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Agricultural Residues as Potential Diluents in Natural Rubber Formulation

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ABSTRACT: Agricultural residues such as Maize Husk, Groundnut Shell, Coconut Shell and Sugarcane Bagasse were collected, sorted, dried and ground to particulate fillers. The various fillers were characterized in terms of density, moisture content and pH value. Single ordinates of 150 µm particle size and 30 parts per hundred of rubber (pphr) loading were respectively adopted for all filler types. They were used alongside with conventional Sulphur vulcanization system (high Sulphur to low organo-accelerator level) in the formulations of natural rubber compounds. Tests such as tensile strength at 400% elongation, constant force compression set, abrasion resistance as a function of percentage mass retention on surface exposure to a rotating abrasive surface and thermal stability using differential scanning calorimeter were carried out. Results obtained revealed that rubber vulcanizate samples filled with coconut shell and sugarcane bagasse had hardness values of 58 and 57 on Shore A scale while unfilled vulcanizate and carbon black filled sample had respective values of 45 and 49 Shore A hardness. However, unfilled vulcanizate and carbon black filled vulcanizate showed superior values of tensile strength at 400% elongation to the ones filled with agricultural residues. Therefore, these agricultural residues can serve as diluents in the formulation of rubber vulcanizates.

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In recent times, biobased composites from renewable sources are taking up a lot of spaces in the material research and development especially those involving the use of agricultural residues as reinforcement materials and agro-based polymer matrix such as natural rubber (Ortega et *al.*, 2021; Oboh *et al.*, 2017; Imanah and Okieimen, 2013; Al-Hayat and Omprakash, 2014). Agricultural residues such as maize husk, groundnut shell, coconut shell and sugarcane bagasse amongst others are low-cost raw materials derived from renewable agricultural crops waste mostly biodegradable and would otherwise be thrown away (Al-Hayat and Omprakash, 2014). They are mostly lignocellulose biomass consisting of about 35 – 55 % cellulose, 25 – 40 % hemicellulose and 15 – 25 % lignin with small percentages of extractive, protein and ash. Also, they generally have elemental constituents of Carbon, Hydrogen, Nitrogen and Oxygen (Shah *et al.*, 2016; Kalia *et al.*, 2011; Rudi *et al.*, 2016). These agricultural residues have also been reported to have structure, composition and properties similar to that of plant fibres making them suitable for the production of polymer composites, textile, pulp and paper making (Ajekwene *et al.*, 2022). The use of these agricultural residues as filler in agricultural polymer-based matrix such as natural rubber as the case in this research will lead to the production of environmentally friendly compound/composite. The expected properties of the resultant composites will strongly depend on the quality of interface formed between the agricultural residues and the natural rubber matrix (Pickering *et al.*, 2016; Lee *et al.*, 2014;

