Bio-sourced Janus Molecule for the Universal Functionalization of sp^2 Carbon Allotropes and Inorganic Oxyhydroxide

Maurizio Galimberti

Vincenzina Barbera, Daniele Locatelli, Fatima Margani, Luciarita Rubino

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

Politecnico di Milano

ISCaMaP

Innovative Sustainable Chemistry and Materials and Proteins Group

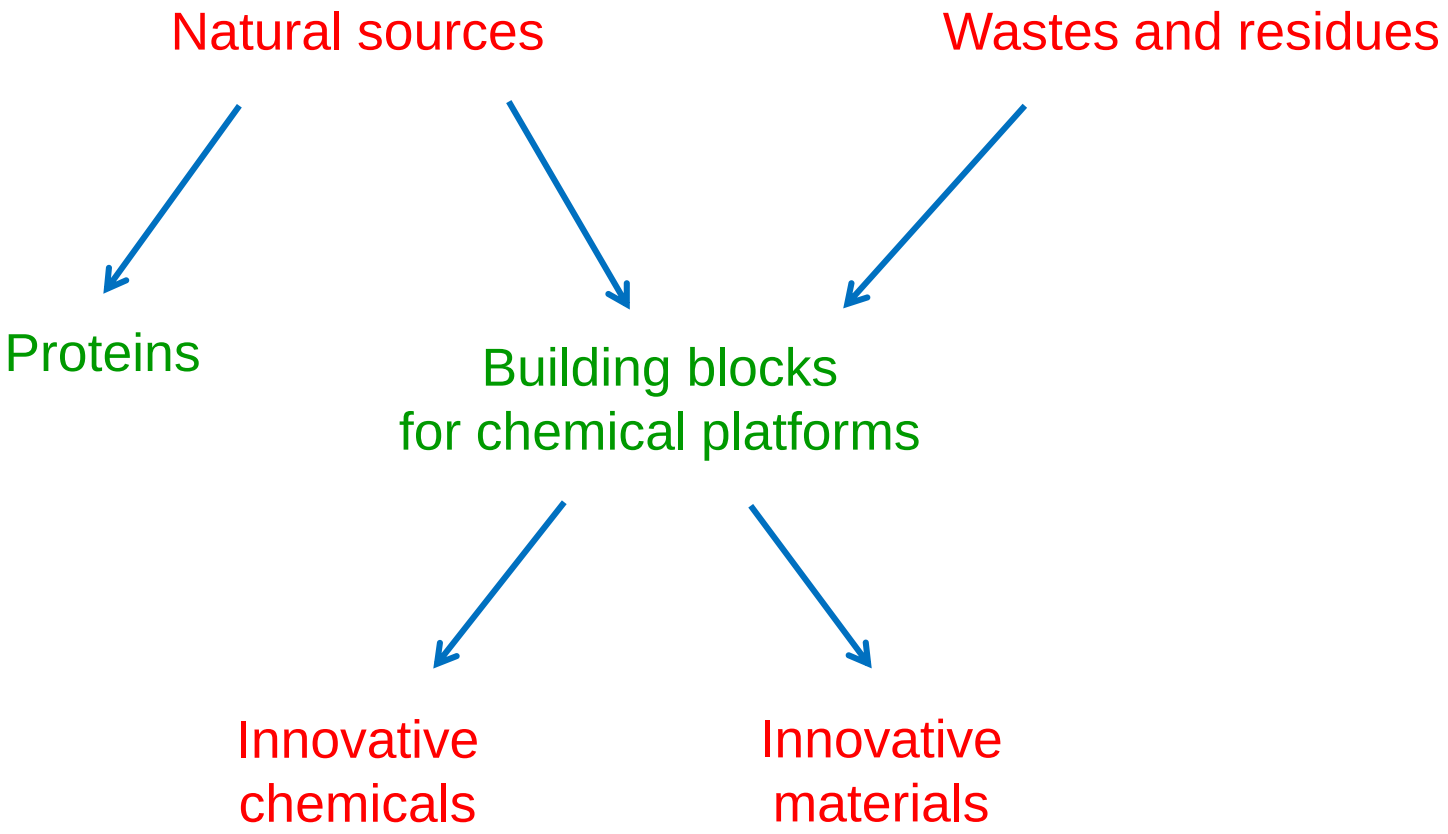
Vincenzina Barbera

Daniele Locatelli

Fatima Margani

Lucia Rubino

Innovative Sustainable Chemistry and Materials and Proteins Group



☞ Chemicals, Additives, Modifiers, Polymers

The DOE's Top Chemical Opportunities

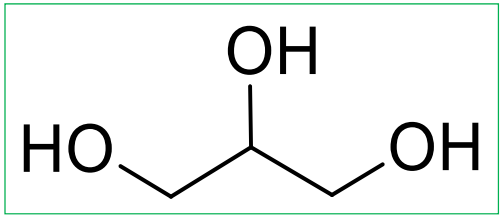
Four Carbon 1,4-Diacids: Succinic, Fumaric and Malic

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

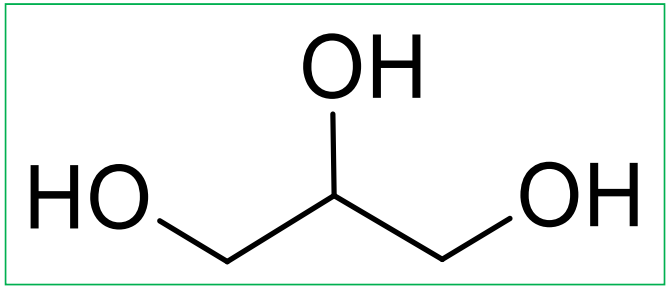
Levulinic acid

DOE = US Department of Energy

The outline of the presentation

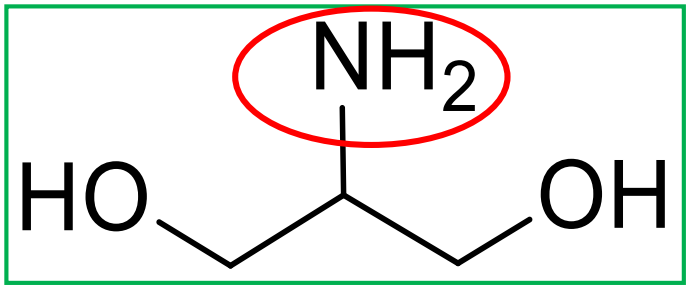
- ☞ Innovative chemicals from glycerol
- ☞ Glycerol derivatives reactive with carbon black and oxyhydroxides: “coupling agents” in elastomeric composites
- ☞ Elastomeric composites for lower dissipation of energy

