HIGH ASPECT RATIO NANOFILLERS FOR RUBBER COMPOSITES

Maurizio Galimberti[1]

Vincenzina Barbera,[1] Andrea Bernardi,[1] Daniele Locatelli,[1] Gea Prioglio,[1]
Luca Giannini[2]

[1]Politecnico di Milano
Department of Chemistry Materials Chemical Engineering
ISCaMaP Group

[2]Pirelli Tyre

IRC 2019

3-5 September 2019, Kia Oval, London (UK)

Co-authors and Acknowledgments

Politecnico di Milano

ISCaMaP

***I**nnovative **S**ustainable **C**hemistry and **M**aterials and **P**rotein Group*

Vincenzina Barbera

Andrea Bernardi

Daniele Locatelli

Gea Prioglio

Pirelli Tyre

Luca Giannini

Luca Michielan

Objective of the research

To take advantage

of nanometric high aspect ratio fillers

for the mechanical reinforcement of rubbers.

Objective of the research

To take advantage

of nanometric high aspect ratio fillers

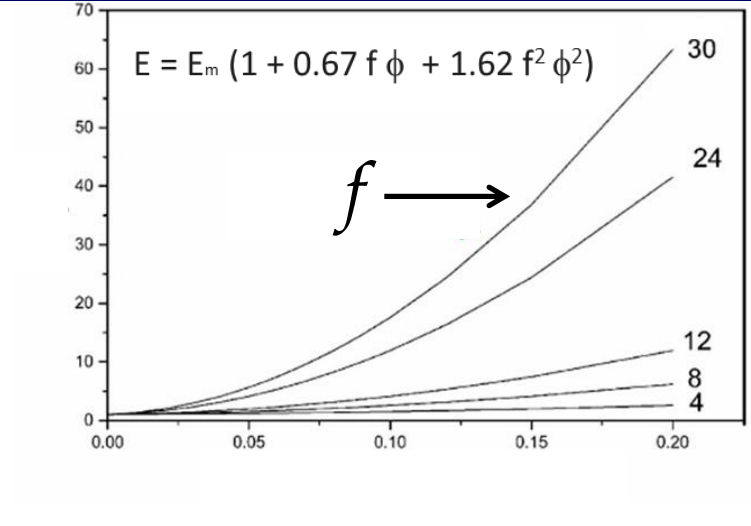
for the mechanical reinforcement of rubbers.

How?

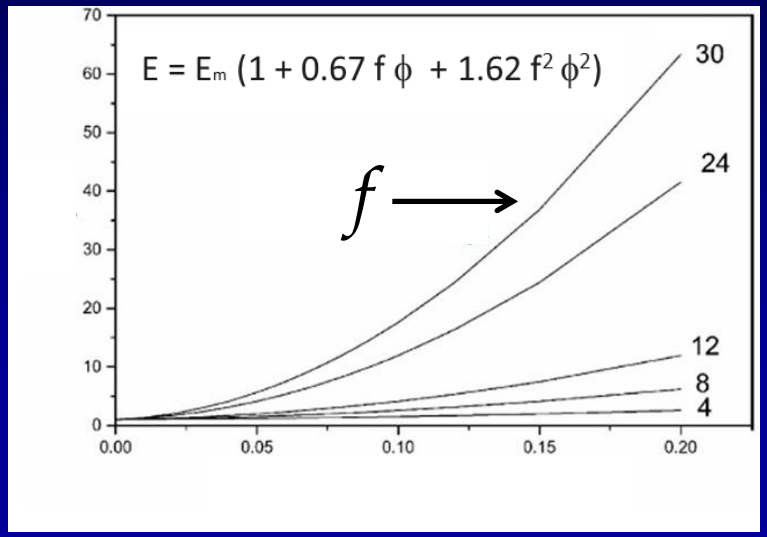
By fostering their chemical reactivity.

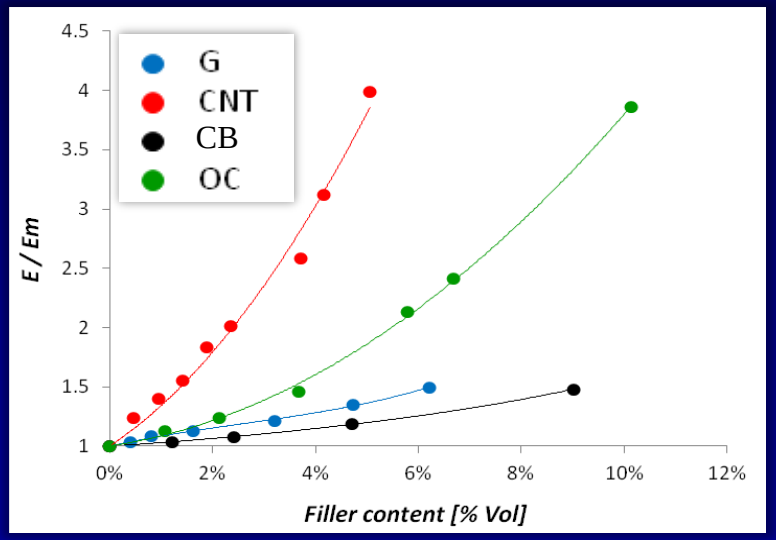
By creating filler – rubber linkages.

Nanometric Fillers: large reinforcement



Nanometric Fillers: large reinforcement





G = nanosized graphite

CNT = carbon nanotubes

CB = carbon black

OC = organoclay

Galimberti M., Coombs M., Riccio P., Ricco` T., Passera S., Pandini S., Conzatti L., Ravasio A., Tritto I., Macromol. Mater. Eng., 298 (2012), 241-251

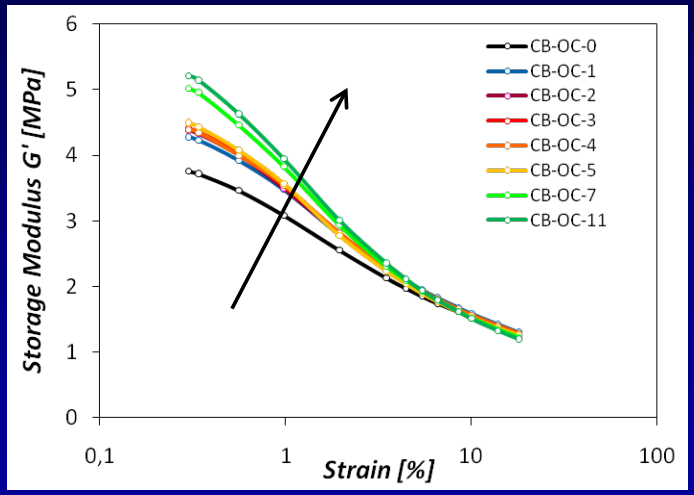
Galimberti M., Coombs M., Cipolletti V., Riccio P., Ricco` T., Pandini S., Conzatti L., Applied Clay Science 65–66 (2012) 57–66.

Galimberti M., Coombs M., Cipolletti V., Riccò T., Agnelli S., Pandini S., KGK 7-8 (2013) 31-36

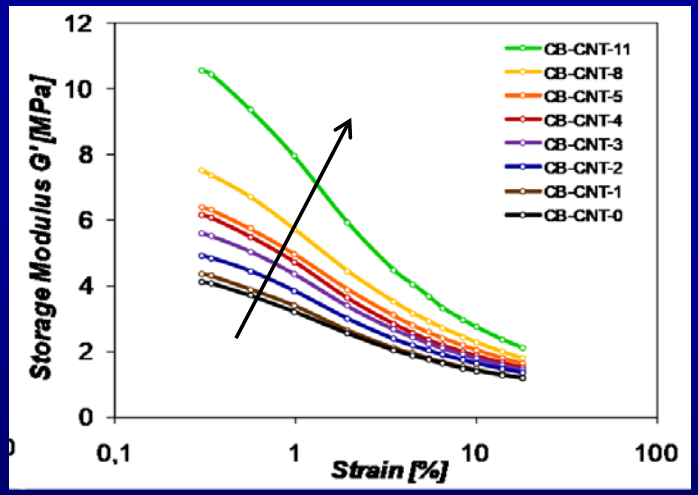
Galimberti M., V. Kumar, M. Coombs, V. Cipolletti, S. Agnelli, S. Pandini, L. Conzatti, RCT 87(2) (2014) 197-218

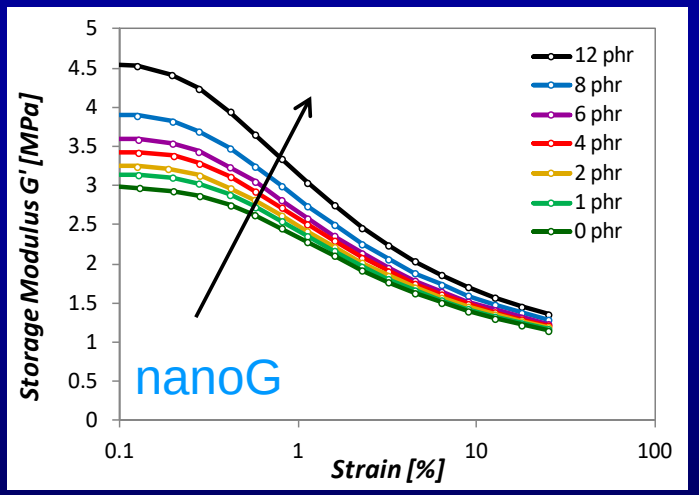
Nanometric Fillers: large Payne Effect

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





Galimberti M., Coombs M., Riccio P., Ricco` T., Passera S., Pandini S., Conzatti L., Ravasio A., Tritto I., Macromol. Mater. Eng., 298 (2012), 241-251
Galimberti M., Coombs M., Cipolletti V., Riccio P., Ricco` T., Pandini S., Conzatti L., Applied Clay Science 65–66 (2012) 57–66.
Galimberti M., Coombs M., Cipolletti V., Riccò T., Agnelli S., Pandini S., KGK 7-8 (2013) 31-36
Galimberti M., V. Kumar, M. Coombs, V. Cipolletti, S. Agnelli, S. Pandini, L. Conzatti, RCT 87(2) (2014) 197-218

To foster the chemical reactivity

of high aspect ratio nanometric fillers

Chemical modification

of high aspect ratio nanometric fillers

inorganic

oxides and hydroxides

sp^2 carbon allotropes

Chemical modification

of high aspect ratio nanometric fillers

Sepiolite

High surface area

nanosized graphite

Chemical modification

of high aspect ratio nanometric fillers

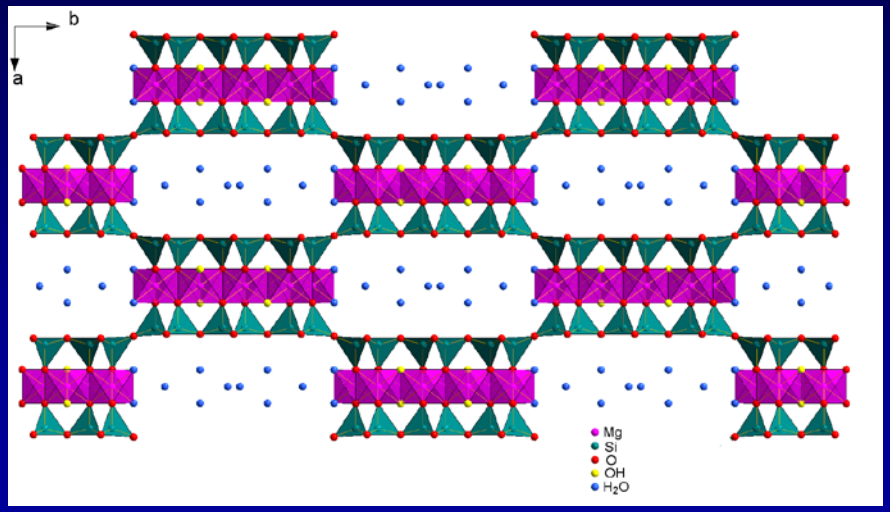
Sepiolite

High surface area

nanosized graphite

A bio-filler: Sepiolite

σήπιον (sepion)
+
λίθος (lithos)



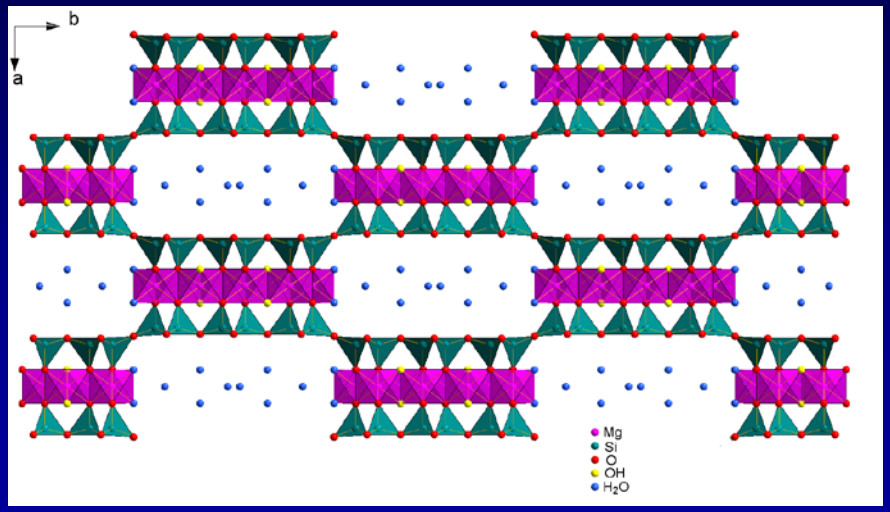
cuttlebone

- naturally occurring, easily available, low cost fibers
  typically 40–150 nm wide and 1–10 μm long
- high mechanical and thermal stability

