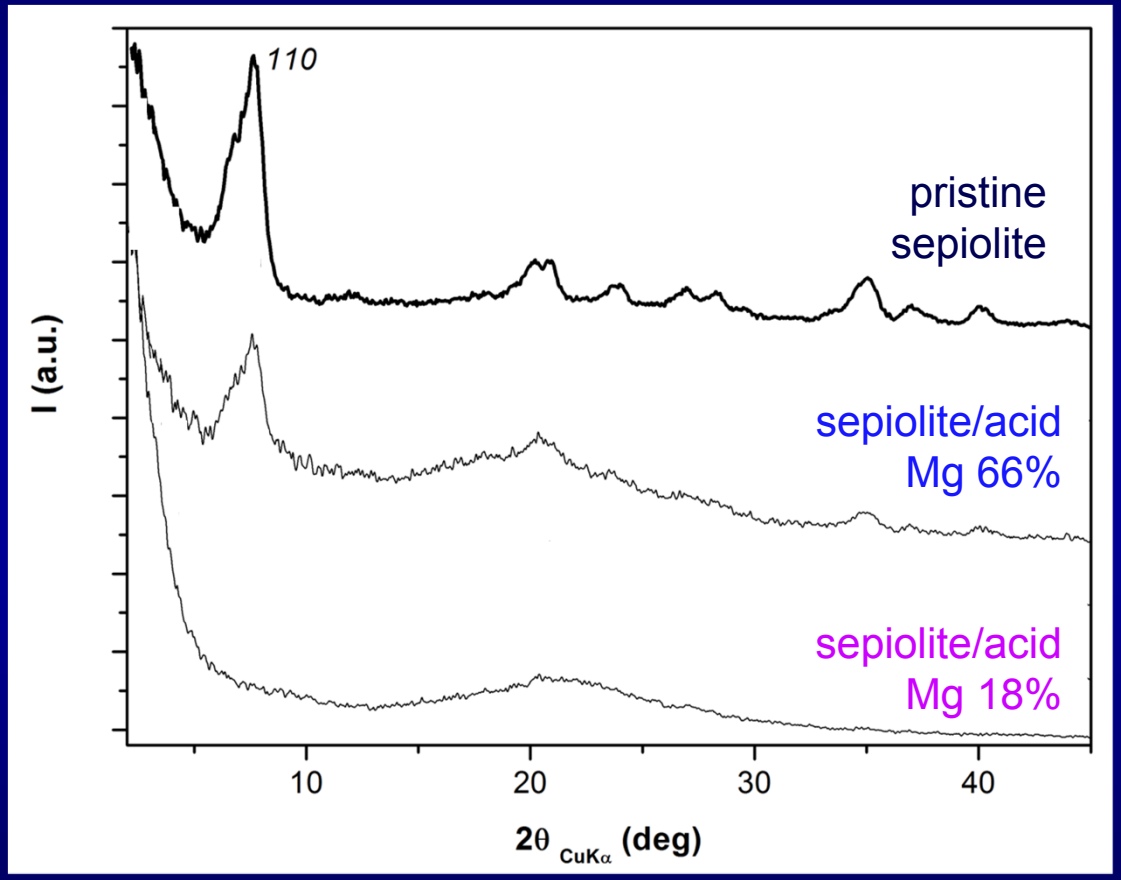


Reduction of the intensity of bands due to

- hydroxyl groups bound to Mg (3688 cm^{-1})
- water molecules bound to the octahedral Mg layers (3566 cm^{-1})

