

# Mechanical and rheological properties of partial replacement of carbon black by treated ultrafine calcium carbonate in natural rubber compounds

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## Research Article

**Keywords:** calcium carbonate, vulcanization, natural rubber, carbon black, composites, hybrid fillers

**Posted Date:** February 23rd, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-226742/v1>

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# Abstract

The present research aimed to develop natural rubber (NR) hybrid composites reinforced with treated ultrafine calcium carbonate/carbon black (CC/CB). The influence of CC/CB with various filler ratios (50/0, 40/10, 30/20, 20/30, 10/40 and 0/50) on mechanical properties and cure characteristics of the vulcanizates was investigated and their reinforcing efficiency was compared aiming to achieve the best ratio for CB partial substitution as compared to composites with CC and CB incorporated separately. The CC<sub>30</sub>/CB<sub>20</sub> composites reached around to 17 MPa similar strength at break response compared to CC<sub>0</sub>/CB<sub>50</sub> (16.83 MPa). Elongation at break increased 48% in relation to CC<sub>0</sub>/CB<sub>50</sub>. Hardness maintain similar values compare to high concentration of CB composites. Crosslink density results revealed similar chain number in rubber matrix representing better interaction between CC/CB. Scanning electron microscopy studies also reveal a good filler dispersion between filler particles and matrix. The results shown that the new material can be an alternative filler for partial substitution of CB conserving mechanical properties.

## Introduction

In order to reduce produce costs and environmental impacts renewable/natural materials sources has been widely used as replacements for industrial products. Mostly rubber products as shoes, soles, sandals, etc. Employed commercial reinforcement fillers to improve mechanical properties as silica [1–3], carbon black [4–6] or even to reduce the rubber mass, loading with calcium carbonate [7, 8], kaolin [9, 10], asphalt [11], grits waste [12], sludge ash [13] and bio composites [14, 15].

The size and shape homogeneity are usually considered, improving surface adhesion in the polymer matrix [7] and, enhancing the reinforcement effect. However, some fillers e.g. carbon black, has been classified as Group 2B by International Agency for Research on Cancer (IARC) as human carcinogenic agent [16, 17]. Fillers as graphene [18], fly ash [19], metakaolin [20] and silica [21] has been used as total or partially carbon black replacement. Some others organic or natural fillers as whittings (chalk) [22], clays [23], sugarcane bagasse [24, 25] and, leather waste [26–28] has been widely tested without reached the carbon black response.

Hybrid composites which mixes one or more kind of fillers/matrix to improve the original material, even organic/inorganic, is growing attention aiming to merge the both properties of fillers such as graphene/silica [29], grain/ground tire [30], Kenaf/CC [31], carbon nanotube/silver nanoparticles [32], hazelnut/walnut [33], etc. Thereby commercial calcium carbonate is a common filler of rubber industry, improving the reinforcement characteristics by particles sized reduced (nanoparticulate) or by using coupling agents as silane [34, 35], Chartwell [36] and many others cited by RAUT et al [37], became an alternative to partial replacing of carbon black in a hybrid composite.

Here, we introduce a new approach from the use of commercial treated ultrafine calcium carbonate (CC) with Chartwell coupling agent as filler substitutive to maintain or even enhance mechanical reinforcement

compare to carbon black (CB) using partial substitution of CC/CB hybrid fillers in natural rubber (NR) composites reducing the production cost and environmental impacts.

## Materials And Methods

### *2.1 Experimentals*

The CC used was received and treated from Aodran do Brasil Ltda with coupling agent *Chartwell* which formula is protected by patent. Obtained commercially, CB used was the N 762 type, commonly used in industry. Crepe Brazilian Clear (CBC) rubber type was commercially obtained. All compounds had the same base composition except the ones that were add CC and CB filler. The CC/CB ratios were 50/0, 40/10, 30/20, 20/30, 10/40 and 0/50 (phr/phr). Other ingredients in NR formulation contain (in phr): natural rubber (CBC rubber type) 100 phr; stearic acid 2 phr; zinc oxide 5 phr; sulfur 1 phr; antioxidant 1 phr; lubricant 5 phr; tetramethyl tiuram monosulfide (TMTM) 0.46 phr; benzothiazole disulphide (MBTS) 0.17 phr.

