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

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Introduction

The research here reported was aimed at the controlled functionalization of carbon black, tuning its solubility parameter, without altering the bulk structure. The selected functionalization method, already patented[1] and published[2], is **simple** and **versatile** and is indeed **sustainable**: it **does not use solvents** or **catalysts** and **does not produce wastes**. Such method, applied to carbon black, is summarized in the following scheme.

Carbon black + Pyrrole compound → (Mixing) → Carbon black / pyrrole compound mixture → (Thermal energy) → Carbon black / pyrrole compound adduct

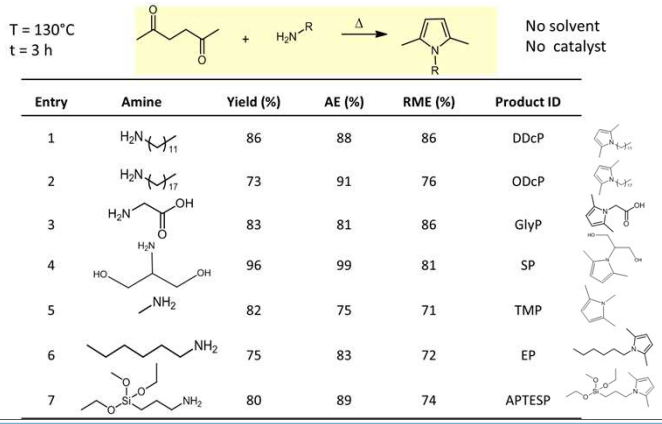
Carbon black (CB)

CB grade	BET surface area [m²/g]	External surface area [m²/g]	Oil adsorption number [cm³/100g]	Heating loss [%]
N234	112	110	125	≤2.5
N326	78	76	72	≤1.0

The grades of CB chosen are the most used as filler for tire tread compounds.

Same results were obtained from both grades of CB.

Pyrrole compounds (PyC)



Entry	Amine	Yield (%)	AE (%)	RME (%)	Product ID
1	H_2N	86	88	86	DDcP
2	H_2N	73	91	76	ODcP
3	H_2N	83	81	86	GlyP
4	H_2N	96	99	81	SP
5	NH_2	82	75	71	TMP
6	NH_2	75	83	72	EP
7	NH_2	80	89	74	APTESP

Functionalization

Procedure

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

1) Mixing in acetone
2) Solvent removal

→ CB - PyC

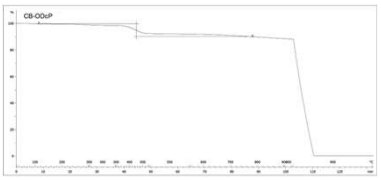
T = 180°C, 4 h, 400 rpm

→ CB/PyC adduct

All adducts were **extracted in Soxhlet** with acetone (16 h).

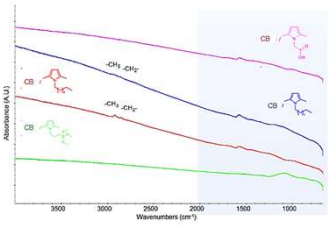
Characterization

Thermogravimetic analysis



Example of TGA analysis on CB-PyC adduct: CB-ODcP(10 mass%)

Infrared spectroscopy



ATR spectra of some examples of CB-PyC adducts: CB/GlyP, CB/HP, CB/DDcP, CB/APTESP

Functionalization yield

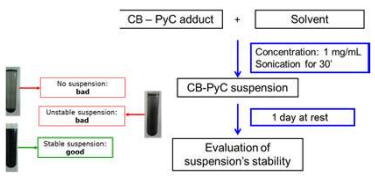
Entry	Adduct	Yield *
1	CB - DDcP	85%
2	CB - ODcP	98%
3	CB -GlyP	82%
4	CB - SP	96%
5	CB -TMP	65%
6	CB - EP	85%
7	CB -APTESP	78%

*Yield calculated through TGA analysis, using the equation:

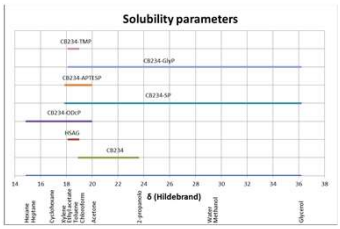
$$\text{Yield (\%)} = \frac{mass\ loss_{after\ washing}[\%]}{mass\ loss_{before\ washing}[\%]} \times 100$$

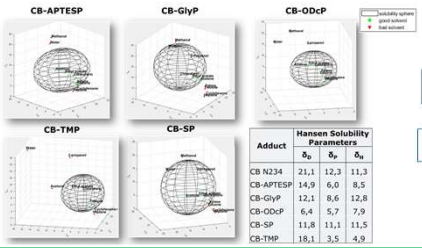
Tuning of solubility parameter

Experimental determination



Solubility parameters of carbon black N234 modified with different pyrrole compounds





Adduct	Hansen Solubility Parameters δ_D	δ_P	δ_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

Theoretical predictions

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

→ The substance is identified by three coordinates (δ_D, δ_P and δ_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

Rubber composites

Recipes

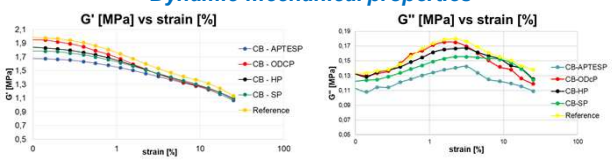
Ingredients[a]	phr	phr
IR	50.0	50.0
BR	50.0	50.0
CBN326	25.0	17.5
CB-PyC[b]	0.0	8.5
CB		7.5
PyC		1.0
Silica	25.0	25.0
TESPT	4.0	4.0

a.Other ingredients (phr): ZnO 4.0, Stearic acid 2.0, S 1.5, 6PPD 2.0, CBS 1.8;
b. Amount of PyC on CB= 5%mol

Vulcanization reaction: results

	Reference	CB-SP	CB-HP	CB-ODcP	CB-APTESP
M_L [dNm]	4,20	4,17	4,06	3,62	4,04
M_H [dNm]	20,83	19,20	19,19	19,29	18,47
$M_H - M_L$ [dNm]	16,63	15,03	15,13	15,67	14,43
ts1 [min]	5,20	5,17	5,06	4,62	5,04
t90 [min]	3,89	3,94	3,96	3,96	4,10

Dynamic-mechanical properties



Strain sweep tests: results

Compound	G' min [Mpa]	G'' max [Mpa]	ΔG'	ΔG'/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-ODcP	1,951	0,175	0,867	0,444	0,117
CB-APTESP	1,679	0,142	0,615	0,366	0,101

Strong modification to composite properties
With **only 1 phr** of PyC:
Less Payne effect, less dissipation of energy

Conclusions

Different grades of CB were efficiently functionalized using a facile and sustainable method. The solubility parameter was tuned in a wide range of values. Enhanced properties of rubber composites were obtained by using functionalized CB. This work paves the way for the facile and sustainable modification of the solubility parameters of carbon black and of sp^2 carbon allotropes and for the predictive assessment of their compatibility with different environments

References:

[1] M. Galimberti, V. Barbera, A. Truscello, R. Sebastiano, EP3180379B1 (2017).
[2] V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti, Pure and Applied Chemistry 2018, 90(2), 253–270.

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