Biobased materials for advanced rubber composites

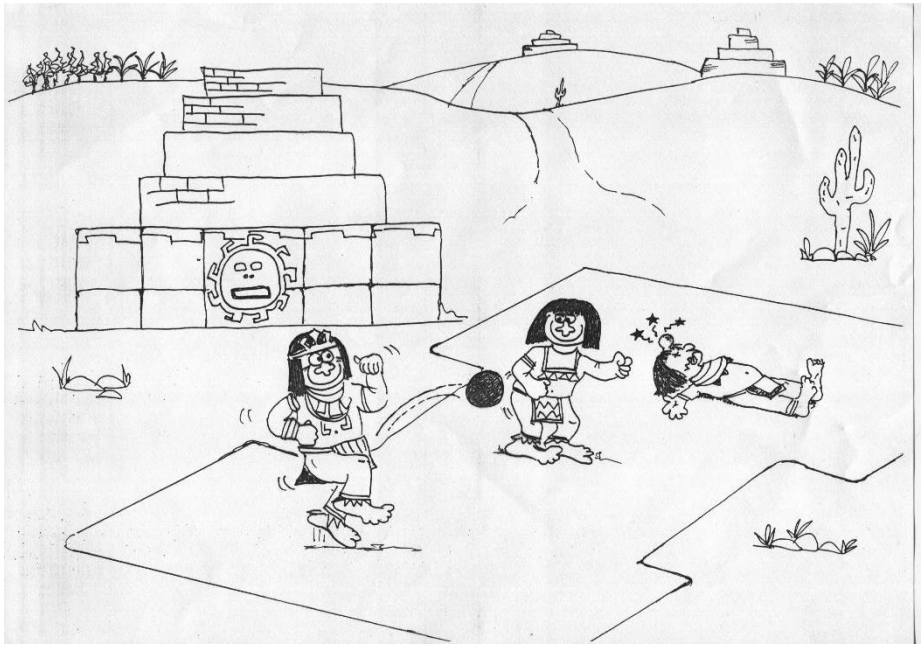
Maurizio Galimberti

Vincenzina Barbera, Andrea Bernardi, Valeria Cipolletti, Giulia Peli, Daniele Locatelli

Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “G. Natta”

Rubber and biosources

Ipomoea alba



Castilla elastica tree

Rubber processed in ancient Mesoamerica, MIT researchers find - MIT News Office

Rubber and biosources

Ipomoea alba

Castilla elastica tree

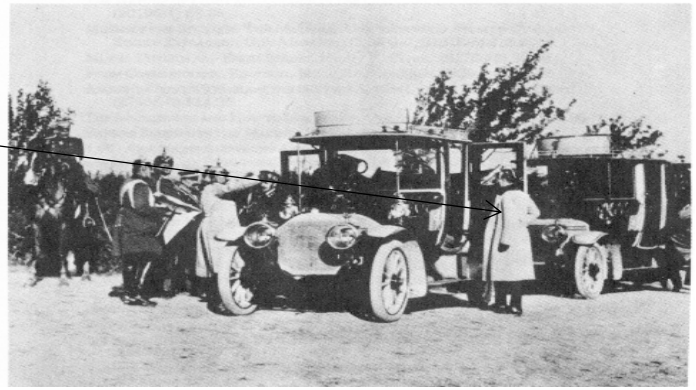
hevea brasiliensis

taraxacum kok-saghyz

partenium argentatum

From rubber to rubber goods

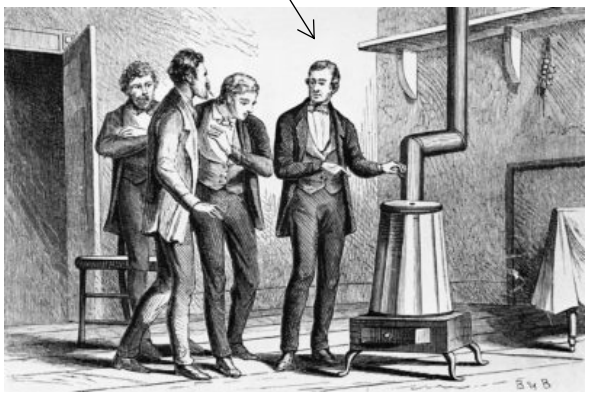
Emperor Wilhelm



Polymers: The Origins and Growth of a Science
Paperback – October 1, 1995
Herbert Morawetz

Reinforcement

Charles Goodyear



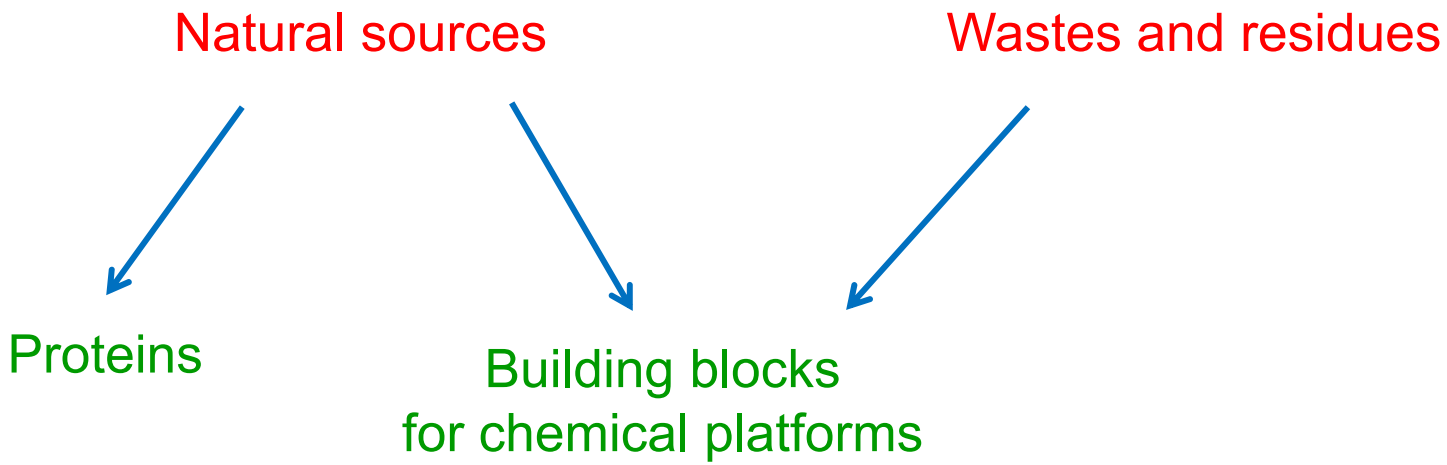
kimyasalgelismeler.com

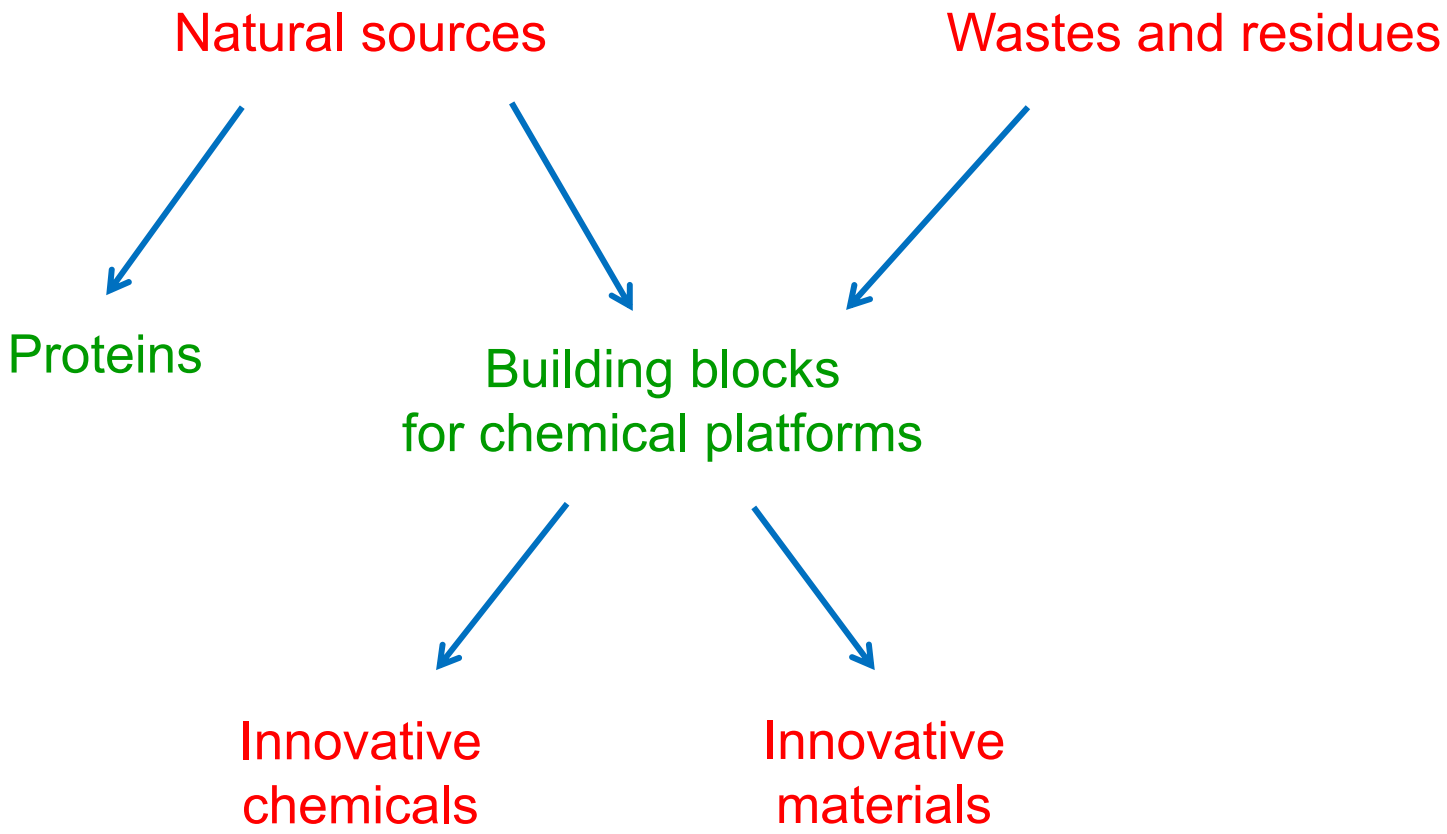
Crosslinking

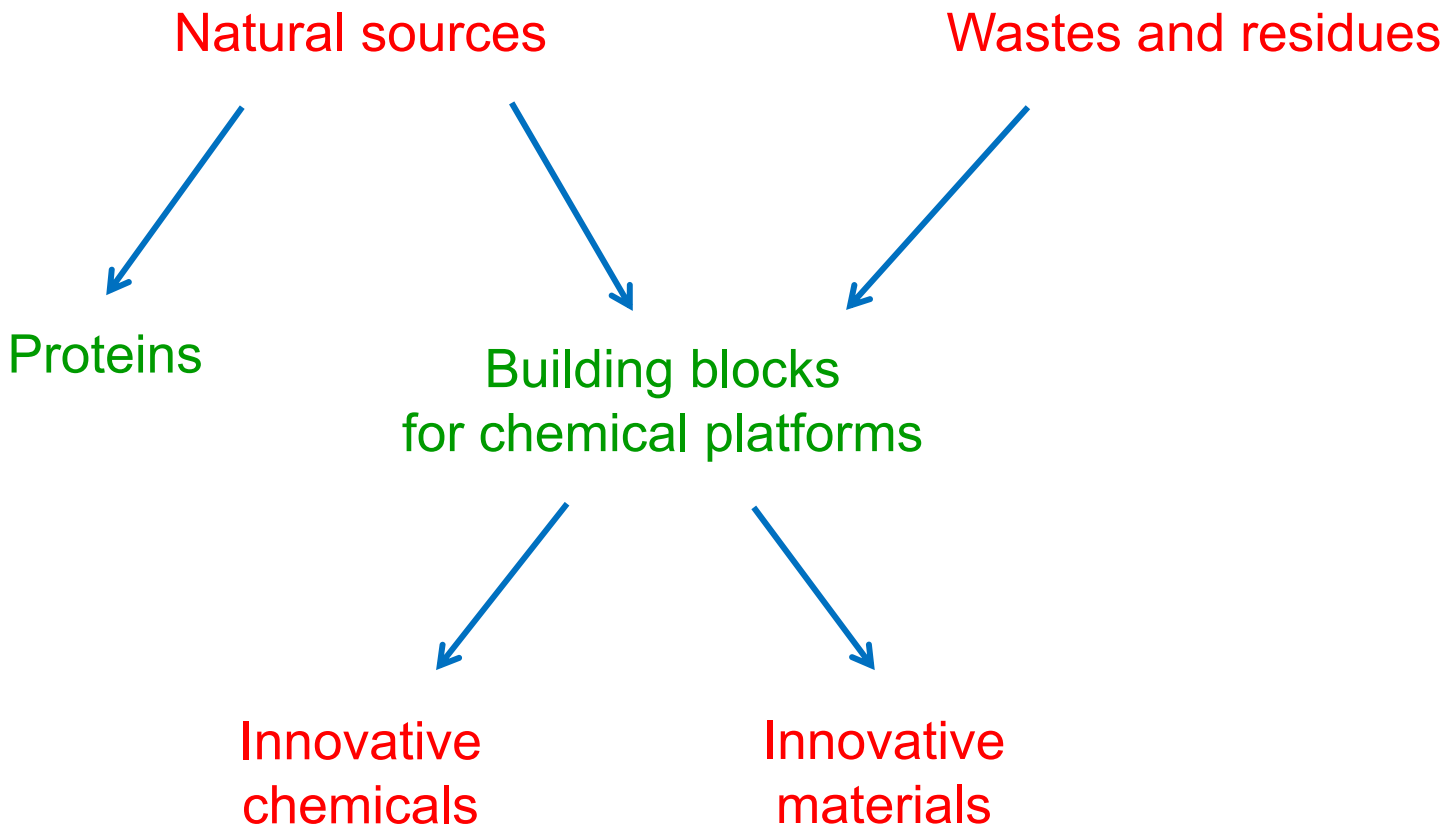
ISCaMaP

Innovative Sustainable Chemistry and Materials and Proteomics Group

Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “G. Natta”


