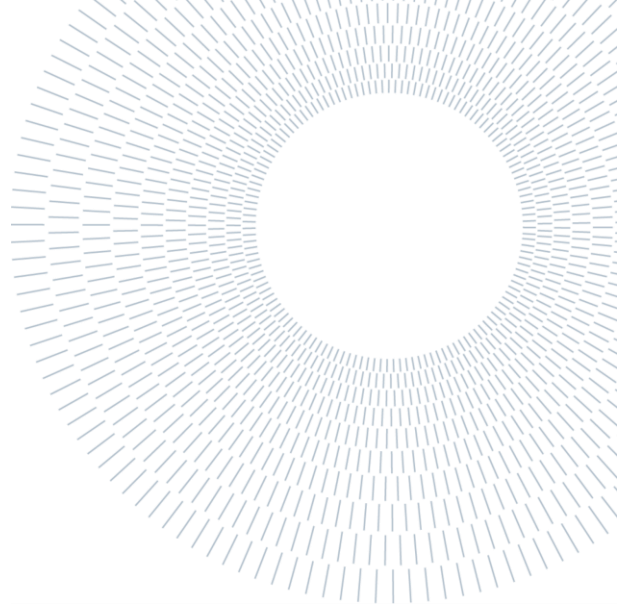




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EXECUTIVE SUMMARY OF THE THESIS

Adduct of carbon black with serinol pyrrole.

From flocculation studies to its use as reinforcing filler in elastomer nanocomposites.

TESI MAGISTRALE IN CHEMICAL ENGINEERING – INGEGNERIA CHIMICA

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1. Introduction

This thesis demonstrates that the functionalization of CB with SP has a clear effect on the properties of a rubber composite and, more in general, of a composite based on a lipophilic matrix.

Furnace CB was functionalized with serinol pyrrole (SP) and elastomeric composites were prepared with CB and CB-SP as such and with their mixtures. Composites were as well prepared in paraffin oil. Flocculation studies were performed, by applying literature protocols and a novel protocol developed during the thesis.

The functionalization reduced the surface area of CB. The reduction of surface area appeared to have the prevailing effect up to a certain level of SP: reduction of Payne Effect. The effect of the OH groups becomes evident above a certain level of SP. The mentioned level of SP likely depends on the type of CB and of the matrix.

The effect of SP on the composite's properties was observed to be dependent on the chemical composition of the surrounding: the reduction of

the Payne effect was promoted by so called small ingredients of the composite, in particular the polar ingredients. Lower Payne effect was in particular obtained in the vulcanized composite.

This thesis reveals the potentiality of the functionalization of CB with OH groups, which are grafted on the CB surface. These results were obtained on the basis of supramolecular interactions. The next step clearly appears to be the use of a suitable coupling agent, to covalently link CB and the polymer chains.

2. Objectives

The objectives of this thesis were:

- 1) to functionalize CB with the OH functional group, through a sustainable process, meaning sustainable essentially from the environmental point of view, performing the functionalization reaction in line with the basic principles of green chemistry
- 2) to study the effect of the OH functional groups on the self assembling of the CB aggregates, performing flocculation studies in masterbatches

obtained through non productive mixing, i.e. in the absence of vulcanizers

3) to perform flocculation studies in oil, to investigate the possibility of using a simple method for studying the self assembling ability of CB, without preparing the rubber composite

4) to use the functionalized CB as filler in rubber compounds, exploiting the ability of the OH groups to react with other ingredients of the compound

3. What has been done

The functionalization of CB was performed by using a methodology developed by the group where this thesis was done: the pyrrole methodology. This methodology consists in the reaction, promoted by either thermal or mechanical energy, of an sp² carbon allotrope with a pyrrole compound. It allows to obtain the formation of a covalent bond between the carbon substrate and the pyrrole ring in a two steps mechanism. The reaction can be performed by simply mixing carbon black and the pyrrole compound, giving then either thermal or mechanical energy, without using solvent or catalyst.

In this thesis, serinol pyrrole (SP), which allows the introduction of OH functional groups. The preparation of CB-SP adduct was done according to the principles of green chemistry. Dangerous and noxious reagents were not used. The reaction was made between beads of industrial CB and serinol pyrrole.