Sepiolite treated with HCl

WAXD analysis

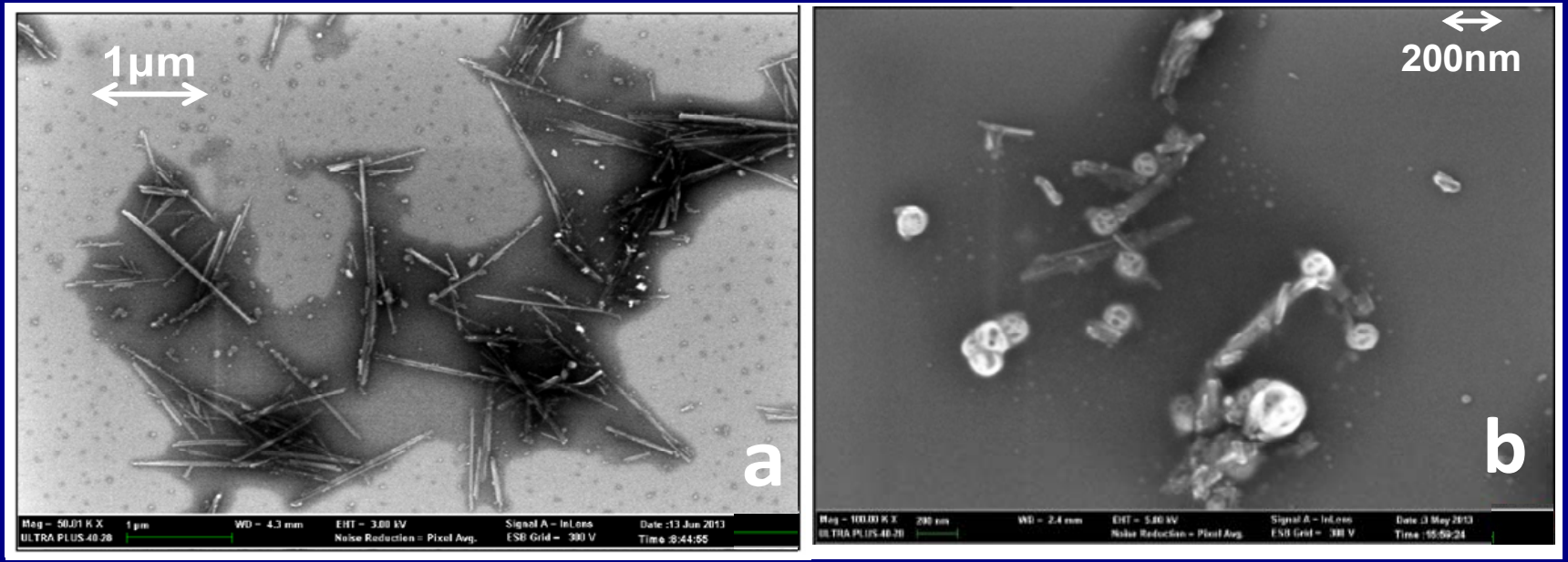


Sepiolite treated with HCl

FESEM analysis

pristine sepiolite

sepiolite / HCl - Mg 18%

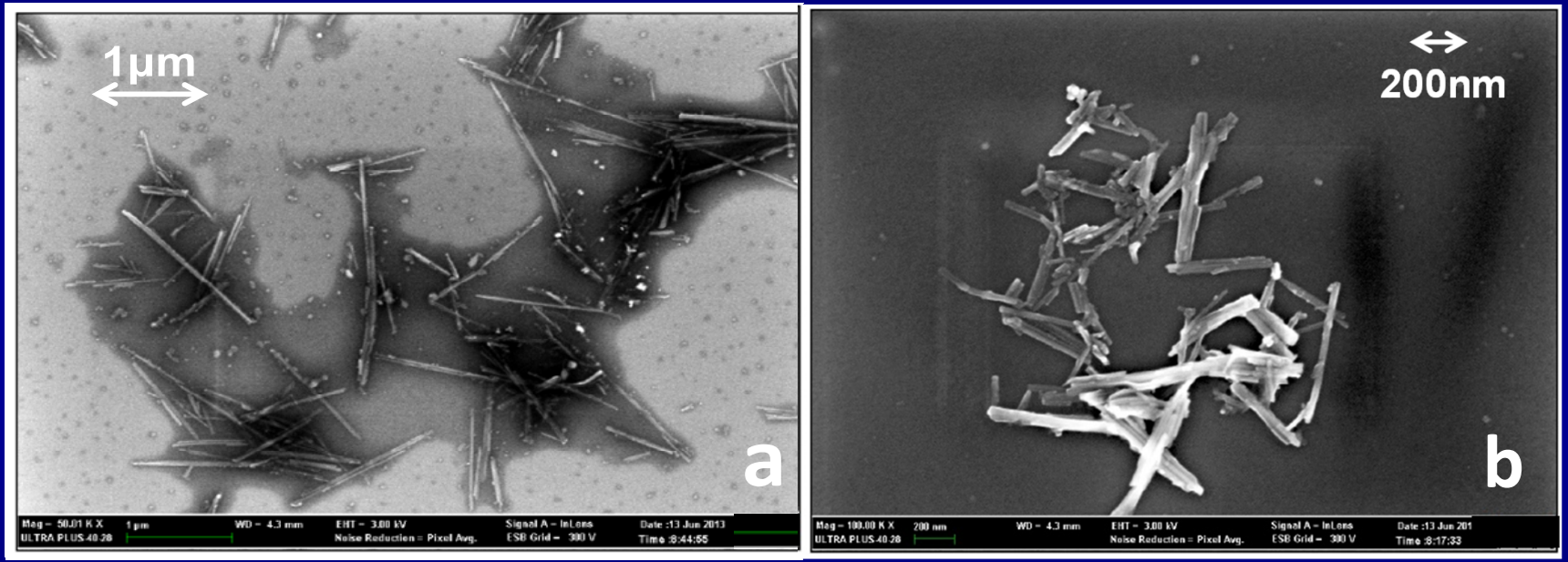


Sepiolite treated with HCl (Sepiolite/HCl)