Serinol: a glycerol derivative



glycerol

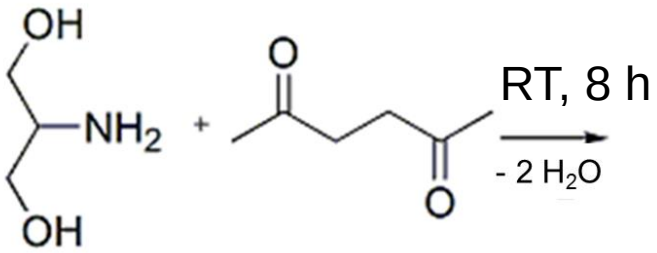
propane-1,2,3-triol

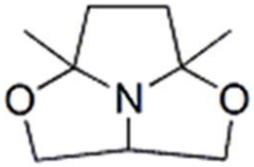


serinol

3-Amino-1,2-propanediol

Serinol pyrrole from neat Paal Knorr reaction

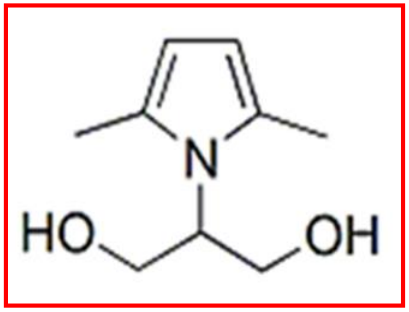




no solvent, no catalyst

Δ 180°C, 3 h

Yield: 95 %



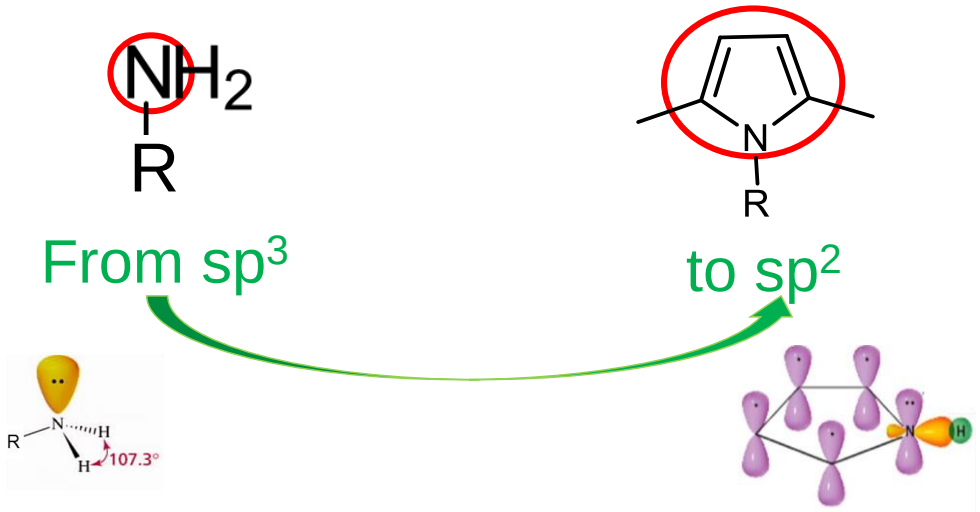
Serinol pyrrole - SP

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 *US10329253B2*

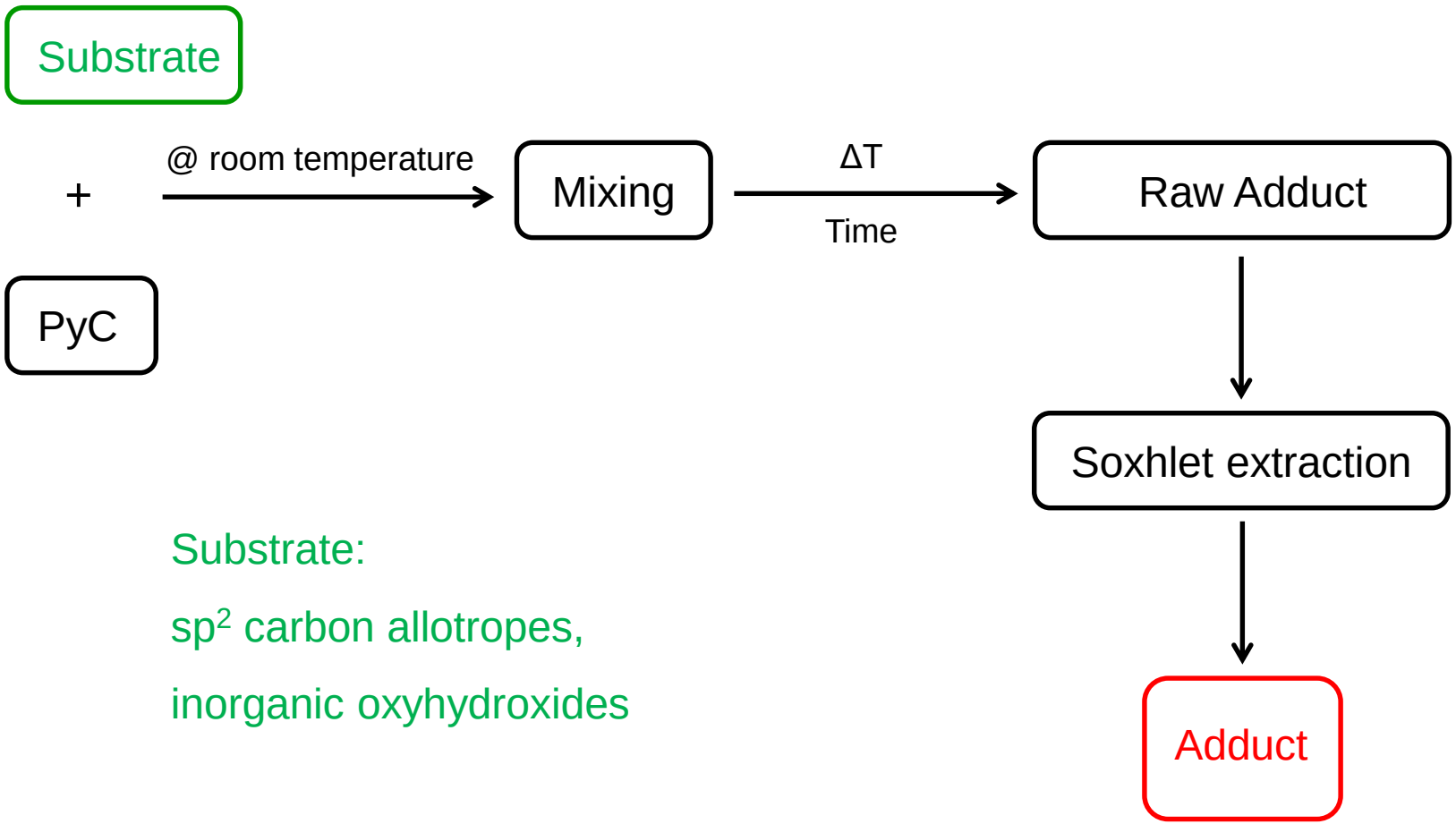
M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini,, *RSC Adv.*, 2015, *5*, 81142-81152

Neat synthesis of PyC



- Yield: up to 96%
- Atom efficiency: up to 85%
- Easy procedure: mixing and heating
- No solvent, no catalyst
- By product: H_2O

Preparation of PyC/Substrate adduct

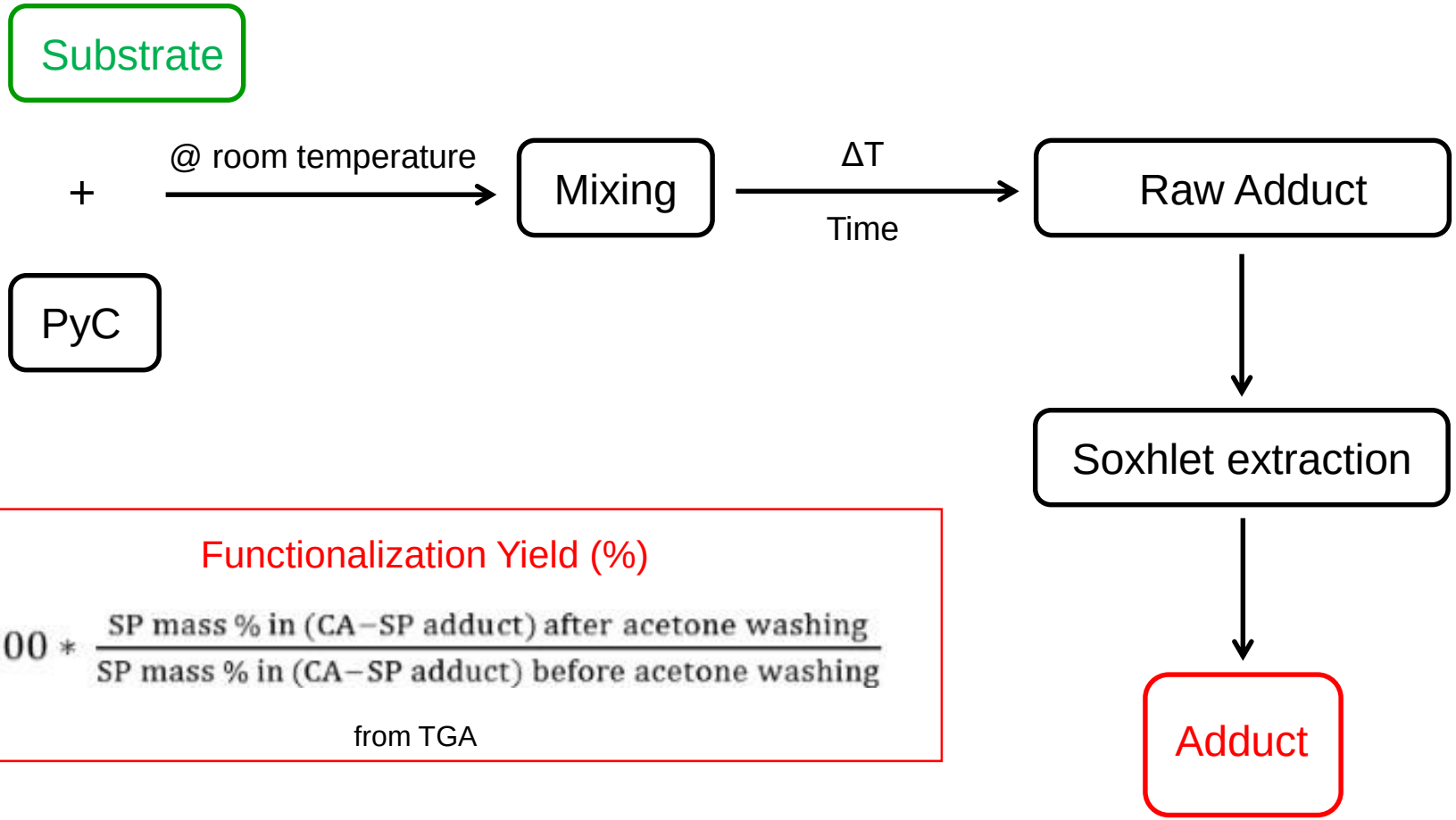


Substrate:

sp^2 carbon allotropes,

inorganic oxyhydroxides

Preparation of PyC/Substrate adduct



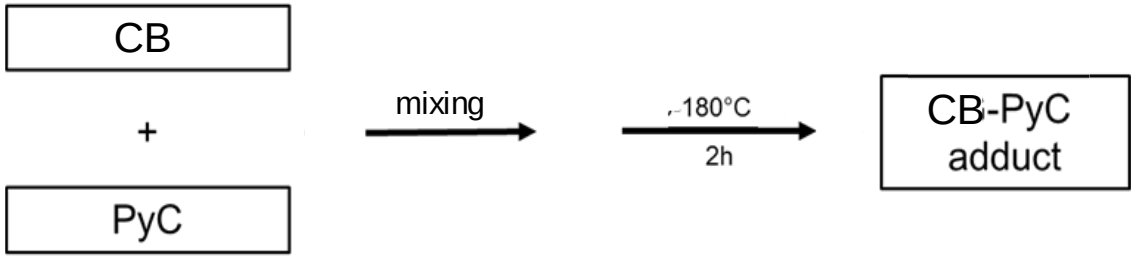
Functionalization Yield (%)

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

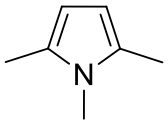
from TGA

Substrate: sp^2 carbon allotropes, inorganic oxyhydroxides

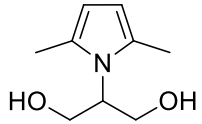
Adducts of PyC with carbon black



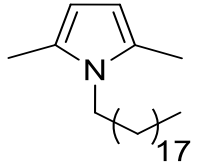
Functionalization Yield %



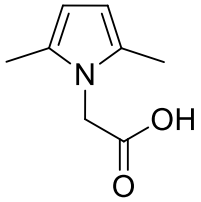
65.6



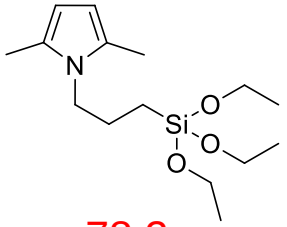
96.0



98.0



81.8



78.2

CB N234 from Cabot

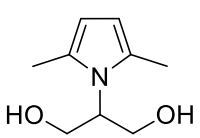
V. Barbera, A.Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, A.M. Valerio *US10160652B2*