### *2.2 Composites preparation*

The CC/CB composites were produced by mixing NR and CC/CB in varying proportions ranging from 0-50 parts of CC/CB per hundred rubber (phr). The samples were processed on industrial mixing roller. As a comparative sample, NR prepared by the same vulcanization process was used. The mixing was carried out in two stages in an open chamber mixer (Makintec, model 379) for 20 min with a friction ratio of 1.0:1.25.

In the first stage, stearic acid and zinc oxide and fillers were incorporated into NR until complete homogenization. Also lubricant oil is incorporated to improve CC and CB dispersion, followed by addition of antioxidant (Vulcanox NS). In a second stage, the mixture was left to stand for 24 h to allow formation of zinc stearate and facilitate the action of accelerators and sulfur. Then, sulfur, Dibenzothiazole disulfide (MBTS) and Tetramethylthiuram monosulfide (TMTM) are added and mixed to improve crosslink formation.

### *2.3 Materials characterization*

To analyze vulcanization behavior, rheometry experiments were performed using a rheometer from Team Equipment Ltda, Brazil, with a disc oscillation of 1° and isotherm of 150 °C. According to ASTM D 2084 curing parameters were determined from obtained results [38]. According to ASTM D 5963, abrasion tests were carried out in triplicate using a rotating cylinder from MAQTEST Automação e Controle Industrial Ltda., Brazil [39]. According to ASTM D 2240, the samples were submitted to 84 rotations in friction with the cylinder (corresponding 40 m of wear contact), under a force of  $5 \pm 0.2$  N ( $1.125 \pm 0.02$  lbf). According to ASTM D 2240, hardness tests were performed on a Kiltler durometer graduated in the Shore A scale [40]. According to ASTM D 412 method A, using type C samples, the tensile tests were performed in

triplicate on an EMIC model DL 2000, at 500 mm/min of stretch and load cell of 0.5 kN, using an internal deformation transducer.

SEM microscopy images were obtained with gold deposition over the samples carried out by a turbo-pumped sputter coater (Quorum, model Q150TE), using a ZEISS, Model EVO LS15.

The study of the interaction of calcium carbonate / carbon black with rubber was determined using the Lorentz-Park methodology with the parameters obtained in the solvent swelling test according to equation (1) [41, 42]:

**See formula 1 in the supplementary files.**

Where the subscriptions “f” and “g” refer to vulcanized with filler and gum. Q is the weight of the toluene absorbed per gram of rubber and determined by equation (2):

**See formula 2 in the supplementary files.**

Using solvent-swelling technique, the cross-link density of the composites was determined. The samples, with a mass of approximately  $0.25 \pm 0.05$  g, were weighed and immersed in toluene for five days. After this period, the samples were removed, surface-dried on absorbent paper, and weighed. They were then placed in an oven at a temperature of 60 °C for 24 h, and weighed again. The cross-link density is calculated according to equation (3) developed by Flory-Rehner [43].

**See formula 3 in the supplementary files.**

Where  $V_b$  is the volume fraction of the polymer in the swollen gel at equilibrium, X is the polymer-solvent interaction parameter,  $p_b$  is the density of the polymer, and  $V_0$  is the molar volume of the solvent.

## Results And Discussion

### *3.1 Composites evaluation*

Rheometry results are given in Table 1 and Table 2. Previous pure filler composites of CC and CB (Table 1) revealed that the presence of CC and CB increased the minimum ( $M_L$ ) and maximum ( $M_H$ ) torque in relation to NR (Table 2) and also, reduction of cure time ( $t_{90}$ ), were CB  $t_{90}$  reduction is due to its capacity to activates the vulcanizing process through the promotion of hydrogen sulfide formation and the rupture of sulfur linkage when heated in rubber either in the presence or absence of other compounding ingredients [44] and CC indicates higher interaction to form sulfur linkage. The insertion of CC/CB as hybrid filler (Table 2) causes an increase in the  $M_L$  and  $M_H$  torque and also significant change in optimum cure time ( $t_{90}$ ), showing better interaction between both fillers in higher phr concentration. The increase in  $M_L$  is due to an increase in viscosity, which is attributed to CB incorporation in the rubber matrix.

