



**POLITECNICO**  
MILANO 1863



## A biosourced *Janus* molecule as universal coupling agent in rubber compounds

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Vincenzina Barbera, Silvia Guerra, Andrea Bernardi, Daniele Locatelli,  
Lucia Rubino, Gea Prioglio, Fatima Margani, Simone Naddeo,  
Francesco Moriggi, Stefania Gallo, Federica Magaletti

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

14th Fall Rubber Colloquium (KHK) ONLINE  
Germany, November 2022, 8 - 10



# The people



Maurizio Galimberti



Vincenzina Barbera



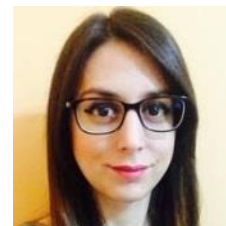
Silvia Guerra



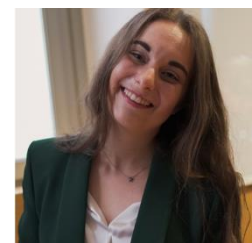
Andrea Bernardi



Daniele Locatelli



Lucia Rubino



Gea Prioglio



Fatima Margani



Francesco Moriggi



Simone Naddeo



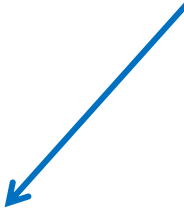
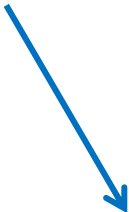
Stefania Gallo



Federica Magaletti

Natural sources

Wastes and residues



Chemicals

Proteins

as building blocks for chemical platforms



Chemicals, Additives, Modifiers, Polymers

# Materials from natural sources and wastes

Estimated global production of biomass: ca.  $10^{11}$  tonnes / year

60% terrestrial

40% aquatic

Only 3%

cultivated, harvested, used: for food and non food

Agricultural dry biomass waste

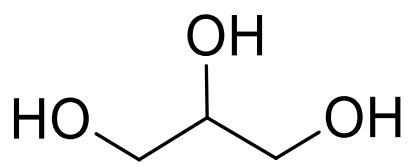
20 Gton/year

👉 Abundant non edible biomass waste

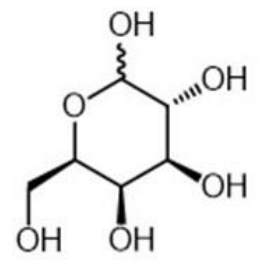
# Items of the presentation

- Biosourced C-3 and C-6 building blocks
- Pyrrole compounds and pyrones
- Adducts of pyrrole compounds  
with  $sp^2$  carbon allotropes and inorganic oxyhydroxides
- Adducts as coupling agents in rubber compounds

# Materials from C3 and C6 building blocks



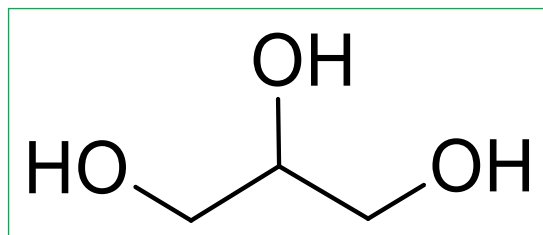
Glycerol, Sugars



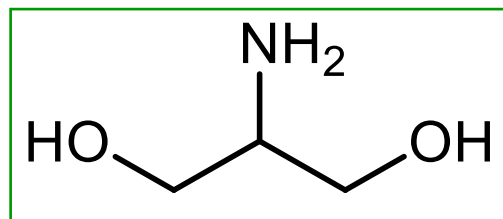
Green Chemistry

Building blocks

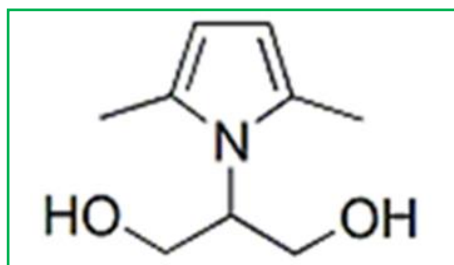
# Glycerol as the C3 building block. From glycerol to serinol to serinol pyrrole



Propane-1,2,3-triol

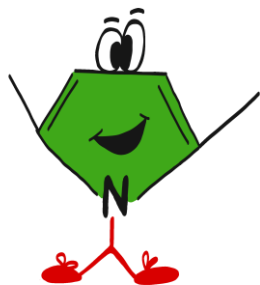
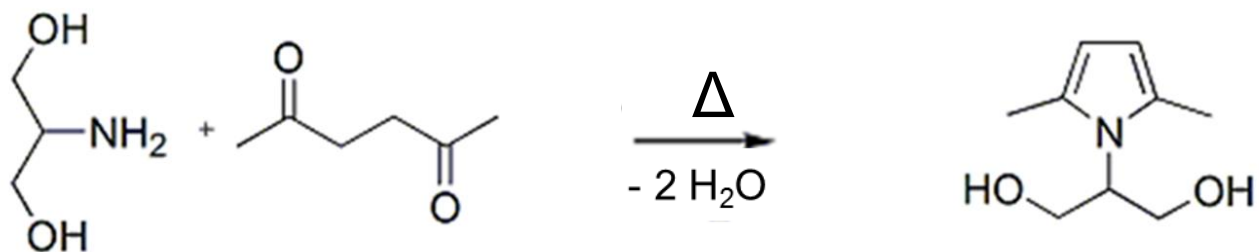


2-Amino-1,3-propanediol



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

# From serinol to serinol pyrrole

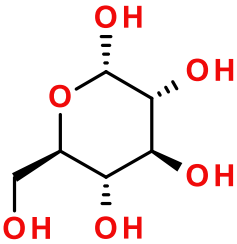


- ➡ Yield: at least 96%
- ➡ Atom efficiency: 85%
- ➡ Easy procedure
- ➡ No solvent
- ➡ Co-product:  $\text{H}_2\text{O}$

Up to hundreds kg

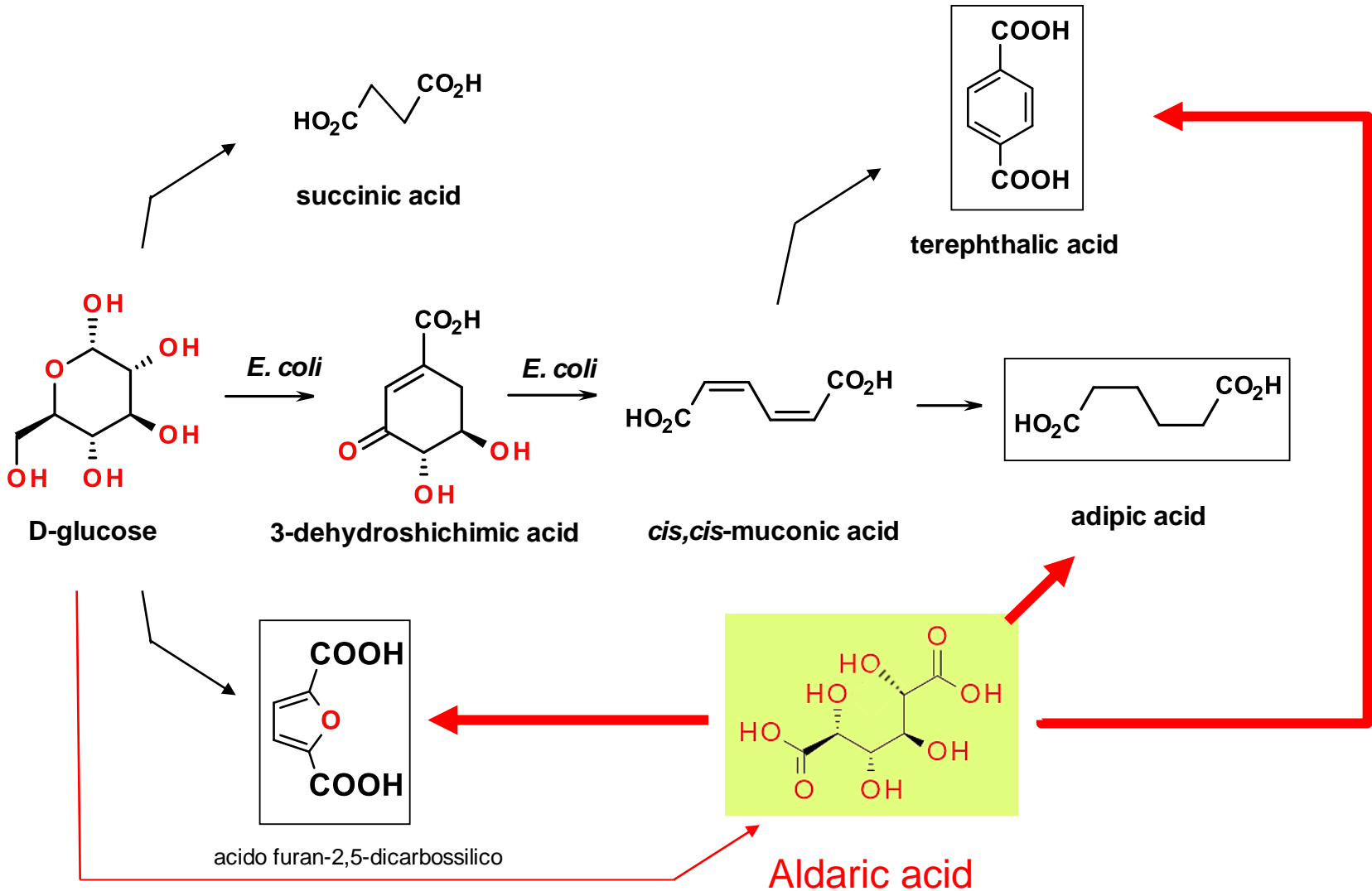


# C6 building blocks from hydrolyzed biomasses

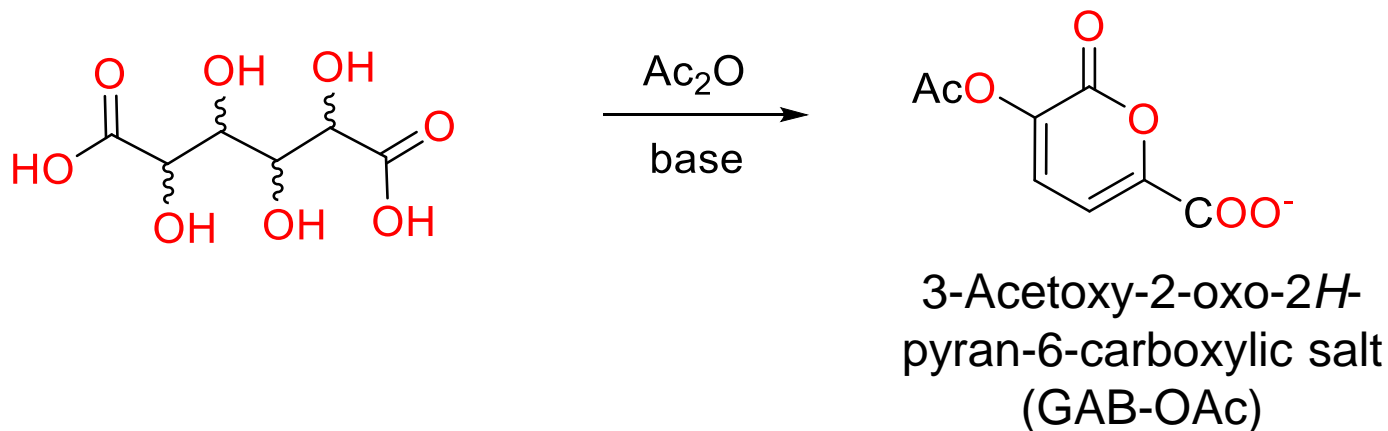


**D-glucose**

# Dicarboxylic Acids from hydrolyzed biomasses as the building blocks

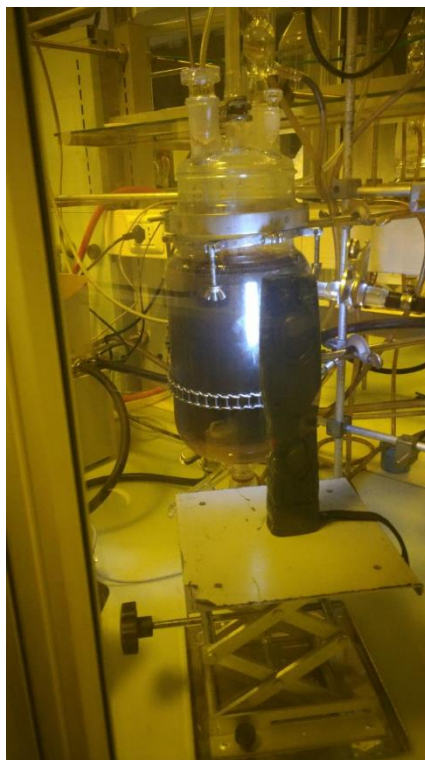
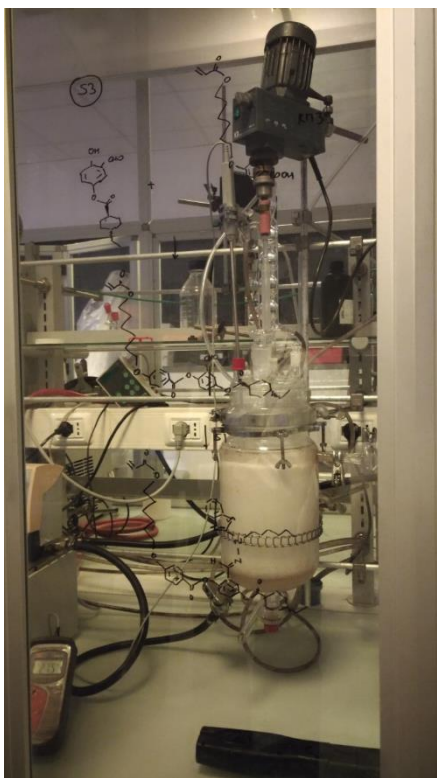


