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Full Length Research Paper

Studies on the Morphology of Natural Rubber Compound Filled Cashew Nut Shell Powder (CNSP)

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Abstract
Cashew nut shell powder (CNSP) was utilized as filler in natural rubber vulcanizates using a particle size of 450 µm and filler loadings 10, 20, 30, 40, and 50 pphr, respectively. The CNSP was characterized in terms of pH and moisture content, this revealed a pH of 4.97, moisture content of 0.72 %. The rubber was vulcanized using efficient vulcanization system with the CNSP as filler and this was compared with commercial filler, Nigerian National Petroleum Corporation (NNPC carbon black).The x-ray diffraction which reveals a quite percentage of elements of silicon carbide and silicon dioxide (0.733 and 0.811) was attributed to the partial reinforcement of the filler. The x-ray diffraction reveals that the distance (d) is an inverse of the 2 θ that is as the 2 θ is increasing the spacing is reducing while the broad peaks were indications that cashew nut shell powder is largely amorphous. The scanning electron microscopy reveals better mixed rubber with carbon black than cashew nut shell powder.

Key words: *Cashew nut shell powder, x-ray, moisture content, vulcanization*

Introduction

The search for means and methods of improving the properties and processing of rubber dates back to over a century ago. One way of achieving this extension of service life of rubber is the incorporation of additives into the polymer matrix. Additives are materials which when incorporated into a polymer base, help to ensure easy processing, reduce cost of production and enhance service properties. The different types of additives used in the processing of rubber into products include vulcanizing agents accelerator, activator, antidegradants, fillers, softener, thickeners, gel sensitizer, colorant etc. (Egwakhide *etal*; 2007).

Filler is one of the major additives used in natural rubber compounding and has marked effect and influence on rubber materials. Filler functions to modify the physical and, to some extent, the chemical properties of vulcanizates (Egwakhide *etal*; 2013). The mechanism of reinforcement of elastomers by fillers has been reviewed by several workers. They considered that the effect of filler is to increase the number of chains, which share the load of a broken polymer chain. It is known that in the case of filled vulcanizates, the efficiency of reinforcement depends on a complex interaction of several filler related parameters. They include particle size, particle shape, particle dispersion, surface area, surface reactivity, structure of the filler and the bonding quality between the filler and the rubber matrix. In the rubber industry, fillers that are commonly used are carbon black, china clay and calcium carbonate. Carbon black is derived from petro-chemical sources but the unstable price of crude oil has led to the search for fillers that are derived from other sources. Agricultural by-products, maize cobs, cocoa pod husk, sugar cane chaff, rice husk, plantain peel etc. are low cost materials and readily available in large quantity for use, of which well over 300 million tones are produced annually in the world (Mary, 2007). In previous reports, the use of cocoa pod husk, rubber seed shells, groundnut husk, and plantain peels etc: were examined (Jawad *et al;* 2011). The results obtained from these studies indicated a potential for the utilization of agricultural residues as fillers in natural rubber compounds.

Scanning electron microscopy (SEM) uses a focused electron probe to extract structural and chemical information point-by-point from a region of interest in the sample. The high spatial resolution of an SEM makes it a powerful tool to characterize a wide range of specimens at the nanometer to micrometer length scales. Cashew nut shell constitutes environmental menace in the southern part of

Nigeria, therefore the need to put it to useful application in rubber as rubber compounding cannot be achieved without the use of fillers. Locally sourced potential fillers may modify the morphological properties of natural rubber vulcanizates

Materials and methods

Materials

The materials used in this work are natural rubber, zinc oxide, stearic acid, trimethylquinoline, cashew nut shell powder, carbon black, mercapto benzolethiazole disulphide and sulphur.

Methodology

Processing of cashew nut shell powder (CNSP)

A large quantity of Cashew nut shell (CNS) was collected around Auchi, and was well separated from debris and dried for 7 days under the sun to obtain total drying; it was then taken to the grinding machine and ground to a powder form. The powder was then sieved into particle size of 450µm using an American Standard for Testing and Materials (ASTM) sieve.

Determination of moisture content

The moisture content of the filler is determined using ASTM D1509 method. A known weight (5g) of the air dried material poured in a petri dish and placed in an hot air oven maintained at $105^0C \pm 5\ ^0C$. The sample was then removed from the oven at 30minutes intervals and allowed to cool at room temperature and in a desiccator: and repeatedly done until there was no further change in weight (ASTM D1509, 1983). Triplicate determinations were carried out and the average change in weight was calculated in percentage asthe moisture content.

$$\text{Moisture Content (MC) \%} = \frac{w_0 - w_1}{w_0} x \frac{100}{1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

Where;
w_0= *Initial weight*
w_1 = *Final weight*

pH determination

The pH is determined using ASTM D1512 method. The slurry of the materials is prepared by mixing 5g of the material in 50cm^3 of boiling distilled water. The mixture was allowed to cool to room temperature. pH measurement was made on a cooled mixture (ASTM D1512, 1983).

