

SUSTAINABLE FUNCTIONALIZATION OF sp^2 CARBON ALLOTROPES AS FILLERS FOR RUBBER COMPOUNDS WITH LOWER DISSIPATION OF ENERGY

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Abstract: A facile and sustainable functionalization method, suitable for all the families of sp^2 carbon allotropes, has been developed. Functionalization was obtained by simply mixing the carbon allotropes and pyrrole derivatives. Reactions were characterized by a yield up to 96%. The structure of the graphitic substrates remained substantially unaltered, after the reaction. Study of the mechanism led to define a domino reaction involving a carbocatalyzed oxidation of the pyrrole compound followed by Diels-Alder cycloaddition. Dispersions of functionalized carbon allotropes were prepared in solvents with different solubility parameters and, from the qualitative results of the dispersion tests, Hansen solubility parameters of carbon allotropes were estimated. Functionalized carbon black was used to prepare rubber compounds based on carbon black and/or silica as the main fillers. Effects on vulcanization and mechanical reinforcement are discussed.

Keywords: carbon allotrope, functionalization, domino reaction, rubber compound.

sp^2 carbon allotropes (CA) are efficient reinforcing fillers for rubber materials. In this field, carbon black (CB) has been used for over a century and nanofillers such as carbon nanotubes (CNT), graphene (G) and graphene related materials (GRM), are dramatically increasing their importance. Ultimate distribution and dispersion of carbon fillers in the rubber compounds must be obtained. To achieve this goal, CA can be used unaltered or functionalized. The introduction of functional groups on sp^2 carbon allotropes allows to dramatically enlarge their range of interesting properties and hence their impact on the properties of rubber materials. The above – mentioned CA can be seen as an assembly of graphene sheets with different arrangements. The single graphene layer is the common feature in all the considered carbon allotropes and it is a good substrate for performing chemical reactions. The reaction with graphene layers, wherever they are, represents a synthetic strategy, which could allow a more efficient functionalization.

Functionalization can be summarized as covalent^[1-9] and non – covalent.^[5-7,10-11] The ideal functionalization method should allow tuning the solubility parameter of CA, promoting their dispersion in a large variety of matrices. Functional groups should be firmly bound to CA, without altering the structure of the carbon substrate and leaving as much surface as possible free and available for further interactions. CA with a controlled variety of functional groups and with carbon atoms in a range of oxidation states could become platform building blocks for the preparation of value-added products.

In our group, the research was inspired to these objectives, aiming at developing a sustainable functionalization method, in line with the basic principles of green chemistry.^[12] Functionalization of graphene layers, carbon black and carbon nanotubes was performed with pyrrole compounds (PyC) obtained from the Paal Knorr reaction of a primary amine with α,δ dicarbonyl compounds.^[1,4,10,11] PyC were obtained with high atom economy and yield. Functionalization of CA was obtained by simply mixing the carbon allotropes and the pyrrole compound, giving thermal energy. Reactions were characterized by a yield up to 96%. The structure of the graphitic

substrates remained substantially unaltered, after the reaction. Study of the mechanism led to defining a domino reaction involving a carbocatalyzed oxidation of the pyrrole compound followed by Diels-Alder cycloaddition.^[1]

1 Experimental part

1.1 Materials

Reagents and solvents commercially available were purchased and used without further purification.

2,5-hexandione (Merck e Schuchardt, Aldrich).

2-amino-1,3-propanediol (kindly provided by Bracco).

Dodecanamine (Merck e Schuchardt, Aldrich).

