Performance Evaluation of Graphite Oxide in Natural Rubber Compounds

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ABSTRACT

The performance of graphite oxides from waste batteries and carbonized maize cobs as filler in natural rubber was evaluated in this study. Graphite from carbon electrodes in waste batteries and carbonized maize cobs respectively were subjected to the conventional Hummers method for conversion to the more reactive graphite oxides. The oxides were characterized in terms of their surface area, ash content, pH, moisture content, conductivity and loss on ignition using standard methods. The oxides were further characterized in terms of their morphology and functional groups. The graphite oxides and N330 carbon black which acts as the control were then used as filler in natural rubber compounding using the two–roll mill and subjected to physico-mechanical characterization. The graphite oxides showed significant enhancement in the reinforcement and mechanical properties of the natural rubber compounds as evidenced from the results obtained when compared with the control. Morphological study of the vulcanizates shows that natural rubber – maize cob graphite oxide (NR/MCGO) vulcanizates showed very good dispersion in the rubber matrix. Mechanical properties study shows that NR/MCGO vulcanizates are having improved properties with tensile strength of 32.79MPa, modulus at 100% elongation of 19.51MPa. However, NR/MCGO vulcanizates show lower elongation at break of 500.02%. The highest hardness value is NR/MCGO of 71.01 IRHD.

Keywords: Maize cob, natural rubber, fillers, g*raphite oxides*

INTRODUCTION

Recently, graphene-based fillers have garnered global attention in the industry and academia due to their promising outstanding physical properties such as high electron mobility, thermal conductivity, mechanical stiffness, strength and elasticity. Rubbers with fillers have been widely applied in various industrial fields due to their outstanding mechanical properties, thermal stability and oil resistance[1]. The most common and widely used filler for rubber in the industry is carbon black. Studies from literatures have demonstrated situations whereby incorporating small amounts of particulate fillers such as carbon-black in rubber can introduce remarkable changes in the mechanical and physical properties[2]. However, fillers at nano scale particulate level presents far better properties for rubber composites when compared with conventional carbon black fillers. Hence Graphite oxide used in this study at the nano scale level interacts well with rubber when they are mixed together. In order to achieve the enhancement of the properties of natural rubber, fillers need to be well dispersed and homogenized with the rubber[1]. Graphite oxide (GO) bears oxygen-containing functional groups, which enable them to disperse well in rubber which ensures the retainership of the precursor graphene properties. The most important property of natural rubber is its elasticity and flexibility. Vulcanization of NR by adding a certain amount (5-8%) of sulfur forms cross-links between the molecular chains which enhances its toughness. Additives such as carbon black and graphene derivatives can be added into the NR during compounding to improve its properties as well as promote the vulcanization process[3].

The main objective of the study is to assess the performance of graphite oxide from waste batteries and maize cob carbon as filler in natural rubber compounds.

MATERIALS AND METHODS

Waste batteries and maize cobs were obtained locally from Auchi, Edo State, Nigeria. All reagents used were products of Sigma Aldrich, Germany sourced from a commercial sales outlet in Ondo State, Nigeria.

Preparation and Characterization of the Graphite and Graphite Oxide

The maize cobs were washed in water and dried in air to remove sand particles and moisture. The dried maize cobs were weighed and carbonized at 300°C, for two hours[4]. The carbonized shells were then milled to fine powder and sieve through the 65µm sieve mesh. The fine powder that passed through were collected and characterized.

Carbon electrodes from waste batteries were removed and crushed to fine powder. The powder was sieved using a mechanical shaker at 65µm.

The conventional Hummers method was used for the synthesis of graphite oxide (GO) in this experiment[1,5].

The graphites and graphite oxides were characterized in terms of pH, Bulk density, moisture content, conductivity, Iodine adsorption number and loss on ignition.

The pH of the graphites and graphite oxides samples were determined using ASTMD 1512 method, the bulk density were determined by the tamping procedure[6], the moisture content were determined by adopting the method described in STMD 1509, Iodine adsorption number (surface area) were determined using ASTMD 1510(1983), while loss on ignition was determined using the procedure described in ASTMD 7348.

Fourier Transform Infrared Spectroscopy Characterization:

Fourier transform infrared (FTIR) spectroscopy was carried out to quantitatively identify the constituents of the various graphite oxides obtained. The dried samples were ground into fine particles and mixed with KBr. The samples were then compressed into pellets and analyzed with Perkin Elmer IR Spectrophotomer operating in a transmission mode in the range of 500-4000 cm^{-1}.

Scanning Electron Microscopy (SEM):

The morphology of the various graphite oxide samples was investigated by using the scanning electron microscopy.