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Syuhada and Azura., 2021). However, the resinous and percolating tendencies of natural rubber matrix makes readily possible for particles of agricultural residues to be embedded in its matrix (Ayo *et al.,* 2019). The reinforcing characteristics of a particulate materials are characterized by its chemical composition, shape, dimensions, volume fraction and spatial distribution in matrix. Therefore, the relative strength and weakness of cellulose, hemicellulose and lignin will determine the overall performance of the resultant compounds (Duangkamol *et al.*, 2017; Oboh *et al*., 2015; Egwaikhide *et al*., 2007). Agricultural residues as reinforcement materials for polymer matrix are continuously attracting tremendous interest due to their specific strength, dimensional stability, wear resistance, renewability, low specific weight, availability and most importantly they do not produce toxic by product during thermal processing unlike their counterpart inorganic fillers such as glass fibre, carbon fibre and clay (Syuhada and Azura, 2021). In practical applications, low-cost agricultural waste fibre reinforced thermoplastic composites are gaining significant roles in building and automobile industries and other commodity applications (Syuhada and Azura, 2021). The major setback of these materials is their poor compatibility with hydrophobic polymer matrix such as natural rubber (Egwaikhide *et al.,* 2008; Okele *et al.,* 2013; Choi *et al.,* 2006). This problem of poor compatibility can be minimized by surface modification and the use of nanotechnology (Oboh *et al.,* 2017; kalia *et al.,* 2011; Rudi *et al.,* 2016; Pickering *et al*., 2016); however, these procedures require additional factors and costs of production which will negate the objectives of producing low-cost commodity. Natural cellulosic materials fiber such as hemp, sisal, jute, kenaf, cotton linter, bamboo amongst others have been extensively used as fillers in polymer composite formation due to their comparative advantage over conventional fillers in terms of low density, low cost and renewability character. Fillers in the context of polymer composite formation are either considered to be reinforcing or non-reinforcing fillers. Reinforcing fillers are capable of improving mechanical properties and commercial importance of composite materials while the non-reinforcing fillers also known as diluents are low-cost materials with potentials to increase material volume with the objective to cheapen overall cost of composites production (Oboh *et al.,* 2017). This is the category which unmodified agricultural waste fillers which is the focus of this study belong to. Agro-based natural rubber is recently playing a fiddle role to synthetic rubber because it is more expensive than synthetic rubber, one of the promising methods to ensure cost effective and competitive natural rubber production is the use of low-cost fillers (Duangkamol *et al.,* 2017). Carbon black filler which is one of the conventionally versatile fillers is produced through heavy industrial combustion of hydrocarbon process. This process requires tremendous energy utilization and constitutes a potential source of pollution and global warming; this has led to the search for more cost effective and eco-friendly materials for replacement (Oboh *et al*., 2015). Raw rubber is usually transformed into a range of materials suitable for application in various uses and in different service environment through compounding and vulcanization. Natural rubber alone does not possess the necessary physio-mechanical properties that are required by rubber manufacturers. Fillers are widely used additives and the largest in quantity among others in the manufacture of rubber product. Particulate fillers such as carbon black, calcium carbonate and China clay are widely used as reinforcing filler in the industries. Agricultural residues are low-cost materials and readily available in large quantity for use everywhere (Egwaikhide *et al*., 2007; Egwaikhide *et al*., 2008). Previous researchers (Egwaikhide *et al*., 2007; Egwaikhide *et al*., 2008; Okele *et al*., 2013) have reported the use of sugarcane bagasse, cocoa pod husk and rubber seed shell as agriculture waste filler in natural rubber formulation and compounding. Similarly, other researchers (Choi *et al*., 2006; Cindy and Katrina, 2019; Hammajam *et al*., 2013; Khalil *et al*., 2014; Khala, 2021) have also extensively dealt with other polymer matrices interaction with other agricultural and industrial waste. The focus of this work is to investigate the effects of Maize Husk, Groundnut Shell, Coconut Shell and Sugarcane Bagasse carbon black based fillers on the tensile strength at 400 % elongation, hardness, compression set, wear resistance hardness and thermal properties of natural rubber vulcanizate.

MATERIALS AND METHOD

Materials: The main materials used in this work are crumb natural rubber of grade NSR-10 and variety of agricultural wastes (Maize Husk, Groundnut Shell, Coconut Shell and Sugarcane Bagasse) collected from some farmers in Zaria, Nigeria at no cost. The other ingredients used in the work were the conventional rubber property enhancing additives such as Sulphur, Stearic acid, Carbon black (N330 HAF with particle size distribution of 50 – 200 nm), Trimethylquinoline (TMQ) and Mercaptobenzothiazole (MBT). All of these additives were of commercial/industrial grades and were obtained from Tony West Chemical Store in Lagos, Nigeria.

*Preparation and Characterization of Agricultural Residue Fillers***:** The agricultural residues were sorted and washed to remove foreign materials, they were subsequently dried under sun for a period of 72hrs and then converted to particulate filler by grinding with the aid of a Thomas Wiley Laboratory mill. The ground particles were screened through 150 µm mesh aperture with the aid of mechanical vibrator. The screened particles referred to as fillers were analyzed on the bases of pH value, density and moisture content (Al-Hayat and Omprakash, 2014; Rudi *et al*., 2016; Ajekewene *et al*., 2022). The pH value various fillers sludge was determined in accordance to ASTM D1293-99 while the density and moisture content of fillers were carried out according to ASTM D 792-09 and ASTM and ASTM D 2216-05 respectively.