Preparation of vulcanizates

The sample preparation will be discussed according to the following processes.

i. Compounding/mixing
ii. Curing/vulcanization

Mixing of natural rubber with compounding additives

The mixing of the fillers and compounding additives with natural rubber was done according to the ASTM D3182 method. The two roll mill was switched on and the nip of the rolls was tightened before the piece of rubber was fed in between the nip of the rolls and allowed to pre-masticate in order to reduce the molecular weight of the rubber; after the pre-mastication a band was formed round the front roll of the mill after which a bank was formed in between the nip of the rollers. The co-activators zinc oxide and stearic acid were added and allowed to mix for 2minutes, the antioxidant (TMQ) was then added and was allowed to mix for another 2 minutes. The filler was then introduced to the compound and the mixing carried out for 5 minutes, the incorporation was done by the help of processing oil (paraffinic). The accelerator (MBT and MBTS) was then added, mixed for 2minutes after which the last additive which is the curative/vulcanizing agent (sulphur) is added. The cross-mixing is done very fast for about $1^1/_2$minutes to avoid premature vulcanization, the nip of the rolls were adjusted to a thickness of 3 mm and the compounded material is sheeted out and kept for 24 hours for relaxation.

***Note:** The mixing of the natural rubber was carried out with a blank sample, carbon black and cashew nut shell powder and all the mechanical and rheological tests were also carried out on them.*

Curing/vulcanization

The curing of the compounded rubber is carried out on a hydraulic machine (hot press) with electrically heated platens. The temperature of the platens is set at 130 ± 2^oC and when the temperature is attained the moulds were preheated to attain the platen temperature. The material is cut to the shape of the mould and placed in between the platen with a pressure of 33.4bar for 8 minutes, and the cured samples were removed from the mould.

Table 1. Formulation table

		Formulations PPHR		
S/No	**Ingredients**	**1**	**2**	**3**
1	Natural rubber	100	100	100
2	Zinc oxide	5	5	5
3	Stearic acid	2	2	2
4	TMQ	1.5	1.5	1.5
5	MBTS	3	3	3
6	Filler	00	--	--
7	Carbon black	--	40	--
8	Cashew nut shell	--	--	40
9	Processing oil	2	2	2
10	Sulphur	3	3	3

TMQ: Trimethylquinoline, MBTS: Mercaptobenzolethiazole disulphide

Morphological tests

Scanning electron microscopy (sem) analysis

A small sample was cut, followed by sectioning, mounting, grinding, polishing and etching to reveal accurate microstructure and contents. Detailed viewing of the sample was done with a microscope that had a system of lenses (objective and eye piece) at 3000x magnifications and the details recorded and saved on the computerized system.

X-ray diffraction (x-rd) analysis

A prepared test sample of the material was placed on the powder sample holder, then the sample was illuminated with x-rays of a fixed wavelength and the intensity of the reflected radiation recorded using a goniometer. This data is then analyzed for the reflection angle to calculate the inter-atomic spacing (d values in Angstrom units -10^{-8}cm). The intensity (I) was measured to discriminate (using I ratios), the various spacing's and the results were then identified with possible matches.

Results and discussion

Filler Characterization Results

The moisture content of cashew nut shell powder was determined to be 0.72% and the pH of 4.92. The moisture content of carbon black is 0.50% and the pH is 4.92. Figure 1 presents the x-ray diffraction spectra of the CNSP

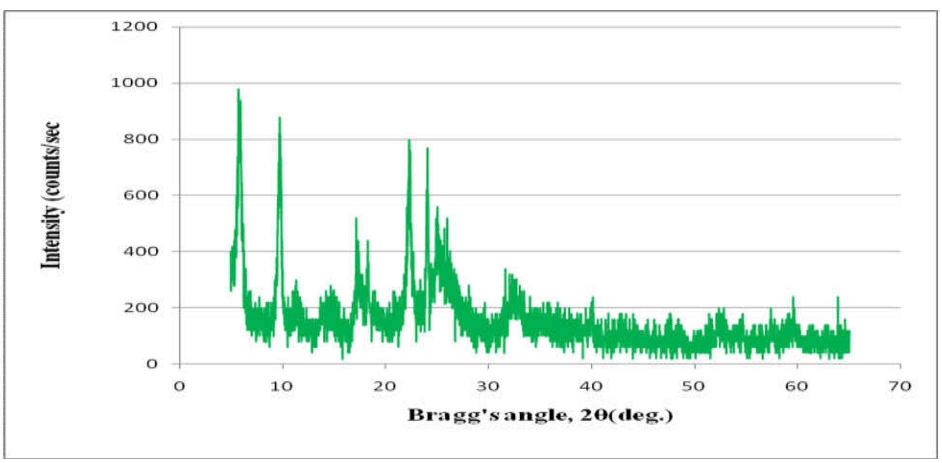
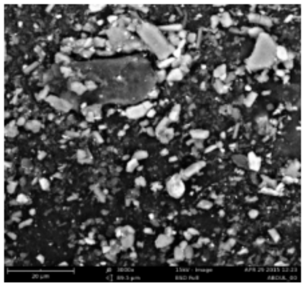
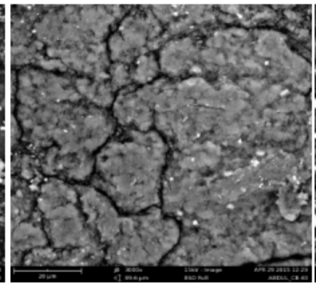


