



**13<sup>th</sup> Kautschuk Herbst Kolloquium**  
Hannover, Germany, November 6-8, 2018



## Facile and sustainable functionalization of carbon black, as filler for rubber composites

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Via Mancinelli 7, 20131 Milano (MI)

## Items of the presentation

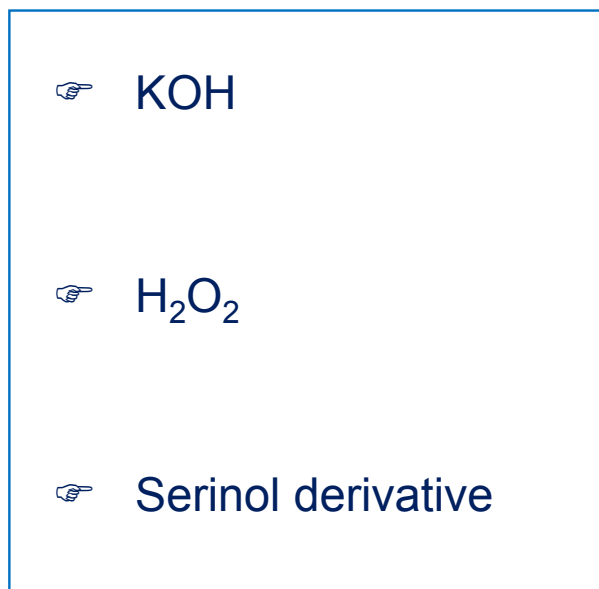
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- ➔ Objectives of the research
- ➔ Sustainable functionalization of carbon allotropes:  
selection of the method
- ➔ Functionalization of Carbon Black
- ➔ Rubber composites with functionalized CB

## Objectives of the research activity

- ☞ To **reduce the synthetic footprint**  
in the functionalization of carbon allotropes  
in view of industrial applications:  
**no wastes**
- ☞ To develop a **sustainable, facile, versatile** method,  
preserving the  $sp^2$  hybridization of carbon atoms
- ☞ To prepare **elastomer composites**

## Methods



A. Porta, [Thesis, Politecnico Milano, 2015](#)

V. Barbera, A. Porta, L. Brambilla, S. Guerra, A. Serafini, A. M. Valerio, A. Vitale, M. Galimberti, [RSC Adv., 2016, 6, 87767-87777](#)

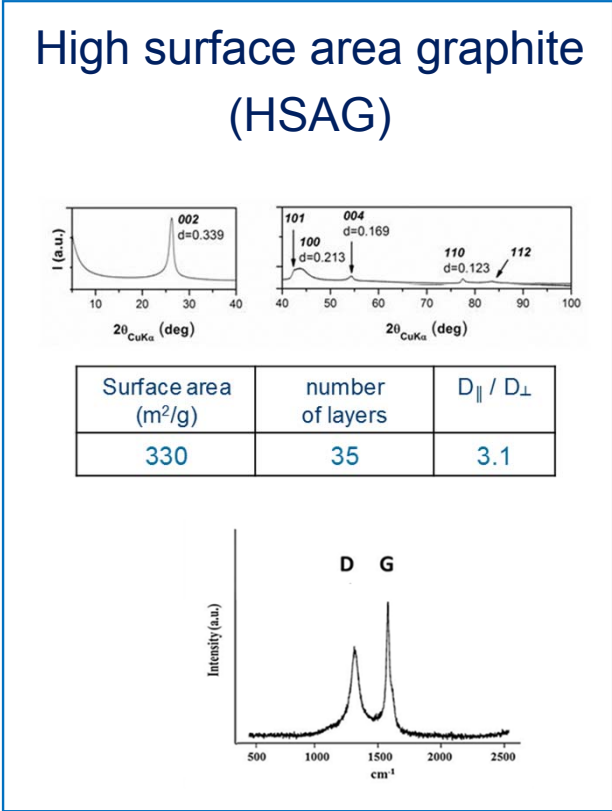
V. Barbera, A. Bernardi, G. Torrisi, A. Porta, M. Galimberti, [Elastomerj, 2017, 21\(4\), 235-251](#)

# Sustainable functionalization of carbon allotropes

## Methods

- ☞ KOH
- ☞ H<sub>2</sub>O<sub>2</sub>
- ☞ Serinol derivative

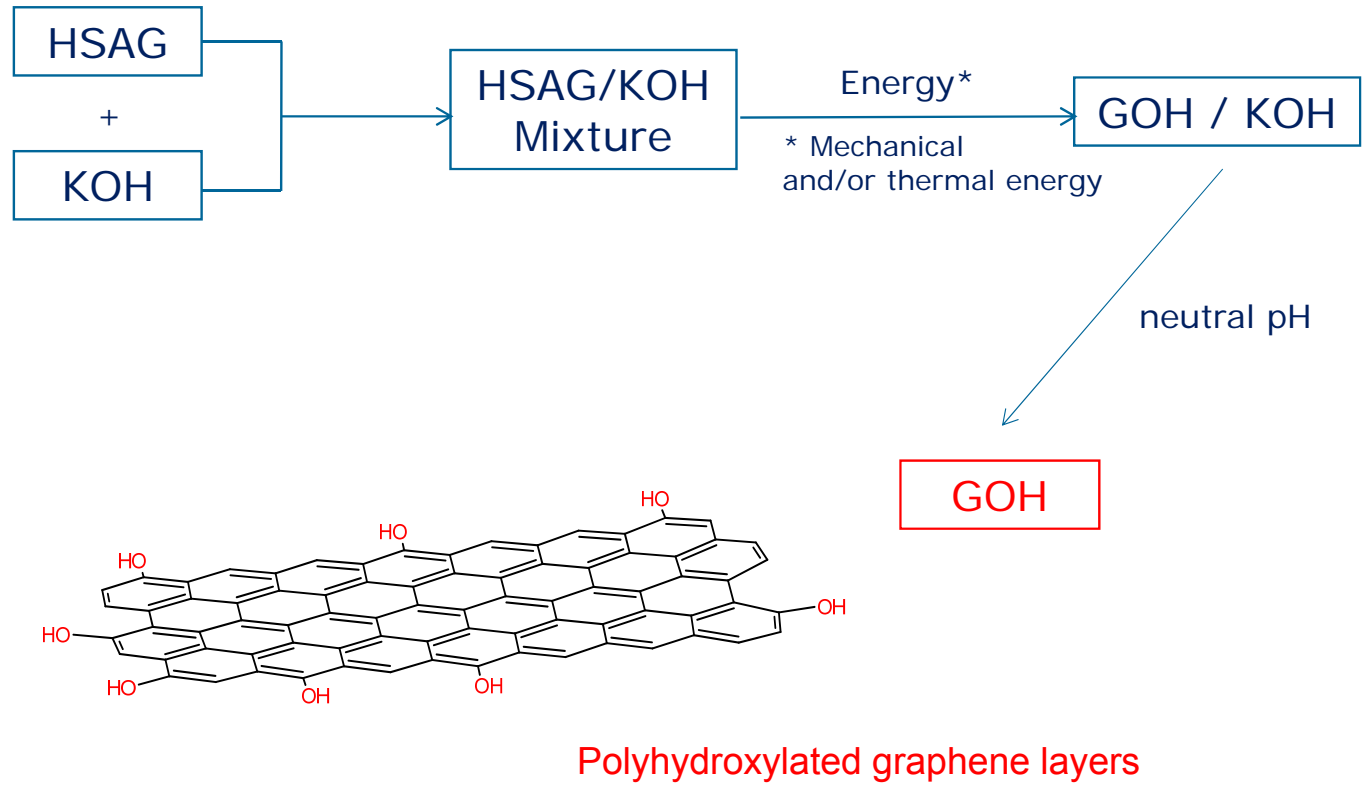
+



M. Mauro, V. Cipolletti, M. Galimberti, P. Longo, G. Guerra, *J. Phys. Chem. C* **116** (2012) 24809–24813

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

# Oxidation of HSAG with KOH



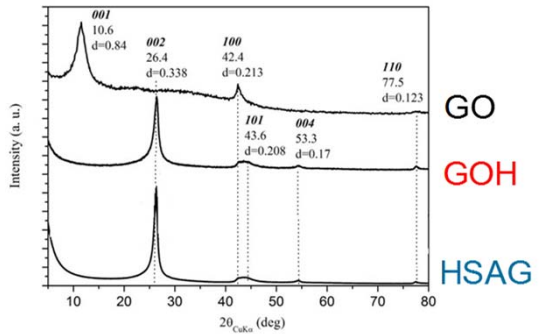
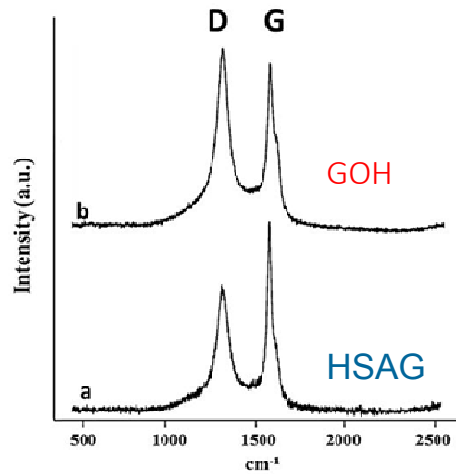
A. Porta, Thesis, Politecnico Milano, 2015

V. Barbera, A. Porta, L. Brambilla, S. Guerra, A. Serafini, A. M. Valerio, A. Vitale, M. Galimberti, RSC Adv., 2016, 6, 87767-87777

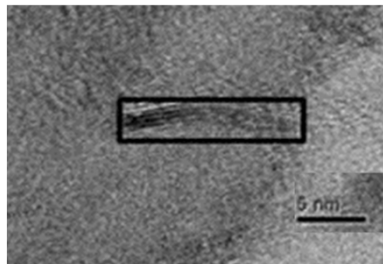
V. Barbera, A. Bernardi, G. Torrisi, A. Porta, M. Galimberti, Elastomerj, 2017, 21(4), 235-251

# Polyhydroxylated graphene layers from HSAG + KOH

- ☞ Selective introduction of OH groups up to 15 mass%
- ☞ In plane order substantially unaltered
- ☞ No expansion of interlayer distance



Few layers graphene

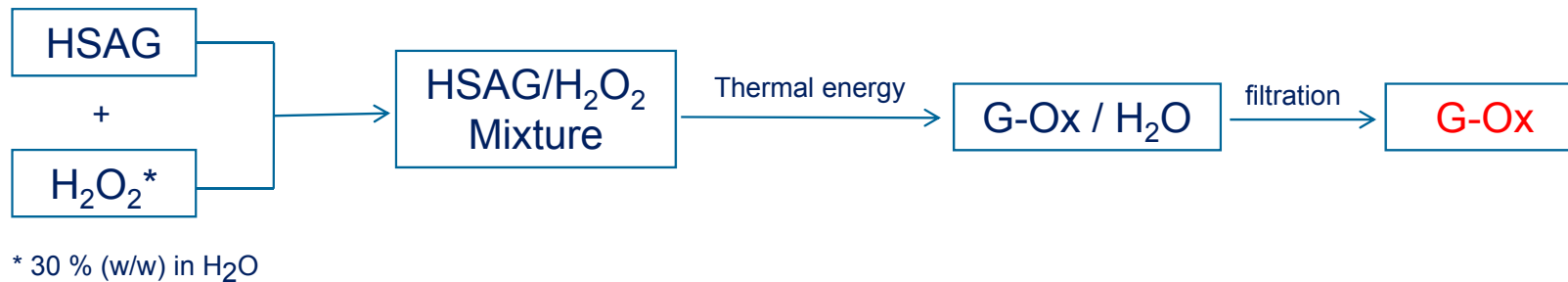


From water suspension

*Results from elemental, TGA, IR, XPS, Raman, XRD, HRTEM analysis*

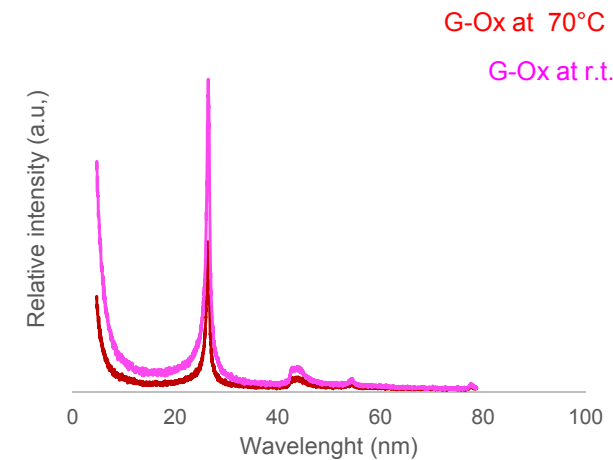
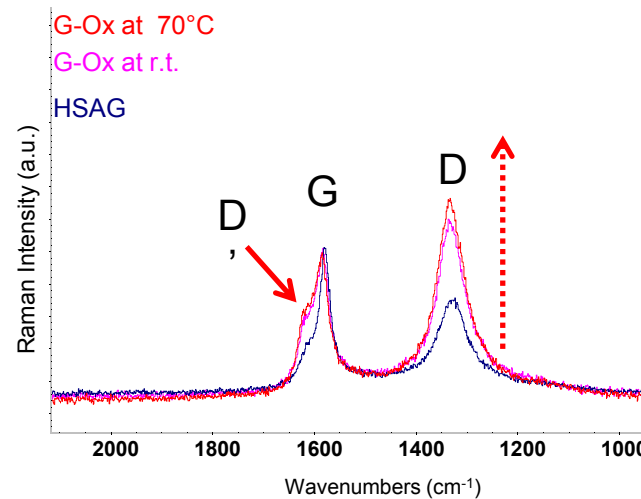
V. Barbera, A. Porta, L. Brambilla, S. Guerra, A. Serafini, A. M. Valerio, A. Vitale, M. Galimberti, *RSC Adv.*, 2016, 6, 87767-87777  
 V. Barbera, A. Bernardi, G. Torrisi, A. Porta, M. Galimberti, *Elastomerj*, 2017, 21(4), 235-251