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

A bio-filler: Sepiolite

TOT units

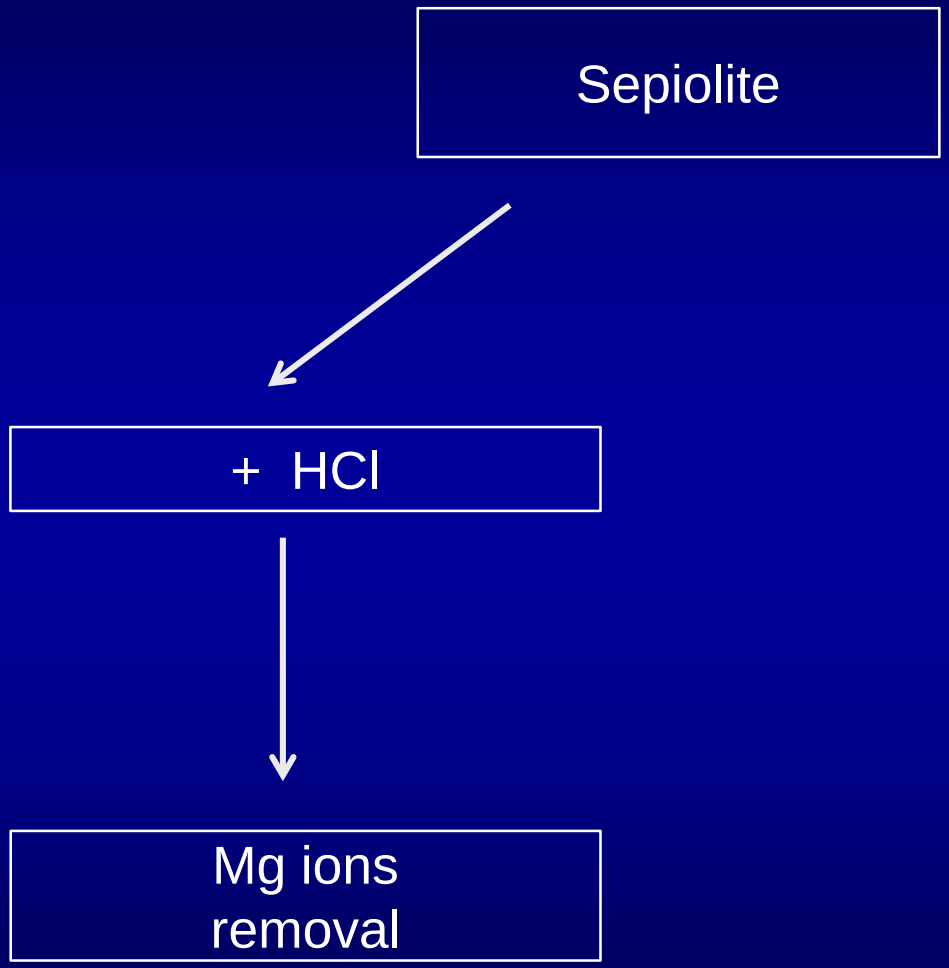


Connections in the direction perpendicular to the layers: due, in part, to covalent bonds.

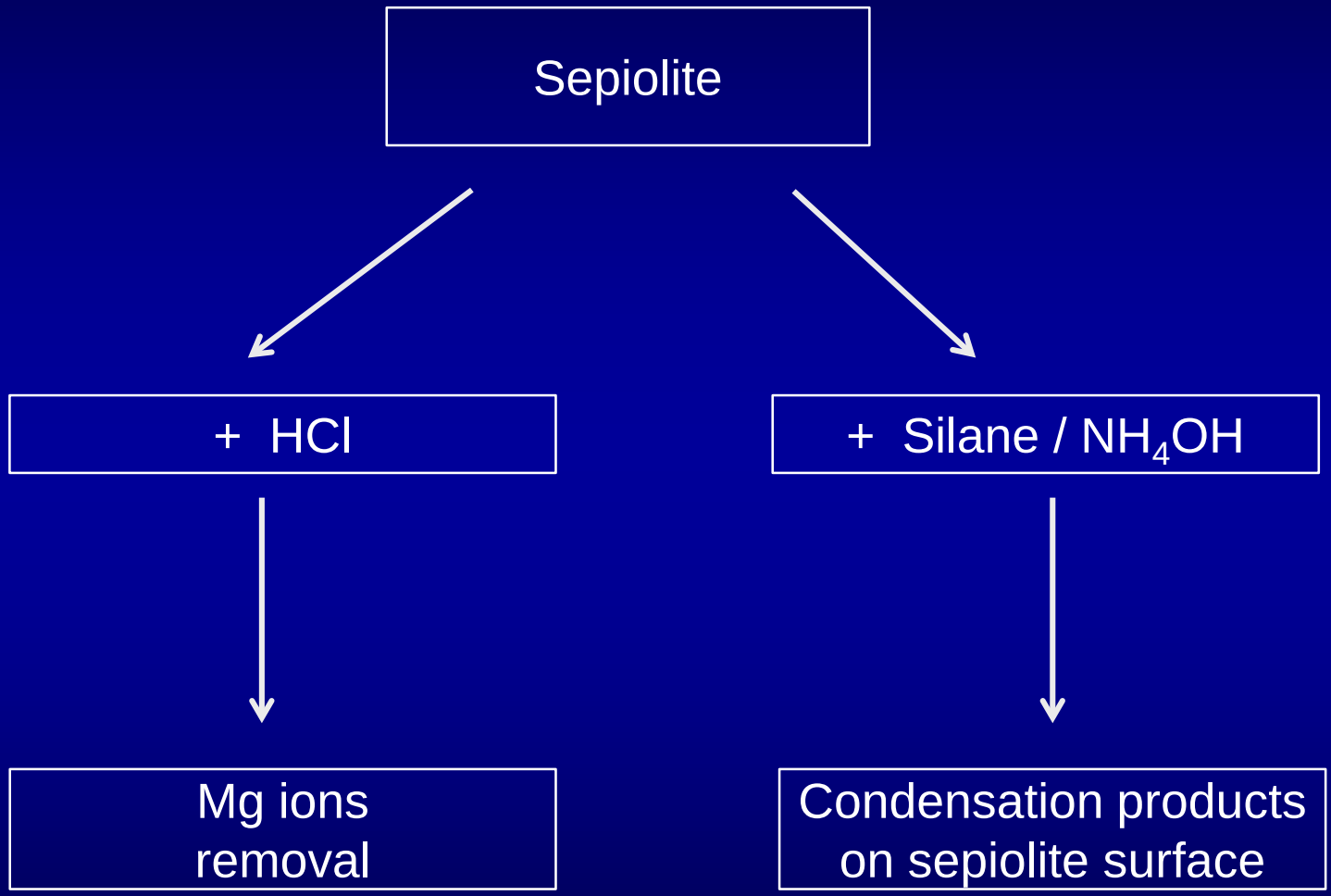
Sepiolite and the minerals of this group cannot swell or exfoliate!

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

Chemical modification of sepiolite



Chemical modification of sepiolite



Treatment of sepiolite with HCl

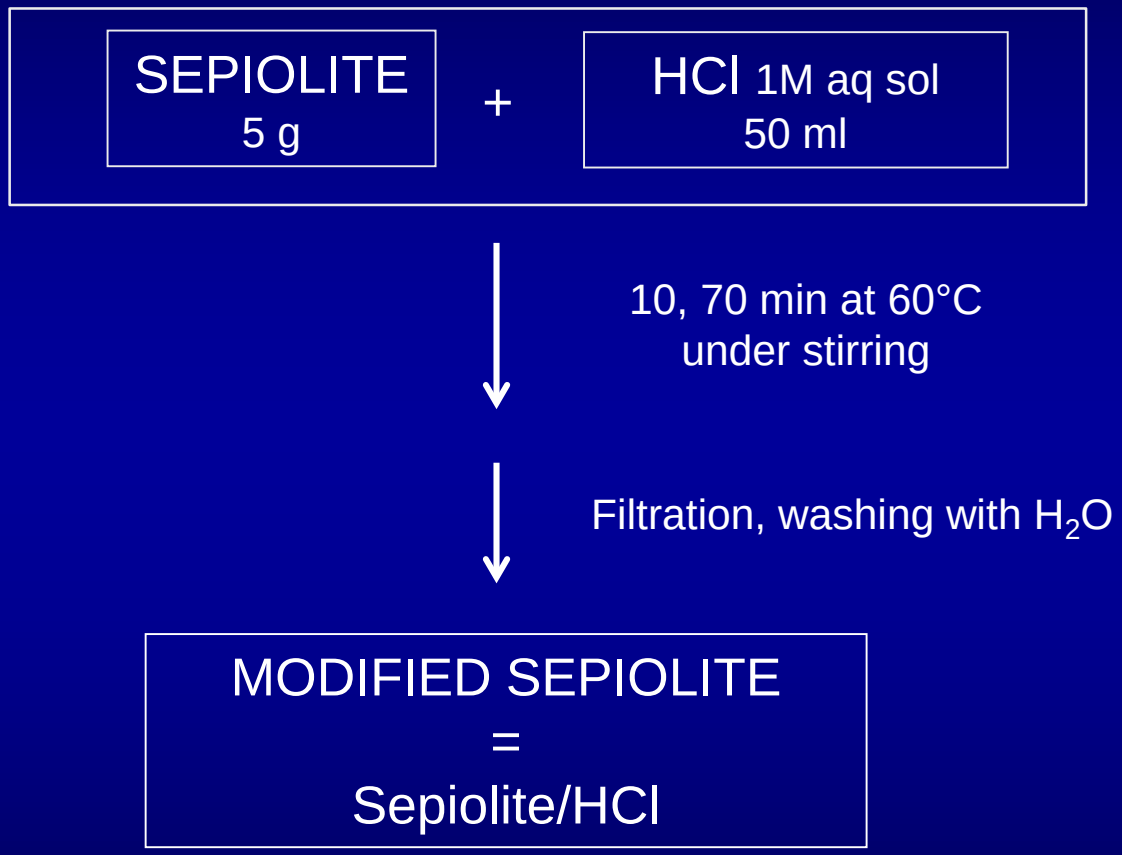
L. Giannini, L. Tadiello, T. Hanel, M. Galimberti, V. Cipolletti, G. Peli, F. Morazzoni, R. Scotti, B. Di Credico WO 2016/174629A1

M. Galimberti, V. Cipolletti, G. Peli, V. Barbera, A. Bernardi, D. Locatelli, L. Giannini, Proceedings of 194th Technical Meeting of the Rubber Division of the American Chemical Society, Inc., October 9 - 11, 2018, Louisville (KY)

M. Galimberti, G. Peli, V. Barbera, D. Locatelli, V. Cipolletti, L. Giannini, rubberworld.com, August 2019, 32-38

D. Locatelli, N. Pavlovic, V. Cipolletti, G. Peli, V. Barbera, L. Giannini, M. Galimberti Submitted to RCT, Frontiers Edition