M. Galimberti, V. Barbera *WO 2018/087685 A1*

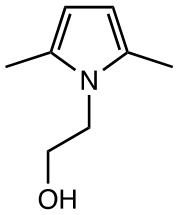
V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

Adducts of Pyrrole compounds with silica

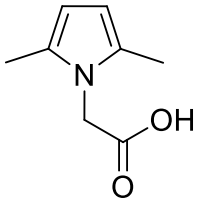
Functionalization Yield %



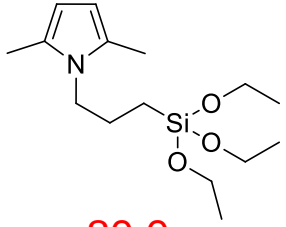
95.1



95.0



93.3



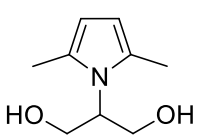
80.0

Silica: Zeosil® 1165 from Solvay

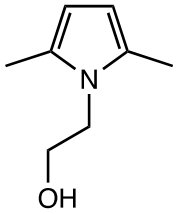
M. Galimberti,, A. Bernardi, V. Barbera, D. Locatelli *WO2019162873A1*

Adducts of Pyrrole compounds with silica

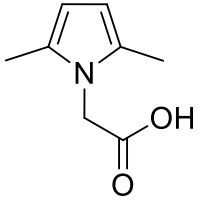
Functionalization Yield %



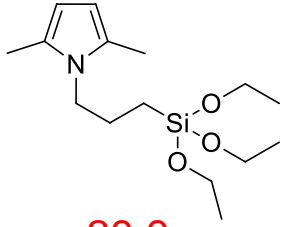
95.1



95.0



93.3



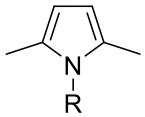
80.0

Silica: Zeosil® 1165 from Solvay

M. Galimberti,, A. Bernardi, V. Barbera, D. Locatelli *WO2019162873A1*

Adducts of Pyrrole compounds with sepiolite

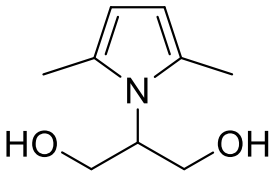
Sepiolite

+ 

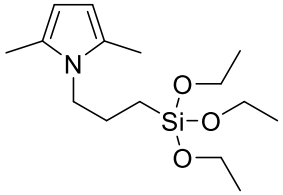
T = 150 °C
time = 2 h

Sepiolite/PyC

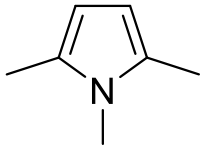
Functionalization Yield %



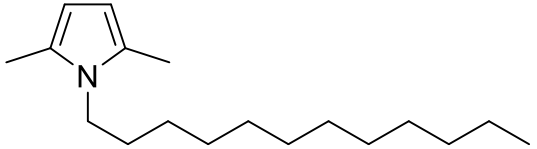
96.0



88.7



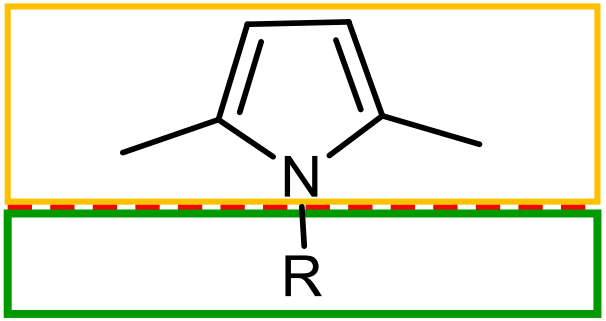
92.8



82.0

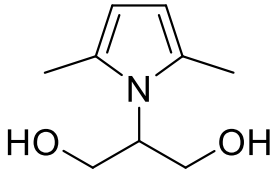
Sepiolite Pangel S9: from Tolsa

Pyrrole compound. A *Janus* molecule



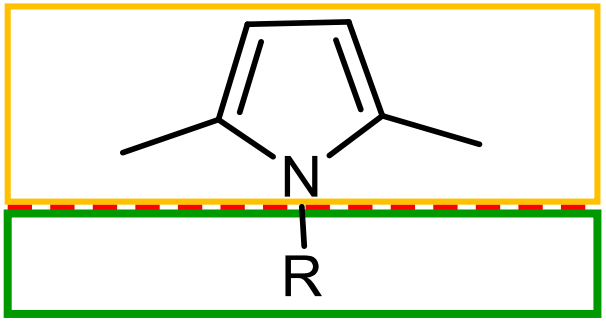
Study of the reactivity

of pyrrole compounds moieties



with sp^2 carbon allotropes and oxyhydroxides

Pyrrole compound. A *Janus* molecule



Study of the reactivity

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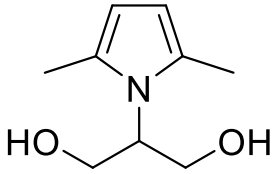
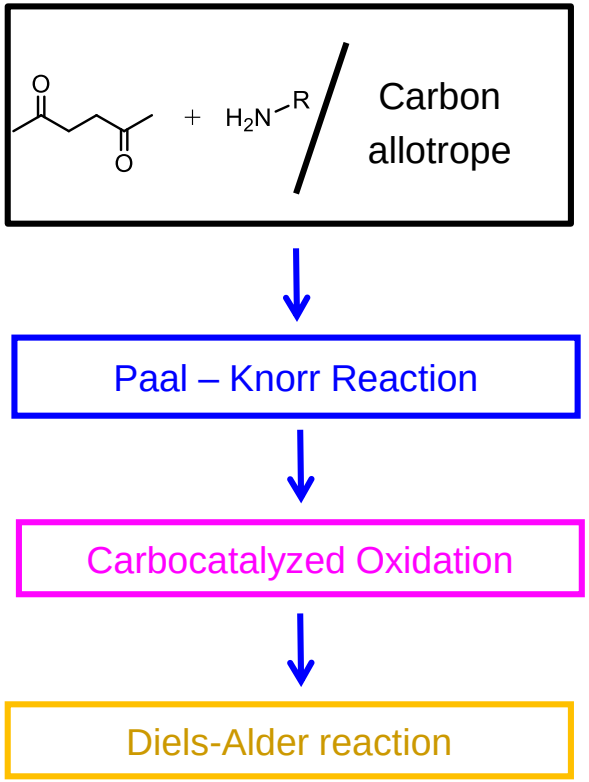
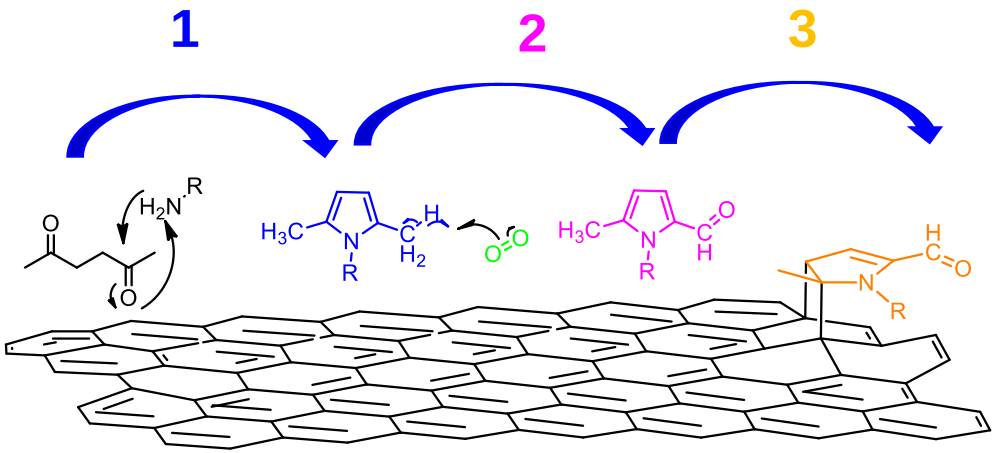


with sp^2 carbon allotropes

Reaction of PyC with an sp^2 carbon allotrope

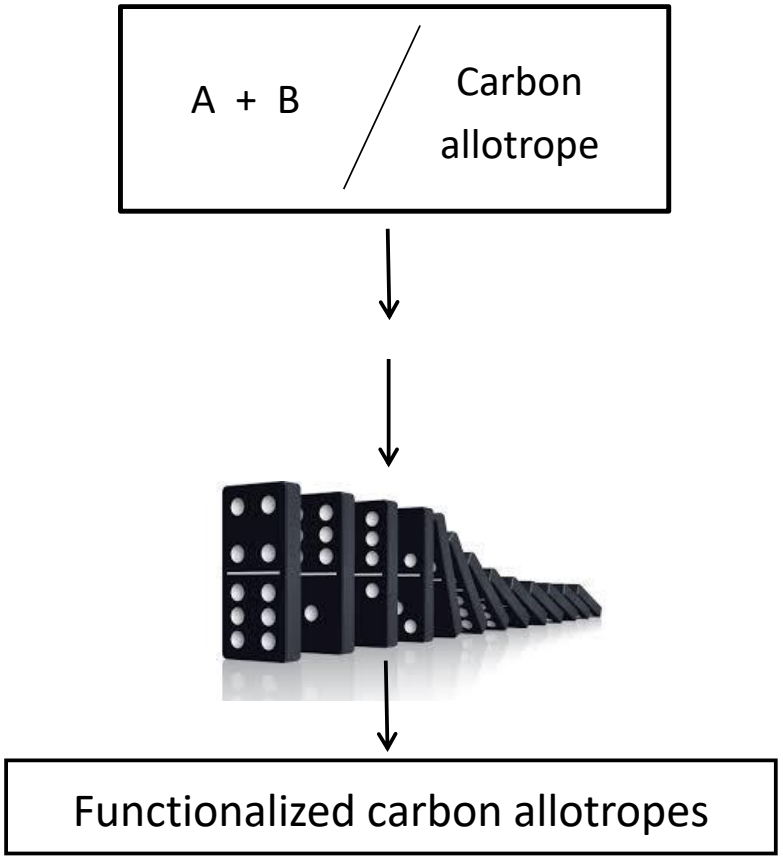
Domino reaction





V. Barbera, L. Brambilla, M. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, R. Bongiovanni, and M. Galimberti, 2019. Nanomaterials, 9(1), p.44.