Bis[3(triethoxysilyl)propyl]tetrasulfide silane (Merck e Schuchardt, Aldrich). Deuterated choloform (CDCl₃) and dimethylsulfoxide (DMSO-d₆) were used to perform ¹H NMR and ¹³C NMR tests. n-hexane, toluene, ethyl acetate, 2-propanol, and water (all from Sigma-Aldrich, used as received) were the solvent used for the solubility test. The following chemicals have been used for the elastomeric compounds preparation: silica Zeosil 1165 MP (Solvay), bis(3-triethoxysilylpropyl) tetrasulfide (TESPT), ZnO (Zinc Oxide), Stearic acid (Sogis), 6PPD ((1,3-dimethyl butyl)-N'-Phenyl-p-phenylenediamine from Crompton), S (sulfur from Solfotecnica), TBBS (N-tert-butyl-2-benzothiazyl) sulfonamide, from Flexsys).

Synthetic poly(1,4-*cis*-isoprene) (IR) was SKY3 from Nizhnekamskneftekhim Export, with 70 Mooney Units (MU) as Mooney viscosity (ML(1+4)100°C), synthetic poly (1,3-butadiene) (BR) was neocis BR 40 from Versalis, with a 43 Mooney Viscosity (ML(1+4)100°C).

Different kinds of sp² carbon allotropes were used: HSAG was Synthetic Graphite 8427® from Asbury Graphite Mills Inc., with 99,5% as carbon content.

Carbon Black N326 (from Cabot) with BET surface area 78 m²/g and External surface area 76 m²/g.

Carbon nanotubes Nanocyl NC7000 from Nanocyl SA are produced by catalytic Chemical Vapor Deposition (CCVD) process. The average diameter of nanotubes were 9,5 * 10⁻⁹ m, average 1,5 μm, surface area = 250 – 300 m²/g.

1.2 Synthesis of pyrrole compound (PyC): general procedure

A mixture of 2,5-hexandione (37,67 g; 0.33 mol) and serinol (30.06 g; 0.33 mol) was poured into a 100 mL round bottomed flask equipped with magnetic stirrer. The mixture was then stirred, at 150°C, for 2 h.

1.2.1 2-(2,5-dimethyl-1H-pyrrol-1-yl)propane-1,3-

diol (SP) (2a)

The resulting compound SP was characterized through ¹H NMR (CDCl₃, 400 MHz); δ (ppm) = 2,27 (s, 6H); 3,99 (m, 4H); 4,42 (q, 1H); 5,79 (s, 2H). ¹³C NMR (DMSO-d₆, 100 MHz); δ (ppm) = 127,7; 105,9; 71,6; 61,2; 13,9.

The yield of the reaction was estimated to be 99%.

1.2.2 1,2,5-trimethyl-1H-pyrrole (TMP) (2b)

The resulting compound TMP was characterized through ¹H NMR (CDCl₃, 400 MHz); δ (ppm) = 5.80 (s, 2H, CH), 2.24 (s, 6H, CH₃), 3.41 (s, 3H, CH₃). ¹³C NMR (CDCl₃, 100 MHz); δ (ppm) = 127.6, 105.6, 32.4, 12.8.

The yield of the reaction was estimated to be 76%.

1.2.3 1-dodecyl-2,5-dimethyl-1H-pyrrole (DdcP) (2c)

The resulting compound DdcP was characterized through ¹H NMR (CDCl₃, 400 MHz); δ (ppm) = 5.75 (s, 2H, CH), 3.68–3.72 (m, 2H, CH₂), 2.21 (s, 6H, CH₃), 1.60 (m, 2H, CH₂), 1.30 (m, 2H, CH₂–CH₂–CH₃), 1.26 (m, 18H, CH₂), 0.90–0.86 (t, 3H, CH₃). ¹³C NMR (CDCl₃, 100 MHz); δ (ppm) = 127.2, 104.9, 43.6, 31.9, 31.0, 29.6, 26.9, 22.6, 14.0, 12.4.

The yield of the reaction was estimated to be 62%.