In order to investigate the influence of SP on the filler – filler interaction, pristine CB and CB-SP were added to the rubber matrix, with poly(1,4-cis-isoprene) as the rubber. The total amount of filler was fixed at 50 phr and CB and CB-SP were used in different relative ratios.

Flocculation studies were performed. The flocculation of CB and CB-SP was investigated by using the procedure proposed by Tunncliffe[1]. The composite was kept at high temperature, to cancel the thermo-mechanical history. A strain sweep experiment was then performed by applying a strain from 0.1 % to 10 %, to check the extent of the filler network. Finally, the sample was kept at high and constant temperature, at constant frequency and at a fixed strain value in order to investigate the re-formation of the filler network

The preparation of rubber composites with a total CB content and different relative amounts of CB and CB-SP were prepared. The preparation was carried out via melt blending in a Brabender® type internal mixer, in two steps. The first one was the so called unproductive mixing. In the second step, vulcanization agents were added. Flocculation study was performed on the uncured composites. Composites were then crosslinked with a sulphur based system. Dynamic-mechanical characterization, in the shear and in the axial mode, was performed. Dispersions of CB and CB-SP in paraffin oil were prepared, by using a speed-mixer. The total filler content was kept constant: 50 phr (per hundred oil). The pristine CB was replaced with CB-SP, at different relative ratios. The procedure proposed by Robertson[2] was first used and optimization of the procedure was studied, by grinding CB and CB-SP before preparing the mixtures.

The flocculation of CB in these compounds was then evaluated with the same method used for the composites in IR matrix.

4. Synthesis and results

4.1. Synthesized CB-SP adducts

Serinol-pyrrole was weighed in a vial and diluted in acetone. CB N326 beads was weighed in a single-neck round bottom flask. The SP/acetone solution and other acetone were added till all the CB was covered by the liquid phase. The flask with solution was sonicate for 15 min. To remove acetone from CB/pyrrole compound the Rotavapor was used (40 °C for the bath, from 550 mbar to 50 mbar going down 50 by 50 mbar). The remaining compound without acetone was transferred in a 2-neck 250 ml round bottom flask that was equipped with a magnetic stirrer. In one neck some cotton was applied to retain possible pour losses. In the other was closed with the tube for the compressed air. The flask was inserted in an oil bath preheated at 160 °C. The stirring velocity was set at 235 rpm. The temperature of the bath went down a little. When the temperature came back to the set point the compressed air was started. The reaction took 2 hours in a temperature range between 160 °C and 180 °C. The product of the reaction was put in a 1000 ml becher and about 300 ml of acetone was added. Stirring slowly to extract all the unreacted pyrrole. After about 30 min the compound was

filtered on a tailed flask connected to a vacuum pump set at 450 mbar. Three washing with acetone were performed. To remove completely the acetone the product was inserted in an oven at 80 °C for an hour.

The value of phc (per hundred carbon black) of the adducts was evaluated through two different analyses. First, it was calculated by a method based on the evaluation of the mass of the unreacted SP extracted by washing of the synthesized adduct. Then, the same data was estimated by the thermogravimetric analysis (TGA). The results are reported in the following Table 1.

	Adduct	phc (mass balance)	phc (TGA)
1°	CB-SP	8,6	6,9
2°	CB-SP	7,7	5,2

Table 1: phc calculated for CB-SP adducts.

It is possible to underline that the pyrrole methodology[3], allows to prepare functionalized adducts of CB-SP with more than 5 phc of pyrrole on the filler. Anyway, the not so high level of functionalized yield obtained indicates a possible diffusion-limited reaction kinetics.

4.2. IR-based composites filled with CB and CB-SP preparation without curing agents

IR-based compounds with carbon black as filler, were prepared without the vulcanization agents to study the flocculation of un-crosslinked composites. The amount of filler was maintained constant at 50 phr CB was replaced with various amounts of CB-SP. For each composite, the content of serinol pyrrole and the values of surface area in the filler system are reported. These parameters were calculated as the weighted average of the values of the pristine CB and the pure CB-SP. The amount of SP of these lasts was evaluated by TGA, while the surface area values were obtained through BET analysis.

To prepare the composites, the procedure, described in Figure 1, was applied.