# Oxidation of HSAG with H<sub>2</sub>O<sub>2</sub>

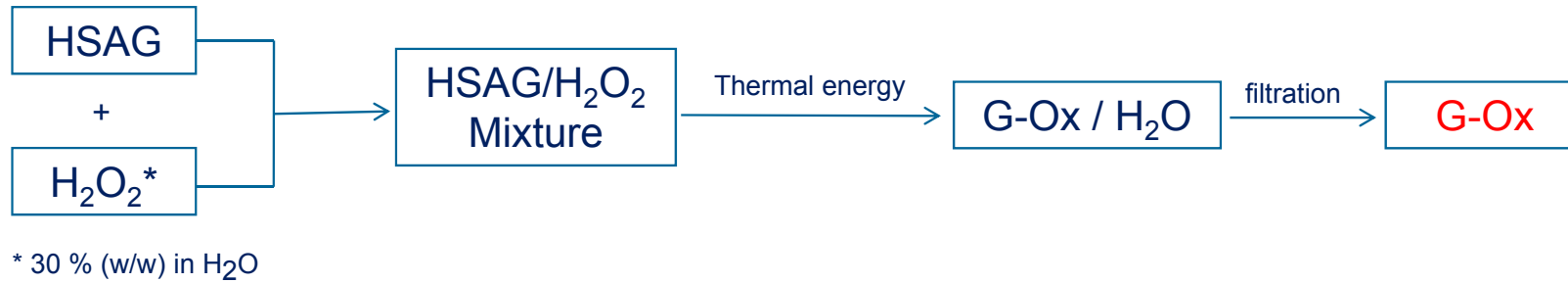


- ☞ Selective introduction of OH groups at room temperature
- ☞ In plane order substantially unaltered
- ☞ No expansion of interlayer distance

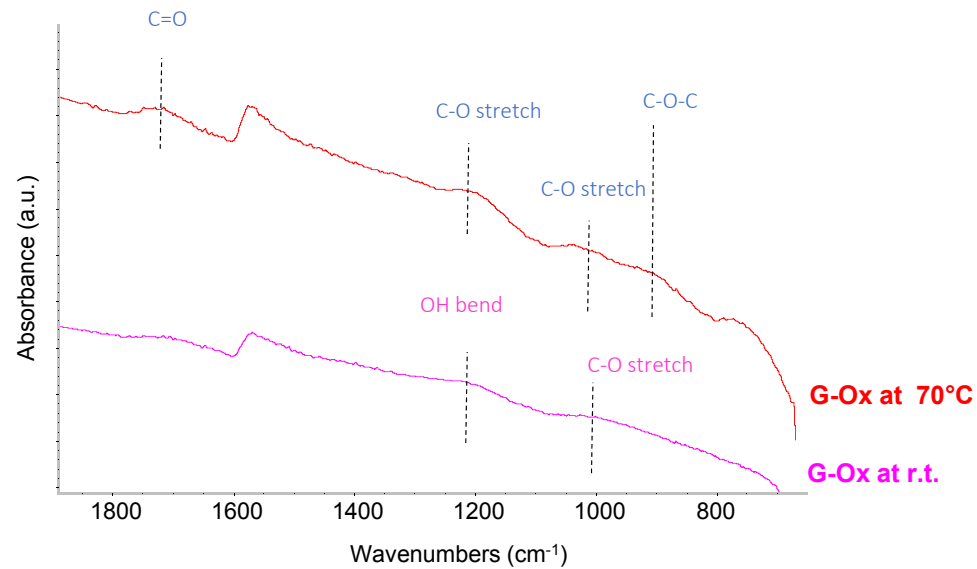
Results from elemental, TGA, IR, XPS, Raman, XRD



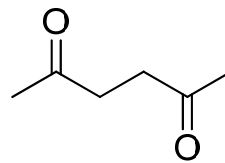
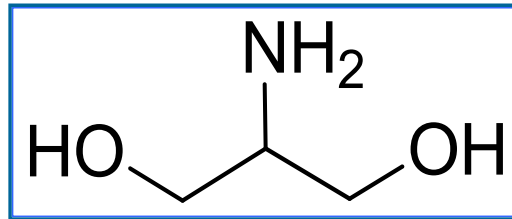
# Oxidation of HSAG with H<sub>2</sub>O<sub>2</sub>



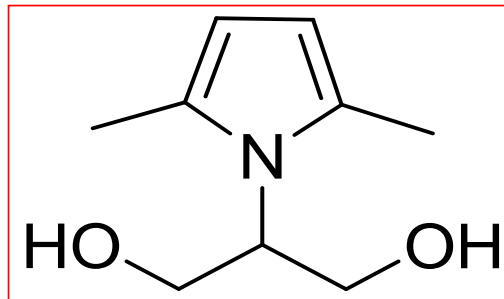
➔ Various types of oxygenated functional groups



# Functionalization of carbon allotropes with serinol derivative



Paal Knorr reaction

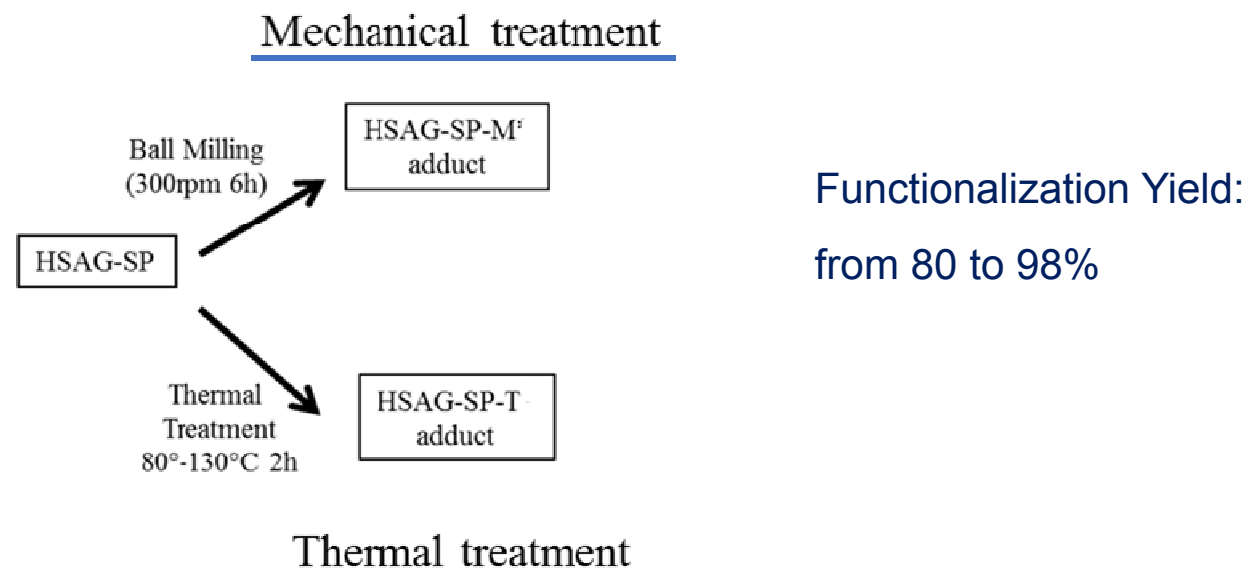


Serinol pyrrole - SP

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



# Adducts of SP with HSAG - Preparation

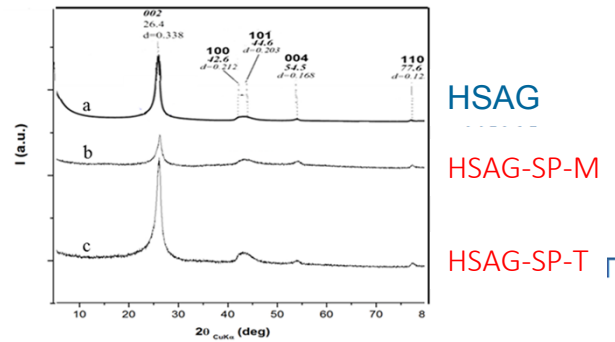
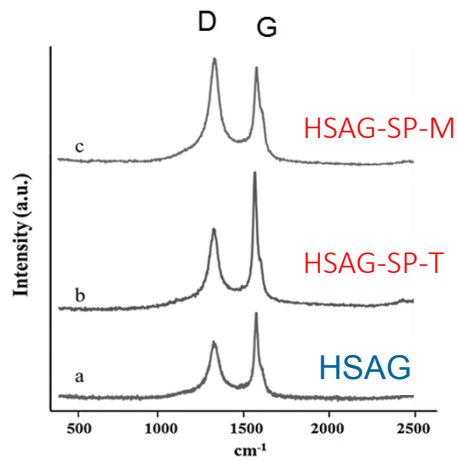


Carbon allotropes: CNT: single and multiwalled,  
carbon black: various grades

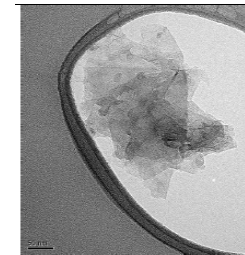
Galimberti, M., Barbera, V., Sebastiano, R., Valerio A.M. Leonardi, G., Citterio, [EP 3209604 B1 - US 2017 0275169 A1](#)  
M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini, [RSC Adv., 2015, 5, 81142-81152](#)  
V. Barbera, A. Bernardi, G. Torrisi, A. Porta, M. Galimberti, [Elastomerj, 2017, 21\(4\), 235-251](#)

# Adducts of SP with HSAG - Characterization

- ☞ Functional groups up to 20 mass%
- ☞ In plane order substantially unaltered
- ☞ No expansion of interlayer distance



Few layers graphene

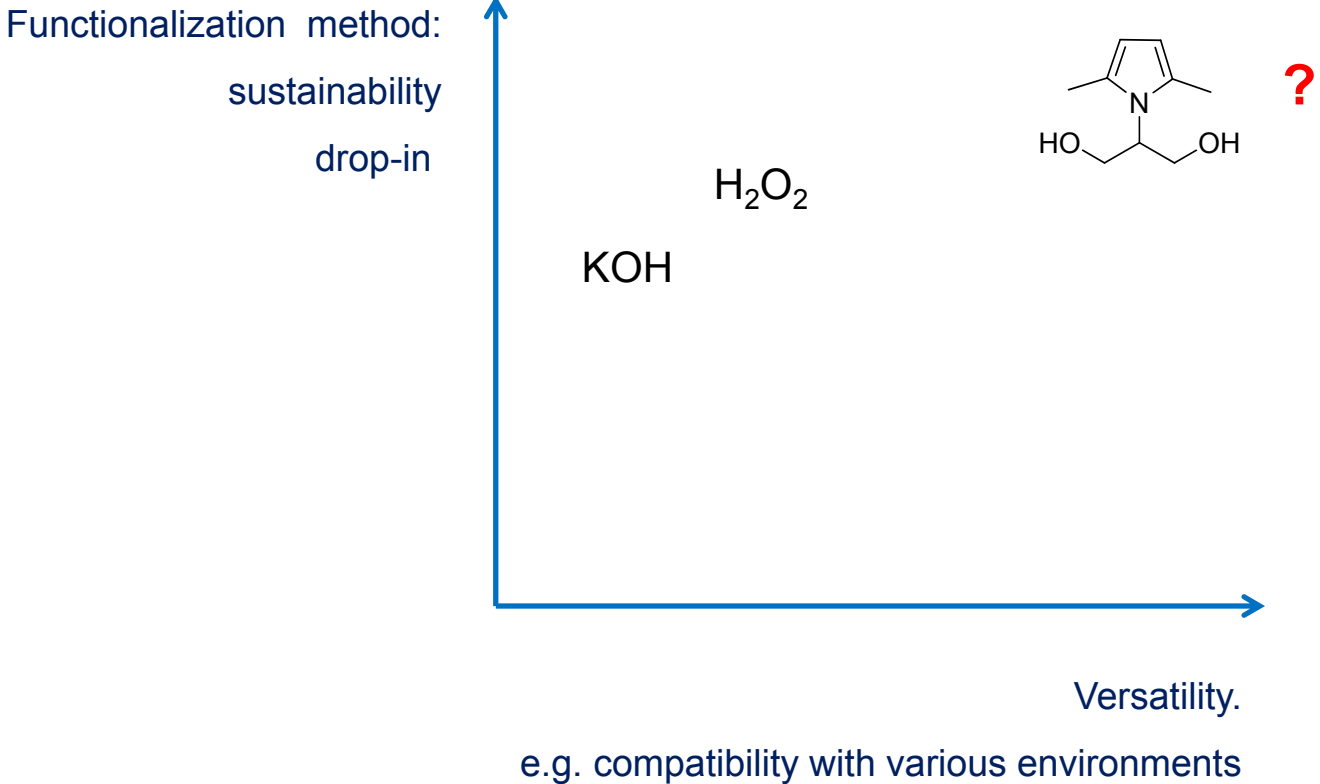


From water suspension

*Results from elemental, TGA, IR, XPS, Raman, XRD, HRTEM analysis*

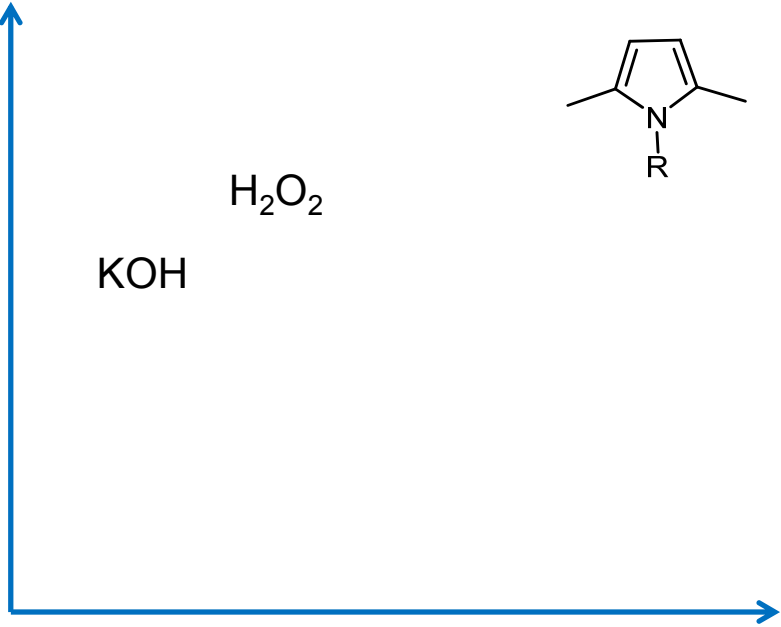
Galimberti, M., Barbera, V., Sebastiano, R., Valerio A.M. Leonardi, G., Citterio, EP 3209604 B1 - US 2017 0275169 A1  
 M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini, RSC Adv., 2015, 5, 81142-81152

# Comparison of functionalization methods



# Comparison of functionalization methods

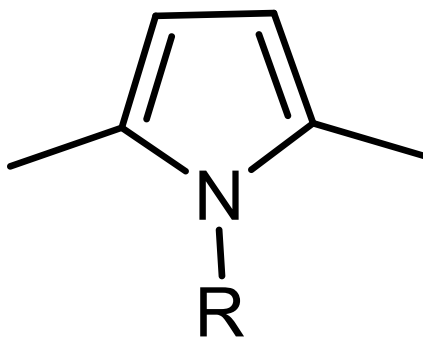
Functionalization method:  
sustainability  
drop-in



Versatility.

