A bio-sourced molecule as carbon black coupling agent in rubber compounds with low hysteresis

Gea Prioglio[1], Simone Naddeo[1], Vincenzina Barbera[1], Ulrich Giese[2], Maurizio Galimberti[1]

[1] Politecnico di Milano, Piazza L. Da Vinci 32, 20131 Milano, Italy [2] Deutsches Institut für Kautschuktechnologie e.V. · Eupener Straße 33 · 30519 Hannover, Germany

gea.prioglio@polimi.it

Introduction

Tire sustainability

- ❑ Nowadays the **environmental impact of a tire is of prime concern**.
- ❑ The majority of the environmental impact of a tire takes place during its use and is related to rolling resistance.
- ❑ An **equilibrium** between **tire performances and rolling resistance** and thus hysteresis **is perused**.

Reinforcing fillers and hysteresis in tire compounds

- ❑ **Silica** employed as reinforcing filler **allows mechanical reinforcement and a great reduction of hysteresis**
- ❑ **Silica's strength** is the formation of a **rubber-filler chemical bond via a coupling agent** (an organosilane containing sulphur atoms)
- ❑ However, **silica has various drawbacks**: the release of ethanol from the silica – silane reaction, the corrosion of compounding equipment, the increase of compound viscosity and the reduction of the shelf life of semifinished products.
- ❑ **Carbon black** (CB) is another main filler for tire compounds, it is highly reinforcing
- ❑ CB **does not have a coupling agent able to promote chemical bonds with the rubber matrix**

→ It would be highly desirable to replace silica, at least partially, with a CB-based filler able to promote strong rubber-filler interactions

Objectives

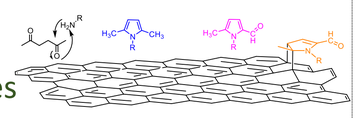
☞ **To prepare a CB-filled compound with the same performances of a silica-based compound**

Hence

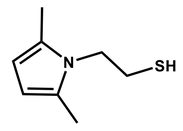
☞ **To prepare a functionalized carbon black able to establish a chemical bond with rubber chains**

How to achieve the objectives?

✓ Exploiting the **pyrrole methodology** to functionalize carbon allotropes



✓ Selecting **pyrrole compounds** able to react with rubber chains

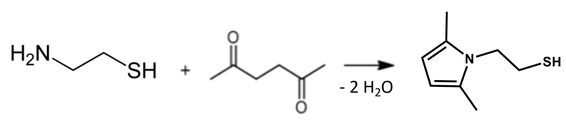


Thiol Pyrrole, SHP

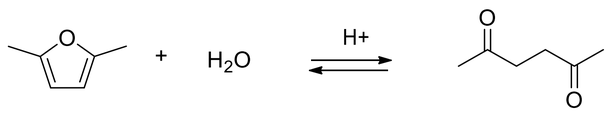
2-(2,5-dimethyl-1*H*-pyrrol-1-yl)ethane-1-thiol

Synthesis of SHP form a bio-based building block

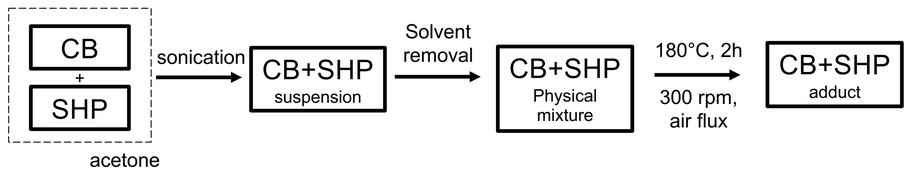
Thiol Pyrrole (SHP) was synthesized starting from 2,5-hexanedione and 2-aminoethanethiol.



2,5-hexanedione was obtained from 2,5-dimethylfuran as bio-based building block.



Synthesis of the CB-SHP adduct via the pyrrole methodology



The obtained adduct was purified via an acetone sohxlet extraction and deeply characterized via TGA, HRTEM, X-Ray diffraction, solubility, BET and desorption analyses.

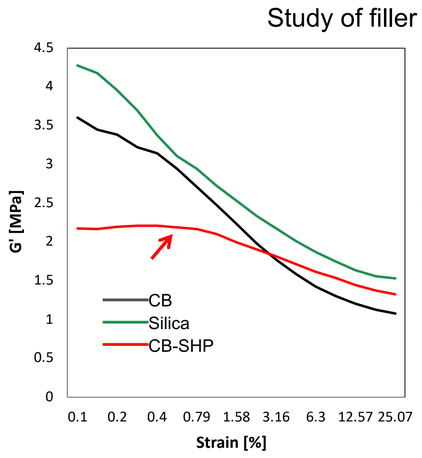
Preparation and characterization of CB-SHP vs Silica vs CB rubber composites

Silica vs CB vs CB-SHP at constant filler volume

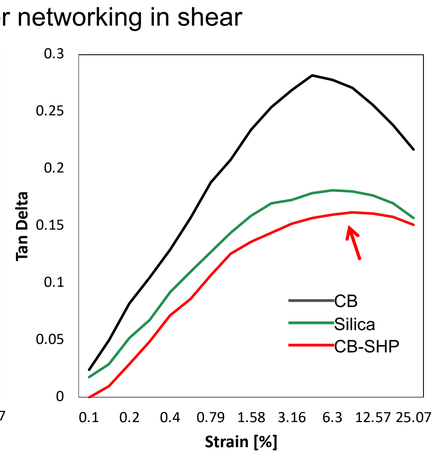
Recipies in phr	**Silica**	**CB**	**CB-SHP**
S-SBR	70	70	70
NR	30	30	30
Silica	65	0	0
Silane	5.2	0	0
CB	0	55	0
CB-SHP	0	0	58.7