Treatment of sepiolite with acid



Sepiolite treated with HCl

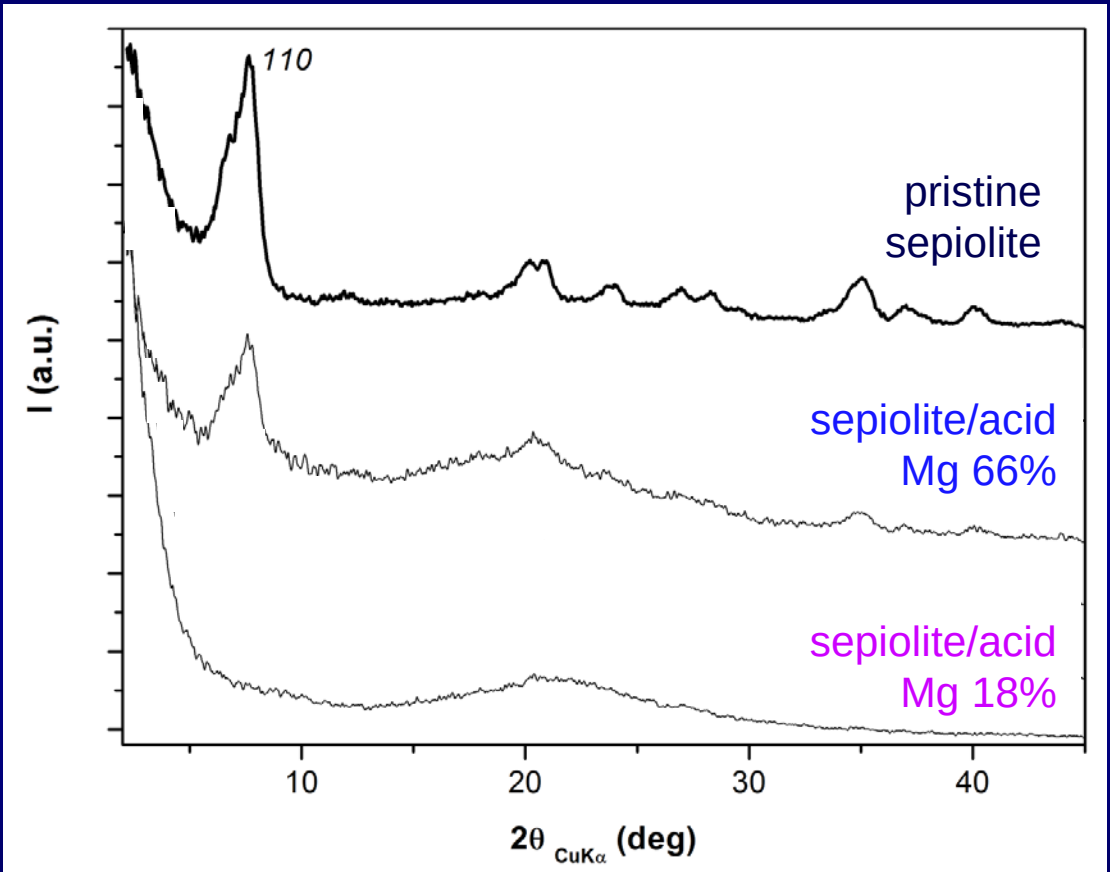
Extracted Magnesium

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

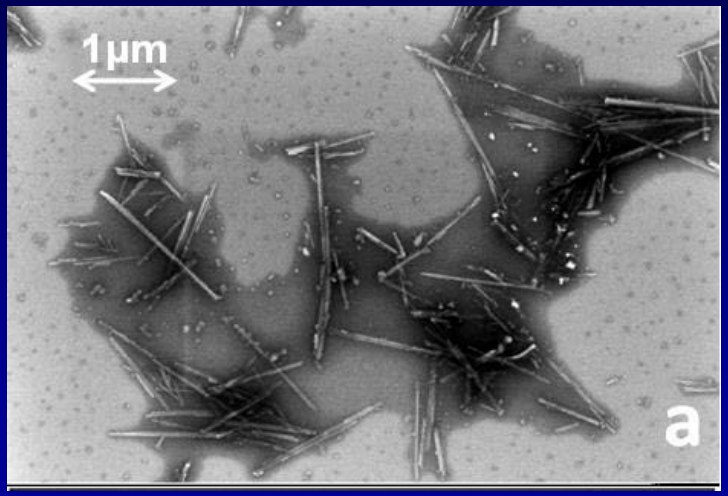
Sepiolite treated with HCl

WAXD analysis

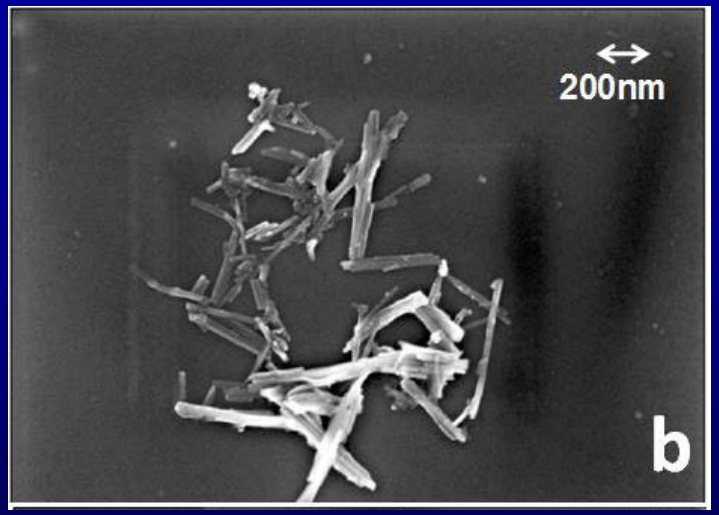


Sepiolite treated with HCl

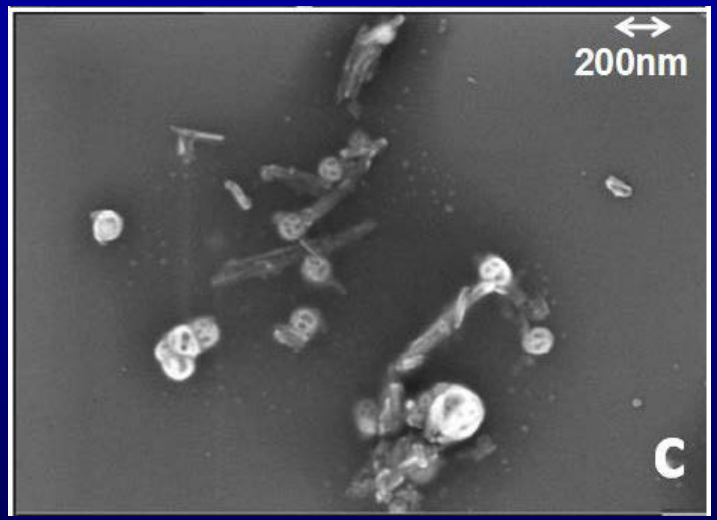
FESEM analysis



pristine sepiolite



sepiolite / HCl - Mg 66%



sepiolite / HCl - Mg 18%

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

Formulations
(phr)

Ingredient	Filler in the composite		
	Silica	Silica + Sepiolite	Silica + Sepiolite (Mg 66%)
NR	100	100	100
Silica	45	35	35
Sepiolite	0	10	0
Sepiolite-HCl	0	0	10
Silane TESPT	3.6	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/HCl (Mg66%)

Dynamic mechanical properties

Property	Filler in the composite		
	Silica	Silica + Sepiolite	Silica + Sepiolite (Mg 66%)
G' (0.4%)	1.51	1.48	1.31
ΔG' (0.4%-35%)/G' (0.4%)	0.30	0.31	0.27

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

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

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 properties

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

Treatment of sepiolite with a silane

Silane:

TEOS

TESPD

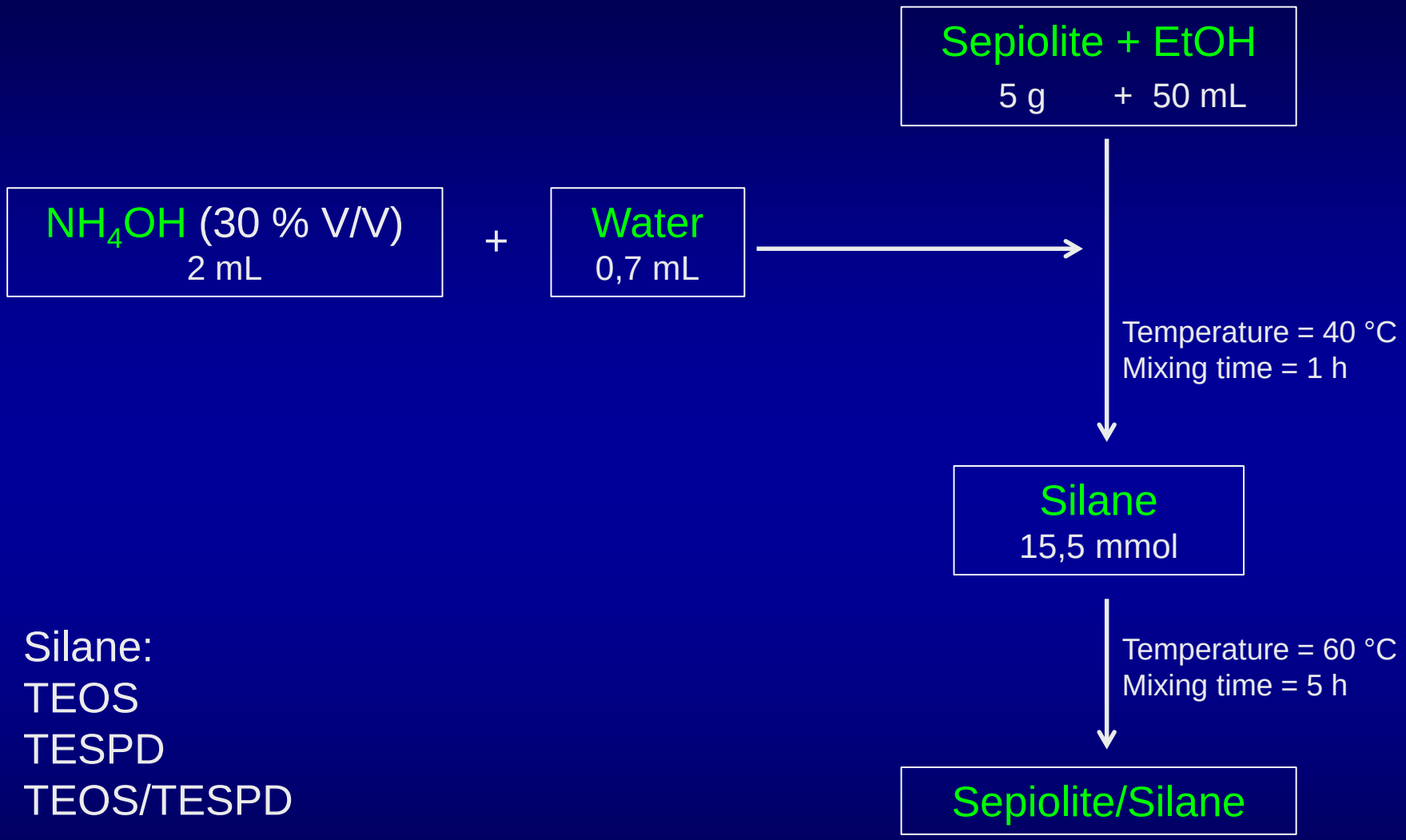
TEOS/TESPD

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

M. Galimberti, V. Cipolletti, G. Peli, V. Barbera, A. Bernardi, D. Locatelli, L. Giannini, Proceedings of 194th Technical Meeting of the Rubber Division of the American Chemical Society, Inc., October 9 - 11, 2018, Louisville (KY)

D. Locatelli, N. Pavlovic, V. Cipolletti, G. Peli, V. Barbera, L. Giannini, M. Galimberti Submitted to RCT, Frontiers Edition

Treatment of sepiolite with a Silane



Silane:
TEOS
TESPD
TEOS/TESPD

Sepiolite treated with a silane

Thermogravimetric analysis

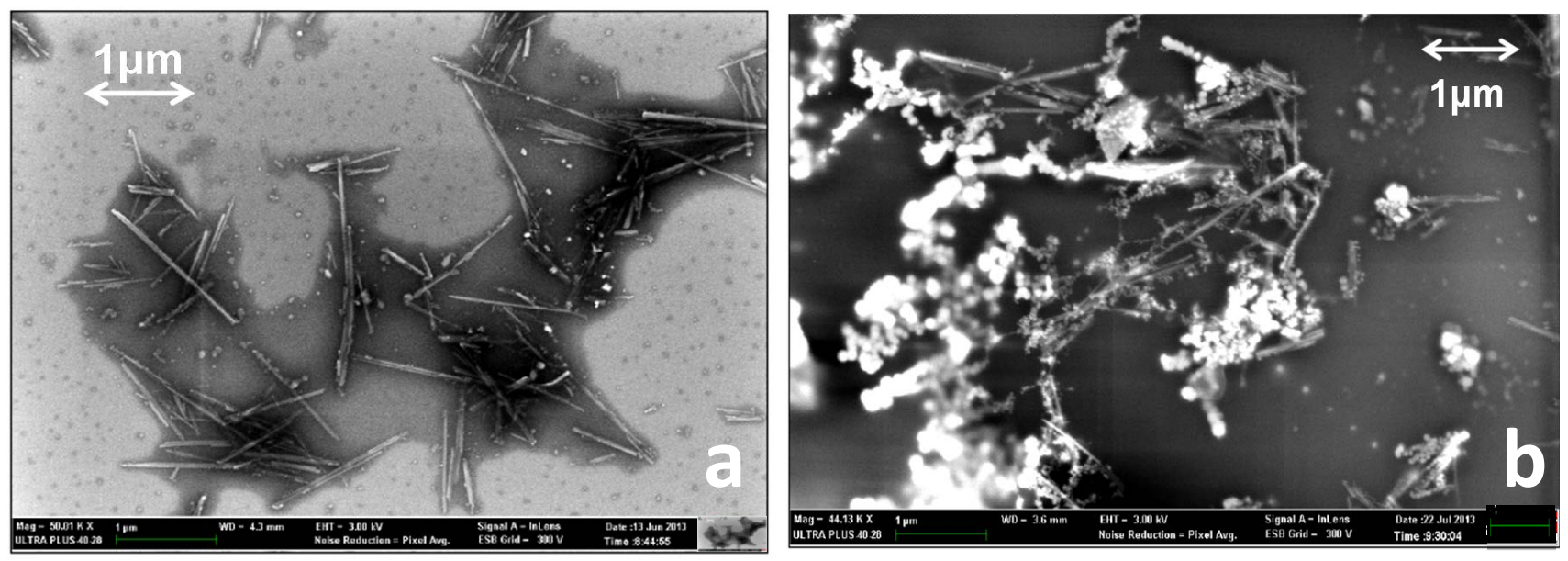
Sample	Mass losses in different T (°C) ranges				Residue
	T < 150	150 < T < 450	450 < T < 750	750< T< 900	T > 900
Sp	8,1	3,3	2,7	2,0	83,6
Sp/TEOS	6,1	5,6	2,8	2,1	83,4
Sp/TESPD	5,6	8,2	4,4	2,3	79,5
Sp/TEOS/TESPD	6,2	6,2	3,3	2,1	82,2

Sepiolite treated with TEOS

FESEM analysis

pristine sepiolite

sepiolite / TEOS



typical fibrillar shape of pristine sepiolite

silica nanoparticles on sepiolite fibrils

Treatment of sepiolite with nanoparticles from silane condensation

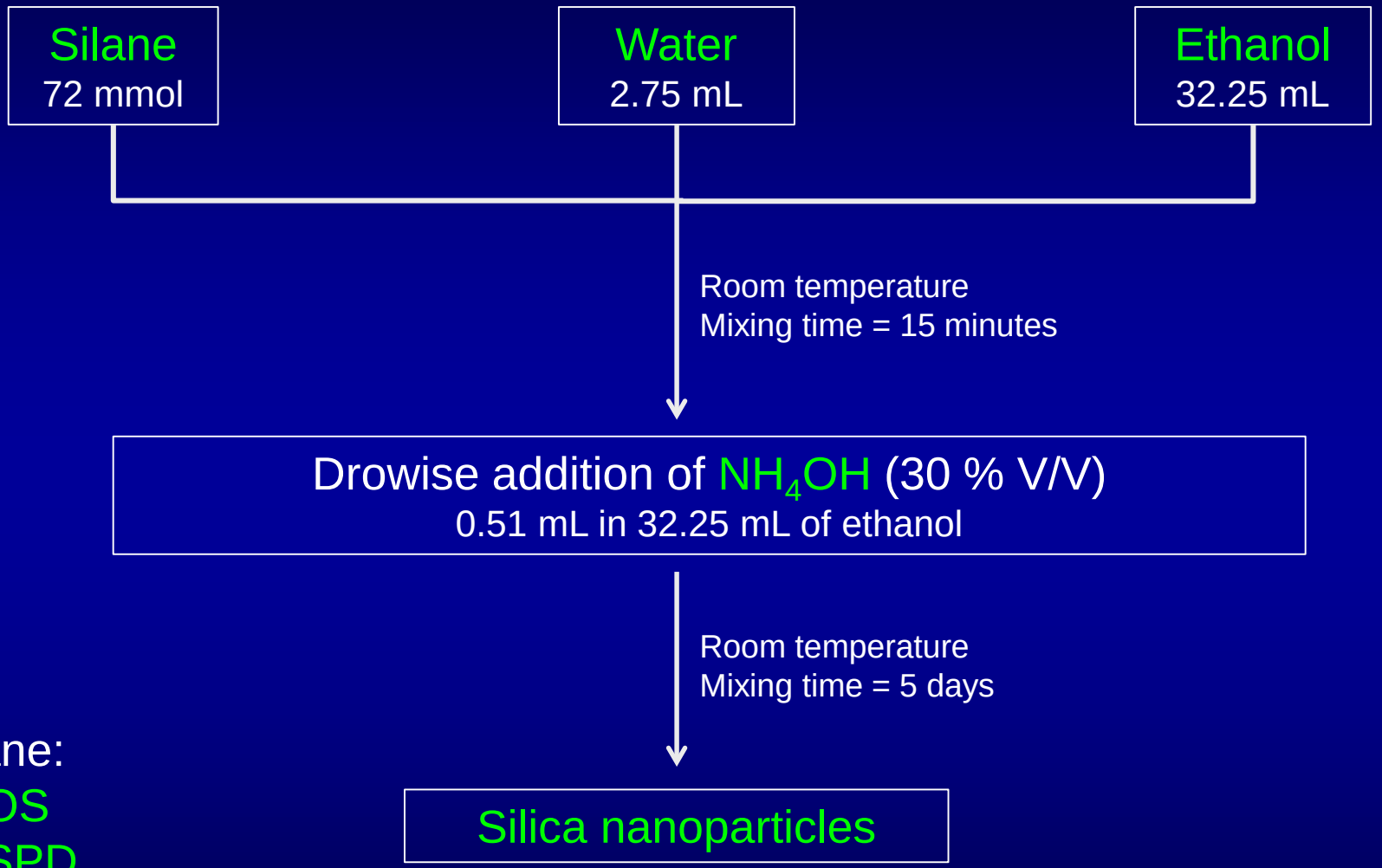
Silane:

