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

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Abstract

The present research aimed to develop natural rubber 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 composites was investigated. Also filler 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 CC30/CB20 composites reached around 17.56 ± 0.3 MPa similar strength at break response compared to CC0/CB50 (16.83 ± 0.6 MPa). Elongation at break increased 48% in relation to CC0/CB50. Hardness maintained similar values compared to high concentration of CB composites. The increase of crosslink density is attributed to a strong interaction between CC and CB and showed a synergism between filler and polymeric matrix in hybrid composites. 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.

Keywords Calcium carbonate · Vulcanization · Natural rubber · Carbon black · Composites · Hybrid fillers
Introduction

Recently, green composites have been gaining most significant attention from researchers worldwide [1–5]. Some of the reasons are its high performance in mechanical properties, aligned with processing advantages, low cost and lightness, in addition to greater availability of renewable resources, enabling ecological composites with greater recyclability and degradability. Generally, the term bio-composite is used when at least one material is derived from natural resources such as natural fiber reinforced petroleum polymers or biopolymers reinforced synthetic fibers (glass and carbon) [6].

In order to reduce produce costs and environmental impacts renewable/natural materials sources have been widely used as replacements for industrial products, mostly rubber products such as shoes, soles, sandals, etc. Commercial reinforcement fillers such as silica [8–10], carbon black [11–13] are used to improved mechanical properties or even used to reduce the rubber mass through loading with calcium carbonate [14, 15], kaolin [16, 17], asphalt [18], grits waste [19], sludge ash [20], bio composites [21, 22], ground tire rubber [23–25], lignocellulosic fibers [26, 27], nanocellulose [28], short sugar palm [29, 30], green olive leaves [31] and rice husk [32, 33].

The size and shape homogeneity are usually considered, improving surface adhesion in the polymer matrix [14] and, enhancing the reinforcement effect. However, some fillers, e.g., carbon black, have been classified as Group 2B by International Agency for Research on Cancer (IARC) as a human carcinogenic agent [34, 35]. Fillers, like graphene [36], fly ash [37], metakaolin [38] and silica [39], have been used as total or partial carbon black replacement. Some other organic or natural fillers, like whitings (chalk) [40] and clays [41] have been widely tested without equaling the carbon black response.

For industrial application, a criteria for selection of materials for reinforced polymer composites are very important and has been evaluated by Faris (2013) [42]. In this investigation, the authors categorized the selection criteria for the types and conditions of natural fibers, as well as the polymer base matrix: chemical, physical, biological, thermal, environmental and mechanical properties. Furthermore, quality and cost must be considered for the fiber selection; the properties mentioned above must also be evaluated for the polymer base (matrix). In addition, the toxicity and cost should be considered; composite characteristics in addition to occupational health and safety characteristics; general composite performance with mechanical strength, resistance to weather and environmental conditions, bio-stability, life cycles and others properties; and specific properties for desired function or application should be considered [42]. Thus, several research works have evaluated the directing of reinforcement materials according to their characteristics, and this selection criteria methodology is a possibility for a comparative effect on different waste materials for application as reinforcement in polymers [43–46] and determination of appropriate polymer matrix [47–50].

Currently, several research works are being carried out to replace conventional fillers with non-conventional, wastes such as sugarcane bagasse [51–53] and,
leather shavings [54–56], or even graphene [57], carbon nanotubes [58, 59] and biofillers [60, 61]. Utrera-Barrios et al. studied self-healing rubbers with epoxidized natural rubber (ENR) and thermally reduced graphene oxide (TRGO), and obtained up to 85% curing efficiency at room temperature without applying external stimuli, where it improved by up to 100% in relation to pure ENR [57]. Le et al. studied the formation and stability of a carbon nanotube (CNT) network in NR, deproteinized NR (DPNR) and polyisoprene (IR), where the cation-π bonding of phospholipids of NR and DPNR with the CNT surface layer was identified, promoting greater filler-rubber interaction [58]. Softwood Kraft Lignin was studied as a functional additive in natural rubber, being produced in two stages: the first by extracting lignin with organic solvents to obtain more appropriate physico-chemical properties and then by chemical modification to increase its affinity with rubber, demonstrating that the adopted method is adequate to increase the potential of lignin reinforcement in elastomeric composites [60]. Barana et al. applied lignin in NR and evaluated its influence on the thermal and mechanical stability of the composites from the incorporation by co-precipitation and dry-mixing, resulting in the increase of both properties, in addition to adding antioxidant properties to the composites [61].

