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ASSESSMENT OF NANO GROUNDNUT SHELL ON THE MECHANICAL PROPERTIES OF NATURAL RUBBER

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ABSTRACT

Assessment of nano groundnut shell on the mechanical properties of natural rubber composite was studied. Samples of groundnut shell were ball milled to obtain nano particles. The characterization results of the nano groundnut shell showed excellent values of pH (6.89), moisture content (2.15%) and bulk density (0.72g/ml). The mechanical properties of the nano groundnut shell filled natural rubber vulcanizates present improved tensile strength (17.50 – 40.25MPa), modulus (6.15 – 23.50MPa), elongation at break (550.05 – 435.09%), abrasion resistance (17.85 – 10.35%), compression set (37.00 – 21.04%), flex fatigue (7.18 – 4.25 kc x 10^3) and hardness (32.60 – 73.80) as filler loading increases from 10 - 50phr. The results obtained from the nano groundnut shell powdered filler showed that particle size of fillers greatly affect the properties of filled natural rubber in no small way

Keywords: Composite, filler, loading, nano, rubber

INTRODUCTION

Polymer nano composites have attracted the attention of researchers all over the world in recent times. There are several advantages, environmental and economical, in various applications such as structural and food packaging of using bio composites over ordinary composites. Perhaps the biodegradability feature of such composites offers a natural solution for the problem in agricultural and marble waste management. Properties of composites are improved using fillers in the size of nano level as reinforcement [1]. However, for the purpose of this work, we shall refer to 124nm to 394nm particles size as semi-nano. Much research has been carried out in the development of nano-filled composites through the incorporation of nano-scaled materials such as ceramics and carbon in polymer matrices. For instance, organo clays, carbon nano tubes, alumina nano particles and silica nano particles have been added to polymers. Polymer nano composites exhibit unique properties even by the addition of low fillers [1]. Incorporation of nano fillers in polymer compounds enhances mechanical, electrical and optical properties of the composites. Other important properties include toughness and stiffness as demonstrated in rubber filled carbon fibres [2]. Several polymers have been used for preparing polymer nano composites such as elastomers (natural rubber), epoxidised natural rubber (ENR), styrene-butadiene rubber (SBR), chloroprene rubber (CR), ethylene propylene diene monomer rubber (EPDM), thermoplastics (nylon 6, 6, polypropylene (PP), polyethyleneterephthalate (PET), polymethylmetacrylate (PMMA), polycarbonate and polymer blends [1]. Many researchers have tried several methods to obtain nano silica from agro-waste; these include chemical, solution, mechanical, etc.

The aim and objectives of this study will include:

i. To obtain a nano particles from groundnut shell
ii. To characterize the nano particles from groundnut shell
iii. To study the effect of nano particles from groundnut shell in natural rubber compound
iv. To study the mechanical properties of the nano composite

MATERIALS AND METHOD

Materials

The materials used in this research include nano groundnut shell powder obtained from Auchi metropolis, natural rubber (NR) from Rubber research Institute, Iyanomoh and the compounding ingredients such as zinc oxide, stearic acid, sulphur, tetramethyl thiuram disulphide (TMTD), mercaptobenzothiazole sulphenamide (MBTS) were obtained from British Drug House, England.

Equipment and Machines

The equipment used during this study are of world class standard and made in England. They include;

i. Retch new planetary mill series (Pm100) with planetary balls made of harden steel as small as 0.1mm (< 0.004inch) in diameter.
ii. Universal Tensile Tester, Manufactured by British Company Limited, England was used for tensile tests properties.
iii. Wallace Hardness Tester, Elektron Technology Series, UK was used for hardness test.

iv. Wallace Akron Abrasion Tester, Elektron Technology Series, UK was used for abrasion test.

v. Flex meter Manufactured by British Company Limited, England was used for flex fatigue test.

vi. Two Roll Mill, Manufactured by British Company Limited, England mills were used in mixing the rubber composite.

vii. Hydraulic press, Elektron Technology Series, UK was used for curing the rubber composite.

viii. Mevler analyzer sizer for particle size analysis was used in determining the sample sizes.

Method

Nano Groundnut Shell Powder Production

In this research investigation, the nano fillers have been synthesized using ball milling technique. Groundnut shell was soaked in water and collected in a mesh sieve (75µm) to prevent sand particles and other impurities. The washed groundnut shell was then ground to reduce the particle size and further subjected to ball milling using the PM100 series which contains a spherical shape media, measuring about 0.24 to 0.95 cm in diameter. The grinding media is made of balls of hardened stainless steel. The material and the media are then agitated by a shaft with arms, which are rotating at high speed. This causes the media to exert both shearing and impact forces on the material resulting in optimum size reduction and dispersion. An internal cascading effect reduces the material to ultra-fine powder. The resultant slurry formed was discharged, dried in air and further dried in a microwave oven to eliminate the water content. The cake is again fed into the ball mill machine using the top-down technique, i.e. critical speed grinding under a continuous process of approximately 78hrs producing nano particles [2]. In general, the particle size decreased with increasing reaction time and temperature. Consequently, the particle size could be controlled by systematic adjustment of the reaction conditions including time, temperature, and concentration of stabilizers.