Compounding

The recipe for compounding of the natural rubber (NSR 5) with the GO for each sample is given in the Table 1. Natural rubber (NR) was masticated on the laboratory open two roll mill for ten minutes. Zinc oxide, stearic acid and other rubber additives were added sequentially into the masticating NR. The compounds were prepared as one part of filler per hundred parts of natural rubber, formulation is provided in Table 1 according to ASTM D3182.

A batch factor of four was used to multiply the weight of the ingredient in parts per hundred of the rubber. Mixing procedure was done according to ASTM D3184-80, 1983

Table 1: Formulation for Compounding Natural Rubber

Ingredients	Phr
Natural Rubber	100
Filler (GOs)	3.0
Stearic acid	4.0
Zinc Oxide	3.0
ZMBT	3.5
Processing oil	2.0
Sulphur	2.5

Determination of the Physico - Mechanical properties of the Composite.

The tensile properties were determined on a Monsanto tensile tester model 1/m at a cross speed of 500mm/min using dumbbell test pieces of dimension (45x 5x 2mm) as contained in ASTMD 412-87 method A ,1983. The hardness of the sample was determined by adopting the standard dead load method. The standard dead load method of measurement covers rubbers in the range of 30 to 85 International Rubber Hardness Degrees (IRHD). The hardness was carried out using the Wallace hardness tester model C8007/25 in accordance with BS 903 Part A26, 1983.

The procedure adopted for the measurement of compression set was based on ASTM 385, 1983. Wallace Compression set machine was used.

Wallace Akron abrasion tester was used to test for the abrasion resistance in accordance to BS method, 1949. The flex fatigue resistance measurement was carried out in accordance to the procedure described in ASTM D430, 1983, using the Du Pont machine, which function by inducing surface cracking of the rubber sample.

RESULTS AND DISCUSSION

Characterization of Graphite and Graphite Oxide

The results of the graphites and graphite oxides obtained from maize cob designated as maize cob graphite (MCG) and maize cob graphite oxide (MCGO) as well as from waste batteries designated as waste batteries graphite (WBG) and waste batteries graphite oxide (WBGO) are presented in Table 2.

Table 2: Characterization of the Graphites and Graphite oxides

Parameters	MCG	WBG	MCGO	WBGO
Yield (%)	-	--	69.8	88.2±0.01
pH of slurry at 28°C	4.79 ± 0.02	5.45 ± 0.01	8.17 ±0.02	11.51 ±0.01
Conductivity (Ω^{-1}m-^{1})	41.93	84.05	143.40	211.25
Bulk density (g/ml)	0.655±0.02	0.751±0.03	0.546 ±0.02	0.588 ±0.01
Iodine adsorp. number (mg/g)	25.10 ± 0.01	52.86 ± 0.04	136.56 ±0.02	172.01 ±0.03
Loss on Ignition (%)	6.1	46.8	88.5	92.5
Moisture Content (%)	0.18	0.25±0.01	0.12	0.10 ±0.01

The change in pH for the samples as shown in Table 2 has been attributed to the lost in residual materials during treatment, the metal content activity increases and hence alkalinity of the GO. The high pH of GO shows high alkaline activity in solution. Electrical conductivity is defined as the conducting power of all ions produced by one gram of electrolyte in solution and it has a reciprocal relationship with resistance[7]. From Table 2; the results showed that the electrical conductivity of GOs (MCGO & WBGO) is higher than that of graphites (MCG & WBG), showing active ionization activity in solution. The high electrical conductivity of GOs is probably due to the high ionization power of the GOs over the Gs. However, the waste batteries graphites and graphite oxides showed superior properties than the maize cob graphites. The bulk density given in Table 2 varied between 0.751 – 0.546 g/ml. Bulk density is principally influenced by the particle size and structure of the fiber and the lower the particle size the lower the bulk density and therefore the better the interaction between the polymer matrix and the reinforcing filler. This will enhance the processing and improve the quality of the end product. The desirable properties for particulate fillers include excellent tensile strength and modulus, high durability, low bulk density, good moldability and recyclability[8]. The bulk density reduction from 0.751 to 0.546

g/ml has been attributed to the opening of the interstitial spaces (microspores) in the GOs.

The iodine adsorption number from the Table 2 reveals that the GOs have high amount of iodine adsorbed per 100 gram of the material when compared with that of the graphites. The iodine adsorption number increases with that of WBGO having the highest of 172.01mg/g. One important application of iodine adsorption number is that it elicits the surface area of the material. It is a parameter that indicates the macrostructure of filler and reflects the reaction and adsorption abilities[6]. Like wood fiber, all kinds of porosities will form inside the GOs, which ascribed to the GOs a certain specific surface area, reaction and adsorption capacity.