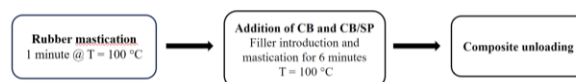


Figure 1: Mixing procedure for un-crosslinked IR composites.

4.3. Preparation of IR-based composites filled with CB and CB-SP with curing agents

Starting from the composites analyzed in section 4.3, that are also called “Masterbatch”, the anti-ozonant, the activators and the curing agents were added in the same Brabender® type internal mixer. The chamber was heated at 50 °C and then the Masterbatch was inserted and mixed for 1 min to prepare the compound for the addition of the ingredients. They were added in two steps keeping the temperature fixed at 50 °C. First, ZnO, Stearic acid and 6-PPD were inserted, then TBBS and sulphur were added. After both the additions, 2 minutes mixing was carried out. The whole mixing procedure is reported in Figure 2.

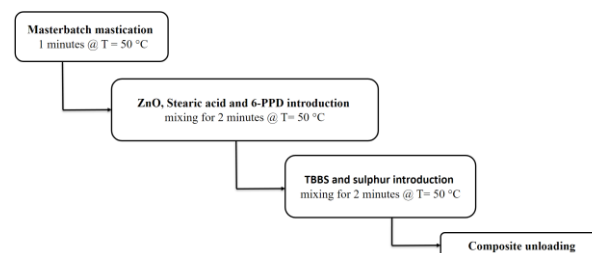


Figure 2: Mixing procedure for crosslinked IR

4.4. Flocculation study

Viscoelastic properties of the sample were characterized in oscillatory shear using a Dynamic Rubber Process Analyzer. The procedure applied was the one proposed by Tunncliffe[1] that is divided in three phases.

In the first phase the composite was kept at 150 °C for 10 minutes, in order to eliminate any possible influence of the thermal history of each sample.

In the second phase, a strain sweep test was performed: a strain from 0.1 % to 10 % was applied at 150 °C with a constant value of frequency, fixed at 1 Hz. The shear dynamic mechanical modulus as a function of the strain was measured. The extent of the filler network and its breakdown are studied.

In the last phase, each sample was kept at constant temperature (150 °C), frequency (1 Hz) and strain

(0.1 %), to inspect the re-formation of the filler network. The values of G' were collected over 20 minutes. Three specimens were analyzed for each sample. The arithmetic average and the standard deviation were calculated for the G' values determined in Phase 2 and in Phase 3.

In Figure 3 a comparison is shown among the graphs from Phase 2 for the Masterbatches (Fig. 3a) and for the composites un-crosslinked (Fig. 3b) and crosslinked (Fig. 3c).

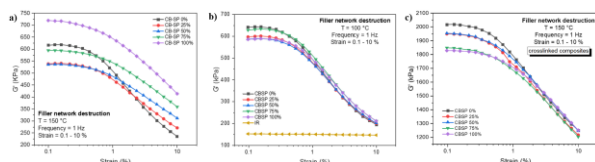


Figure 3: G' vs strain % of Masterbatches, G' vs strain % of un-crosslinked composites with vulcanization agents (b), G' versus strain % of cured composites (c)

It is evident that the dependence of G' vs strain is different for the three classes of composites. The composites with 100% CB-SP give the maximum value of G' γ min in the masterbatch without other ingredients and the minimum value of G' γ min in the composites with other ingredients, particularly after vulcanization.

Also the graphic of the curves obtained from Phase 3 is different for the masterbatch and for the composites, as it is shown in Figure 4.

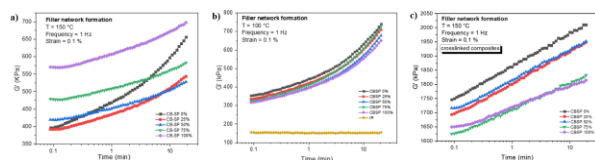


Figure 4: G' vs time of Masterbatches (a), G' vs time of un-crosslinked composites with vulcanization agents (b), G' versus time of cured composites (c)

This is a clear indication that the presence of other ingredients and, in particular, the vulcanization help the dispersion of CB-SP. Moreover, it could be hypothesized that the basic nitrogen can lead to more efficient interactions of CB with the polymer chains, reacting with the sulphur chains and favoring the formation of chemical bonds between sulphur and the surface of CB, as hypothesized by the Group[4] where this thesis was done.