Filler Characterization

Determination of Moisture Content

The moisture content of the filler sample was determined by adopting the method described in ASTMD 1509 [3] at 125^{o}C. This method is used to determine the percentage of water in a sample by drying the sample to a constant weight. The moist sample was weighed and recorded as initial weight of sample. The wet sample was dried to a constant weight at a temperature of 125^{o}C in an oven. The sample was allowed to cool, reweighed and recorded as the final weight of the sample.

$$\text{Moisture Content (\%)} = \frac{\text{Initial Weight} - \text{Final Weight}}{\text{Initial Weight}} \times 100$$

Determination of Bulk Density

Bulk density of the various samples was determined by the tapping procedure. Accurately weighed samples were poured into a uniform cylinder of cross sectional area and were then tapped several times until there was no change in the volume occupied [4]. This volume was then recorded and the bulk density calculated.

Determination of pH

The pH of the nano groundnut shell powder sample was determined using ASTMD 1512 method by immersing 1.0g samples in 20.0mL of deionized water in a 250mL beaker. The mixture was stirred for 15mins and the pH meter used to obtain reading directly from solution [5].

Determination of Particle Size

The size of groundnut shell powder was determined using Malvern optical and digital imaging system. Nano groundnut shell powder was dispersed in a cuticle using methanol as the suitable dispersant to obtain a medium capable of been focused by dynamic light scattering system and reflecting on a transducing medium which help to measure the aggregation of the particles. As the light passes through the sample, image is formed by reflection on the transducing medium which detects the resultant size of the material by volume of aggregates and the level of light intensity that passes through the medium. The peaks and percentage volume and intensity are measured for particle data.

Processing of the Composites

This involves the compounding of natural rubber with nano groundnut shell fine powdered particles using the formulation given in Table 2.1

Table 2.1: Formulation for Compounding Natural Rubber.

Ingredient	Parts per hundred rubber
Natural rubber	100
Nano Groundnut Shell Powder (NGS)	Variable (10 - 50)
Zinc Oxide	5.0
Stearic acid	2.5
Sulphur	1.5
MBTS	1.5
TMTD	3.5
Processing Oil	5.0

Mixing Procedure

The rubber mixes were prepared on a laboratory size two roll mill according to the mixing cycle shown in Table 2.2 following ASTMD 3184 - 80 Standard [6].

Table 2.2: Mixing Steps and Mixing Time

Mixing Steps	Time (Minutes)
Natural rubber mastication	3
Addition of Stearic acid	2
Addition of Zinc Oxide	1
Addition of filler	8
Addition of MBTS	1
Addition of TMTD	1
Processing Oil	2
Addition of Sulphur	2
Total	**20**

Composite Curing

The curing of test pieces was done in a compression moulding machine at 115^{o}C and 2bar for 5 mins.

Mechanical Properties of the Vulcanizates

Tensile Tests

The test specimens were cut from the moulded dump-bell rubber sheets along the grain direction. The thickness and width of each test piece at the middle was maintained at 2.5mm and 6mm respectively. Each test piece was clamped into the grips of the tensometer. The stress applied, the load and elongation at break was recorded. The test samples were tested in the machine giving straight tensile pull, without any bending or twisting. The machine measured both the tensile stress and the tensile strain. The tensile stress is the strength of pull in the area between the notch marks; it is based on original cross sectional area. The tensile strain is a measure of how the test sample has been stretched by the pull.

Hardness Test

Test pieces from the moulded spherical rubber pieces were clamped onto a Wallace Hardness Tester, Elektron Technology Series, made in United Kingdom for hardness test and the penetration of the indenter measured. The standard dead method of measurement covers rubber in the range of 30 to 85 International Rubbers Hardness Degrees (IRHD). The test was carried out using the Shore "A" Wallace Hardness Tester.

Compression Set Test

The Wallace Compression Set machine was used. Compression set evaluates the extent by which the specimen fails to return to its original thickness when subjected to standard compression load for a given period of time at a given temperature. The test samples were cut to standard dimension and compressed between parallel steel plates under stress of 2.8MP and allowed for 24 hours at 70^{o}C for 30mins. The compression set is the difference between the original thickness of the sample and the thickness after the test expressed as a percentage of the original thickness.

$$\text{Compression Set (\%)} = \frac{t_o - t_r}{t_o} \times 100$$

Where: t_o = Initial Thickness and t_r = Recovered thickness of Sample.