It can be seen that the loss on ignition percentage increases from 6.1% to 88, the loss on ignition percentage increased rapidly with treatment of Gs to GOs, this might be caused by the almost completed volatilization of the volatile matter during the treatment.

Fourier Transform Infrared Spectroscopy (FTIR)

IR spectrum of MCG and MCGO are shown in Figures 1 and 2 and that of the WBG and WBGO are shown in Figures3 and 4.

Peak at 1519 and 1651cm^{-1} in Figure 1 and Figure 3 respectively indicate the presence of C=C bonds for MCG. In Figure 2 and 4, the peak at 1149 and 1242cm^{-1} indicate the vibration of C-O-C epoxide functional groups or C-O stretching of alcohol or carboxylic acid. Another peak at 1481 and 1512cm^{-1} show the presence of unoxidized C=C bonds in graphene oxide for MCGO and WBGO respectively. The next peak at 1635 and 1728cm^{-1} in Figure 1 and 3 represent the stretching vibration of C=O bonds. At 3279 and 3402cm^{-1}, in Figure 1 and 3 the peak signifie the stretching vibration of OH groups. In Figure 1, a peak at 1427cm^{-1} and in Figure 3, a peak at 1620cm^{-1} were observed and this indicates the presence of C=C aromatic bond. Next, the peak at 3271 and 3379cm^{-1} represents the unreduced OH bond.

The presence of oxygen-containing groups in Figure 2 and Figure 4 have proven that the oxidation of graphite to GO is feasible. Similar absorption peaks were reported by Olanipekun et al[5], another study conducted by Tran et al[9] also shown similar absorption peaks for both Gs and GOs.

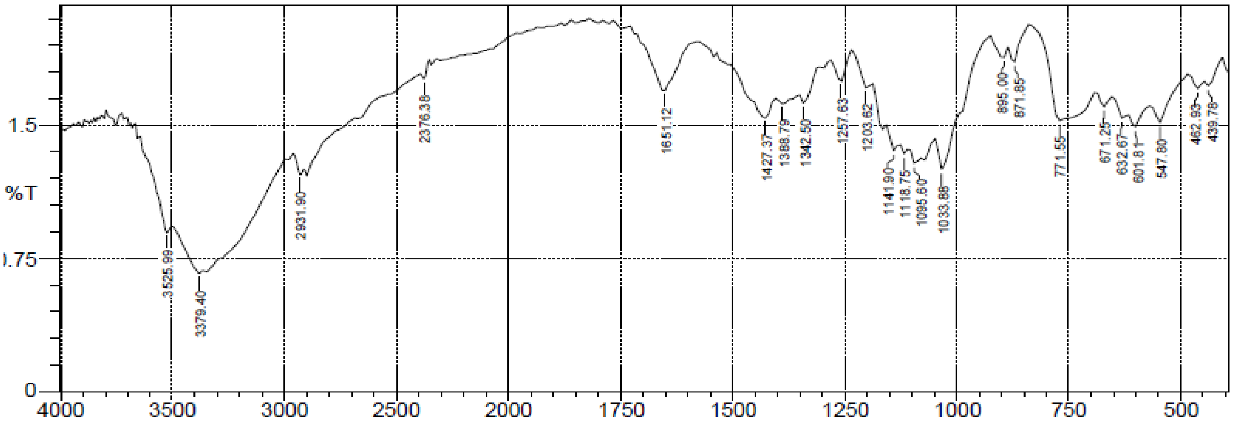

Figure 1: FTIR spectrum for the maize cob graphite (MCG)