Furthermore, the increase in  $M_H$  is attributed to surface area of filler particles that promote higher interaction between filler/matrix with increases stiffness of the material [45].

The composites with CC and/or CB decrease in  $t_{90}$  and scorch time ( $t_{S2}$ ). This is attributed to enhanced adhesion between fiber/matrix, the increasing of viscosity as consequence of CC/CB incorporation, which corroborates the higher  $M_L$ . Curing time was improved due to a high number of reactive sites at matrix in the presence of fillers, which allowed more reactions between accelerators and rubber [46].

At Figure 1, hybrid filler composites showed an increase in the values of the cross-link density compared to NR, this is related to fillers acting as crosslinks with difficulty the interaction between solvent/rubber, reducing its degradation [47], this also indicate a tangle of crosslink formed by molecules and/or filler particles. In an attempt to improvise the performance of industrial production, carbon black has been partially replaced by many alternative types of filler, where there is shorter  $t_{90}$  and consequently less time to produce crosslink. The results shown satisfactory interaction with CB by not reducing the number of crosslink density to obtain better mechanical response; this is also show satisfactory interaction between CC/CB and rubber matrix.

The results of the abrasion tests are shown in Table 3 and Table 4. The incorporation of CC/CB decreased the abrasion loss; that is, it increased the composite abrasion resistance. Abrasion resistance was enhanced by all hybrid filler composites. Compounds with elevated concentration of CC shown higher abrasion loss, this is due to the filler promote formation of aggregates resulting in higher number of tension points in rubber structure as reported by Santos et al. [48].

The CC<sub>0</sub>/CB<sub>50</sub> composite shows the best result with a reduction of 237% in abrasion loss due to its reinforcing characteristics [49]. All CC/CB composites exhibited significant reduction in abrasion loss compared to NR composite, and this is associated with better filler dispersion and interaction with the polymer matrix in the former.

The hardness of the composites increases with the filler insertion (Figure 2). Since the CC/CB particles are more rigid than the matrix, the greater amount of filler in the composites restricts the movement of the polymer chain, leaving the composite more resistant to penetrating forces, that is, the composite becomes more elastic. It is possible to observe in Figure 2 that the CC/CB composite maintains mechanical properties compared to the composites NR/CB. The composites with higher concentration of CC present values of hardness lower than those with higher concentration of CB, this occurs due to the reinforcing characteristics of filler [50].

We can observe that the presence of CC/CB generated reinforcement in the composite. The increase of the resistance is related to the addition of filler in the polymeric matrix that restricts the movement of the grooves characteristic of the chains [51]. As NR shows only the crosslinks produced by sulfur, the addition of pure calcium carbonate (CC<sub>50</sub>/CB<sub>0</sub>) generated reinforcement of 23% in relation to the sample

without addition of filler. For the samples with CC<sub>40</sub>/CB<sub>10</sub> (17,02 MPa), CC<sub>30</sub>/CB<sub>20</sub> (17,56 MPa) and CC<sub>20</sub>/CB<sub>30</sub> (17,48 MPa), was presented higher values than composites with 20, 30, 40 phr of NR/CB pure and, better results of tensile strength in relation to the others CC/CB composites. This fact may be related to the coupling agent that covalently bound the structure of the calcium carbonate to the polymer chain, increasing the ability of the matrix to withstand higher tensile stresses due to a greater amount of crosslinking. Furthermore, the insertion of filler into the composites reduces the deformation capacity, that is, it increases the stiffness of the material. This relationship also occurs when we relate the decrease of the concentration of CC and the increase of the concentration of CB. This tendency is associated with the higher stiffness caused by CB and a greater restriction of the polymer chains.

The values of  $Q_f/Q_g$  are calculated according to equation 1 and shown in Figure 4. The linear relationship with positive slope is shown with the curve  $Q_f/Q_g$  by  $e^{-z}$ . Parameters "**a**" and "**b**" are constant with numerical values of **1.3247** and **-0.3169**, respectively, with the correlation coefficient (R) equal to **0.91**. The difference between these constants reveals the excellent matrix load interaction and synergism between loads [52]. According to Lorentz and Park [52], constant values greater than **0.7** indicate "**a**" strong interaction of calcium carbonate with rubber, making it difficult for solvent to penetrate the composite.