1.2.4 1-(3-(triethoxysilyl)propyl)-2,5-dimethyl-1H-pyrrole (APTESP) (2d)

The resulting compound APTESP was characterized through ¹H NMR (CDCl₃, 400 MHz); δ (ppm) = 5.73 (s, 2H, CH), 3.80 (m, 6H, O–CH₂), 3.70 (m, 2H, N–CH₂), 2.20 (s, 6H, CH₃), 1.71 (m, 2H, CH₂), 1.22 (m, 2H, CH₂), 0.62 (m, 3H, CH₃). ¹³C NMR (CDCl₃, 100 MHz); δ (ppm) = 127.6, 105.6, 56.1, 51.05, 27.01, 19.2, 13.01, 12.51.

The yield of the reaction was estimated to be 80%.

1.3 Functionalization of sp² carbon allotropes with pyrrole compounds (PyC) - General procedure

10,0 g of CA and 25 mL of acetone were poured in sequence in a 250 mL round bottomed flask. The system was sonicated for 10 minutes.

Then, 1,00 g of PyC was poured into the round bottomed flask. The system was sonicated for 30 minutes. The temperature was raised at 180 °C for 2 hours. After the reaction the adduct CA-PyC was cooled at room temperature. The mixture was washed by using acetone and filtered.

The same procedure was adopted for the preparation of all the adducts reported in this manuscript. In all preparations, a mass ratio equal to 10:1 between the

carbon allotrope and PyC was used. Adducts were obtained as a black powder. Functionalization yield was determined through the following equation (Eq.1):

$$\text{Functionalization yield (\%)} = \frac{\text{mass loss (\% of PyC after washing)}}{\text{mass loss (\% of PyC before washing)}} \times 100$$

1.3.1 HSAG-SP adduct

The yields of functionalization were estimated by means of TGA, determining the amount of pyrrole compound in the adduct after washing. According to the equation 1 the yields was estimated to be 92%.

1.3.2 CB-SP adduct

The yields of functionalization were estimated by means of TGA, determining the amount of pyrrole compound in the adduct after washing. According to the equation 1 the yields was estimated to be 87%.

1.3.3 CNT-SP adduct

The yields of functionalization were estimated by means of TGA, determining the amount of pyrrole compound in the adduct after washing. According to the equation 1 the yields was estimated to be 90.6%.

1.3.4 HSAG-DdcP adduct

The yields of functionalization were estimated by means of TGA, determining the amount of pyrrole compound in the adduct after washing. According to the equation 1 the yields was estimated to be 73%.

1.3.5 CB-DdcP adduct

The yields of functionalization were estimated by means of TGA, determining the amount of pyrrole compound in the adduct after washing. According to the equation 1 the yields was estimated to be 88%.

1.3.6 CNT-DdcP adduct

The yields of functionalization were estimated by means of TGA, determining the amount of pyrrole compound in the adduct after washing. According to the equation 1 the yields was estimated to be 93.1%.

1.3.7 HSAG-APTESP adduct

The yields of functionalization were estimated by means of TGA, determining the amount of pyrrole compound in the adduct after washing. According to

the equation 1 the yields was estimated to be 70%.

1.3.8 CB-APTESP adduct

The yields of functionalization were estimated by means of TGA, determining the amount of pyrrole compound in the adduct after washing. According to the equation 1 the yields was estimated to be 78%.

1.3.9 CNT-APTESP adduct

The yields of functionalization were estimated by means of TGA, determining the amount of pyrrole compound in the adduct after washing. According to the equation 1 the yields was estimated to be 98.5%.

1.4 Rubber compounds

1.4.1 General procedure

Synthetic isoprene (IR) and butadiene (BR) rubber were fed into a Brabender® internal mixer and masticated at 145 °C for 1 minute. Then silica and silane TESPT were added at T=145°C and mixed for 4 minutes. The obtained composite was discharged at T=145°C. The temperature of the internal mixer was then set to 80°C, and the composite obtained in the first step was charged and mixed for 1 minute. At that point, CB (as it was or modified with SP) was fed and mixed for further 4 minutes, then the composite was discharged at T=80°C. The composite thus prepared was then fed into the internal mixer at 50 °C, masticated for 1 minute, then stearic acid, zinc oxide and 6PPD were added and mixed for 2 minutes. Finally, TBBS and sulfur were added and mixed for 2 minutes. The composite was then unloaded at 50 °C.