## Synthesis of Pyrone Derivatives from Aldaric Acids @ ISCaMaP



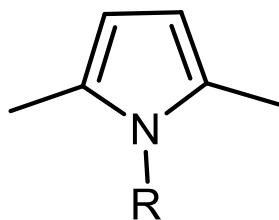
- ➡ Easy procedure
- ➡ No solvent
- ➡ No catalyst
- ➡ High Conversion
- ➡ High Atom efficiency

## Synthesis of Pyrone - Scale up

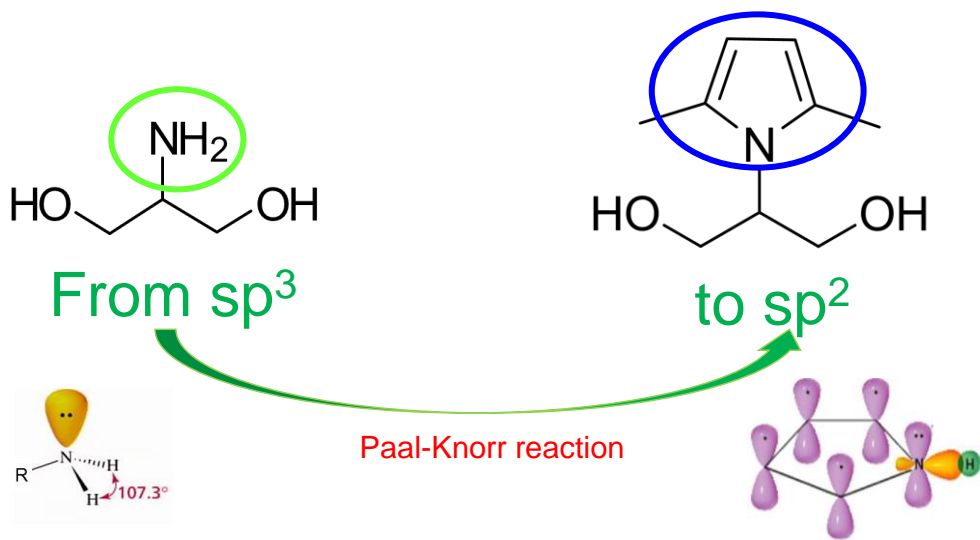
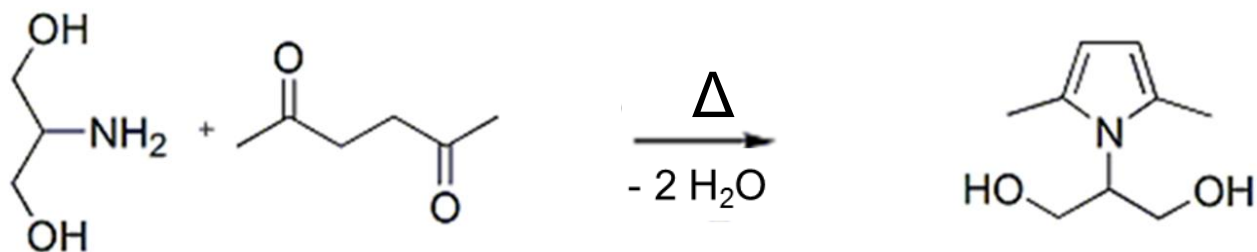


One Pot, 2 hours, Yield = 75%  
kgs of product

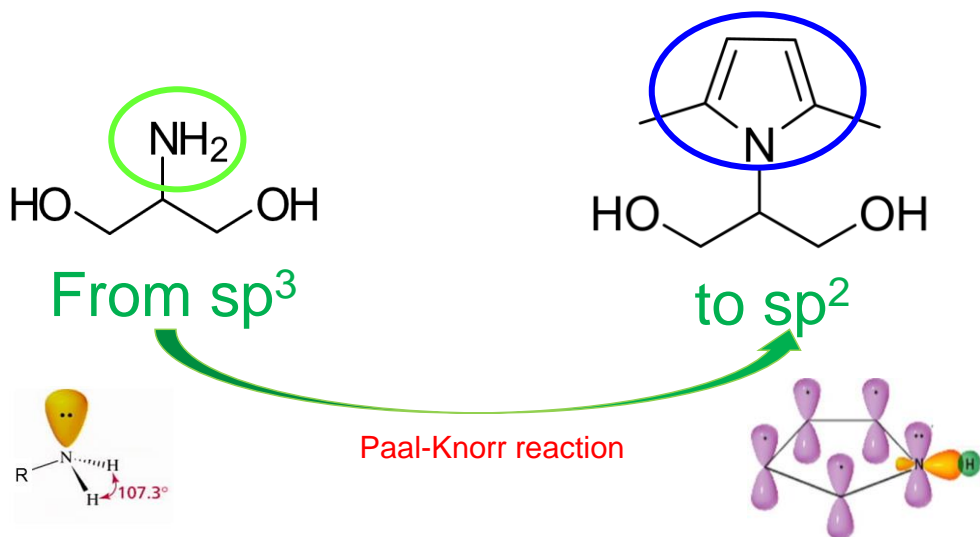
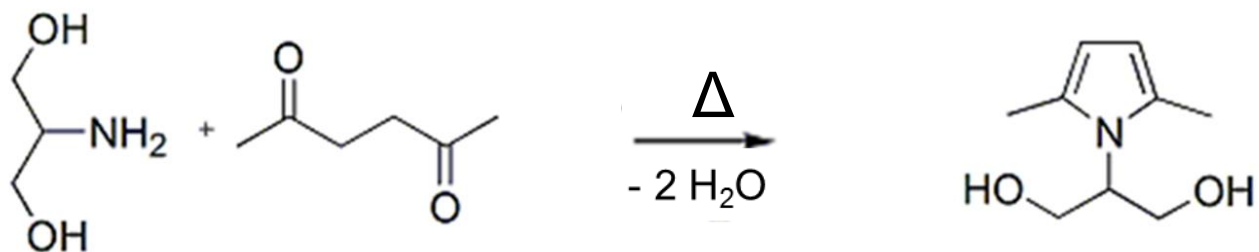
## C3 building blocks



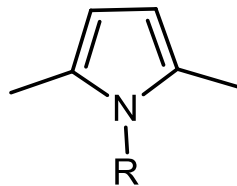
# Serinol pyrrole as coupling agent?



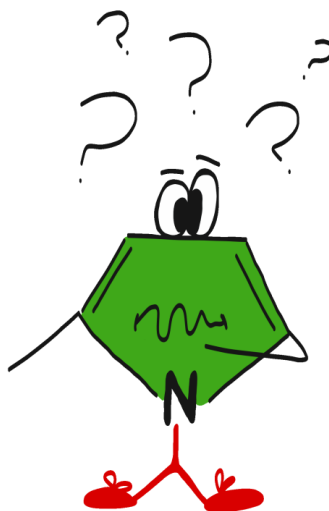
# Serinol pyrrole as coupling agent?



# “Universal coupling agent for carbon black and silica”

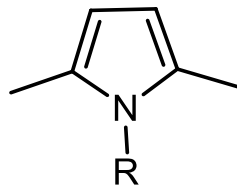


Is a coupling agent for carbon black and silica?

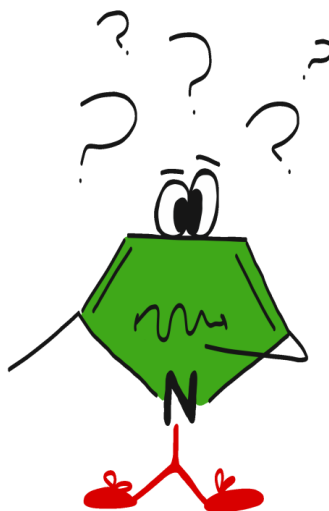




# “Universal coupling agent for carbon black and silica”

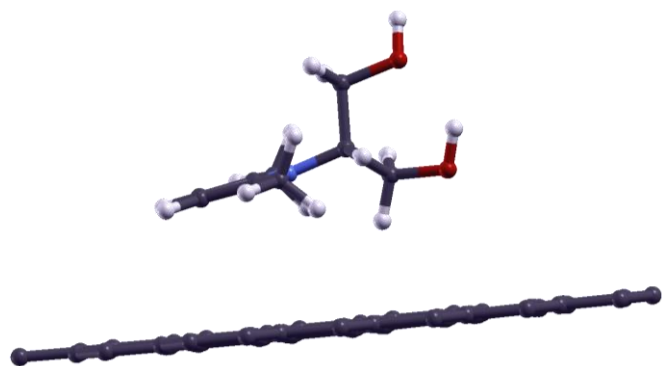


Is a coupling agent for carbon black?



# Supramolecular interaction of pyrrole compounds with $sp^2$ carbon allotropes

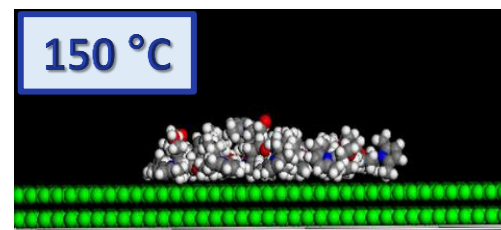
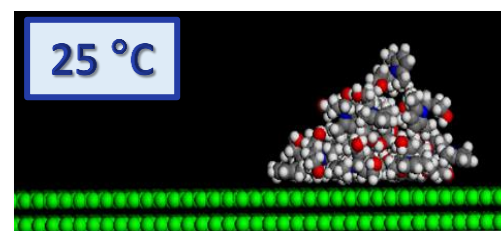
Density functional theory (**DFT**) and molecular dynamics (**MD**) simulations



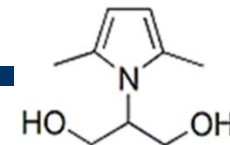
☞ pyrrole  $sp^2$  configuration:  
 $\pi$ - $\pi$  bonding with the graphene surface

☞ Long alkyl chains:  
London interactions

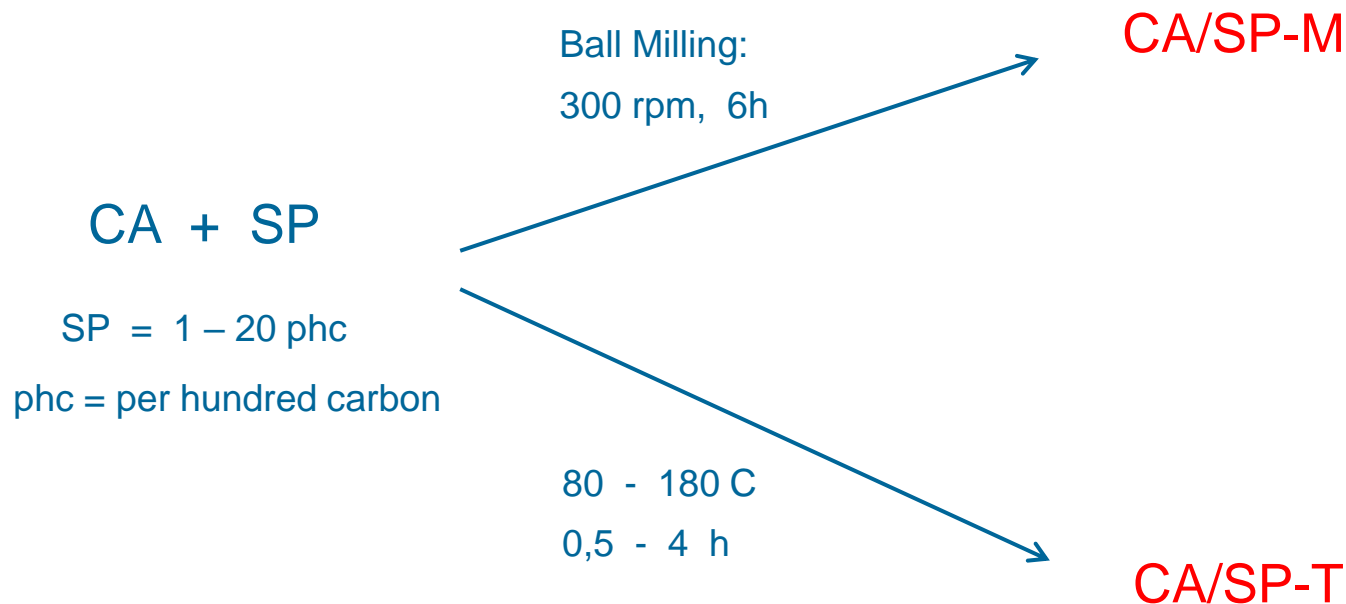
☞ Temperature increase  
promotes the spreading on the surface  
of the pyrrole molecule