TEOS

TESPD

TEOS/TESPD

Preparation of nanoparticles

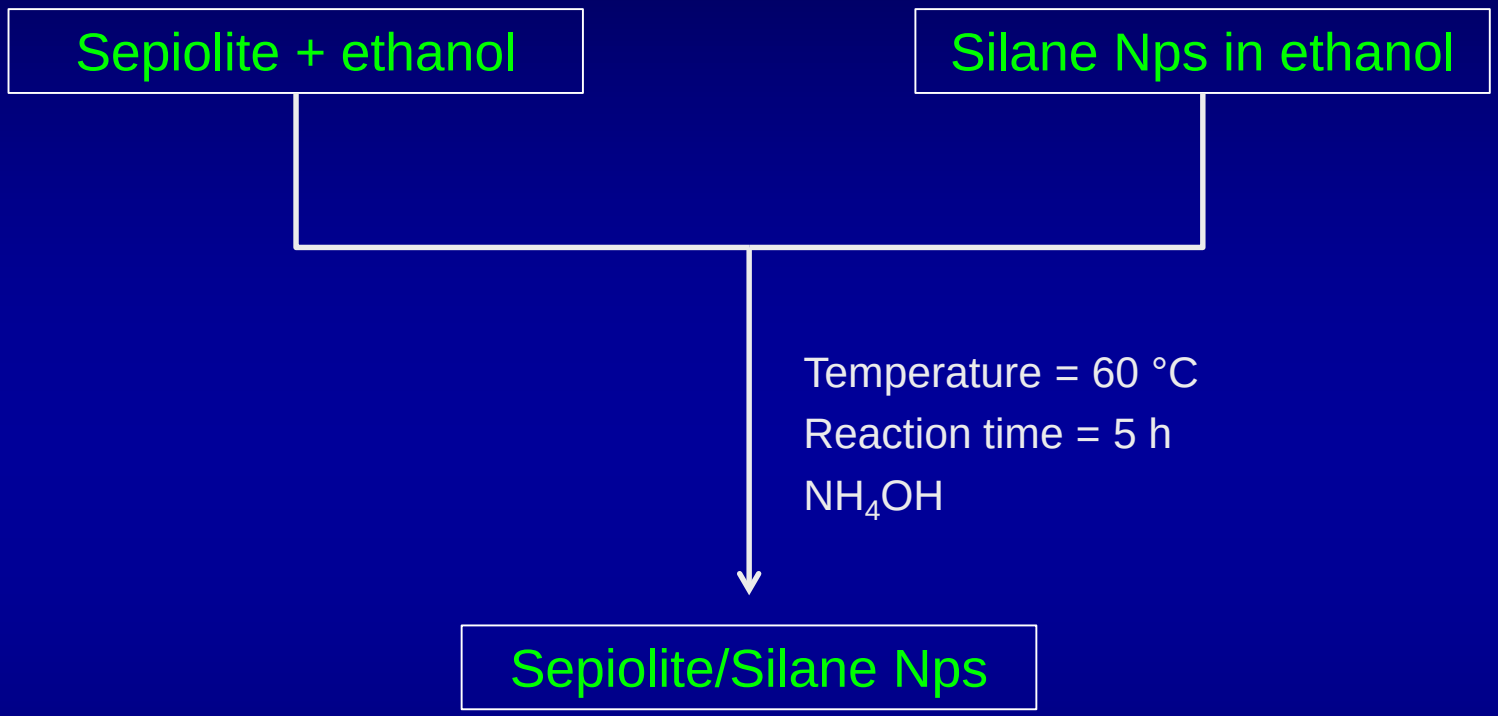


Silane:
TEOS
TESPD
TEOS/TESPD

Nanoparticles from silane(s) condensation

Nanoparticle from	Average diameter [nm]	PdI
TEOS	25,50	0,280
TEOS/TESPD	37,80	0,262
TESPD	n.d.	n.d.

Treatment of sepiolite with nanoparticles from silane condensation



Washing with ethanol

Adducts of sepiolite with silanes' condensation products

Elemental analysis

	Sp/Silane		Sp/silane Nps	
	C (%wt)	**S (%wt)**	**C (%wt)**	**S (%wt)**
Sp/TEOS/TESPD	3,39	0,56	3,13	1,27
Sp/TESPD	5,45	2,89	2,89	0,87

NR based compounds with silica and sepiolite

treated with silanes' condensation products

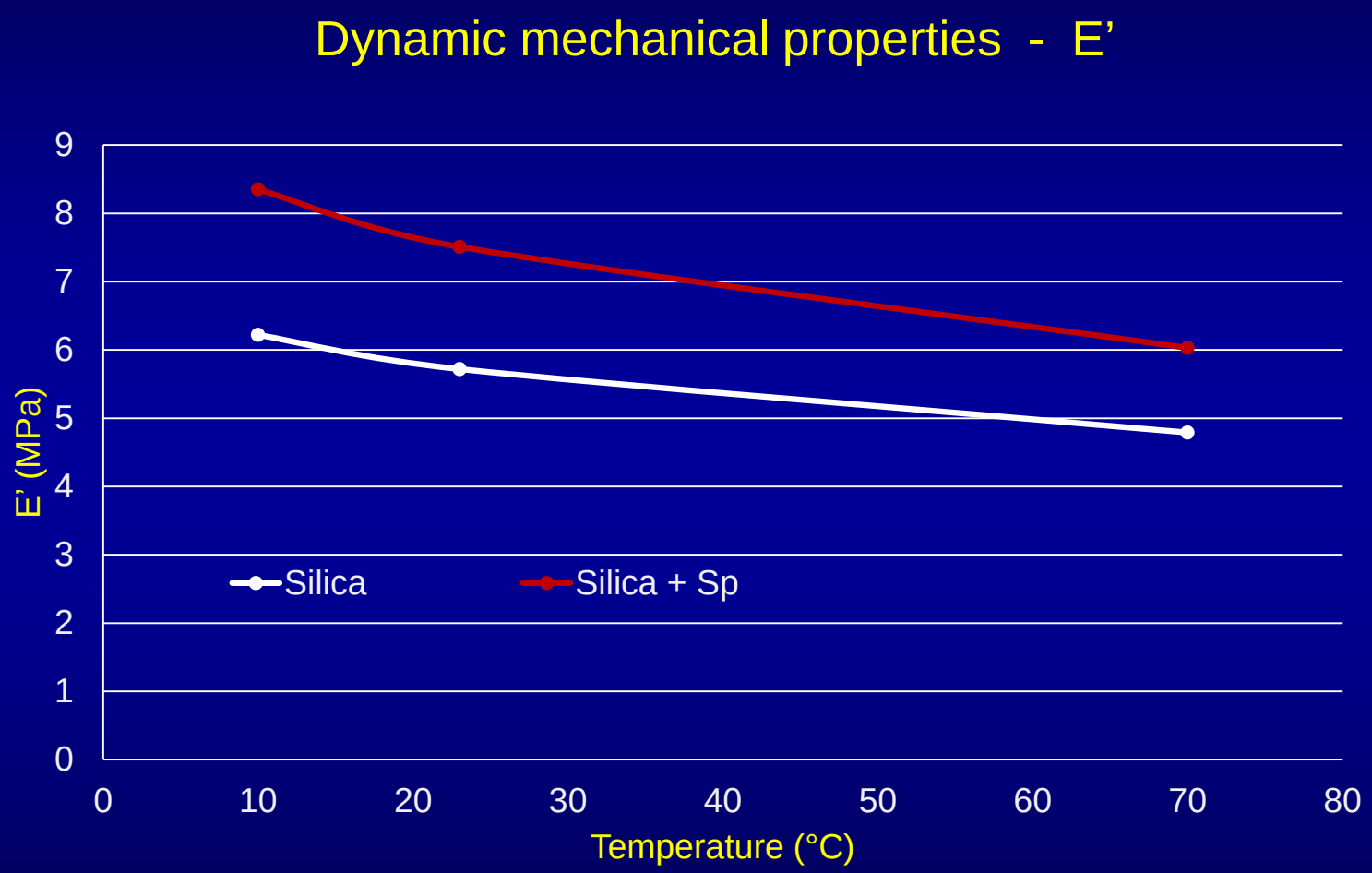
Formulations

Ingredient	Filler in the composite				
	Silica	Silica + Sp	Silica + Sp/TEOS	Silica + Sp/TESPD	Silica + Sp/TEOS/TESPD
NR	100	100	100	100	100
ZEOSIL 1165	46,6	35	35	35	35
Sp	0	11,6	0	0	0
Sp/TEOS	0	0	11,6	0	0
Sp/TESPD	0	0	0	11,6	0
Sp/TEOS/TESPD	0	0	0	0	11,6

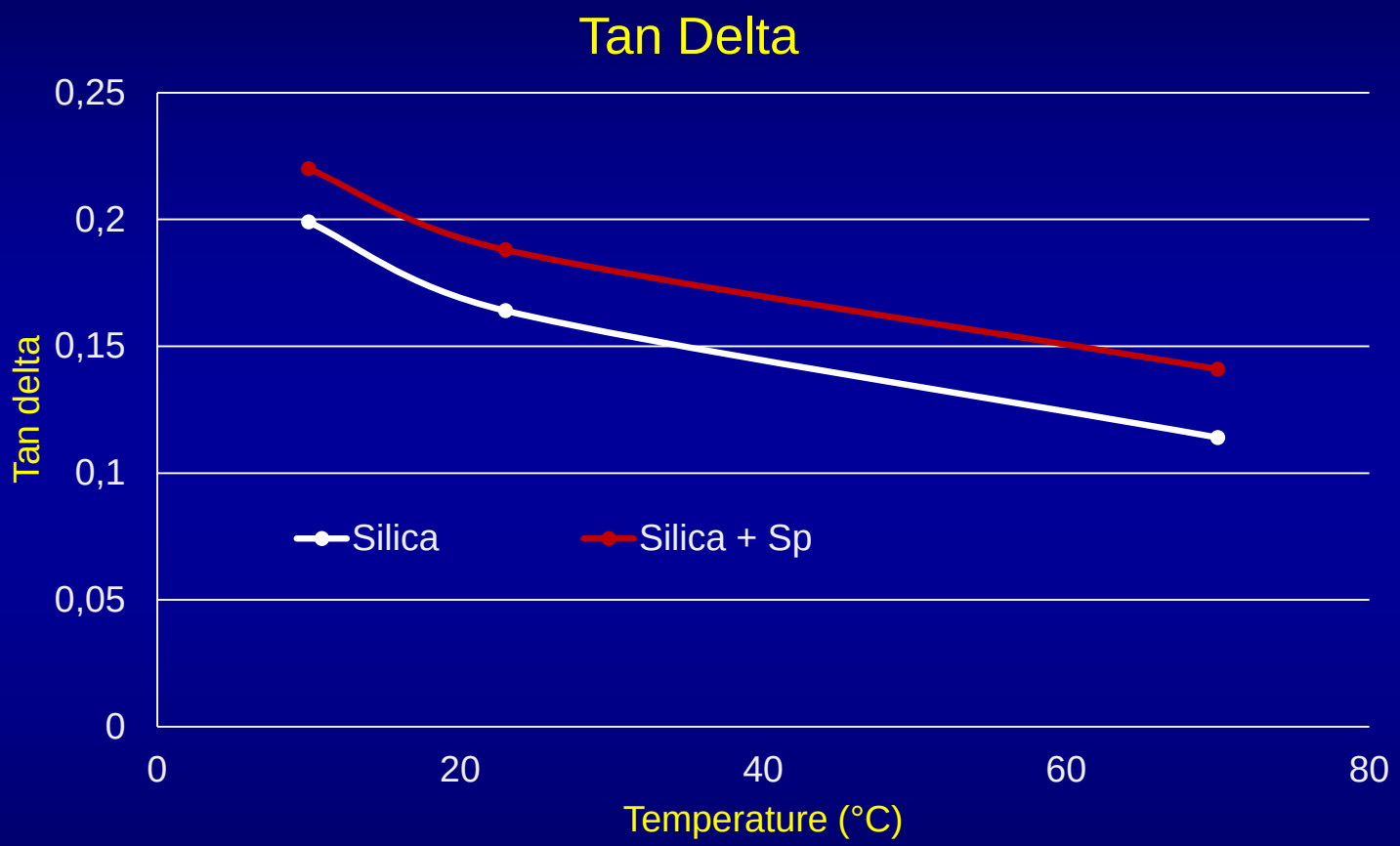
Other ingredients: ZnO 3.6, Stearic acid 2, TESPT 3.6, 6PPD 2, TBBS 1.8, Sulphur 2

