An Investigation on the Reinforcing Potential of Red Earth as Filler for Natural Rubber Compounds

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ABSTRACT: Locally sourced red earth (RE) was air-dried, pulverized, and screened with a sieve of mesh size 75 nm. It was characterized in terms of its moisture content, loss on ignition, silica content, iodine adsorption number, oil absorption, pH, and metal oxide compositions. Natural rubber, standard Nigerian rubber used for this work was first characterized in terms of its dirt, ash and nitrogen contents, volatile matter, plasticity retention index, and Mooney viscosity. The RE was applied as filler wholly and in blends with standard carbon black, CB (N330) filler in the natural rubber compounding using efficient vulcanization system. The cure and the physicomechanical properties of the compounds and vulcanizates were, respectively, measured as function of filler loading. The results were compared with those of the standard carbon black (N330)-filled natural rubber. It was found, that the RE-filled natural rubber showed substantial reinforcement of the rubber, though inferior to carbon black (N330) filled vulcanizates, the tensile strength of the carbon black-filled vulcanizates is about one half times that of the RE-filled vulcanizates. The tensile properties of the RE-filled vulcanizates improved markedly by blending the RE-filler with the carbon black (N330). J Appl Polym Sci 105: 515–520, 2007

Key words: fillers; rubber; compounding; curing; reinforcement

INTRODUCTION

Rubber manufacturing requires the addition of many ingredients known as additives. This is to allow the rubber compounds to be easily processed and when vulcanized improve the application properties of the rubber products. Filler is one of the most important second largest additives, following the base polymer in rubber formulation and compounding. Fillers improve processability, physicomechanical properties, and may cheapen the final product. They achieve performance enhancement by forming bonds with the rubber molecules producing strong filler-elastomer interactions. Fillers are majorly used for reinforcing polymers. A reinforcing filler is one which can increase the tensile strength, tear strength, hardness, and abrasion resistance of the rubber article. Carbon black and silica are examples of reinforcing fillers. A nonreinforcing filler may cause reduction in strength properties but may increase hardness and modulus of the rubber product. They are usually applied as diluents or extenders to cheapen the polymer product. Examples include $CaCO_3$ and China clay. A good reinforcing filler should posses fine particle size, usually less than 1000 nm, a chemically active, porous, and irregular surface to facilitate contact between it and rubber matrix. The efficiency of rubber reinforcement is dependent on the filler particle size, shape, dispersion, surface reactivity, structure, and the bonding quality between the filler and rubber matrix.[1–5]

Precipitated silica and petroleum derived standard carbon black fillers are quite reinforcing but expensive commercially. There is the need, therefore, to develop cheaper fillers from among the underutilized renewable natural resources in our society today. These natural resources include, rice husks, cocoa pod husk, corn cobs, peanut shells, egg shells, limestones, rubber seed shells etc. They can be used directly or converted by simple chemical processes to valuable materials in polymer or related applications.[6–12] Red earths (RE) or sands the subject of this research work are earths rich in iron oxides or hydroxides as a result of chemical weathering in humid regions.[13] They are naturally occurring iron oxide pigments having hematite iron ore. They are mined in various parts of the world including Nigeria. They are natural inorganic pigments or colorants that can be used in surface coatings.[14,15]

This research work is focused on the need to develop a cheaper filler for rubber that can be an alternative, wholly and/or partially substituted for carbon black filler. REs are present in abundance in Nigeria and are only majorly used for sand filling roads during road surfacing. It is used here as filler

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TABLE I
The Characteristics of the Natural Rubber, Standard Nigerian Rubber (SNR_{10}), Standard African Rubber (SAR), and Standard Malaysian Rubber (SMR)

Test parameter	SNR_{10}	SAR_{10}	SMR_5
Dirt content (%)	0.02	0.02	0.05
Ash content (%)	0.30	0.32	0.50
Nitrogen content (%)	0.18	0.23	0.70
Volatile matter (%)	0.25	0.40	1.00
Plasticity retention index (PRI)	71.05	67.00	–
Mooney viscosity ML (1 + 4) 100°C	76.00	70.00	60.00

for natural rubber whose properties were compared with the standard carbon black filled natural rubber.