Abrasion Resistance Test

Wallace Akron abrasion tester was used. The angle between the test sample and the wheel was adjusted to an angle of 15^{o}. The abrasion was carried out for 1000 revolutions and the material loss for each run was noted. The specimen was re-reweighed between each test run. The mean of the four revolutions of the abrasive wheel was calculated.

$$\text{Abrasion Resistance} = \frac{\text{Weight Loss of the Standard}}{\text{Weight Loss of the Sample}} \times 100$$

Flex Fatigue Test

The measurement was carried out in accordance to the procedure described in ASTMD 430 using the Flex machine, which function by inducing surface cracking of the rubber vulcanizates sample.

RESULTS AND DISCUSSION

Table 3.1: Particle Size Analysis

Parameter	Volume		Intensity	
	Peak 1	Peak 2	Peak 1	Peak 2
Percentage (%)	83.2	16.8	81.8	18.2
Size (d.nm)	939.8	5030	748.7	4700
PDI	0.425		0.425	
Result Quality	Good		Good	

Table 3.2: Characteristics Results of the Powdered Fillers

Parameter	Value
Moisture content (%)	2.15
pH of slurry	6.89
Bulk Density (g/ml)	0.72

Table 3.3: Mechanical Properties of the Vulcanizates

Property	Filler Loading (phr)					
	0	**10**	**20**	**30**	**40**	**50**
Tensile Strength (MPa)	21.50	29.10	33.30	34.50	35.60	40.25
Modulus (MPa)	6.15	15.00	19.60	20.20	21.00	23.50
Elongation @ Break (%)	550.05	506.17	489.35	474.48	450.55	435.09
Hardness (IRHD)	32.60	46.30	50.50	58.70	66.40	73.80
Compression Set (%)	37.00	28.90	25.00	22.20	21.90	21.04
Abrasion Resistance (mm^3/100rev)	17.85	16.78	15.40	14.16	13.40	10.35
Flex Fatigue (kc x 10^3)	7.18	6.25	5.59	5.02	4.57	4.25