Natural sources
Wastes and residues
Proteins
Building blocks
for chemical platforms


Natural sources
Wastes and residues
Proteins
Building blocks
for chemical platforms
Innovative
chemicals
Innovative
materials



☞ Chemicals, Additives, Modifiers, Polymers

Items of the presentation

- Vulcanization
  - Biosourced accelerator for guanidines replacement
- Reinforcement by nanometric fillers
  - Biobased chemical compatibilization
  - Biofiller

The DOE's Top Chemical Opportunities

Four Carbon 1,4-Diacids: Succinic, Fumaric and Malic

2,5-Furan dicarboxylic acid

3-Hydroxypropionic acid

Glucaric acid

Glycerol

Aspartic acid

Itaconic acid

3-Hydroxybutyrolactone

Sorbitol (Alcohol Sugar of Glucose)

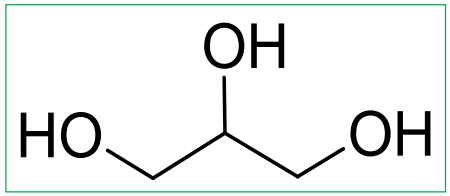
Xylitol/arabinitol (Sugar alcohols from xylose and arabinose)

Glutamic acid

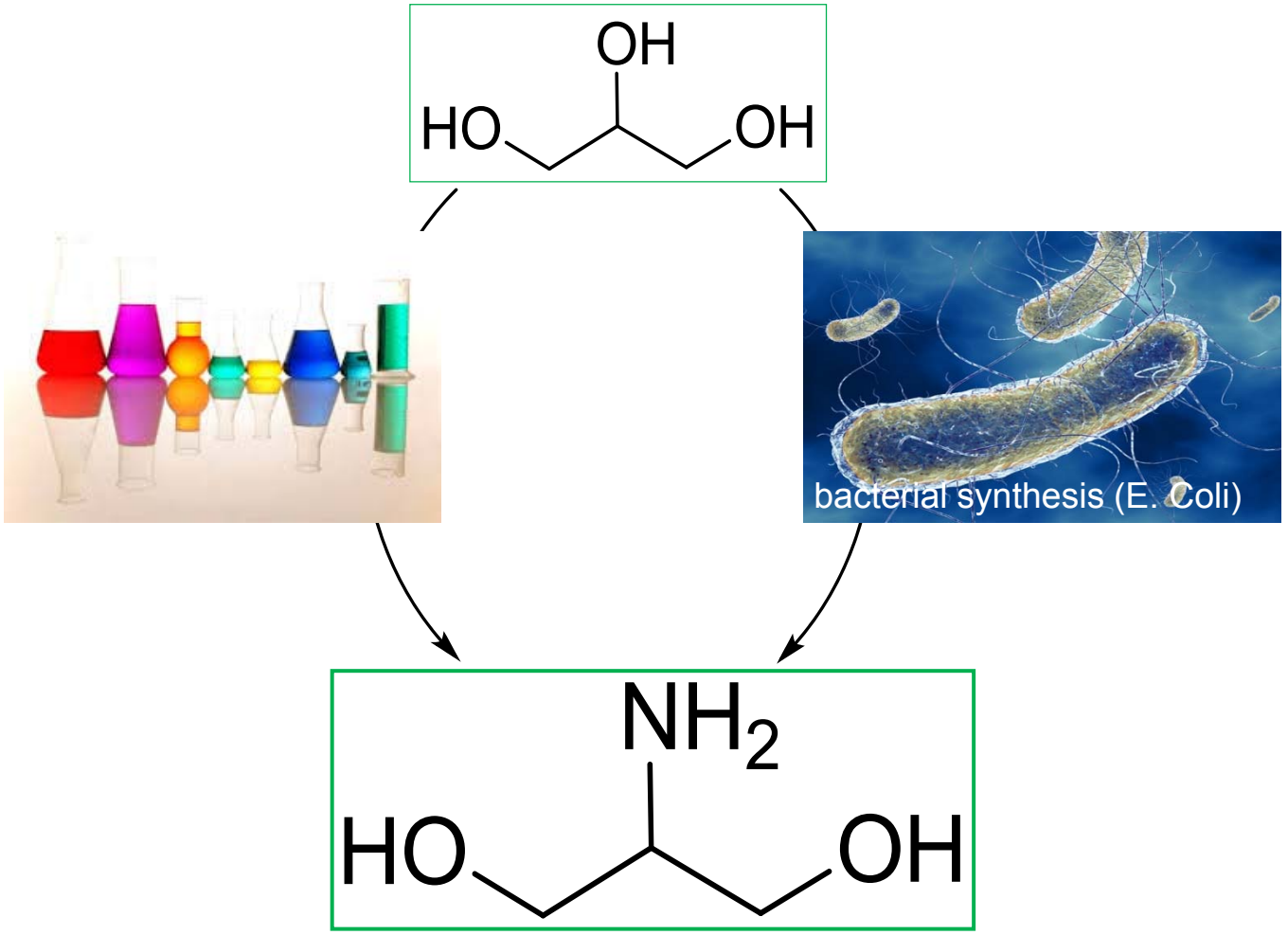
Levulinic acid

DOE = US Department of Energy

Selection of the building block: glycerol



Selection of the building block: serinol

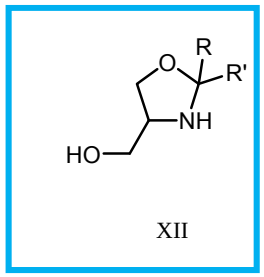


- Starting building block for many reaction pathways
- Chemoselectivity

Specific reactions of serinol with carbonyl compounds.

Without steric hindrance

and aromatic substituents

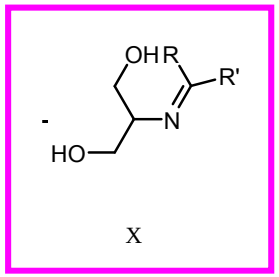


XII

Oxazolidines

With steric hindrance

and aromatic substituents



X

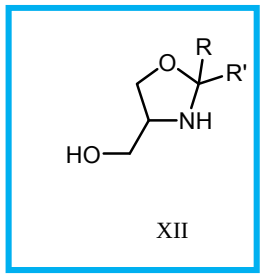
Imines

M. Galimberti, V. Barbera, G. Infortuna, V. Cipolletti, A. Citterio, S. Sun Proceedings of International Elastomer Conference Cleveland (OH), October 9-12, 2017
M. Galimberti, V. Barbera, S. Musto, G. Infortuna, V. Cipolletti, A. Citterio, S. Sun, Submitted to Rubber Chemistry and Technology, Frontiers Edition

Specific reactions of serinol with carbonyl compounds.

Without steric hindrance

and aromatic substituents

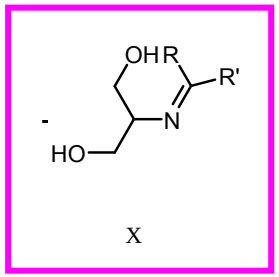


XII

Oxazolidines

With steric hindrance

and aromatic substituents



X

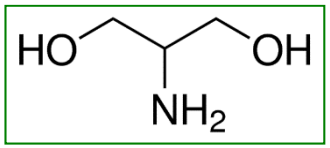
Imines

☞ Secondary accelerators for silica based compounds

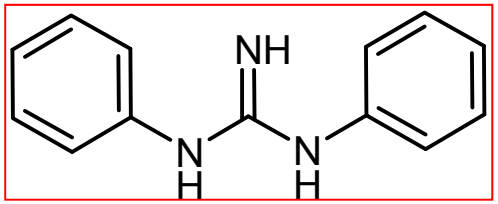
for DPG replacement

M. Galimberti, V. Barbera, G. Infortuna, V. Cipolletti, A. Citterio, S. Sun Proceedings of International Elastomer Conference Cleveland (OH), October 9-12, 2017
M. Galimberti, V. Barbera, S. Musto, G. Infortuna, V. Cipolletti, A. Citterio, S. Sun, Submitted to Rubber Chemistry and Technology, Frontiers Edition

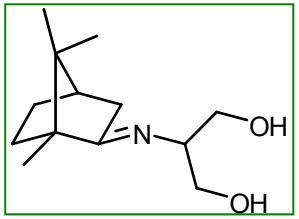
Serinol and serinol derivatives as secondary accelerators for silica based compounds



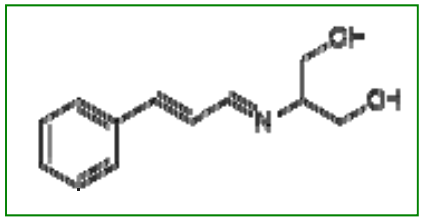
Serinol



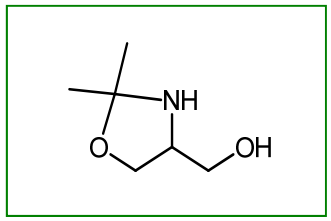
DPG



Serinol camphor imine



Serinol cinnamaldehyde imine

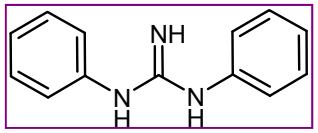


Serinol acetone oxazolidine

M. Galimberti, R. Sebastiano, V. Barbera, V. Cipolletti, G. Leonardi, S. Sun, L. Rossiello WO 2017/115253 A1

Serinol and serinol derivatives as secondary accelerators in silica based compounds

Ingredient	phr
S-SBR	96.3
NR	15
BR	15
Silica	65
Silane TESPT Si69	5.6
Oil MES	10
Stearic Acid	2
ZnO	2.5
6PPD	2
Sulphur	1.8
TBBS	1.2
Secondary accelerator	X

Secondary accelerator	X phr
	2.4
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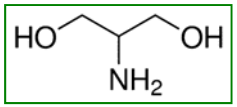
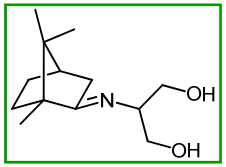
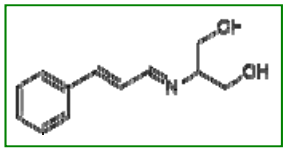
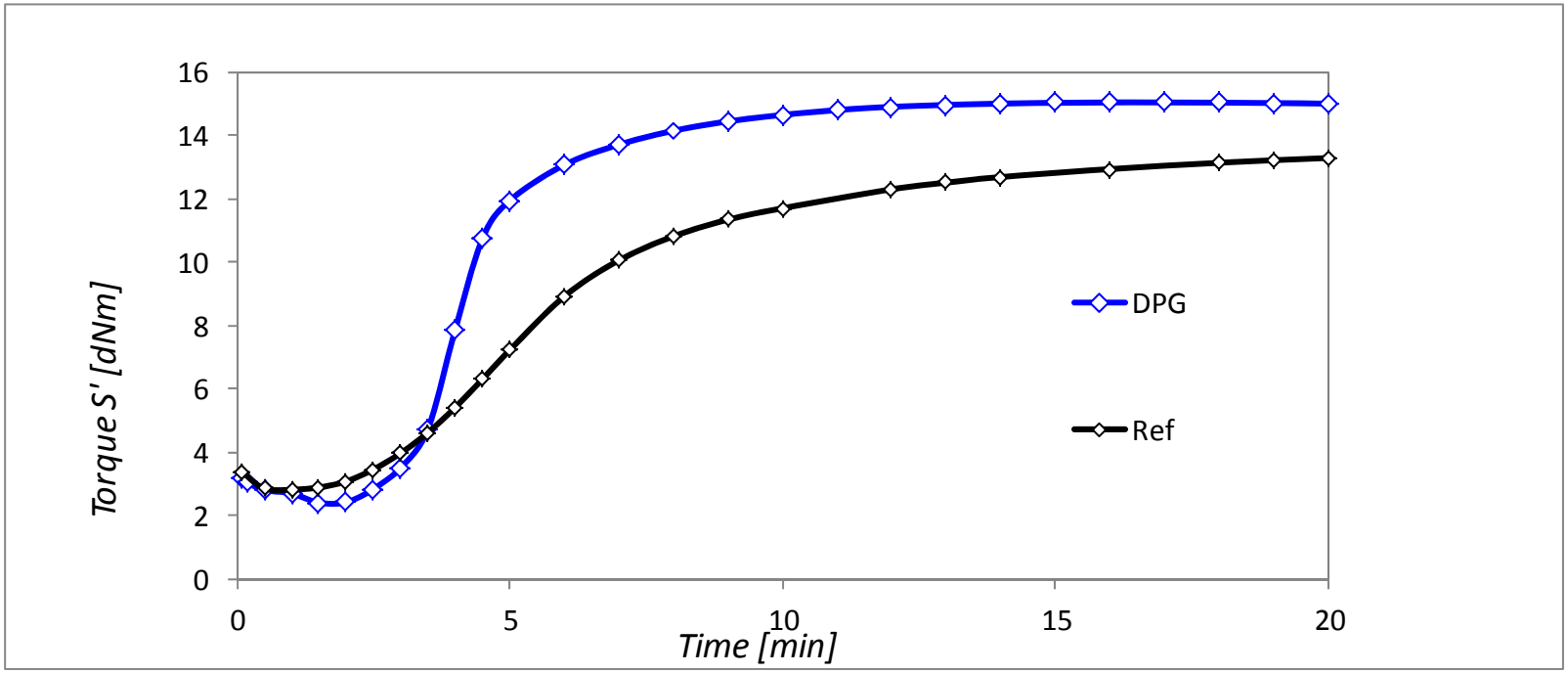
	0.83
or	
	2.04
or	
	1.87