EXPERIMENTAL

Materials

The RE used for this work was collected from Ikpoba hill, Benin-City, the carbon black (N330), was got from the carbon black production unit of the Nigerian National Petroleum Company, Warri. The natural rubber grade, standard Nigerian Rubber, (SNR_{10}), was obtained from FAMAD (formerly BATA), Benin-City, all in Nigeria. Industrial grade chemicals and rubber ingredients were used for characterization and compounding. Standard rubber manufacturing equipment for this work were got from the Department of Polymer Technology, Auchi Polytechnic, Auchi, Edo State, Nigeria and Dunlop Nigeria, Ikeja, Lagos. The atomic absorption spectrometer, Pye Unicam SP 2900 model, used for the metal analysis was obtained from Tudaka Environmental Consultants, Warri, Delta State, Nigeria.

Characterization of the standard Nigerian rubber (SNR_{10}) and red earth

The natural rubber, SNR_{10} used was characterized in terms of its dirt, ash, and nitrogen contents, volatile matter, initial and final plasticities, plasticity retention index (PRI), and Mooney viscosity using standard techniques.[1,16,17] The RE used was first air dried, pulverized, and screened with a sieve of mesh diameter 75 nm. The fine particle RE obtained was characterized in terms of its moisture content, loss on ignition, silica content, iodine adsorption number, oil absorption, pH of aqueous slurry density, metal oxides, and particle size using standard methods,[18–22] in comparism with the characteristics of standard carbon black (N330).

Formulation, compounding, and curing

The formulation given in Table III, using efficient vulcanization system was employed in the rubber compounding. Mixing was done on a laboratory size (160 × 320 mm^2) two-roll mill maintained below 80°C. The cure characteristics were measured using the Mosanto Rheometer, MDR 2000 model. The curing of the test pieces was done by compression molding in a steam heated, hydraulically operated press with a pressure of 150 kg/cm at a temperature of 185°C. The cure times predicted by the Mosanto rheographs were used as guide to obtain vulcanizates for the test specimens.[1]

Measurement of the physicomechanical properties

The tensile properties of the natural rubber vulcanizates obtained were determined using Instron 4301, tensile tester at a cross speed of 500 mm/min. Dumb-bell test specimens of dimension (45 × 5 × 2 mm^3) were used as described in ASTMD412. The specific gravity (S.G.) and hardness of the test pieces were measured with the aid of automatic machines, Mosanto Densitron 2000 and Mosanto Duratron 20001, respectively. The Dunlop resilience, and abrasion resistances of the test specimens were determined using the Wallace Croydon resiliometer 2A, and abrader, the DIN to ISO 4649 Akron to BS 903 part A9 method C, respectively.[23]

RESULTS AND DISCUSSION

The results of the aforementioned tests, are shown in Tables I–VI. The RE-filled vulcanizates were compared with the standard carbon black-filled systems.

Tables I and II show the properties of the natural rubber, SNR_{10}, standard African rubber (SAR_{10}), standard Malaysian rubber (SMR_5) and the fillers, respectively. The properties of SNR followed similar trends in properties with other rubbers, the SMR, and SAR.[1,17,24] It showed lower, dirt, ash, volatile matter, and nitrogen contents indicating high purity.

TABLE II
Physicochemical Properties of the Red Earth and Carbon Black

Test parameter	Red earth	Carbon black (N330)
Moisture content 110°C (%)	1.66	1.45
Loss on ignition 100°C (%)	15.55	96.05
Iodine adsorption number (mg/g)	64.24	79.92
Oil absorption (g/100g)	53.45	54.50
Density (g/cm^3)	2.00	1.80
pH of aqueous shury	6.35	6.65
Silica, $Si0_2$ (%)	55.50	Trace
Iron oxide, Fe_2O_3 (%)	25.30	Trace
Aluminium oxide, Al_2O_3 (%)	1.60	Trace
Sodium oxide, Na_2O (%)	0.30	Trace
Potassium oxide, K_2O (%)	0.10	Trace
Particle diameter range (nm)	15.0–75.0	28.0–32.0

