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Mechanical properties and microstructure of hybrid vulcanized natural rubber filled with carbon black and Nano-$CaCO_3$ from *achatina achatina* shells

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Abstract

Nano-$CaCO_3$ (NCC) obtained from *Achatina achatina* shells were used as single filler and as partial replacement of carbon black (CB) to produce vulcanized natural rubber (NR) filled at 5, 10, 15, 20, 25 and 30 pphr. The SEM micrographs showed that the dispersion of the fillers in the hybrid composites up to 15wt% replacement of CB was very good. Higher strengths were obtained up to 25 pphr for composites that contained 95wt%CB/5wt%NCC and 90wt%CB/10wt%NCC, while the composites that contained 85wt%CB/15wt%NCC showed higher strength up to 20 pphr compared to the CB filled samples. The NR filled with hybrid CB/NCC up to 15wt% replacement of CB offered comparative hardness and abrasion resistance; while 95wt%CB/5wt% NCC filled sample showed lower compression set over CB reinforced samples up to 30 pphr and comparative tensile strength, hardness, elastic modulus and abrasion resistance. As single filler, the synthesized nanoparticles imparted significant improvement in the mechanical properties of vulcanized NR; however, the properties were inferior to the CB reinforced sample due to poor dispersion of the NCC in vulcanized NR. The thermal and oxidative stability of the hybrid composites up to 15wt% replacement of CB were better than those of the CB filled samples.

1. Introduction

Calcium carbonate is a very useful material that serves as semi-reinforcing filler in the rubber industry for many applications such as tyre, conveyor belt and bearings [1-3]. In a research carried out to compare the properties of natural filled with various fillers, it was observed that the hardness of natural rubber vulcanizate reinforced with $CaCO_3$ was 86.67% and 76.47% of those reinforced with carbon black and silica respectively; while the tear strength of the $CaCO_3$ reinforced natural rubber was 74.03% and 37.96% of those of carbon black and silica respectively [2]. Generally, the reinforcing ability of fillers in natural rubber depends on the filler properties such as particles sizes and shapes, chemical nature and porosity of the surface, filler dispersion and agglomeration in the matrix [3]. Since the reinforcing abilities of fillers improve as the particles sizes reduce, efforts are channeled towards the production of nanoparticles of calcium carbonate in order to improve its reinforcing ability in rubber.

The production of nanoparticles of calcium carbonate dates back to over 25 years [4]. Research findings revealed that nanoparticles of calcium carbonate improved the elastic modulus and impact strength of acrylonitrile-butadiene-styrene elastomer higher than the values obtained with micro-size calcium carbonate [5]. In epoxy system, nanoparticles of calcium carbonate have been reported to improve compressive strength and elastic modulus [6]. It has been reported that the use of nano-$CaCO_3$ improved the tensile strength, tear strength, elongation at break, elastic modulus and hardness far beyond the properties obtained with micro-size precipitated $CaCO_3$ as filler in natural rubber/expandable graphite vulcanizate [7].

In hybrid composites, the fillers combine their good properties to enhance the properties of the composites due to the synergistic effects of two fillers resulting to higher filler dispersion and cross-linking densities [8-9]. Hybrid filled rubber components are applied in tyre treads, sidewalls, inner liner, conveyor belts, and bumper strips [9].

Due to the interest in the use of nano-$CaCO_3$ as filler in rubber composites, the possibility sourcing

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nano-CaCO$_3$ for the rubber industry from renewable agro-waste such as the shells of *Achatina achatina* is considered in this work. The research seeks to establish the effectiveness of partial replacement of carbon black with nano-CaCO$_3$ obtained from *Achatina achatina* as filler for the production of vulcanized natural rubber. This work reports the mechanical properties of vulcanized natural rubber filled with hybrid carbon black and nano-CaCO$_3$ from *Achatina achatina* shells.

2. Materials and method

2.1 Production of the vulcanized natural rubber samples

A report of the production and properties of precipitated nano-CaCO$_3$ from *Achatina achatina* shells with 50 nm average particle size has earlier been presented [10]. The produced nano-CaCO$_3$ was used for this work. Natural rubber grade NSR10 in form of ribbed smoke sheet and the other compounding ingredients were supplied by the Rubber Research Institute of Nigeria. The type of carbon black used for this work is high abrasion furnace (HAF) grade N330 by ASTM designation. The formulation used to produce the vulcanized rubber samples is shown in Table 1. The compounding operation was done on a laboratory size two-roll mill maintained at temperature of 50°C with flowing water to avoid premature cross-linking as specified by ASTM-D 3184-89 [11]. The compounded rubber composite samples were conditioned in the laboratory for 24 h before vulcanization. The different compounded rubber samples were vulcanized in laboratory size compression moulding press using different moulds. The hot press was maintained at a temperature of 150°C and pressure of 10 MPa was applied on the closed moulds and held for five minutes before the moulded samples were brought out. The cured rubber composites were conditioned at room temperature for 14 days before testing.