As all composites are made of the same elastomer, with the same crosslinking system, it can be said that a decrease in the ratio  $Q_f/Q_g$ , as is observed in Figure 5, due to the increase of calcium carbonate, indicates an important improvement in the interfacial load-rubber interaction, reflecting in the mechanical properties of the composites. Higher values of  $Q_f/Q_g$  indicate lower load / rubber interactions [53, 54]. These results are in agreement with the tensile strength.

In Figure 6 is shown the FT-IR spectrum of vulcanized natural rubber, filler composites, CC/CB powders and coupling agent *Chartwell* it is observed that there are variations of new peaks, characterizing the physical and chemical interaction between the fillers and polymeric matrix.

Analyzing the FT-IR spectrum for high frequencies it is noted the first bands regions, in  $2960\text{ cm}^{-1}$  is attributed to CH<sub>3</sub> asymmetric stretching modes, and the bands  $2915\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$  related to the stretching asymmetric and symmetric vibrations of methyl groups [55]. The band in  $1514\text{ cm}^{-1}$  is related to the stretching of C=C bonds. The band in  $1440\text{ cm}^{-1}$  is attributed to the CH<sub>3</sub> deformation mode. Absorption peaks of calcite-type calcium carbonate crystals are attributed to the asymmetric  $1415\text{ cm}^{-1}$  of C-O in carbonate roots, with is also attribute to the CH<sub>3</sub> deformation vibrations [56]. Bands between  $950$  and  $1380\text{ cm}^{-1}$  are characteristics of functional groups in rubber, being in the region between  $950$  e  $1150\text{ cm}^{-1}$  is related the CH<sub>3</sub> rocking vibration of the unsaturated hydrocarbons, while the region among  $1150$ - $1385\text{ cm}^{-1}$  is linked to the twisting and wagging CH<sub>2</sub>. At  $873\text{ cm}^{-1}$  absorption peaks of calcite-type calcium carbonate crystals are attributed to the surface deformation and vibration of carbonate roots [57]. The band in  $835\text{ cm}^{-1}$  is attributed to CH out-of-plane bending [58–60]. In the region of  $713\text{ cm}^{-1}$

absorption peaks of calcium carbonate crystals are attributed to the O-C-O deformation vibration in the plane [61, 62].

Figure 7 shows SEM images from CC/CB composites. It is observed that both fillers were well dispersed into the polymeric matrix. It is possible to identify particles at microscopy up to 50 phr samples. Some aggregates are noticed evaluating the CC/CB samples. In Figure 7a and 7b it is possible to observe particulate material where the CC presents a higher concentration of agglomerates in relation to CB. It is also possible to note in Fig.7d that the addition of the fillers provided a more plastic break in the cryofracture which indicates better mechanical property by the restriction in the movement of the chains

## Conclusions

It can be concluded that it is possible to insert the CC with coupling agent in the natural rubber for the production of composites with mechanical properties suitable for industrial application. The analysis of rheometry, tensile strength, elongation at break, abrasion loss, hardness, showed that the CC generated reinforcement for the composite with respect to BN, increasing the mechanical properties, and that samples CC<sub>30</sub>/CB<sub>20</sub> (17.56 MPa) and CC<sub>20</sub>/CB<sub>30</sub> (17,48 MPa) represented an improvement in tear strength up to 4% in relation to CC<sub>0</sub>/CB<sub>50</sub> and elongation at break results shown similar deformation to the average.

FTIR analyzes revealed that the interaction between CC/coupling agent and rubber was of a chemical nature where Chartwell covalently attached calcium carbonate to the structure of the rubber chain to form crosslinks. Furthermore, crosslink density analysis by swelling showed that in relation to the crosslinking system, calcium carbonate is crosslinked to the composite structure due to the presence of *Chartwell* which revealed an increase in crosslinking density generating reinforcement in the rubber.

The dispersion of the crosslinking agents and also of the fillers is the main factor for the preparation of the composites. The satisfactory dispersion and interaction of the accelerators with the filler and the polymer matrix provided a homogeneous crosslinking, resulting in a larger and more uniform crosslink distribution.