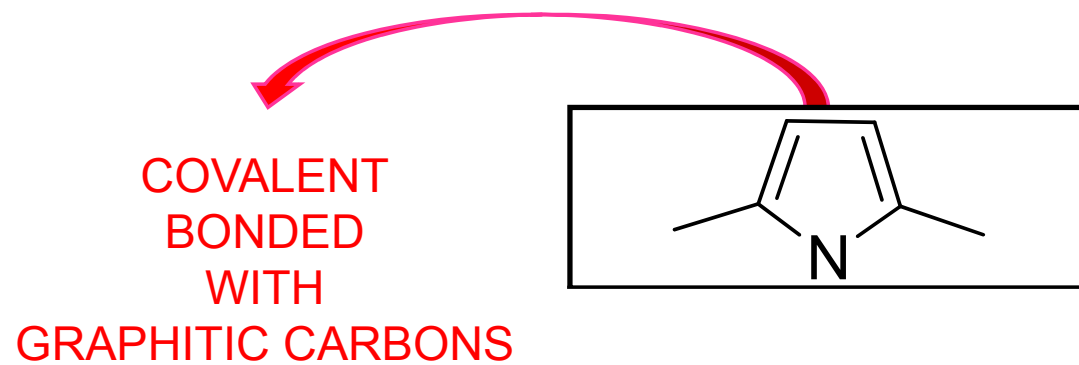
e.g. compatibility with various environments

## Functionalization of Carbon Black with pyrrole compounds

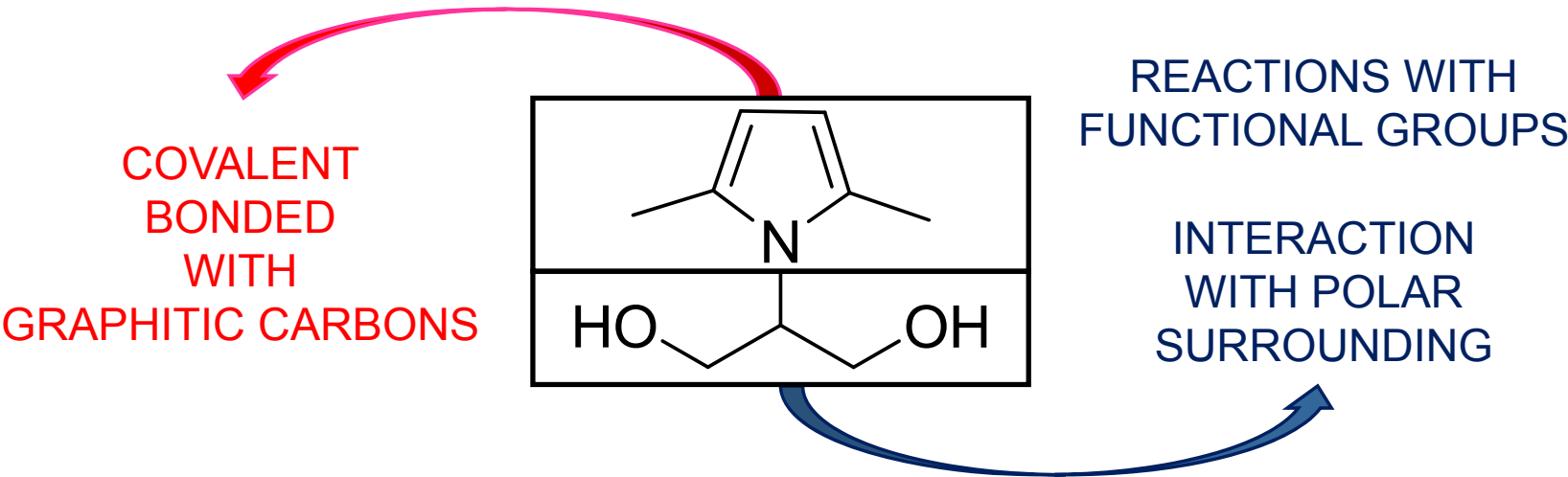


PyC

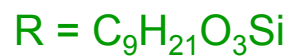
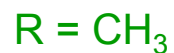
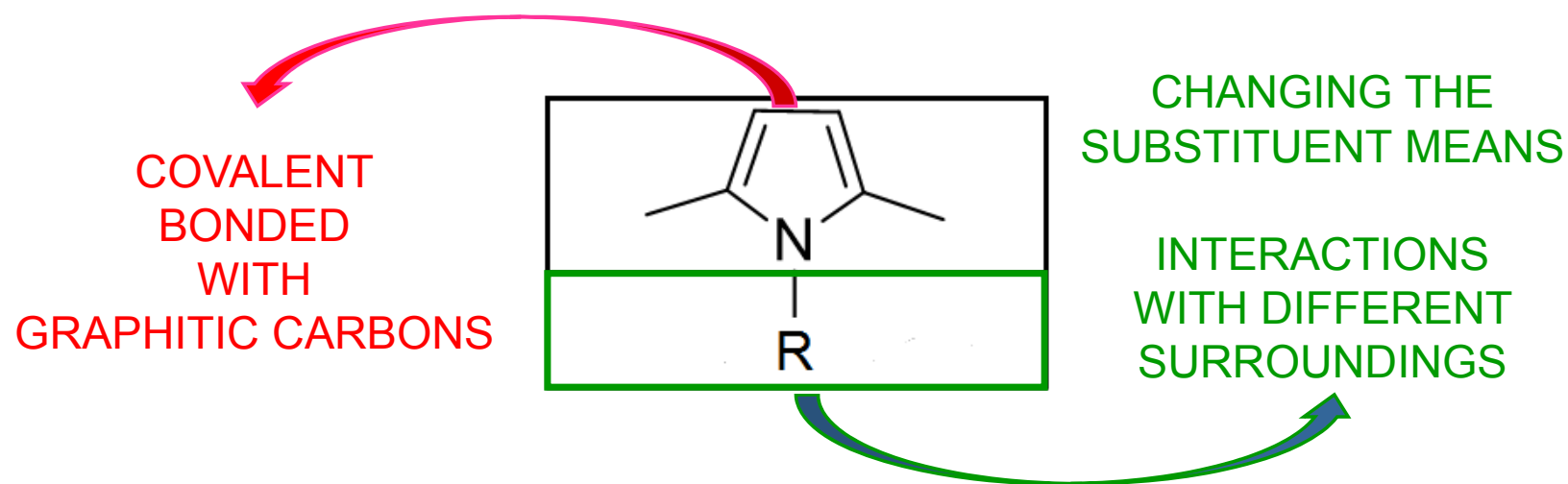
# Janus molecule - Serinol pyrrole



# Janus molecule - Serinol pyrrole

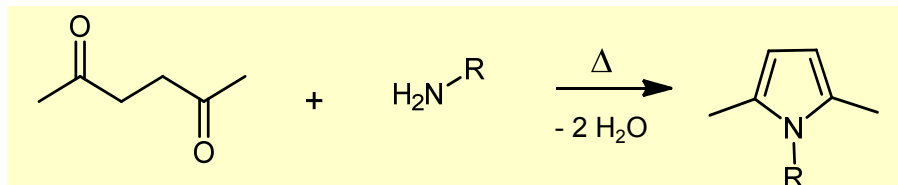


# Janus molecules - Pyrrole Compounds (PyC)



# Pyrrole Compounds (PyC) - Preparation

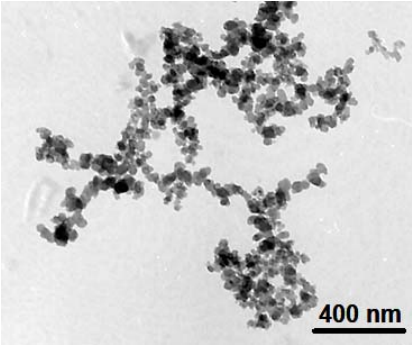
**T = 130°C**  
**t = 3 h**



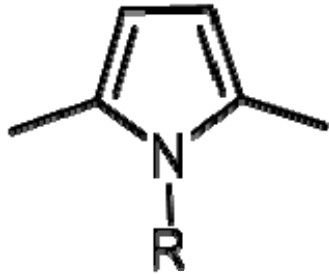
**No solvent**  
**No catalyst**

Entry	Amine	Yield (%)	AE (%)	RME (%)	Product ID	Structure
1		<b>86</b>	88	86	DDcP	
2		<b>73</b>	91	76	ODcP	
3		<b>83</b>	81	86	GlyP	
4		<b>96</b>	85	81	SP	
5		<b>80</b>	75	61	TMP	
6		<b>75</b>	83	62	HP	
7		<b>70</b>	89	74	APTESP	

# Functionalization of carbon black: general procedure



Carbon black (CB) (\*) + Pyrrole compound  
10 : 1 mass



1) Mixing in acetone  
2) Solvent removal

(\*) CB grades used: N234, N326.

Step 1

CB - PyC

Step 2

T = 180°C,  
4 h, 400 rpm

CB/PyC adduct

All the so-formed adducts were **extracted** in **Soxhlet** for at least 12 hours.

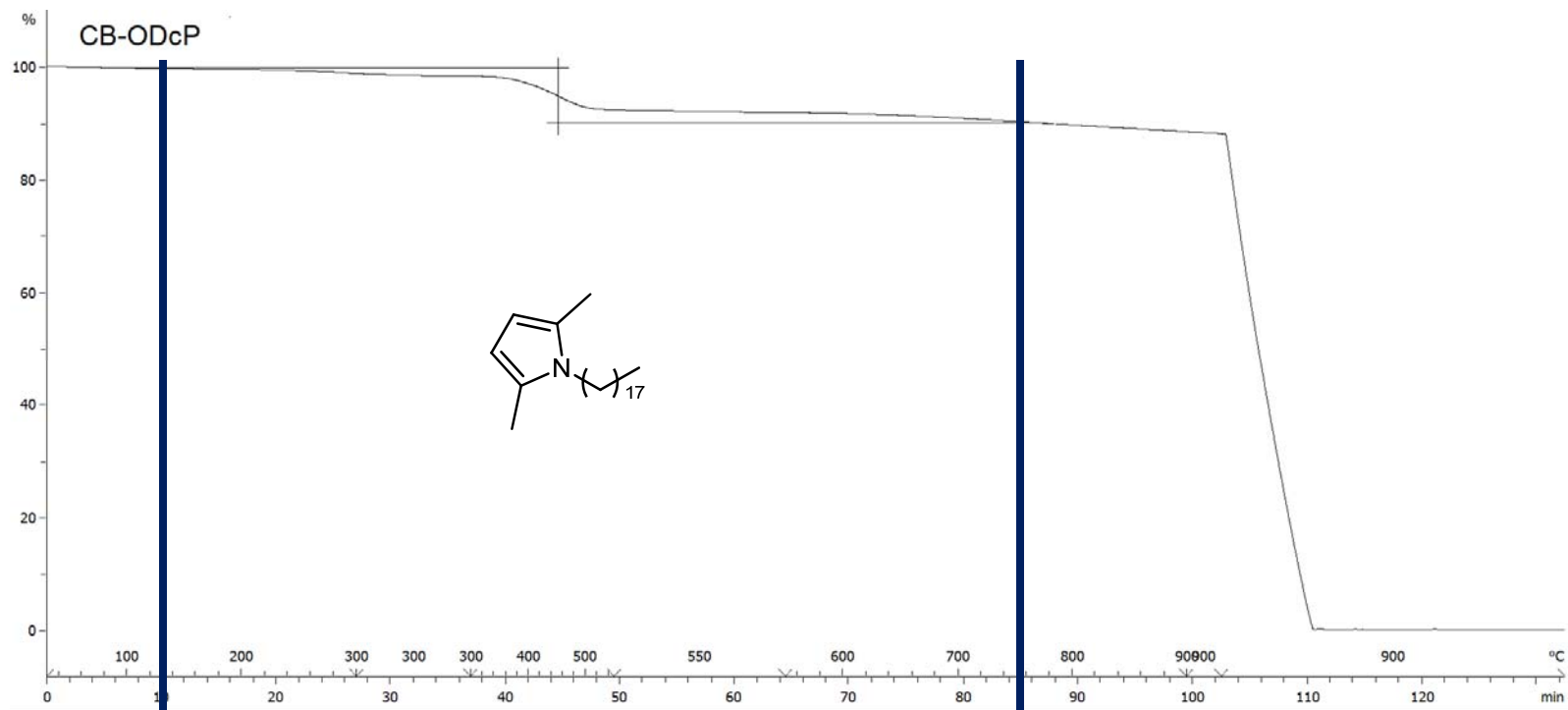
## Functionalization yields

Entry	Adduct	Yield *
1	CB - DDcP	85%
2	CB - ODcP	98%
3	CB -GlyP	82%
4	CB - SP	96%
5	CB -TMP	65%
6	CB - EP	85%
7	CB -APTESP	78%

\*Yield calculated through TGA analysis, using the equation:

$$\text{Yield (\%)} = \frac{\text{mass loss}_{\text{after washing}} [\%]}{\text{mass loss}_{\text{before washing}} [\%]} \times 100$$

# Characterization of the adducts: thermogravimetric analysis



T < 150°C:  
residual solvent

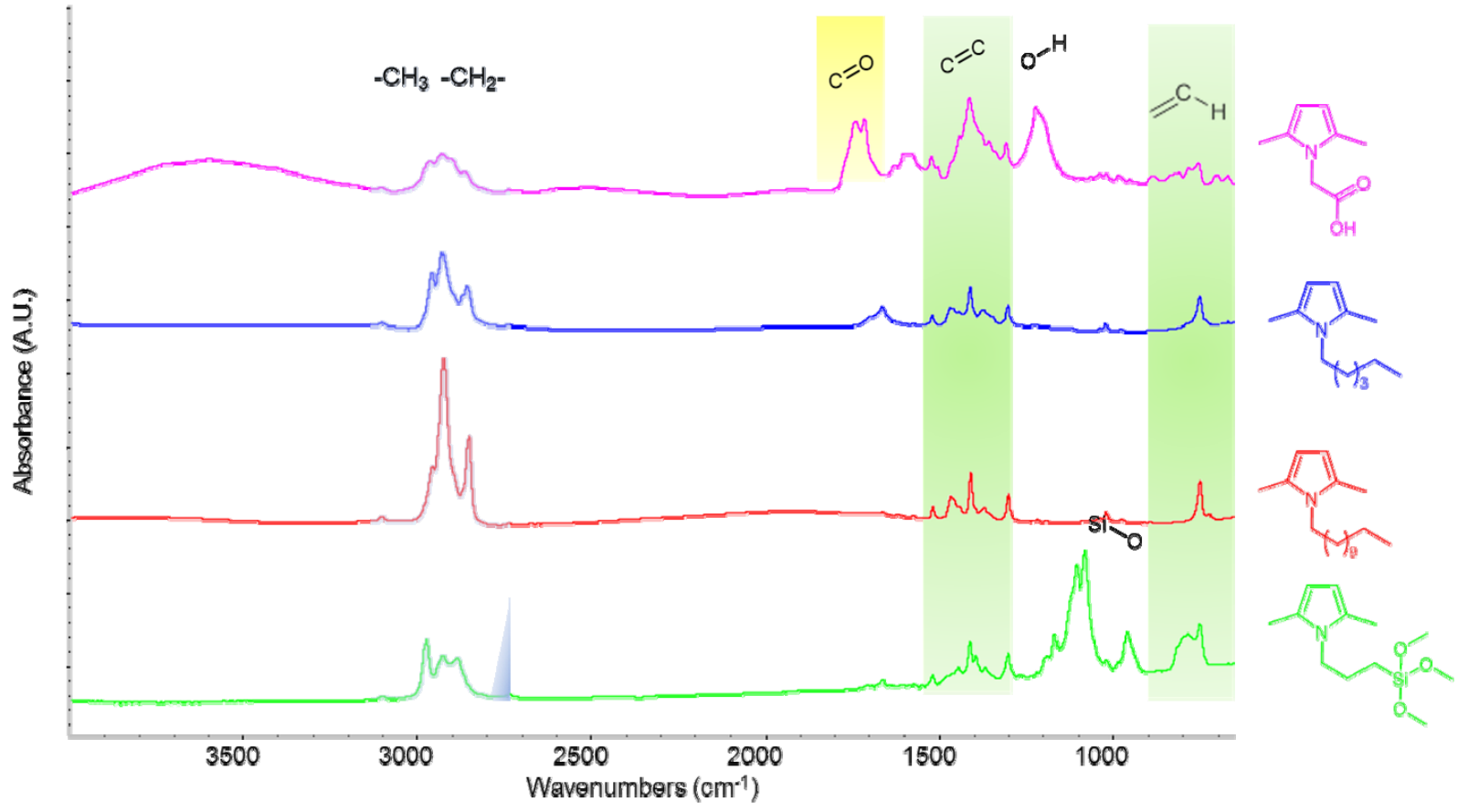
150°C < T <: 750°C  
%mass loss  
due to covalently bonded PyC