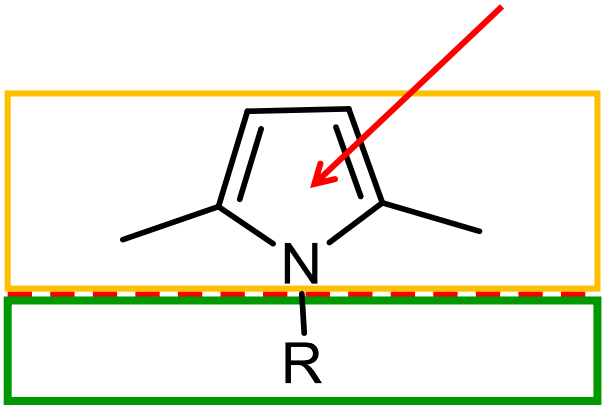
Functionalization of carbon materials with PyC



- Functional group:
  from few % to 20%
- 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*

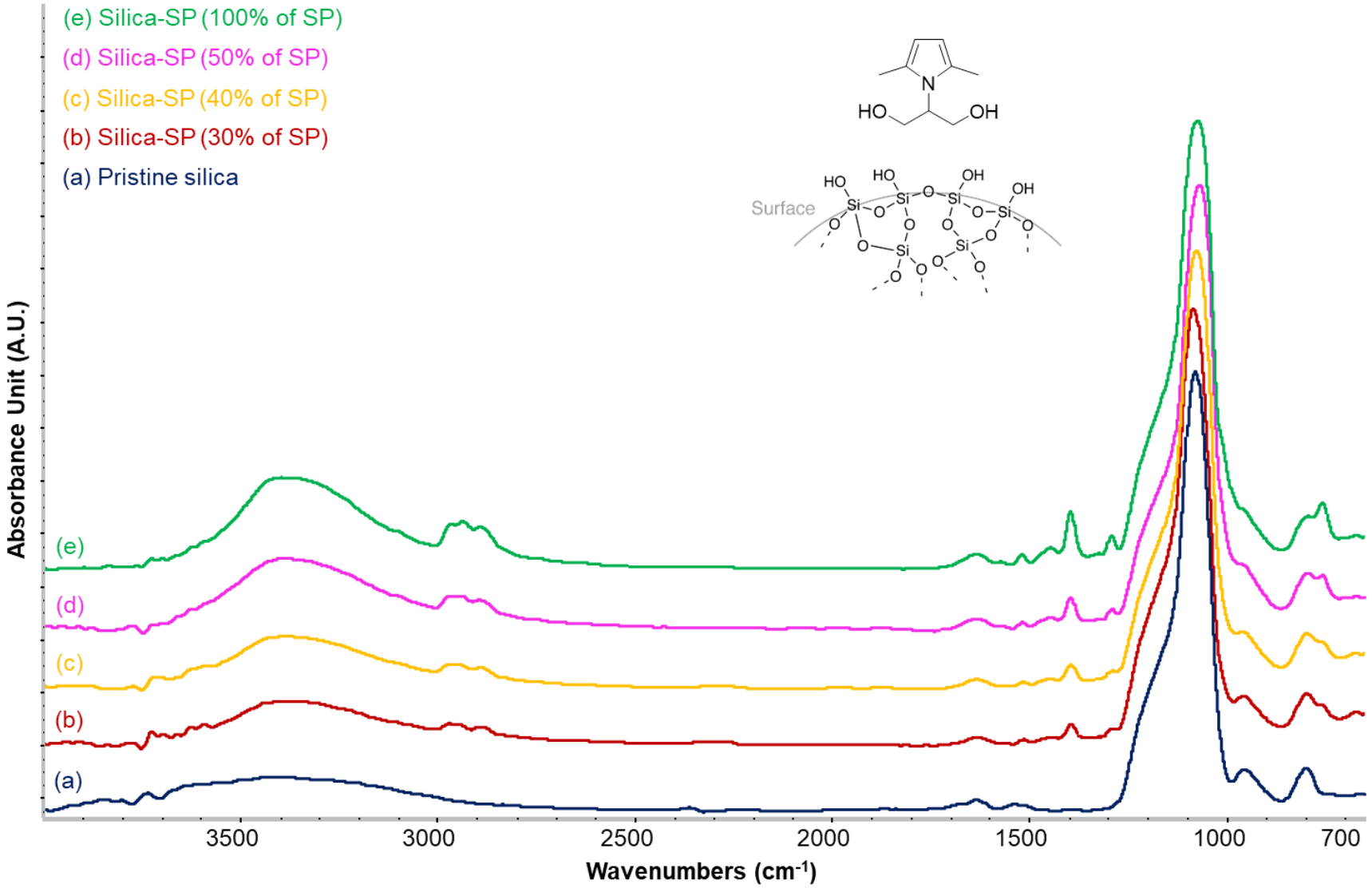
Pyrrole compound. A *Janus* molecule