2.2 Characterizations of the vulcanized rubber samples

(a) Mechanical Testing

Dumbbell shaped samples for tensile testing conforming to ASTM D 412-06a [12] were cut from each sample of the vulcanized rubber with a cutting die. The tensile tests were performed at room temperature with a Zwick/Roell Universal Testing Machine, model Z005 at a cross head speed of 500 mm/min until the specimen ruptured in accordance with ASTM D 412-06a. Three tensile specimens of each sample were tested and the average results reported to ensure reliability.

Samples for hardness tests with dimension 20×20×6.4 mm (length x width x thickness) were cut from each of the vulcanized rubber samples that were already conditioned. Shore A hardness test was performed on each cut sample at room temperature using a durometer in accordance with ISO 7619-1 [13]. Five locations on every sample were penetrated and the average computed as the hardness in IRHD in order to ensure reliability

The abrasion resistance of each vulcanized rubber sample was determined with the aid of rotary drum abrader in terms of volume loss according to ISO 4649-2010 (E) [14]. Four abrasion specimens of each sample with thickness 6.5 mm and internal diameter 16 mm were prepared with a drill. The abrasion resistance of each sample was computed from equation (1).

$$\%\text{ARI} = \frac{\Delta m_r \times \rho_t}{\Delta m_t \times \rho_r} \times 100\% \qquad (1)$$

Table 1. Formulation of the vulcanized rubber samples.

S/N	Additive		Quantitity (pphr)
1	Natural rubber		100.0
2	Sulphur		2.0
3	2-Mercapto benzothiazole (MBT)		1.0
4	Stearic acid		1.0
5	Zinc oxide		5.0
6	Tetramethylthiuram disulphide (TMTD)		2.0
7	Processing oil		1.0
8	Fillers	Carbon black (CB) nano-CaCO$_3$ (NCC) 95wt%CB/5wt% NCC 90wt%CB/10wt% NCC 85wt%CB/15wt% NCC 80wt%CB/20wt% NCC 50wt%CB/50wt%NCC	0, 5, 10, 15, 20, 25, 30

where Δm_t is the mass loss of the test specimen (mg), Δm_{cont} is constant mass of 200 mg, Δm_r is the mass loss of reference test piece (mg), ρ_r is the density of the reference compound (g/cm^3), ρ_t is the density of the vulcanized rubber sample (g/cm^3) and ARI is the abrasive resistance index.

The compression set of each vulcanized rubber specimen was determined using a compression set machine in line with ASTM D 395-03 (2008) method [15]. A cylindrical specimen of diameter 29.0$\underline{+}$0.5 mm and thickness 12.5$\underline{+}$0.5 mm was cut with a die from each vulcanized rubber sample. The test specimen was mounted on the machine and a force of 1.8 kN was applied on the specimen through the plate and spring of the machine. The assembled test specimen was left for 26 h at room temperature. Compression set was calculated from equation (2). Where $\%C_a$ is the percentage compression, t_o is the initial thickness and t_1 is the final thickness.

$$\%C_a = \frac{t_0 - t_1}{t_0} \times 100\% \tag{2}$$

(b) Microstructural Characterization

In order to evaluate the dispersion of the fillers, the microstructure of the unfilled sample, and all the vulcanized rubber samples with filler loadings of 30 pphr, as well as and that of the sample filled with only nano-CaCO$_3$ at 15 pphr were studied with Phenom Prox Scanning Electron Microscope at accelerated voltage of 15 kv, 80 µm resolution and x1000 magnification.

(c) Thermogravimetric analysis (TGA)

The thermal and oxidative stability of the composites were studied through thermogravimetric (TG) and derivative thermogravimetric (DTG) analysis on the unfilled sample and the samples filled at 25 pphr using DTG 60 Shimadzu Thermo-gravimetric Analyzer. Small amounts (2.1 - 3.6 mg) of the samples were used for the analysis. The heating was done in air atmosphere at flow rate of 50 ml/min and heating rate of 10°C/min from 32^{o}C up to 600°C using alumina crucible. The TGA and DTG curves were plotted for each sample in order to assess their thermal and oxidative stability.

3 Results and Discussion

3.1 Mechanical Properties of the Vulcanized Rubber Samples Filled with the Nanoparticles

Figures 1-6 represent the tensile strength, percentage elongation, compression set, hardness, elastic modulus at 100% elongation and abrasion resistance respectively of the various samples of the vulcanized rubber with respect to filler loading.