Hybrid composites which mix one or more types of fillers/matrices to improve the original material, even being organic/inorganic, are receiving increased attention aiming to merge the properties of fillers such as graphene/silica [62], grain/ground tire [63], Kenaf/CC [64], carbon nanotube/silver nanoparticles [65], hazelnut/walnut [66], cellulose nanocrystal/silica [67], DDSA-modified porous starch/CB [68], cellululosic cypress/pine [69] and others. Currently, research is also being carried out with the development of self-healing elastomers with the possibility of functional applications such as coatings, sensors, actuators, controlled release of drugs, seals and others applications [70]. As such, commercial calcium carbonate is a common filler used by the rubber industry, improving the reinforcement characteristics by particle size reduction (nanoparticulate) or by using coupling agents like silane [53, 71], Chartwell [72] and many others cited by Raut et al. [73], which have become an alternative to partial replacement of carbon black in a hybrid composite.

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

**Materials**

The CC used was received from Aodran do Brasil Ltda and treated with coupling agent Chartwell whose formula is protected by patent. The CB used was the N 762 type, commercially obtained from Delquimica Commercial Ltda, commonly used in the industry. Crepe Brazilian Clear (CBC) type rubber was commercially obtained...
from DLP Indústria e Comércio de Borracha e Artefatos Ltda, Brazil, with Mooney Viscosity higher than 98, measured at 100 °C. All compounds had the same base composition except those that were added with CC and CB filler. The CC/CB ratios were 50/0, 40/10, 30/20, 20/30, 10/40 and 0/50 parts per hundred rubber (phr). Other ingredients in the NR formulation contain (in phr): natural rubber (CBC rubber type) 100 phr; stearic acid 2 phr; zinc oxide 5 phr; sulfur 1 phr; antioxidant vulkanox 1 phr; lubricant 5 phr; tetramethylthiuram monosulfide (TMTM) 0.46 phr; dibenzothiazole disulfide (MBTS) 0.17 phr.

Stearic acid and sulfur reagents were purchased from Jand Química Indústria e Comércio de Produtos Químicos Eireli, Jandira, SP, Brazil. Zinc oxide was purchased from LABSYNTH Laboratory Products, Diadema, SP, Brazil. Lubricant Oil A – ONU 3082 – III- 9 reagent was purchased from FRAGON Produtos para Indústria de Borracha Ltda, Guarulhos, SP, Brazil. TMTM was purchased from Zhejiang Huangyan Zhedong Rubber Auxiliary Co., Ltd, Huangyan Laobei Road, Zhejiang Province, China. MBTS was purchased from Shandong Shanxian Chemical Co., Ltd, Shanxian, Shandong Province, China. Antioxidant Vulkanox 4020/LG reagent was purchased from LANXESS Deutschland GmbH, Leverkusen, Germany.

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 in a rotating industrial mixer. 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 was incorporated to improve CC and CB dispersion, followed by addition of an 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, MBTS and TMTM were added and mixed to improve crosslink formation.

Materials characterization

To analyze vulcanization behavior, rheometry experiments were performed using a rheometer from Team Equipment Ltda, Brazil, with a disk oscillation of 1° and isotherm of 150 °C. According to ASTM D 2084, curing parameters were determined from the obtained results [74]. According to ASTM D 5963, abrasion tests were carried out in triplicate using a rotating test piece (Method B) configuration from MAQTEST Automação e Controle Industrial Ltda., Brazil [75]. According to ASTM D 5963, the samples were submitted to 84 rotations under friction with the cylinder (corresponding 40 m of wear contact), under a force of 5 ± 0.2 N (1.125 ± 0.02 lbf). According to ASTM D 2240, hardness tests were performed on a Kiltler durometer graduated in the Shore A scale [76]. 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 of composites in the region of cryogenic fractures 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 Eq. (1) [77, 78]:

\[
\frac{Q_f}{Q_g} = a e^{-z} + b
\]

Where: \( \frac{Q_f}{Q_g} \): ratio of the absorbed mass of toluene per gram of rubber; \( z \): ratio of load mass per unit mass of rubber; \( a \): constant angular coefficient of the straight; \( b \): constant linear coefficient of straight.

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

\[
Q = \frac{W_s - W_d}{W_r} \times 100 \times W_f
\]

Where: \( Q \): mass of toluene absorbed per gram of rubber; \( W_s \): mass of the swollen composite, after reaching equilibrium (g); \( W_d \): dry composite mass (g); \( W_r \): mass of rubber in the dry composite (g); \( W_f \): total formulation mass (g).

