# Properties of Vulcanizates from Blends of Natural Rubber and Thioglycolic Acid Modified, Epoxidized, Low-Molecular-Weight Natural Rubber Filled with Carbonized Rubber Seed Shell

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**ABSTRACT:** Vulcanizates from blends of natural rubber and thioglycolic acid modified, epoxidized, low-molecular-weight natural rubber filled with mixtures of carbon black and carbonized rubber seed shell, with semiefficient sulfur vulcanization recipes, were critically investigated and characterized. The investigated properties were the processing and rheological properties (the cure rate, cure time, scorch time, total oscillating disc rheometry torque, and Mooney viscosity), physicomechanical and chemical properties, solvent resistance, solubility, and swelling properties. On the basis of the investigated properties, it was observed that the carbonized rubber seed shell acted as a plasticizer and not as a reinforcing filler such as carbon black. The replacement of carbon black with up to 20% carbonized rubber seed shell produced vulcanizates having processing advantages in time gain and energy consumption, with their physical, chemical, and mechanical properties around the acceptable level for natural rubber compounds but lower than the properties obtained for a 100% carbon black filled vulcanizate. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2830–2838, 2007

**Key words:** modification; processing; reinforcement; rheology; vulcanization

## INTRODUCTION

The wide and commercial acceptance of natural rubber (NR) has been attributed to some of its outstanding properties over some known elastomers.[1] NR is a renewable agricultural resource that does not naturally possess the necessary hardness and modulus required for its commercial acceptability,[2] but the incorporation of various materials (additives or compounding ingredients) increases these aid characteristics to the level desired for NR's demands.[3] The additives, which are added to enhance the processability and properties of rubber vulcanizates, are usually sourced from combinations of any of the following:[4] accelerators, activators, fillers, antioxidants, vulcanizing agents, softeners, plasticizers, and so forth. An alternative way of enhancing the processability or improving some of the inherent limitations of NR is the blending of NR with different rubbers.[4] These developments for the blending of rubbers have gained commercial interest and wider acceptability from rubber users by providing rubber vulcanizates that can combine improved processing characteristics with modifications of the limitation areas of NR. For example, some of the limitations suffered by NR, such as poor resistance to oxygen and ozone and high permeability to gases, were found to improve after the blending of NR with some new generic family of polymers of lesser solubility problems and good processing characteristics, as reported by Perera et al.[5]

These recent developments concerning the use of copolymers and rubber blends have engineered our idea of using modified forms of NR, that is, low-molecular-weight natural rubber (LMWNR), epoxidized, low-molecular-weight natural rubber (ELMWNR), and thioglycolic acid modified, epoxidized, low-molecular-weight natural rubber (TGA-ELMWNR), as copolymers with NR with the aim of making NR available in new forms with new uses, thereby increasing its commercial and technological acceptability by making it more competitive even with synthetic rubbers. Previous studies have taken account of the use of LMWNR[2] and ELMWNR.[6] This study therefore focused on the use of TGA-ELMWNR as a cobase polymer with NR in the presence of carbonized rubber seed shell (CRSS) as a filler in the hope that the presence of sulfur in the structure of thioglycolic acid

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might increase and facilitate the extent of crosslinking in the rubber matrix, thereby enhancing the incorporation of other additives and consequently improving the reinforcing power of CRSS.