In Figure 1, it can be seen that the nanoparticles of calcium carbonate obtained from *Achatina achatina* shells significantly increased the strengths of the vulcanized natural rubber samples with increase in filler loading up to 30 pphr. Compared to the works earlier reported where micro sized calcium carbonate obtained from snail shells [16] and sea shells [17], the nano-CaCO$_3$ offered higher improvement in strength due to the higher surface area of the nanoparticles which enhanced their interaction with the natural rubber matrix [18]. The values of the strength of the natural rubber composites reinforced with the nanoparticles of calcium carbonate obtained from the shells are in agreement with the values earlier report where commercial nanoparticles of calcium carbonate was used as filler in natural rubber [1]. The vulcanized rubber samples reinforced with carbon black offered superior strength than the samples reinforced with the nano-CaCO$_3$ obtained from *Achatina achatina* shells at all filler loading. This is because carbon black has higher loss on ignition of 92.6% compared to 44.37% for the synthesized nanoparticles [10] due to higher carbon content which offers higher reinforcement in natural rubber. The good interaction of carbon black with natural rubber matrix ensures the entanglement of the rubber molecules on the surface of the carbon black which prevents the movement of the rubber chain and thus improves the mechanical properties of the rubber composite [19]. Also, the hydrophobic nature of calcium carbonate has been reported to reduce its reinforcing ability in natural rubber due to poor interfacial adhesion between rubber and the particles [1].

Comparing the strengths of the samples reinforced with carbon black and those reinforced with hybrid fillers (mixtures of carbon black and the synthesized nanoparticles), higher strengths were obtained up to 25 pphr for composites that contained 95wt%CB/5wt% NCC and 90wt%CB/10wt%NCC, while the composites that contained 85wt%CB/15wt%NCC showed higher strength up to 20 pphr. The maximum strength in the experiment was at 10 pphr with 85wt%CB/15wt% NCC. The value was higher than the strength obtained at 30 pphr in the composite filled with only carbon black. However, as the percentage of carbon black in the hybrid composites reduced, the strength of composites also reduced. This is because, at higher proportion of the synthesized nanoparticles in hybrid composites, the interfacial bonding between the fillers reduced and agglomeration of the nano-CaCO$_3$ became dominant. The results obtained in the hybrid composites are also in agreement with literature [9]. The significant improvement in the strength of the hybrid composites is due to the synergistic effects of the two fillers which imparted higher filler dispersion ensuring effective transfer of stress from matrix to filler as well as higher cross-linking density which enhanced the strength [8] [20]. In hybrid composites, the fillers combine their good properties to enhance the properties of the composites [9]. Hybrid filled rubber components are applied in tyre treads, sidewalls, inner liner, conveyor belts, and bumper strips [9].

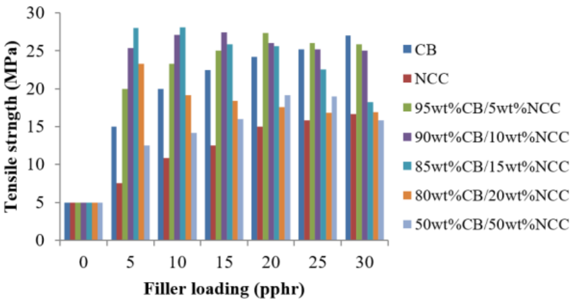


Figure 1. Tensile strength of the vulcanized rubber samples.

The compression set results of the samples are shown in Figure 2. Compression set a measure of permanent plastic deformation on the vulcanized rubber samples under compressive loading. Low compression sets are desired for applications where the materials are subjected to compressive loads such as car engine seats, bearing pads, seals and bushings. From Figure 2, it can be seen that the compression set decreases with increase in filler loading (increase in strength). The hybrid composites 95wt%CB/5wt% NCC, 90wt%CB/10wt%NCC and 85wt%CB/15wt% NCC showed similar low compression set compared to the carbon black reinforced samples up to 25 pphr filler loading. At 30 pphr filler loading, 95wt%CB/ 5wt%NCC composite showed the lowest compression set. Samples filled with only the nanoparticles or higher proportions of the nanoparticles exhibited higher compression set than carbon black reinforced sample as from 10 pphr filler loading because as the volume fraction of the nano-$CaCO_3$ increased, filler agglomeration also increased thereby reducing the bond between the rubber matrix and the filler. The low compression set obtained in the hybrid composites is as a result of enhanced filler interaction with the rubber matrix which improved the bonding between filler and rubber. The low compression set obtained in the hybrid composites makes them suitable for applications in where compression resistance is desired. The compression sets obtained in the composites are also in agreement with earlier report [9]. Similarly, calcium carbonate nanoparticles have been reported to increase the compressive strength of concrete [21].