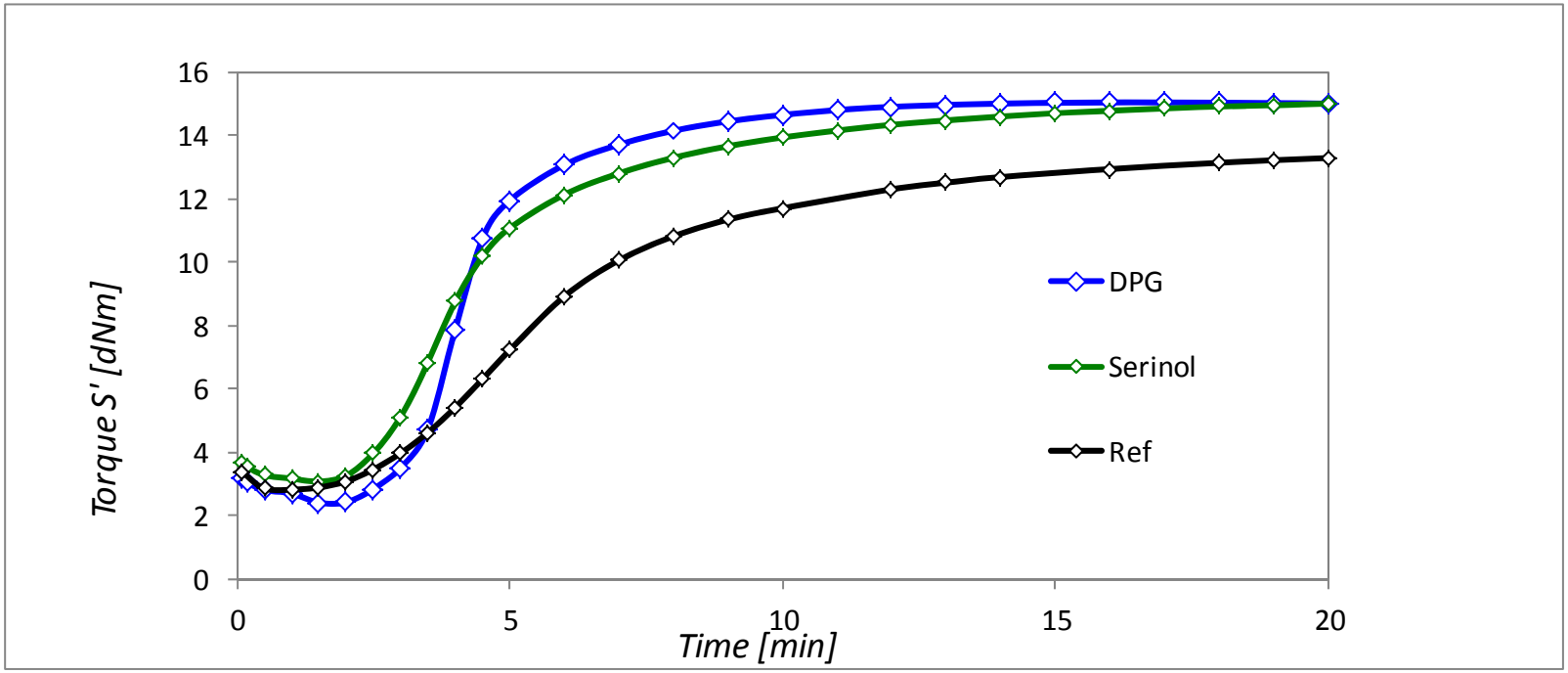
Secondary accelerators were used in equal molar amount

Curing at 170°C



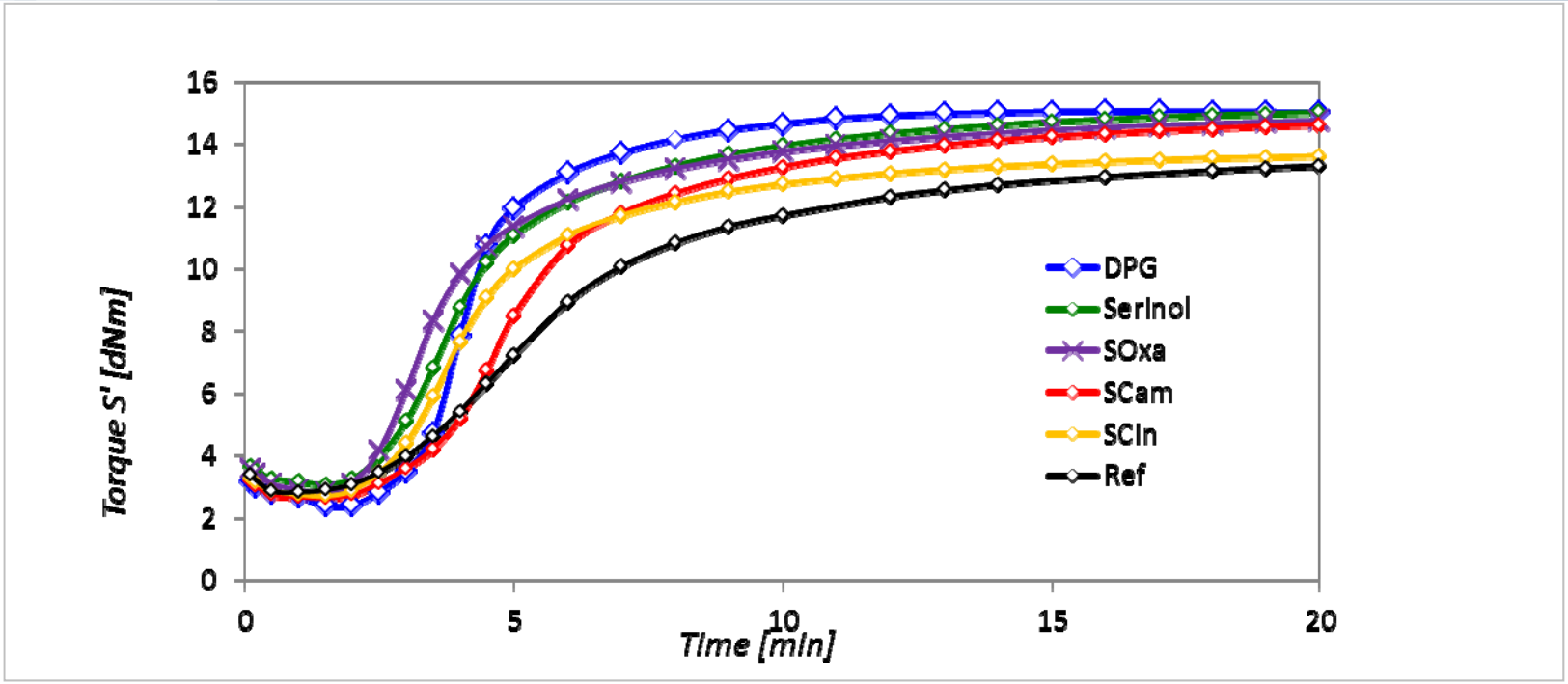
Secondary accelerator = DPG			
Parameter			
M_L	[dNm]	2.8	2.3
M_H	[dNm]	13.3	15.1
t_{s1}	[min]	2.8	2.9
t_{90}	[min]	11.5	7.1

Curing at 170°C



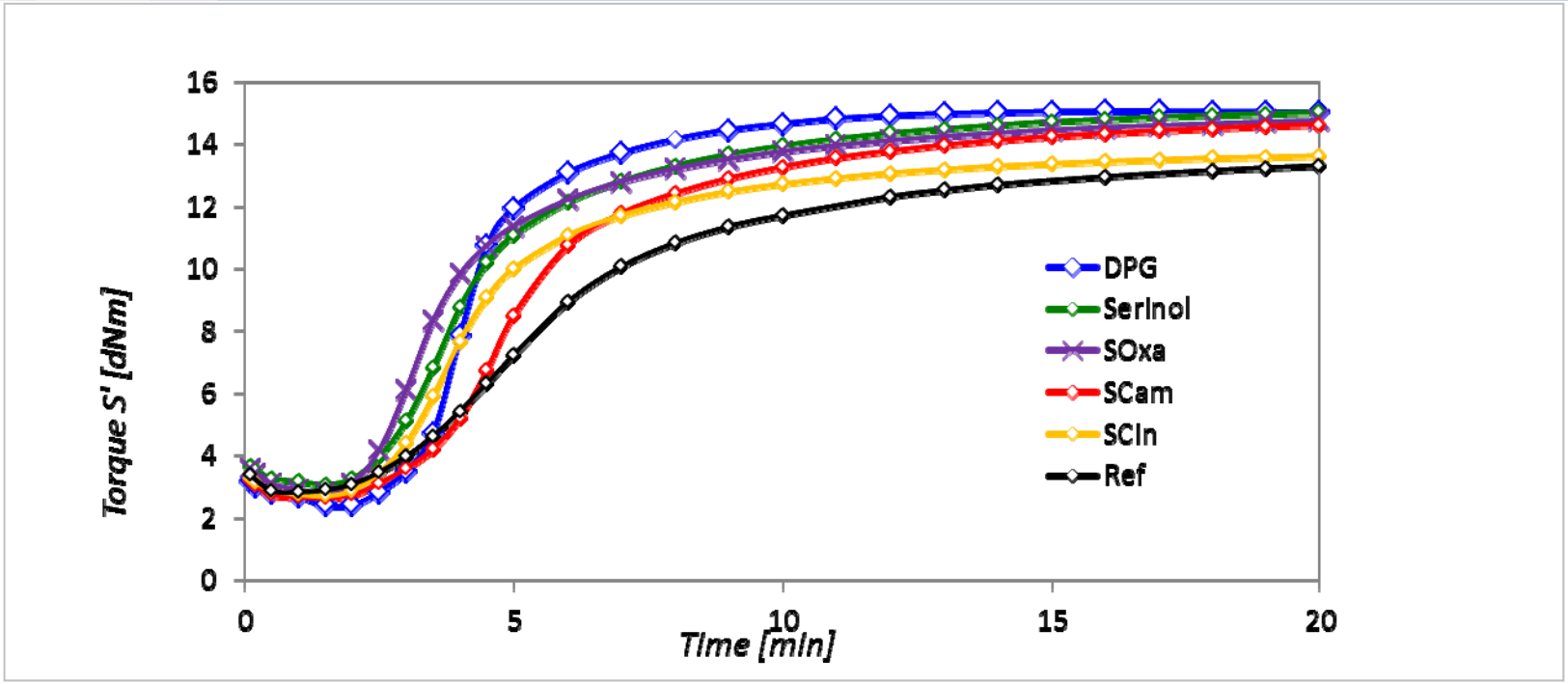
Secondary accelerator	=	DPG	Serinol
Parameter			
M_L [dNm]	2.8	2.3	3.1
M_H [dNm]	13.3	15.1	15.0
t_{s1} [min]	2.8	2.9	2.6
t_{90} [min]	11.5	7.1	9.5

Curing at 170°C



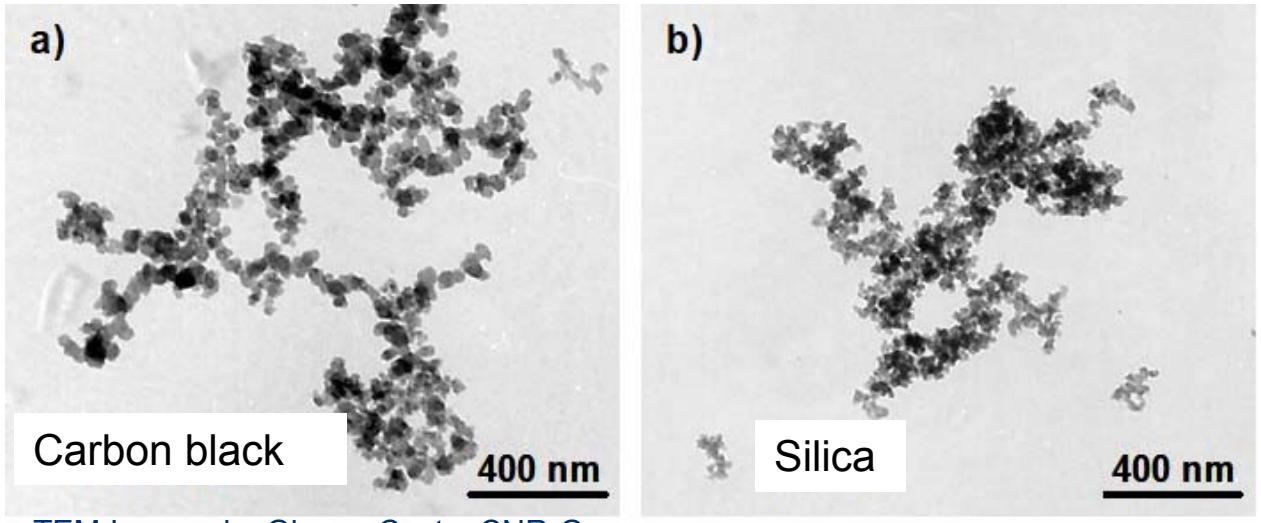
Secondary accelerator	=	DPG	Serinol	SCam	SCin	SOxa
Parameter						
M_L [dNm]	2.8	2.3	3.1	2.6	2.7	2.8
M_H [dNm]	13.3	15.1	15.0	14.6	13.6	14.8
t_{s1} [min]	2.8	2.9	2.6	3.0	2.7	2.4
t_{90} [min]	11.5	7.1	9.5	10.5	9.2	9.2

Curing at 170°C and compound properties



- Tuning of crosslinking kinetics
- Similar, lower dissipation of energy
- No leakage of accelerator from rubber compound

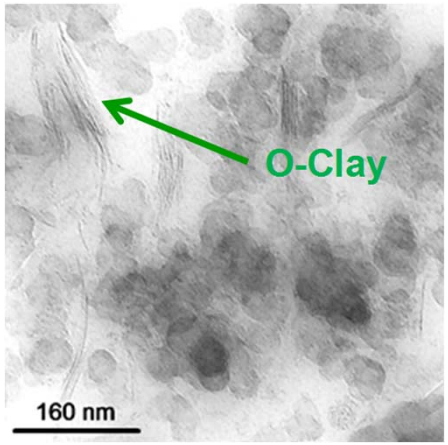
Nanostructured fillers for rubber reinforcement