Fig 1: X-ray diffraction test on cashew nut shell powder

Results for the Morphological Properties of Rubber

The result of scanning electron microscopy for unfilled rubber is presented in plate 1





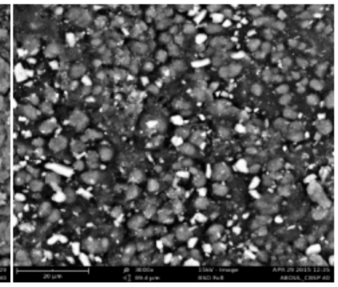


Plate 1 **Plate 2** **Plate 3**

Plate 1: Scanning electron microscopy for control sample (unfilled rubber).

The result of scanning electron microscopy for carbon black filled rubber is presented in plate 2

Plate 2: Scanning electron microscopy for carbon black filled rubber.

The result of scanning electron microscopy for cashew nut shell filled rubber is presented in plate 3

Plate 3: Scanning electron microscopy for cashew nut shell powder filled rubber.

Discussion

Moisture content of fillers

The filler characterization result obtained reveals the moisture content of cashew nut shell powder to be 0.72% which is within the limit of 1 % of fillers moisture content used in rubber compounding as reported by Gent, (2003).The moisture content of the carbon black is 0.50 %. The moisture content of fillers is often used to predict the degree of defects arising from shrinkage during curing.

pH of fillers

The pH of the filler slurry shows that cashew nut shell powder (CNSP) is acidic with pH of 4.97 while that of the carbon black is alkaline with pH value of 8.07. It is generally well known that acidic fillers retard cure rate or vulcanization (longer cure time) while alkaline fillers accelerate it (shorter cure time): as the proper vulcanization time for carbon black were lower than those of cashew nut shell powder used.

X-ray diffraction of cashew nut shell powder

The XRD measurement revealed the formation of different phases of mineral components such as silicon dioxide, silicon carbide, beryllium carbide, cerium oxide, calcium fluoride, iron carbide, molybdenum boride, arsenic oxide, nickel sulfide, iron oxide, sodium, magnesium, aluminum silicate, ammonium, and germanium iodate. Amongst all the elements present, silicon dioxide was the most abundant with 0.811wt% followed by silicon carbide with 0.770wt% and are the most important of all the elements present in terms of filler reinforcement (Appendix 17 and 18). Generally, silicon is stable and it is a group 14 element as carbon which makes it more versatile and finds a wide range of applications in polymer and electronic industry for conducting polymers. Silicon carbide and silicon dioxide have a good wear resistant and resistance to oxidation at high temperatures. Peaks 6, 1 and 2 are the three strongest peaks with 2θ values of 9.8215, 5.9887 and 22.3332 and with a distance (d) of 8.99843, 14.74612 and 3.97754, respectively. As the Bragg angle (2θ) values were increasing from peak one to peak 86 (5.9887 to 59.9743) the distance (d) were reducing (14.74612 to 1.54120). The broad peaks were indication that cashew nut shell powder is largely amorphous and from the X-RD and SEM analysis, it was revealed that the addition of cashew nut shell powder (CNSP) caused morphological changes on the vulcanizates.

Scanning electron microscopy on rubber

The morphological analysis was carried out using a scanning electron microscopy (Phenon Prox). The results obtained showed that at 3000x magnification, the plates revealed similar pore areas but with the carbon black filled rubber having largest pore area compared with the sample filled with cashew nut shell powder. The sample filled with carbon black showed better compartment over that of cashew nut shell powder and this can be attributed to the surface area of the fillers. From the control sample down to the samples filled with carbon black and cashew nut shell powder, it is obvious that there cannot be 100% homogeneity in a compound mix as the additives incorporated in the compound still found their way revealed in the micrographs (Plates 1, 2, and 3, respectively). The compound filled with carbon black revealed a better homogeneous mix over the control and cashew nut shell powder filled vulcanizates. The whitish spots detected on micrographs are all cylindrical in nature while the main body is octagonal and circular. As for a better mix, cashew nut shell powder should be well processed to ensure reduction of the particle size and surface area to a nano particle in order to be closely compared to compounds filled with carbon blacks.

Conclusion

The micrographs revealed that vulcanizates filled with carbon black had better mix/interaction than those filled with CNSP and this could be attributed to the particle nature and surface area of the filler. The characterized fillers revealed that cashew nut shell powder has low moisture content and it is acidic in nature while the commercially used filler (carbon black) is alkaline in nature and the XRD revealed that silicon dioxide and silicon carbide were found to be more in the filler making it to have the reinforcing property as carbon black.

Recommendation

Agricultural waste like cashew nut shell should be treated in other to modify the surface area of the filler to yield a better interaction with the rubber compounds.

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