Using solvent-swelling technique, the crosslink density of the composites was determined. The samples, with a mass of approximately 0.25 ± 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 crosslink density (\( n \)) is calculated according to Eq. (3) developed by Flory-Rehner [79] and determined experimentally, according to ASTM D 297 [80].

\[
n = -\frac{(\ln(1 - V_B) + V_B + \chi(V_B)^2)}{(\rho_B)(V_0)(V_B^{1/3} - \frac{V_B}{2})}
\]

Where \( V_B \) is the volume fraction of the polymer in the swollen gel at equilibrium, \( \chi \) is the polymer-solvent interaction parameter, \( \rho_B \) is the density of the polymer, and \( V_0 \) is the molar volume of the solvent. Polymer-solvent interaction parameter is 0.42, toluene molar volume \( V_0 \) is 106.2 mL/mol and density is 0.87 g/cm³, density of NR is 0.997 g/cm³.
Results and discussion

Composites evaluation

Rheometry results are given in Tables 1 and 2. Previous composites filled with CC and CB separately (Table 1) revealed that the presence of CC and CB increased the minimum \( M_L \) and maximum \( M_H \) torque compared to NR (Table 2) and also decreased the cure time \( t_90 \). The \( t_90 \) reduction by CB incorporation is attributed to its capacity to activate the vulcanizing process through the promotion of hydrogen sulfide formation and the rupture of sulfur linkage when heated [81]. Also, CC incorporation promotes 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 a significant change in optimum cure time \( t_90 \), most evident in higher phr filler concentrations. 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 the surface area of filler particles that promotes higher interaction between filler/matrix with increased stiffness of the material [82].

The separately filled NR/CC and NR/CB composites also show a scorch time \( t_{52} \) reduction. This is attributed to enhanced adhesion between filler/matrix and the increasing of viscosity as a consequence of CC or CB incorporation, which corroborates the higher \( M_L \). Curing time was improved due to a high number of reactive sites in the matrix in the presence of fillers, which allowed more reactions between accelerators and rubber [83].

In Fig. 1, hybrid filler composites showed an increase in the values of the cross-link density compared to NR, which is attributed to the strong interaction between fillers and rubber matrix, acting as barriers to the entrance of solvent, deferring the degradation process [84]. The literature report this behavior as the bound rubber phenomenon (BdR), where chemical bonding occurs, enabling the stabilization of a thin rubber layer around single particles and agglomerates of CB. This binding model restricts molecular chains and this spatial limitation can result in an interface more resistant to solvents, in addition to increased resistance to mechanical deformations, as investigated by several authors [85, 86]. Also, the increase in crosslink density can be attributed to a simple decrease in the free volume of the material.

The results of the abrasion tests are shown in Tables 3 and 4. The incorporation of pure CC and CB decreased the abrasion loss; that is, it increased the composite abrasion resistance. Abrasion resistance has also been enhanced by all hybrid filler composites in comparison with unfilled NR. Compounds with elevated concentration of CC shown higher abrasion loss, this is due to the filler promoting the formation of aggregates resulting in higher number of tension points in the rubber structure as reported by Santos et al. [87].

The CC_{0}/CB_{50} composite shows the best result with a reduction of 237% in abrasion loss due to its reinforcing characteristics in comparison to unfilled NR, already expected as compared to that reported in the literature [88]. All CC/ CB composites exhibited significant reduction in abrasion loss compared to NR.
| (phr) | CC     | CB     |
|-------|--------|--------|
|       | $M_L$ (dN.m) | $M_H$ (dN.m) | $\Delta M$ (dN.m) | $t_{52}$ (min.) | $t_{90}$ (min.) | $M_L$ (dN.m) | $M_H$ (dN.m) | $\Delta M$ (dN.m) | $t_{52}$ (min.) | $t_{90}$ (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 2  Rheometric parameters of NR compared to composites of CC/CB

| Samples         | $M_{L}$ (dN.m) | $M_{H}$ (dN.m) | $\Delta M$ (dN.m) | $t_{s2}$ (min.) | $t_{90}$ (min.) |
|-----------------|----------------|----------------|-------------------|-----------------|-----------------|
| NR              | 1              | 10.37          | 9.37              | 3.95            | 5.07            |
| CC$_{50}$/CB$_{0}$ | 1.03          | 19.03          | 18                | 2.38            | 3.15            |
| CC$_{40}$/CB$_{10}$  | 1.07          | 23.3           | 22.23             | 2.35            | 3.18            |
| CC$_{30}$/CB$_{20}$  | 1.57          | 24.57          | 23                | 2.55            | 3.32            |
| CC$_{20}$/CB$_{30}$  | 2.07          | 27.3           | 25.23             | 2.52            | 3.35            |
| CC$_{10}$/CB$_{40}$  | 2.67          | 28.87          | 26.2              | 2.38            | 3.42            |
| CC$_{0}$/CB$_{50}$   | 3.33          | 32.23          | 28.9              | 2.32            | 3.45            |