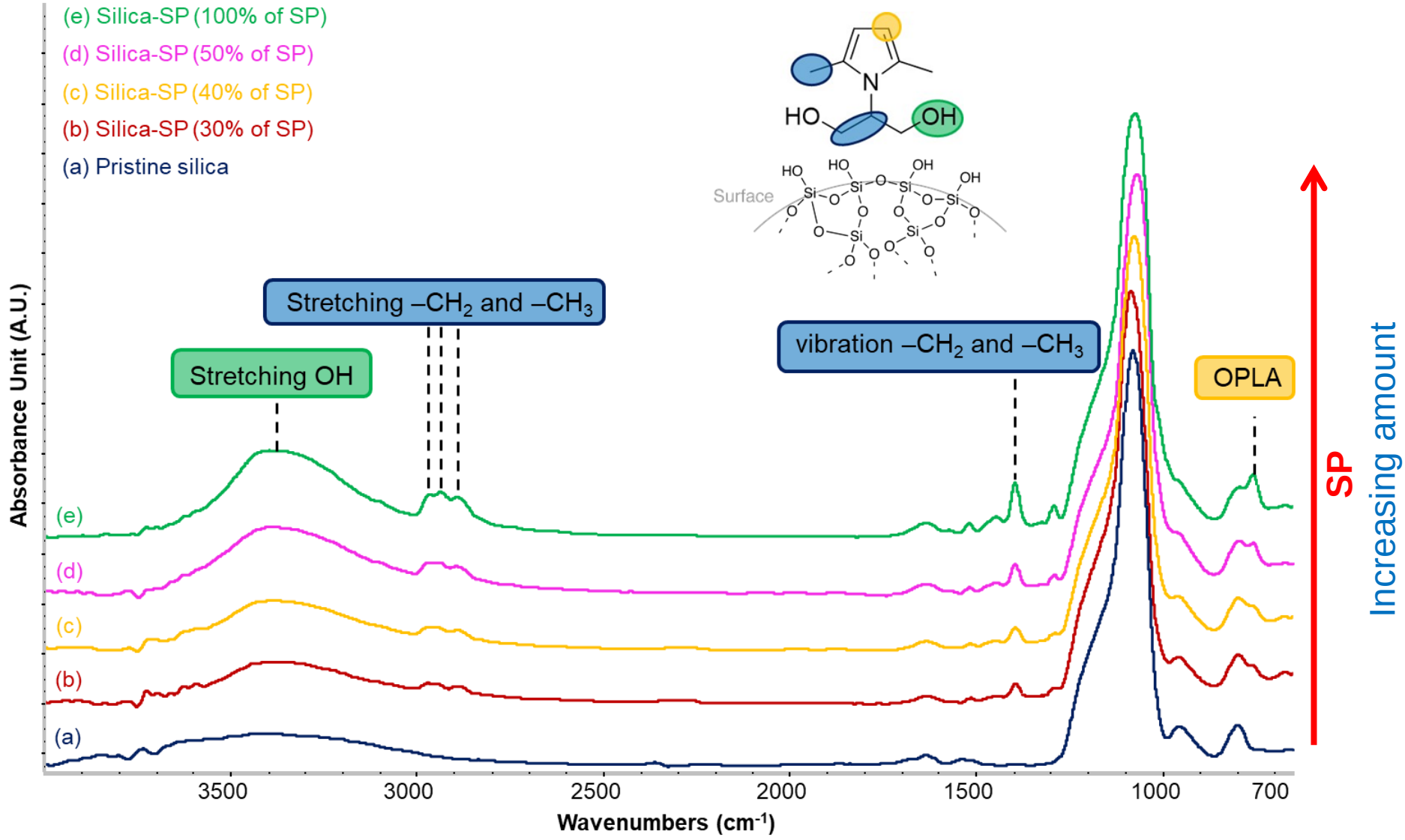
Study of the reactivity

with silica

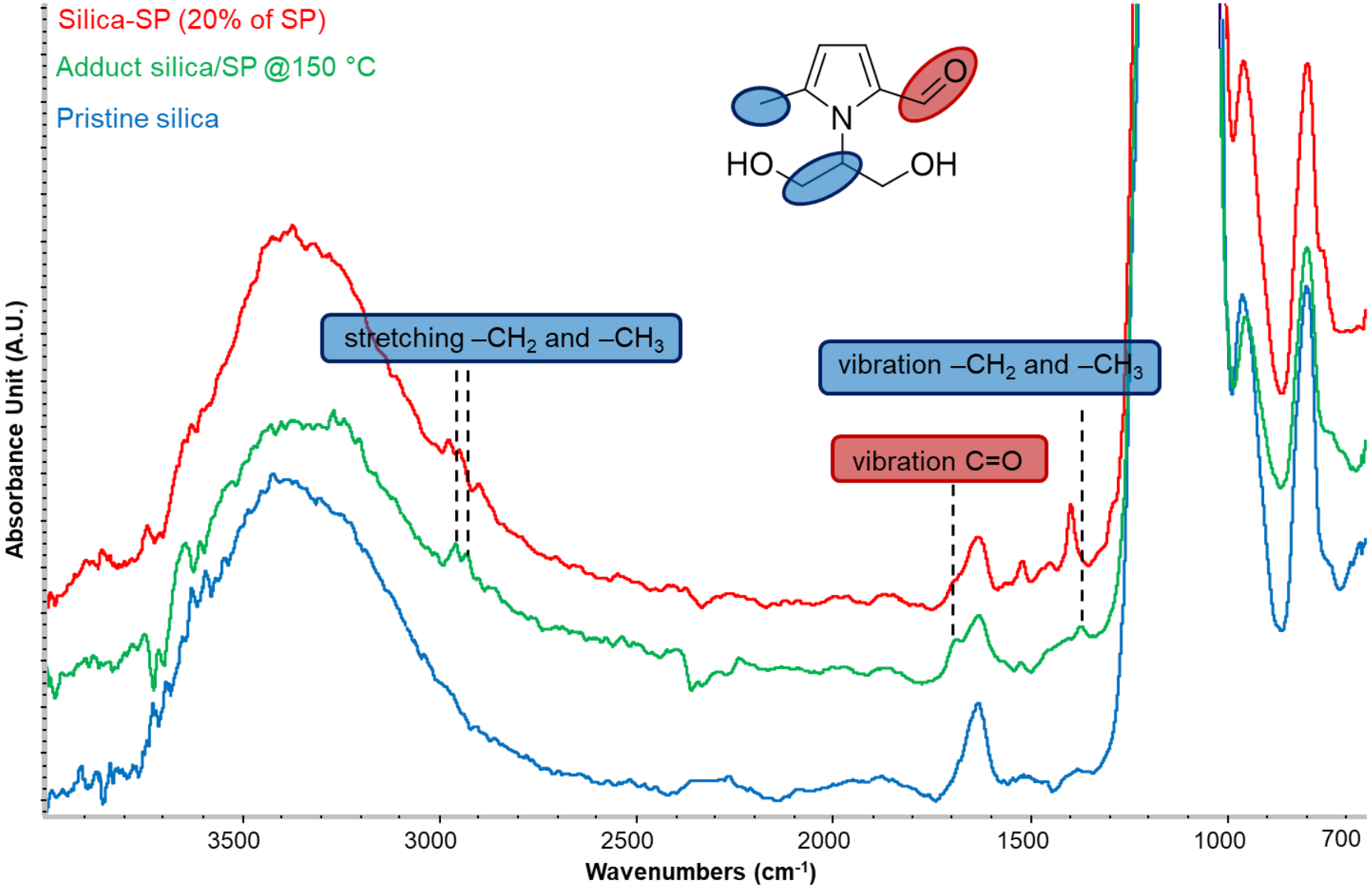
Silica + serinol pyrrole - Physical mixture



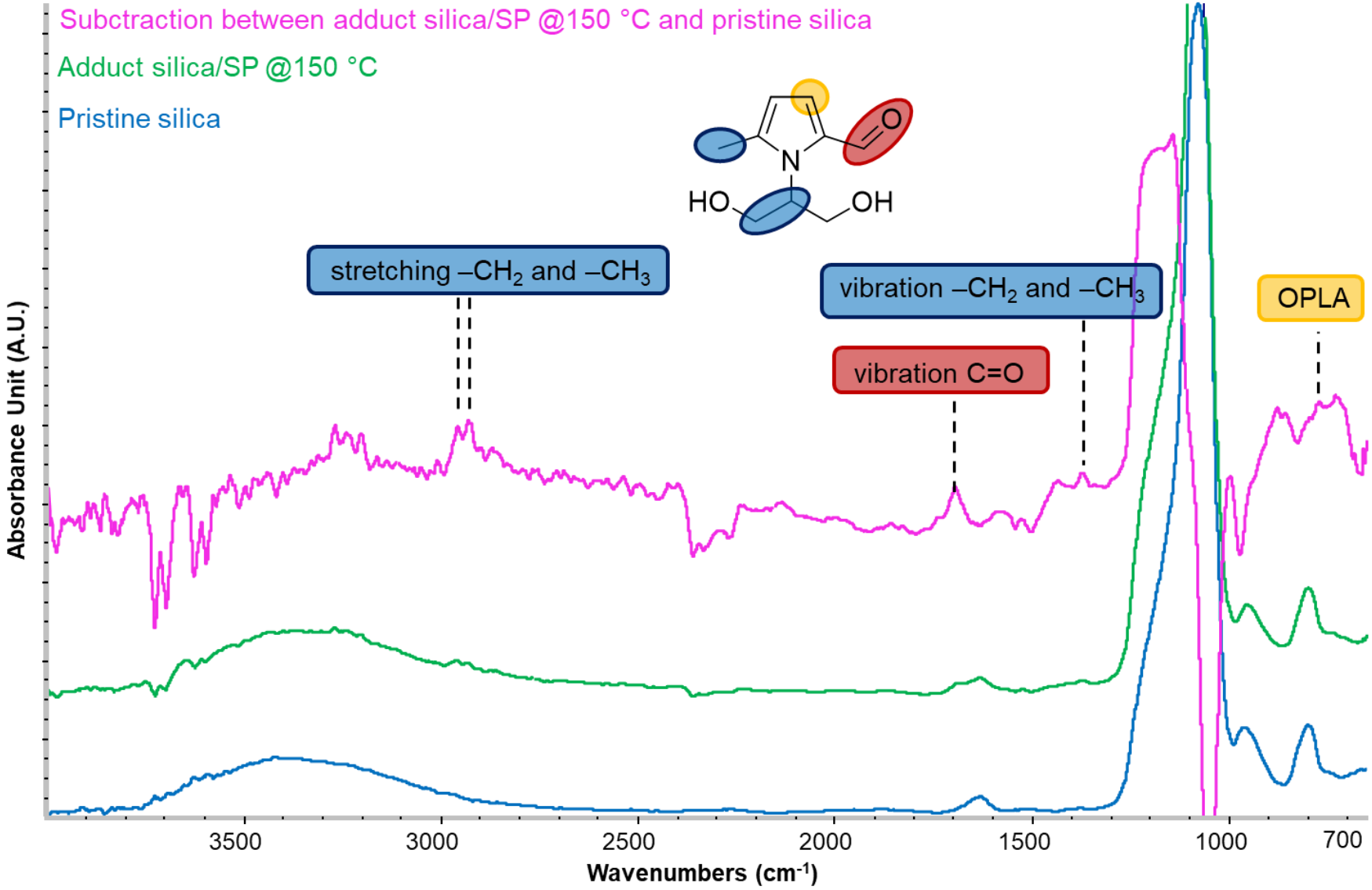
Silica + serinol pyrrole - Physical mixture