In general, it is possible to replace up to 60% of CB by CC maintaining satisfactory mechanical properties without compromising reinforcement, and this replacement can significantly reduce the costs for producing rubber artifacts in industry.

## Declarations

### Acknowledgements

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001.

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## Tables

(phr)	CC					CB				
	M <sub>L</sub> (dN.m)	M <sub>H</sub> (dN.m)	DM (dN.m)	t <sub>s2</sub> (min.)	t <sub>90</sub> (min.)	M <sub>L</sub> (dN.m)	M <sub>H</sub> (dN.m)	DM (dN.m)	t <sub>s2</sub> (min.)	t <sub>90</sub> (min.)
50	1.03	19.03	18.00	2.38	3.15	3.33	32.23	28.90	2.32	3.45
40	1.02	17.82	16.80	2.42	3.22	2.48	30.25	27.77	2.47	3.47
30	1.02	17.02	16.00	2.71	3.54	1.51	29.51	28.00	2.39	3.51
20	1.01	16.73	15.72	2.38	3.87	1.12	27.12	26.00	2.27	3.56
10	1.01	16.12	15.11	2.55	4.01	1.04	24.16	23.12	2.53	3.58

**Table 1** Previous rheometric parameters of pure composites CC and CB.

Samples	M <sub>L</sub> (dN.m)	M <sub>H</sub> (dN.m)	DM (dN.m)	t <sub>s2</sub> (min.)	t <sub>90</sub> (min.)
NR	1	10.37	9.37	3.95	5.07
CC <sub>50</sub> /CB <sub>0</sub>	1.03	19.03	18	2.38	3.15
CC <sub>40</sub> /CB <sub>10</sub>	1.07	23.3	22.23	2.35	3.18
CC <sub>30</sub> /CB <sub>20</sub>	1.57	24.57	23	2.55	3.32
CC <sub>20</sub> /CB <sub>30</sub>	2.07	27.3	25.23	2.52	3.35
CC <sub>10</sub> /CB <sub>40</sub>	2.67	28.87	26.2	2.38	3.42
CC <sub>0</sub> /CB <sub>50</sub>	3.33	32.23	28.9	2.32	3.45

**Table 2** Rheometric parameters of NR compared to composites of CC/CB.

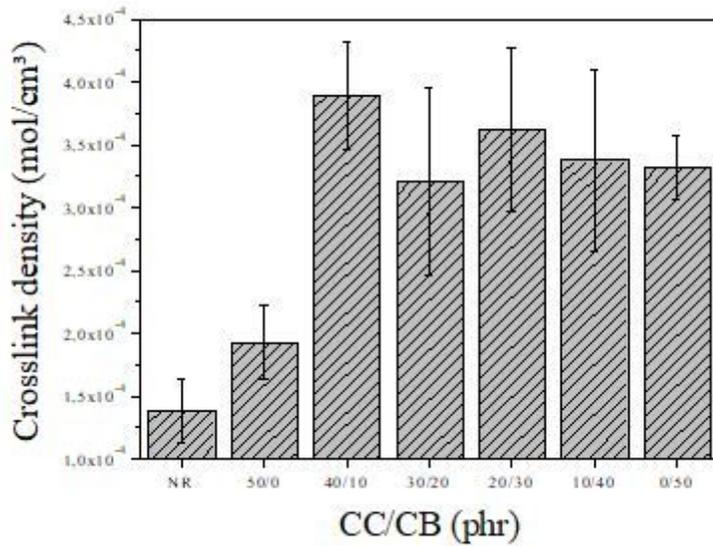
Samples	Hardness (Shore A)	Elongation at Break (%)	Tear Strength (MPa)	Abrasion (mm <sup>3</sup> /40 m)
NR	30 ± 2	843.2 ± 82	11.92 ± 0.2	279.3
CC <sub>50</sub> /CB <sub>0</sub>	40 ± 2	752.3 ± 37	14.63 ± 0.3	196.1
CC <sub>40</sub> /CB <sub>10</sub>	50 ± 2	622.5 ± 35	17.02 ± 0.4	151.7
CC <sub>30</sub> /CB <sub>20</sub>	52 ± 2	637.1 ± 20	17.56 ± 0.3	127.6
CC <sub>20</sub> /CB <sub>30</sub>	60 ± 2	523.8 ± 57	17.48 ± 0.3	117.2
CC <sub>10</sub> /CB <sub>40</sub>	62 ± 2	531.4 ± 27	16.08 ± 0.7	101.3
CC <sub>0</sub> /CB <sub>50</sub>	68 ± 2	421.9 ± 32	16.83 ± 0.6	42.0