4.5. Axial compression tests

The dynamic-mechanical properties of the cured composites were evaluated by axial compression tests. The values of E' , E'' and Tan Delta were calculated at three different values of frequency (1, 10 and 100 Hz) and at three different values of temperature (10 °C, 23 °C and 70 °C). In the following Figure 5, the trends of E' , E'' and Tan Delta ($\tan \delta$) versus the temperature are reported at 100 Hz.

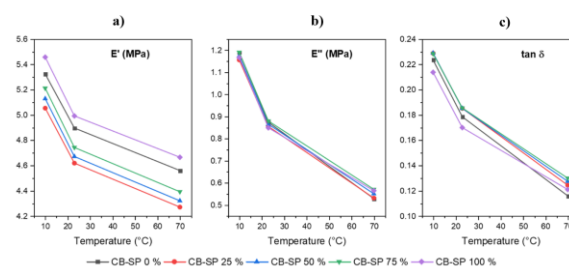


Figure 5: E' versus T (a), E'' versus T (b) and Tan Delta versus T (c) calculated at 100 Hz

By exploring the Figure 5, for each composite all the parameters decrease monotonically with the increasing of the temperature. The decrease of E' is obviously not due to the entropic elasticity but to the presence of the filler network.

Considering the values of the elastic modulus (Figure 5a), the composite with 100% CB-SP adduct shows the highest values of E' at each temperature. On the other hand, the composites prepared with the blended fillers have lower elastic modulus than the compound made with pristine CB. In this case, the lower is the amount of SP, the lower is the value of E' . However, the differences can be considered not remarkable. As already commented, the reduction of E' with CB-SP could be attributed to the reduction of surface area, whereas the increase with CB-SP 100% could be attributed to the prevailing effect of the OH functional groups.

In the Figure 5c, it appears that the composites with CB-SP 100% shows lower Tan Delta with respect to the composite prepared with the pristine CB at low temperatures and similar/higher at the highest temperature. The composites with mixtures of fillers (CB-SP 25 %, CB-SP 50 % and CB-SP 75 %) have always higher values of Tan Delta than the composite with pristine CB. These results are in line with the values of E' . Also for the values of Tan delta, the differences are not remarkable.

4.6. Oil based composites

Dispersions based on oil and containing either CB or CB-SP had a total filler content of 50 pho (per hundred oil). This level was kept constant. CB was replaced with an increasing amount of CB-SP, obtaining five binary mixtures with a content of the functionalized filler from 0 % (the pristine carbon black) to 100 % (only CB-SP). As anticipated in the previous paragraph 2, the procedure to prepare the oil-filler composites required the introduction of a pre-mixing step to improve the dispersibility of the filler in the oil matrix.

The new dispersion procedure (named Procedure 2) was developed at Polimi. First, in order to reduce the size of the CB/CB-SP agglomerates, the dry mixture was grinded into powder using a Moulinex® blender. This additional step required 20 seconds for the pristine CB while the grinding of CB-SP took 2 minutes. Then, the blended fillers of each dispersion, were obtained by simply placing together the relative quantities of CB and CB-SP adducts in the speed mixer cups. After this, the paraffin oil was added to each cup and the mixtures were rotary mixed in the Hauschild Speedmixer DAC-150. The mixing steps in this case were two: 1 minute at 800 rpm, then 15 minutes at 3100 rpm.

4.7. Characterization

Viscoelastic properties of the sample were characterized in oscillatory shear using a Dynamic Rubber Process Analyzer. An important change of the procedure was made. The three phases of the procedure proposed by Tunncliffe[1] were performed at 50 °C instead of 150 °C. In the first phase (named Phase 1) the composite was kept at 50 °C for 2 minutes, in order to eliminate any possible influence of the thermal history of each sample. In the second phase, a strain sweep test was performed: a strain from 0.1 % to 10 % was applied at 50 °C with a constant value of frequency, fixed at 1 Hz. The shear dynamic mechanical modulus as a function of the strain was measured. The extent of the filler network and its breakdown are studied. In the last phase, each sample was kept at constant temperature (50 °C), frequency (1 Hz) and strain (0.1 %), to inspect the re-formation of the filler network. The values of G' were collected over 5 minutes. Five specimens were analyzed for each sample. The arithmetic average and the standard