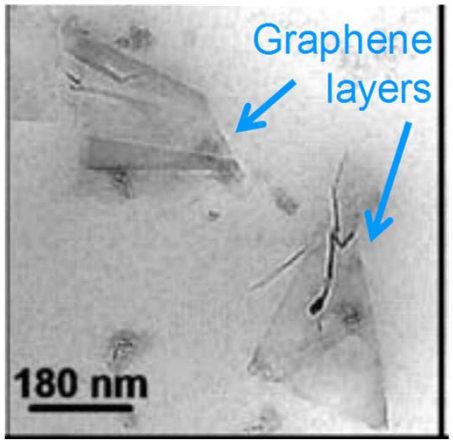


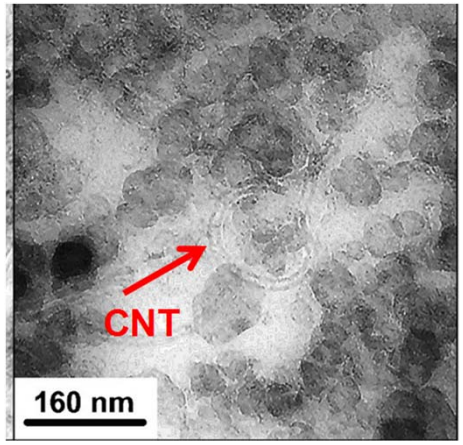
TEM Images by Gianna Costa, CNR-Genova

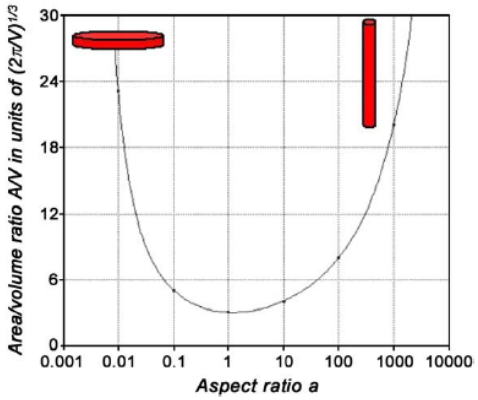
- Surface area
- Structure
- Surface activity
- Aspect ratio? ⟶ f

Nano fillers for rubber reinforcement









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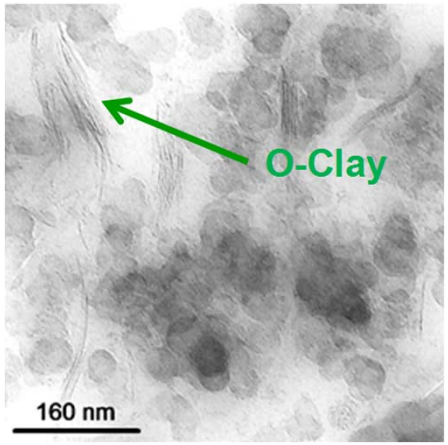
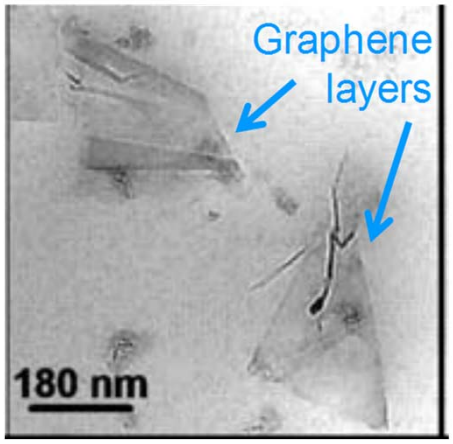
Galimberti M., Coombs M., Riccio P., Ricco` T., Passera S., Pandini S., Conzatti L., Ravasio A., Tritto I., Macromol. Mater. Eng., 298 (2012), 241-251

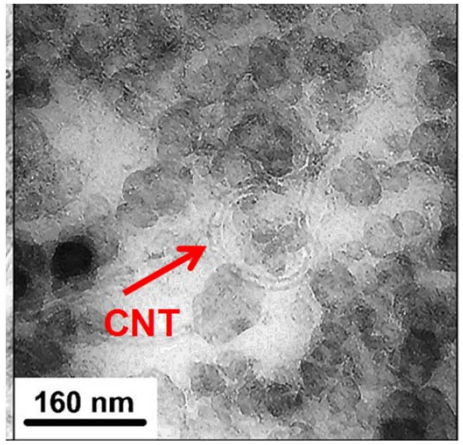
Galimberti M., Coombs M., Cipolletti V., Riccio P., Ricco` T., Pandini S., Conzatti L., Applied Clay Science 65–66 (2012) 57–66.

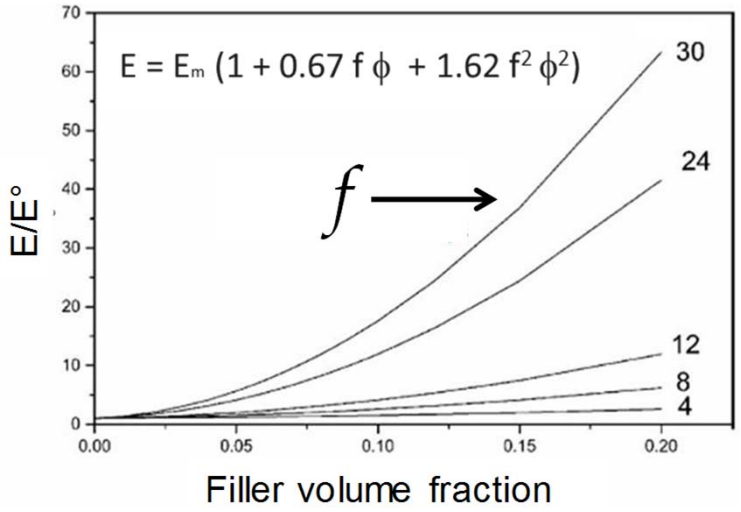
Galimberti M., V. Kumar, M. Coombs, V. Cipolletti, S. Agnelli, S. Pandini, L. Conzatti, RCT 87(2) (2014) 197-218

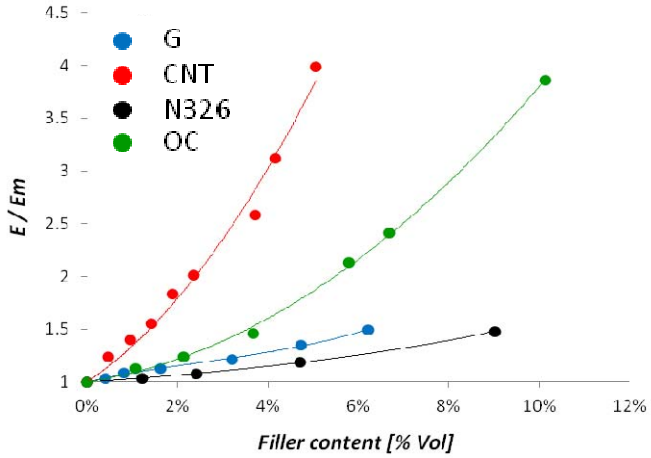
Nano fillers for rubber reinforcement









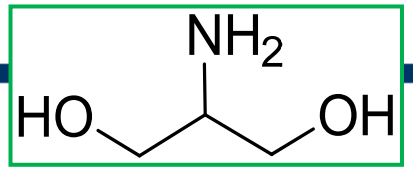


Galimberti M., Coombs M., Riccio P., Ricco` T., Passera S., Pandini S., Conzatti L., Ravasio A., Tritto I., Macromol. Mater. Eng., 298 (2012), 241-251

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

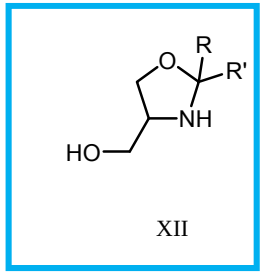
Galimberti M., V. Kumar, M. Coombs, V. Cipolletti, S. Agnelli, S. Pandini, L. Conzatti, RCT 87(2) (2014) 197-218

Reaction of serinol with carbonyl compounds.



Without steric hindrance

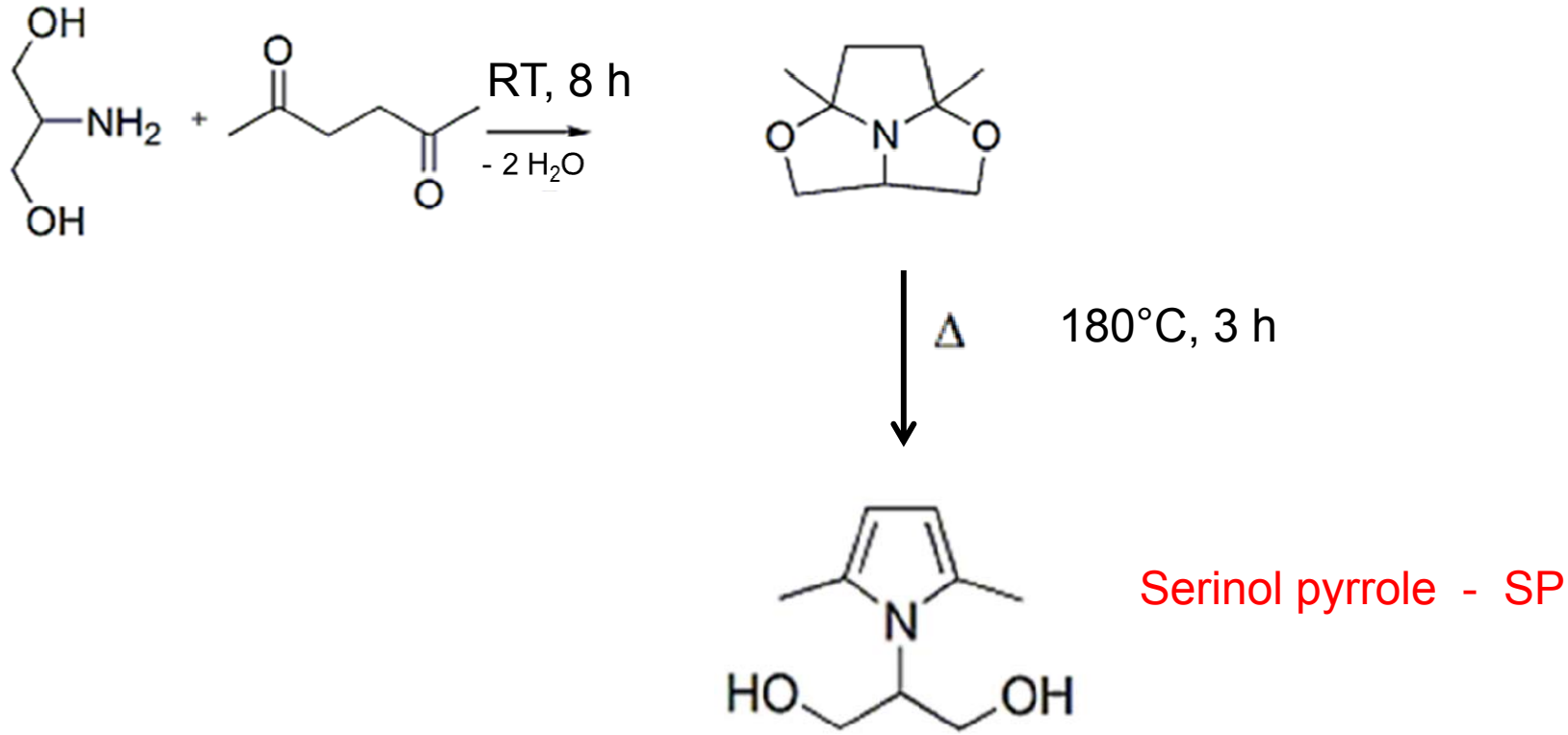
and aromatic substituents



XII

Oxazolidines

Reaction of serinol with dicarbonyl compound



Serinol pyrrole - SP

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

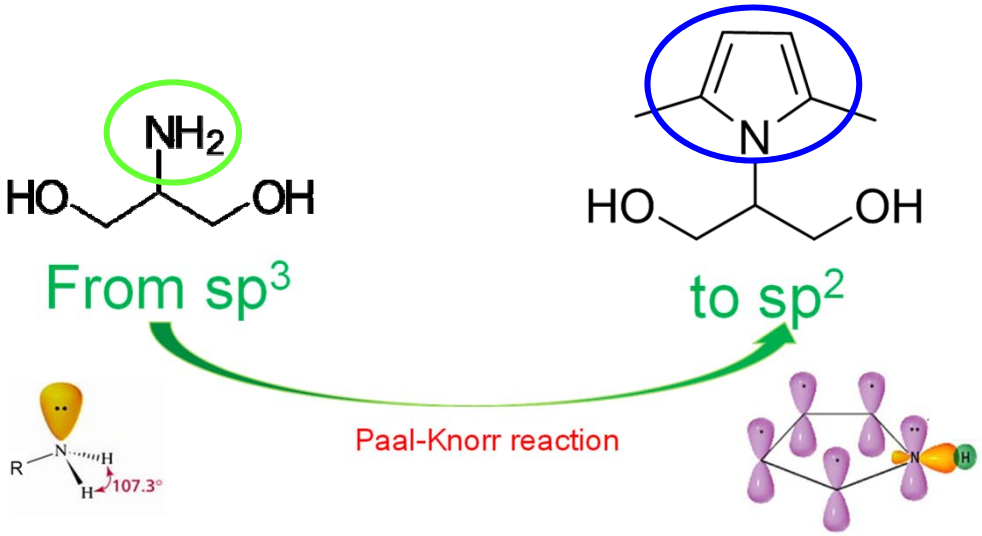
V. Barbera, A.Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U.Shisodia, A.M. Valerio *WO 2015 189411 A1*

M. Galimberti, V. Barbera, A. Citterio, R. Sebastiano, A. Truscello, A. M. Valerio, L. Conzatti, R. Mendichi, *Polymer*, vol 63, 20 April 2015, Pages 62–70

M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini,, *RSC Adv.*, 2015, *5*, 81142-81152 DOI: 10.1039/C5RA11387C

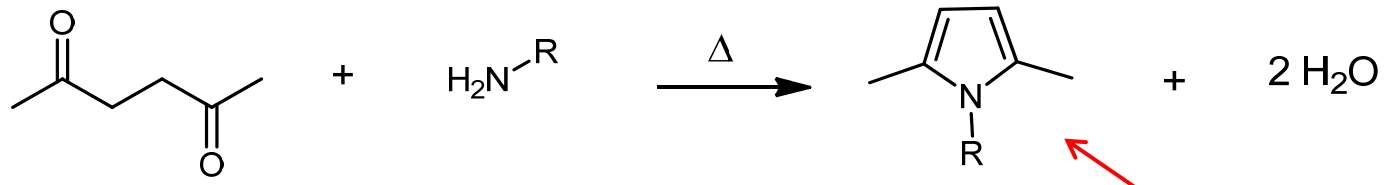
V. Barbera, S. Musto, A. Citterio, L. Conzatti, M. Galimberti,, *eXPRESS Polymer Letters* 2016, *10* (7) 548–558