# CA-SP Covalent Adducts - Preparation

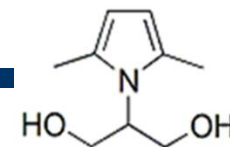


Mechanical treatment



Thermal treatment

# CA-SP Covalent Adducts - Yield of functionalization\*



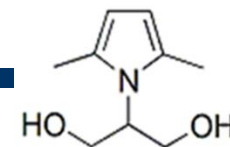
Thermal treatment  
SP = 5 phc; 150°C, 2 h

	HSAG	CB	MWCNT
BET Surface area: [m <sup>2</sup> /g]	300	77	275
Functionalization Yield(%)*:	96	82	92

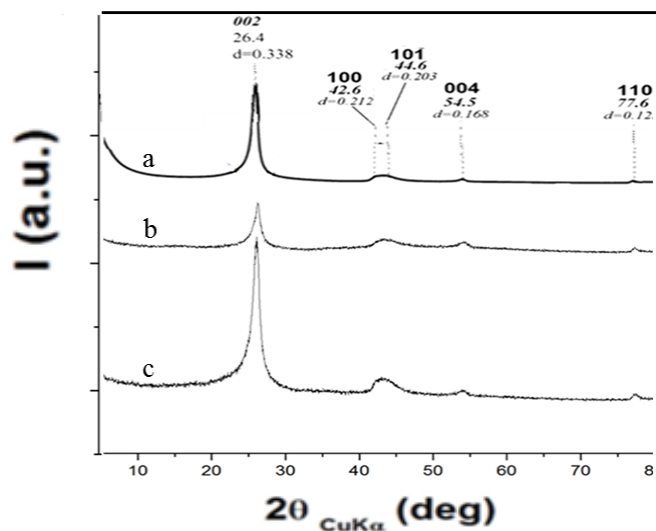
\* Functionalization Yield (%) =  $100 * \frac{\text{SP mass \% in (CA-SP adduct) after acetone washing}}{\text{SP mass \% in (CA-SP adduct) before acetone washing}}$  from TGA

HSAG (High Surface Area Graphite) from Asbury, CB from Cabot, CNT from Nanocyl

# Covalent Adducts of SP with high surface area graphite (HSAG)



## WAXD

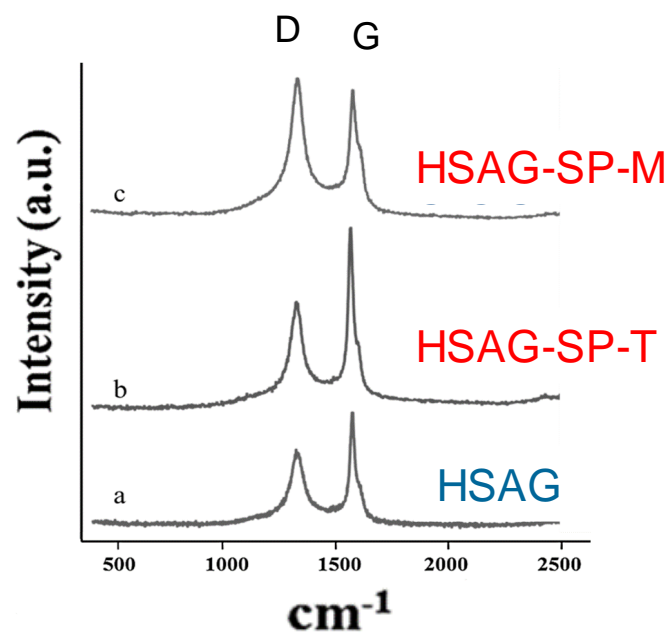


HSAG

HSAG-SP-M

HSAG-SP-T

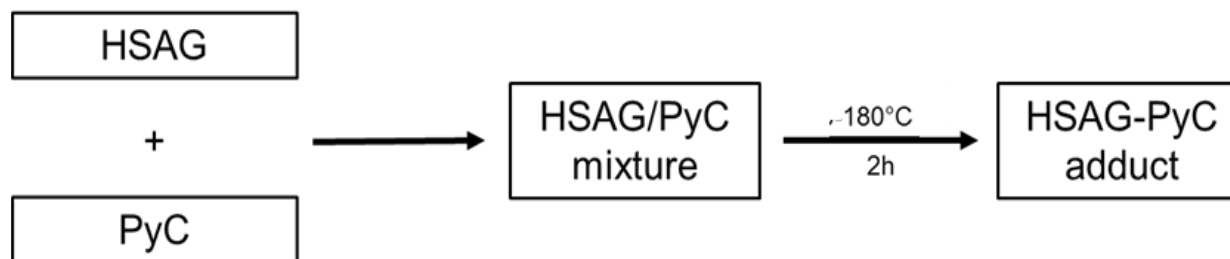
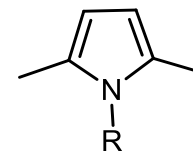
## Raman



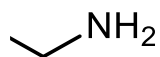
Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, *RSC Advances*, 5(99), (2015) 81142-81152

Galimberti M., Barbera V., Guerra S., Bernardi A., *Rubber Chemistry and Technology*, 2017, 90(2), 285-307.

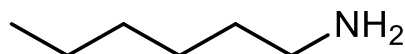
# HSAG / PyC covalent adducts



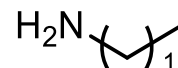
Functionalization Yield %



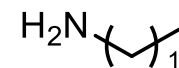
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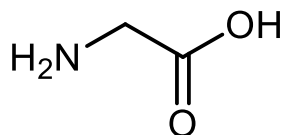
53



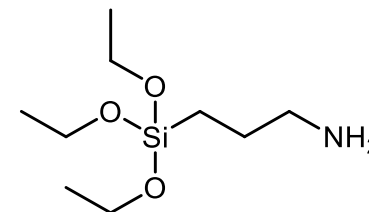
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55

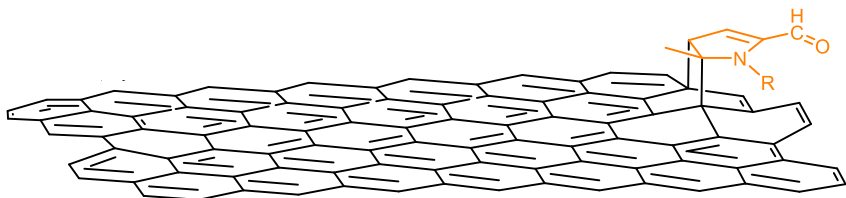


63

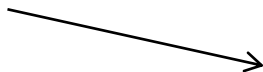


70

# CA/PyC covalent adducts

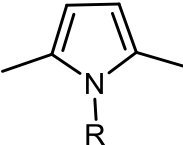


➡ Scale up for CB



- ➡ **Modifier:**  
from few % to 10%
- ➡ **Functionalization yield:**  
from 85% to quantitative
- ➡ **Covalent bond**  
between functional group and carbon allotrope
- ➡ **Bulk structure of graphitic materials:**  
substantially unaltered

V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio. [US10329253B2](#)  
M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio. [US10160652B2](#)  
M. Galimberti, V. Barbera, R. Sebastiano, A. Truscello, A.M. Valerio. [EP3180379B1](#)  
M. Galimberti, V. Barbera, [EP3538511A1](#)  
M. Galimberti, V. Barbera, [EP3538481A1](#)



Experimental determination



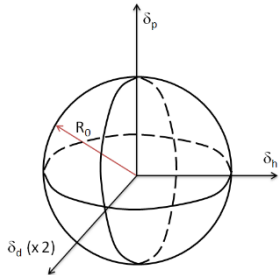
Stable suspensions  
in solvents  
with different  $\delta$

Adduct	solvents				
	water	isopropanol	ethyl acetate	toluene	heptane
TMP	bad (↓)	good	good	good	good
EP	bad (↑)	bad (↓)	good	bad (↓)	good
DDcP	bad (↑)	good	good	bad (↓)	bad (↓)
APTESP	bad (↑)	bad (↓)	bad (↓)	good	good
Gly	bad (↓)	good	good	good	bad (↓)
SP	good	good	good	bad (↓)	bad (↓)