**Table 3** Hardness, tear strength, elongation at break and abrasion results of NR and composites with CC/CB.

Samples		CC			CB			
(phr)	Hardness (Shore A)	Tensile Strength (Mpa)	Elongation at break (%)	abrasion (mm <sup>3</sup> /40 m)	Hardness (Shore A)	Tensile Strength (Mpa)	Elongation at break (%)	Abrasion (mm <sup>3</sup> /40 m)
50	40 ± 2	14.63 ± 0.30	752.3	196.1	68 ± 2	16.83 ± 0.56	421.9	42.0
40	42 ± 2	13.65 ± 0.87	773.3	212.3	62 ± 0	16.79 ± 0.29	497.7	57.9
30	42 ± 0	12.49 ± 0.59	786.7	223.7	54 ± 2	16.02 ± 0.41	595.4	72.5
20	40 ± 2	11.71 ± 0.31	802.4	245.8	52 ± 0	15.27 ± 0.52	673.1	101.4
10	38 ± 2	11.89 ± 0.15	810.5	251.2	48 ± 2	15.01 ± 0.17	752.3	115.7

**Table 4** Hardness, tear strength, elongation at break and abrasion results of composites with pure CC or CB.

## Figures



**Figure 1**

The cross-link density of composites with CC/CB in different proportions.

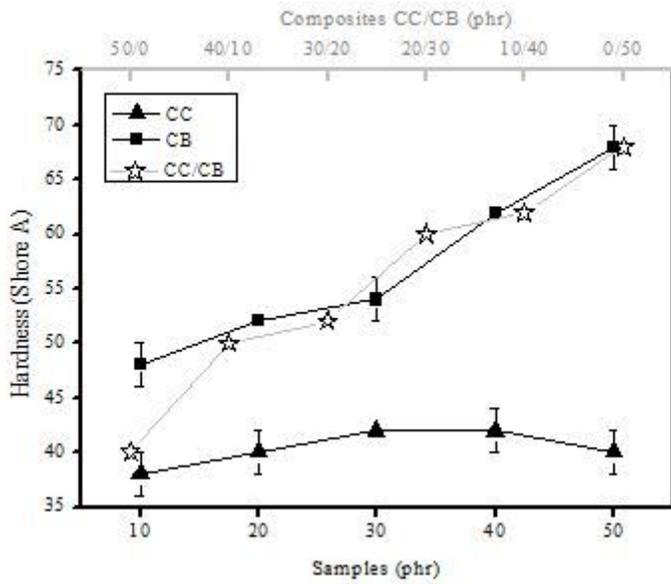


Figure 2

Hardness (Shore A) from produced composites (CC/CB).