1.5 Methods

1.5.1 Thermogravimetric analysis

TGA test under flowing N₂ (60mL/min) were performed with a Mettler TGA SDTA/851 instrument according to the standard method ISO9924-1. Samples (10 mg) were heated from 30 to 300°C at 10°C/min, kept at 300°C for 10 min, and then heated up to 550°C at 20°C/min. After being maintained at 550°C for 15 min, they were further heated up to 700°C and kept at 700°C for 30 min under flowing air (60 mL/min).

1.5.2 Nuclear magnetic resonance (NMR)

¹H NMR. The NMR spectra were recorded on a Bruker AV 400 (400MHz). To record ¹H NMR spectra it was used a 5 mm multinuclear probe with reverse detection. 64 scans were used with an acquiring time of 6 minutes.

Chemical shifts were reported in ppm with the solvent residual peak as internal standard (DMSO-d6: $\delta_H = 2.50$ ppm, CDCl3: $\delta_H = 7.26$ ppm)

¹³C NMR. The NMR spectra were recorded on a Bruker AV 400 (400MHz) equipped with a 5 mm multinuclear probe with reverse detection was used to record ¹³C NMR spectra, 1400 scans and an acquiring time of 15 minutes.

1.5.3 Sonication

A 2L ultrasonic bath (power 260 W) from Soltec Ultrasonic Cleaner was used.

1.5.4 Calculation of the Hansen solubility parameters (HSP)

Calculation of HSP for carbon black was performed applying the Hansen solubility sphere representation of miscibility. The idea at the basis of this geometrical approach is the calculation of the cohesive energy density (UT/V) of a compound as the sum of three interaction contributions, as given by equation 2; dispersion (non-polar van der Waals forces) (δ_D), polar (δ_P), and hydrogen bonding (δ_H) (Eq.2).

$$\frac{U_T}{V} = \delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

The compound is therefore identified by three coordinates (δ_D , δ_P , and δ_H) in the Hansen parameters space. The distance between points (e.g a solute and its solvent) is related to their cohesive energy density difference, which is related to the enthalpy of mixing. As the enthalpy of mixing is minimal for miscible substances, two points close to each other in the Hansen space correspond to miscible compounds.

To estimate the HSP of a solute i, a dispersion test is performed on different solvents j, distinguishing good solvents (providing stable solutions/dispersions) and bad solvents, which are not able to give stable dispersions. Given the parameters (coordinates) of the solvents, it is possible to define a sphere, centered on the solubility parameters of the solute, which encompasses the good solvents points and excludes the non-solvents.

The sphere radius is defined as R_0 , the radius of interaction, while the distance between the solute and the solvent is R_a , calculated as (Eq.3):

$$R_{a,ij}^2 = 4(\delta_{D,i} - \delta_{D,j})^2 + (\delta_{P,i} - \delta_{P,j})^2 + (\delta_{H,i} - \delta_{H,j})^2$$

The ratio between $R_{a,ij}$ and R_0 is defined as RED, relative energy difference. Solutes and solvents with good affinity have relative energy difference lower than 1 (Eq.4).

$$RED = \frac{R_{a,ij}}{R_0}$$

An optimization problem is therefore defined: the center coordinates of the Hansen solubility sphere are calculated by minimizing the radius of interaction (i.e. the distance from the coordinates of the good solvents), including the good solvents (RED<1) and excluding the bad ones. The sphere center coordinates correspond to the three unknown HSP of the solute.

The fitting sphere program was adapted and solved in Matlab environment using the Nelder-Mead simplex algorithm.