Formulation of Rubber Vulcanizate The formulation used in this experiment is based on a single ordinate particle size and loading system of 150µm and 30 pphr respectively for the different fillers as presented in Table 1. The crumb Natural rubber and its associated additives (see Table 1) was masticated and mixed with chemicals/additives as well as the fillers using two roll mixing mills in accordance with standard methods (ASTM D3184-80) for all the rubber compound samples. Appropriate test pieces were vulcanized using 11 metric tons Carver Inc. model 3851-0 lab curing press at temperature of 150 ºC for 30 minutes each.

Table 1: Formulation of Compounds Samples

	Vulcanizates samples codes/Compostion					
Ingredients	Blank NR (Pphr)	NR/MH (Pphr)	NR/GS (Pphr)	NR/CS (Pphr)	NR/SB (Pphr)	NR/CB (Pphr)
Natural rubber	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
TMQ	1	1	1	1	1	1
MBT	2	2	2	2	2	2
Sulphur	3	3	3	3	3	3
Fillers	0	30	30	30	30	30

NR (Natural rubber), (MH) Maize Husk, GS (Groundnut shell), CS (Coconut shell) CB (Carbon black), Pphr (parts per hundred of rubber)

Properties Determination of Rubber Vulcanizates: Tests piece were prepared from the vulcanizates into appropriate shapes and dimensions for various tests and analysis. Hardness, abrasion resistance (Duangkamol *et al*., 2017), compression set (Oboh *et al*., 2017; Duangkamol *et al*., 2017; Oboh *et al*., 2015), tensile strength at 400 %, and differential scanning calorimetric analysis were carried out. The tensile strength, hardness, abrasion resistance and compression set tests of the vulcanizates samples were conducted in accordance to ASTM D412, ASTM D2240, ASTM D4060 and ASTM D575 respectively. The thermal property was studied using DSC according to method described by Oboh *et al* (2017).

RESULTS AND DISCUSSIONS

The results for the characterization of fillers are shown on Table 2. The proximate analysis based on pH value, moisture content and density of the fillers are shown in Table 2. The pH values of biomass can be slightly affected by the soil condition surrounding area of cultivation due to transport phenomena between the soil and the plant source while the moisture content is a function of the drying conditions of the particulate materials. The pH values obtained indicated that the ago-fillers were slightly acidic with the exemption of carbon black hence they could attempt to retard cure rate of Sulphur vulcanization system (Egwaikhide *et al*., 2007). The moisture content of groundnut shell and coconut shell corresponding to 5.59 and 7.27 % respectively were found to be higher than that of maize husk and sugarcane bagasse. High moisture content can lead to porosity as well as reduction in elastic modulus and tensile strength due to hydrolytic degradation during processing and in particular the plasticizing action of the presence of moisture in polymer matrix (Khala, 2021).

Table 2: Proximate Analysis of Filler

Parameters	Maize husk (MH)	Groundnut shell (GS)	Coconut shell (CS)	Sugarcane bagasse (SB)	Carbon black (CB)
pH value	5.54	6.47	6.45	6.56	8.03
Density (g/cm^3)	0.43	0.97	0.76	0.87	0.92
Moisture content (%)	3.87	5.79	7.27	3.27	0.9

The tensile strengths values as shown in Figure 1 where all obtained at 400% elongation. That is the force per unit area required to elongate the various samples to 400 % of their initial length was expressed as tensile strength at 400 % elongation. The values obtained for unfilled vulcanizate (blank NR) and vulcanizate filled with carbon black (NR/CB), sugarcane bagasse (NR/SB), maize husk (NR/MH), groundnut shell (NR/GS), and coconut shell (NR/CS) were 2.1, 6.0, 1.3, 1.5, 1.2 and 1.8 MPa. All fillers except carbon black used at the same particle size of 150 µm and loading content of 30 pphr gave tensile strength values lower than that unfilled vulcanizate.

The tensile strength of a polymer composites measures the ability of stress transfer between the matrix and the filler with minimal localized stress point or stress concentration. Therefore, the nature of interface formed (weak or strong) between the natural rubber matrix and the agro-based filler is of tremendous importance (Oboh, 2017).