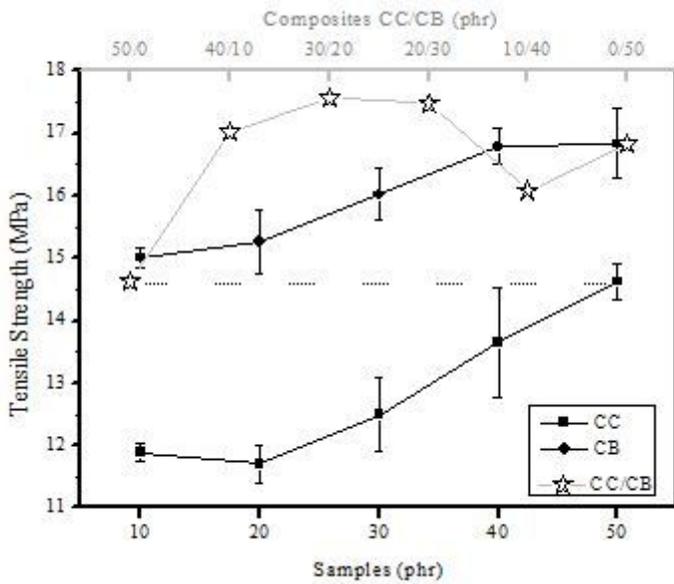
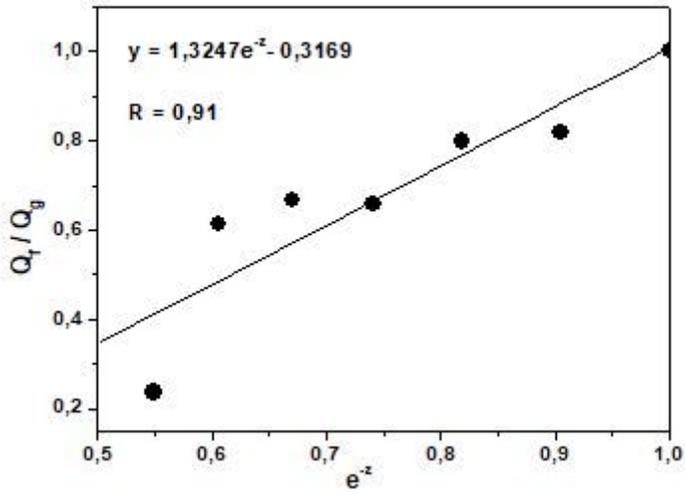


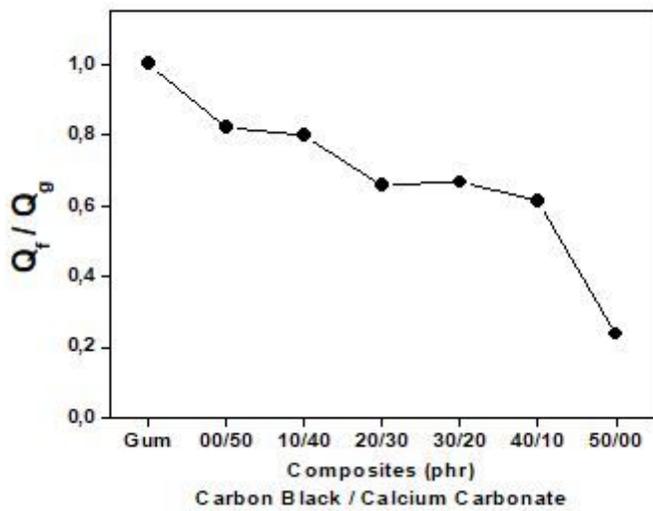
Figure 3

Tensile Strength (MPa) from CC/CB composites.



**Figure 4**

Variation of  $Q_f/Q_g$  with  $e^{-z}$  of composites.



**Figure 5**

Effect of filling load on  $Q_f/Q_g$  of hybrid BN composites with carbon black (NC) and calcium carbonate ( $CaCO_3$ ) treated with 2% Chartwell® and gum as a reference.