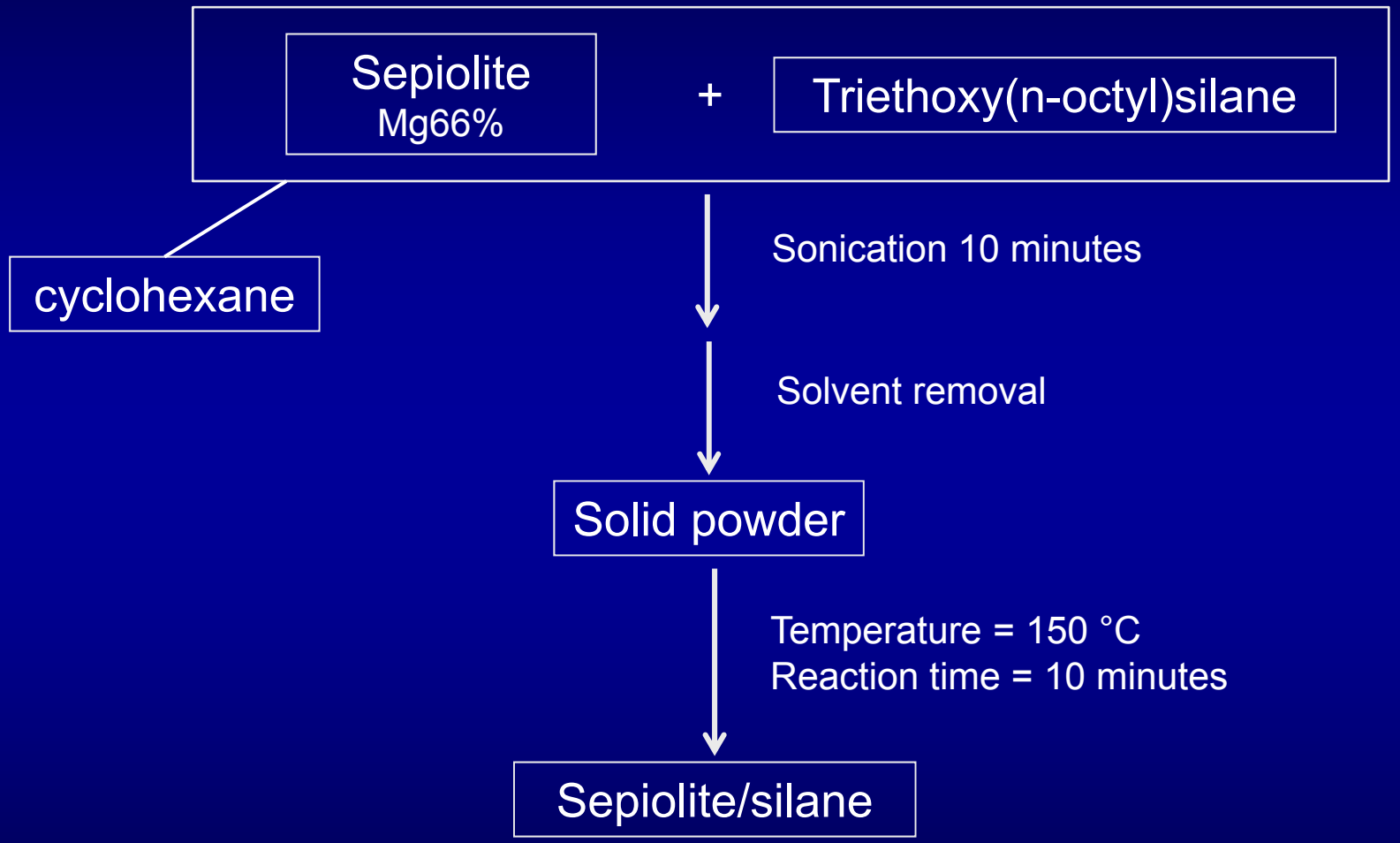
FESEM analysis

pristine sepiolite

sepiolite / HCl - Mg 66%



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

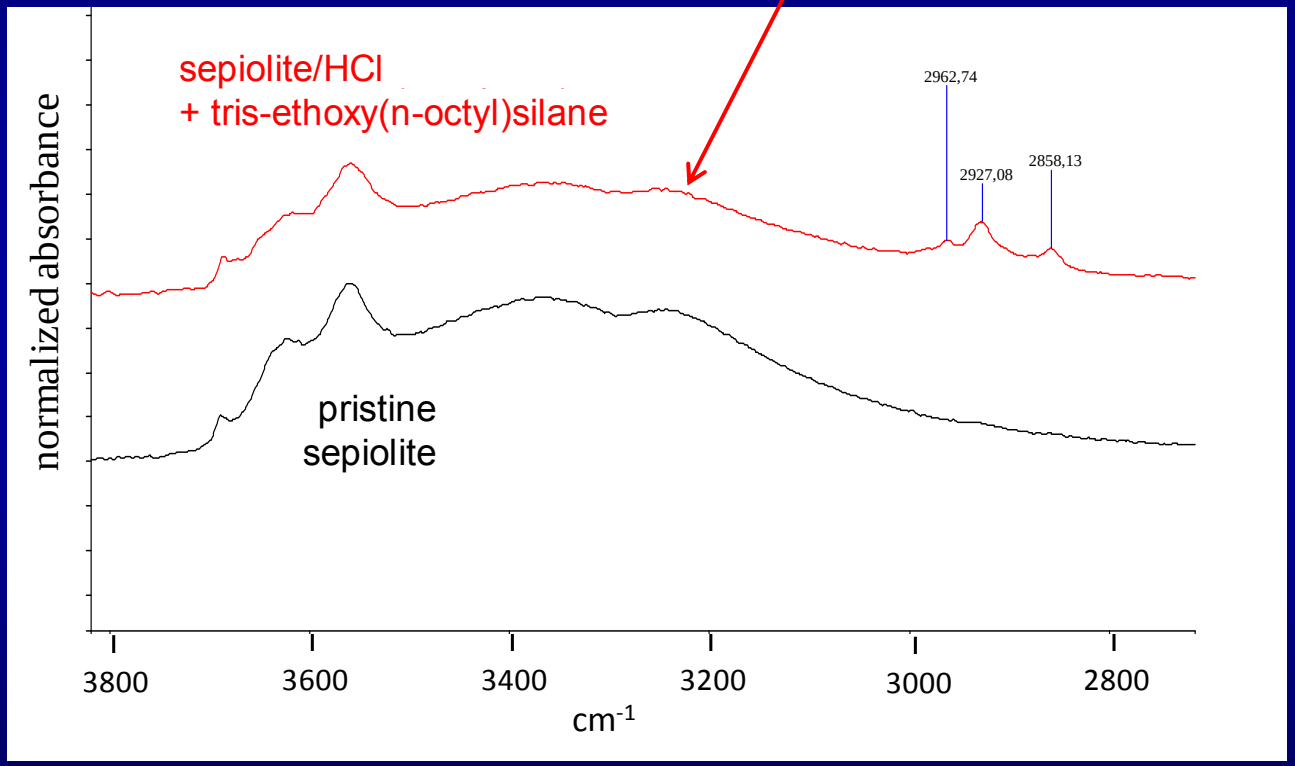


Sepiolite/HCl - Silanization with triethoxy(n-octyl)silane

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

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

typical stretching of CH and CH_2 (2964 cm^{-1} ; 2856 cm^{-1})