Neat synthesis of Serinol pyrrole



- Yield: at least 96%
- Atom efficiency: 85%
- Easy procedure
- No solvent
- By product: H_2O

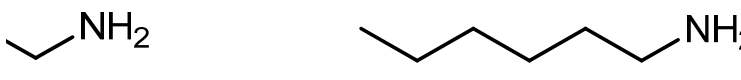
Pyrrole compounds (PyC) from neat Paal Knorr reaction



Same reaction conditions used for SP

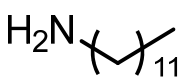
PyC

Yield %



80

75



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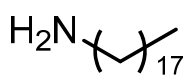

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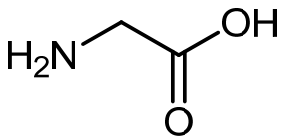

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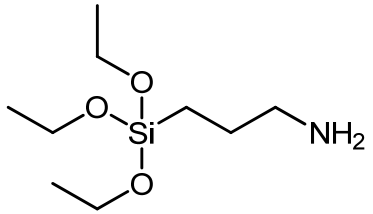
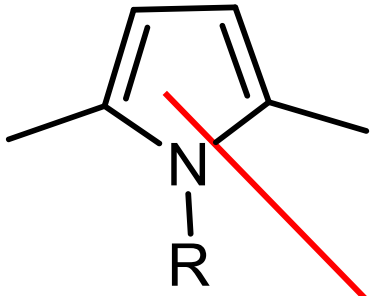


70

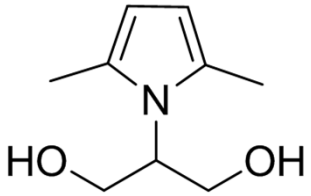
V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270



Functionalization

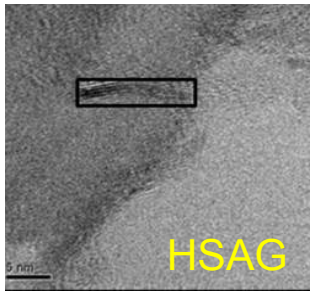
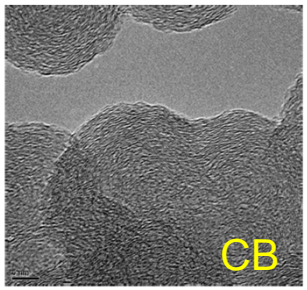
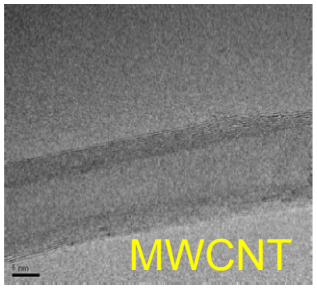
of sp^2 carbon allotropes (CA)

CA-SP Adducts - Yield of functionalization*



Thermal treatment

SP = 5 phc; 150°C, 2 h

	High surface area graphite	Carbon black	Carbon nanotubes
			
BET Surface area: [m^2/g]	300	77	275
Functionalization Yield(%)*:	96	82	92

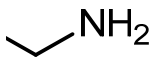
$$* \text{ Functionalization Yield } (\%) = 100 * \frac{\text{SP mass \% in (CA–SP adduct) after acetone washing}}{\text{SP mass \% in (CA–SP adduct) before acetone washing}}$$

from TGA

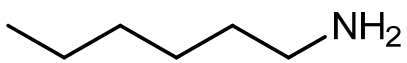
HSAG from Asbury, CB from Cabot, CNT from Nanocyl

HSAG / PyC adducts

Functionalization Yield %



73



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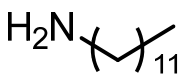

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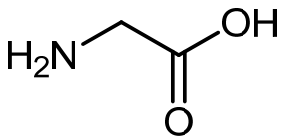
98



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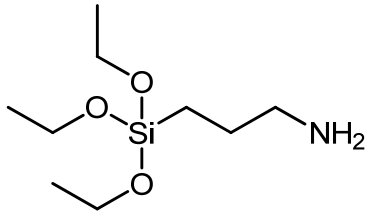

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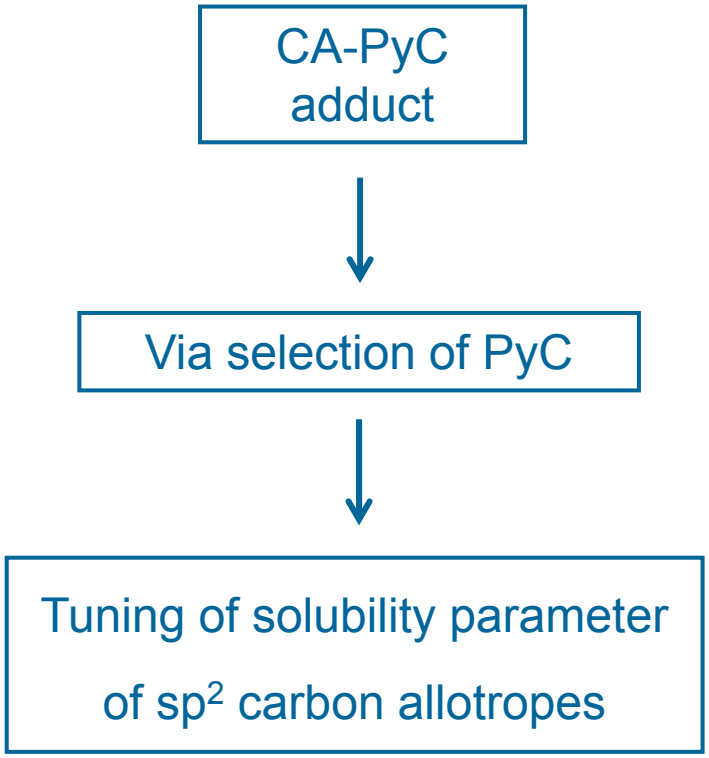
Tuning of solubility parameter of sp^2 carbon allotropes



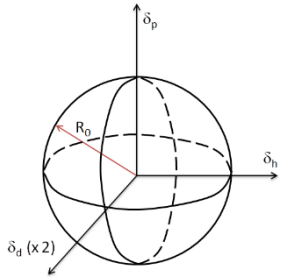
CA / PyC adducts - Tuning of solubility parameters

Experimental determination

Suspensions
in solvents
with different δ

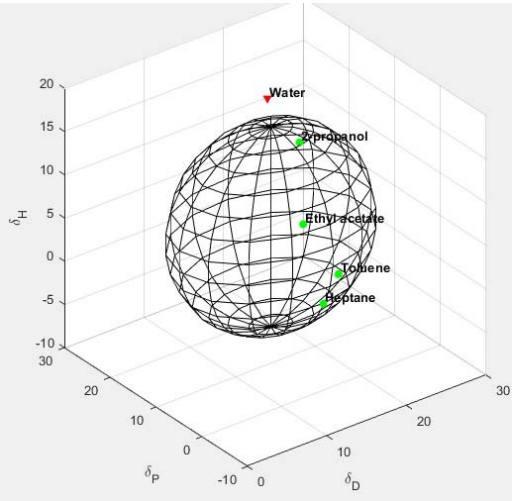
Theoretical predictions

Computational model:
Hansen solubility parameters

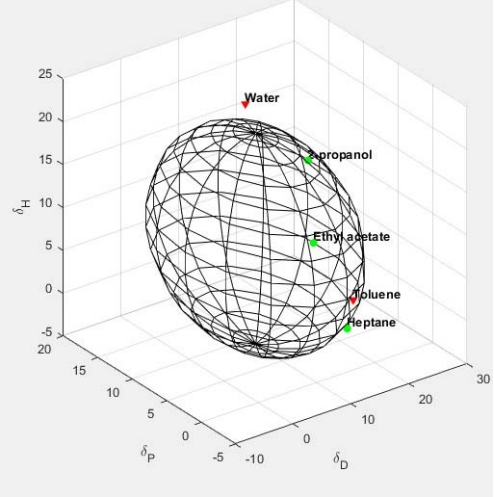


Evaluation of solubility parameters of HSAG-PyC - Hansen sphere

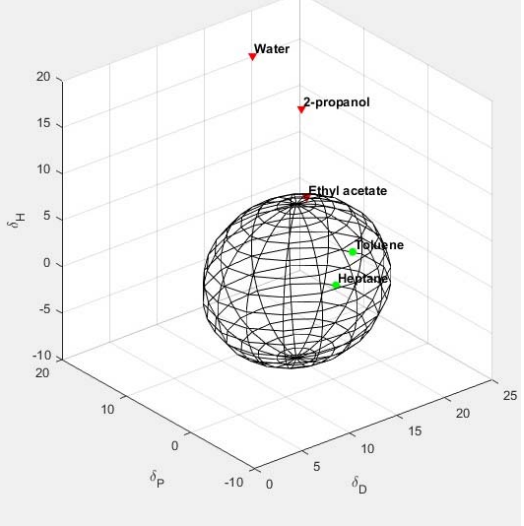
HSAG-TMP



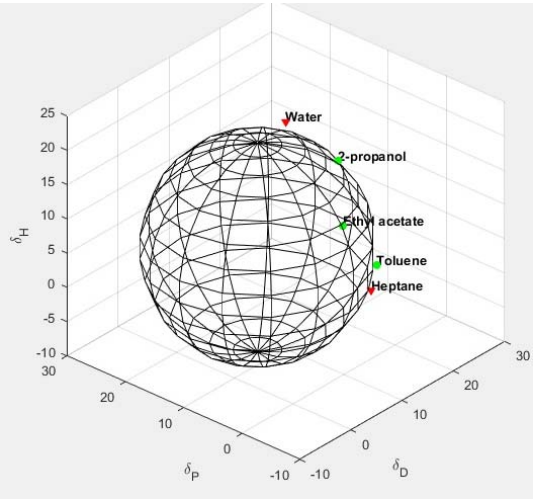
HSAG-DDcP



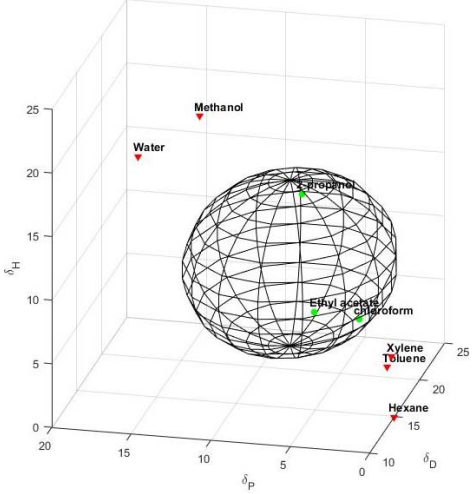
HSAG-APTESP

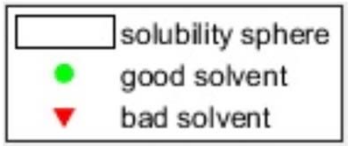


HSAG-GlyP



HSAG-SP





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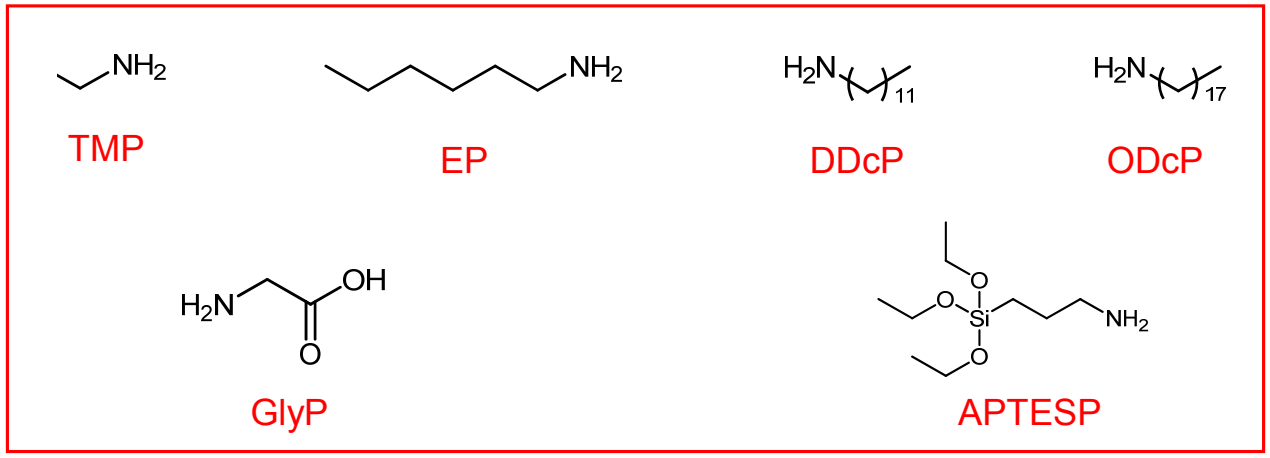
Evaluation of solubility parameters of HSAG-PyC - δ values

Sample	δ_D	δ_P	δ_H	Radius
HSAG	17.8	3.1	5.7	1.0
HSAG-TMP	14.6	10.3	5.6	11.6
HSAG-DDcP	8.5	7.5	8.3	12.3
HSAG-APTESP	12.7	2.3	0.5	8.3
HSAG-SP	12.8	2.0	8.9	13.8
HSAG-GlyP	6.9	12.1	5.3	15.3