Fig. 1  The crosslink density of composites with CC/CB in different proportions

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

| Samples         | Hardness (Shore A) | Elongation at Break (%) | Tensile Strength (MPa) | Abrasion (mm$^3$/40 m) |
|-----------------|-------------------|------------------------|------------------------|------------------------|
| NR              | 30 ± 2            | 843.2 ± 82             | 11.92 ± 0.2            | 279.3 ± 17             |
| CC$_{50}$/CB$_{0}$  | 40 ± 2           | 752.3 ± 37             | 14.63 ± 0.3            | 196.1 ± 8.3            |
| CC$_{40}$/CB$_{10}$  | 50 ± 2           | 622.5 ± 35             | 17.02 ± 0.4            | 151.7 ± 10.9           |
| CC$_{30}$/CB$_{20}$  | 52 ± 2           | 637.1 ± 20             | 17.56 ± 0.3            | 127.6 ± 10.4           |
| CC$_{20}$/CB$_{30}$  | 60 ± 2           | 523.8 ± 57             | 17.48 ± 0.3            | 117.2 ± 6.5            |
| CC$_{10}$/CB$_{40}$  | 62 ± 2           | 531.4 ± 27             | 16.08 ± 0.7            | 101.3 ± 7.3            |
| CC$_{0}$/CB$_{50}$   | 68 ± 2           | 421.9 ± 32             | 16.83 ± 0.6            | 42.0 ± 3.7             |
Table 4  Hardness, tensile strength, elongation at break and abrasion results of composites with pure CC or CB

| Samples (phr) | CC          | CB          |
|---------------|-------------|-------------|
|               | Hardness (Shore A) | Tensile Strength (MPa) | Elongation at break (%) | Abrasion (mm$^3$/40 m) | Hardness (Shore A) | Tensile Strength (MPa) | Elongation at break (%) | Abrasion (mm$^3$/40 m) |
| 50            | 40 ± 2      | 14.63 ± 0.30 | 752.3 ± 46 | 196.1 ± 10.2 | 68 ± 2      | 16.83 ± 0.56 | 421.9 ± 28 | 42.0 ± 3.2 |
| 40            | 42 ± 2      | 13.65 ± 0.87 | 773.3 ± 49 | 212.3 ± 15.5 | 62 ± 0      | 16.79 ± 0.29 | 497.7 ± 33 | 57.9 ± 4.1 |
| 30            | 42 ± 0      | 12.49 ± 0.59 | 786.7 ± 35 | 223.7 ± 14.2 | 54 ± 2      | 16.02 ± 0.41 | 595.4 ± 25 | 72.5 ± 5.6 |
| 20            | 40 ± 2      | 11.71 ± 0.31 | 802.4 ± 57 | 245.8 ± 12.3 | 52 ± 0      | 15.27 ± 0.52 | 673.1 ± 47 | 101.4 ± 5.1 |
| 10            | 38 ± 2      | 11.89 ± 0.15 | 810.5 ± 62 | 251.2 ± 18.7 | 48 ± 2      | 15.01 ± 0.17 | 752.3 ± 51 | 115.7 ± 7.3 |
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. Since the CC/CB particles are more rigid than the matrix, the higher amount of filler in the composites restricts the movement of the polymer chain [89], making the composite more resistant to penetrating forces, that is, the composite becomes more elastic. Table 3 indicates that all NR/CC and hybrid CC/CB composites decreased the hardness properties compared to the composite NR/CB. The composites with higher concentration of CC present hardness values lower than those with higher concentration of CB, this occurs due to the reinforcing characteristics of filler [90].

The mechanical reinforcement characteristics of the fillers are most evidenced in stress–strain tests. 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. 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), presented higher values than composites with 20, 30, 40 phr of NR/CB pure and, better results of tensile strength in relation to the other CC/CB composites. As the polymeric matrix stretches, the strain is transferred to the incorporated inorganic and solid filler, requiring higher forces to reach similar deformations. In the case of calcium carbonate, the reinforcement can be enhanced due to the coupling agent that improves the interaction of the calcium carbonate with the polymeric chain increasing the ability of the matrix to withstand higher tensile stresses. 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 higher restriction of the polymer chains.