NR based compounds with silica and sepiolite/HCl (Mg66%)

Formulations (phr)

Ingredient	Filler in the composite	
	Silica	Silica + Sepiolite (Sample 1)
NR	100	100
Silica	45	35
Sepiolite/HCl Mg 66%	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

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

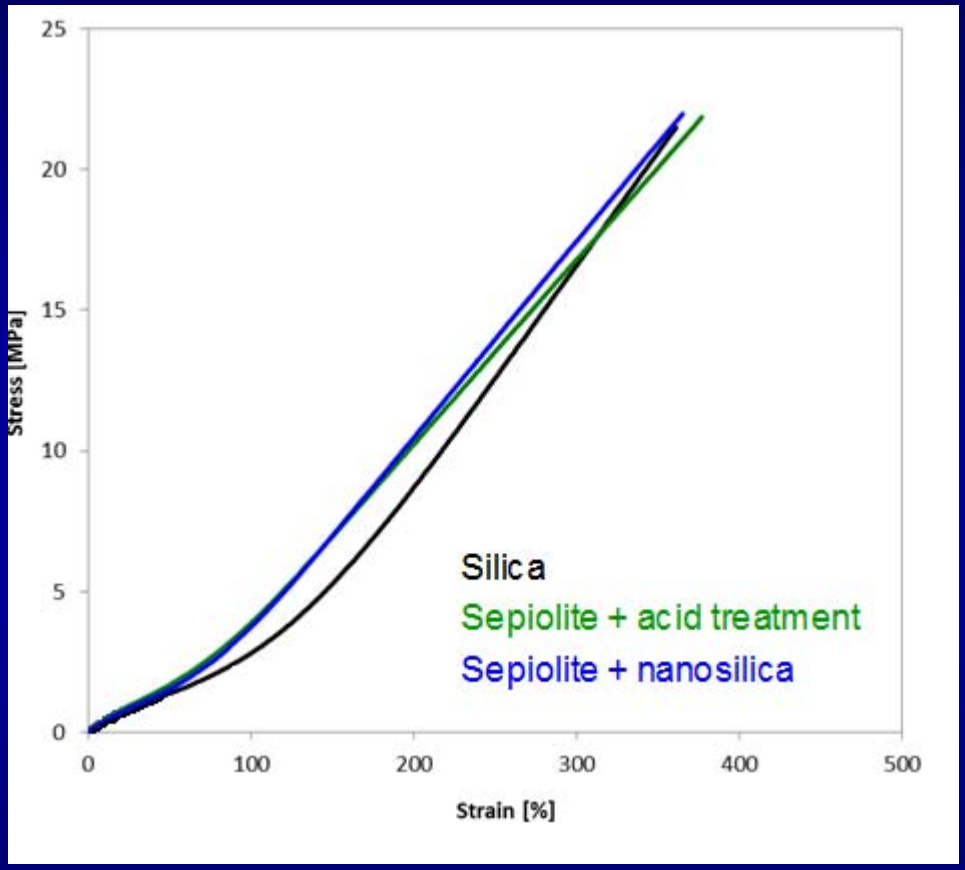
NR based compounds with silica and sepiolite/HCl (Mg66%)

Dynamic mechanical properties

Property	Filler in the composite	
	Silica	Silica + Sepiolite/HCl (Mg 66%)
E' (23°C) 100 Hz	10.57	13.95
E' (70°C) 100 Hz	7.70	9.72
Tan Delta (23°C) 100 Hz	0.296	0.281
Tan Delta (23°C) 100 Hz	0.152	0.141

☞ Tan Delta: the lower, the better

NR based compounds with silica and modified sepiolite



Phr: NR 100, Silica 45, Silane TESPT 3.6, Stearic acid 2.0, 6PPD 2, ZnO 3.6, S 2.8, TBBS 1.8

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

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IR/BR based compounds with silica and sepiolite/HCl (Mg 80%)

Formulations
(phr)

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

Other ingredients: ZnO 4.0, Stearic acid 1, 6-PPD 1.5, TMQ 1, Sulphur 2.3, TBBS 80 4