Silica + serinol pyrrole - Physical mixture vs adduct

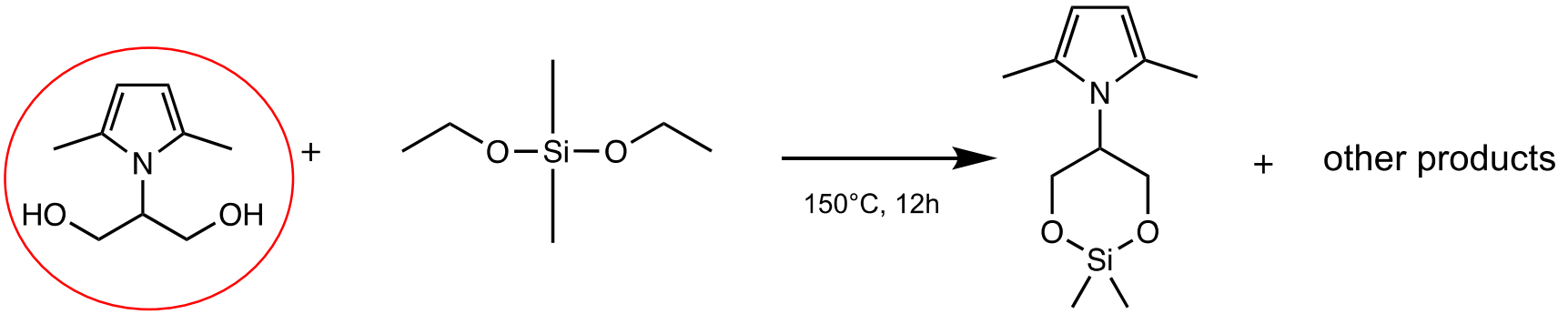


Silica + serinol pyrrole - Physical mixture vs adduct

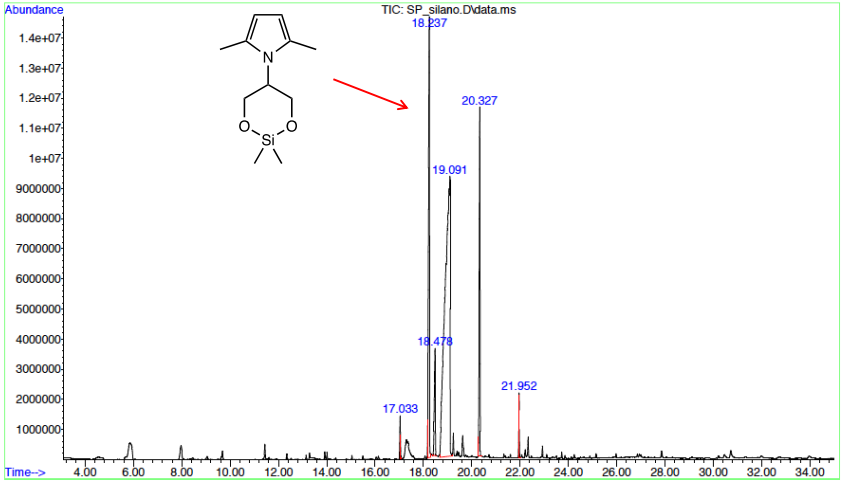


Reactivity of pyrrole compounds with silanes

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



GC-MS

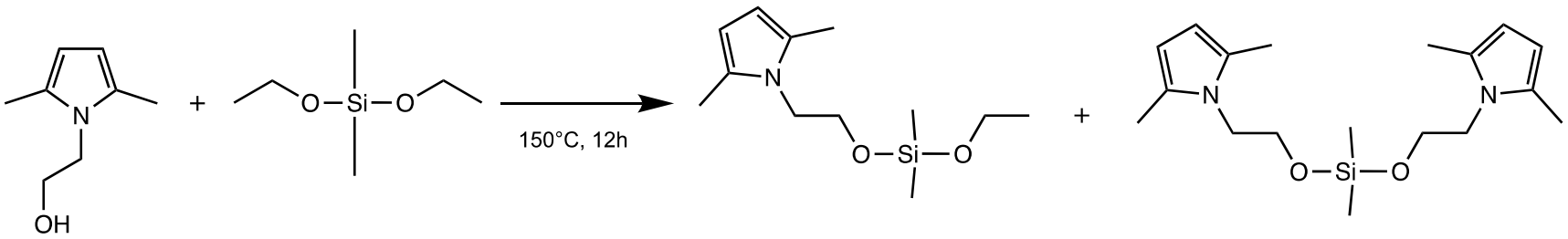


Synthesis of spirosilicates directly from silica and ethylene glycol

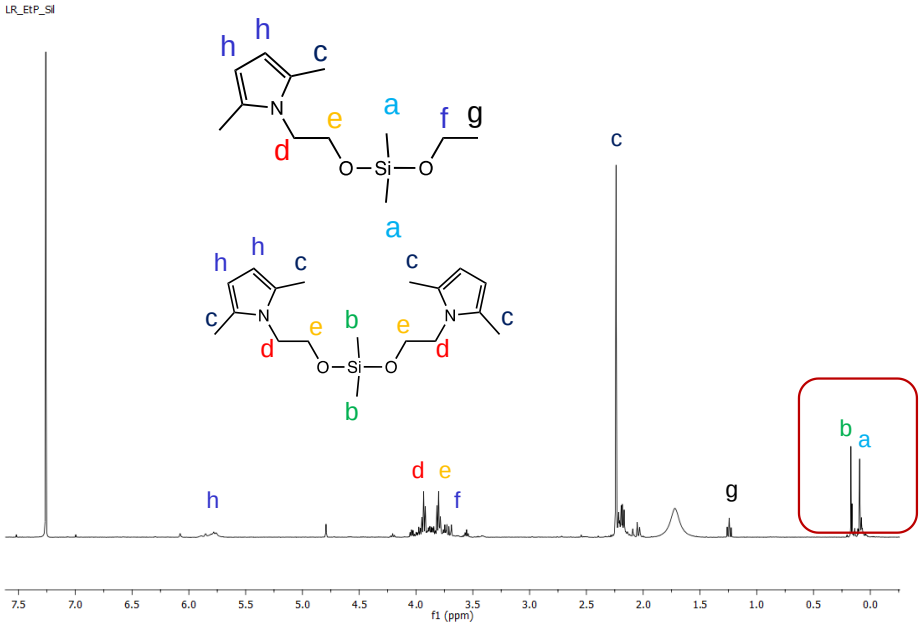
Jitchum, V., Chivin, S., Wongkasemjit, S., Ishida, H. (2001). *Tetrahedron, 57(18), 3997-4003.*

Reactivity of pyrrole compounds with silanes

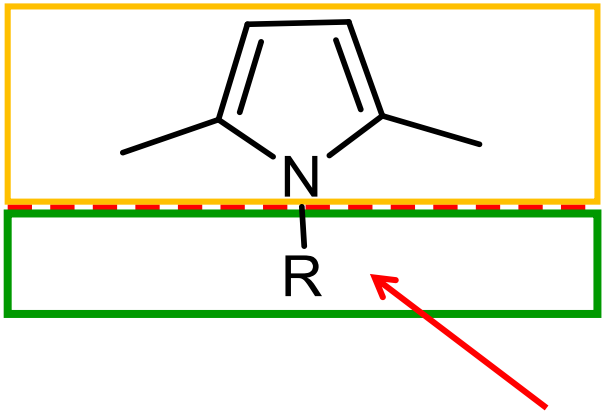
1-hexyl-2,5-dimethyl-1*H*-pyrrole + Diethoxydimethyl silane



1H-NMR



Pyrrole compound.



Why PyC as coupling agent

in elastomeric composites?

The most important application: tyre

Sustainability as the objective of tyre

Green tyre

Renewable resources for tyre compounds

energy input for the production (1)

NR: 15-16 MJ/kg

synthetic rubber: 100 MJ/kg

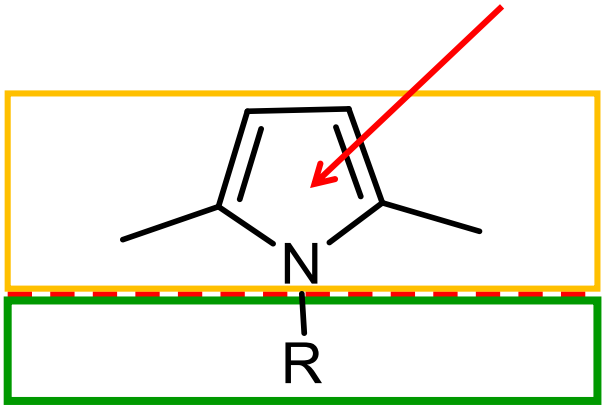
carbon sequestration by the *Hevea* tree (2)

photosynthetic rate

Hevea leaves: about 11 μmol/m^2·s

other trees: 5–13 μmol/m^2·s

Pyrrole compound. A *Janus* molecule



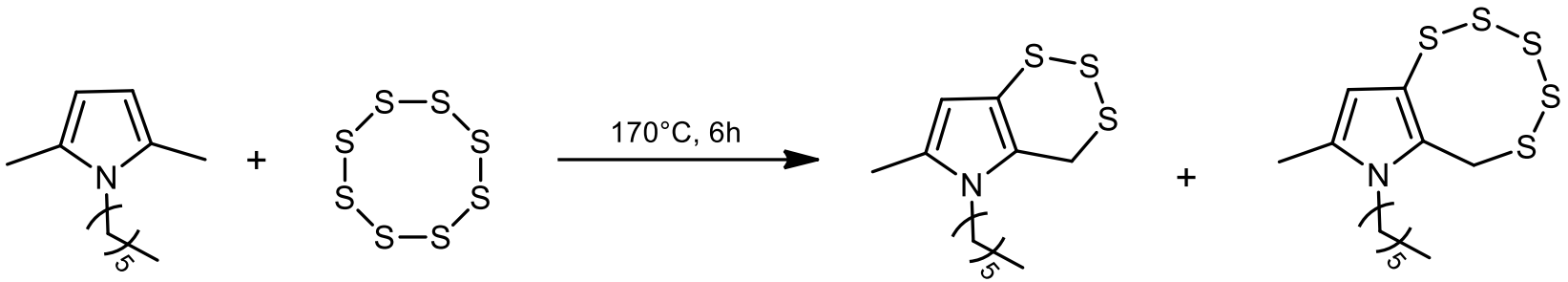
Study of the reactivity

of the pyrrole ring

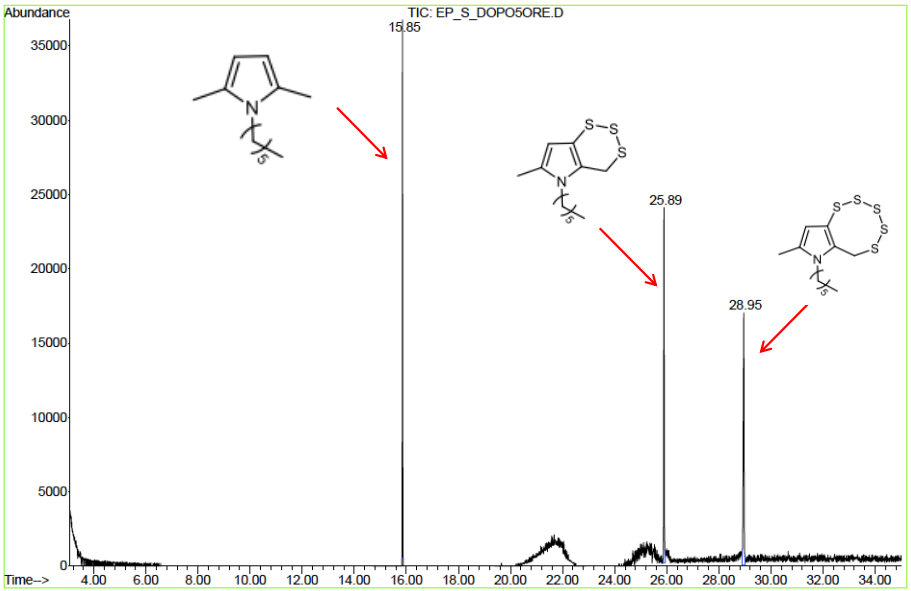
With sulphur and sulphur based chemicals