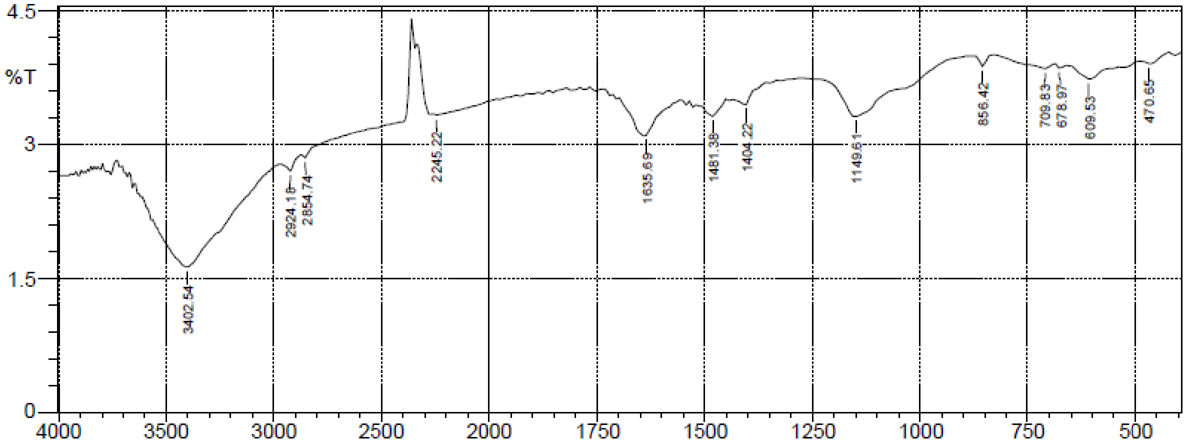

Figure 2: FTIR spectrum of the graphene oxide (MCGO)

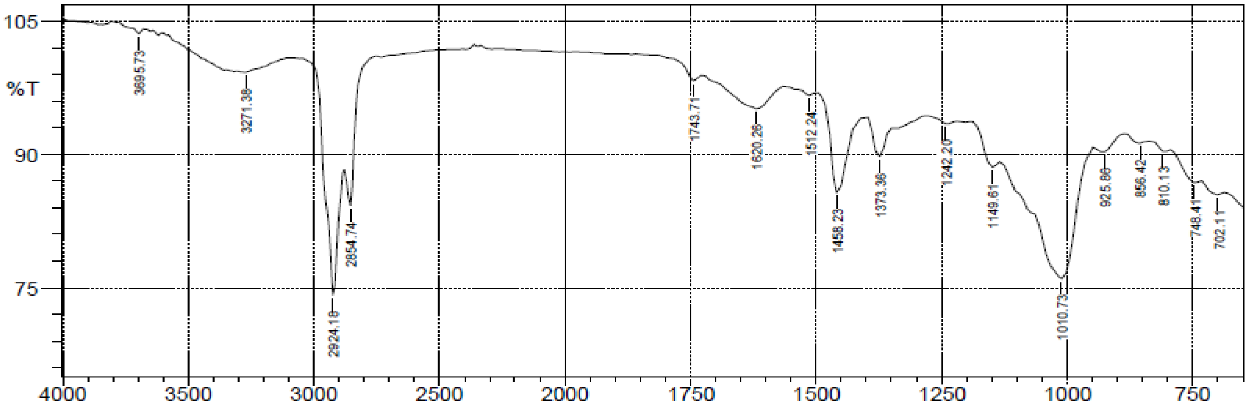

Figure 3: FTIR spectrum for the graphite (WBG)

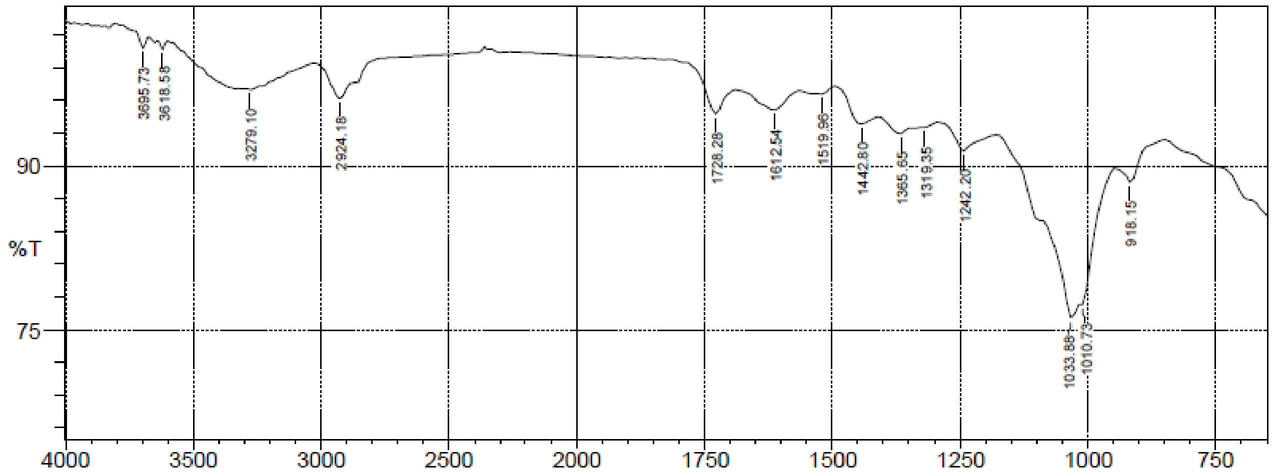

Figure 4: FTIR spectrum of the graphene oxide (WBGO)