Amount of PyC on HSAG: about 5% mol



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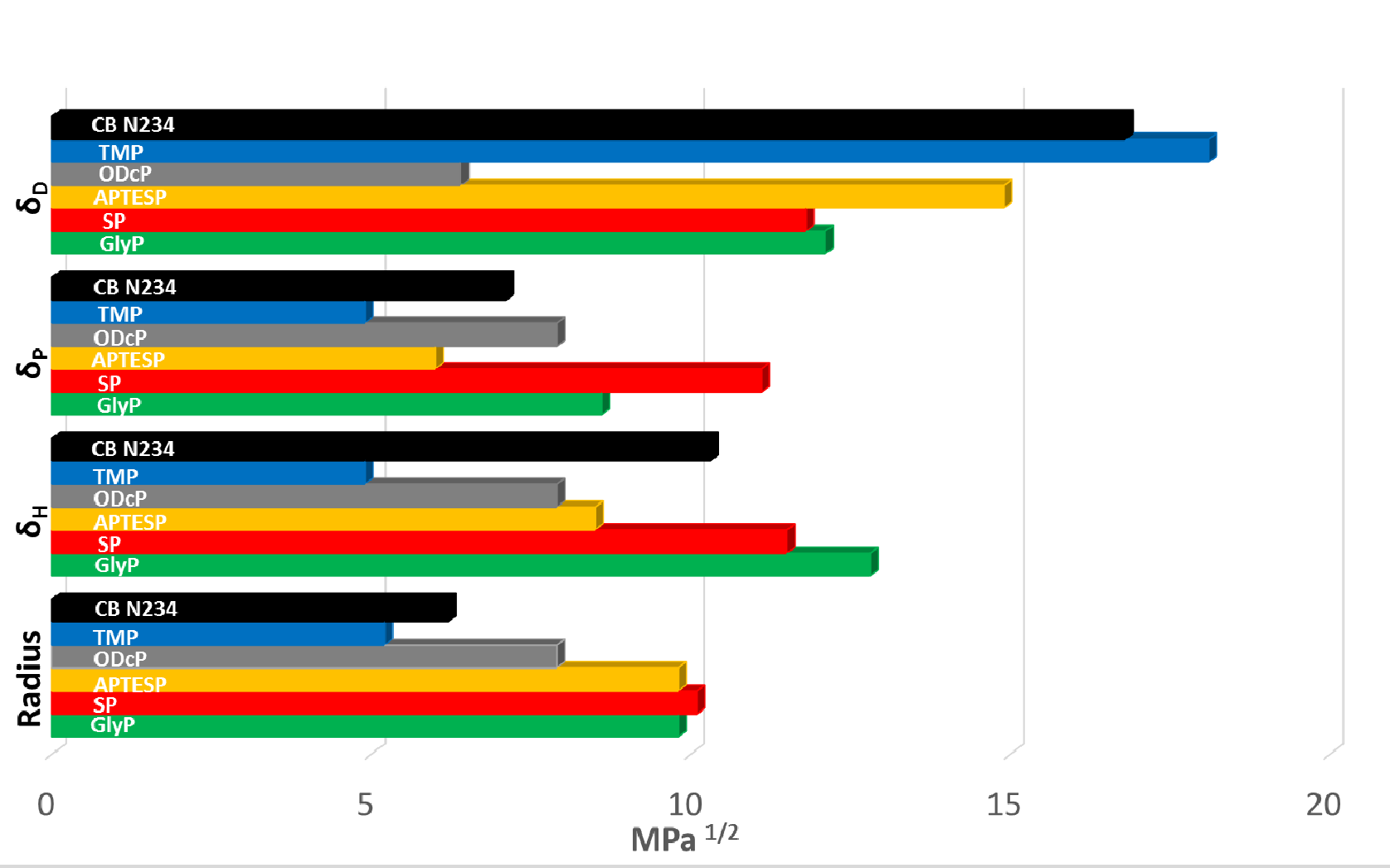
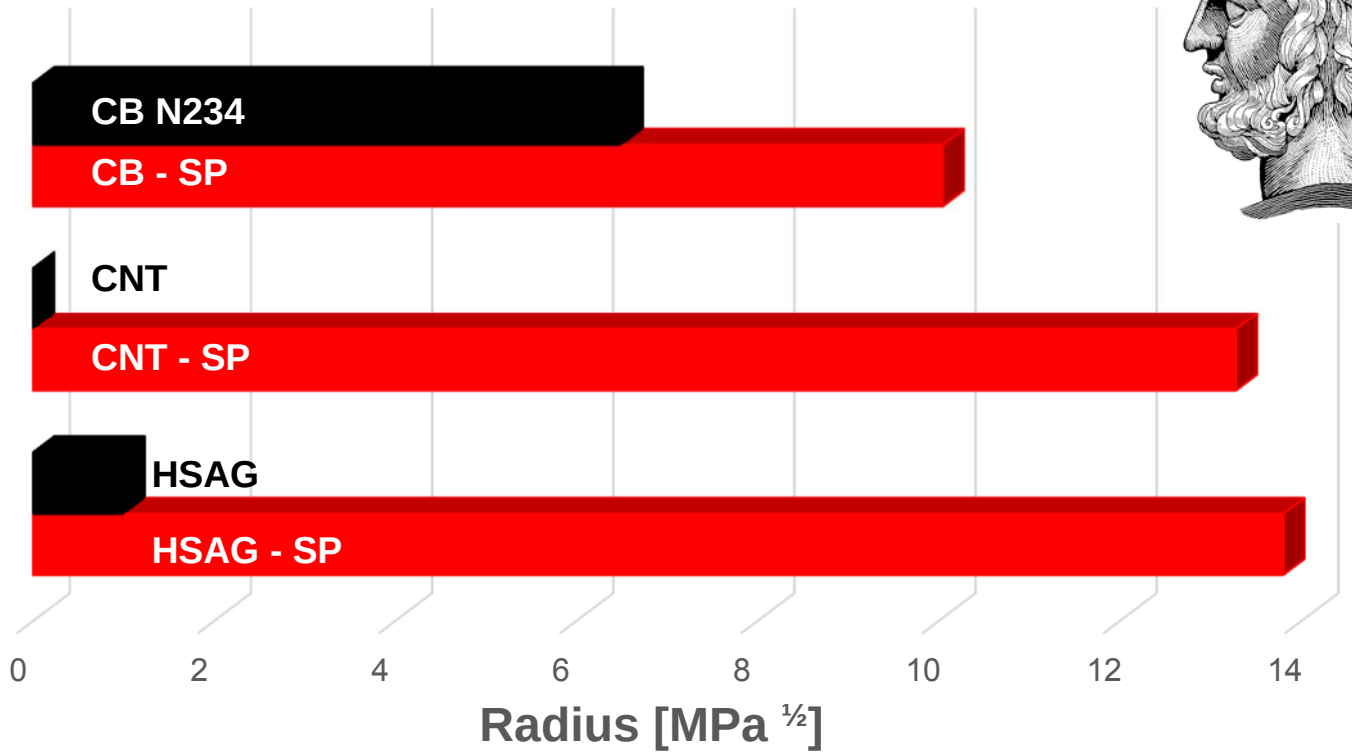
Evaluation of solubility parameters of CB-PyC - comparison