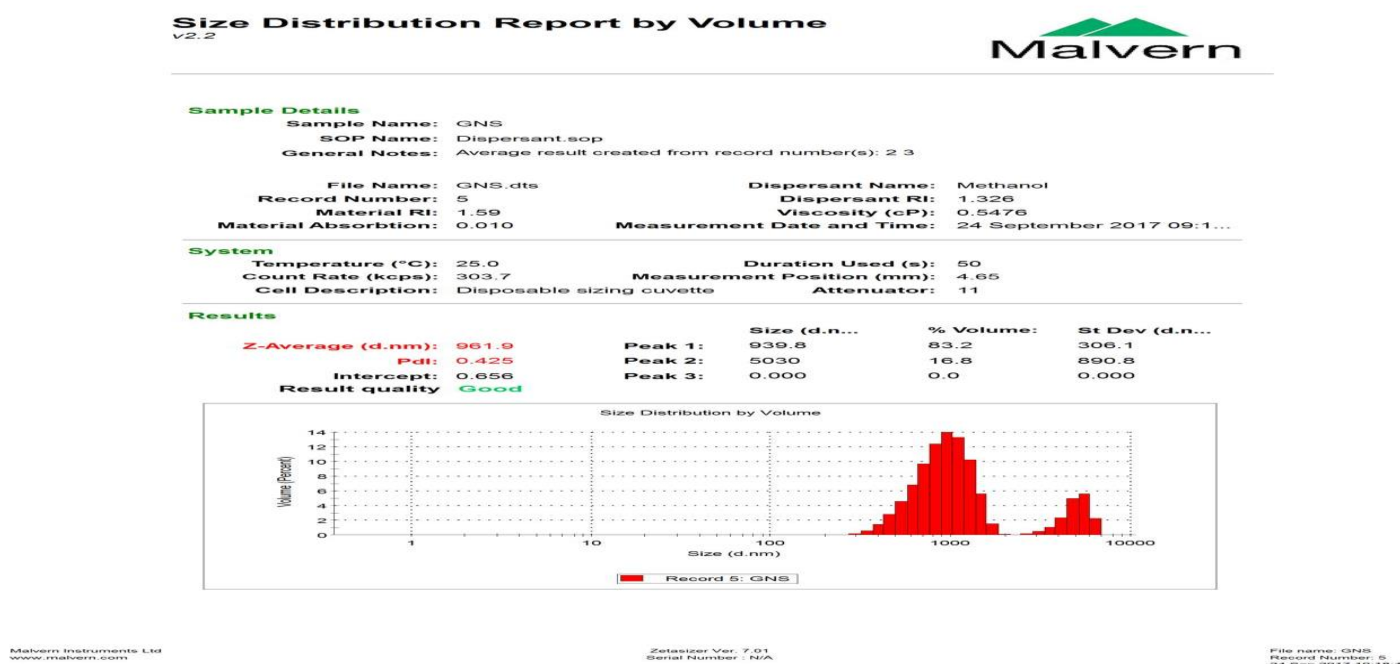

Figure 3.1: Nano Groundnut Shell Powder Size Distribution by Volume

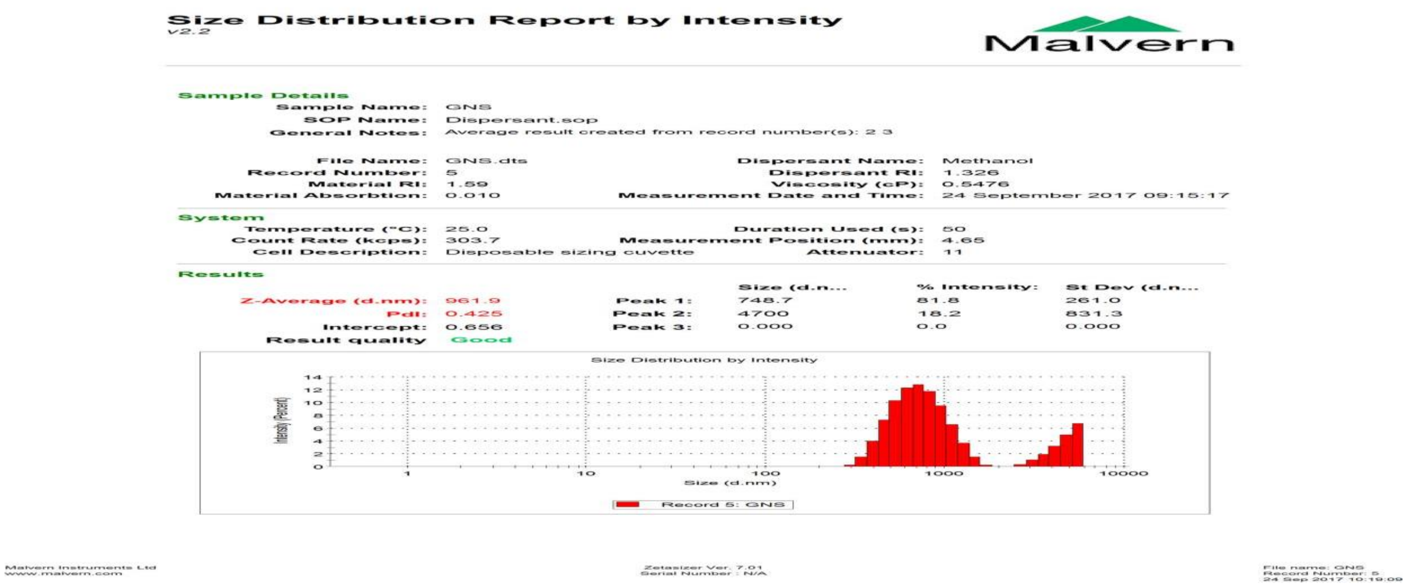

Figure 3.2: Nano Groundnut Shell Powder Size Distribution by Intensity

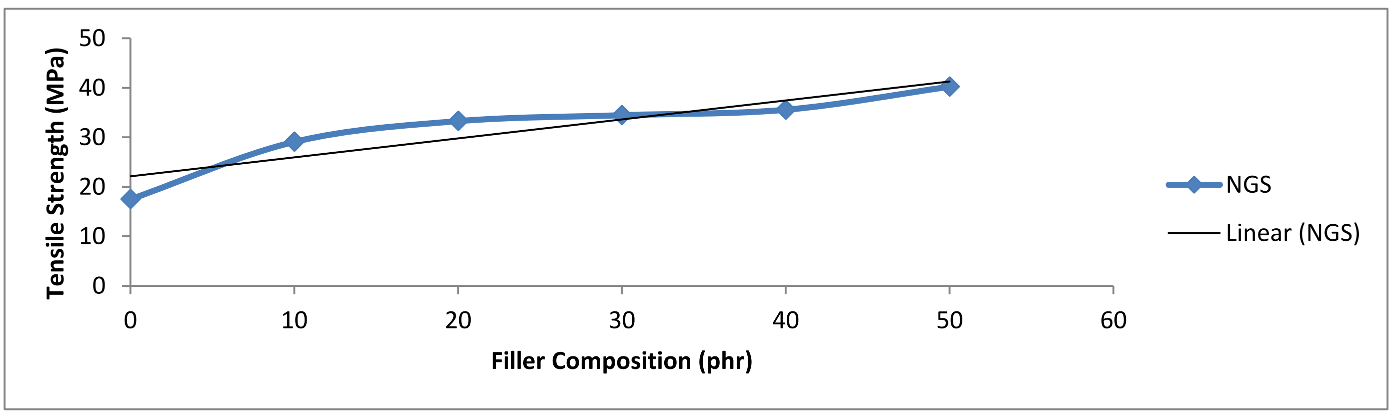

Figure 3.3: Tensile Strength of Nano Groundnut Shell filled Vulcanizates

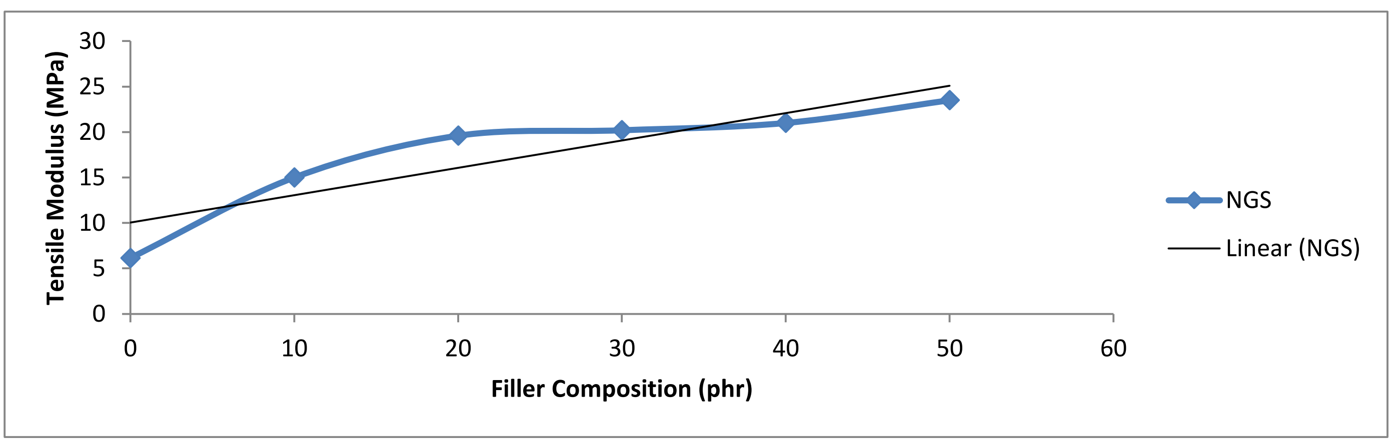

Figure 3.4: Tensile Modulus of Nano Groundnut Shell filled Vulcanizates

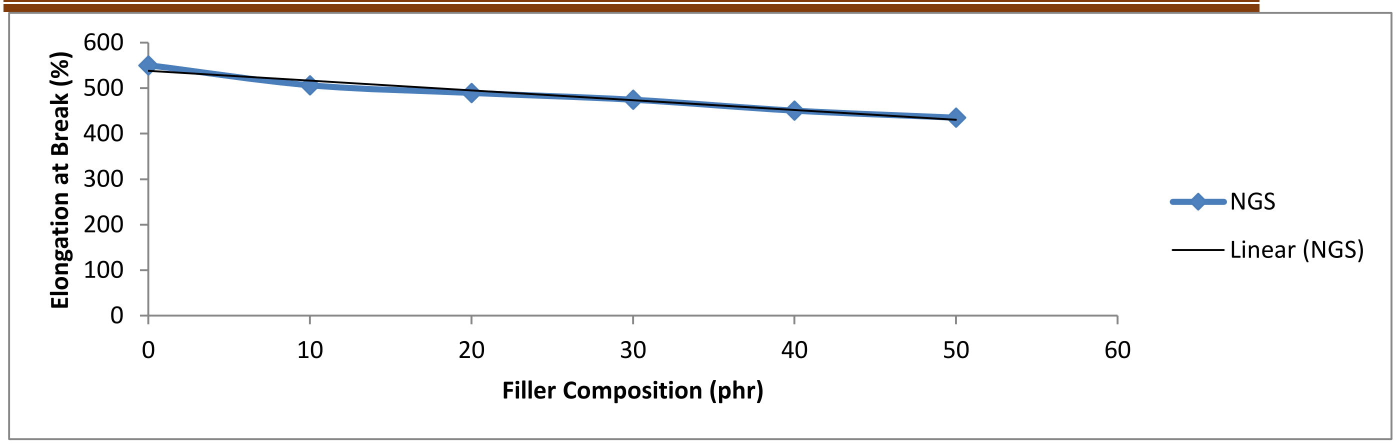

Figure 3.5: Elongation at Break of Nano Groundnut Shell filled Vulcanizates

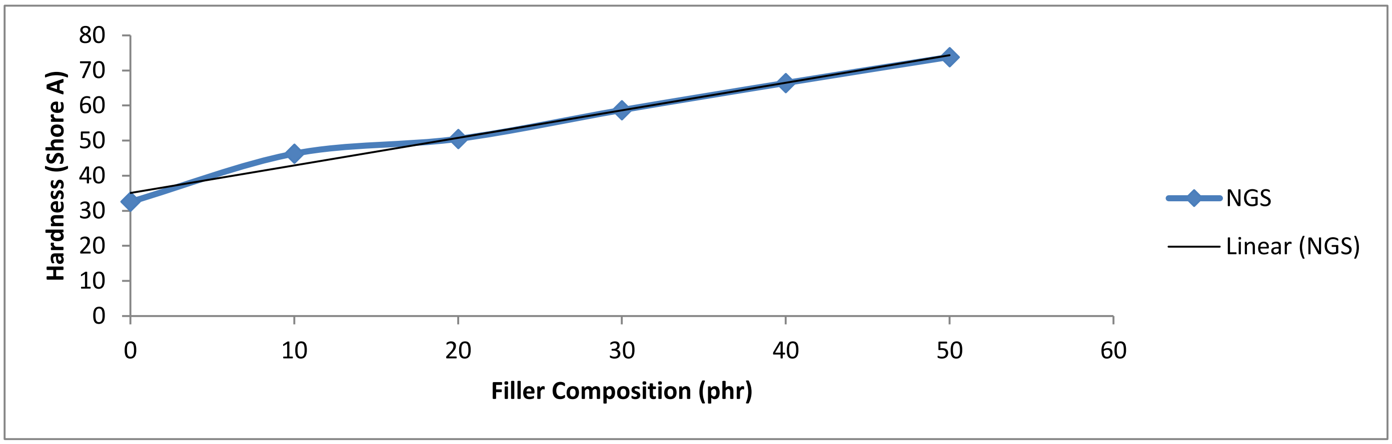

Figure 3.6: Hardness of Nano Groundnut Shell filled Vulcanizates

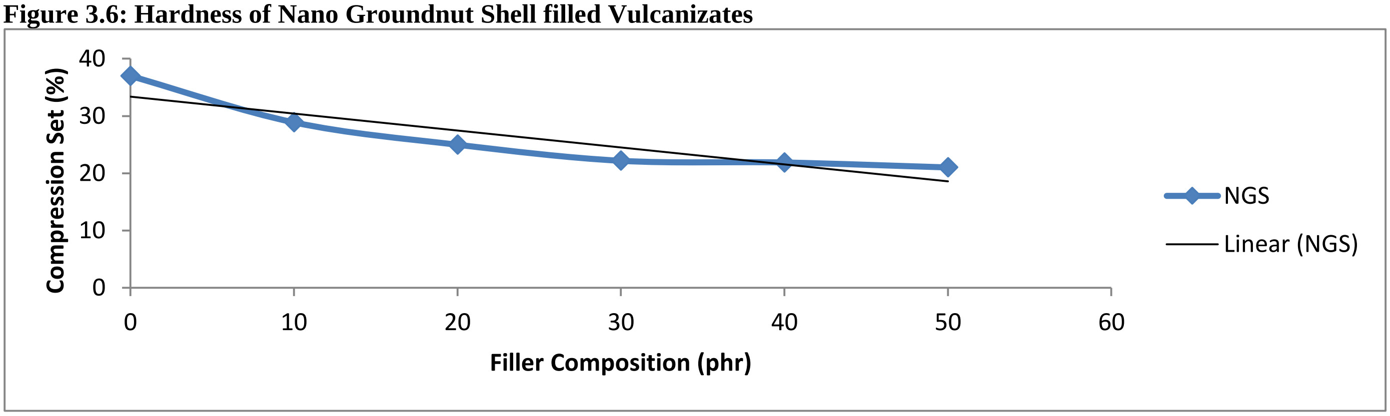

Figure 3.7: Compression Set of Nano Groundnut Shell filled Vulcanizates

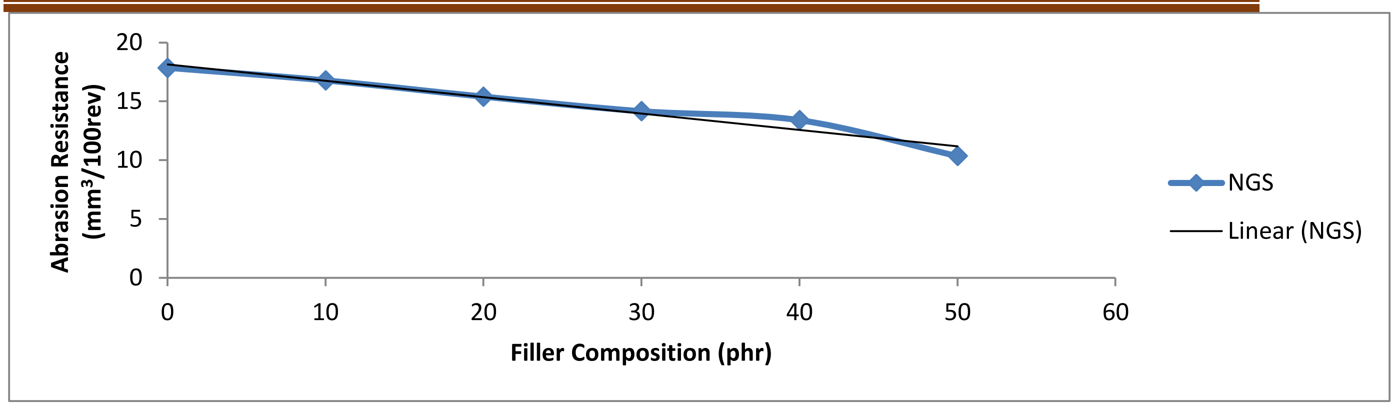