From Figures 3 and 4, it can also be seen that natural rubber filled with hybrid CB/NCC up to 15% replacement of carbon black with the synthesized nanoparticles also offered comparative hardness and abrasion resistance compared to carbon black filled natural rubber due to the good fillers interaction and dispersion in the hybrid composites.

Figure 5 shows the elongation at break of the vulcanized rubber composites. Generally, the elongation decreased with increase in filler loading because lower filler loading will not cause obstruction in the sliding of the entangled natural rubber chains [1].

Composites with higher loading of the synthesized nanoparticles showed lower elongation than those with less filler loading due to the low modulus associated with the addition small particles in natural rubber matrix. Figure 6 shows that the elastic moduli of the hybrid composites are superior to those of the carbon black reinforced vulcanizate up to 15 wt% substitution of the carbon black and at lower filler loading except 95wt%CB/5wt%NCC composite which had higher elastic modulus than every other sample at all filler loadings.

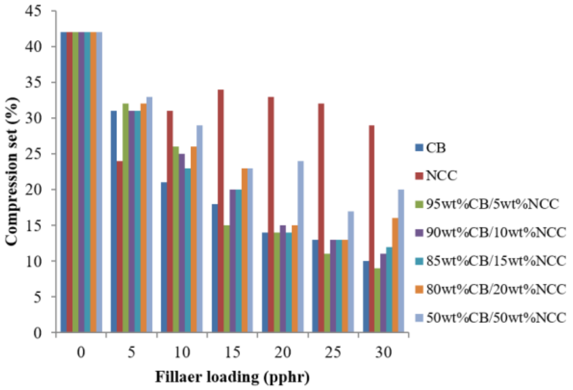


Figure 2. Compression set of the vulcanized rubber samples.

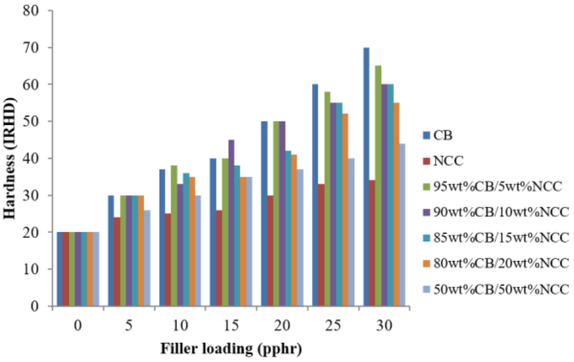


Figure 3. Hardness of the vulcanized rubber samples.

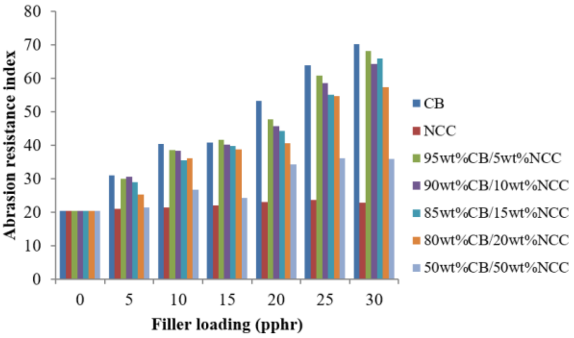


Figure 4. Abrasion resistance indices of the vulcanized rubber samples.

Generally, the reinforcing ability of fillers in elastomers is dependent on the chemical and physical interaction between the fillers and the rubber matrix [22].

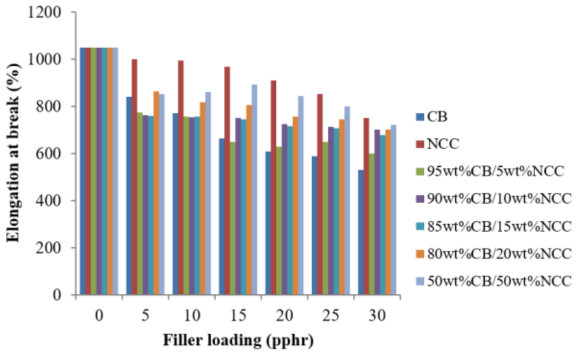


Figure 5. Elongation at break of the vulcanized rubber samples.