T > 750°C:  
impurities on CB

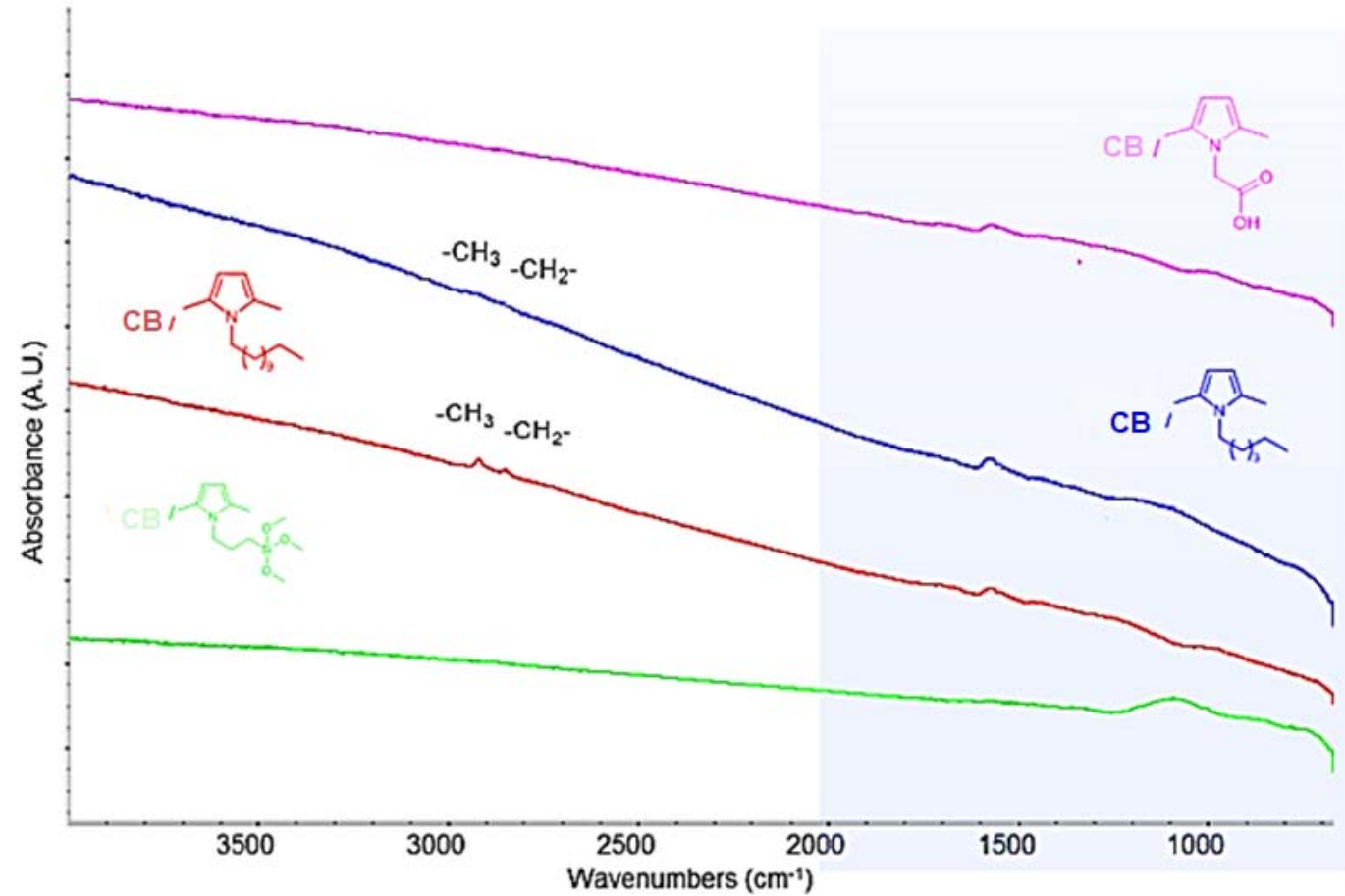
\*Yield calculated through TGA analysis, using the equation:

$$\text{Yield (\%)} = \frac{\text{mass loss}_{\text{after washing}} [\%]}{\text{mass loss}_{\text{before washing}} [\%]} \times 100$$

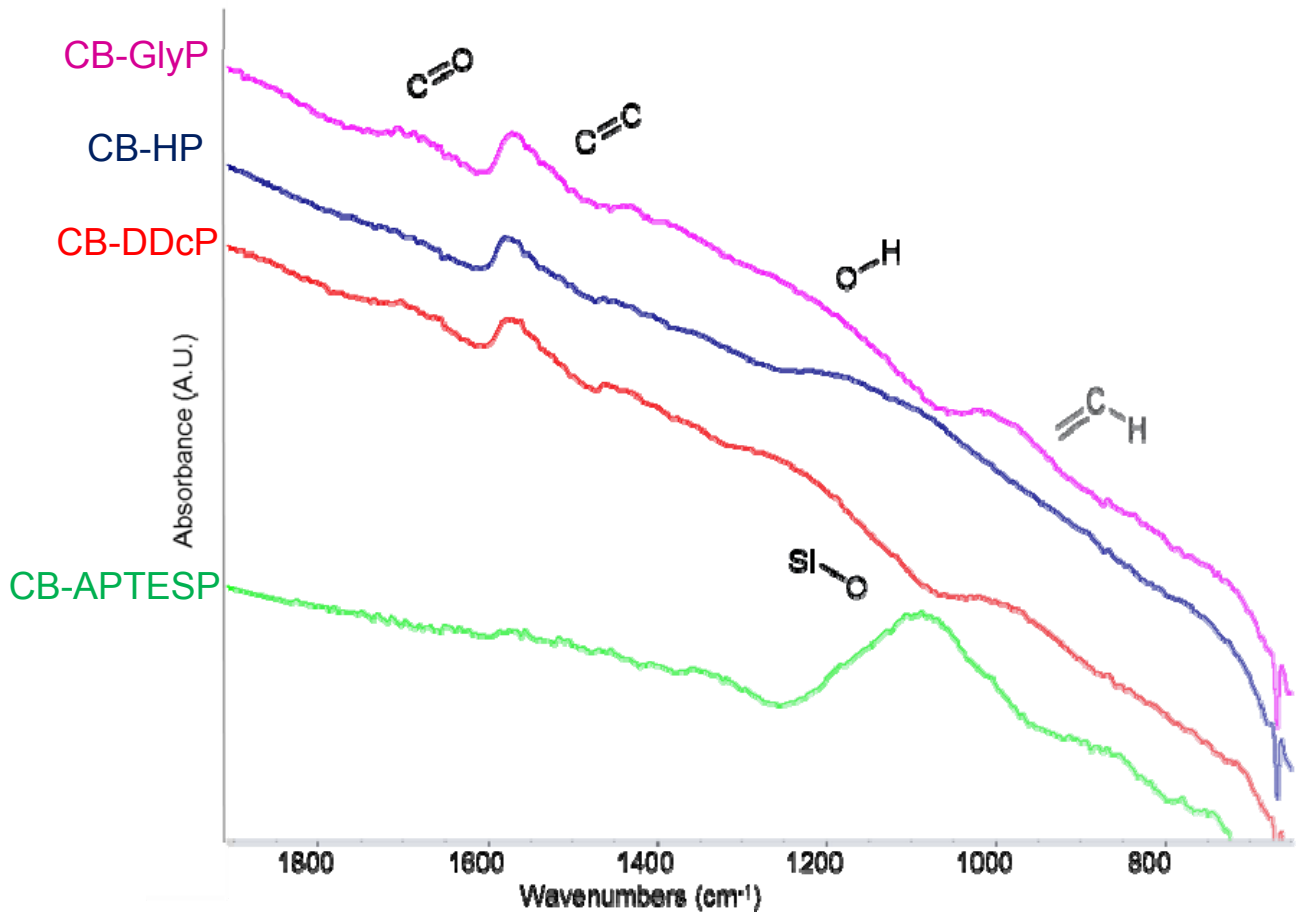
# Characterization of the adducts: infrared spectroscopy of PyC



# Characterization of the adducts: infrared spectroscopy of CB-PyC(5 mass%) adducts



# Characterization of the adducts: infrared spectroscopy of CB-PyC(5 mass%) adducts



# UV-vis analysis

CB-PyC \*  
powder

+

Selected  
solvent

*Concentration:  
from 0.01 to 1 mg/ml*

1) Sonication: 30'  
2) Rest: 30'

UV-vis analysis

Evaluation of linear response to  
Beer-Lambert law

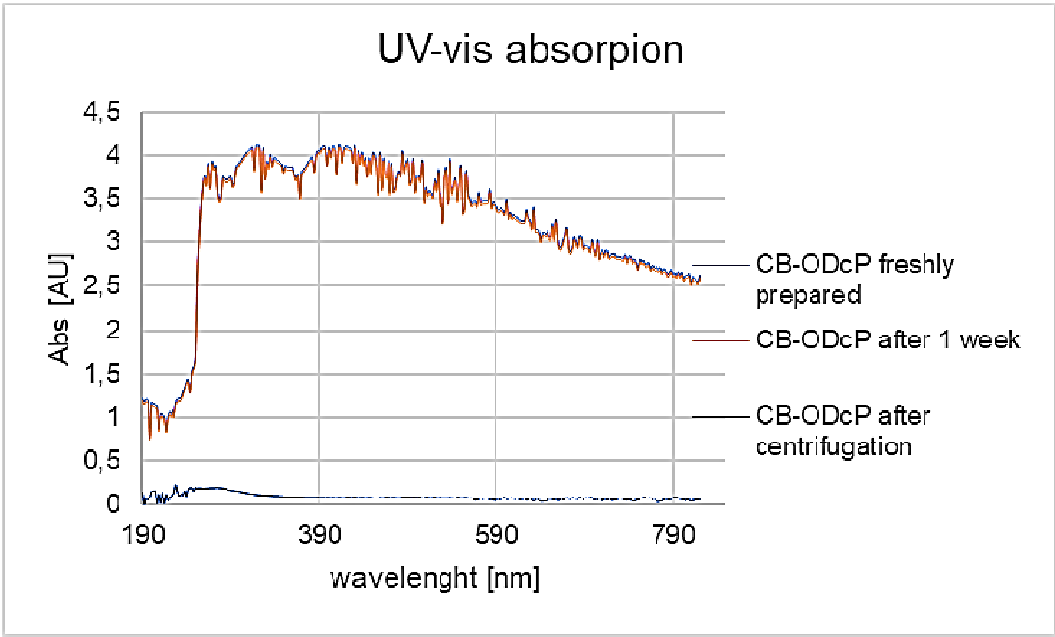
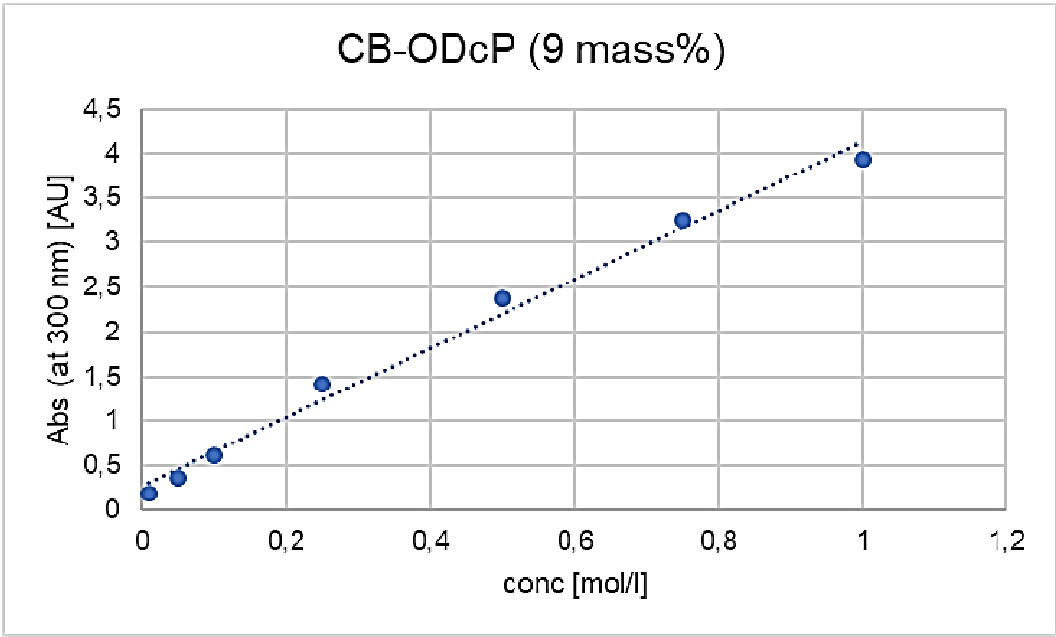
3) Rest: 1 week

UV-vis analysis

Evaluation of suspension  
stability

\* amount of PyC on CB:  
from 8 to 10 mass%

# Characterization of the adducts: UV-vis absorption



Absorbance monotonously increases with the adduct concentration

- Concentration of the suspension: 1 mg/ml
- After 1 week storage: absorbance slightly decreases
- After centrifuge (6000 rpm, 30') absorbance drastically decreases (still remaining detectable)