Silanes: pristine or nanoparticles

NR based compounds with silica and sepiolite treated with silanes

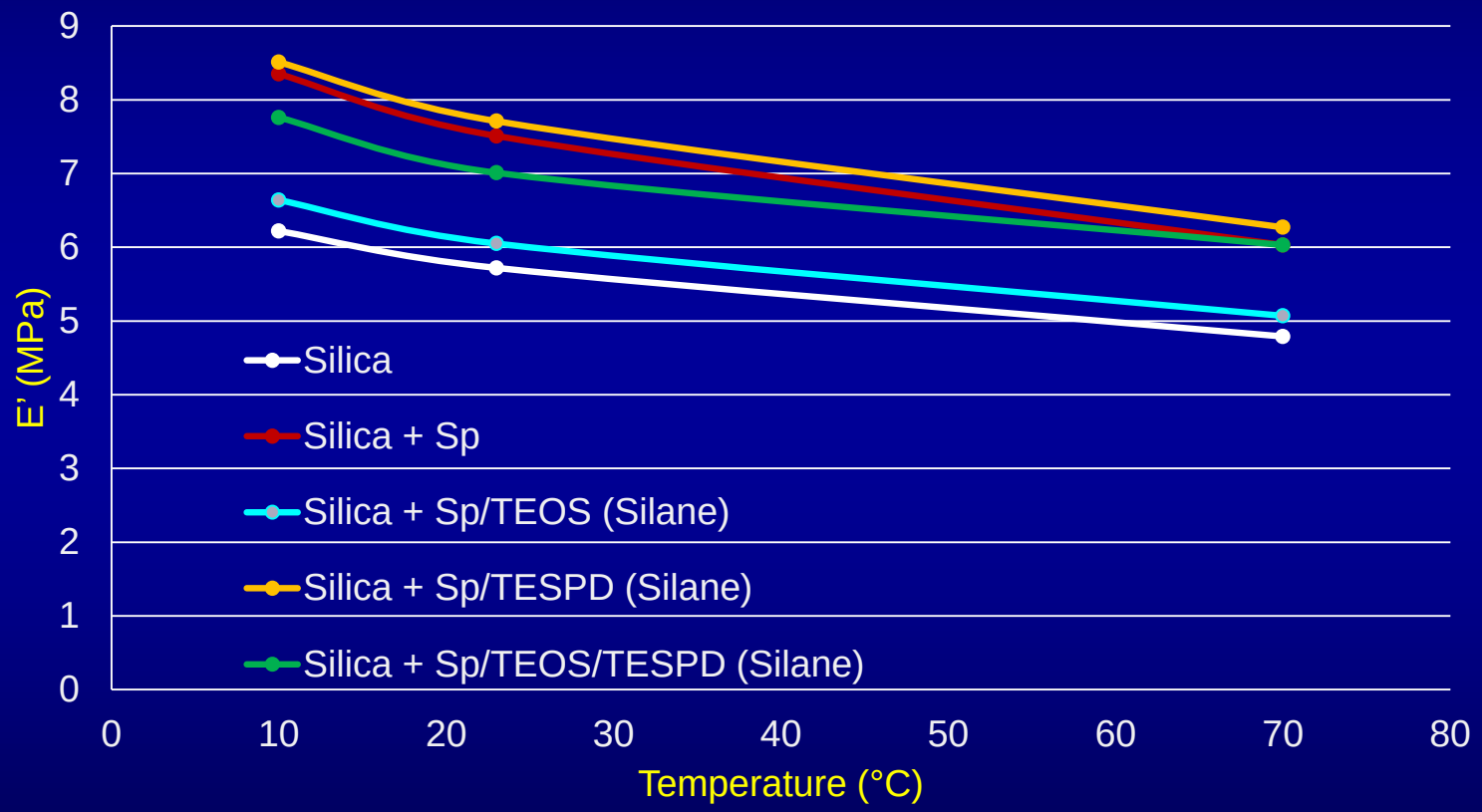


NR based compounds with silica and sepiolite treated with silanes

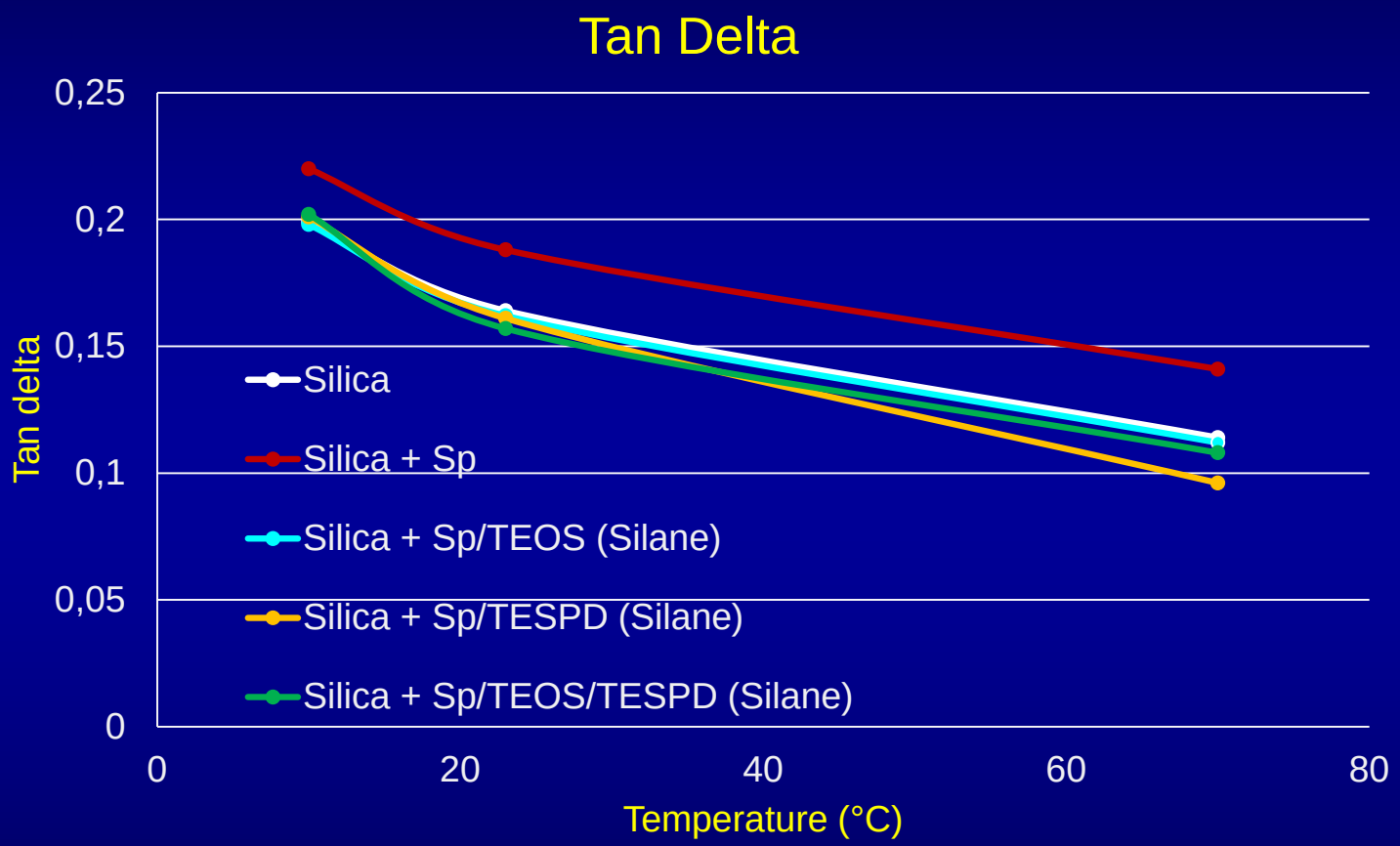


NR based compounds with silica and sepiolite treated with silanes

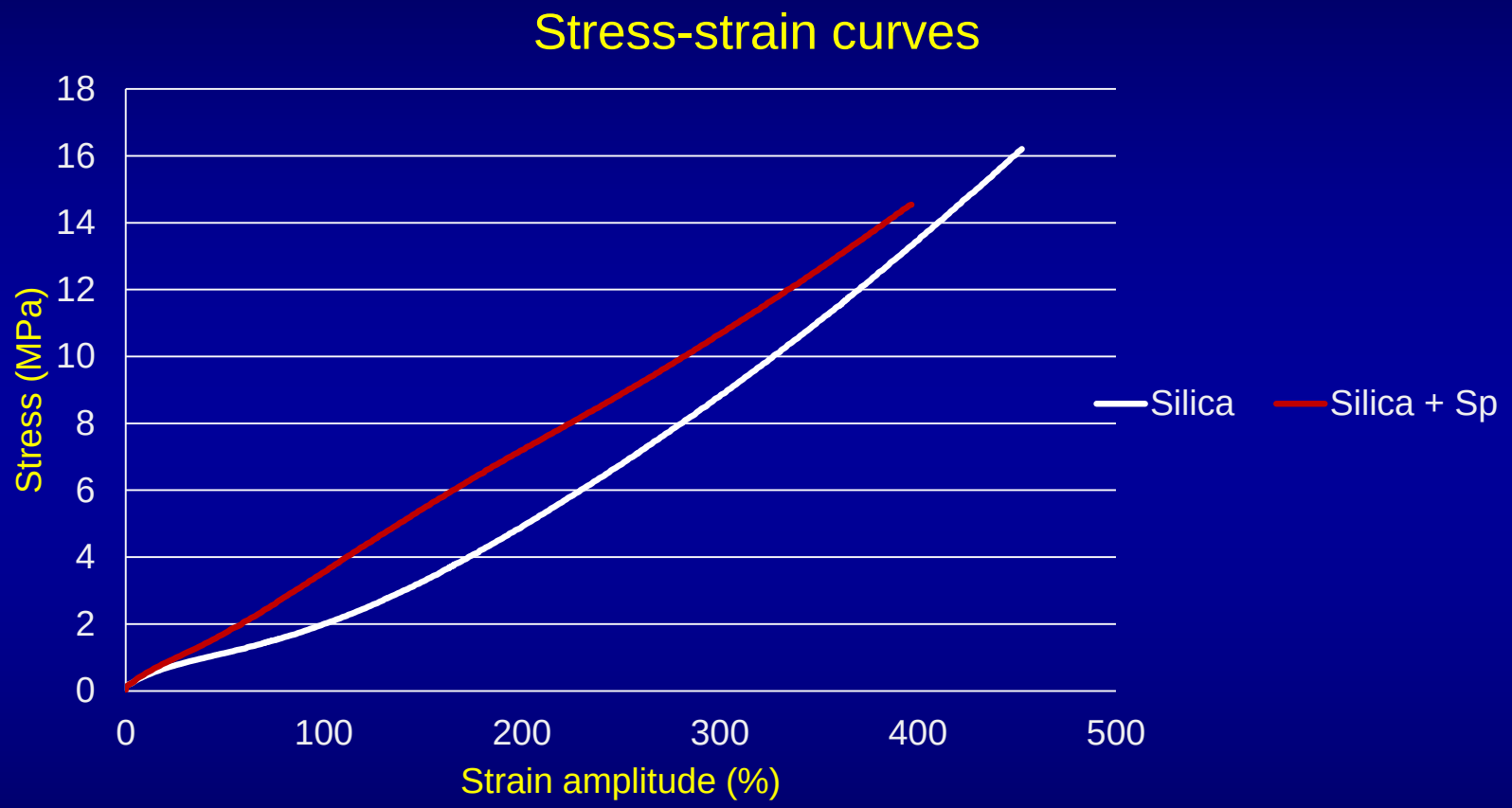
Dynamic mechanical properties - E'



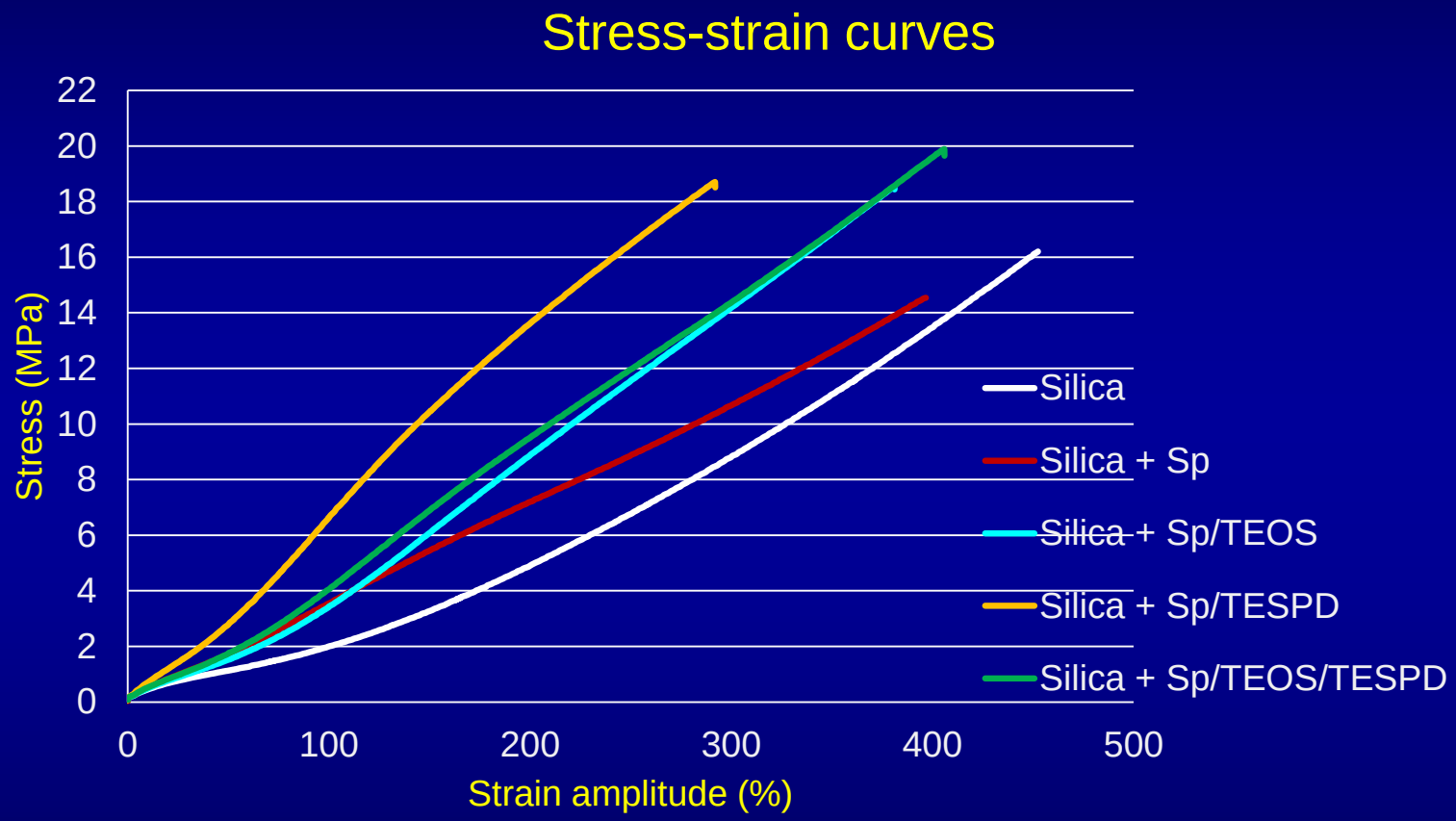
NR based compounds with silica and sepiolite treated with silanes