SEM Analysis of Graphites (MCG and WBG), and Graphite Oxides (MCGO AND WBGO)

Plates 1-6 show the micrographs of MCG (Plates 1, 3, 5), and MCGO (Plates 2,4,6). Also, Plates 7-12 show the micrographs of WBG (7,9,11) and WBGO (Plates 8,10,12) powders under SEM with magnification of 50-100X. From Plates 1.3.5,7,9,11 MCG and WBG show coral tree-like structures. Plates 2,4,6, 8,10,12 show the structures of MCGO AND WBGO with a rougher surfaces. This is due to the presence of oxygen containing groups on the surface of graphitic layers. Similar results were reported by Zhao et al[10]. Plates 2,4,6, 8,10,12 also show a wrinkled paper-like structure of GO. A study done by Silwana et al[11] had shown similar results.

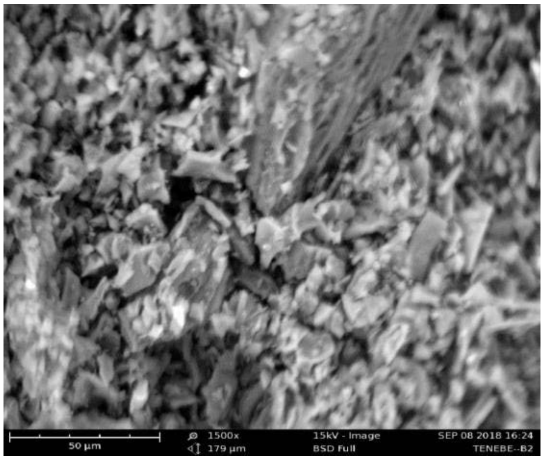

Plate 1: SEM of Maize cob graphite (MCG x 50µm)

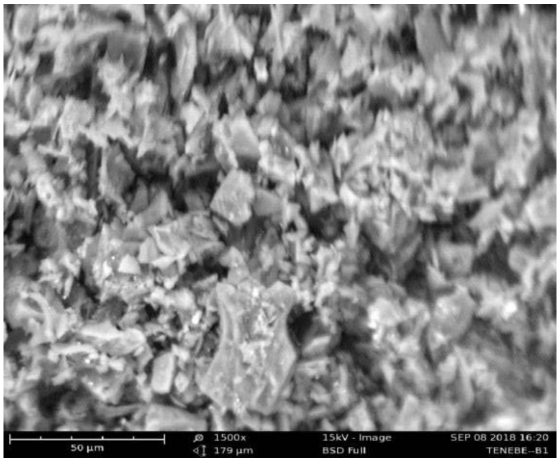

Plate 2: SEM of Graphene Oxide from MCG(x50 µm)

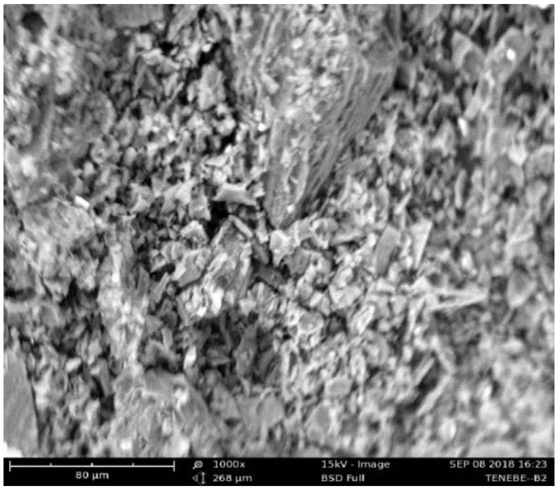

Plate 3: SEM of Maize cob graphite (MCG x 80µm)

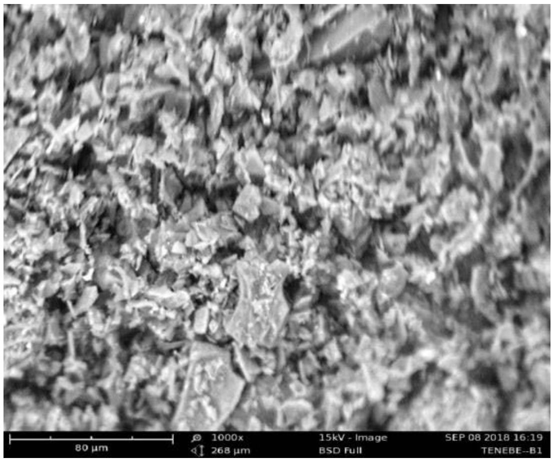

Plate 4: SEM of Graphene Oxide from MCG(x80 µm)