The use of fillers as some of the additives in NR compounding is as old as NR itself and has a larger percentage (next to the base polymer rubber) in compounding formulations. Fillers are usually added to rubber to cheapen the cost of production of a given rubber article, to enhance a set of mechanical properties to increase the longevity of the article in service, or to facilitate various shaping processes to which a rubber may be subjected during manufacture.[4] Particulate fillers, of which carbon black (CB) is a notable example, are very important and are widely used as reinforcing fillers in industry. Commercially available CB is obtained from petroleum products, whereas thermal black comes from the thermal cracking of natural gas and furnace black comes from the incomplete combustion of oil feedstocks.[7] Because petroleum refinery residues are limited and unstable, it is of interest to develop fillers from renewable resources that could serve as viable alternatives. The trial of agricultural residues as fillers is of interest from both economic and environmental viewpoints: it converts unwanted, low-value agricultural residues into useful, high-value materials. Agricultural residues are low-cost materials and are readily available in a large quantity for use everywhere; well over 300,000,000 tons are produced annually.[8–10] The use of carbonized forms of cocoa pod husks and ground nut husks as fillers has been previously documented,[10–12] and it is further thought that the use of CRSS, an agricultural waste, as a filler in TGA-ELMWNR compounding could be of technological interest in the development of useful value-added products from locally available renewable resource that are not used in food with the belief that the agricultural residue will be converted into some useful material in the rubber industry. Nevertheless, findings from this study will serve as a new set of data and information for rubber technology.

## EXPERIMENTAL

### Materials

NR latex from a NIG 902 clone, having the characteristics shown in Table I, was obtained from the estates of the Rubber Research Institute of Nigeria (Benin City, Nigeria); crumb rubber, conforming to Technically Specified Rubber 3 but usually denoted in Africa as Standard African Rubber grade 3, was also obtained from the Rubber Research Institute of Nigeria. The reagents used in the preparation and characterization of NR, LMWNR, ELMWNR, and TGA-ELMWNR were analytical-grades, whereas the rubber compounding chemicals were commercial grades.

**TABLE I**
**Some Characteristics of NIG 902 *Hevea* Latex from the Rubber Research Institute of Nigeria**

| Parameter | Value |
|---|---|
| Total solid content (%) | 43.0 |
| Dry rubber content (%) | 39.5 |
| Mechanical stability (s) | 550 |
| Volatile fatty acids (%) | 0.17 |

CRSS was obtained from the Rubber Research Institute of Nigeria. The rubber seed shell was smashed into smaller pieces, dried in an oven to remove any moisture present, and later ground into a fine powder. The powder was then passed through a mesh with a 150-μm particle size. The sieved portion of the powder was carbonized with the procedure described by Ishak and Bakar[11] with a slight modification. In a typical experiment, the rubber seed shell was tightly packed in a 500-mL can, which was placed in a muffle furnace at a temperature ranging between 250 and 300°C for 1.5 h. The upper and lower parts of the can, which produced burnt or uncarbonized rubber seed shell, were discarded. The middle layer, which gave the real CRSS powder, was retained for use.

### Methods

#### Preparation of LMWNR

The method described by Okieimen and Akinlabi[3] was adopted with a slight modification with nitrobenzene as the depolymerizing agent; the extent of depolymerization was determined by size exclusion chromatography (SEC)[5] and viscosity measurements with an Ubbelohde viscometer.[3] The SEC apparatus was designed by Waters-Millipore (Milford, MA) and consisted of a Waters 717 Plus autosampler, a Waters 600E system controller, a Waters 510 HPLC pump and automatic injector, a Waters 486 UV-tunable absorbance detector (220 nm), a Waters R1410 refractometer, and two PLgel 30-cm, mixed columns with a porosity of 20 μm. The installation was computer-controlled by special software (baseline). The column temperature was fixed at 55°C. The cyclohexane flow rate was 0.81 mL/min, and the injected volume was 100 μL (at a concentration of 0.2 mg/mL) for the LMWNR samples and 25 μL for the standard solutions. Calibration was carried out with synthetic poly(*cis*-isoprene) with molecular weights of 3660, 7000, 33,900, 68,500, 108,000, 293,000, 590,000, 963,000, and 3,000,000 g/mol. Before the injection, the solutions were filtered (porosity = 0.45 μm).