deviation were calculated for the G' values determined in Phase 2 and in Phase 3. The mean values of G' vs strain determined in Phase 2 and the ones of G' vs time determined in Phase 3 are in Figure 6. In particular, in Figure 6a, the modulus G' at minimum strain ($G' \gamma \min$) was obtained at the end of the Phase 1, so after 2 min at 50 °C while the values at high strain ($G' \gamma \max$) were registered at the end of the strain sweep, so at the end of Phase 2.

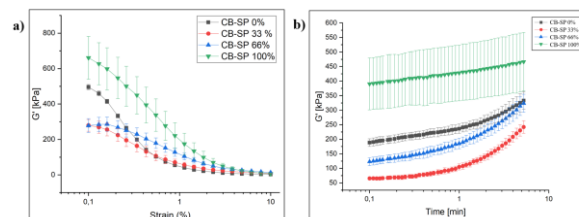


Figure 6: Oil dispersions flocculation study. G' vs strain of Phase 2 (a), G' vs time of Phase 3 (b)

By exploring the results of Phase 2 of the flocculation study it can be commented as follow. There is no monotonic behaviour of the value of G' vs strain with respect to the content of SP. In fact, the composites with 33% and 66% of CB-SP show a significant reduction in $G' \gamma \min$ compared to the compound with only CB. On the other side, the composite with 100% CB-SP shows a higher $G' \gamma \min$ value than that of the composite with CB. Also in this case, a possible interpretation is the following: for composites with small amount of functionalized filler, the reduction of the surface area plays the main role, while, for the composites with high content of the filler it seems that the interactions among the OH groups prevail. It is indeed worth commenting that this behaviour and trend are the same observed for the rubber composites analyzed, as if, with the modified procedure, the oil could remain in the composite and could act as the matrix of the composite, analogously to the rubber.

5. Conclusions

CB and CB-SP were used, as such or in mixture, as filler in the isoprene rubber matrix, in the absence of other ingredients.

Flocculation studies were performed, by applying a protocol available in the literature, proposed by Tunncliffe[1], monitoring the G' modulus in three phases: after storage at high temperature, performing a strain sweep test and keeping the

samples at high temperature. The results were taken as indication of the formation, disruption and re-formation of the filler network.

The filler networking was observed to increase by using CB-SP in place of CB and to decrease by using mixtures of this filler. The interpretation is that the reduction of surface area prevails over the interaction between the OH groups, unless CB-SP is being used as the only filler.

Masterbatches were prepared in paraffin oil, by applying a protocol available in the literature, proposed by Robertson[2].

Flocculation studies were performed by applying a protocol available in the literature, proposed by Tunncliffe[1], analogously to what reported above.

Results similar to those obtained in isoprene rubber were obtained by applying a modified protocol: CB and CB/SP were grinded and a moderate temperature was used for the tests, to avoid the migration of oil.

A monotonous increase of the G' values with the SP amount in the filler system was observed when the same protocol used in the rubber mixture was used. This could be due to the migration of oil, which leads to a direct contact among the filler particles.

In brief, the flocculation in oil highlights that the functionalization of CB with SP strongly influences the rheological behaviour of the composites. Moreover, the results of the rheological measurements depend heavily on the experimental protocol adopted.

Composites based on isoprene rubber (IR) were prepared with CB and CB-SP, either as such or in mixture, in the presence of the other composite's ingredients.

Flocculation studies were performed on the uncured and cured composites. The Figure 3, summarizes the effect of the composite's ingredients (from (a) to (b)) and then of the vulcanization (from (b) to (c)). The Payne effect decreases from (a) to (b) to (c) and, in (c), the composite with CB-SP clearly becomes the composite with the lowest Payne Effect. It is worth underlining that

The composite with 100% CB-SP adduct showed the highest values of E' at each temperature. Hence, in spite of the lower surface area, the composite with CB-SP revealed the higher dynamic rigidity.

In conclusion, the functionalization of CB with SP has a clear effect on the properties of a rubber composite and, more in general, of a composite based on a lipophilic matrix.

6. References

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