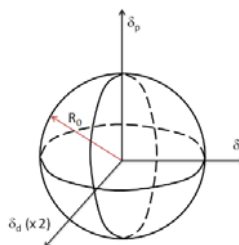
Solvent used for suspensions: toluene

# Tuning of solubility parameters – Hansen approach

Experimental determination



Stable suspensions  
in solvents  
with different  $\delta$



Theoretical predictions



Computational model:  
Hansen solubility parameters

Hansen Solubility Parameters: A User's Handbook", Second Edition, C. M. Hansen  
Hansen solubility parameters for a carbon fiber/epoxy composite", H. Launay, C. M. Hansen, K. Almdal, Carbon 45 (2007) 2859–2865  
Handbook of Solubility Parameters and Other Cohesion Parameters, 2nd edition", Barton, AFM (1991) CRC Press

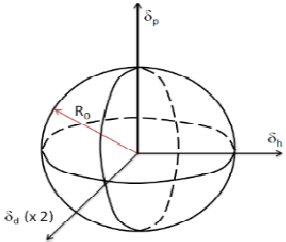


# Evaluation of solubility parameters of CB-PyC adducts

Cohesive energy (Hildebrand model) of a substance  
as sum of three contributions:  
dispersion, polar, hydrogen bonding:  
 $U_D, U_P, U_H$



The substance is identified by three coordinates ( $\delta_D, \delta_P$  and  $\delta_H$ )  
in the Hansen Parameters space



The distance between two points (e.g. of a solute and a solvent)  
is related to the cohesive energy difference



Two points close to each other in the Hansen space  
indicate miscible substances

## Evaluation of HSP of a solute $i$

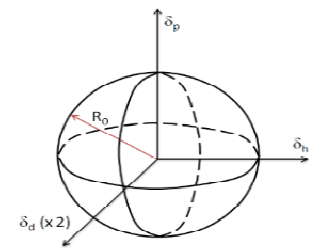
Dispersion tests are performed with different solvents  $j$ , distinguishing:

- **good** solvents, which provide stable dispersions
- **bad** solvents, which do not give stable dispersions

Minimization of the ratio \*  $\frac{\text{Distance between the solute and the solvent}}{R_0 \text{ radius of interaction}}$

Calculation of the center coordinates of the Hansen solubility sphere

The sphere center coordinates correspond to the three unknown HSP of the solute



\* Fitting sphere program adapted from *J. Polym. Sci. Part B Polym. Phys* **47**(21), 2091 (2009) and solved in Matlab environment using the Nelder-Mead simplex algorithm.



# Evaluation of solubility parameters of CB-PyC - Experiments

Adduct	Solvents										
	Hexane	Heptane	Cyclohexane	Toluene	Xylene	Chloroform	Ethyl acetate	Acetone	2-propanol	Methanol	H <sub>2</sub> O
=	Bad	Bad	Bad	Bad	Bad	Good	Good	Bad	Good	Bad	Bad
TMP	Bad	Bad	Bad	Bad	Bad	Good	Good	Bad	Bad	Bad	Bad
ODcP	Good	Bad	Good	Good	Good	Good	Good	Good	Bad	Bad	Bad
APTESP	Bad	Bad	Bad	Good	Good	Good	Good	Good	Bad	Bad	Bad
SP	Bad	Bad	Bad	Bad	Good	Good	Good	Good	Good	Bad	Good
GlyP	Bad	Bad	Bad	Bad	Bad	Good	Good	Good	Good	Bad	Good



No suspension:  
**bad**



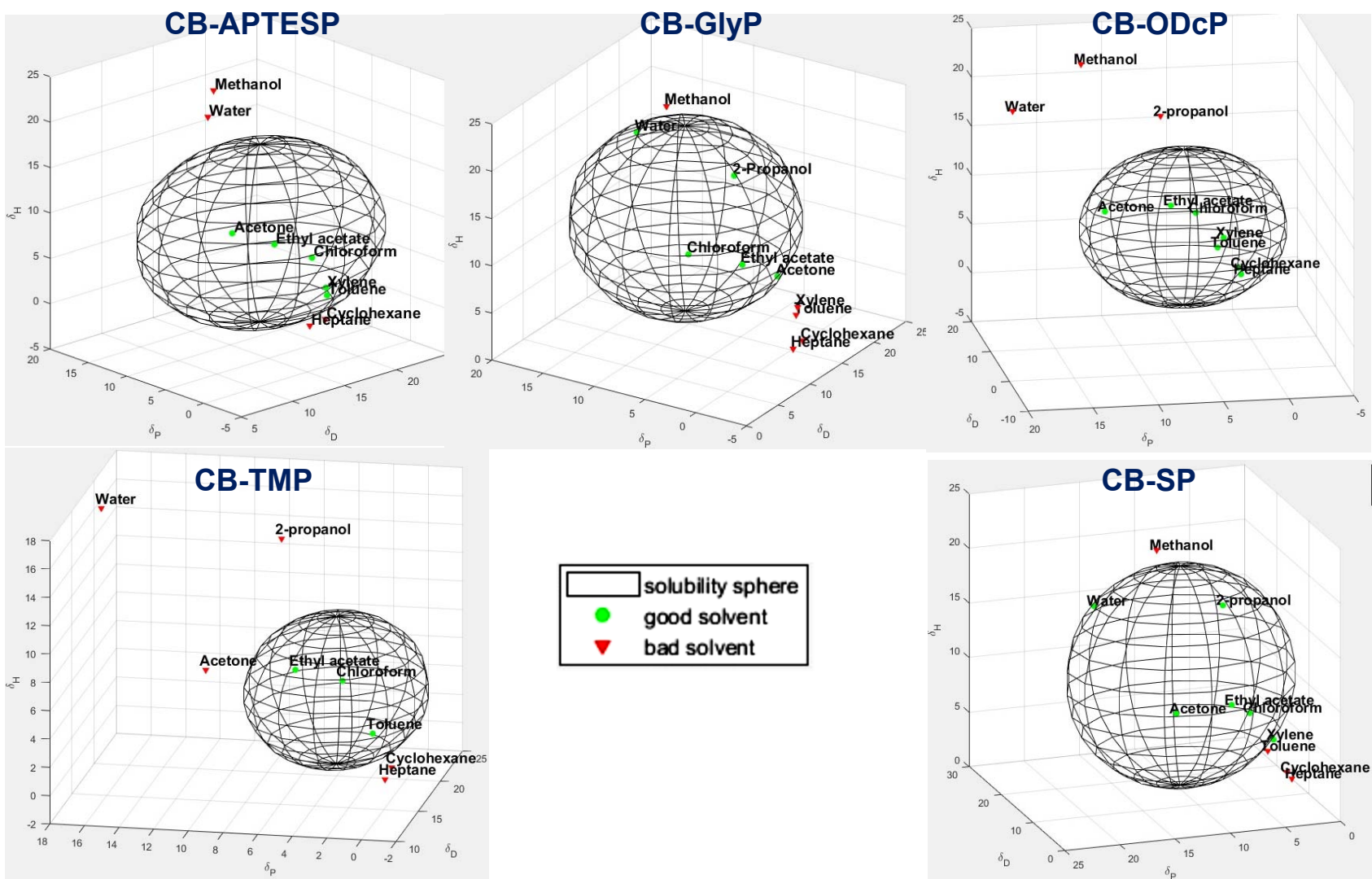
Unstable suspension:  
**bad**



Stable suspension:  
**good**

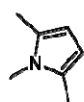
Concentration: 1 mg/ml

# Hansen solubility spheres of CB-PyC adducts

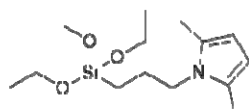


# Hansen solubility parameters for CB-PyC adducts

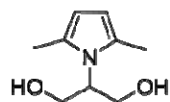
Sample	$\delta_D$	$\delta_P$	$\delta_H$
CB N234	21.1	12.3	11.3
CB-APTESP	14.9	6.0	8.5
CB-GlyP	12.1	8.6	12.8
CB-ODcP	6.4	5.7	7.9
CB-SP	11.8	11.1	11.5
CB-TMP	18.1	3.5	4.9



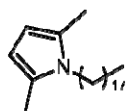
**TMP**



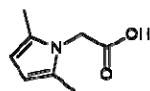
**APTESP**



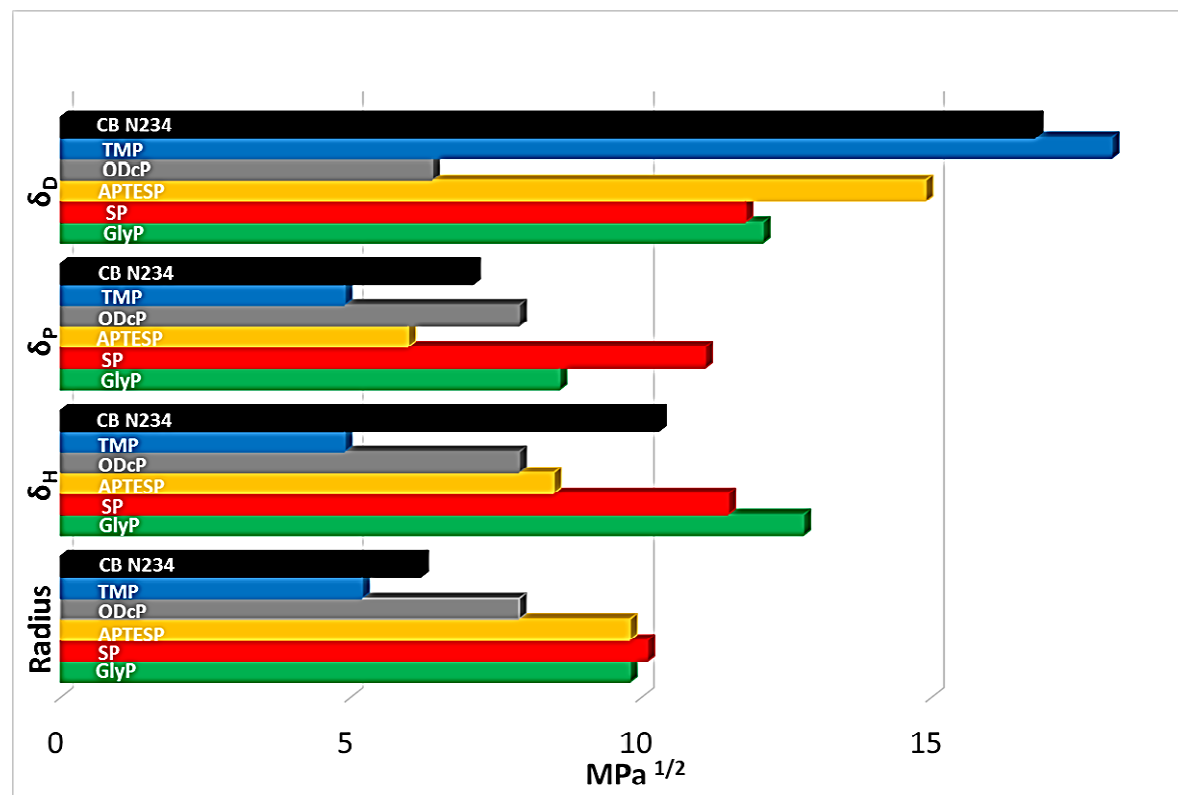
**SP**



**ODcP**

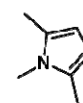
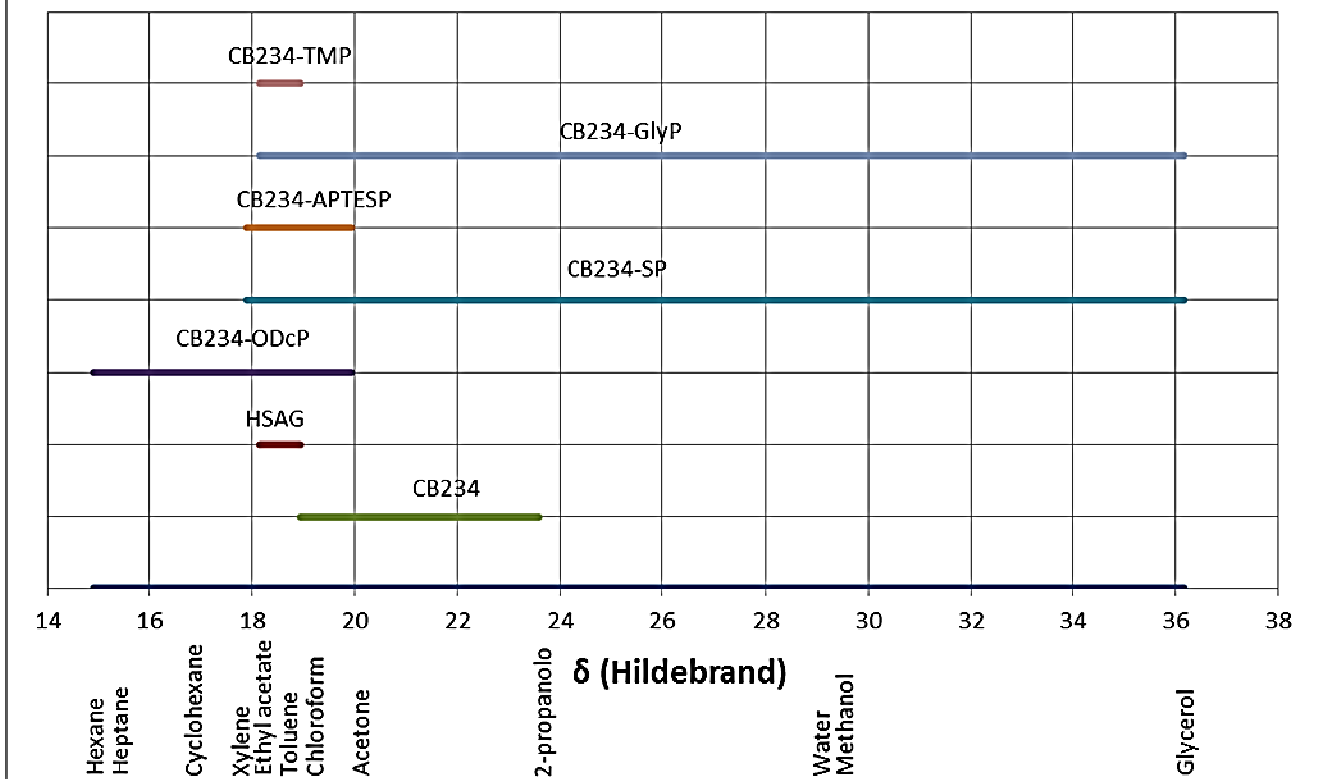