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IR/BR based compounds with silica and sepiolite/HCl (Mg 80%)

Dynamic mechanical properties

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

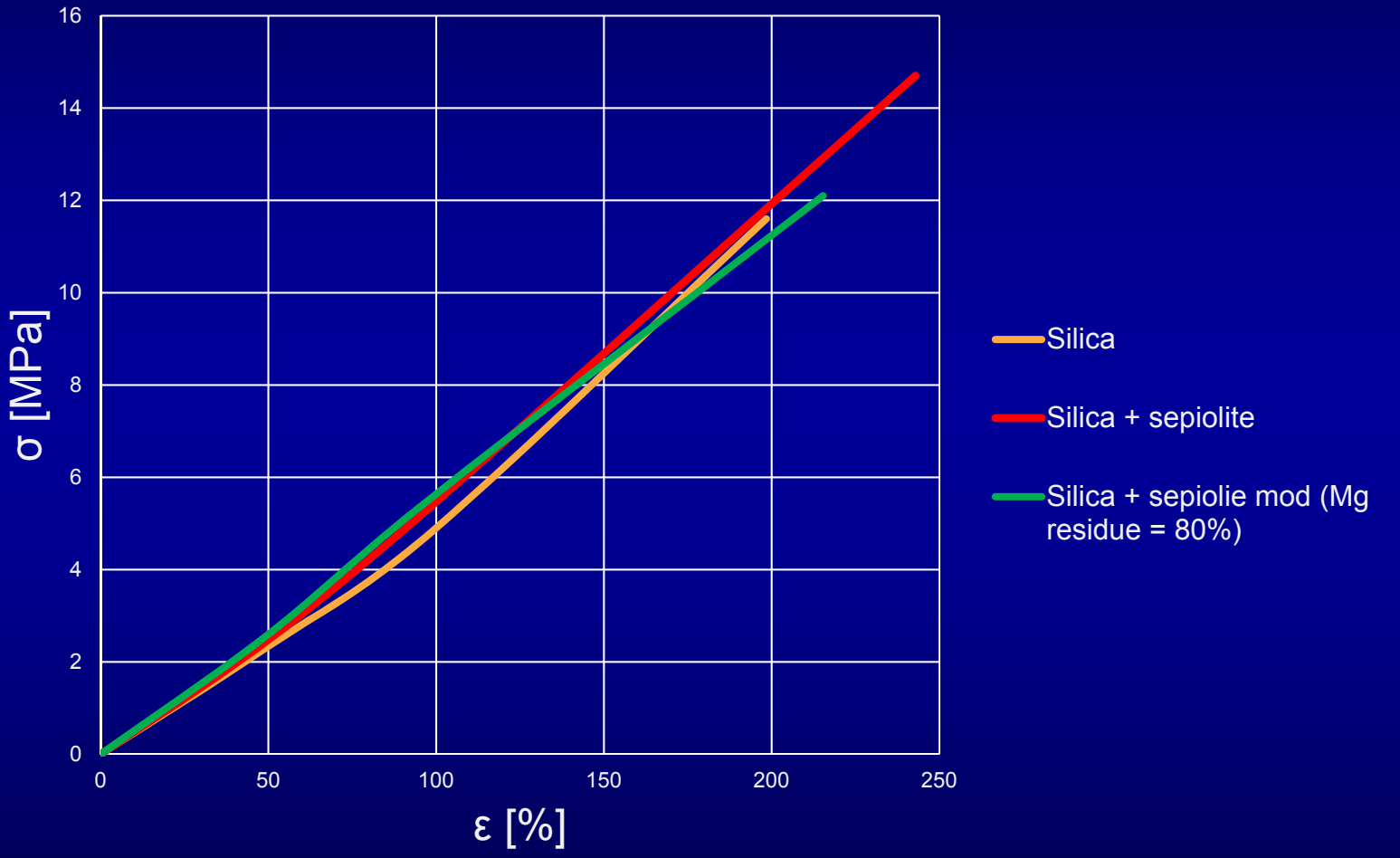
IR/BR based compounds with silica and sepiolite/HCl (Mg 80%)

Tensile tests

Property	Filler in the composite		
	Silica	Silica + Sepiolite	Silica + Sepiolite/HCl (Mg 80%)
σ_{50} (MPa)	100	106	111
σ_{100} (MPa)	100	112	115
σ_B (MPa)	100	127	104
ε_B (%)	100	122	109