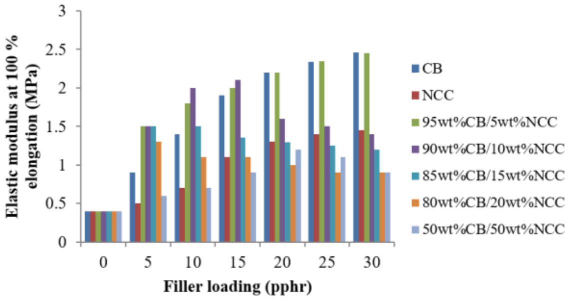
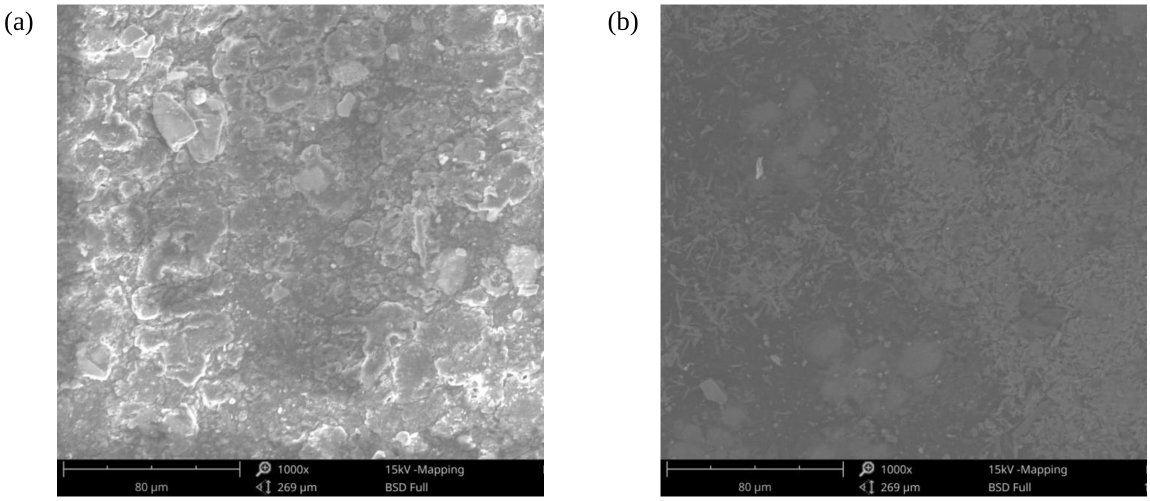


Figure 6. Elastic modulus at 100% elongation of the vulcanized rubber samples.

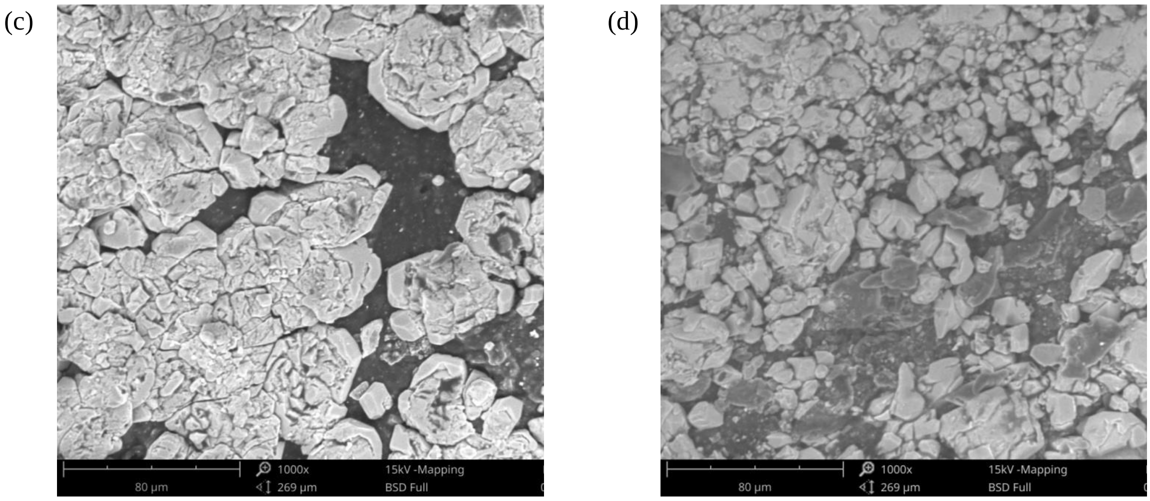
Microstrcture of the Vulcanized Rubber Samples

The SEM micrographs of the unfilled samples are shown in Figure 7. The samples with the micrographs shown in Figure 7 (a-i) are shown in Table 2.