The values of \( Q_f/Q_g \) are calculated according to Eq. 1 and shown in Fig. 2. The linear relationship with positive slope is shown with the curve \( Q_f/Q_g \) by \( e^{-z} \). Parameters “a” and “b” are constants with numerical values of 1.3247 and −0.3169.

![Graph](image)

**Fig. 2** Variation of \( Q_f/Q_g \) with \( e^{-z} \) of composites
respectively, and the correlation coefficient ($R$) is 0.91. The difference between these constants reveals the excellent matrix load interaction and synergism between loads [91]. According to Lorentz and Park [91], constant values greater than 0.7 indicate a strong “a” interaction of calcium carbonate with rubber, making it difficult for the 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 $Q_f/Q_g$ ratio, as is observed in Fig. 3, due to the increase of calcium carbonate, indicates an important improvement in the interfacial filler-rubber interaction, reflecting in the mechanical properties of the composites. Higher $Q_f/Q_g$ values indicate lower filler-rubber interactions [92, 93]. These results are in agreement with the tensile strength.

Figure 4 presents the FT-IR spectrum of vulcanized natural rubber, filler composites, CC/CB powders and Chartwell coupling agent.

Analyzing the FT-IR spectrum for high frequencies, the peak at 2960 cm$^{-1}$ is attributed to CH$_3$ asymmetric stretching modes, and the bands at 2915 and 2850 cm$^{-1}$ are related to the asymmetric and symmetric stretching vibrations of methyl groups [94]. Those peaks are associated to the vibrations of the rubber monomer. The peak at 1514 cm$^{-1}$ is related to the stretching of C=C bonds. The band in 1440 cm$^{-1}$ is attributed to the CH$_3$ deformation mode. Considering the relative intensity of the peaks, for NR, the peak at 1514 cm$^{-1}$ is more evident compared to 1440 cm$^{-1}$. However, with the increase in the amount of filler incorporated, the peak at 1440 cm$^{-1}$ overcame that at 1514 cm$^{-1}$. This can be associated to the high absorption peaks of calcite-type calcium carbonate crystals, attributed to the asymmetric 1415 cm$^{-1}$ of C-O in carbonate roots [95]. A characteristic NR peak at 1000 cm$^{-1}$ disappears as the CB content increase. This change is associated with a strong physical–chemical interaction between NR and CB. This type of positive interaction can explain the strong reinforcing character of the CB network in NR [96]. The CB has relatively high surface reactivity, as a result of

![Fig. 3](image) **Fig. 3** 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
which, the loss of this band is associated with the surface area and the structure of the CB [97]. Bands between 950 and 1380 cm\(^{-1}\) are characteristics of functional groups in rubber, while the region among within 1150–1385 cm\(^{-1}\) is linked to the twisting and shaking CH\(_2\). At 873 cm\(^{-1}\) absorption peaks of calcite-type calcium carbonate crystals are attributed to the surface deformation and vibration of carbonate roots [98]. The band at 835 cm\(^{-1}\) is attributed to CH out-of-plane bending [99–101]. In the region of 713 cm\(^{-1}\) absorption peaks of calcium carbonate crystals are attributed to the O-C-O deformation vibration in the plane [102, 103].

Figure 5 shows SEM images from unfilled NR and hybrid CC/CB composites. In Fig. 5a and b, it is possible to observe particulate material where the CC presents a higher concentration of agglomerates in relation to CB. It is possible to identify particles under microscopy of up to 50 phr in samples. Figure 5c shows the presence of small particles in the unfilled NR, which may be associated with components of the vulcanization such as zinc oxide and stearic acid. In Fig. 5d presents the presence of fine particles, but also a higher presence of agglomerated particles of CC. Some aggregates are noticed evaluating the CC/CB samples, but in smaller dimensions and proportions in comparison with the NR/CC50. It is also possible to note in Fig. 5e that the addition of the fillers provided a more plastic break in the cryofracture which indicates a 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 and hardness, showed that the CC generated reinforcement
for the composite with respect to NR, increasing the mechanical properties, and that samples CC$_{30}$/CB$_{20}$ (17.56 MPa) and CC$_{20}$/CB$_{30}$ (17.48 MPa) represented an improvement in tensile strength of up to 4% in relation to CC$_{0}$/CB$_{50}$ and elongation at break results shown deformation similar to the average. The increase of crosslink density prove the strong interaction of fillers, which avoid the entrance of solvents into the polymeric matrix during the swelling tests, mainly related to carbon black, which is not significantly altered by calcium carbonate partial replacement. Finally, 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 use of carcinogenic components and even the cost for producing rubber artifacts in the industry.

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