Theoretical predictions

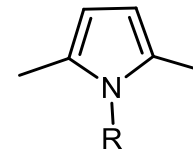


Computational model:  
Hansen solubility parameters



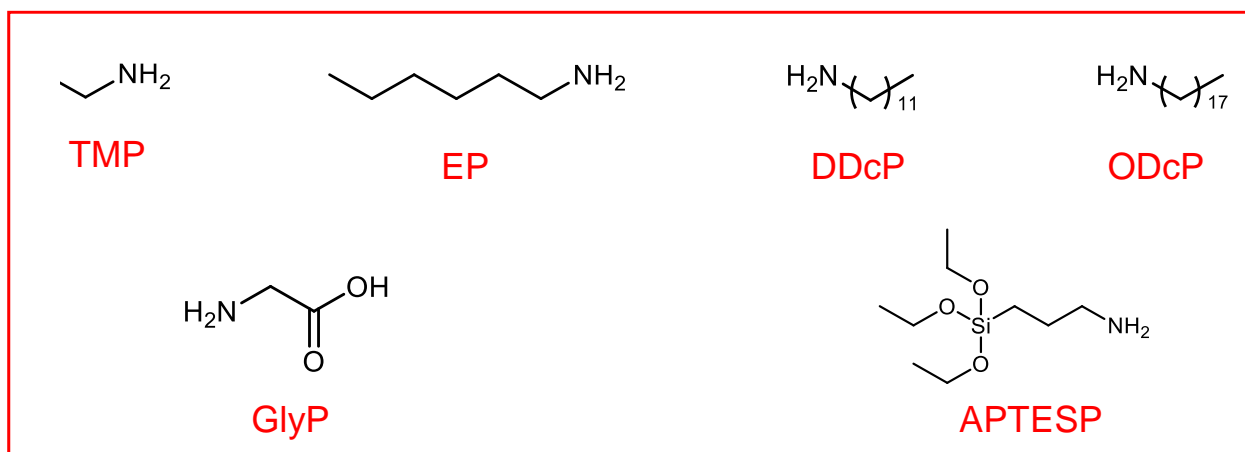


# HSAG / PyC covalent adducts - Hansen solubility parameters

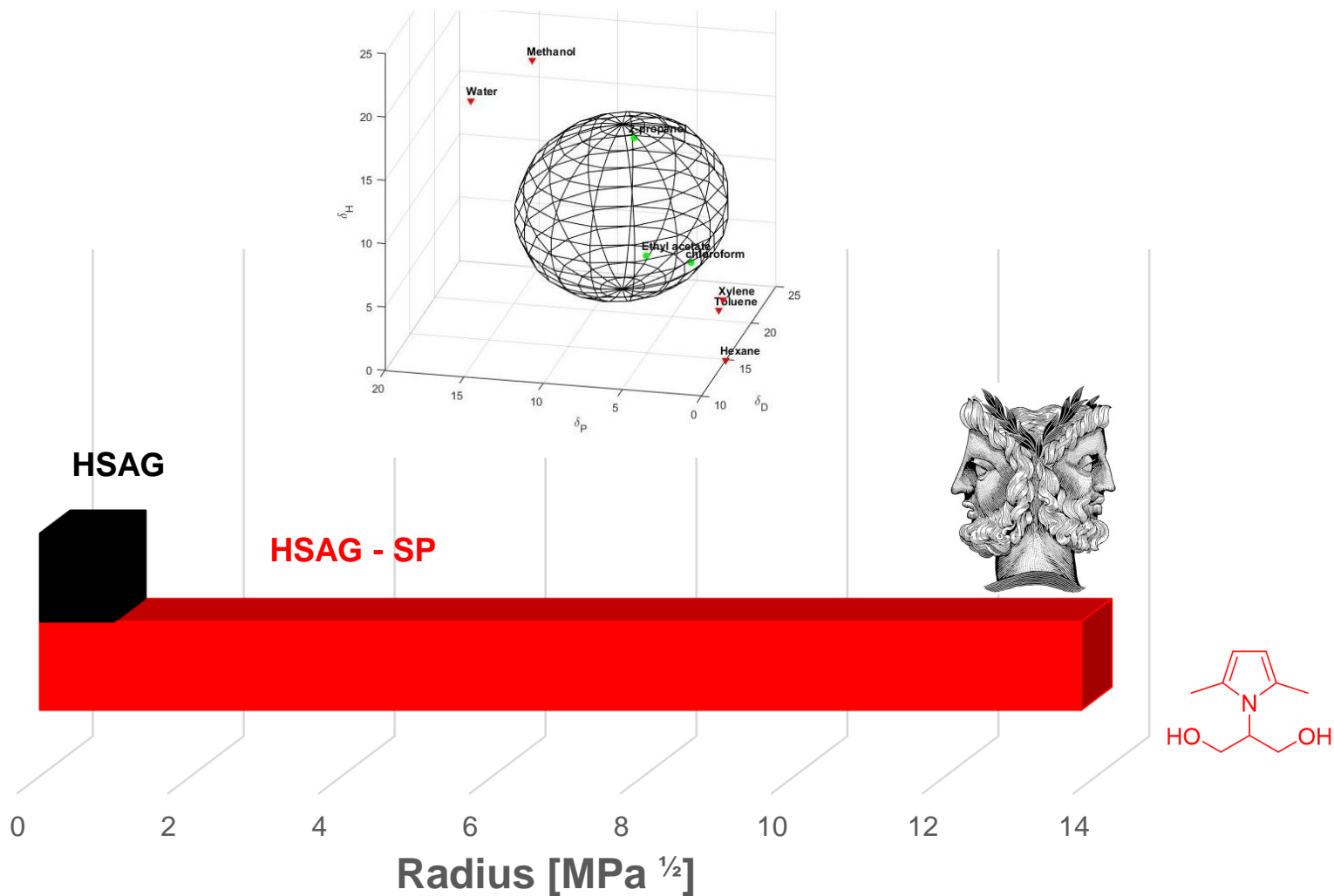


Sample	$\delta_D$	$\delta_P$	$\delta_H$	Radius
HSAG	17.8	3.1	5.7	1.0
HSAG-TMP	14.6	10.3	5.6	11.6
HSAG-DDcP	8.5	7.5	8.3	12.3
HSAG-APTESP	12.7	2.3	0.5	8.3
HSAG-SP	12.8	2.0	8.9	13.8
HSAG-GlyP	6.9	12.1	5.3	15.3

Amount of PyC on HSAG:  
about 5% mol

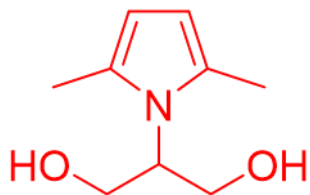
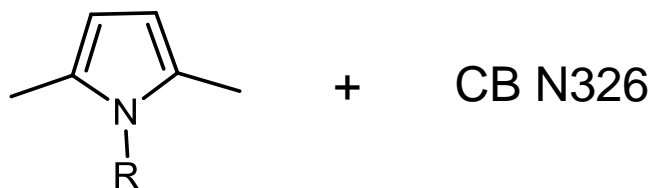


# HSAG and HSAG/SP - Hansen sphere radius comparison

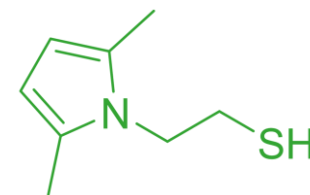


(\*) Amount of SP on CA: 10 mass%

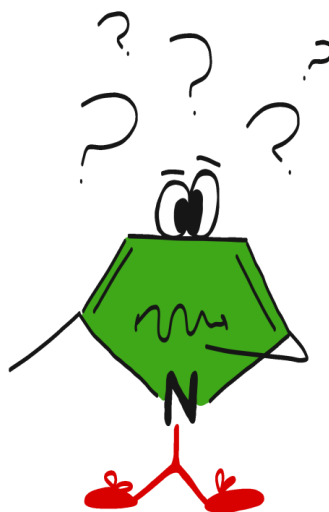
# “Universal coupling agent for carbon black and silica”



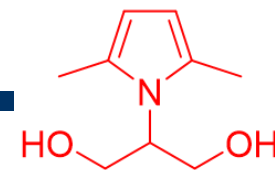
6.2 phc



6.5 phc



Is a coupling agent for carbon black  
in a rubber compound?



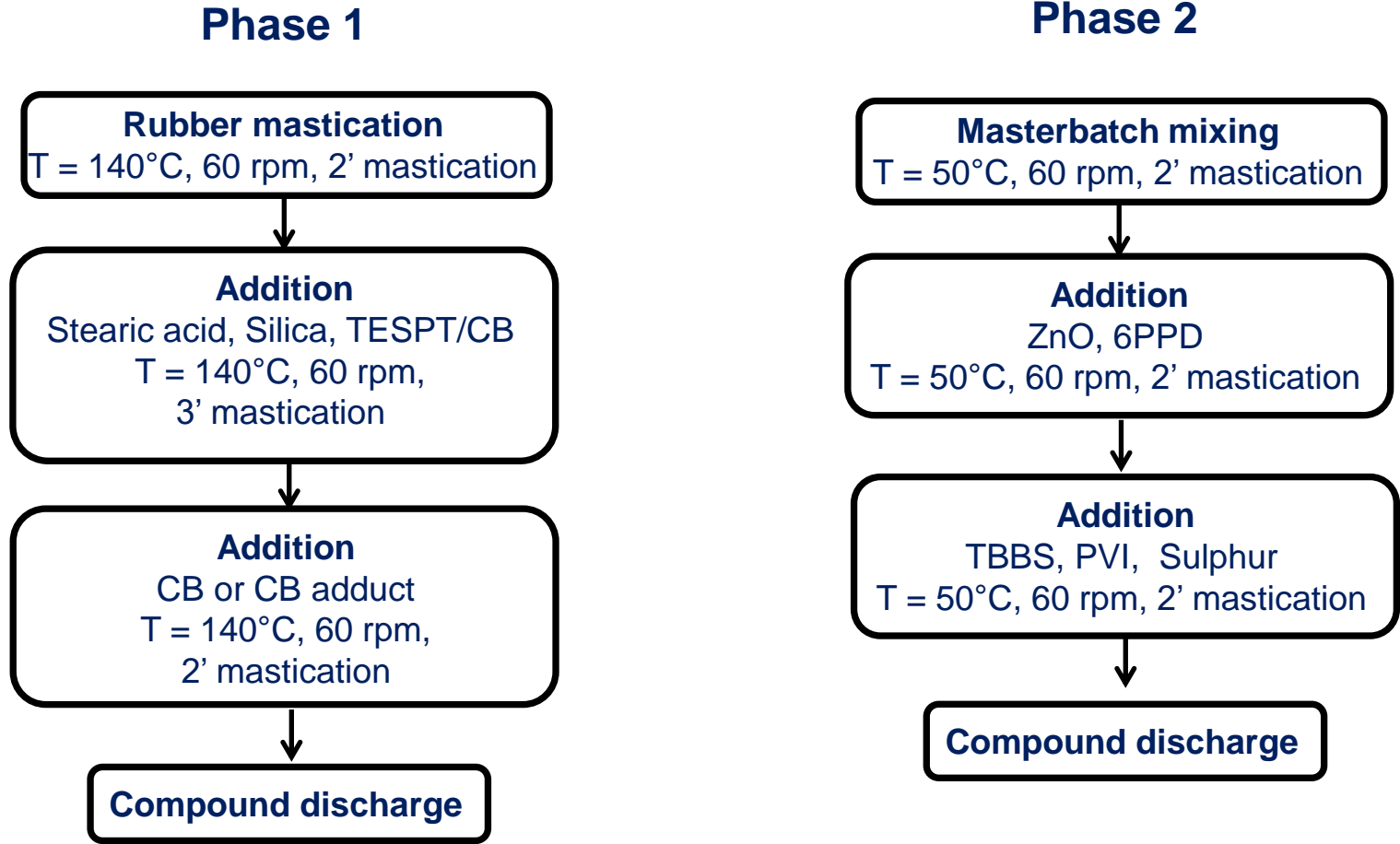
## Recipes

Ingredient	CB	CB-SP
NR	70	70
BR	30	30
Silica	35	12
CB N326-SP	0	19.7
CB N326	30	30
TESPT/CB (1/1)	5.6	5.6
Sulphur	2	2

ZnO 4 phr, stearic acid 2 phr, 6PPD 2 phr,  
TBBS 1.8 phr, PVI 0.5 phr.