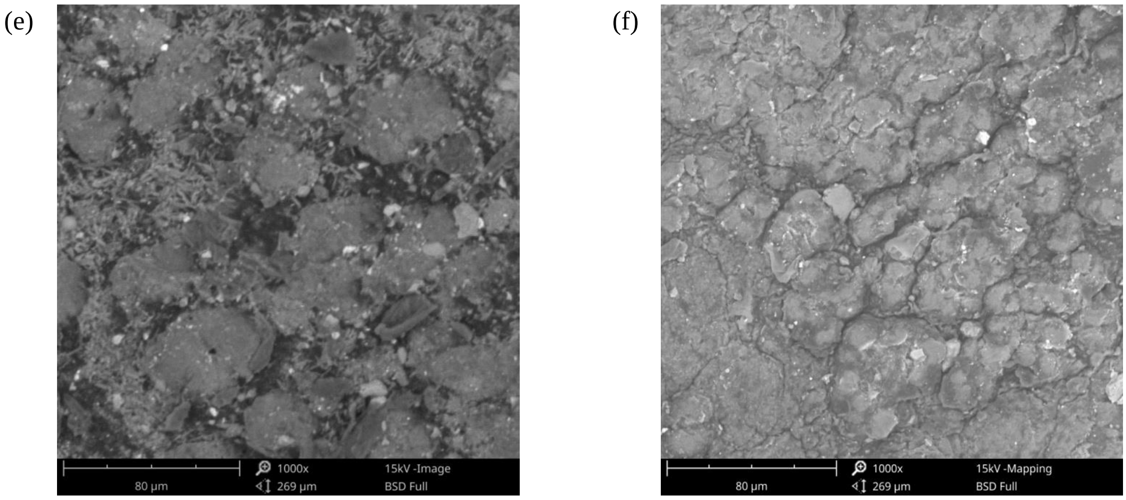


7(a): Unfilled vulcanized rubber matrix

7(b): Vulcanized rubber matrix with well dispersed CB

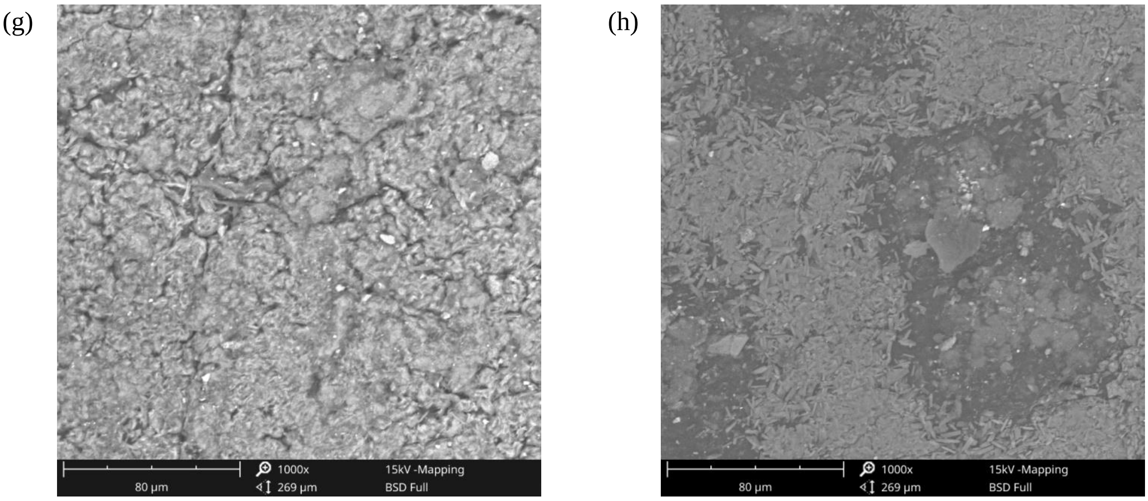


7(c) and 7(d) respectively, the white areas represent agglomerated NCC, while the dark areas represent poor NCC in the rubber matrices.



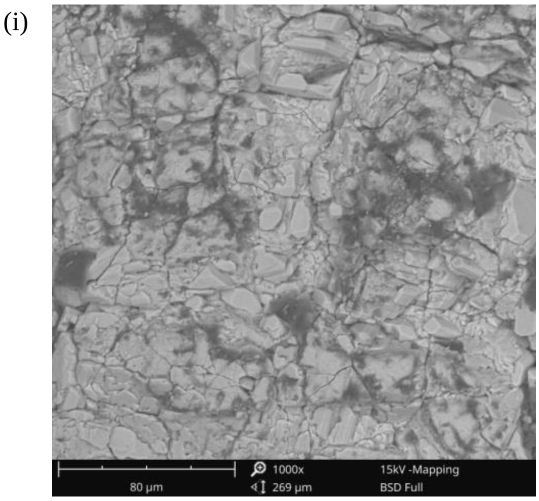
7(e): Entire matrix of hybrid composite with good fillers interaction

7(f): Entire matrix of hybrid composite with good fillers interaction



7(g): Entire matrix of hybrid composite with good fillers interaction

7(h): Areas not so rich in NCC are seen



7(i): NCC tend to interact more with themselves, though there is relatively high dispersion

Figure 7 (a-i). SEM micrographs of the samples.