Figure 3.8: Abrasion Resistance of Nano Groundnut Shell filled Vulcanizates

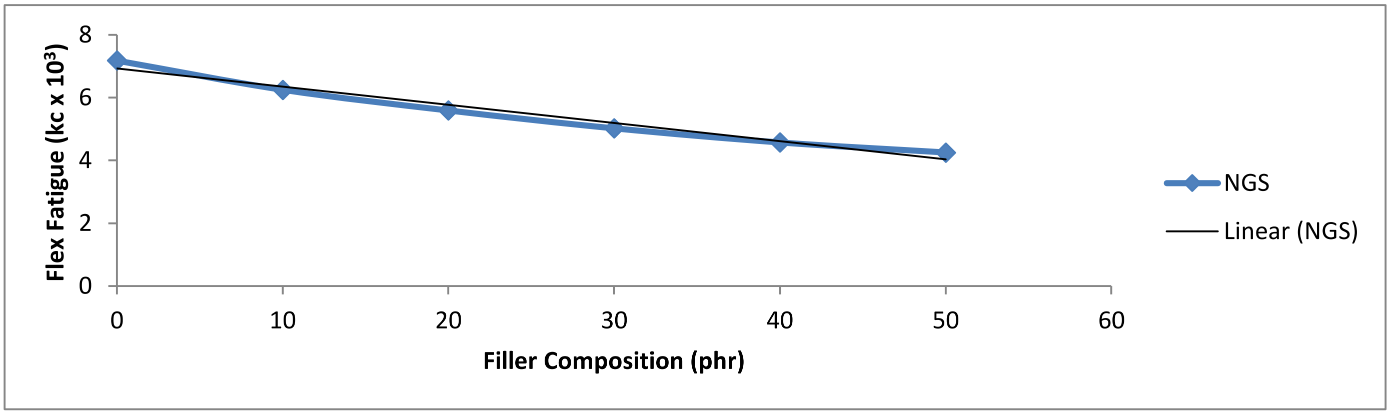

Figure 3.9: Flex Fatigue Resistance of Nano Groundnut Shell filled Vulcanizates

Table 3.1 showed the result of particle size of groundnut under studied in this research work. The powdered groundnut shell was adequately dispersed using methanol as the dispersing medium. The result showed that the particle sized distribution by volume of sample was 83.2% in the first peak and 16.8% in the second peak while the amount of light reflectance on the sample by volume was 81.8% in the first peak and 18. 2% in the second peak which showed a very high level of dominance of particles within the nanometer range over the quasi or coarse particles in the agglomerate. However, it revealed that an aggregation is often formed with powdered particles [5]. The result showed that the groundnut shell powdered particles were of nanometer sizes.

The moisture content of the filler is often used to predict the degree of defects arising from shrinkage during curing particularly for products processed at elevated temperatures [6]. The relationship between moisture contents of the nano groundnut shell powder sample as a function of the surface area is presented in Table 3.2. However, the moisture content present in a sample was 2.15%.

The bulk density of the nano groundnut shell powder sample presented in Table 3.2 is 0.72g/mL. Bulk density is principally influenced by the particle size and structures of the fibre and the lower the particle size, the lower the bulk density and therefore betters the interaction between the polymer matrix and the reinforcing fibre which will thus enhance the vulcanizate processing [6]. This help to improve quality of the final product as desirable properties for fibre include excellent tensile strength and modulus, high durability, low bulk density, good moldability and recycleability. Reduction in bulk density shows that the interstitial spaces (micro-pores) in the residue are opened and thus resulting in easy compaction and interaction with the polymer matrix.

The pH of the powdered fillers is presented in Table 3.2. The results showed that the pH of the nano groundnut shell powder sample was near alkalinity. This is possible because residuals materials are being lost on combustion, leading to the alkalinity [5]. However, pH at alkaline level tends to accelerate cure rate and hence increases the cross-links density in forms the choice of accelerators and activators in the mixing formulation.