Other ingredients used for each compound: stearic acid, ZnO, 6PPD, TBBS, PVI, sulphur

Study of filler networking in shear

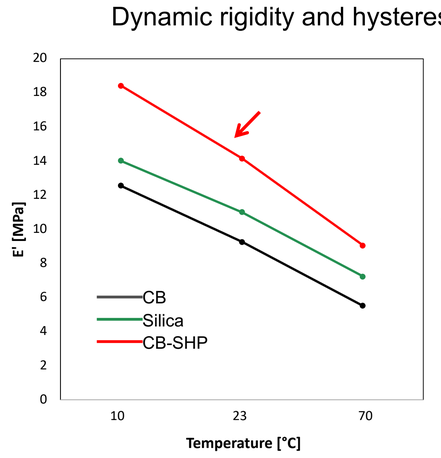


→ *lower Payne Effect*

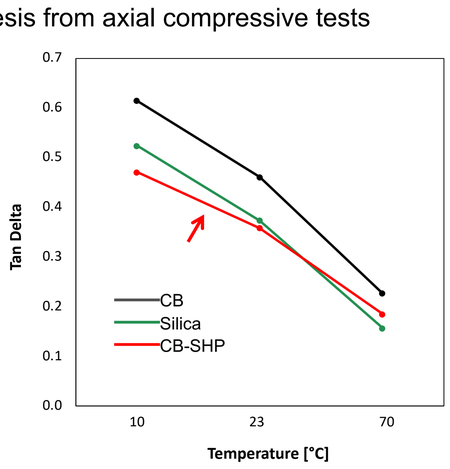


→ *lower hysteresis*

Dynamic rigidity and hysteresis from axial compressive tests



→ *higher rigidity*



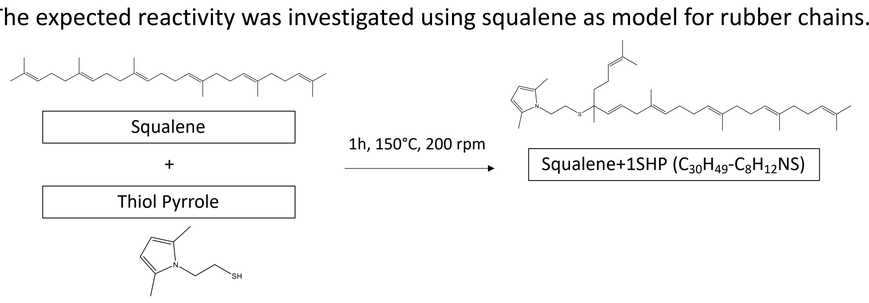
→ *comparable hysteresis to silica*

Curves from axial and shear dynamic-mechanical analyses of S-SBR-based rubber composites filled with 65 phr of pristine silica (green), 55 phr of prisinte carbon black (black) and 58.7 phr of CB-SHP (red).

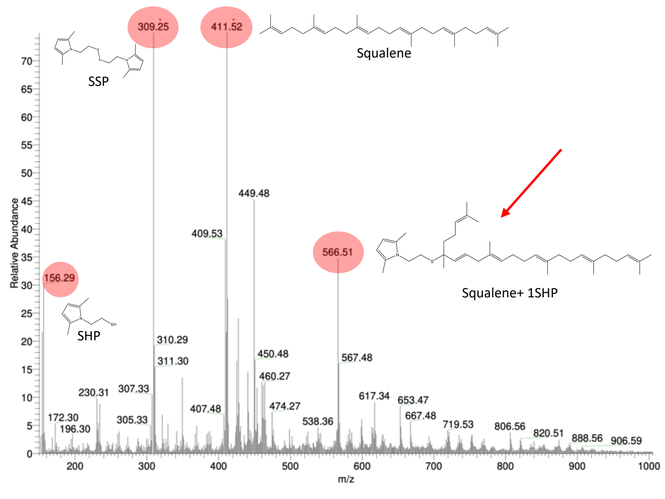
Studying the reactivity of SHP with rubber chains

CB-SHP results in rubber compounds suggest the formation of strong rubber-filler bonds.

The expected reactivity was investigated using squalene as model for rubber chains.



The LC-MS mass spectrum of the reaction product **confirmed SHP-rubber bonding**



Conclusions

- Composites with **CB-SHP** have the same or **even better dynamic mechanical properties with respect to silica-based composites**
- SHP was synthetized starting from a **bio-based building block**
- CB-SHP was prepared via the **pyrrole methodology**, through a simple and sustainable technology based on pyrrole compounds
- The **reactivity** of SHP with rubber chains was **confirmed**

→ Results demonstrate that CB-SHP is a valid alternative to silica for green elastomer compounds for tires since it lowers rolling resistance

References:

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

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

[3] Barbera, V., Bernardi, A., Palazzolo, A., Rosengart, A., Brambilla, L., & Galimberti, M.. Pure and Applied Chemistry, 2018, 90(2), 253-270.

[4] Barbera, V., Brambilla, L., Milani, A., Palazzolo, A., Castiglioni, C., Vitale, A., ... & Galimberti, M. (2019). Domino reaction for the sustainable functionalization of few-layer graphene. Nanomaterials, 9(1), 44.

[5] Maurizio Stefano Galimberti, Vincenzina Barbera, Gea Prioglio, Luca Giannini, WO2020225595A1

[6] Italian Patent Application n. 102021000032138, inventors: V. Barbera, M. Galimberti, L. Giannini. S. Naddeo

Acknowledgments:

We thank Pirelli Tyre S.p.A. for financial support

Innovative Sustainable Materials GROUP in ISCaMaP

@ismaterials.polimi