Table 2. Identification of the Samples with the Micrographs Shown in Figure 7 (A-I).

A	B	C	D	E
Unfilled sample	CB filled at 30 pphr	Nano-CaCO3 filled at 15 pphr	Nano-CaCO3 filled at 30 pphr	95wt%CB/5wt%NCC filled at 30 pphr
F	**G**	**H**	**I**	**-**
90wt%CB/10wt% NCC filled at 30 pphr	85wt%CB/15wt% NCC filled at 30 pphr	80wt%CB/20wt% NCC filled at 30 pphr	50wt%CB/50wt% NCC filled at 30 pphr	-

The micrograph showing the matrix of the unfilled vulcanized natural rubber is shown in Figure 7(a). In Figure 7 (b), it can be seen that the dispersion of carbon black in the vulcanized natural rubber was very good due to the good interaction between rubber and carbon black. As single filler, the synthesized nano-$CaCO_3$ depicted poor interaction with vulcanized natural rubber above 10 pphr filler loading as agglomeration of the filler was observed at 15 pphr and 30 pphr as shown in Figure 7 (c and d). This is due to the hydrophobic nature of calcium carbonate compared to carbon black [23], which resulted in lower strength in the composites filled with on the nano-$CaCO_3$ compared to those filed with carbon black. In the hybrid composites, the dispersion of the fillers in the vulcanized natural rubber matrix was observed to depend on the percentage substitution of carbon black with nano-$CaCO_3$ and the volume fraction of the filler in the matrix. From 5-15 wt% substitution, the fillers dispersion in the matrix was excellent up to 30 pphr as shown in Figure 7 (e, f and g). This is due to the synergistic interaction between carbon black and nano-$CaCO_3$ used in the hybrid composites which resulted to improved mechanical properties of the hybrid composites. For 20 wt% substitution of carbon black with nano-$CaCO_3$, good filler dispersion was also observed; however, as fillers loading got to 30 pphr, the interaction between the fillers and rubber matrix started reducing as depicted in Figure 7 (h).

At 50 wt% substitution of carbon black, though the hybrid nature of filler tends to improve dispersion, the high percentage of nano-$CaCO_3$ promoted agglomeration of nano-$CaCO_3$ and poor interaction with the rubber matrix. The microstructures of the composites correlated with the results reported in the mechanical properties as composites with 5-15% replacement of carbon black which exhibited better filler dispersion also showed better mechanical properties.

3.2 Thermal and Oxidation Resistance of the Vulcanized Rubber Samples

The thermogravimetric (TGA and DTG) curves of the vulcanized rubber samples at 25 pphr are shown in Figures 8 and 9 respectively. From Figures 8 and 9, there was no significant degradation of all the vulcanized rubber samples up to 300°C because natural rubber undergoes both scission and cross-linking when heated within that temperature range [24]. The degradation observed between 300°C and 350°C was due to the volatilization of the plasticizers and other materials used in the rubber compound [25]. The degradation observed in the temperature range of 350°C to 550°C was due to chain scission in natural rubber [26]. From the DTG curve in Figure 9, the major peaks were observed in 390°C to 400°C. The introduction of the nano-$CaCO_3$ imparted significant improvement in thermal resistance in rubber due to the higher thermal resistance of the particles compared to natural rubber. Among the composites, sample 95CB/5NCC showed the greatest improvement in thermal resistance at temperatures above 390°C due to the excellent filler dispersion which resulted to the formation of more cross-links and prevented volatilization of materials. The percentage of weight loss (TGA %) of the samples from 200°C to 550°C respectively are shown in Table 3. It can be seen that samples 90wt%CB/10wt%NCC and 85wt%CB/15wt% NCC offered superior thermal resistance to the carbon black filled samples up the temperature of 550°C. Also, sample 95wt%CB/5wt%NCC offered superior thermal resistance to the carbon black filled sample up the temperature of 200°C and at temperatures from 350°C; its thermal resistance is similar to that of carbon black reinforced sample. For samples with 20 wt% and 50 wt% replacements of carbon black, the thermal and oxidation resistance were inferior to the carbon black reinforced samples. This could be attributed to poor interaction of fillers and agglomeration observed as from that filler loading.

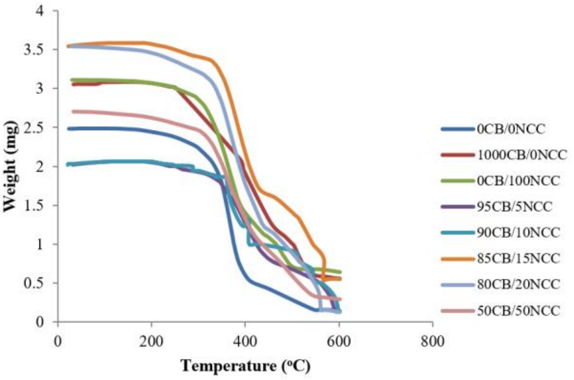


Figure 8. TGA curves of the vulcanized rubber samples.