Reaction of a PyC with sulphur

1-hexyl-2,5-dimethyl-1*H*-pyrrole + S_8

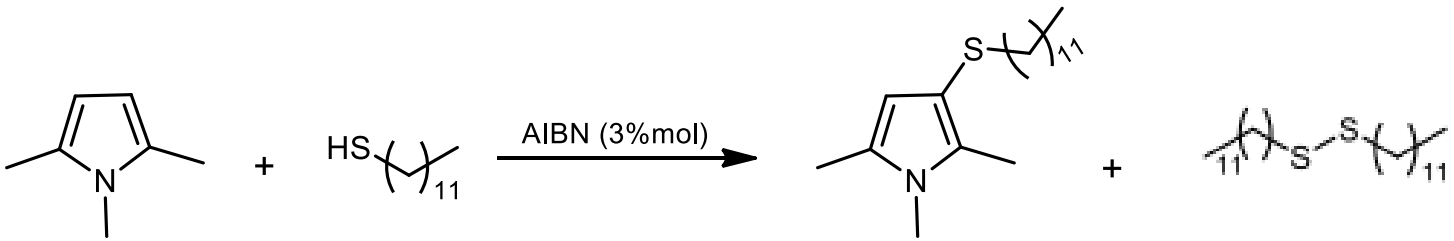


GC-MS



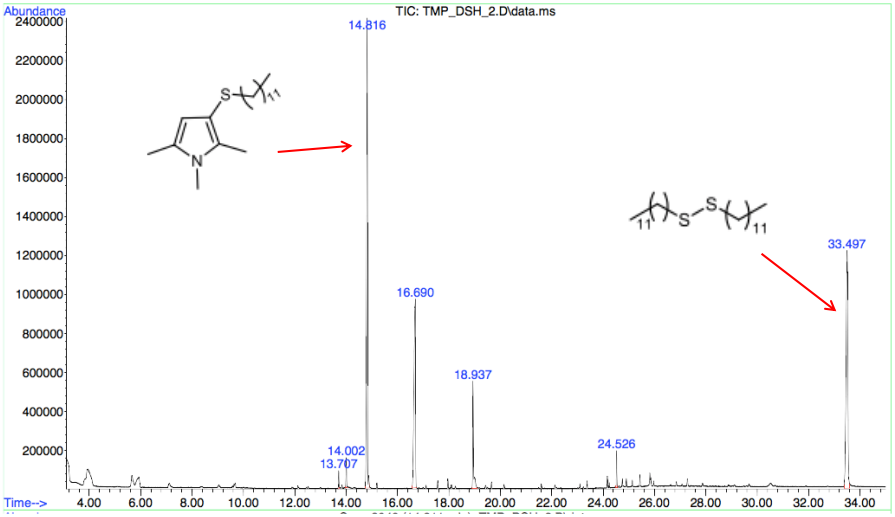
Reaction of a PyC with 1-dodecanthiol

1,2,5-trimethylpyrrole + 1-dodecanethiol



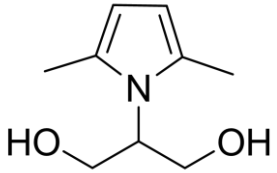
sulphurated products

GC-MS



AIBN = 2-2'-azaisobutyronitrile

CB-SP in CB/Silica based composite



Recipes

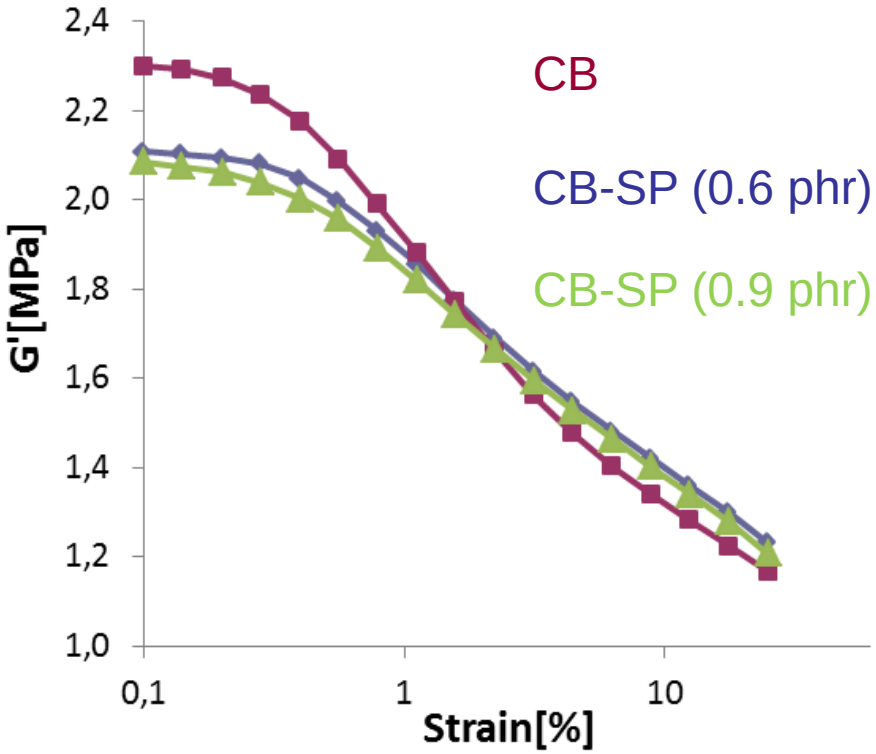
Ingredient	Compound with CB	Compound with CB-SP 0,6 phr of SP	Compound with CB-SP 0,9 phr of SP
IR	50	50	50
BR	50	50	50
Silica	25	25	25
CB N326	25	20	17.5
CB N326-SP	0	6.1	9.1
CB N326	0	5.5	8.2
SP	0	0.6	0.9

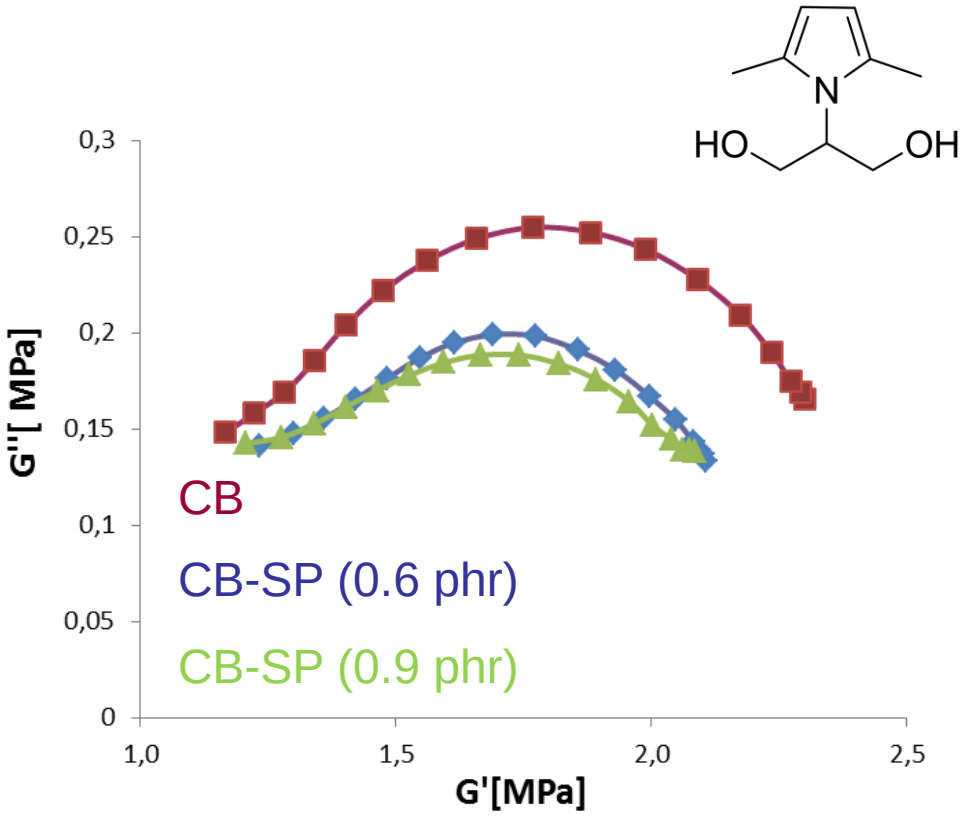
Silane TESPT 2, Stearic acid 2, ZnO 4, 6PPD 2,

Sulphur 3, TBBS 1.8

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

CB-SP in CB/Silica based composite





With CB-SP

☞ Lower Payne effect and crossover of the G' vs strain curves

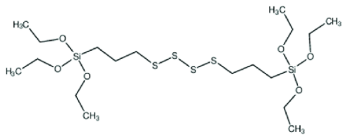
☞ Lower Tan delta

Silica based composites. TESPT vs PyC as coupling agent

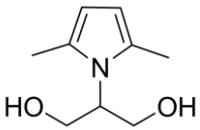
Ingredient	Compund with silica	Compound with silica-TESPT	Compound with silica-SP	Compound with silica-APTESP
S-SBR	110	110	110	110
NR	20	20	20	20
Silica	50	50	0	0
SilaneTESPT	0	4.0	0	0
Silica-SP	0	0	54	0
Silica	0	0	50	0
SP	0	0	4	0
Silica-APTESP	0	0	0	54
Silica	0	0	0	50
APTESP	0	0	0	4
Sulphur	2	1.2	2	2