IR/BR based compounds with silica and sepiolite/HCl (Mg 80%)

Tensile tests



From basic research to commercial development

From basic research to commercial development

Aramid Pulp and Nanobase (Nano.Co)

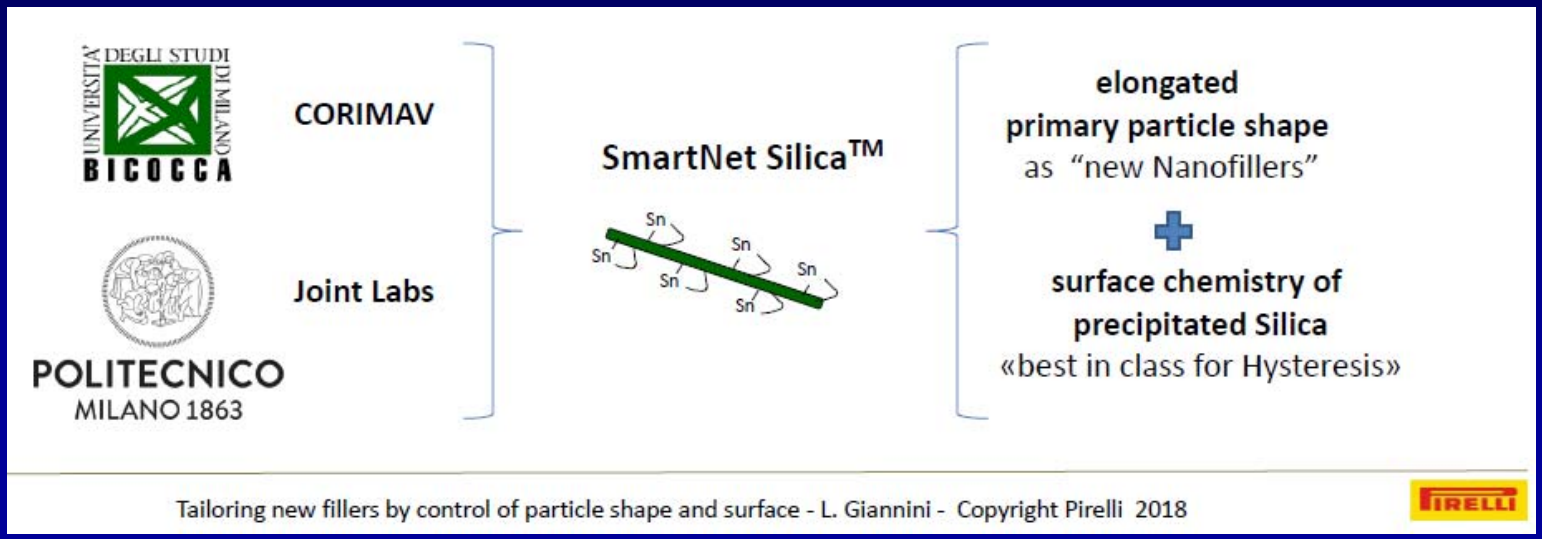
Anisotropic behavior:
high strength
in longitudinal direction

Isotropic behavior: equal performance in longitudinal and lateral directions

- **Higher Stiffness**
- **Better Trade-off Handling/Comfort**
- **Thermoplastic stability**
- **No Decay**

Maurizio Boiocchi
Mission Zero
PZero Technical Presentation
Dubai, February 2007

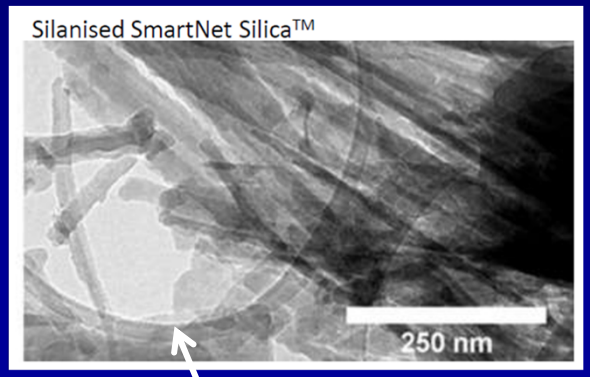
From basic research to commercial development