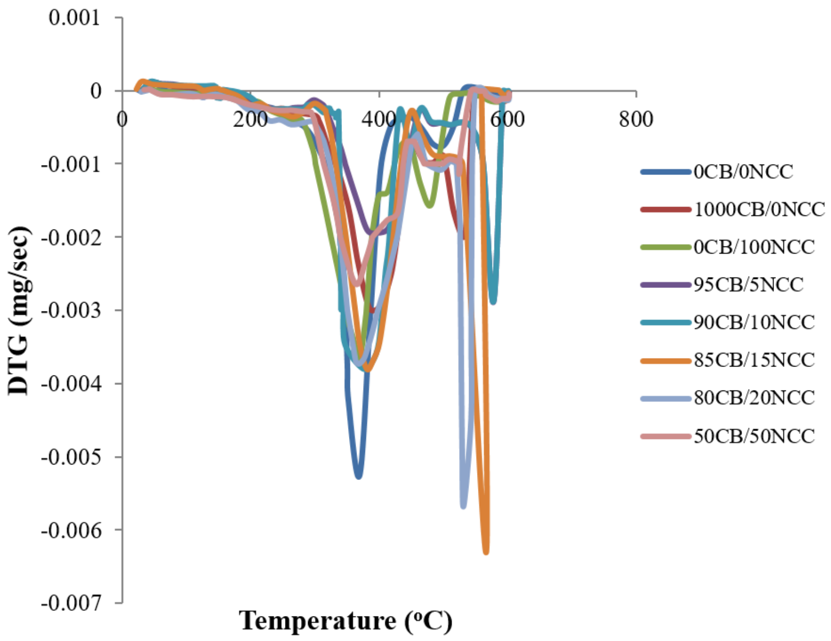


Figure 9. DTG curves of the vulcanized rubber samples.

Table 9. Percentage weigh loss of the samples from 200°C to 550°C.

Temperature (°C)	Percentage weight loss (%)							
	0CB/0NCC	100CB/0NCC	0CB/100NCC	95CB/5NCC	90CB/10NCC	85CB/15NCC	80CB/20NCC	50CB/50NCC
200	-1.5299	0.537723	-1.1626	1.51581	0.92419	0.767078	-2.38309	-2.9663
250	-4.3249	-1.57418	-3.38195	-1.7638	-1.47635	-1.29938	-5.41065	-5.69787
300	-9.9778	-4.53462	-7.81631	-5.0083	-4.00155	-3.8454	-9.21447	-8.8851
350	-28.5412	-13.0172	-26.8279	-12.039	-11.0938	-10.5471	-20.4533	-24.7904
400	-76.4043	-38.0845	-38.939	-37.165	38.5682	-38.939	-50.0532	-50.9363
450	-82.8601	-57.6555	-64.9636	-60.175	-56.1191	-54.0746	-67.1097	-66.7339
500	-90.4408	-66.9979	-77.2117	-66.315	-62.0988	-60.1671	-75.2706	-78.2136
550	-93.7038	-80.6585	-78.0872	-73.434	-72.9865	-72.6846	-95.7362	-88.3822

4. Conclusions

The mechanical properties of the natural rubber vulcanizates filled with the synthesized nanoparticles and carbon black revealed that the tensile strength of the vulcanizates filled with hybrid carbon black and nano-CaCO$_3$ fillers are superior to those filled with only carbon black up to 25 pphr filler loading for 95wt%CB/5wt%NCC and 90wt%CB/10wt%NCC; while 85wt%CB/15wt%NCC showed higher tensile strength up to 20 pphr. The other mechanical properties of the samples filled with 95wt%CB/5wt%NCC were comparable to carbon black reinforced samples up to 30 pphr while offering lower compression set. The improved properties of the hybrid composites are due to the synergistic effect between the two fillers in the matrix resulting to improved filler dispersion, higher cross-linking density and effective transfer of stress from the matrix to the fillers. As a single filler, the synthesized nanoparticles imparted significant improvement in the mechanical properties of vulcanized natural rubber, however, the properties were inferior to carbon black reinforced natural rubber due to poor dispersion of the nano-CaCO$_3$ as a single filler in vulcanized natural rubber. The thermal and oxidative stability of the hybrid composites with 5-15 wt% replacement of carbon black were superior to those of other samples. Further work could be on the surface modification of the nano-CaCO$_3$ obtained from *Achatina acahtina* to enhance its interaction and dispersion in natural rubber.

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