The inferior tensile strength of all the agro-filler based vulcanizates to control samples (unfilled and carbon black filled vulcanizates) is an indication of weak interface formation due to several factors such as the hydrophilic nature of the various biomass, relatively small surface area provided by the filler due to their large particle size (150µm) compared to that of carbon black filler which is in nanometer range (50-200nm) (Oboh, 2017) in addition to the multiple constituents (cellulose, hemicellulose and lignin) of these residues might have contributed to the formation of weak interfacial interaction between the rubber and filler. Bear in mind that these fillers were targeted as low-cost filler and we try as much as possible to avoid treatment procedures that will culminate to additional cost. Hence the multiple constituents of these residues might have hindered adequate interfacial arrangement to support the improvement of tensile strength. This is an indication that this filler can only be used as diluents (Hammajam *et al*., 2013; Khalil *et al*., 2014; Khala, 2021). The result of hardness test as presented in Figure 2 showed that agricultural residues based vulcanizate (NR/NR/CS, NR/MH, NR/GS, NR/SB) possessed superior hardness to their counterpart NR blank and NR/CB. The higher values of hardness obtained for agricultural residues based vulcanizates over carbon black filled vulcanizate could be attributed to their fibrous nature with a potential to stiffen the rubber chain and reduce chain extensivity (Oboh, 2017). The result of compression set as shown in Figure 3 represents the dimension stability of the various vulcanizate when subjected to a constant compression force at room temperature for a period of 48 hrs. The compression set values presented on the chart are the percentage of the initial thickness of samples retained after a period of stress relaxation and elastic recovery. Usually when a rubber sample is in a compressed state, physical and chemical change will inevitably occur, when the compression force is removed, these changes prevent the rubber from returning to its original state and permanent deformation occurs.

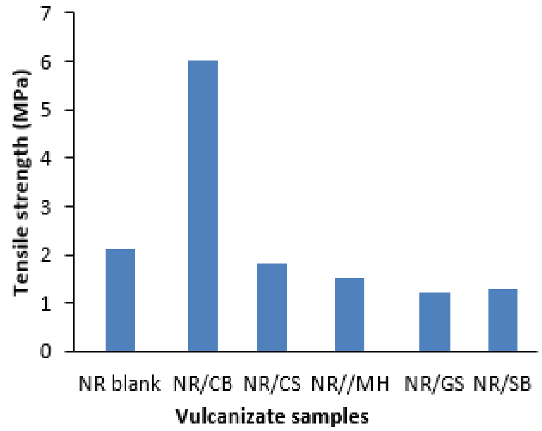

Fig. 1: Effect of filler type on tensile strength @ 400% elongation of vulcanizate

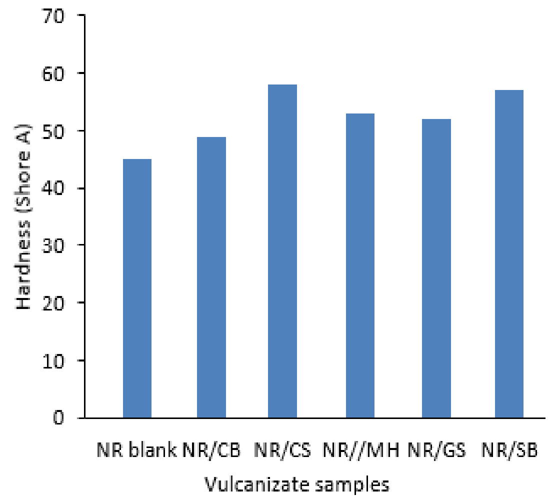

Fig. 2: Effect of Filler Type on Hardness of Vulcanizate

The size of this permanent deformation depends on time and temperature of the compressed state, varieties and loading of additives (Olatunji and Richard, 2016). The vulcanizates of NR/SB and NR/GS samples demonstrated superior dimensional stability with initial thickness retention of 97.3% and 98.5 % respectively against vulcanizates of unfilled rubber and carbon black filled rubber with 92.4 and 96.3 % respectively. The abrasion resistance as presented in Figure 4 measures the resistance of the vulcanizates to mechanical action of rubbing, scraping or erosion that tends progressively to remove material from the vulcanizate surfaces. The result presented showed the percentage of initial volume of vulcanizate samples retained after abrading action of the sample. The vulcanizate sample of NR/GS gave the highest abrasion resistance with a value of 90.54 % while NR blank gave the lowest value of 72.96 %. Result also reveal that the vulcanizations filled agro-based fillers (NR/CS, NR/GS, NR/MH and NR/SB) gave superior abrasion resistance to both control samples (NR/CB and unfilled NR). This is due to nonabrasive characteristics of natural fibre present in the various biomass (Syuhada and Azura, 2021; Cindy and Katrina, 2019).