Silicate route to SmartNetSilica™

L. Giannini. Tailoring new fillers by control of particle shape and surface. Presentation at TyreTech 2018

From basic research to commercial development



Silanised route to SmartNetSilica™

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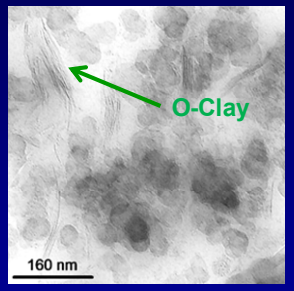
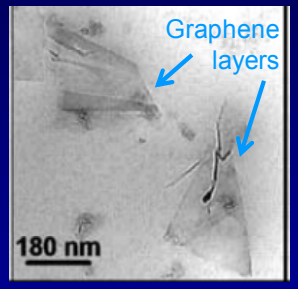
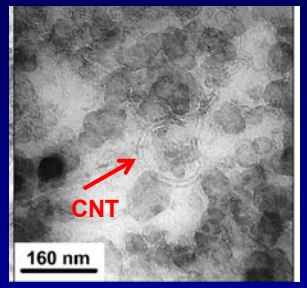
Conclusions







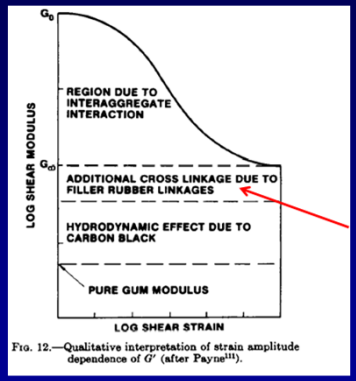


FIG. 12.—Qualitative interpretation of strain amplitude dependence of G' (after Payne[11]).

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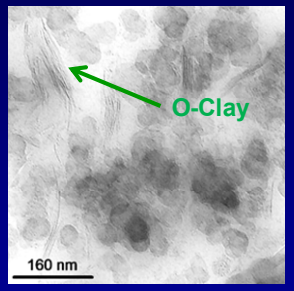
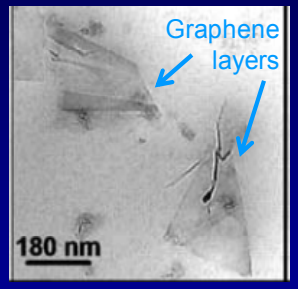
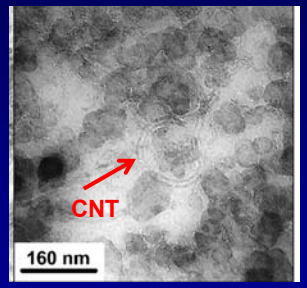
Conclusions







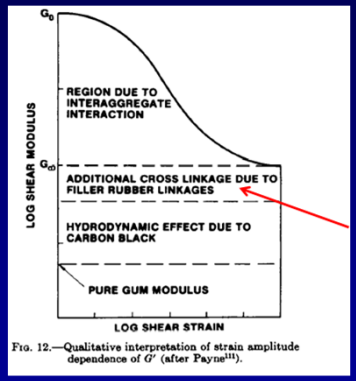
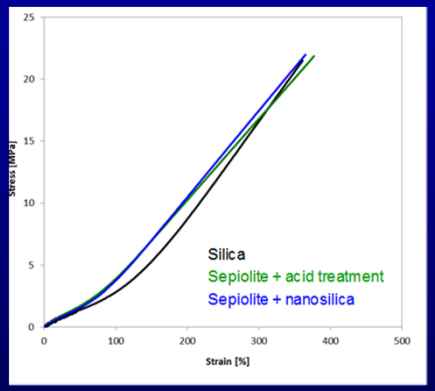


FIG. 12.—Qualitative interpretation of strain amplitude dependence of G' (after Payne[11]).

Enhancement of chemical reactivity
of high aspect ratio nanometric fillers



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ISCaMap

Innovation for sustainability

LiDuP
Lightweight Construction and Durability Performance

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Acknowledgments

Luciano Tadiello Pirelli Tyre

Rubber Division
American Chemical Society

*Enhancing science, technology and business across the **evolving elastomeric community**.*

Thanks
for the attention!