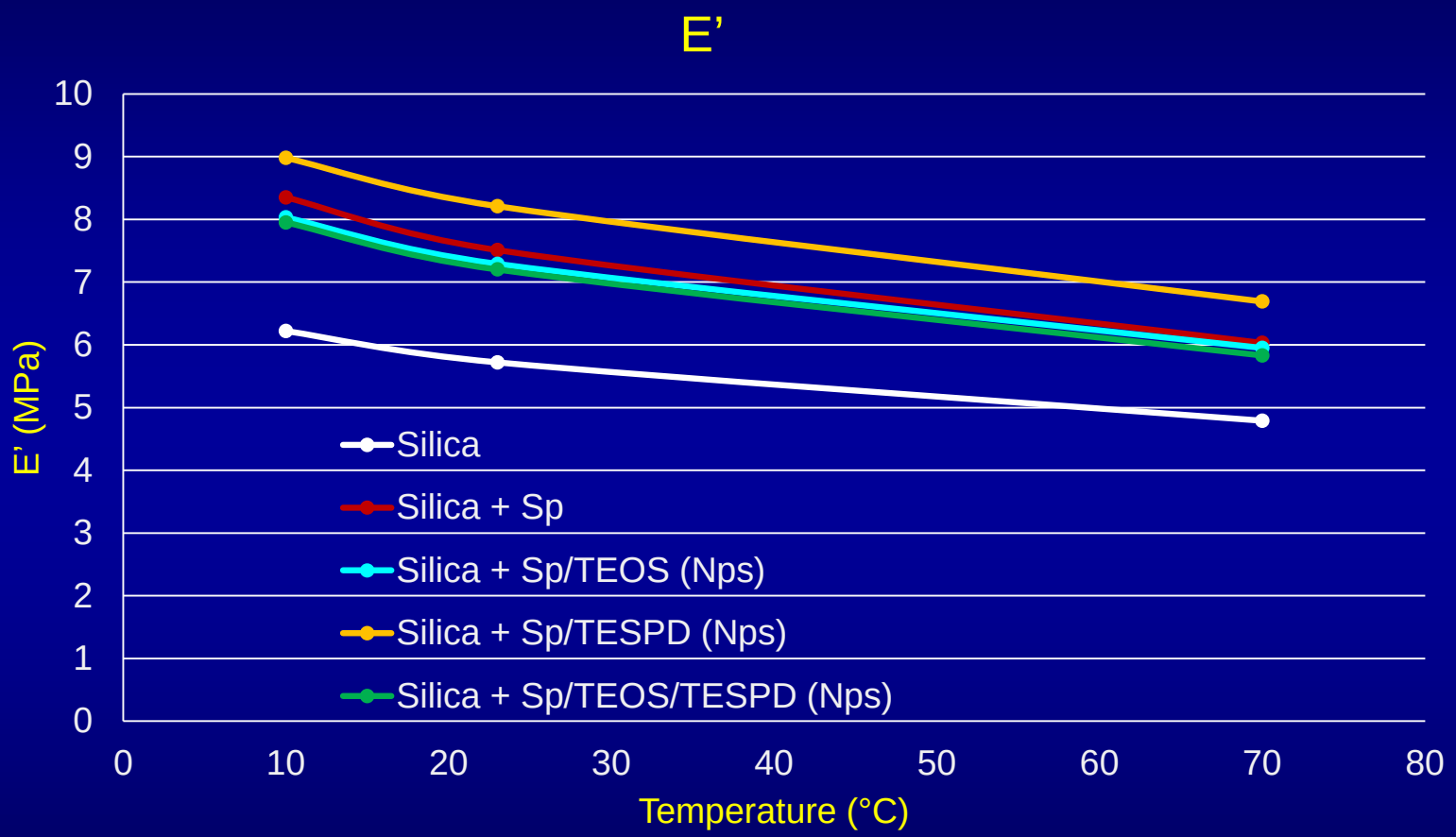
NR based compounds with silica and sepiolite treated with silanes



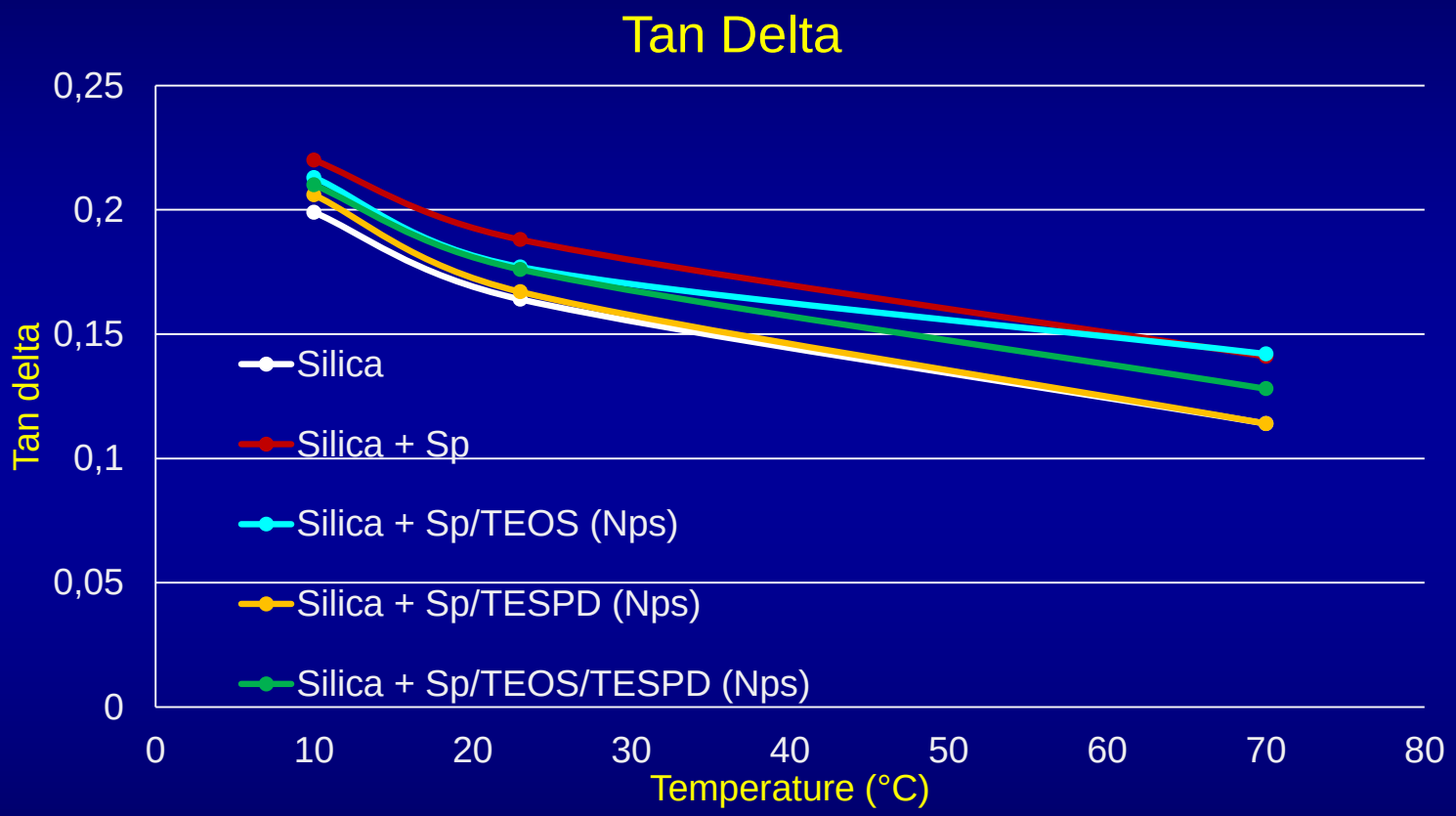
NR based compounds with silica and sepiolite treated with silanes



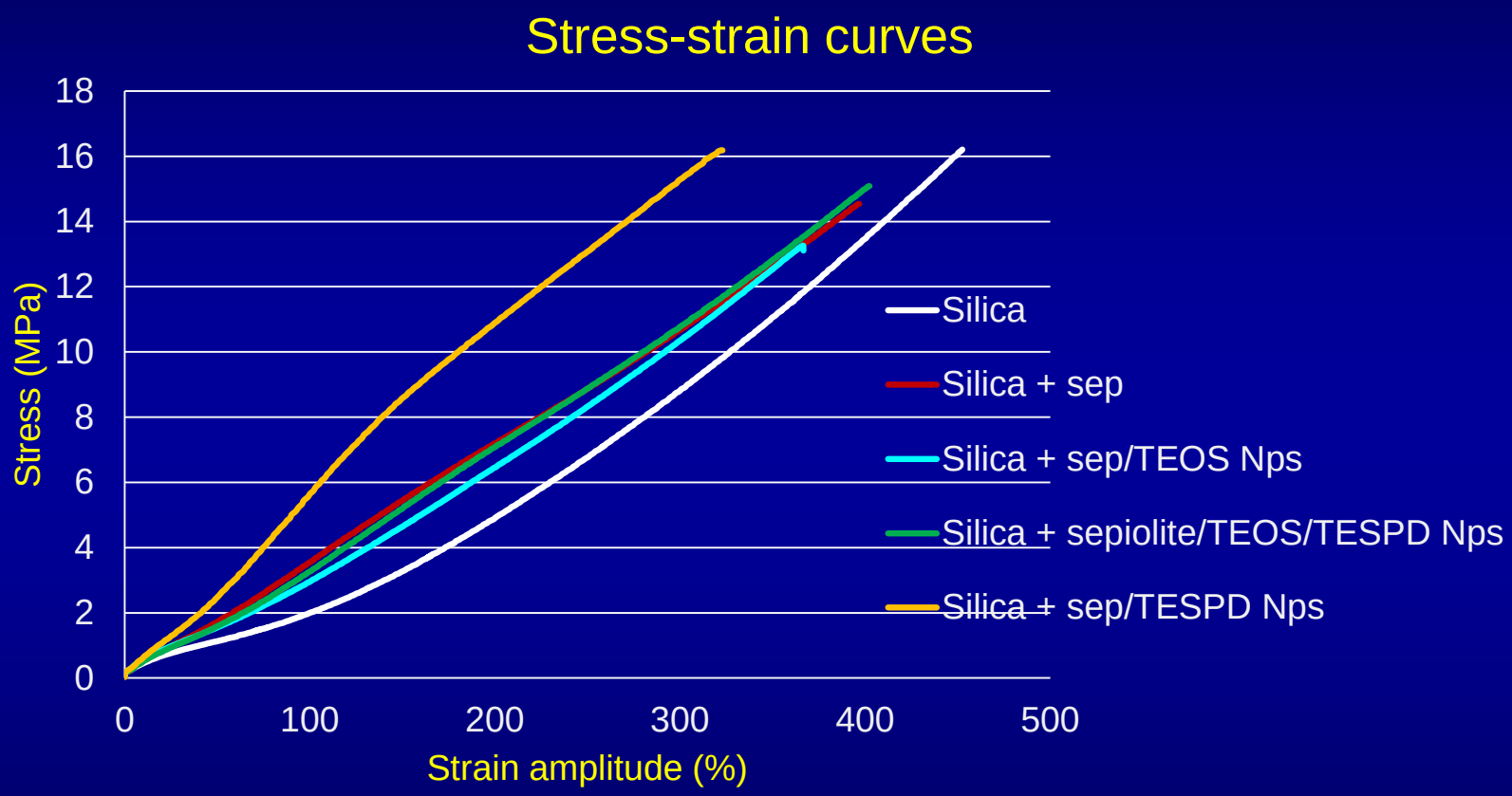
NR based compounds with silica and sepiolite treated with silanes' nanoparticles



NR based compounds with silica and sepiolite treated with silanes' nanoparticles



NR based compounds with silica and sepiolite treated with silanes' nanoparticles



Chemical modification

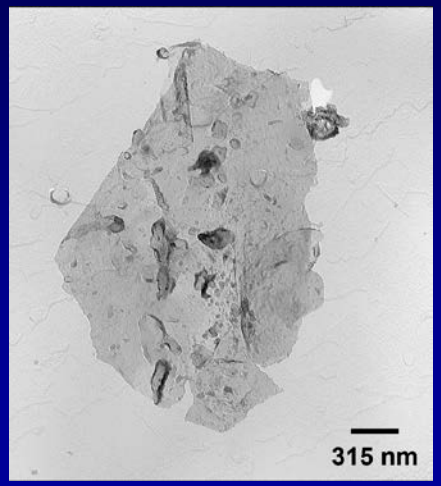
of high aspect ratio nanometric fillers

Sepiolite

High surface area

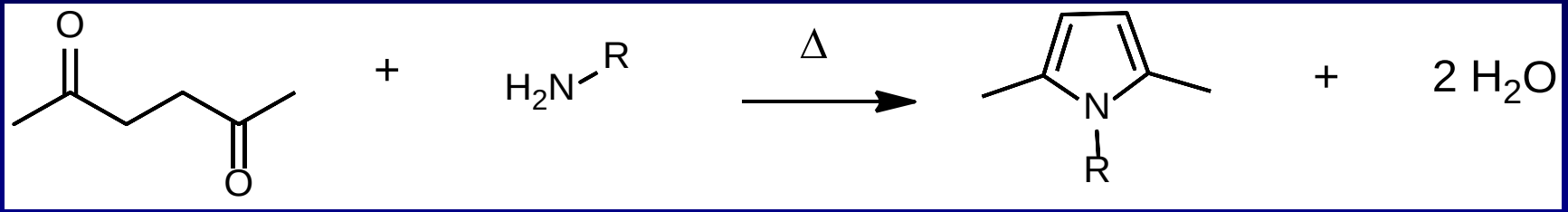
nanosized graphite

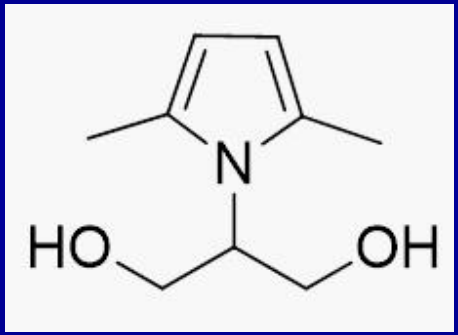
High surface area graphite (HSAG)