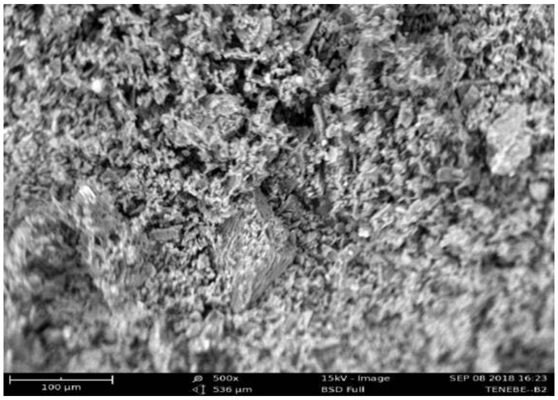

Plate 5: SEM of Maize cob graphite (MCG x 100µm)

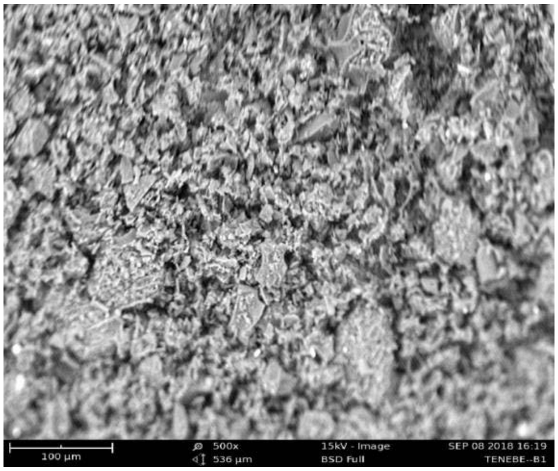

Plate 6: SEM of Graphene Oxide from MCG(x100 µm)

The surface morphology of Gs and GOs were characterized using Scanning electron microscope (SEM). Plates 1-6 show SEM images bring out the comparison between the Gs and GO samples. As shown in Plates 2,4,6 the Gs have irregular form, and its lateral dimensions range from 1016 mm to 1080 mm. The larger Gs consists of small flakes on their surfaces as shown in plates 2,4,6. After chemical treatment, the morphology of Gs was completely changed and a visible difference was observed in the SEM images of all GOs. The images of the GOs (Plates 1,3,5) under low magnification reveals its bound morphology. The high magnification image of GO reveals its multi-layered feature with crumpling and scrolling morphologies, which is consistent with the study reported in literature for GO[12]. The SEM image of GO reveals its flake like configuration with size ranges from 1016 mm to 1080 mm. GO has well-exfoliated feature and consists of randomly aggregated sheets with soft morphologies as shown in plates 1,3,5.