TABLE III
Typical Formulation of the Natural Rubber, Standard Nigerian Rubber Compounds

Ingredient	Phr
Natural rubber (SNR_{10})	100.0
Zinc oxide (ZnO)	4.0
Stearic acid	2.0
Filler[a]	0.0–90.0[b]
Processing oil	2.0
N-Cyclohexylbenzthiazylsuphenamide (CBS)	2.0
Flectol H (TMQ)	1.5
Sulphur	1.5

[a] Filler: The red earth and carbon black (N330) fillers were used in blends (at total filler loading of 50 phr having proportions of the red earth as 0, 10, 20, 30, 40, and 50 phr).
[b] Filler: 0, 10, 30, 50, 70, and 90 Phr. For red earth and carbon black (N330) separately.

TABLE V
Cure characteristics of Standard Nigerian Rubber (SNR10) Filled with Blends of Red Earth and Carbon Black (N330) at Total Filler Loading of 50 phr

Filler blend (% red earth)	0	10	20	30	40	50
Scorch time (s)	28.2	22.8	23.4	22.4	28.8	36.6
Cure time, t_{90} (s)	41.8	32.4	33.0	33.6	34.2	52.8
Maximum torque (Ib-in)	10.26	9.60	11.09	13.43	11.27	7.13

It has high PRI and Mooney viscosity, which are indications of good ageing resistances and rigidity. In comparing the physicochemical properties of the fillers (Table II), RE and carbon black (N330), there were appreciable differences in the values of the moisture content, loss on ignition silica content iodine adsorption number, metal oxides, and mean particle diameter. The loss on ignition is a measure of the carbon content or organic materials present in the sample. The iodine adsorption, member is a measure of the surface area of the filler, the higher it is, the smaller or finer the particle size and the more the reinforcement potential.[4,6] The oil absorption is a measure of the aggregate structure of the filler, the results obtained predicted similar aggregate structures for both fillers, RE and carbon black (N330). RE filler has higher silica content (Table II), and silica itself has been known to be a good reinforcing filler as demonstrated by Ishak and Baker and Gelling.[6,25]

Tables IV–VI summarize the values of the cure characteristics (scorch times, cure times, and maximum torques) of the RE and carbon black (N330) filled SNR_{10}. The fast curing nature of both the RE and carbon black (N330) filled SNR_{10} when compared with other similar works[7,26] may be due to the accelerator used, CBS is very active at curing temperatures.[1] Also, it may be due to the high purity of the rubber in terms of its dirt, moisture, ash and nitrogen contents when compared with other rubbers (Table I). The scorch time and cure time for carbon black (N330) filled SNR_{10}, appear to decrease with increasing filler loading, this means cure enhancement or faster cure rates. A reverse trend was recorded for the RE filled standard Nigeria rubber. This observation may be attributed to the differences in the filler properties. According to Wagner,[27] a faster cure rate is obtained with fillers having low surface area, high moisture content, and high metal oxide contents. The RE filler has high metal oxide contents, low surface area, and cured fast but experienced cure retardation. The reasons for the cure retardation of the RE-filled SNR may either be due to slower interactions between the Fe_2O_3 and SiO_2 particles of the RE (Table II), and the rubber molecules during vulcanization or the existence of two different types of components (Fe_2O_3 and SiO_2) having different particle sizes, surface areas, and surface reactivities. Here, the two different SiO_2 and Fe_2O_3 particles present in the RE filler may contribute to the retardation of the accelerator activity, which in turn can slow down the sulfur reaction leading to increased scorch and cure times.[6] The influence of silica on cure behavior of rubber has been studied by Patterman.[28] The impact of silica on cure retardation is directly proportional to the surface area available for reaction, and the sulfur reactivity is dependent on the amount and particle size of silica present. Therefore, cure retardation can be attributed to silica-accelerator interactions. The silica and iron oxide present in the RE filler here can react with the activator, ZnO in the rubber compound and consequently reduce the activity of the activator, which ultimately slows down the sulfur reactivity.[29]

The RE-carbon black (N330) blend filled vulcanizates gave slight increases in the scorch and cure