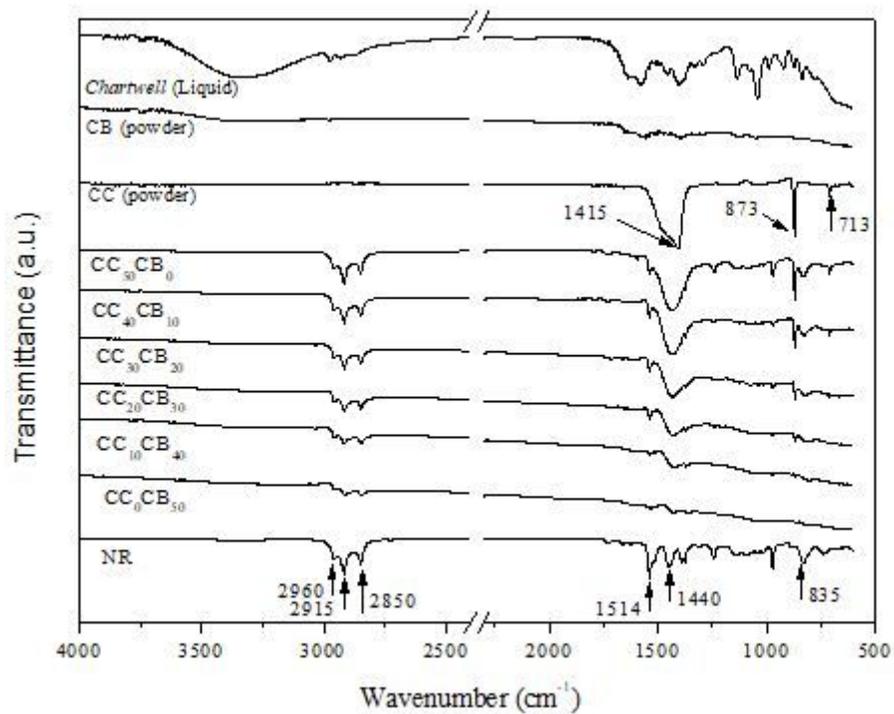


Figure 6

FT-IR of NR, CC/CB composites and Chartwell/CB/CC pure.

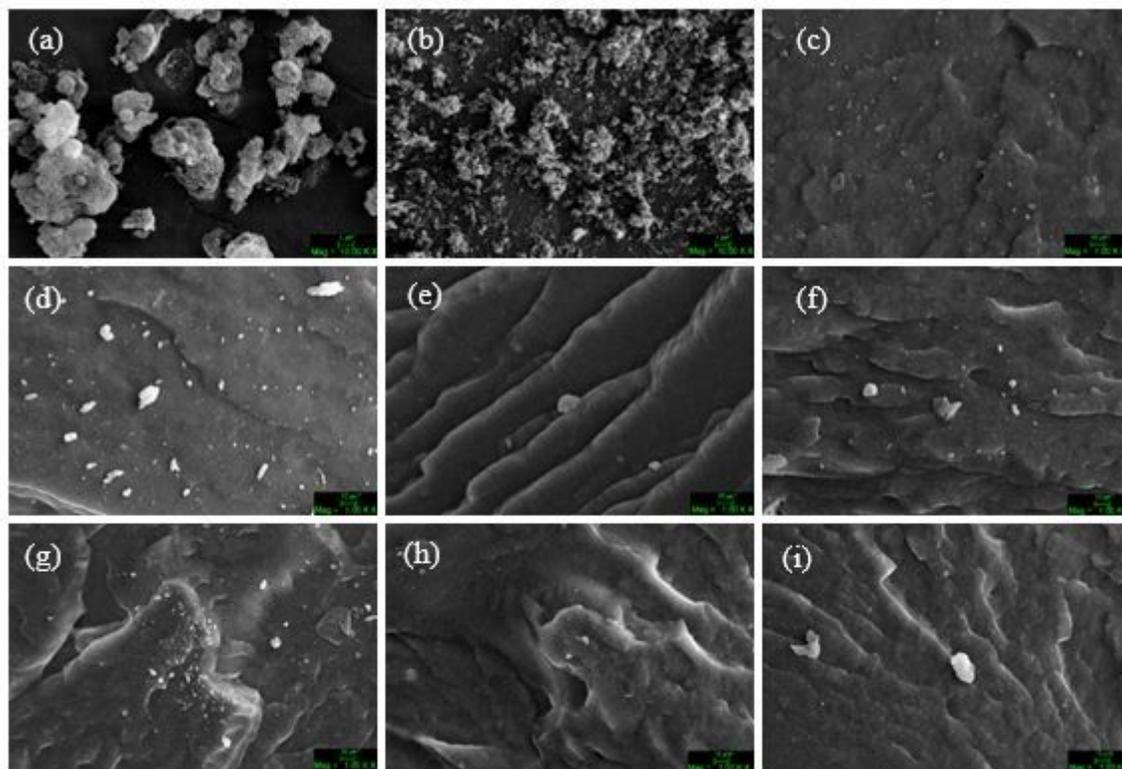


Figure 7

Transversal section of SEM images with EHT = 30 kV, WD= 8,5 mm from composites (NR, CC/CB powder and compounds): (a) CC powder, (b) CB powder, (c) NR, (d) CC50/CB0, (e) CC40/CB10, (f) CC30/CB20, (g) CC20/CB30, (h) CC10/CB40, (i) CC0/CB50.

## Supplementary Files

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