Tensile stress-strain measurements have been one of the standard methods for characterizing rubber vulcanizates. The tensile properties of the nano groundnut shell powder sample filled natural rubber vulcanizate at different filler compositions are given in Table 3.3 and Figure 3.3. The tensile strength increases gradually with increase in filler composition. On incorporating fibres into the matrix, the regular arrangement of rubber molecules is disrupted resulting in loss of strain-induced crystallization [7].

Introduction of unfilled natural rubber produced a rubber composite with lower tensile strength compared to the filled natural rubber. At lower compositions, the rubber composites have lower tensile strength, However, the tensile strength of the filled vulcanizates increases with filler loading from 29.10 – 40.25MPa as filler composition increases from 10 – 50phr which may be due to the improved distribution of the fillers in the rubber matrix and as a result of reduced particle sizes, which has resulted in an improved rubber filler interaction. The increase in tensile strength of rubber vulcanizates as filler loading increases has also been reported by Tenebe et al [8] who worked on coconut shell and palm fruit fibre reinforced rubber composites and found that the tensile strength of rubber vulcanizates increased with increase in coconut shell and palm fruit fibre content. Other researchers had also reported similar trend in tensile strength of rubber vulcanizates with increase in filler loading when working with palm kernel shell reinforced natural rubber. The factors that affect the reinforcing potentials of fillers include filler dispersions, surface area, surface reactivity, bonding capacity (quality), particle size between the filler and the elastomeric matrix.

The modulus results in Table 3.3 and Figure 3.4 increased with filler loadings of nano filler contents in natural rubber vulcanizates. The high tensile modulus has been attributed to a stronger interaction between the rubber matrix and filler particles.

Table 3.3 and Figure 3.5 showed the elongation at break (EAB) of the groundnut shell powder filled vulcanizates values which decreased with the increased composition. As the reinforcing capacity increases, generally the EAB % decreases. A decrease in elongation at break is explained in terms of adherence of the filler to the rubber polymer matrix leading to the stiffening of the polymer chain and hence resistance to stretch when the strain is applied [8]. But the nano groundnut shell powder filled vulcanizate showed a little higher values of elongation at break. The increase in the elongation at break is due to the inclusion of filler particles in the intermolecular space in the rubber matrix.

The hardness results of nano groundnut shell powder filled vulcanizates increased with increasing filler composition. 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 vulcanizates [8]. The hardness results of nano groundnut shell powder filled vulcanizates are higher as showed in Table 3.3 and Figure 3.6.

The results of compression set in Table 3.3 and Figure 3.7 showed that as filler composition increases, the compression of filled vulcanizates decreases for nano groundnut shell powder filled vulcanizates. This observation is connected with the degree of filler dispersion and its particle size which may have enhanced the nano groundnut shell powder vulcanizates [6].

Abrasion resistance (reciprocal of abrasion loss), a measure of reinforcement was found to improve with filler loading. The abrasion resistance of a solid body is defined as its ability to withstand the progressive removal of the material from its surface as a result of the mechanical action of rubbing, scraping or erosive nature [3]. Table 3.3 and Figure 3.8 showed a pattern of increase with increasing the filler composition for nano groundnut shell powder filled vulcanizates. This indicates that filler composition is a function of the measured parameter attributed to the degree of dispersion of the fillers. An improvement in this property was related to the secondary structure of the fillers. Filler aggregates in elastomer matrix have a tendency to form agglomerates, especially at high loading, leading to chain like filler structure or cluster, generally termed as 'secondary structure or filler network [5]. Such a network has a significant effect on the properties of filled rubber. High structure increases abrasion resistance and hardness.

The result of flex fatigue decreased with increased filler composition of the mixes for all the fillers as presented in Table 3.3 and showed in Figure 3.9. A decrease in flex fatigue 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 [4].

CONCLUSION

This research study was aimed at assessing and evaluating nano groundnut shell powder on the mechanical properties of natural rubber compound. The groundnut shell samples were obtained washed and ball milled to nano particles. The obtained particles were then characterized in terms of pH, moisture content, particle size and bulk density and used to compound natural rubber using 2-roll mill. The mechanical properties results investigated showed improvement in the composite as filler loadings on the matrices increases. This revealed that groundnut shell powdered fillers have reinforcing effect on natural rubber which is closely related to earlier research work of Ayo et al [6]. The results further showed that nano groundnut shell can serve as potential reinforcement in natural rubber for the production of rubber based articles and could serve as a replacement for traditional fillers used in the polymer industries such as carbon back. However, the authors wish to recommend that groundnut shell should be chemically treated through mercerization, acetylation, benzoylation or carbonized to investigate the effect of such treatments or carbonization on natural rubber matrices.

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