2 Results and Discussions

The synthesis of the pyrrole compounds (PyC) was performed in the absence of solvents and catalysts, by simply mixing and heating the reagents.^[4] The structures of the primary amines used for the reactions and of the obtained pyrrole compounds therefrom are shown in Figure 1.

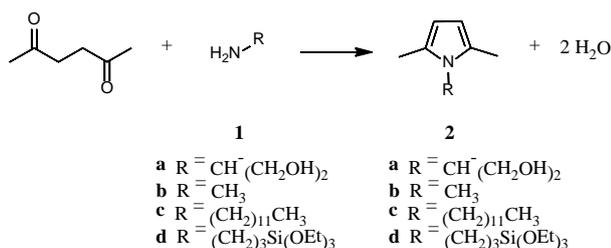


Figure 1. Synthesis of pyrrole compounds (PyC) (2a-d)

All the reactions of Figure 1 are characterized by very good atom economy (from 81 % to 90 %), the only byproduct being water.^[4] Detailed procedures are reported in the experimental part and in previous works.^[4]

Thanks to the reactions of Figure 1, a library of pyrrole – based compounds became available. These compounds were used for the functionalization of CA.

In this work, functionalization reactions of CA with the pyrrole compounds of Figure 1 were performed to prepare CA-PyC adducts. The CA/PyC molar ratio (considering the moles of C6 rings as the moles of the graphitic substrate) was 10:1 and thermal energy was used to favor the formation of the adduct. Details of the reactions are in the experimental part and the process is schematically shown in the block diagram in Figure 2.

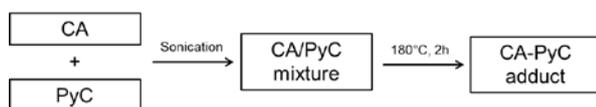


Figure 2. Block diagram for the preparation of CA-PyC adducts with the help of thermal energy

In brief, CA and the selected pyrrole compound were mixed and the CA/PyC mixture was then heated in a flask for 2 h at 180 °C. Very high yield and, thus, high atom economy was obtained. The bulk structure

of the carbon substrate (graphene layers) remained substantially unaltered.^[13]

The formation of covalent bonds between the carbon substrate and the pyrrole compound was demonstrated.^[1] Experimental findings (FT-IR, Raman, XPS) and DFT calculations seem to suggest that domino reactions occur: the pyrrole compound undergoes oxidation in presence of air, thanks to the catalytic activity of the carbon substrate. Such oxidized products are mainly oligomers and 1,5-dimethyl-2-pyrrolylcarbaldehyde (DMP-CHO). DMP-CHO could act as dienophile in cycloaddition reaction with dienes of the graphene layers. Structure of DMP-CHO and hypothesized reaction mechanism are in Figure 3.

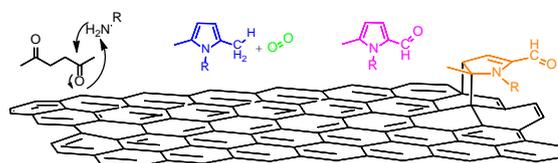


Figure 3. Domino reaction for the functionalization of sp² carbon allotropes

Functionalization with different pyrrole compounds leads to the modification of the solubility parameter of the CA. The variation range is quite broad.

Dispersions were prepared with HSAG-PyC, CB-PyC and CNT-PyC adducts prepared as reported in the experimental part. In Table 1 CA-PyC in solvents having different solubility parameter are reported: water, isopropanol, ethyl acetate, toluene and n-hexane. The stability of the dispersions was studied, as described in the experimental part.