Amount of PyC on CB: 10 mass%

Evaluation of solubility parameters of CA-SP - Radius comparison



(*) Amount of SP on CA: 10 mass%

NR/HSAG composites - Electrical conductivity

NR latex dispersion of HSAG

↓

Addition of vulcanizers via melt blending

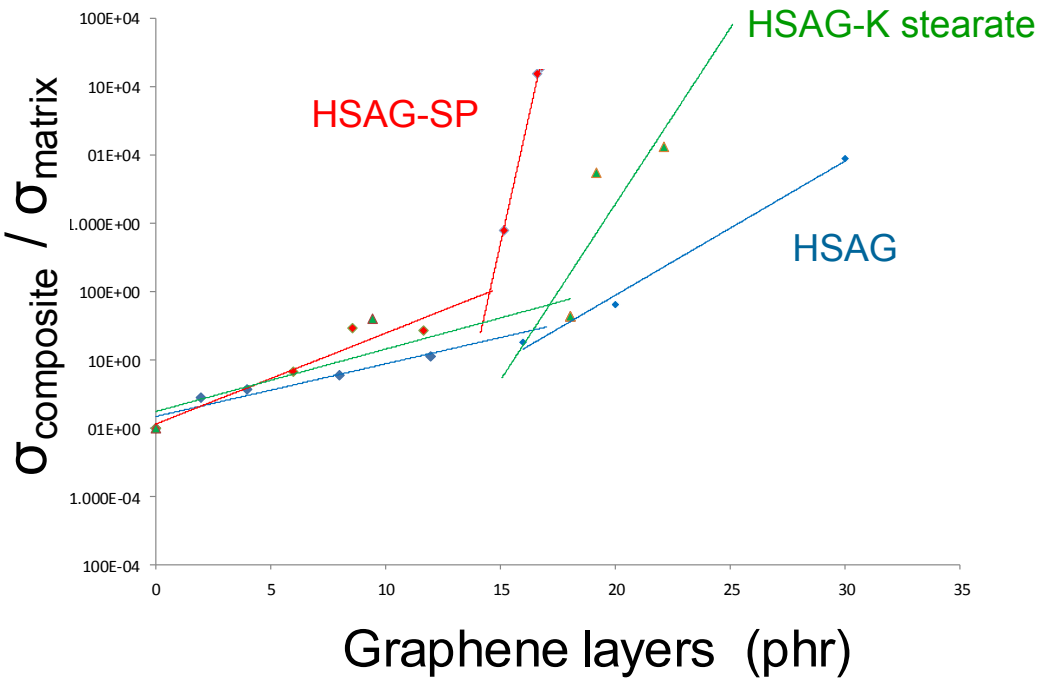
↓

Vulcanization

↓

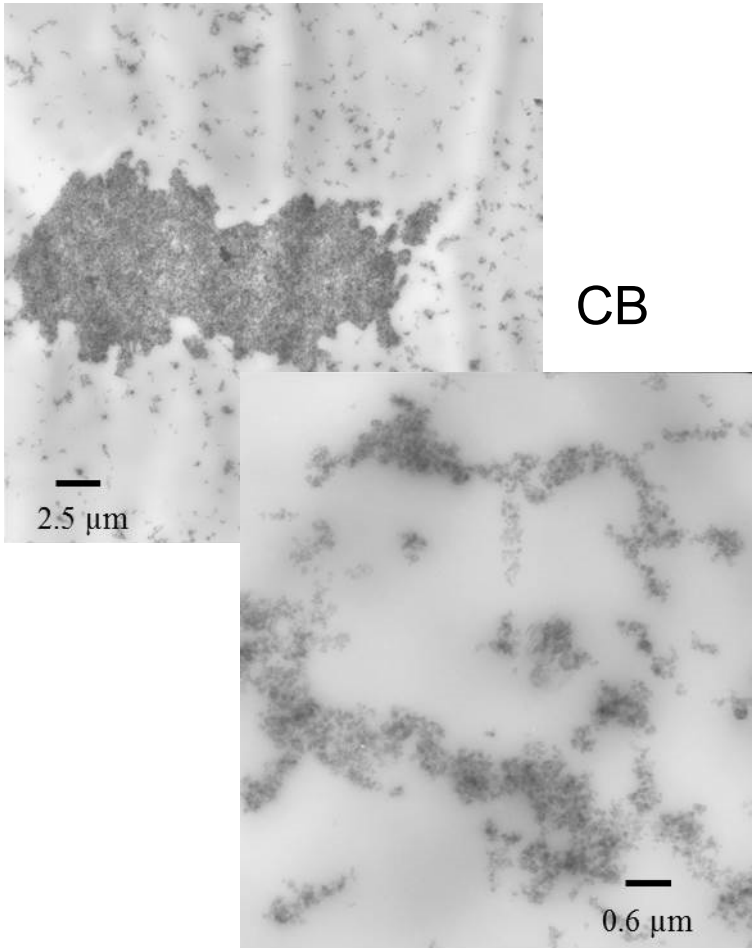
Electrical conductivity

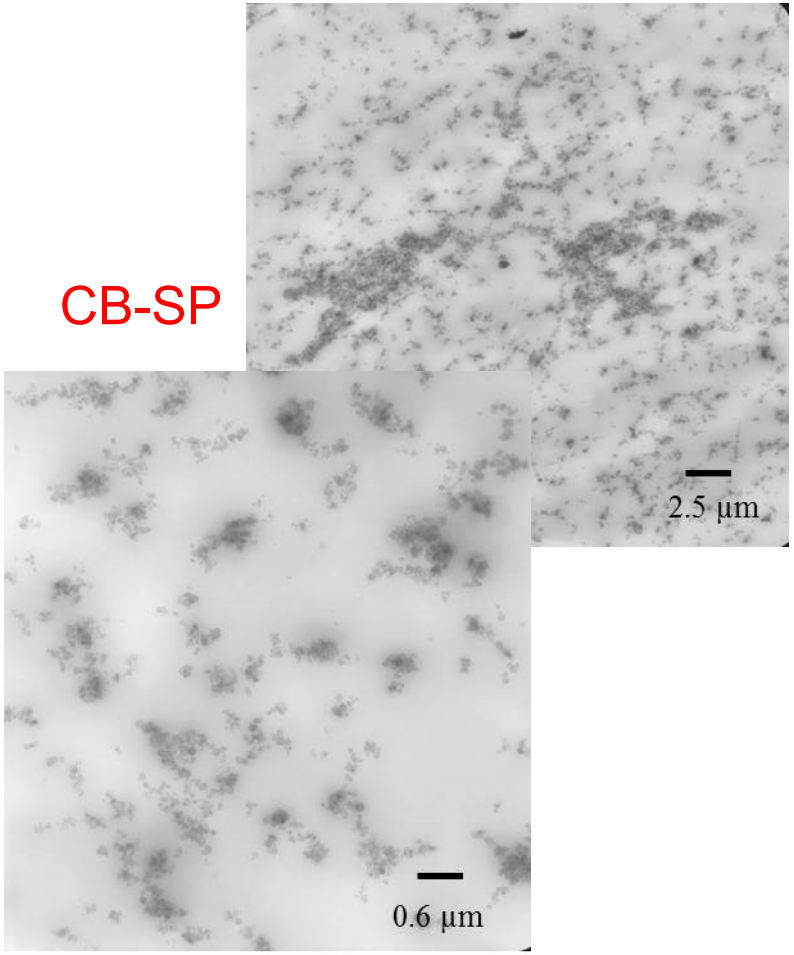
Electrical conductivity



Composites form NR latex dispersions of CB-SP adducts

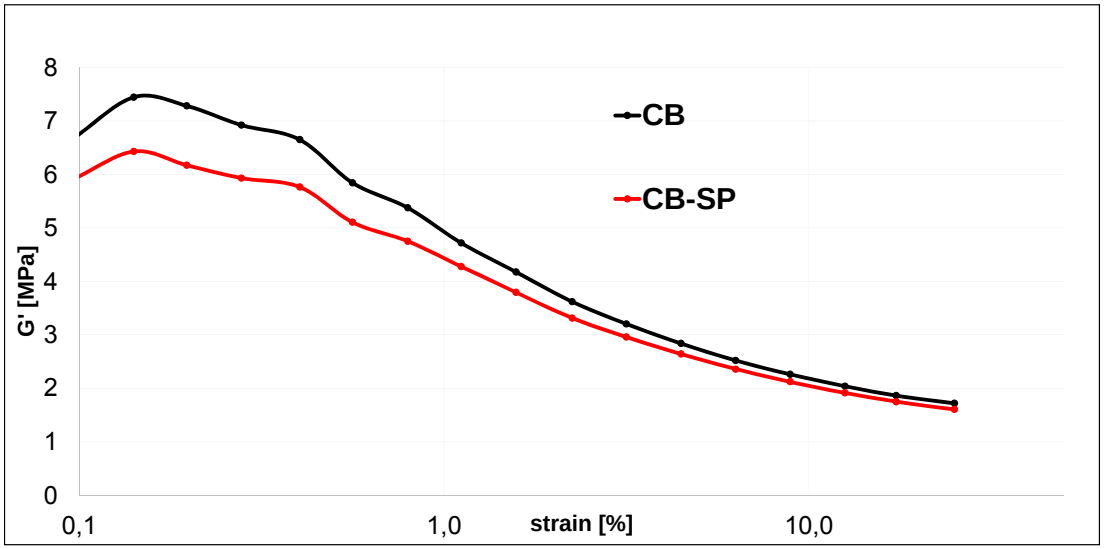
TEM





NR based compounds with CB-SP

G’ vs strain

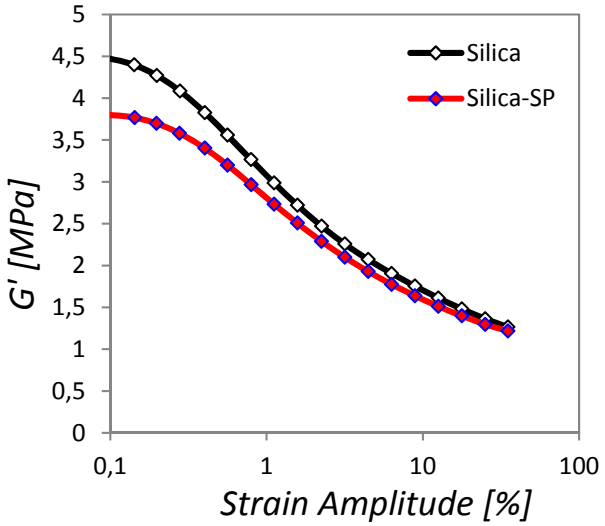


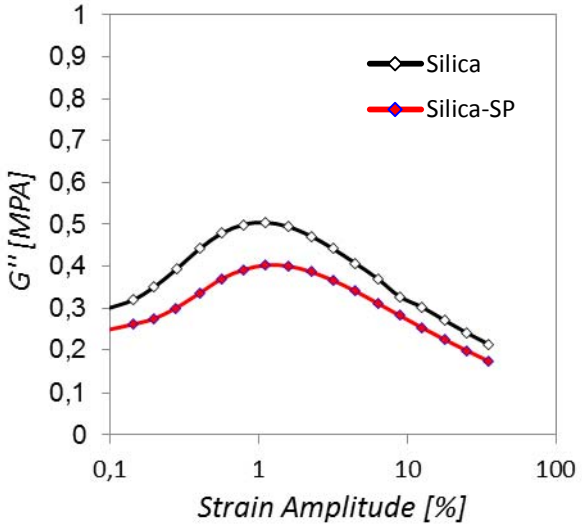
Compound with:	CB	CB-SP
NR	100,00	100,00
CB N234	60,00	0,00
CB-SP	0,00	62,40
Ac Stearico	2,00	2,00
ZnO	4,00	4,00
6PPD	2,00	2,00
TBBS	1,80	1,80
Sulphur	1,80	1,80

CB/SP adducts in silica based composites for lower dissipation of energy

Ingredients	without SP	with SP
IR	100	100
CB	30	30
Silica	30	30
SP	0	3

ZnO 4.0, Stearic acid 2.0, 6PPD 2.0, Sulphur 3, TBBS 1.8





Galimberti, M., Barbera, V., Sebastiano, R., Valerio A.M. Leonardi, G.,Citterio, US 2017 0275169 A1

NanoCarbon Up Technology

V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio.
WO/2015/189411 A1 (2015)

M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio.
WO/2016/050887 A1 (2016)

M. Galimberti, V. Barbera, R. Sebastiano, A. Truscello, A.M. Valerio.
WO/2016/023915 A1 (2016)

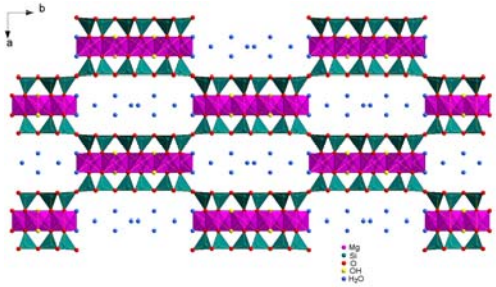
M. Galimberti, V. Barbera,
Italian Patent 102016000113012 (2016)

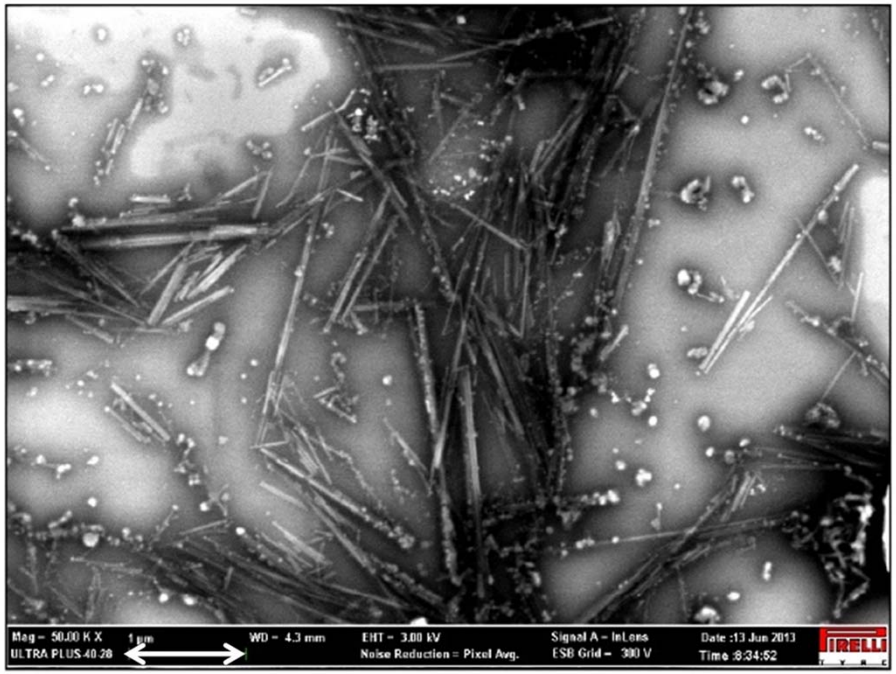
M. Galimberti, V. Barbera,
Italian Patent 102016000113070 (2016)

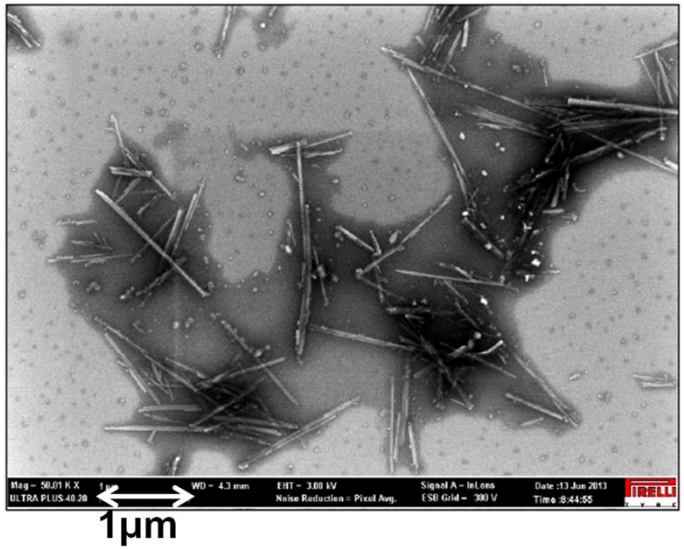
Biofiller - Sepiolite

Sepiolite: a white clay mineral, a complex magnesium silicate.

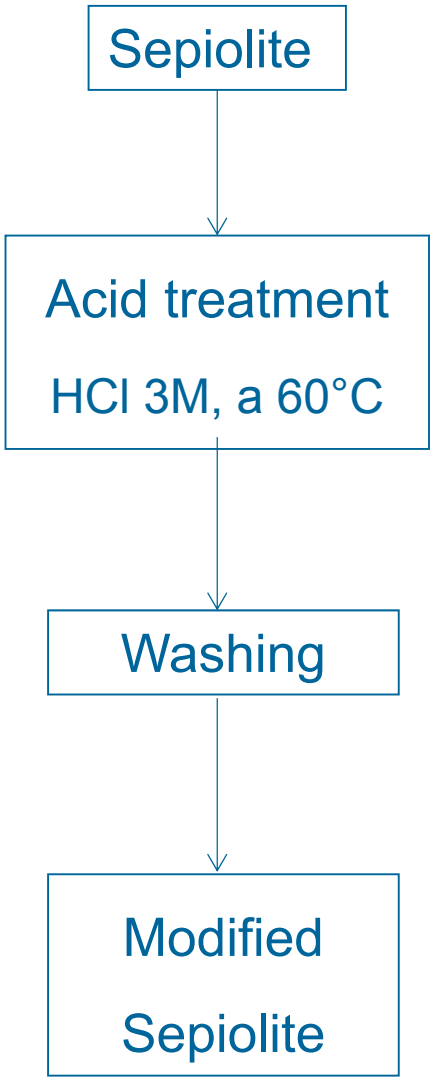
Typical chemical formula: $Mg_4Si_6O_{15(}OH)_2 \cdot 6H_2O$.







Modified Sepiolite - by acid treatment



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

Modified Sepiolite - by acid treatment

Sepiolite

↓

Acid treatment

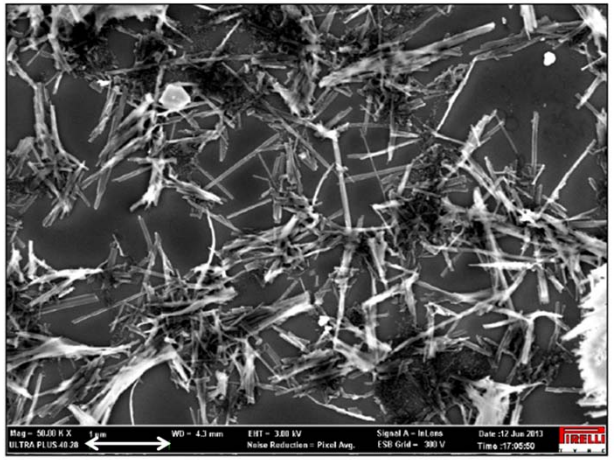
HCl 3M, a 60°C

↓

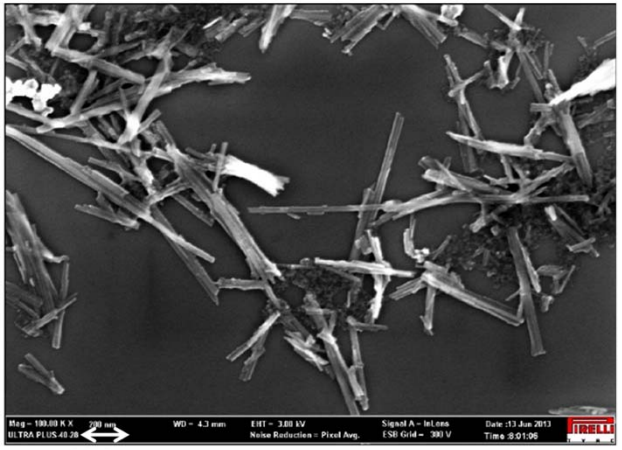
Washing

↓

Modified Sepiolite



1µm



200nm

Extraction of Mg: from 25% to 85%

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Modified Sepiolite - by nanosilica

TEOS / EtOH / H_2O

↓

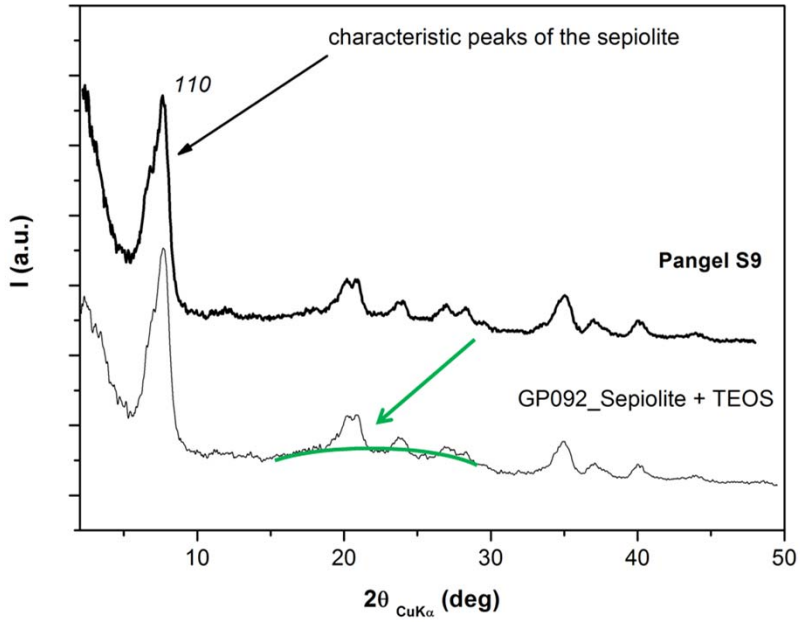
Sepiolite

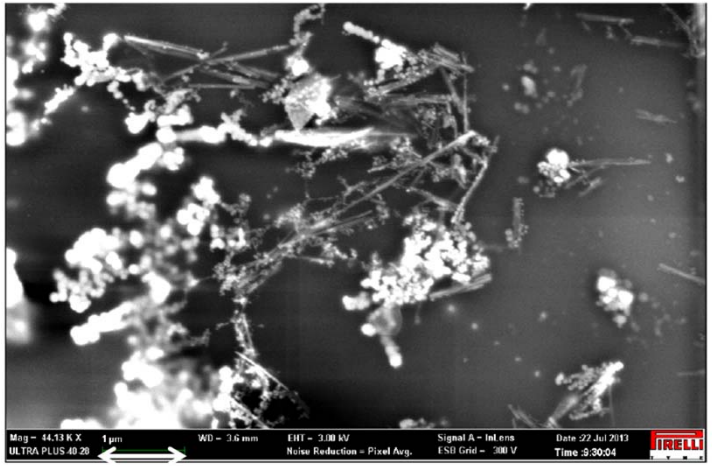
↓

NH_4OH

↓

Modified Sepiolite





1µm

L. Giannini, M. Galimberti, V. Cipolletti, G. Peli MI2015A000611

Rubber composite with Sepiolite modified by acid treatment

10 parts of sepiolite

in place of

10 parts of silica

Phr: NR 100, Silica 45, Silane TESPT 3.6, ZnO 3.6, 6PPD 2, S 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