**GlyP**

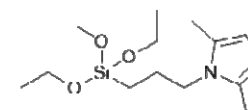


# Hildebrand solubility parameters for CB-PyC adducts

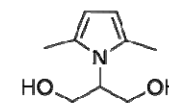
## Solubility parameters



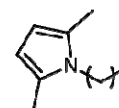
**TMP**



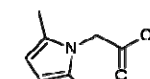
**APTESP**



**SP**

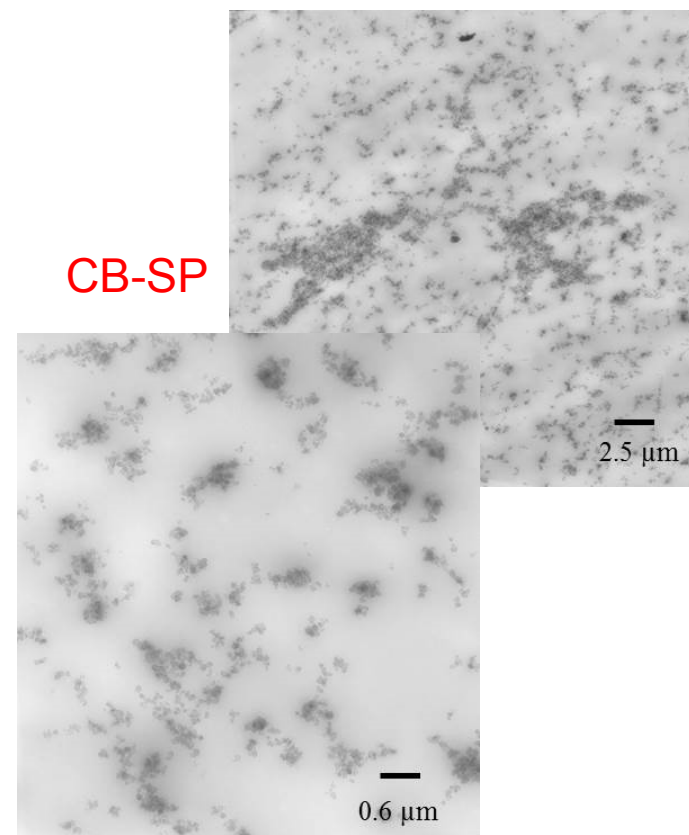
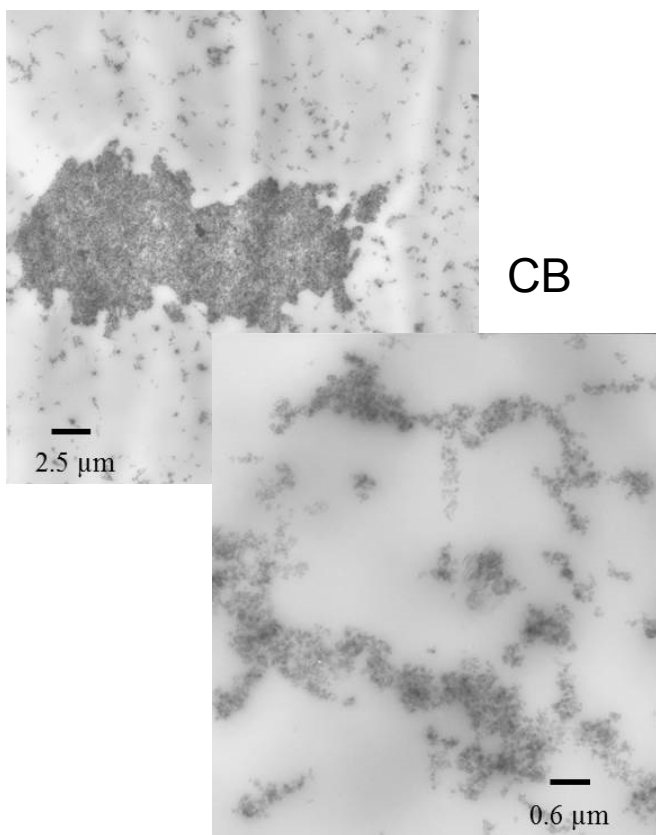


**ODcP**



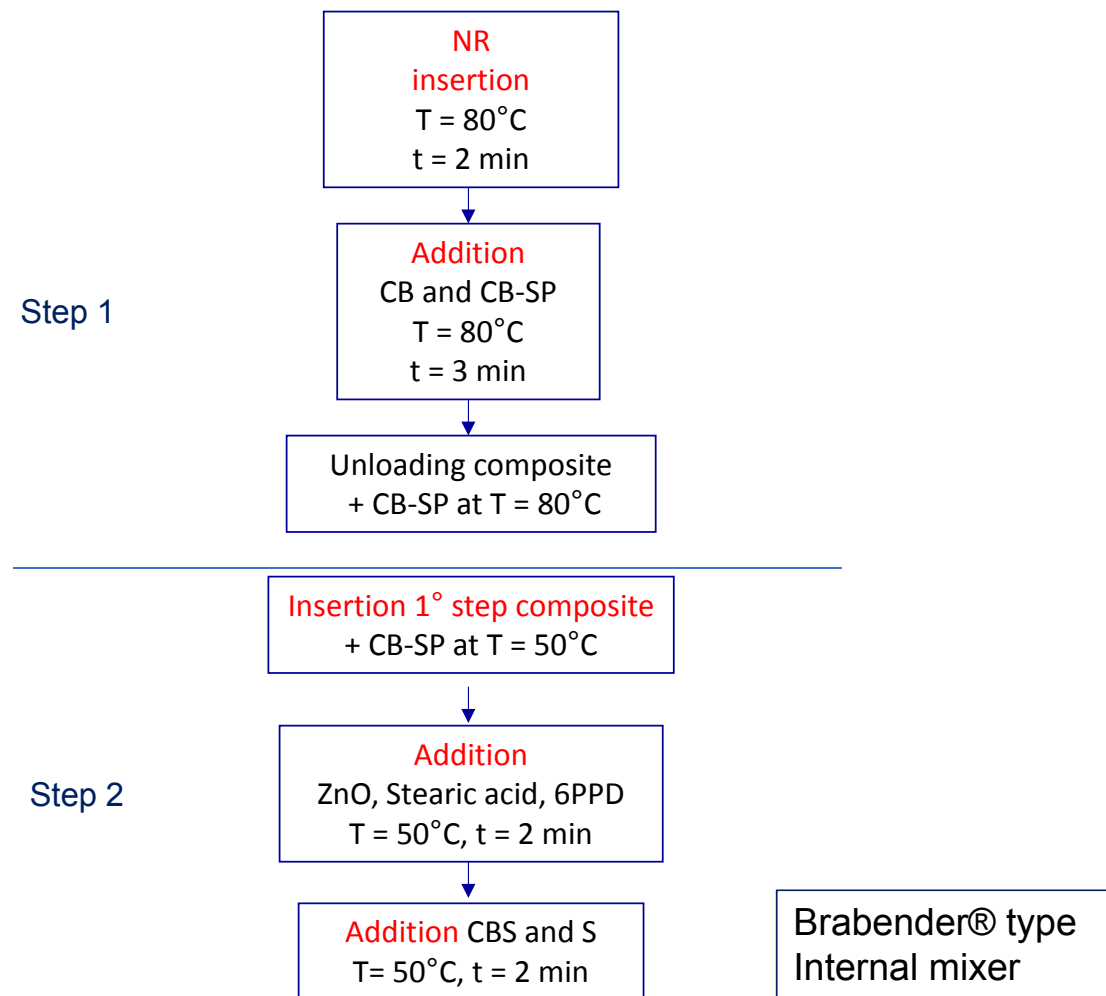
**GlyP**

## TEM Analysis



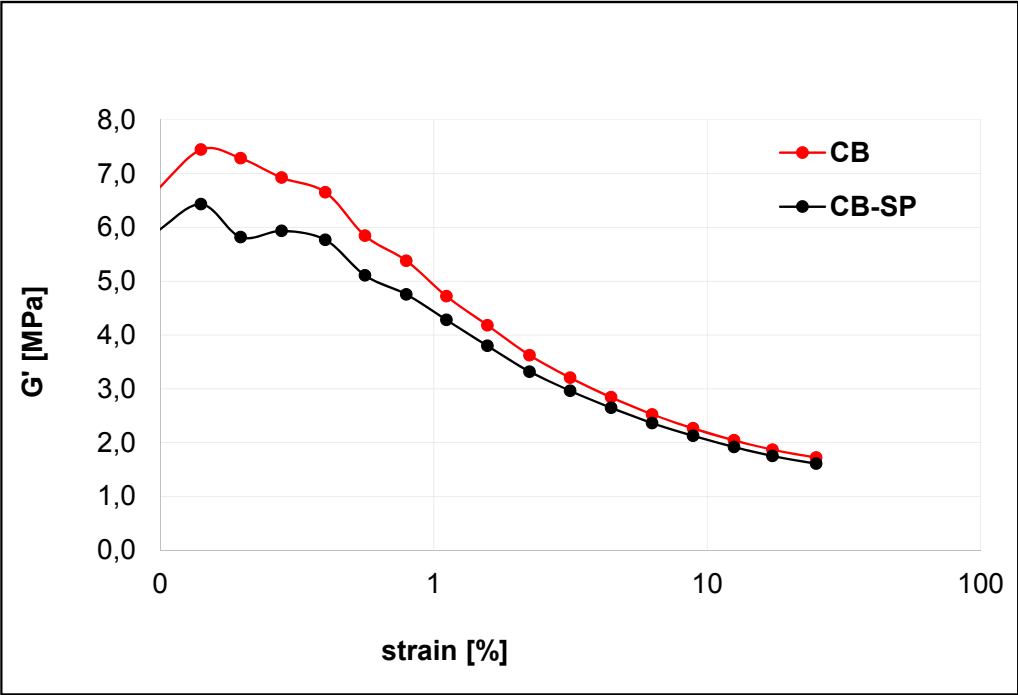
# NR/CB-SP composites from melt blending

<b>Ingredients</b>	<b>CB phr</b>	<b>CB-SP phr</b>
NR	100.0	100.0
CB N234	<b>60.0</b>	0.0
CB-SP(4 mass%)	0.0	<b>62.4</b>
Stearic acid	2.0	2.0
ZnO	4.0	4.0
6PPD	2.0	2.0
TBBS	1.8	1.8
Sulphur	1.8	1.8