# Rubber compounds based on CB/Silica with CB/SP

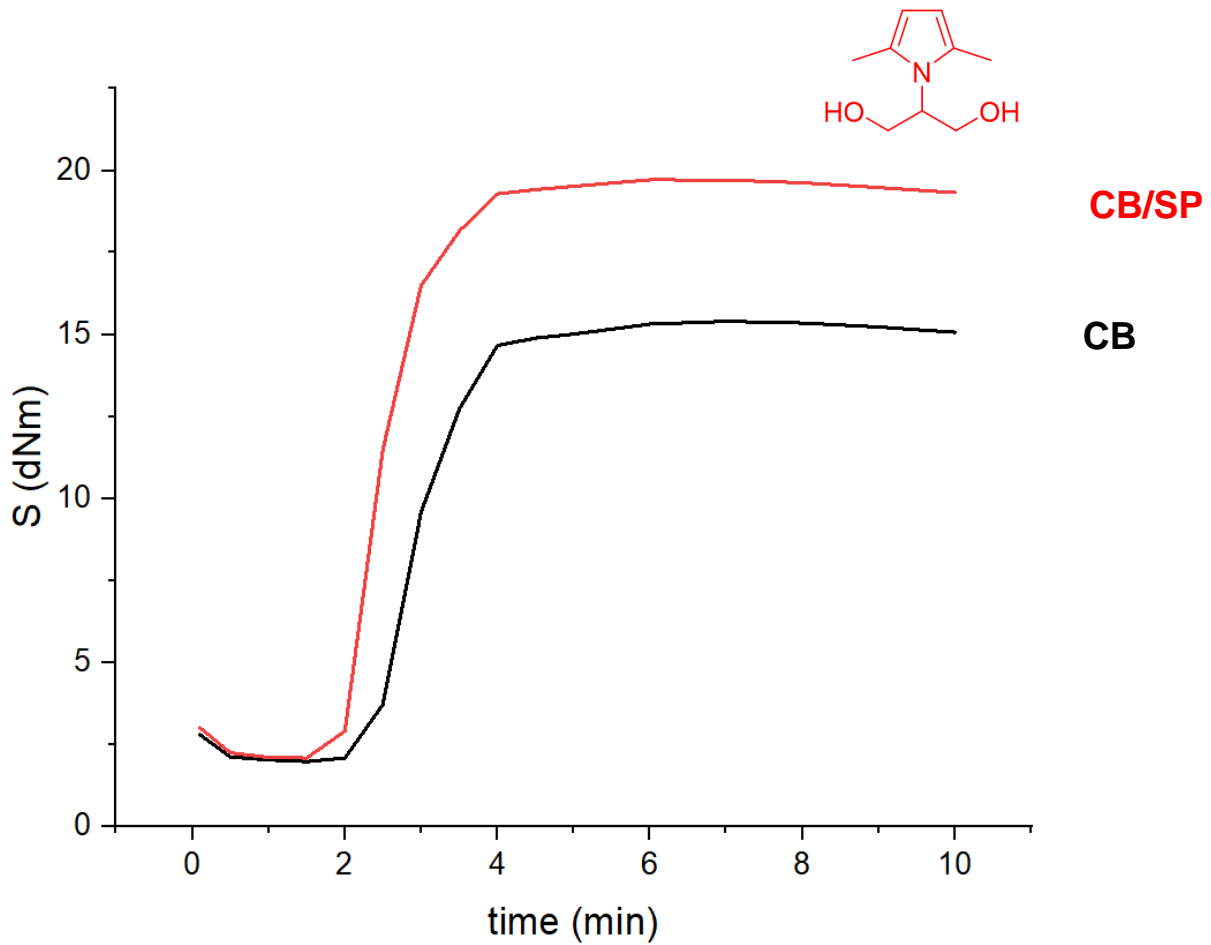
## Compound preparation



Brabender® type internal mixer

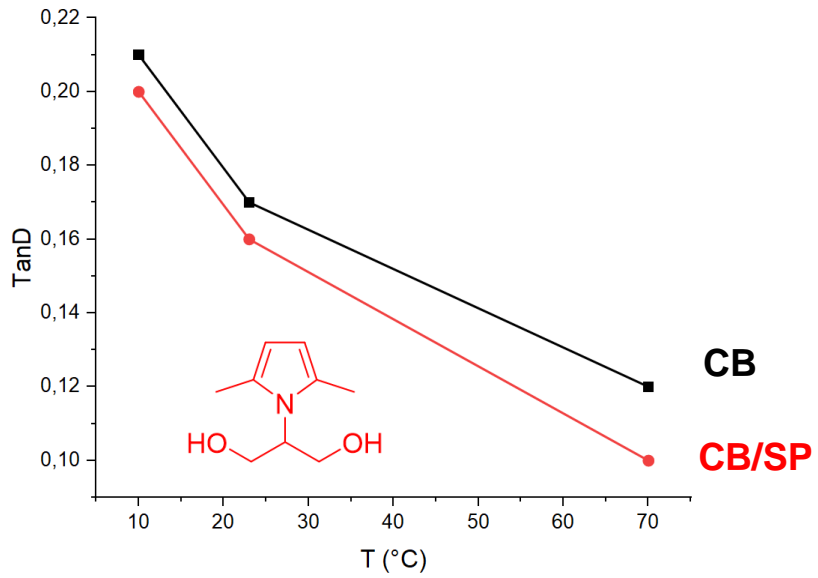
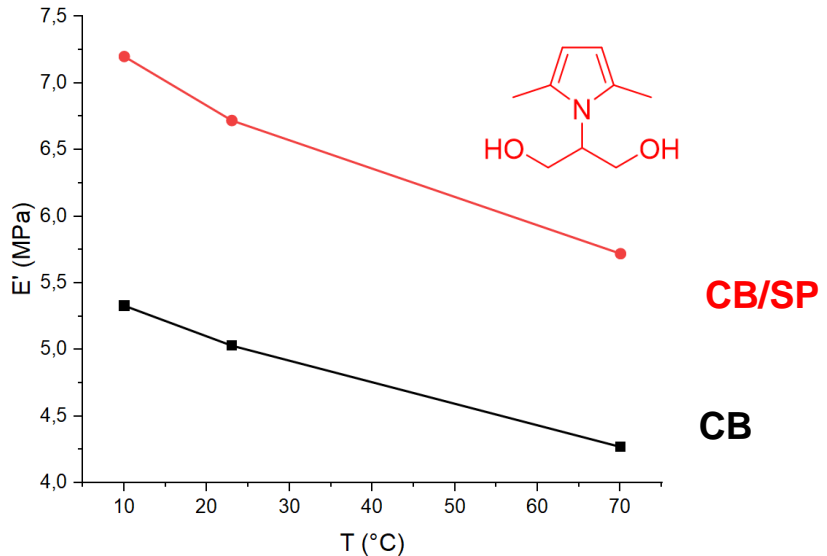
# Rubber compounds based on CB/Silica with CB/SP

## Crosslinking curves

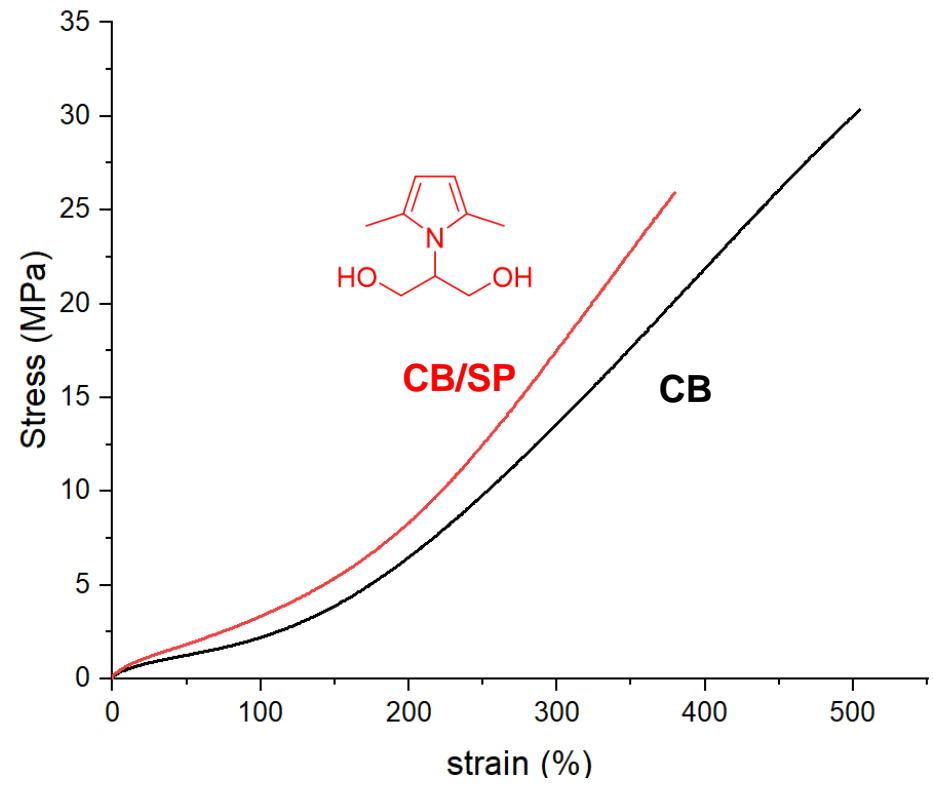


# Rubber compounds based on CB/Silica with CB/SP

## Axial dynamic-mechanical properties

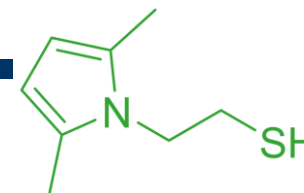


## Tensile properties





# Rubber compounds with CB/SHP. Silica vs CB as the filler



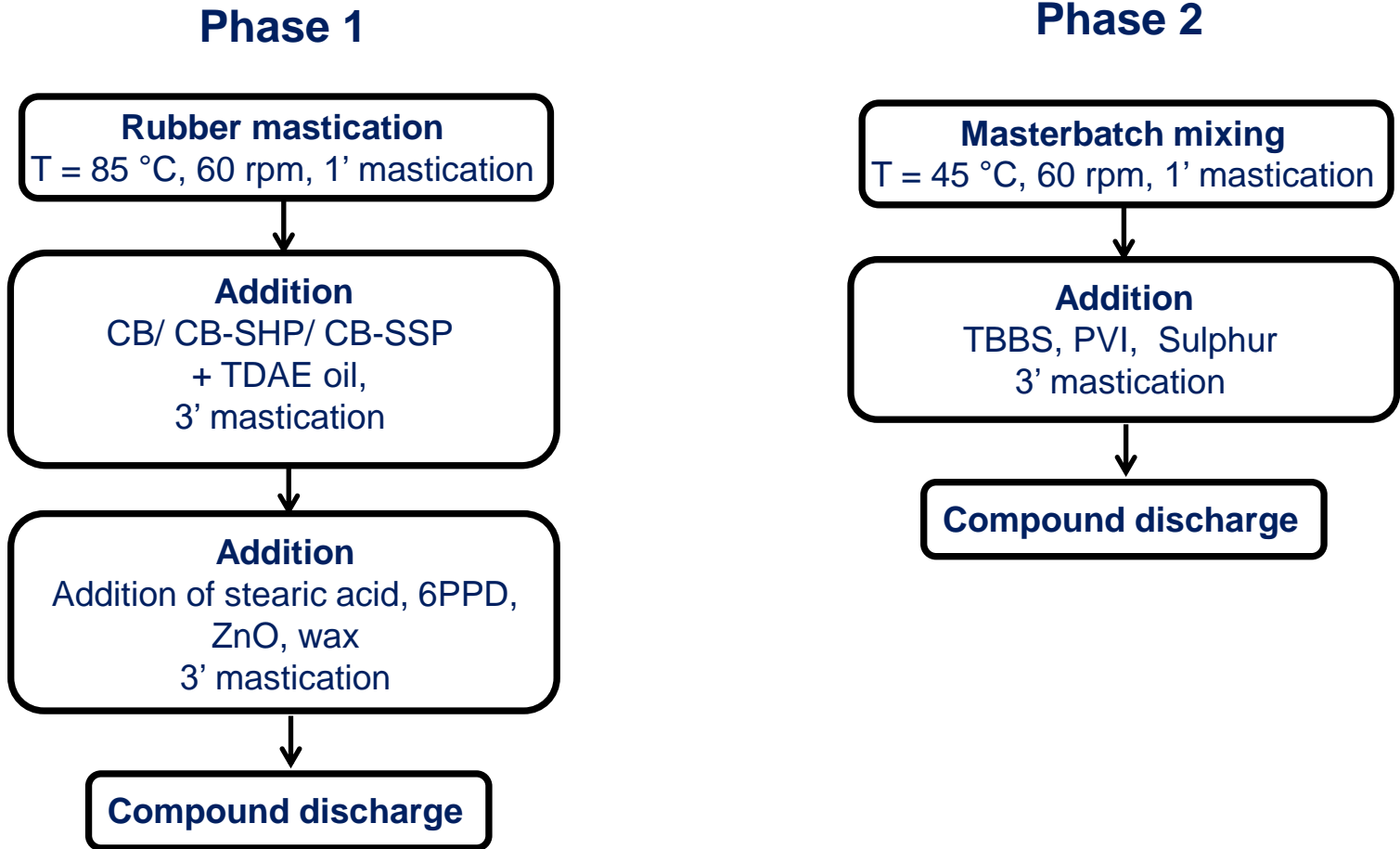
## Recipes

Ingredient	Silica	CB	CB-SHP
S-SBR 4630	70	70	70
NR	30	30	30
Silica	65	0	0
CB N234	0	55	0
CB N234-SHP	0	0	58.70
Silane TESPT	5.2	0	0
Sulphur	1.80	1.80	1.80

ZnO 2.5 phr, stearic acid 2 phr, 6PPD 2 phr,  
TBBS 1.8 phr, PVI 0.5.