Rubber composite with Sepiolite modified by acid treatment

Filler	Silica	Silica + Sepiolite
% ext. Mg	--	35%
CA 0.5 [MPa]	1.49	1.46
CA 1 [MPa]	2.46	2.62
CA 3 [MPa]	9.88	10.64
CR [MPa]	14.68	15.32
AR %	436.1	441.2
IRHD	77.6	72.7
IRHD 100 °C	70.8	68.2
delta IRHD	6.8	4.5
E' [MPa] 0 °C 100 Hz	15.11	13.95
E' [MPa] 23 °C 100Hz	10.57	9.72
E' [MPa] 100 Hz	7.70	7.17
Tan Delta 0 °C 100 Hz	0.501	0.504
Tan Delta 100 Hz	0.296	0.281
Tan Delta 100 Hz	0.152	0.141
d_G'(0.5-10) MPa	2.7	1.9

10 parts of sepiolite

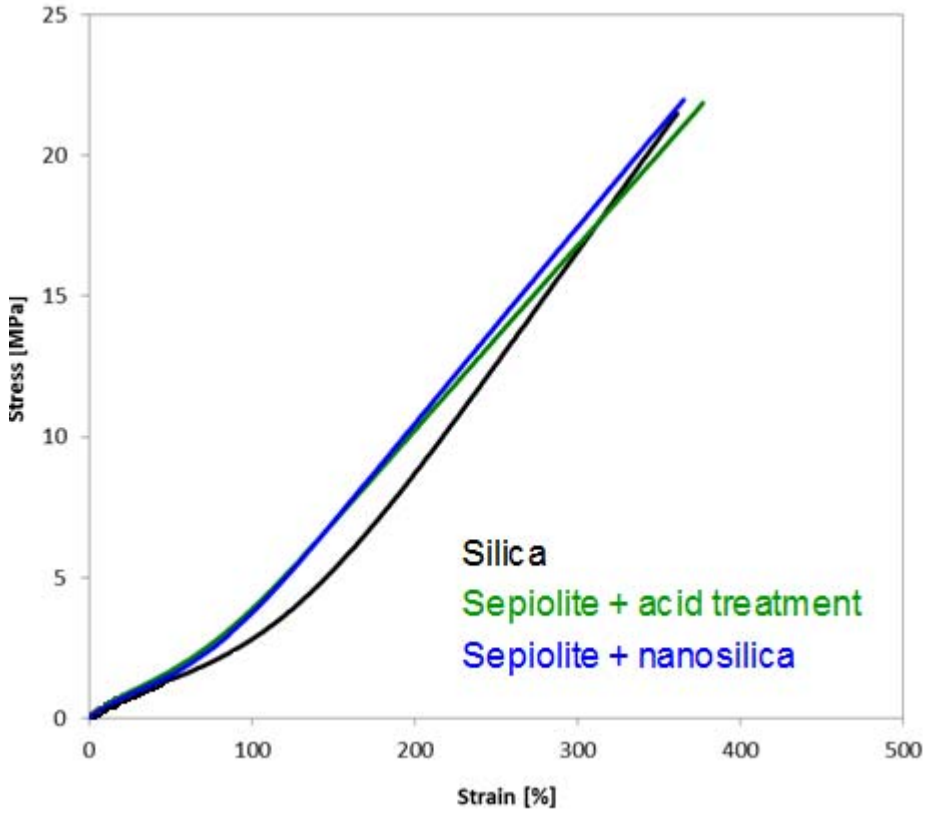
in place of

10 parts of silica

Phr: NR 100, Silica 45, Silane TESPT 3.6, ZnO 3.6, 6PPD 2, S 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

Rubber composite with Modified Sepiolite



Addition of

10 parts of 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

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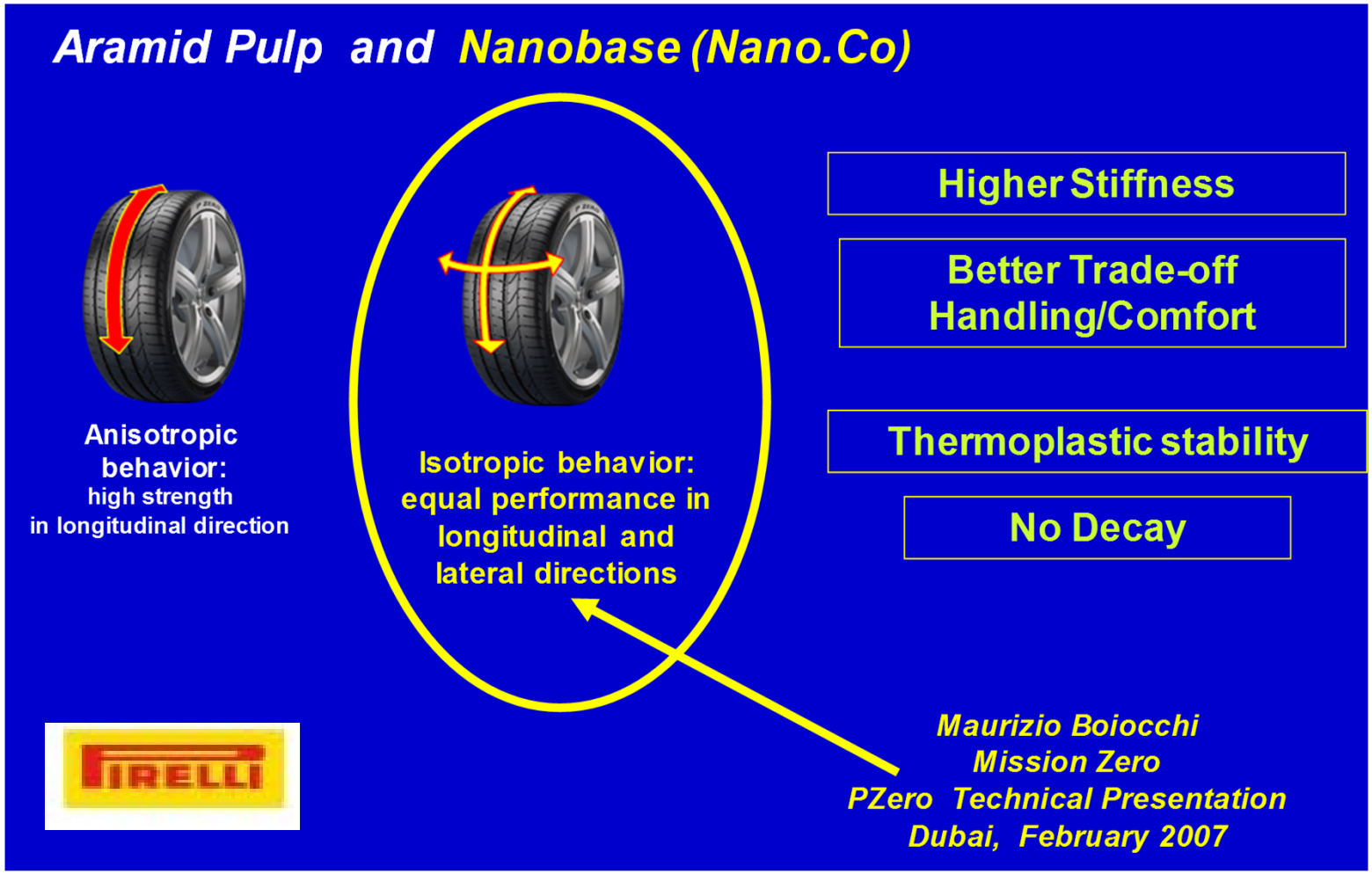
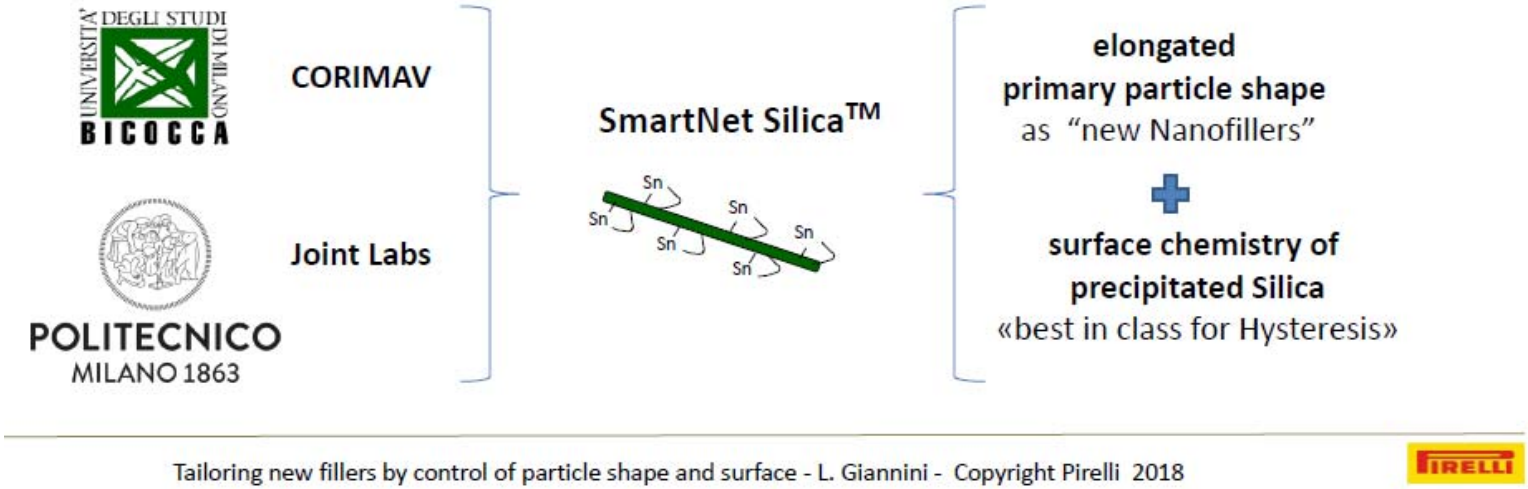
From basic research to commercial development



From basic research to commercial development

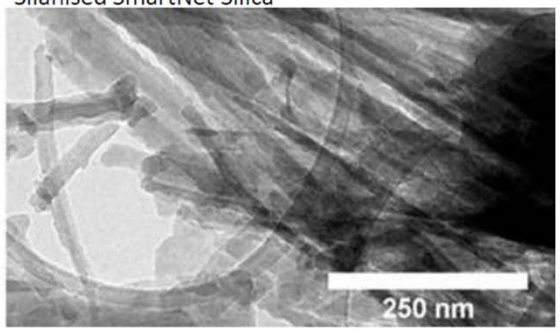


Silicate route to SmartNetSilica™

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

From basic research to commercial development

Silanised SmartNet Silica™



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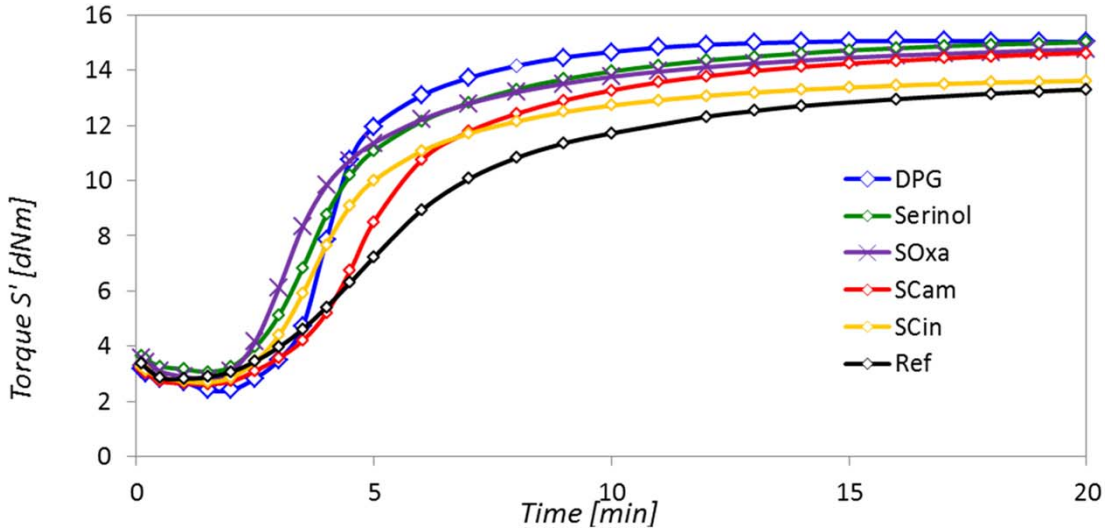
PIRELLI

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

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

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

Conclusions



Thanks
for the attention!

Associazione Italiana
di Scienza e Tecnologia delle Macromolecole

Giornate Tecnologiche

In occasione del PLAST 2018, AIM organizza la GIORNATA TECNOLOGICA

"ELASTOMERI 4.0"