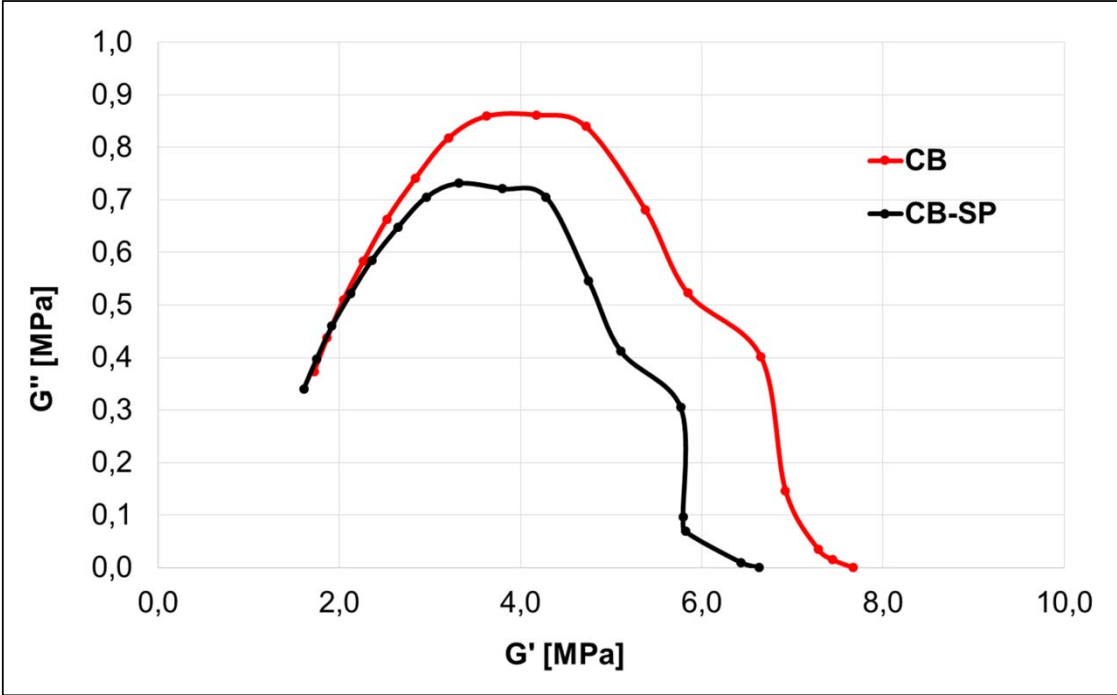


# NR/CB-SP composites from melt blending

## G' [Mpa] vs strain [%]



## Cole-Cole plot

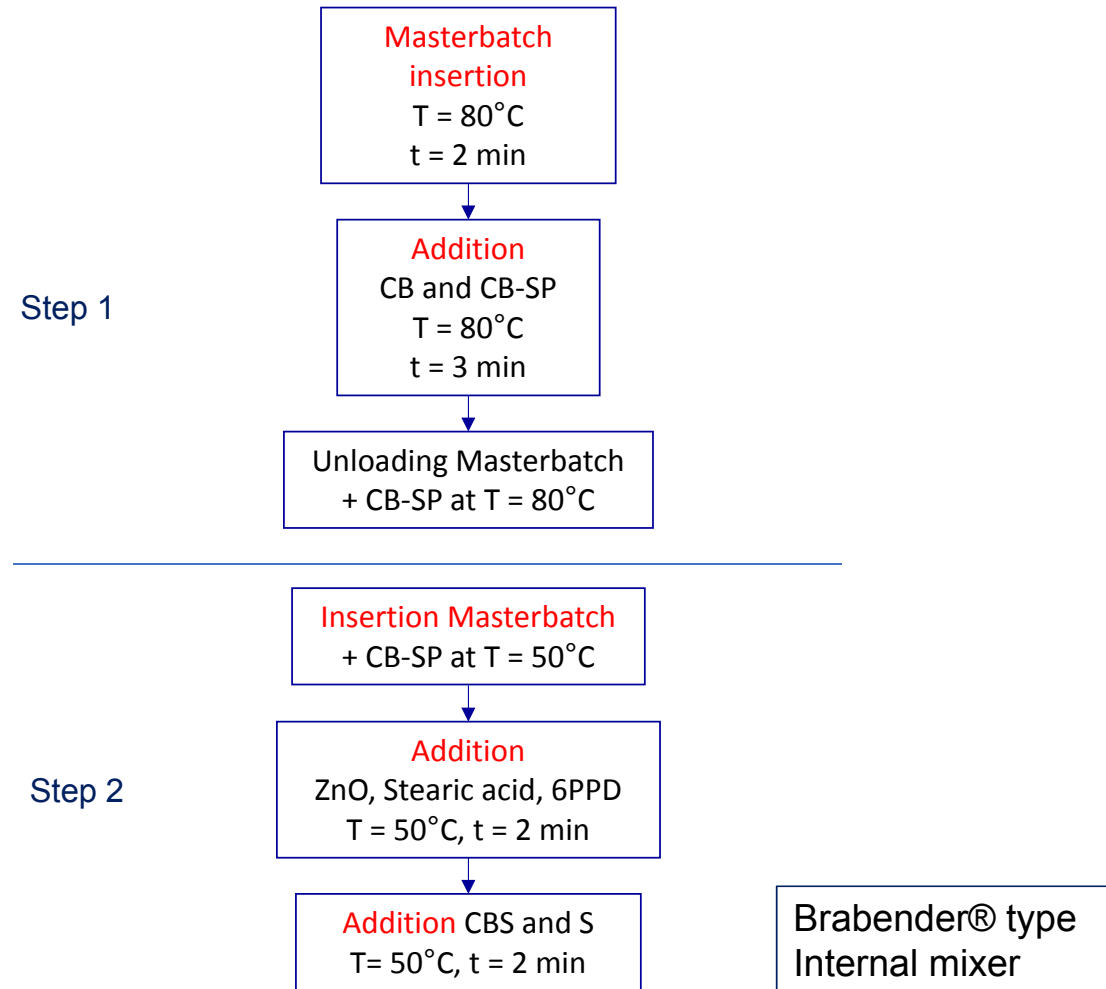


No effects on vulcanization kinetic

Results obtained with R.P.A.2000 Strain @50°C

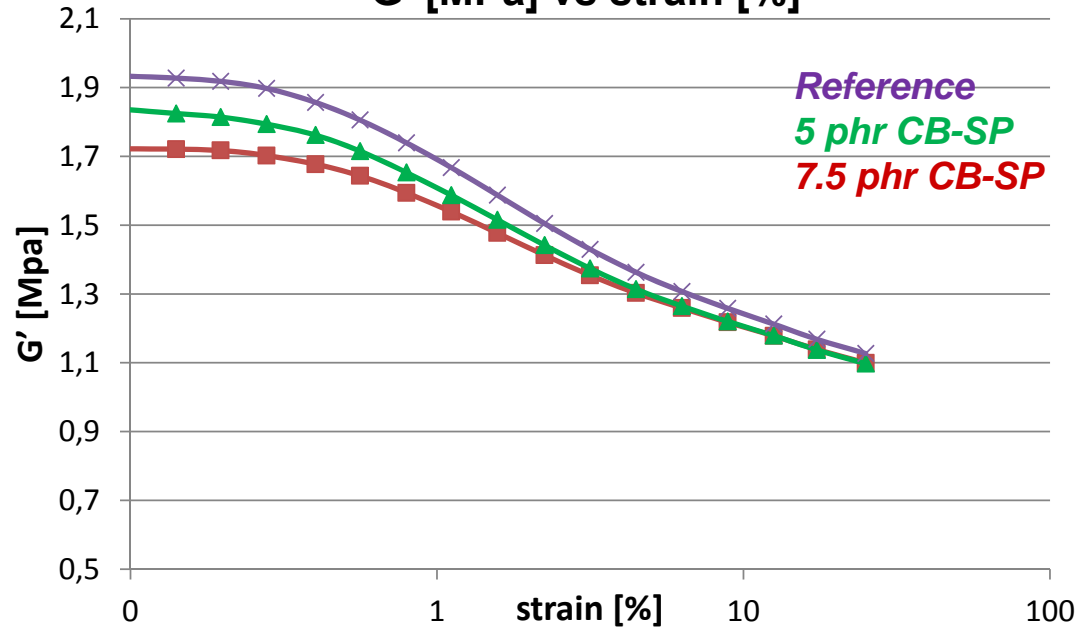
# IR-BR / CB-SP / silica composites from melt blending

<i>Ingredients<sup>a</sup></i>	<i>phr</i>	<i>phr</i>	<i>phr</i>
IR	50.0	50.0	50.0
BR	50.0	50.0	50.0
Silica	25.0	25.0	25.0
TESPT	4.0	4.0	4.0
CB N326	25.0	20.0	17.5
CB-SP(10 mass%)	0.0	5.5	8.25
CB		5.0	7.5
a. Other ingredients (phr): ZnO 4.0, Stearic acid 2.0, S 1.5, SP 2.0, CBS 0.5, SPPD 2.0, CBS 0.5, S 0.75			

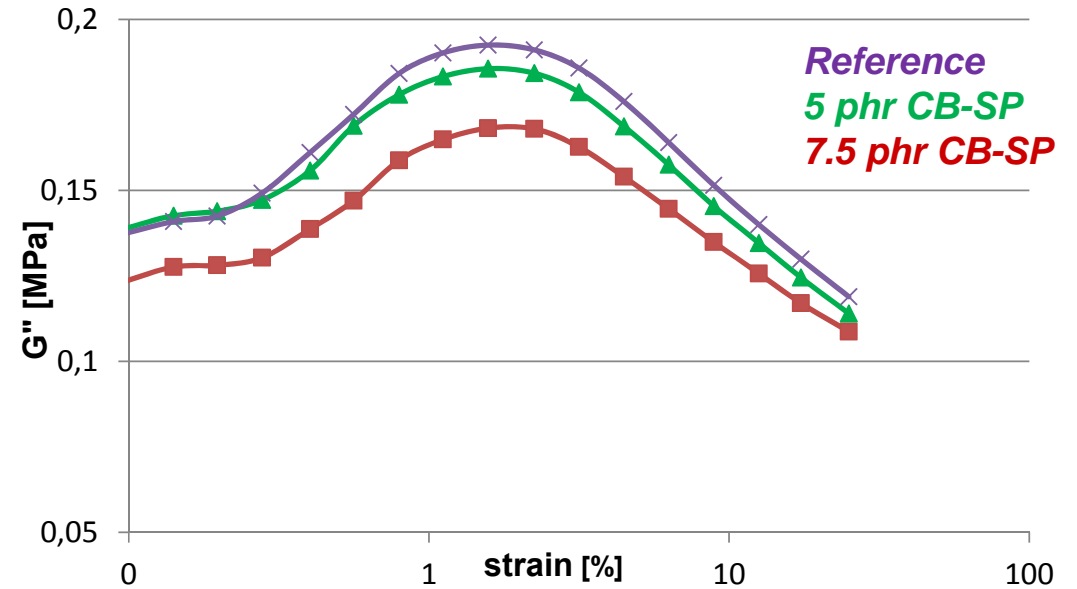


# Dynamic-mechanical properties: strain sweep test

**G' [MPa] vs strain [%]**



**G'' [MPa] vs strain [%]**

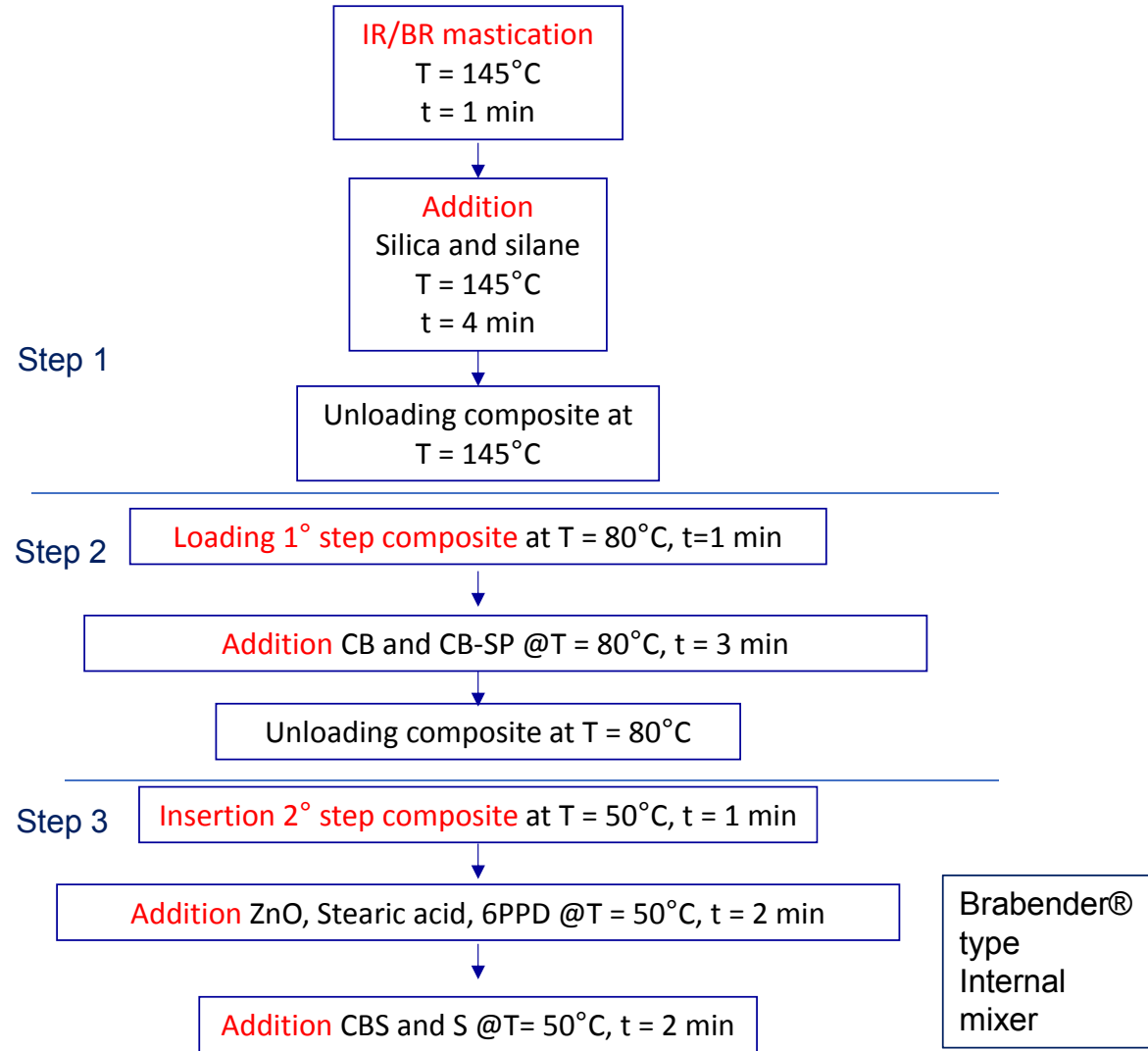


sample	phr SP *	G' min [Mpa]	G'' max [Mpa]	$\Delta G'$ [Mpa]	$\Delta G'/G'_{min}$	Tan delta max
<i>Reference</i>	0.0	1.93	0.19	0.81	0.42	0.13
<i>5 phr CB-SP</i>	0.5	1.84	0.19	0.74	0.40	0.13
<i>7.5 phr CB-SP</i>	0.75	1.72	0.17	0.62	0.36	0.12

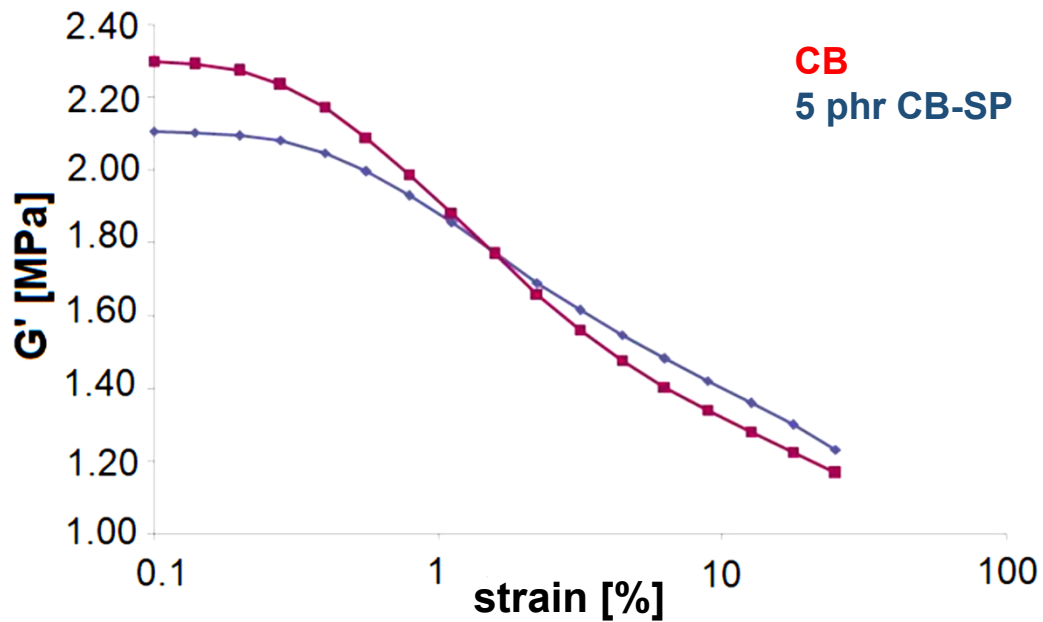
Results obtained through R.P.A.2000

# IR-BR / CB-SP / silica composites from melt blending

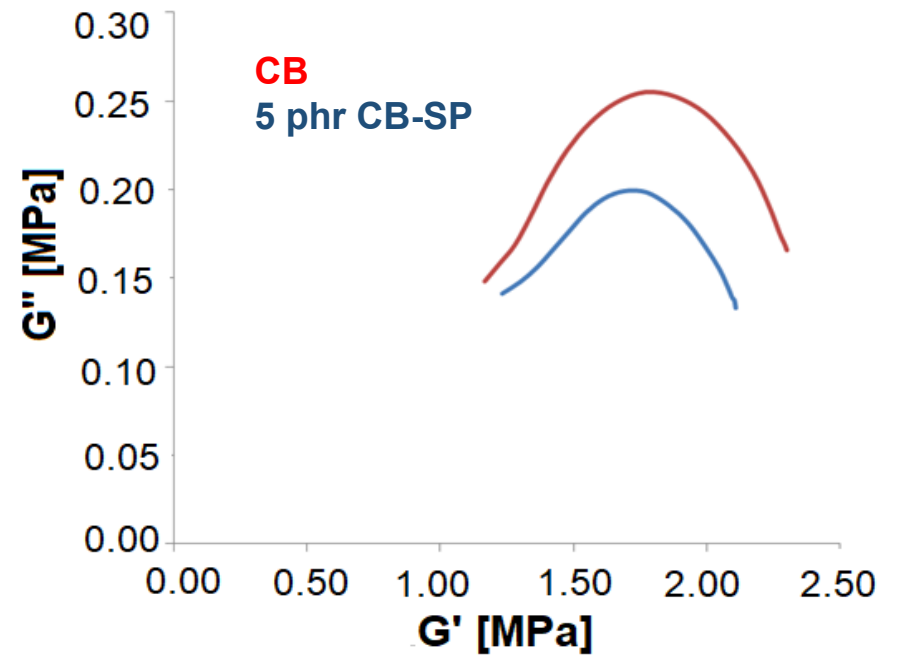
<i>Ingredients<sup>a</sup></i>	<b>CB</b> <i>[phr]</i>	<b>CB-SP</b> <i>[phr]</i>
IR	50.0	50.0
BR	50.0	50.0
Silica	25.0	25.0
TESPT	4.0	4.0
<b>CB N326</b>	<b>25.0</b>	<b>20.0</b>
<b>CB-SP(10 mass%)</b>	<b>0.0</b>	<b>5.5</b>
	<b>CB</b>	<b>5.0</b>
a. Other ingredients (phr): ZnO 4.0, Stearic acid 2.0, S 1.5, 6PPD 2.0, TBBS 1.8, <b>SP 0.5</b>		