# Rubber compounds with CB/SHP. Silica vs CB as the filler

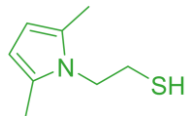
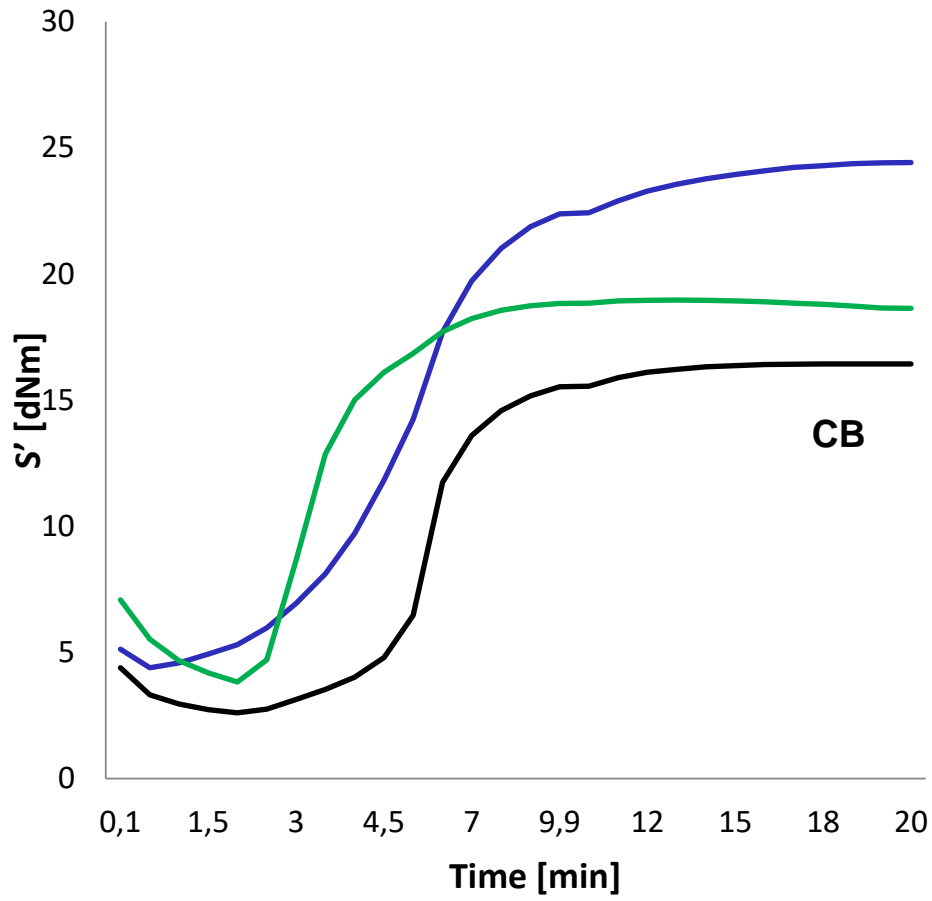
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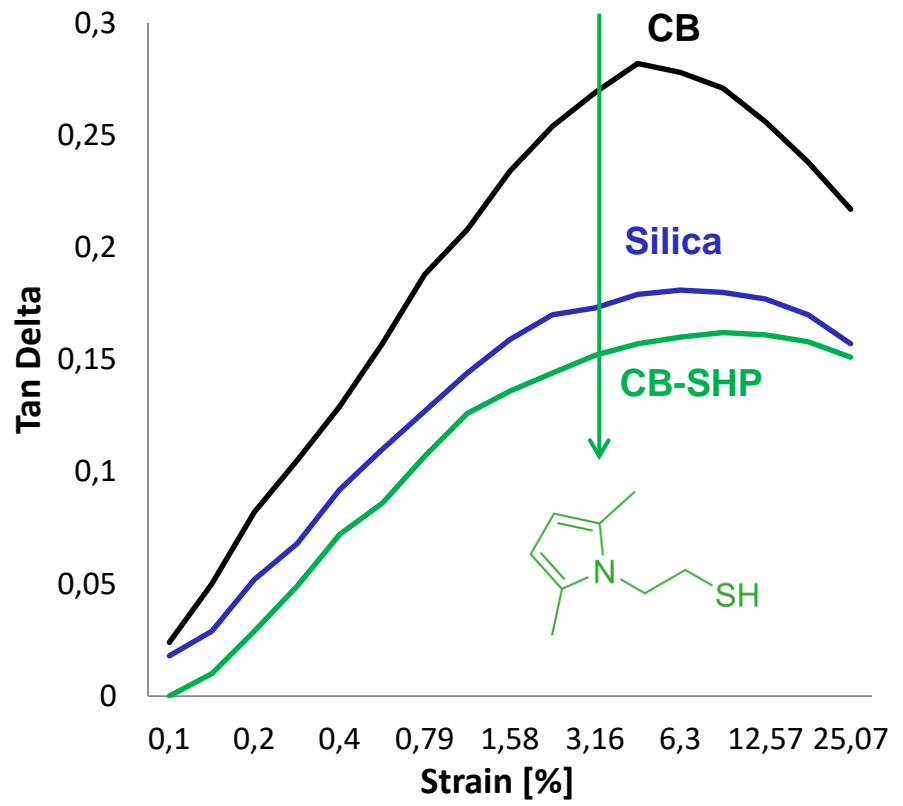
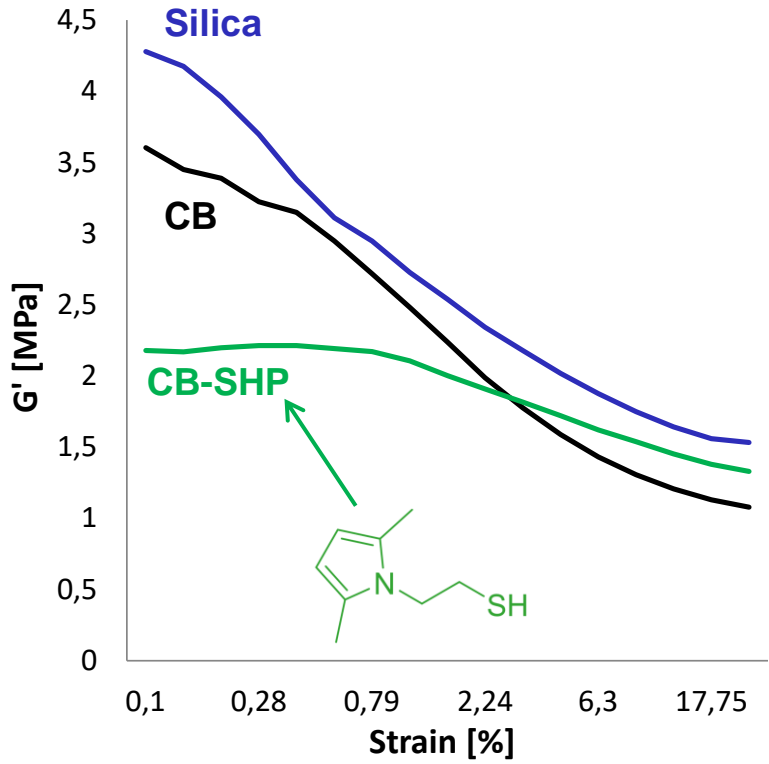
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## Crosslinking curves



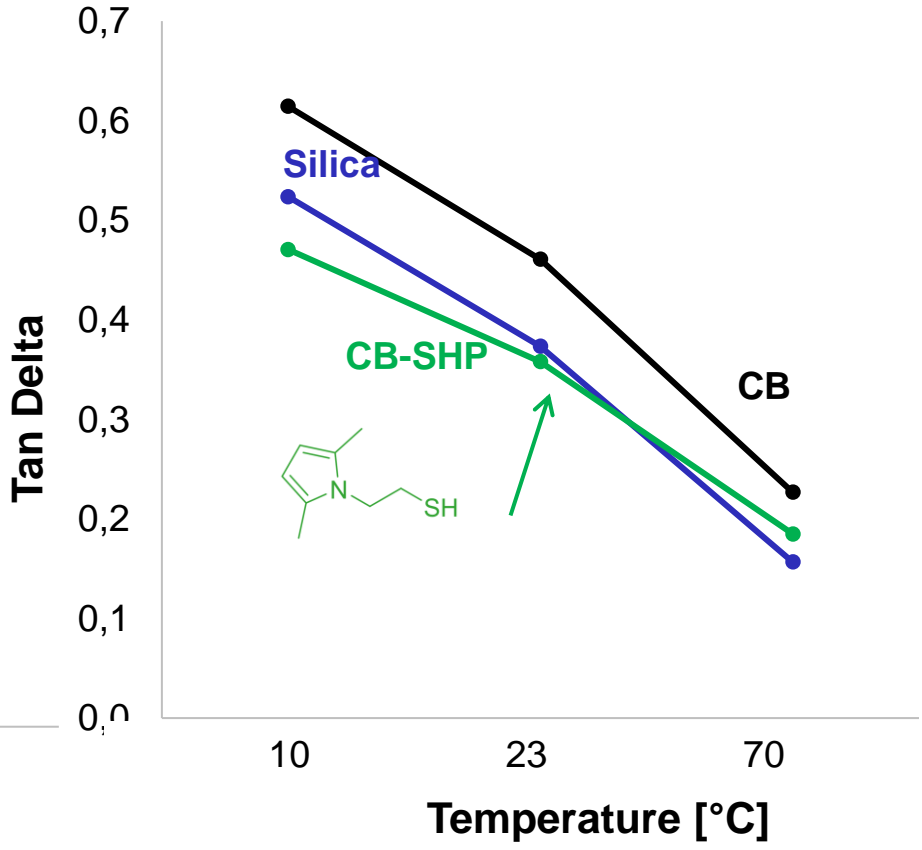
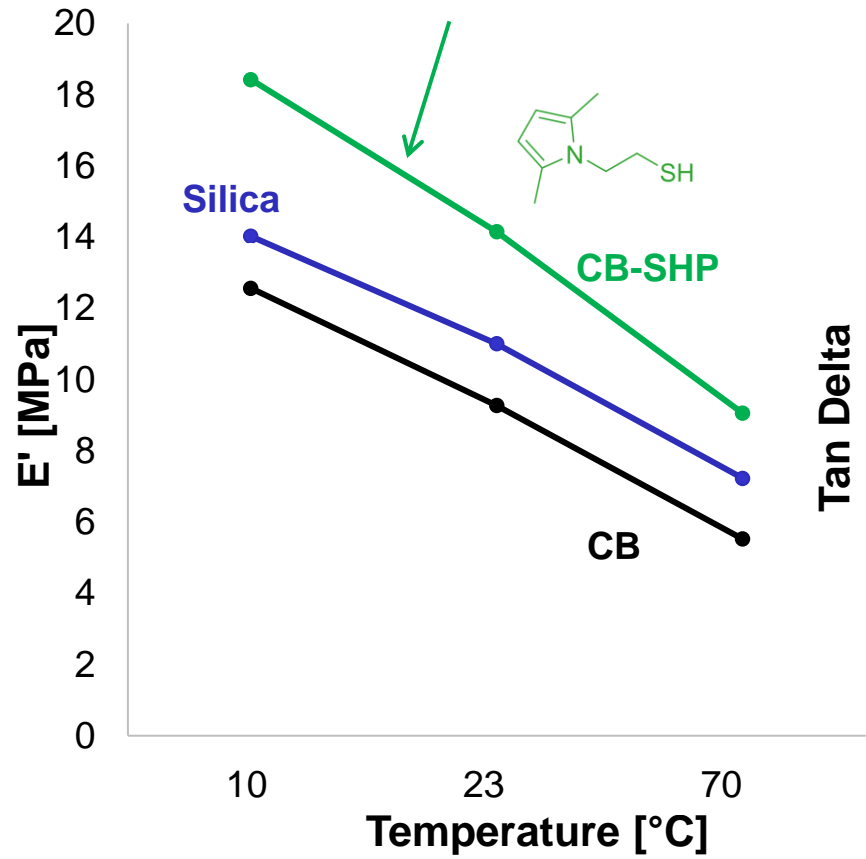
# Rubber compounds with CB/SHP. Silica vs CB as the filler

## Shear dynamic-mechanical properties

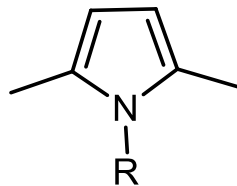


# Rubber compounds with CB/SHP. Silica vs CB as the filler

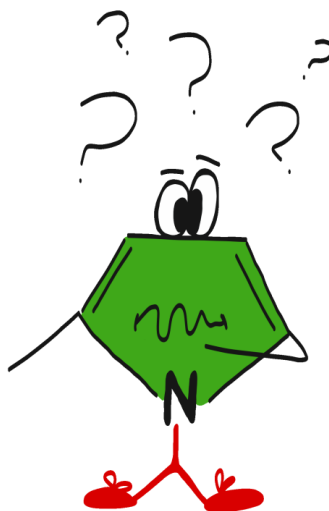
## Axial dynamic-mechanical properties



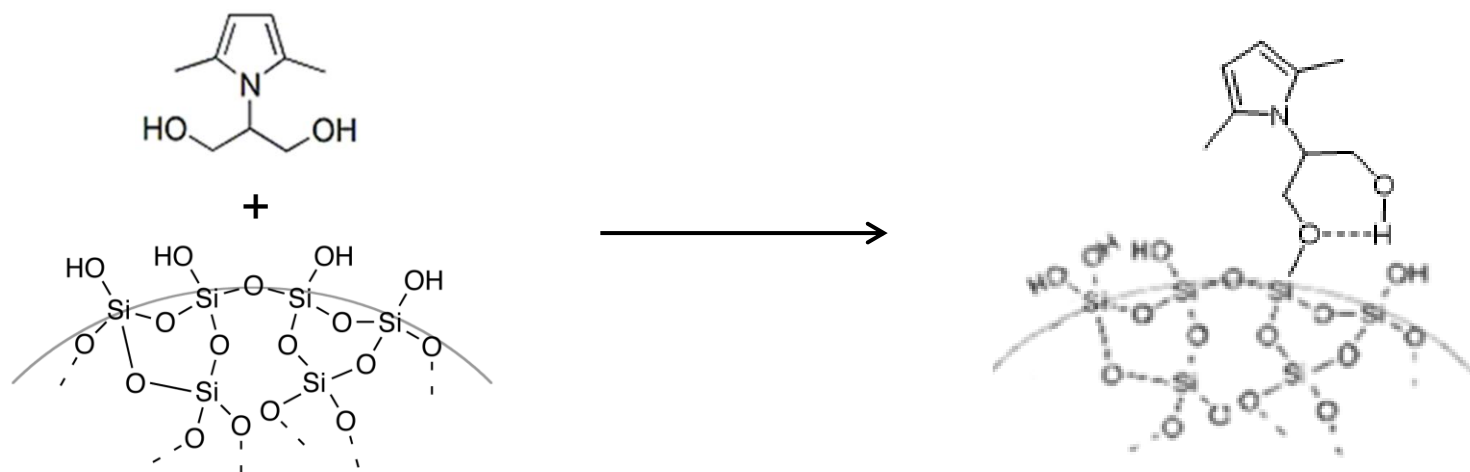
# “Universal coupling agent for carbon black and silica”



Is a coupling agent for silica?