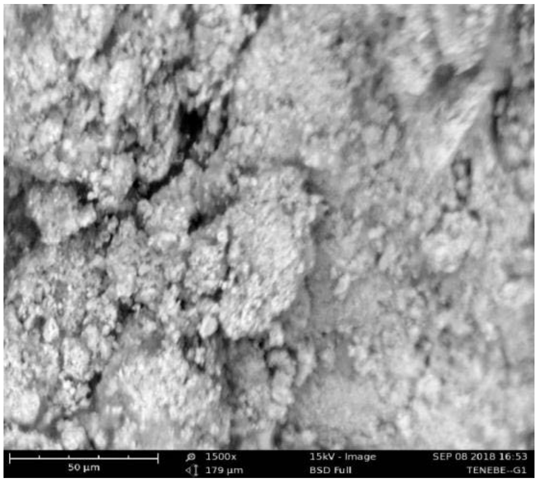

Plate 1: SEM of graphene Oxide x50µm

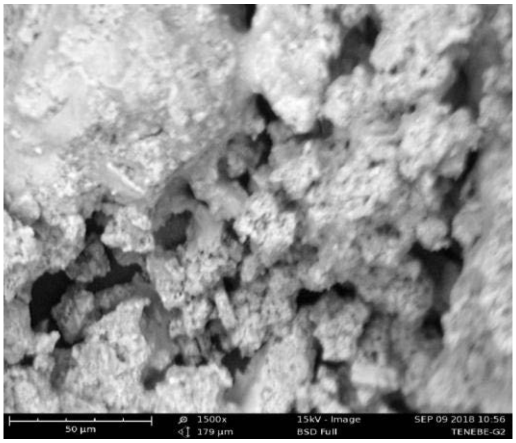

Plate 2: SEM of graphite x50µm

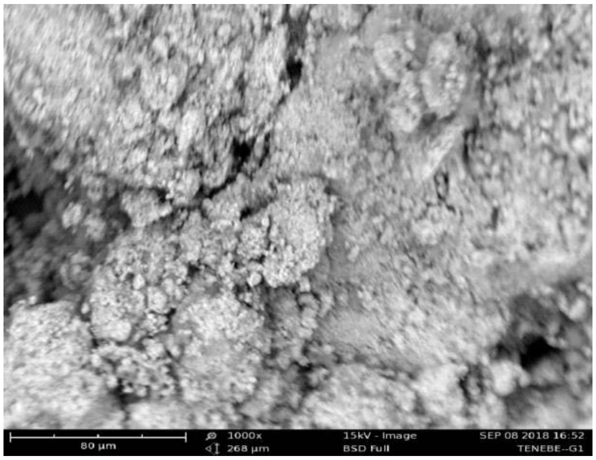

Plate 3: SEM of graphene Oxide x80µm

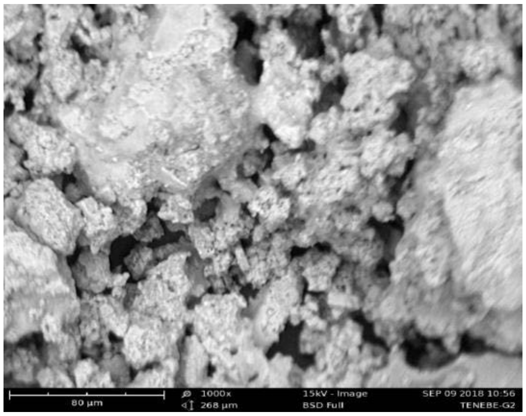

Plate 4: SEM of graphite x80µm

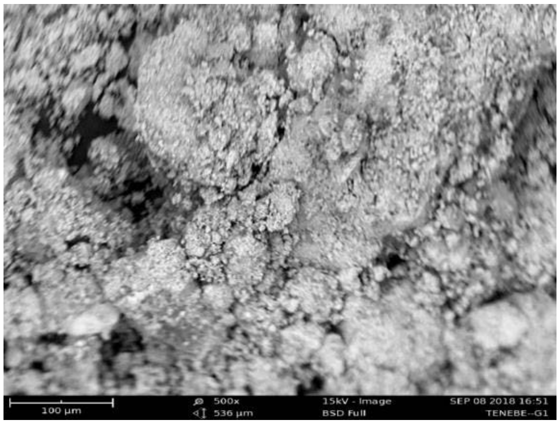

Plate 5: SEM of graphene Oxide x100µm

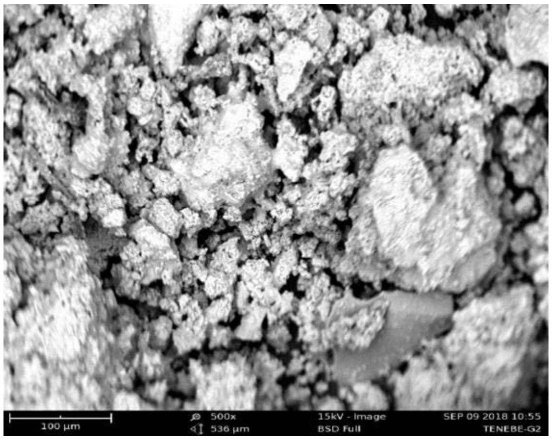

Plate 6: SEM of graphite x100µm

Mechanical properties of graphite and graphene oxide filled natural rubber vulcanizates

Mechanical properties of the natural rubber vulcanizates

The evaluation of tensile strength, elongation at break, modulus at 100%, flex fatigue, hardness, compression set and abrasion resistance has been studied.

Table 3: Mechanical properties of the vulcanizates

Properties	**Filler Loading**	**MCG**	**MCGO**	WBG	WBGO	**CB (N330)**
Tensile Strength (MPa)	5phr	27.06	32.79	15.09	19.80	18.60
Modulus at 100%	5phr	14.80	19.51	6.72	8.78	4.33
Elongation at break (%)	5phr	709.45	500.02	651.05	603.58	525.02
Flex Fatigue (Kc x 10^3)	5phr	0.00	0.00	0.00	0.00	0.00
Hardness IRHD	5phr	65.73	71.01	49.35	53.00	45.20
Abrasion Resistance (mm^3/rev)	5phr	35.11	37.45	33.66	37.34	35.54
Compression Set (%)	5phr	37.75	39.05	31.90	35.88	16.34
Energy at Break(N.mm2)	5phr	7.75	10.41	5.87	6.47	5.21
Force at Break (N)	5phr	187.05	210.36	168.12	172.12	160.8