**G' [Mpa] vs strain [%]**



**Cole-Cole plot**



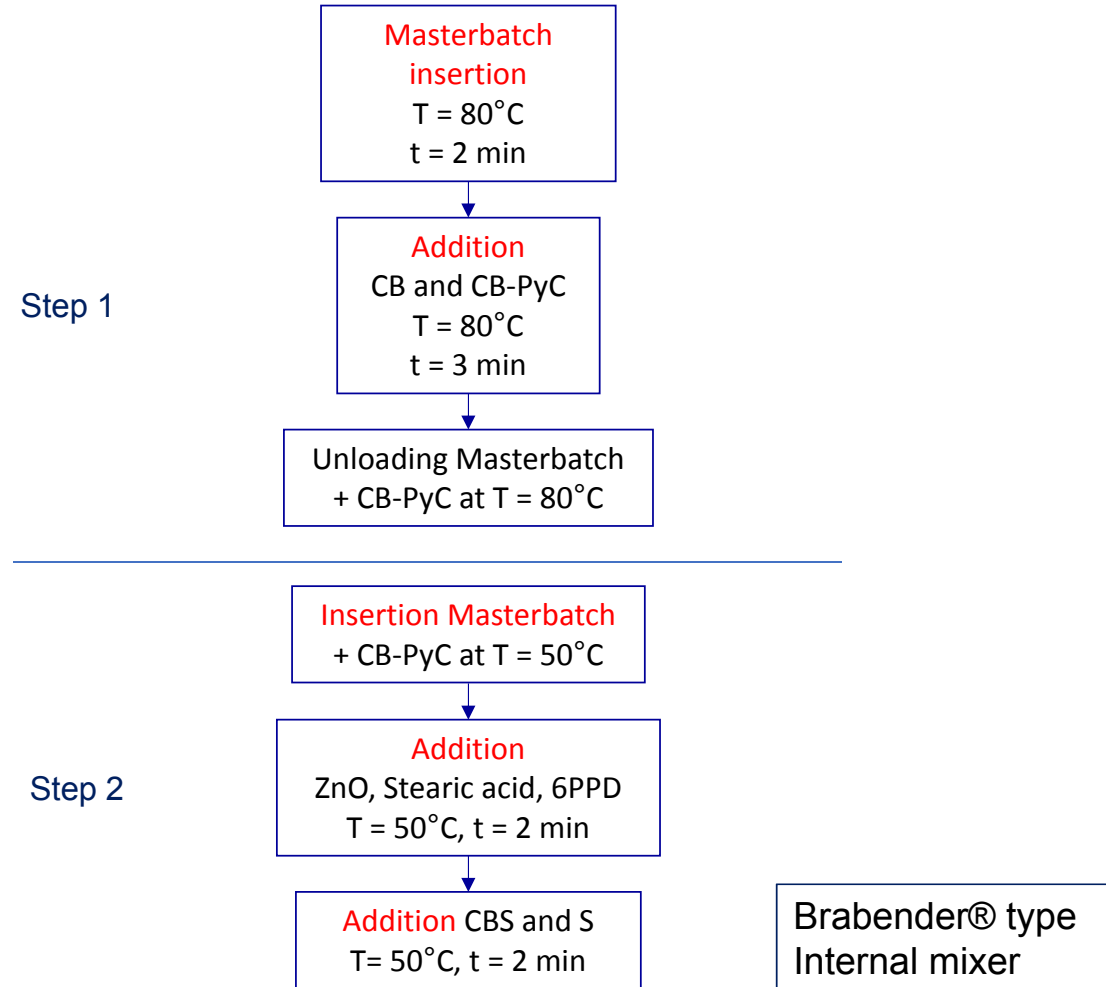
**No effects on vulcanization kinetic**

Results obtained  
with R.P.A.2000  
Strain @50°C

# IR-BR / CB-PyC / silica composites

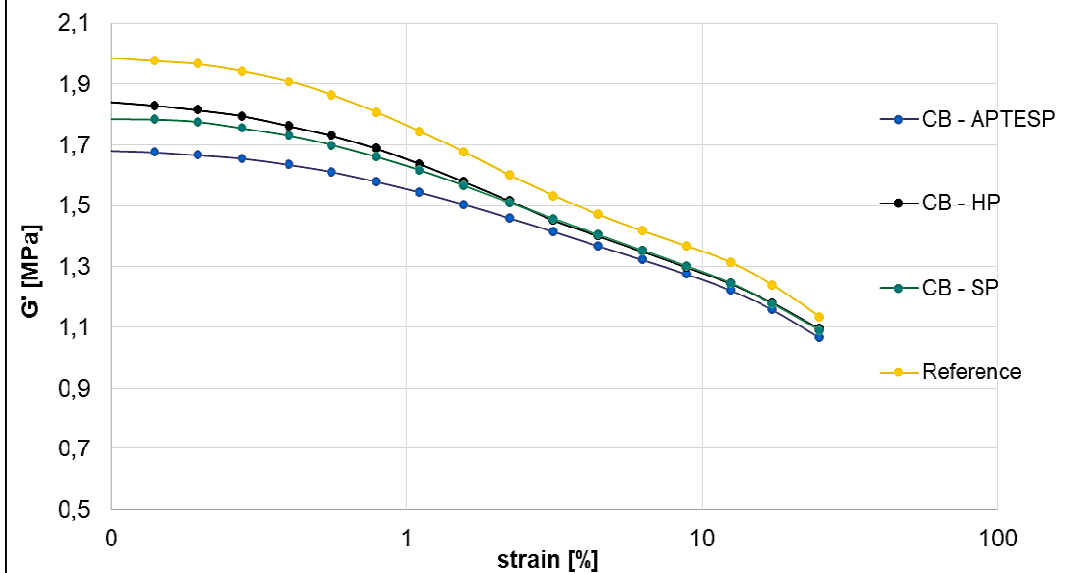
<i>Ingredients<sup>a</sup></i>	<i>phr</i>	<i>phr</i>
IR	50.0	50.0
BR	50.0	50.0
Silica	25.0	25.0
TESPT	4.0	4.0
CB N326	25.0	17.5
CB-PyC	0.0	8.5
CB		7.5

a. Other ingredients (phr): ZnO 4.0, Stearic acid 2.0, S 1.5, 6PPD 2.0, CBS 1.8,

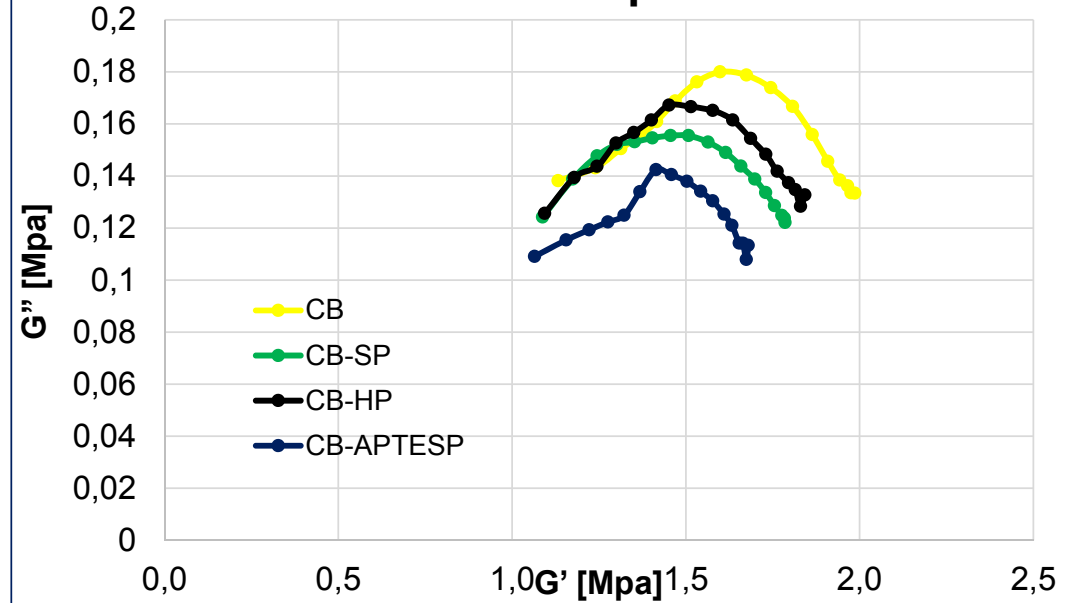


# Dynamic-mechanical properties: strain sweep test

## G' [MPa] vs strain [%]



## Cole-Cole plot



Compound	G' min [Mpa]	G'' max [Mpa]	$\Delta G'$ [Mpa]	$\Delta G'/G'_{min}$	$\tan \delta_{max}$
Reference	1.986	0.180	0.854	0.430	0.115
CB-SP	1.785	0.156	0.698	0.391	0.107
CB-HP	1.843	0.167	0.749	0.406	0.115
CB-APTESP	1.679	0.142	0.615	0.366	0.101

Results obtained through R.P.A.2000 Strain @50°C

# Conclusions



- ☞ A sustainable, efficient, versatile functionalization method was developed for the chemical modification of carbon black using pyrrole compounds
- ☞ The introduction of different functional groups on CB leads to a controlled modulation of the solubility parameters of the modified CB
- ☞ The total or partial replacement of pristine CB with CB-PyC as filler for rubber composites leads to enhanced properties: less Payne effect, lower hysteresis



Thanks for your attention

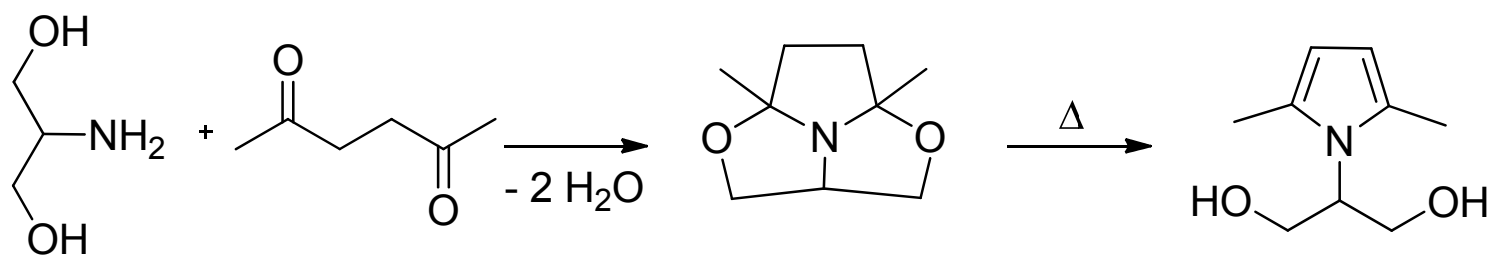
## Acknowledgement

Pirelli Tire:  
Raw Material Lab  
Chemical Lab  
Physical Lab

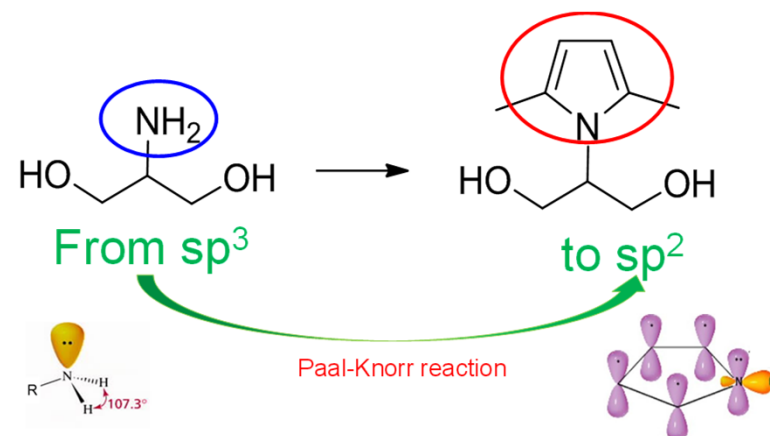
## Special thanks to:

Dr. A. Rosengart  
Dr. L. Brambilla  
Dr. A. Serafini

## Neat synthesis of Serinol Pyrrole (SP)



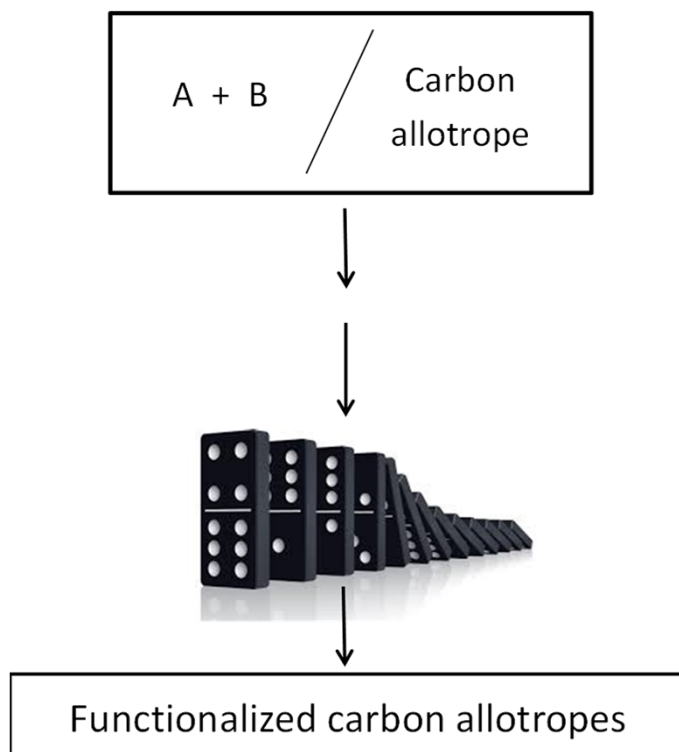
- ➡ Yield: at least 96%
- ➡ Atom efficiency: 85%
- ➡ Easy procedure
- ➡ No solvent
- ➡ Only by product: H<sub>2</sub>O



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](#)

# Facile functionalization of carbon materials



- Functional group:  
from few % to >20%
- Functionalization yield:  
from 85% to quantitative
- Covalent bond  
between functional group  
and graphene layer
- Bulk structure of graphitic materials:  
substantially unaltered

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 \(2016\)](#)  
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M. Galimberti, V. Barbera, [Italian Patent 102016000113070 \(2016\)](#)