TABLE IV
Cure Characteristics of Standard Nigerian Rubber Filled with Red Earth

Filer (phr)	0	10	30	50	70	90
Scorch time (s)	34.2	34.8	35.4	36.6	37.2	39.0
Cure time, t_{90} (s)	43.8	46.2	49.2	52.8	54.0	56.4
Maximum torque (Ib-in)	6.47	6.57	6.67	7.13	6.63	7.61

TABLE VI
Cure Characteristics of Standard Nigerian Rubber, Filled with Carbon Black (N330)

Filler (phr)	0	10	30	50	70	90
Scorch time (s)	34.2	32.4	28.8	28.2	24.0	21.6
Cure time, t_{90} (s)	43.8	44.2	43.2	41.8	40.2	37.8
Maximum torque (Ib-in)	6.47	7.57	11.07	10.26	13.18	22.51

TABLE VII
Physicomechanical Properties of Standard Nigerian Rubber Filled with Red Earth

Filler (phr)	0	10	30	50	70	90
Tensile strength (Mpa)	9.98	14.72	18.90	24.66	16.34	15.90
Modulus, M100 (Mpa)	0.86	0.93	1.15	1.33	1.11	1.21
Elongation at break (%)	835.4	655.5	596.2	498.3	459.5	453.0
Specific gravity (S.G)	1.001	1.001	1.080	1.120	1.174	1.300
Dunlop resilience at 250 (%)	83.6	79.9	76.1	72.4	68.6	65.1
Hardness (IRHD)	40.3	40.4	40.8	44.7	44.9	49.4
Abrasion resistance index	40.4	40.8	41.1	42.0	42.2	43.3

times with increasing filler loading. The improved cure rate over the RE-filled SNR, was a contribution by the carbon black (N330) filler in the blend. The maximum torque (T_{max}) generally increased with increasing filler content for both the RE and the carbon black (N330)-filled SNR, except at 70 phr RE-filled vulcanizate. This may be due to lower filler-rubber interactions, which may be due to the phenomenon of ''phase inversion.'' The higher the filler-rubber interactions, the more the restriction to macro molecular motion and consequently, the higher the torque.[30] This higher filler-elastomer interactions is the reason for the higher torques observed in the carbon black (N330)-filled vulcanizates. The maximum torque for the filler blend natural rubber compounds increased to a maximum at 30 phr RE content then decreased (Table V). This observation could be due to the degree of dilution of the carbon black filler by the RE filler.

Tables VII–IX summarize the physicomechanical properties of the RE and carbon black (N330)-filled standard Nigerian rubber, SNR_{10} vulcanizates. The tensile strength increased up to a maximum at 50 phr RE and carbon black (N330) filled vulcanizates before declining. There were appreciable increases in tensile strength at any filler loading for RE-filled vulcanizates, though the increases were more for the carbon black-filled vulcanizates. The filler blend filled vulcanizates showed marked improvement in tensile strength over the RE-filled vulcanizates (Tables VII and VIII). The inferiority in tensile strength between the blends and carbon black-filled vulcanizates were slight particularly at 10–30% RE filler content in the blends. Increases in tensile strength of polymers mean reinforcement, and it has been reported that substantial reinforcement is normally attainable at 0.02–0.05 μm filler particle size.[31–32] The smaller or finer the filler particle size, the more reinforcing the filler will be.[1,5,33] The modulus is a measure of the stiffness of the rubber article. The moduli for both RE and carbon black-filled vulcanizates generally increased with increasing filler loading, with the exception at 70 and 90 phr RE-filler loadings, which decreased in moduli after reaching maximum at 50 phr filler content. A reduction in modulus was also observed at 30 phr carbon black-filled vulcanizate (Tables VII and IX). The moduli for the filler blends (Table VIII) decreased with increasing RE filler content. These observations may be due to the differences in the filler properties (Table II). It has been noted that modulus of filled polymer articles can be enhanced by improving the surface area, surface reactivity of fillers, filler dispersion, and filler-elastomer interaction.[5,27] In this work, the inferiority in stiffnes of RE-filled vulcanizates over the carbon black-filled types may be due to larger particle diameter of the RE filler, (Table II), and also lower filler-elastomer interaction in the system. Lower filler-elastomer interactions or bonding may arise from the phenomenon of ''phase inversion'' and agglomeration of filler particles.[1,6]