Table 1: Results of inspection of dispersions of CA-PyC adducts in various solvents^{a, b}

Adduct	Solvents				
	Water	isopropanol	Ethyl acetate	Toluene	Hexane
CNT-SP (2a)	GOOD	GOOD	GOOD	GOOD	BAD
CB-SP (2a)	GOOD	GOOD	GOOD	BAD	BAD
HSAG-SP (2a)	GOOD	GOOD	GOOD	BAD	BAD
CNT-DdcP (2c)	BAD	GOOD	GOOD	GOOD	GOOD
CB-DdcP (2c)	BAD	BAD	GOOD	GOOD	GOOD
HSAG-DdcP (2c)	BAD	GOOD	GOOD	BAD	BAD
CNT-APTESP (2d)	BAD	GOOD	GOOD	GOOD	BAD
CB-APTESP (2d)	GOOD	BAD	GOOD	GOOD	BAD
HSAG-APTESP(2d)	BAD	BAD	BAD	GOOD	GOOD

^aconcentration: 1 mg/mL; ^bgood: homogenous dispersion

was observed soon after sonication and after one week storage at rest; bad: separation of adduct from the solvent

In brief, dispersions were first sonicated, stored for one week at rest and then centrifuged. Visual inspection of the dispersions was carried out immediately after sonication and after one week of storage at rest. In Table 1 results of the inspections on dispersions of CA-PyC adducts in the different solvents are qualitatively summarized with ‘good’ or ‘bad’ as indicators (‘good’ means that a homogenous dispersion was observed and ‘bad’ that the adduct either settled down or floated on the solvent).

The CB-SP (2a) adduct was considered for the estimation of its Hansen solubility parameter. The qualitative “good” or “bad” classification of Table 1 was used to identify the unknown Hansen Solubility Parameters of CB-SP, applying a fitting sphere algorithm. The sphere shown in Figure 4 was generated, as explained in the experimental part, to encompass the good solvent points and to exclude the bad solvent, being centered on the solubility parameters of the CB-SP adduct. Solubility parameters of the adduct δ_D , δ_P and δ_H values were estimated to be 11.8, 11.1, 11.5, respectively, while the solubility radius was found to be 10.1.

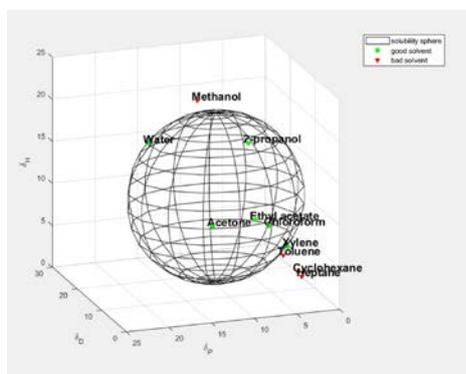


Figure 4. Hansen solubility sphere calculated for CB-SP. The calculated HSP are δ_D 11.8 MPa^{0.5}, δ_P 11.1 MPa^{0.5} and δ_H 11.5 MPa^{0.5}. The green circles correspond to the good solvents (within the radius of interaction), the red triangles to the bad solvents (outside the sphere).

Rubber compounds, based on carbon black and silica as the filler systems, were prepared and sulphur-based crosslinking behavior and dynamic-mechanical

properties were investigated.

Table 2: Formulations of elastomer nanocomposites based on IR, BR as the rubber and CB and silica as the fillers. CB-SP as the functionalized CA^{a,b}

Ingredient	Composite	
	(1)	(2)
IR	50.0	50.0
BR	50.0	50.0
CB N326	25.0	20.0
CB-SP	0.0	5.5
Silica	25.0	25.0
TESPT	2.0	2.0

^aOther ingredients: ZnO 4.0, Stearic acid 2.0, 6PPD 2.0, S 1.5, TBBS 1.8;; ^b amount of SP on CB 1 : 10 mass

Composites were based on IR and BR as the rubbers and CB and silica as the fillers. A furnace carbon black (CB N326) was functionalized with serinol pyrrole (10% by mass of functionalization). Objective of the research was the reduction of the silica networking, thanks to the affinity between silica and the functionalized CB. Recipes are in Table 2, all the amounts are expressed in phr.

Both the nanocomposites contained the same amount of CB; SP was an extra ingredient in composite (2). Also in this case, crosslinking was performed with a sulphur – based system. It was found that functionalization had no effect on the vulcanization behaviors, as it is shown by the curves in Figure 5.