Sample	Surface area (m^2/g)	number of stacked layers	$D_{\parallel} / D_{\perp}$
HSAG	330	35	3.1

Pyrrole compounds for the functionalization of sp^2 carbon allotropes



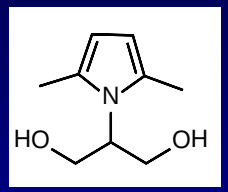


2-(2,5-dimethyl-1*H*-pirrol-1-yl) -1,3-propanediol

serinol pyrrole

V. Barbera, A.Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U.Shisodia, A.M. Valerio WO 2015 189411 A1
M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini,, RSC Adv., 2015, 5, 81142-81152
V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

Domino reaction for the functionalization of sp^2 carbon allotropes



HSAG

Domino reaction
for the functionalization of HSAG

HSAG-SP

HSAG 100 SP 4

Barbera, V., Brambilla, L., Milani, A., Palazzolo, A., Castiglioni, C., Vitale, A., Bongiovanni R., Galimberti, M., Nanomaterials, 2019, 9(1), 44.
Galimberti M., Barbera V., Guerra S., Bernardi A., Rubber Chemistry and Technology, 2017, 90(2), 285-307.

S-SBR / NR based compounds with silica and HSAG

Formulations (phr)

Ingredient	Filler in the composite					
	Silica	HSAG (15%)	HSAG (30%)	HSAG-SP (15%)	HSAG-SP (30%)	*
S-SBR 4630	110	110	110	110	110	
NR (SIR - 20)	20	20	20	20	20	
Silica 1165	50	42.5	35	42.5	35	
HSAG	0	8.2	16.4	0	0	
HSAG-SP	0	0	0	8.5	17.06	

Other ingredients: ZnO 2.5, 6PPD 2, Sulphur 2, TBBS 1.8

* Silica was partially substituted by pristine or modified HSAG at constant volume

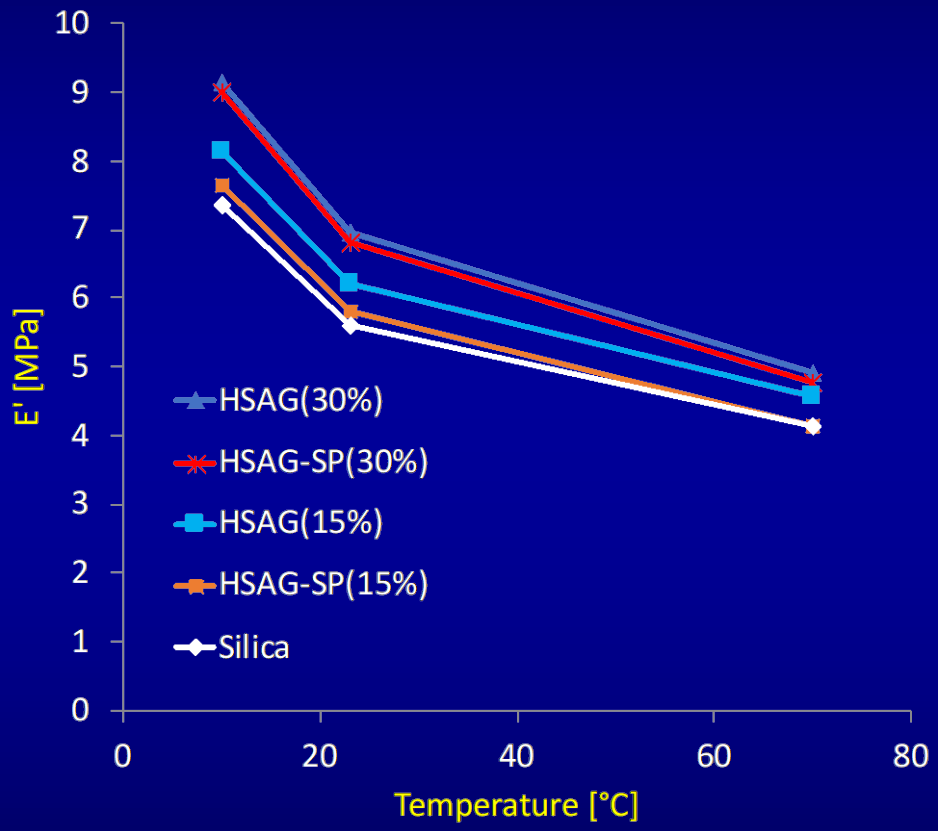
S-SBR / NR based compounds with silica and HSAG

Curing behaviour.
Data from rheometer test

	Silica	HSAG 15 %	HSAG 30 %	HSAG-SP 15 %	HSAG-SP 30 %
M_L [dNm]	2.71	2.71	2.01	1.71	1.86
M_H [dNm]	**13.67**	**13.52**	**12.36**	**11.91**	**12.36**
t_{90} [min]	11.66	11.08	11.39	12.39	12.32

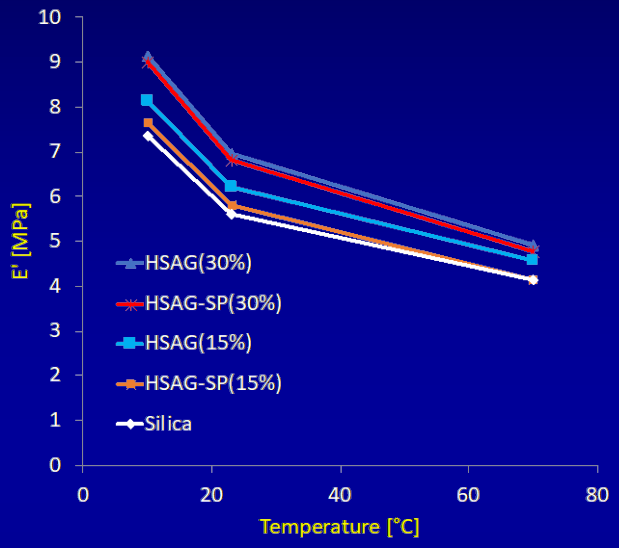
S-SBR / NR based compounds with silica and HSAG

Dynamic-mechanical properties



S-SBR / NR based compounds with silica and HSAG

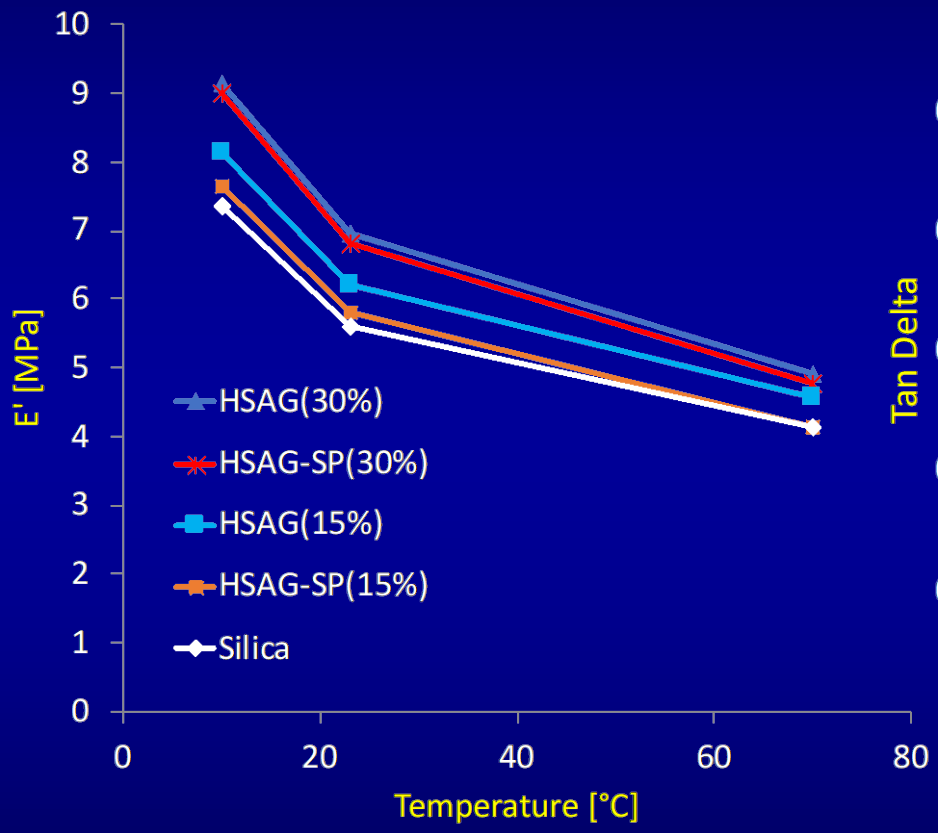
Dynamic-mechanical properties

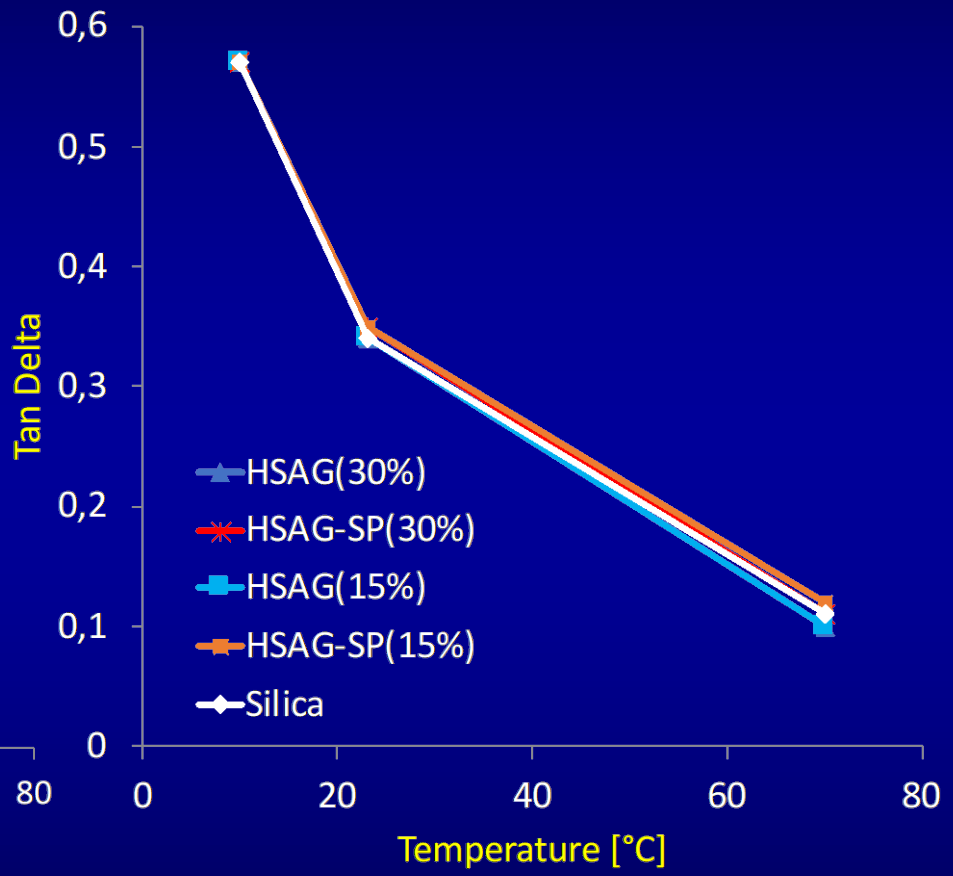


	Silica	HSAG 15 %	HSAG 30 %	HSAG-SP 15 %	HSAG-SP 30 %
E'@10°C	**7.35**	**8.15**	9.14	7.64	**9**
Tan Delta@10°C	0.57	0.57	0.56	0.57	0.57