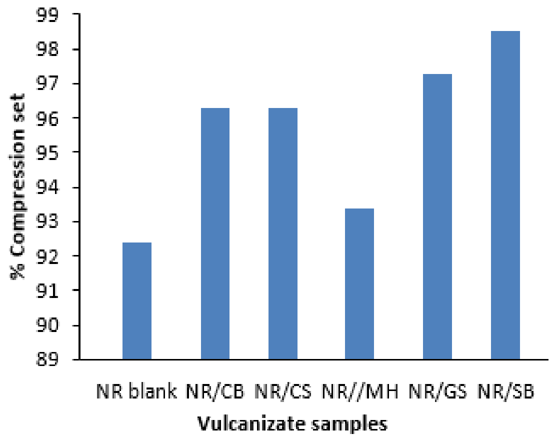

Fig. 3: Effect of Filler Type on Compression Set of Vulcanizate

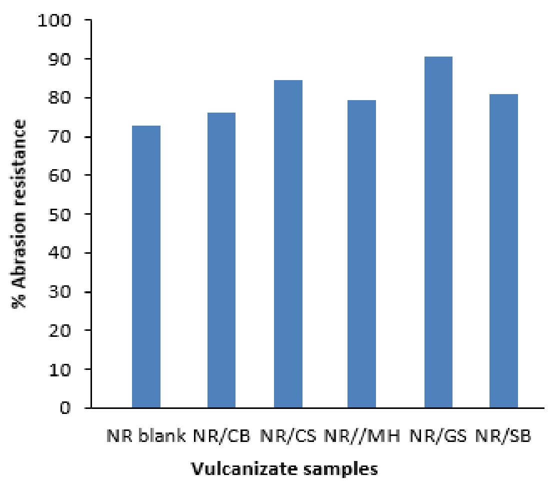

Fig. 4: Effect of Filler Type on Abrasion Resistance of Vulcanizate

The thermal properties of various samples were studied using Differential Scanning Calorimeter (DSC) in a power compensation mode. The cold crystallization temperature Tcc, minimum decomposition temperature and maximum decomposition temperature obtained from the associated curves are presented in Table 3.

Table 3: Thermal Properties from DSC Curves

Samples	Tcc (^{0}C)	Tm_{min} (^{0}C)	Tm_{max} (^{0}C)
Blank NR	65.9	163.75	262.99
NR-MH	64	149.58	257.56
NR-GS	62	162.71	264.81
NR-CS	63.5	149.04	298.74
NR-SB	62	110.61	229.75
NR-CB	70.4	167.44	256.38

Tcc: Crystallization Temperature, Tm_{min}: Minimum Decomposition Temperature, $Tm_{max:}$ Maximum Decomposition Temperature

The cold crystallization temperature (TCC) is the onset of molecular crystallization and it is an exothermic event while the decomposition temperature is the crystalline melting temperature (Tm) and it is an endothermic occurrence (Olatunji and Richard, 2016). The inclusion of these agro-fillers into the rubber matrix did not significantly affect the Tcc as indicated in Table 3 rather there was slight reduction in Tcc with the exemption of carbon black filled vulcanizate with Tcc of 70 ^{0}C, this same trend is almost replicated in the case of crystalline melting temperature (Tm_{min} and Tm_{max}) however coconut shell filled sample had the highest crystalline melting temperature of 298.74 ^{0}C.

Conclusion: The potential utilization of agricultural wastes such as maize husk, coconut shell, groundnut shell and sugarcane bagasse as low-cost fillers in natural rubber products have been studied and compared with blank and carbon black based vulcanizates. Coconut shell filled vulcanizate had the highest value (58 Shore A) of Hardness, while coconut shell filled vulcanizates (NR/GS) and Sugarcane bagasse filled Vulcanizate (NR/SB) has the highest values of Permanent set (97.3 and 98.5% thickness retention respectively) and Abrasion resistance (90.54 % volume retention).

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