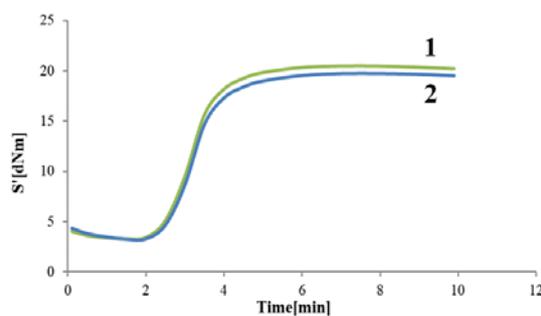


Figure 5. Rheometric curves taken at 170°C for composites of Table 2. Content of CB-SP: 1) 0 phr; 2) 5.5 phr.

Silica networking was investigated by performing strain sweep experiments at 50°C, on crosslinked samples. The dependence of shear storage modulus G' on strain amplitude and the dependence of loss module G'' on G' are in Figure 6.

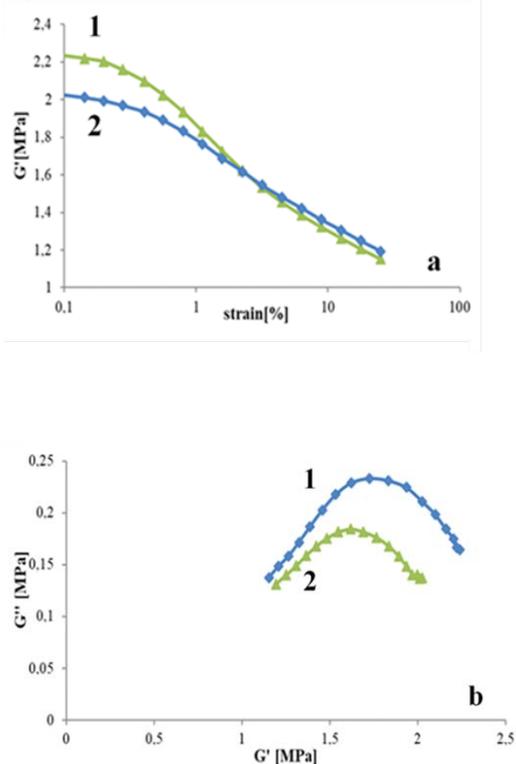


Figure 6. Storage modulus G' versus strain amplitude (a); loss modulus G'' versus storage modulus G' , for crosslinked composites of Table 2. Content of CB-SP: 1) 0 phr; 2) 5.5 phr

From the graphs of Figure 6a it is clear that the addition of CB-SP led to the reduction of the non-linearity of the G' modulus, i.e. of the Payne Effect.^[14] More interestingly, crossover of the curves can be seen. This is usually taken as indication that a chemical bond was established between the filler and the polymer chains. Most likely, CB is able to establish a stable interaction with silica and such a “hybrid filler system” reacts with the polymer, through the sulphur-based silane. Indeed, as it appears from the Cole-Cole plot in Figure 6b, for a given level of dynamic stiffness, the use of CB-SP allows to have lower loss modulus.

In conclusion, functionalization of CB with SP leaves the vulcanization behaviour substantially unaltered but leads to larger moduli at large strain and to lower dissipation of energy.

3 Conclusions

This work demonstrates that a sustainable, efficient functionalization of carbon allotropes is indeed possible, such as carbon black, graphene related materials and carbon nanotubes, with pyrrole derivatives obtained through the reaction of primary amines and a diketone. This functionalization reaction, which does not produce wastes, is able to modify the solubility parameter of the carbon allotrope in a wide range of values, thus allowing their compatibilization with different matrices. Functionalized carbon black was used in rubber – based compounds consisting in diene rubber and CB and silica as the fillers, promoting a reduction of Payne effect.

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