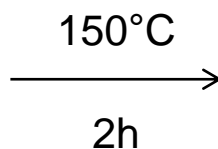
# Silica /PyC covalent adducts



Inorganic  
oxy hydroxide

+

PyC



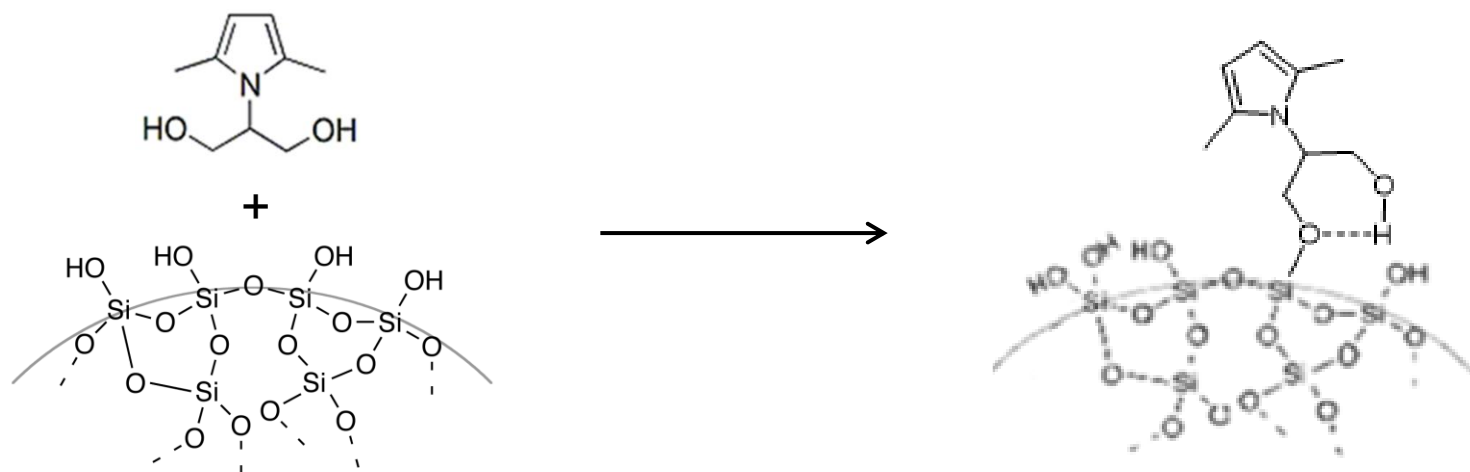
Adduct

M. Galimberti,, A. Bernardi, V. Barbera, D. Locatelli [WO2019162873A1](#)

S. Naddeo, S. Gallo, V. Barbera, M. Galimberti [Poster at KHK 2022](#)

M. Zambito Marsala, G. Stanzione, V. Barbera, M. Galimberti [Poster at KHK2022](#)

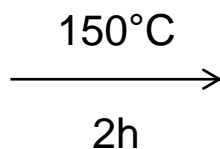
# Silica /PyC covalent adducts



Inorganic  
oxy hydroxide

+

PyC



Adduct

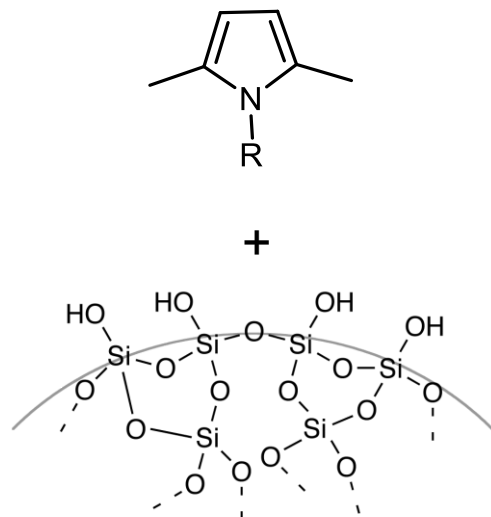
M. Galimberti,, A. Bernardi, V. Barbera, D. Locatelli [WO2019162873A1](#)

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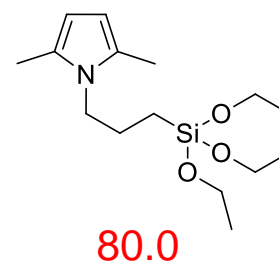
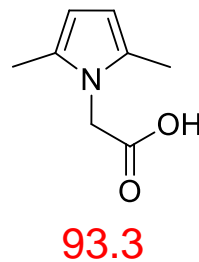
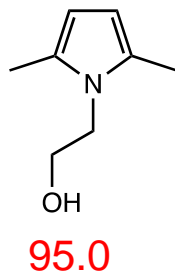
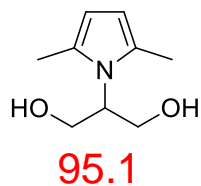
M. Zambito Marsala, G. Stanzione, V. Barbera, M. Galimberti [Poster at KHK2022](#)



# Silica /PyC covalent adducts

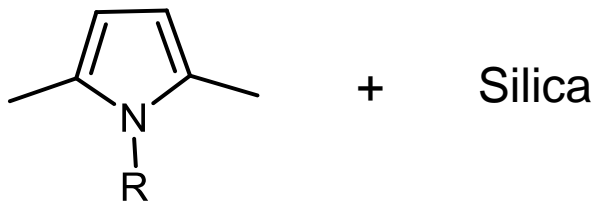


Functionalization Yield %

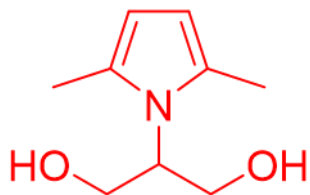


Silica: Zeosil® 1165

# “Universal coupling agent for carbon black and silica”

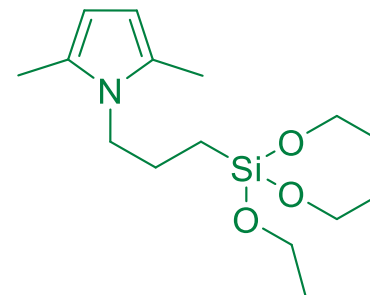


SP

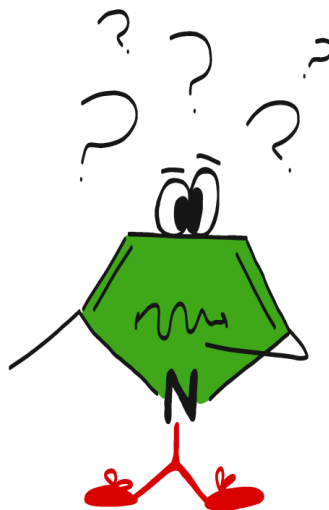


9.5 phs

APTESP



9.6 phs



Is a coupling agent for silica  
in rubber compounds?

# Rubber composites with silica/PyC

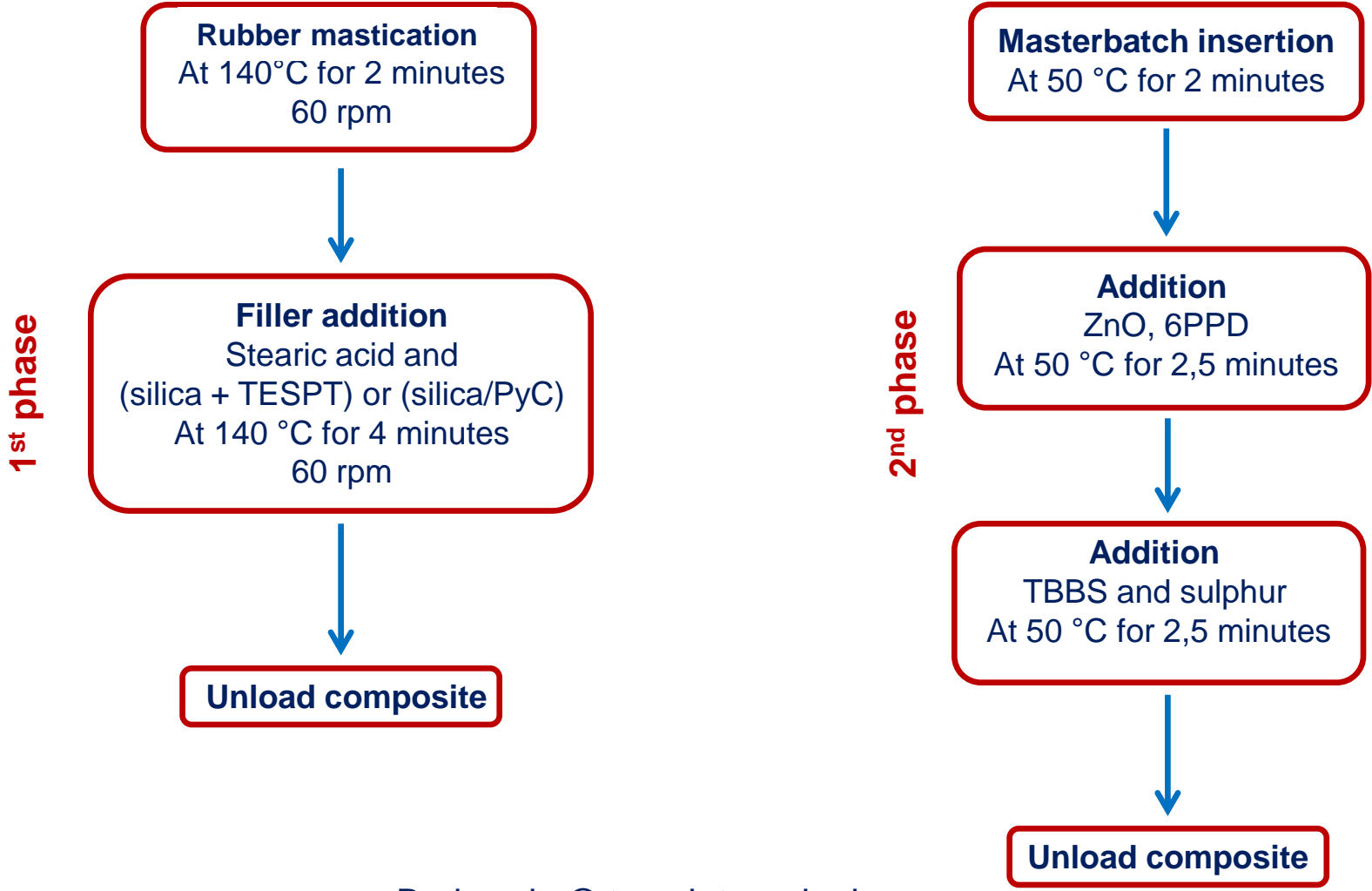
## Recipes phr

	Silica/TESPT	Silica/SP	Silica/APTESP
S-SBR	110	110	110
NR	20	20	20
Silica	50	0	0
TESPT	4	0	0
Silica/SP	0	54.5	0
Silica/APTESP	0	0	54.5
Sulphur	2	2.92	2.92