Stearic acid 2, ZnO 4, 6PPD 2, TBBS 1.8

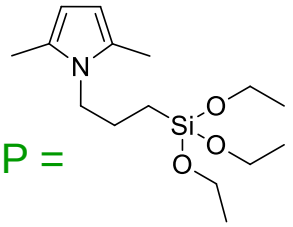
TESPT
Bis(triethoxysilylpropyl)tetrasulfide
=



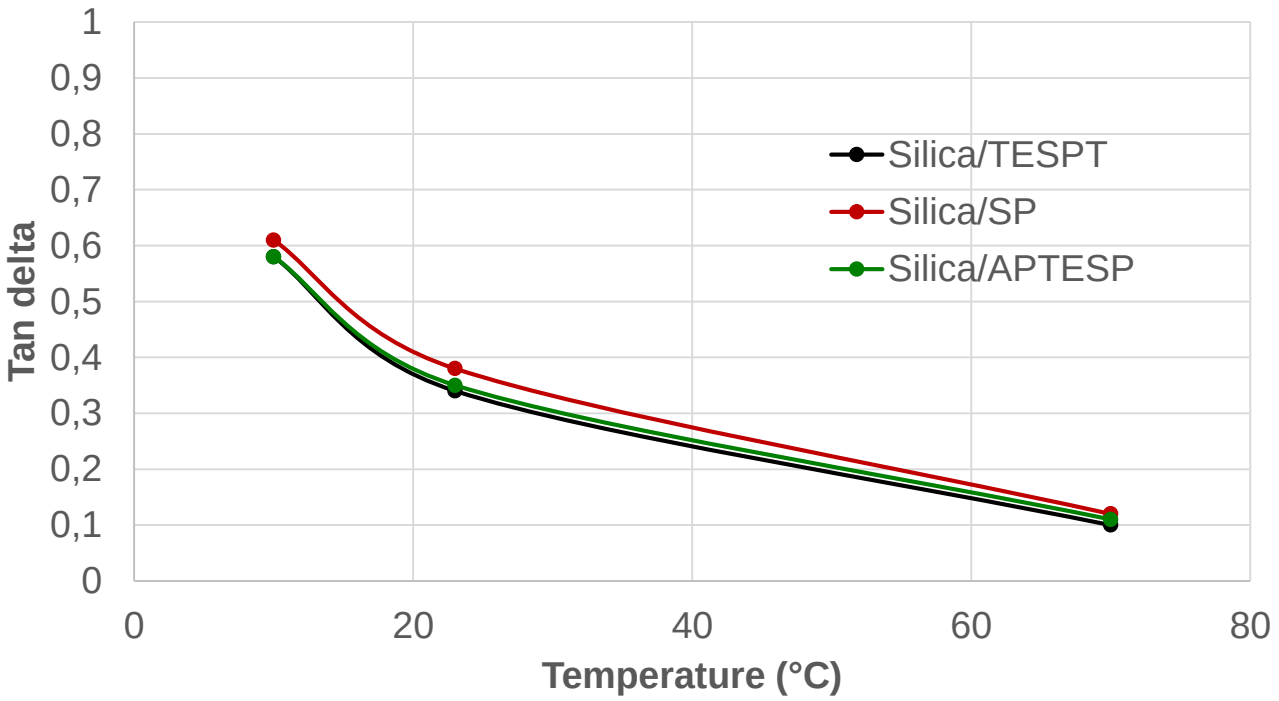
SP =



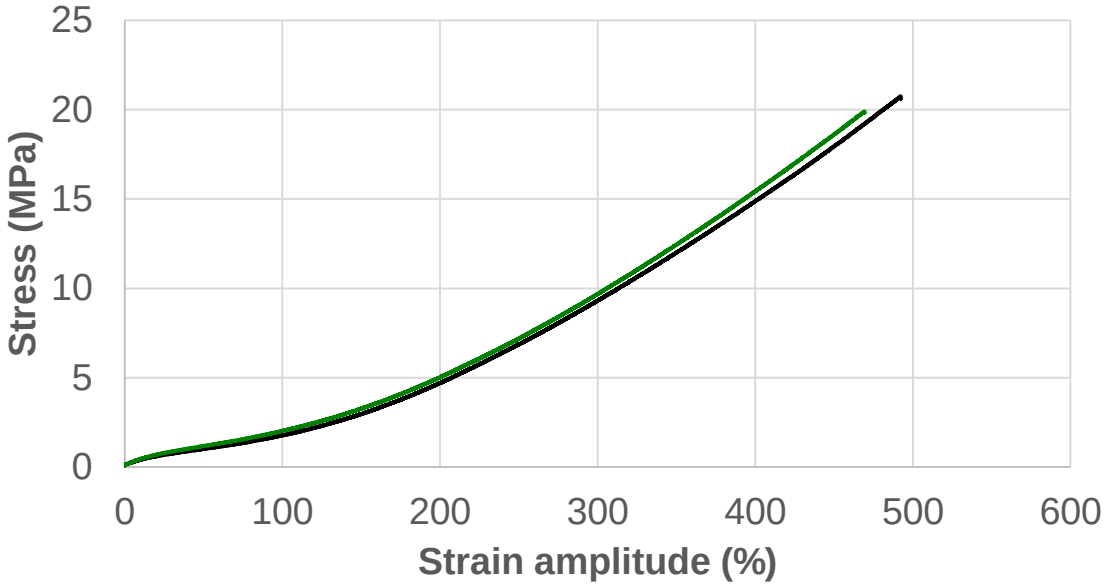
APTESP =



Silica based composites. TESPT vs PyC as coupling agent



Silica based composites. TESPT vs PyC as coupling agent

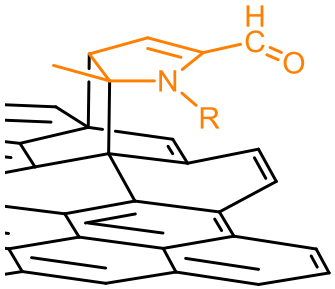


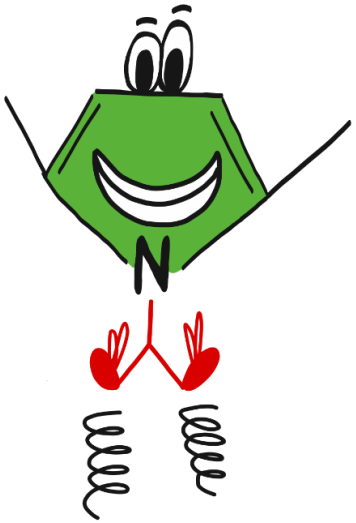
	Silica/TESPT	Silica/PyC
σ_{50}	1,02	1,18
σ_{100}	1,77	2,04
σ_{300}	9,35	9,69
$\sigma_{300}/\sigma_{100}$	5,28	4,75
σ_B	20,59	19,81
ε_B	492,3	469,3

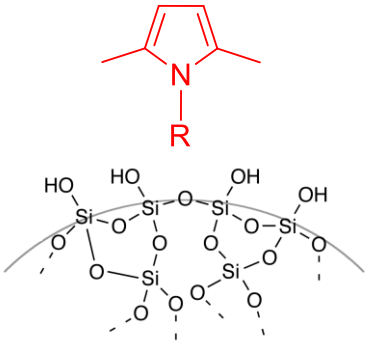
PyC = APTESP

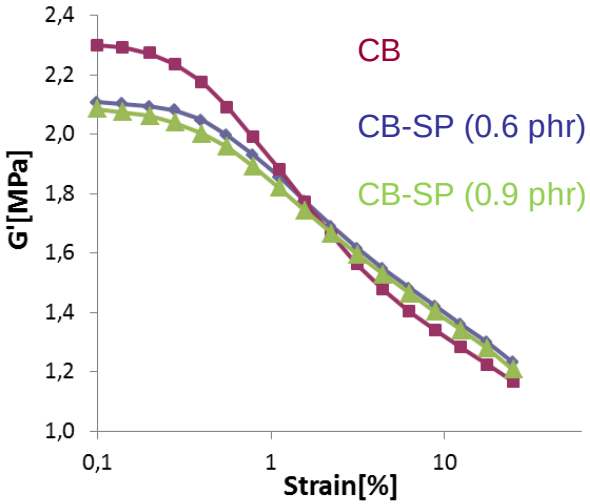
Conclusions

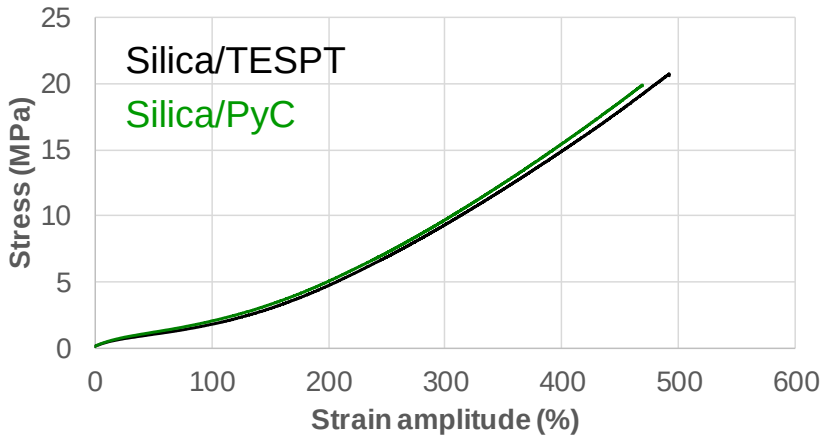
Universal coupling agent for carbon black and silica











Acknowledgment: to Pirelli Tyre for the financial support

Thanks

for your attention!

Innovative Sustainable Materials GROUP in ISCaMaP

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