The RE-filled natural rubber vulcanizates gave slightly higher specific gravity at 30–90 phr filler loadings. The vulcanizates arising from the filler

TABLE VIII
Physicomechnical Properties of Standard Nigerian Rubber, Filled with Blends of Red Earth and Carbon Black (N330) at Total Filler Loading of 50 phr

Filler blend (% red earth)	0	10	20	30	40	50
Tensile strength (Mpa)	36.28	34.42	33.48	33.12	25.88	24.66
Modulus, M100 (Mpa)	3.42	3.84	3.49	2.63	1.54	1.33
Elongation at break (%)	324.2	272.1	281.2	353.3	394.8	498.3
Specific gravity (S.G)	1.118	1.123	1.145	1.168	1.176	1.120
Dunlop resilience at 25°C (%)	68.6	72.4	76.1	83.6	83.8	72.4
Hardness (IRHD)	66.9	54.8	59.2	52.6	50.1	44.7
Abrasion resistance index	42.1	41.8	42.5	42.8	43.1	42.0

TABLE IX
Physicomechanical Properties of Standard Nigerian Rubber, Filled with Carbon Black (N330)

Filler (phr)	0	10	30	50	70	90
Tensile strength (Mpa)	9.98	19.74	31.04	36.28	30.48	26.78
Modulus M100 (Mpa)	0.86	1.02	1.75	3.42	7.51	8.40
Elongation at break (%)	835.4	603.2	499.6	324.2	216.8	179.2
Specific gravity (S.G)	1.001	1.001	1.065	1.118	1.178	1.201
Dunlop resilience at 25°C (%)	83.6	77.7	69.9	68.6	58.4	55.0
Hardness (IRHD)	40.3	43.9	52.2	66.9	76.0	78.2
Abrasion resistance index	40.4	40.9	41.6	42.1	42.5	43.5

blends gave highest specific gravity compared to the RE and carbon black-filled systems up to 50 phr filler loading. This may be attributed to the higher density of RE filler (Table II). The elongation at break and Dunlop resilience generally decreased with increasing filler content. These properties many be determined largely by two factors; the stiffness and specific gravity of the vulcanizates. The higher the stiffness and specific gravity the less resilient and also the less strained the elastomer may be. The RE-filled vulcanizates showed higher elongation at break and higher Dunlop resilience than the carbon black-filled vulcanizates. This observation implies superior resilience for the RE-filled elastomer systems, and consequently lowers heat build-up and less hysterisis for the rubber articles. The decrease in elongation at break with increasing filler content may be due to the adherence of the filler particles to the rubber matrix causing stiffening effects on the polymer chain and decreasing stretching.[1] The elongation at break and Dunlop resilience for the filler blends vulcanizates (Table VIII) increased gradually with increasing RE content. This is as a result of the synergistic effect of the RE filler in producing higher elongation (strain) and resilience of the vulcanizates over carbon black filler. The carbon black-filled vulcanizates showed superior hardness and abrasion resistance properties over the RE-filled vulcanizates. This may be due to better filler dispersion, filler-rubber interaction, and smaller particle size of the carbon black filler. The gradation in the physicomechanical properties of the RE and carbon black-filled vulcanizates follow closely the work of Okieimen and Imanah.[7,12]

CONCLUSIONS

This study has revealed the reinforcing potentials of RE as filler in natural rubber. The cure characteristics, and the vulcanizate properties of RE-filled natural rubber investigated showed comparable results with that of standard commercial carbon black (N330) filled vulcanizates. These properties were improved by blending commercial carbon black filler with the RE filler in the natural rubber compounding. Though slight inferiorities in the cure and physicomechanical properties were noticed in the RE-filled rubber systems, the situation could be remedied by employing modern methods of wet and dry grinding techniques and size separation to obtain finer particle RE-filler comparable to carbon black commercial filler. So, RE could be used in blends with carbon black fillers to achieve optimum performance with a consequent reduction in the cost of the final rubber article.

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