stearic acid 2, ZnO 2.5, 6PPD 2  
TBBS 1.8

# Rubber composites with silica/PyC

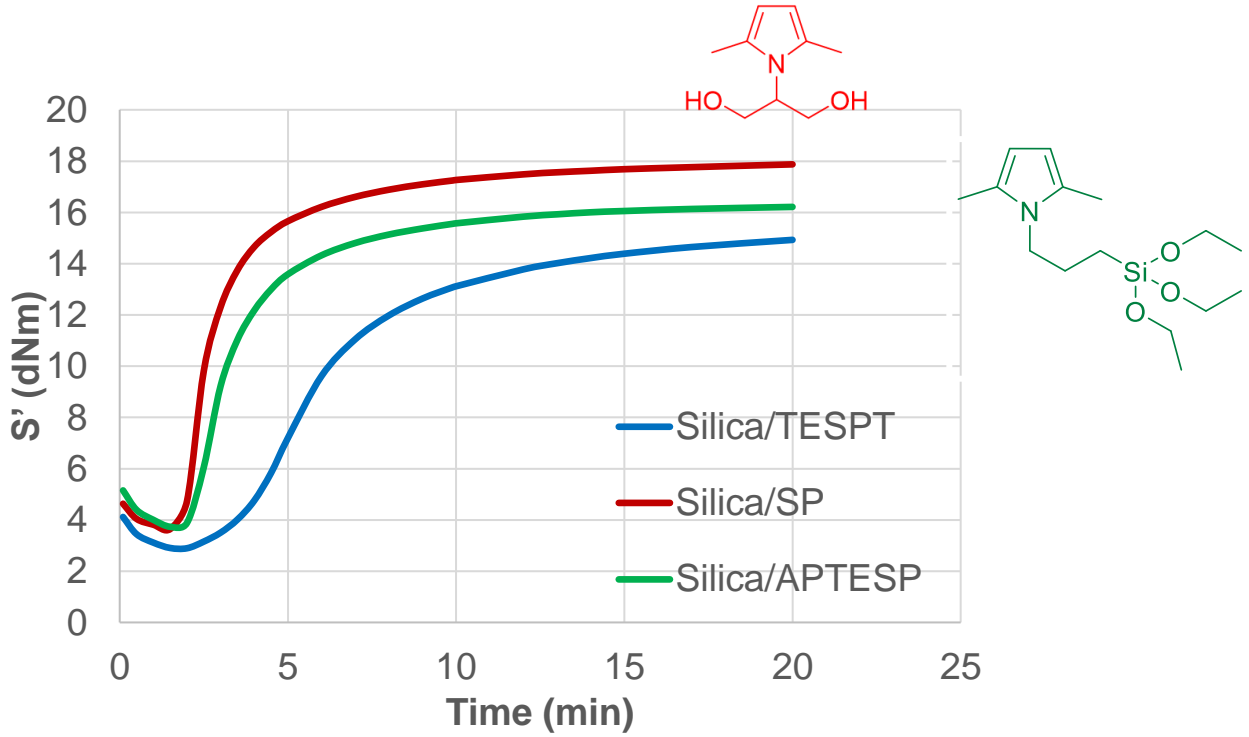
## Compound preparation



Brabender® type internal mixer

# Rubber composites with silica/PyC

## Crosslinking curves

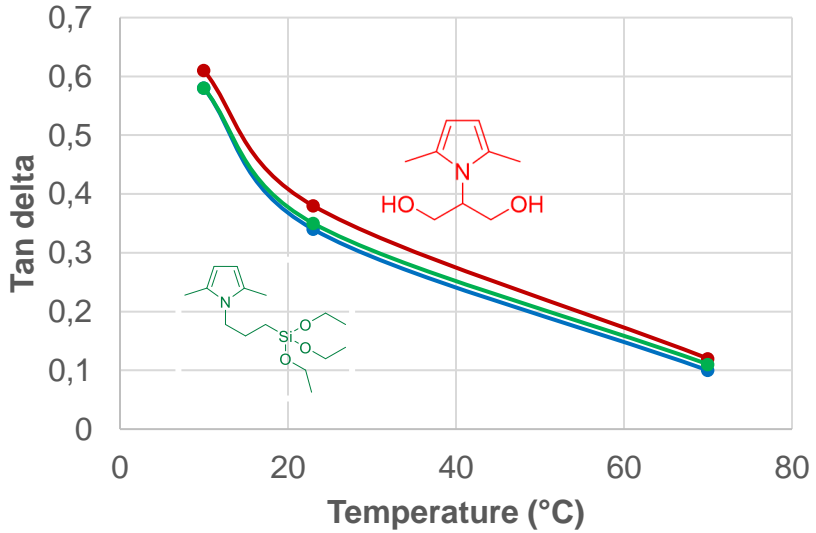
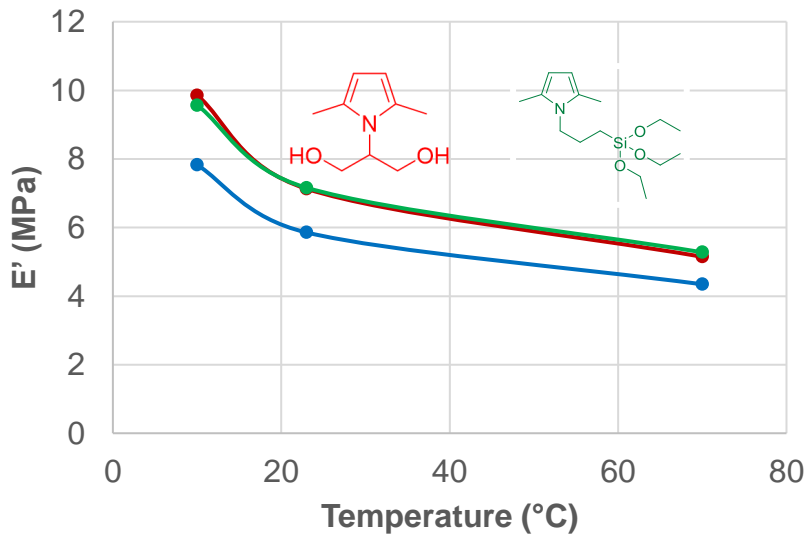


## Crosslinking network

	Silica/TESPT	Silica/SP
Total crosslinks (mol/g)	2.4	2.2
Mono and di-sulphides (% mass)	52.4	63.5
Poly-sulphides (% mass)	47.6	36.5

# Rubber composites with silica/PyC

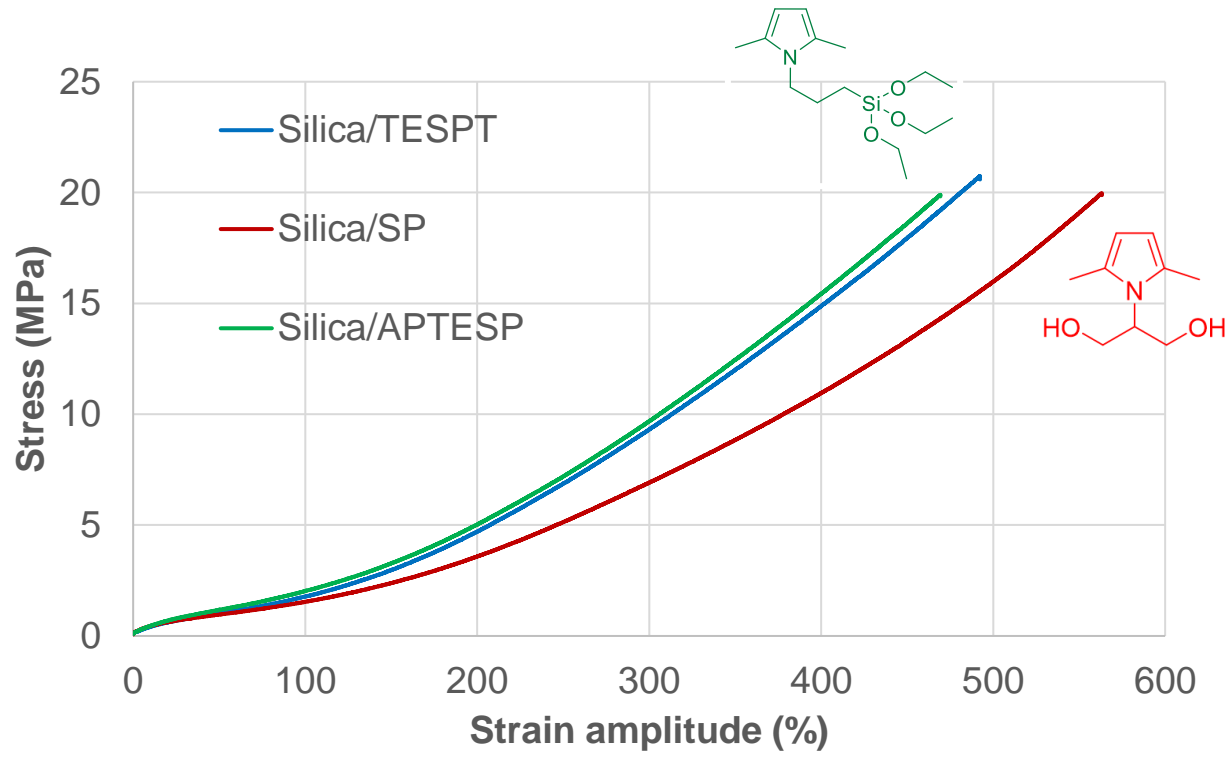
## Axial dynamic-mechanical properties



- Silica/SP
- Silica/APTESP
- Silica/TESPT

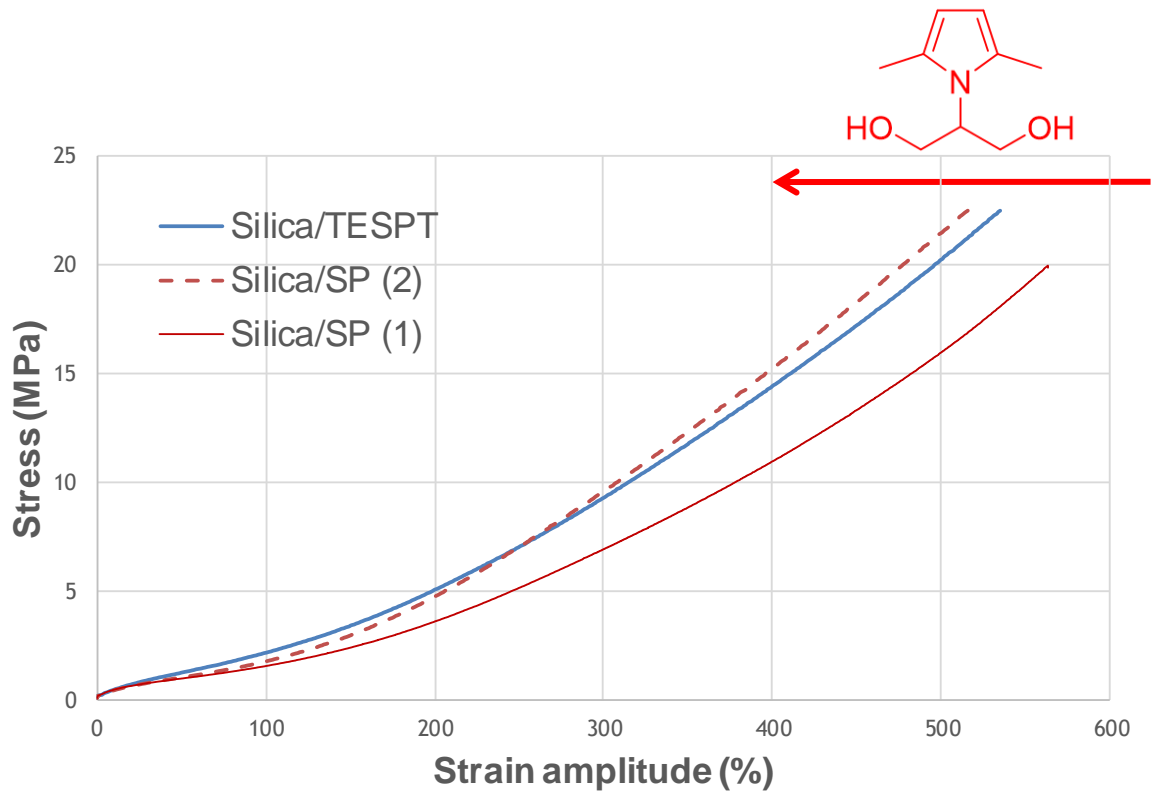
# Rubber composites with silica/PyC

Tensile curves





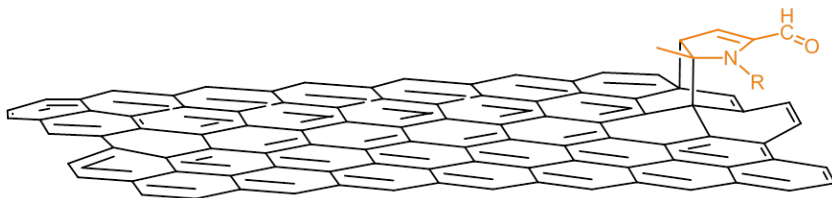
# Rubber composites with silica/PyC



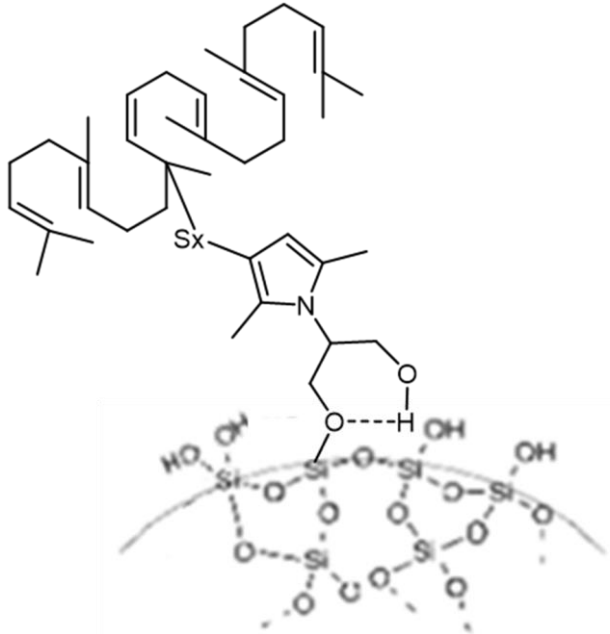
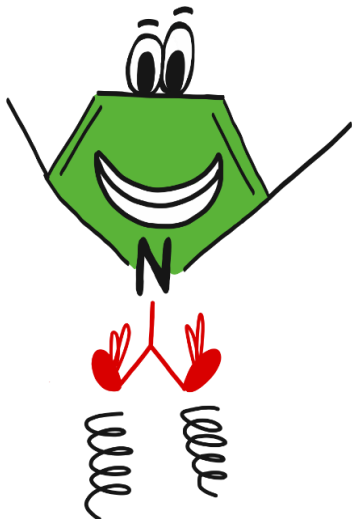
←

By modulating the amount of SP and of compound ingredients

# Conclusions



R = OH, SH



# Acknowledgments

👉 **Pirelli Tyre for the financial support.**

Pirelli Tyre; Annual Report: The Human Dimension. 2020, 106.

[https://corporate.pirelli.com/var/files2020/EN/PDF/PIRELLI\\_ANNUAL\\_REPORT\\_2020\\_ENG.pdf](https://corporate.pirelli.com/var/files2020/EN/PDF/PIRELLI_ANNUAL_REPORT_2020_ENG.pdf)



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MILANO 1863

***Thanks***  
***for your attention!***



instagram: [@ismaterials.polimi](https://www.instagram.com/ismaterials.polimi)

14th Fall Rubber Colloquium (KHK) ONLINE  
Germany, November 2022, 8 - 10



# Greetings from Milan !