Tensile Properties Results

Table 3 shows the variation of tensile strength and modulus of the Vulcanizates with the filler type and loading. An increase in tensile strength as well as modulus with the graphite oxide filler over that of the graphite was observed. It clearly indicates the high level of the graphite oxide filler-polymer matrix interaction compared to that of the graphite filler interaction with the polymer with the maize cob graphite oxide filler showing better results. It may be mentioned here that both tensile strength and modulus are important for recommending any composite as a candidate for structural applications[13].

Improvement of tensile strength in NR/MCGO NR-vulcanizates is because there is better stress transfer. MCGO is able to disperse well than WBGO and form better interaction with rubber matrix. On the other hand, the modulus increased and the elongation at break (EB) of NR/MCGO NR-vulcanizates decreased. This is due to the delocalization of natural rubber chain on the surface of MCGO which reduce the elasticity and increase modulus.

In all filled systems, tensile strength and modulus at 100% increase with increasing filler type and content. The factors that affect the reinforcing potential of fillers include filler dispersions, surface area, surface reactivity, particle size, bonding quality between the filler and the polymer matrix. The results in Table 3 also gave the values of elongation at break as a function of filler type and loading. The values of Elongation at break (EB) decreases with the filler type and content of the mixes for both fillers. Decrease in elongation at break has been explained in terms of adherence of the filler to the polymer phase leading to the stiffening of the polymer chain and hence resistance to stretch when strain is applied[14,15]. However, the values of the graphene oxide filler is low when compared with that of graphite showing high stiffening of the polymer chains and high resistance to strain compared to that of graphite filled natural rubber vulcanizates.

Hardness Results

Table 3 shows the micro-hardness values for both compositions. It is seen that with the graphite oxide filled vulcanizates there was a high hardness over that of the graphite filled vulcanizates for both compositions. This result is expected because as more filler particles get into the rubber, the elasticity of the rubber chain is reduced, resulting in more rigid composites[16].

Compression Set Results

The compression set results in Table 3 shows that the GO-filled type has high compression set compared to that of the graphite-filled vulcanizates. The observation may not be unconnected with the amount of filler incorporated into the matrix, the degree of dispersion of the filler and its particles size.

Abrasion Resistance Results

The abrasions resistance of a solid body is defined as its ability to withstand the progressive removal of material from its surface as the result of mechanical action of a rubbing, scrapping or erosive nature. The variation of abrasion resistance with the filler type is presented in Table 3. It showed a regular pattern of increase with increasing filler type. This indicates that filler loading is a function of the measured parameter. This observation may therefore be attributed to the degree of dispersion of the filler[17].

Results of Flex Fatigue, Energy at Break and Force at Break.

The results in Table 3, give the values of flex fatigue, force at break and energy at break as a function of filler type. The values of these parameters were higher for GO vulcanizates compared with that of graphite filled vulcanizates. This observation has been explained in terms of adherence of the filler to the polymer phase leading to the stiffening of the polymer chain and hence resistance to stretch when strain is applied[18] demanding more force and energy to break the bonds.

CONCLUSION

The main aim of this work was to assess the effect of graphite oxide as filler on the mechanical properties of natural rubber vulcanizates and the possibility of comparative study of the mechanical properties of the composites with that of graphite and N330 carbon black. The preliminary results show that graphite oxide exhibit high reinforcing properties as filler for natural rubber compounds compared to the untreated graphite and N330 carbon black.

This work shows successful fabrication of graphite oxide-reinforced Natural Rubber vulcanizates by simple hand lay-up technique.

GO was produced through conventional Hummers method using graphite from waste batteries and maize cob. Characterization of the filler materials were carried out via FTIR, and SEM Other than that, NR/G, and NR/GO, vulcanizates were successfully produced through two roll mill. Morphology study of the vulcanizates shows that only NR/GO vulcanizates are having very good dispersion in rubber matrix. Mechanical properties study shows that only NR/MCGO vulcanizates is having improved properties with tensile strength of 32.79MPa, modulus at 100% elongation of 19.51MPa. However, NR/MCGO vulcanizate shows low elongation at break of 500.02%. The highest hardness value is NR/MCGO of 71.01 IRHD. The study showed the feasibility of using GOs as filler without using dispersing agent. The mechanical and physical properties of the vulcanizates were enhanced when compared to the use of N330 carbon black as filler.

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