S-SBR / NR based compounds with silica and HSAG

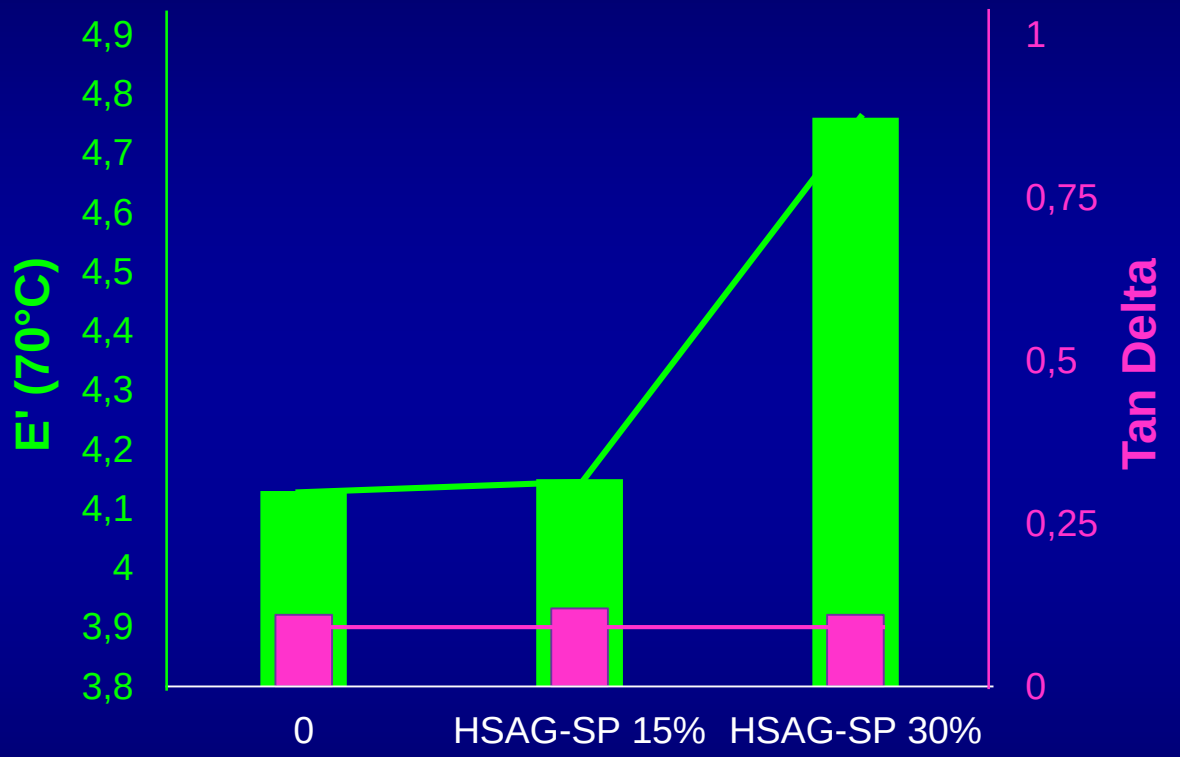
Dynamic-mechanical properties



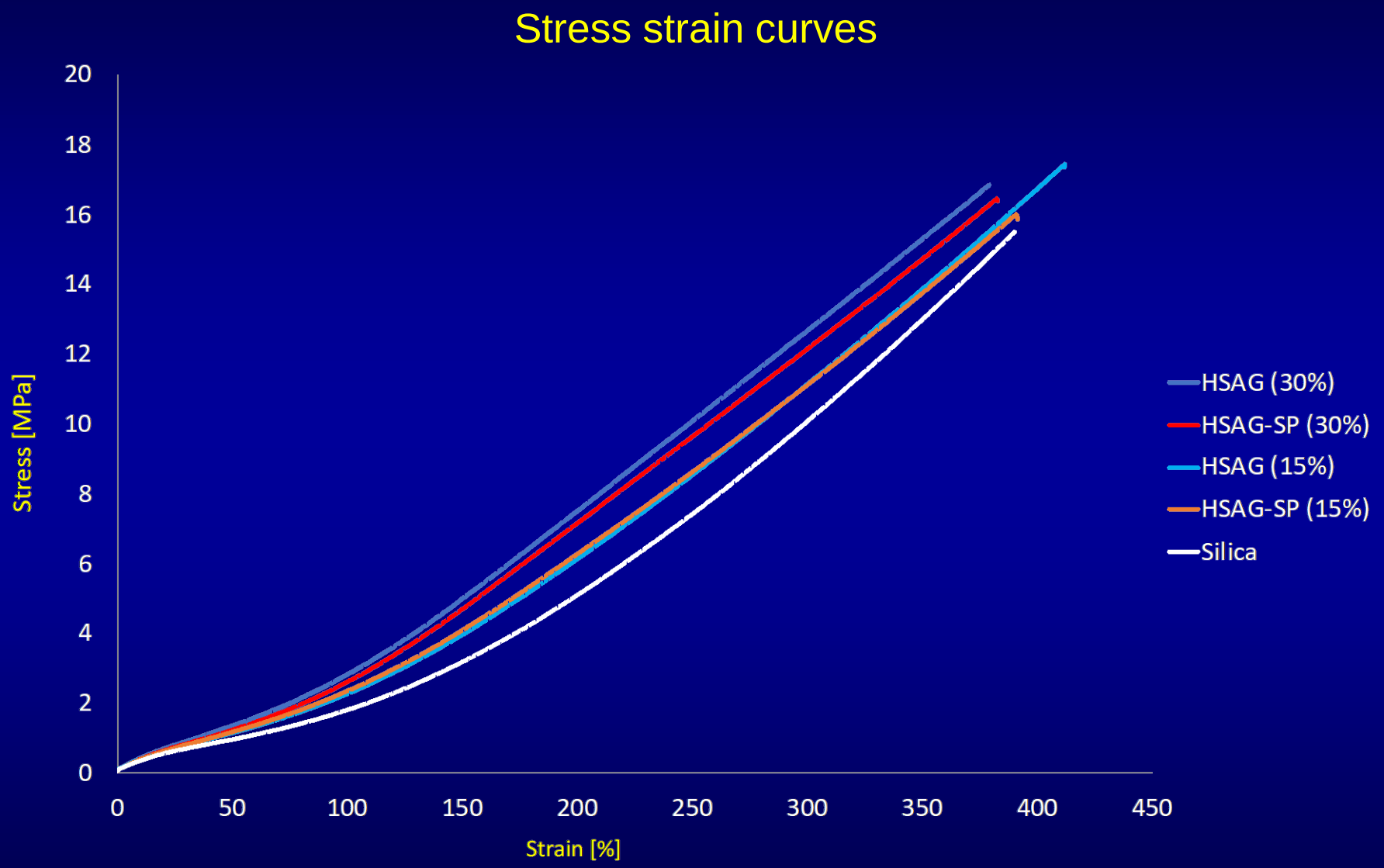


S-SBR / NR based compounds with silica and HSAG-SP

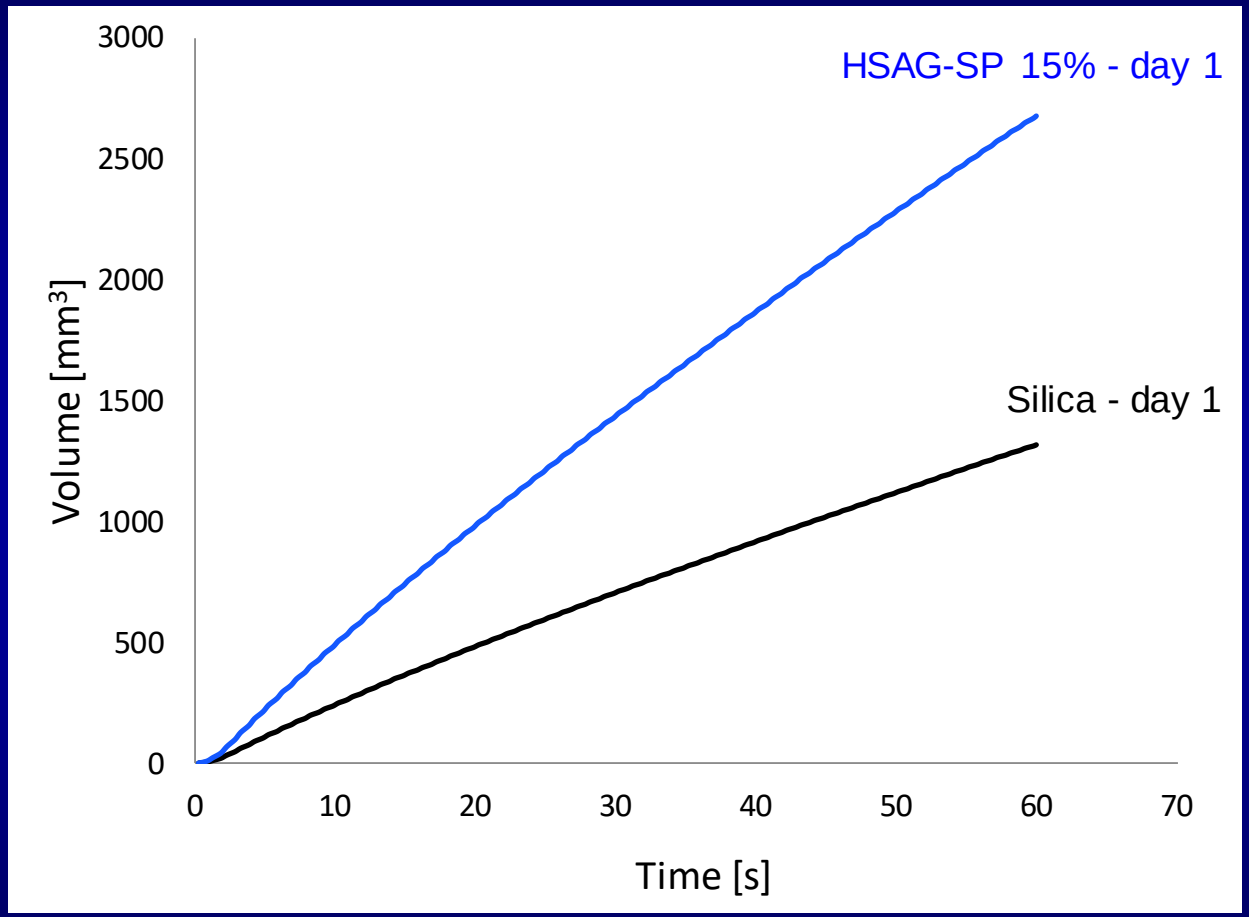
Dynamic-mechanical properties as a function of HSAG-SP content



S-SBR / NR based compounds with silica and HSAG



Rheo-vulkameter test



Rheo-vulkameter 78.90 Göttfert. Capillary: 20 mm length, 2 mm diameter

P: 130 bar, T: 100°C, pre-heating: 180 sec, injected for 60 sec

Rheo-vulkameter test

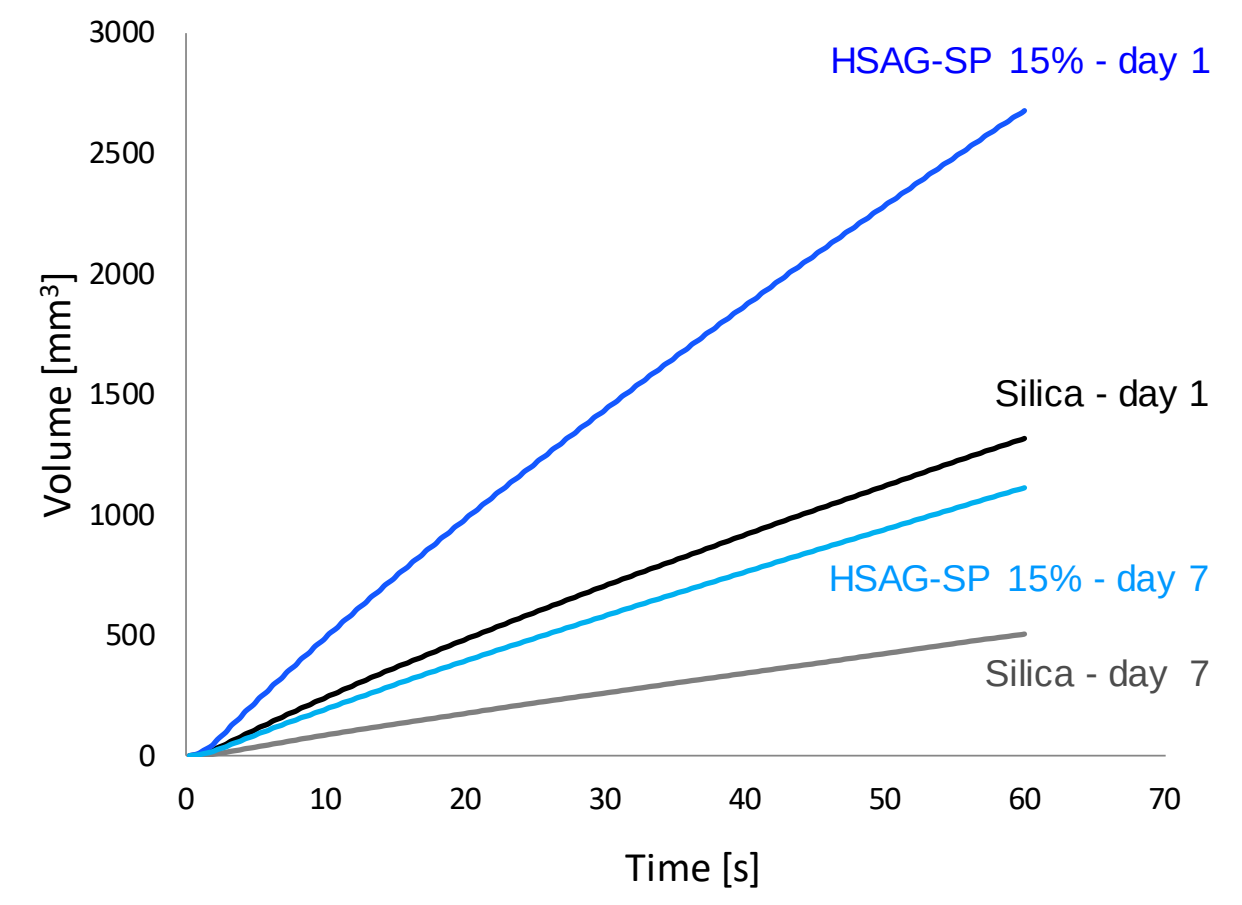
HSAG-SP
15%

Silica

Rheo-vulkameter 78.90 Göttfert. Capillary: 20 mm length, 2 mm diameter

P: 130 bar, T: 100°C, pre-heating: 180 sec, injected for 60 sec

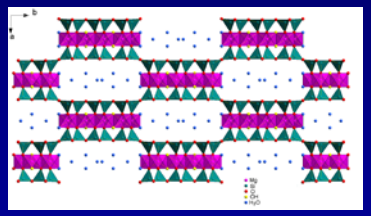
Rheo-vulkameter test

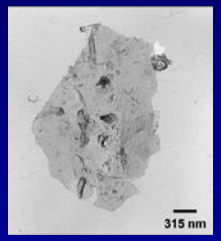


Rheo-vulkameter 78.90 Göttfert. Capillary: 20 mm length, 2 mm diameter

P: 130 bar, T: 100°C, pre-heating: 180 sec, injected for 60 sec

Conclusions





Larger static and dynamic-mechanical reinforcement

Equal or lower hysteresis

Better processability