#### Epoxidation of LMWNR

The epoxidation of the LMWNR was carried out at about 5°C with performic acid generated *in situ* from

**TABLE II**
**Characteristics of CRSS**

| Parameter | Value |
|---|---|
| Loss on ignition at 875°C | 58.20 |
| Moisture content at 125°C | 6.10 |
| pH of the slurry | 8.1 |
| Iodine adsorption number (g/kg) | 534 |
| Oil adsorption (g/100 g) | 53.97 |
| Particle size (mu) | ≤155 |

the reaction between formic acid and 30% hydrogen peroxide.[12,13] During the epoxidation reaction, the acid was slowly added to the stirred LMWNR solution containing 10 g of LMWNR in chloroform (100 mL) for 30 min. The peroxide (135 mol/100 isoprene units) was introduced dropwise over a period of 30 min. The reaction was allowed to proceed for various periods. The reaction mixture was washed with water and soaked in an aqueous solution of $0.1M$ $Na_2CO_3$ for a period of about 14 h. The modified NR was washed with distilled water and dried in an air-circulating oven at 55°C for 4 h.

### Reaction of ELMWNR with thioglycolic acid

The method described by Okieimen et al.[6] was adopted with a slight modification. In a typical experiment, thioglycolic acid (0.12 mol/L of solvent) was added to a freshly prepared ELWMNR (15.7 mol % epoxide) solution at room temperature over 1 h with occasional stirring. The reaction was allowed to proceed for 17 h more. At the end of this period, the modified material (TGA-ELWMNR) was dried in air for 24 h. The unreacted epoxy groups were estimated from the difference between the epoxide levels (%) of ELMWNR before and after the reaction.

### Compounding of the mixes

The compounding formulation for a semiefficient vulcanization system recommended by Akinlabi et al.[5] was adopted. The formulation used in the compounding is shown in Table II while the recipes for the rubber blends are shown in Table III.

### Processing and cure characteristics

The cure characteristics of the mixes were measured at 170°C with an Alpha ODR 2000 (Alpha Technologies, Kingston, UK) oscillating disk rheometer in accordance with the ISO 3417 method.[12] The respective cure times, as measured by the time to attain 90% cure ($t_{90}$), scorch times, torque, and cure rates were read and recorded from the rheometer as displayed. The Mooney viscosity of the samples was determined with a Wallace MK III shearing disc viscometer (HW Wallace & Co., Ltd., Croydon, UK) according to ISO 289.[14] The results were expressed in terms of ML(1 + 4) at 100°C.

### Mechanical properties

The test specimens were molded in an electrically heated hydraulic press (Techno Loire, Paris, France) at 160°C for 5 min as predetermined from the rheograph. The tensile properties of the vulcanizates were measured with a Mosanto model 1/M tensile tester (Paris, France) at a crosshead speed of 500 mm/min with a dumbbell test specimen (type II) according to ASTM D 412-87 (method A).[16] Thereafter, the tensile strength at break, modulus, and elongation at break were calculated.

### Compression set measurements

A Wallace model/reference no. C2 compression set machine (50 Hz) was used. The compression set was designed to evaluate the extent to which a specimen

**TABLE III**
**Recipes for Compounding Blends of NR with TGA-ELMWNR with CRSS as a Filler**

| Component (phr) | Sample | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | A | B | C | D | E | F | G | H | I |
| NR | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 | 70 |
| TGA-ELMWNR (20% conversion) | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| CB (HAF) | 40 | 38 | 36 | 34 | 32 | 30 | 20 | 10 | — |
| CRSS[a] | — | 2.0 | 4.0 | 6.0 | 8.0 | 10.0 | 20.0 | 30.0 | 40.0 |
| Zinc oxide | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 |
| Sulfur | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Stearic acid | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| MBTS[b] | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Flectol H[c] | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |

[a] Measured by the percentage of CB (i.e., 0, 5, 10, 15, 20, 25, 50, 75, and 100% CB).
[b] Dibenzothiazyl disulfide.
[c] Polymerized 1,2-dihydro-2,2,4-trimethyl quinolene.
HAF, high abrasion furnace.

failed to return to its original thickness when subjected to a standard compression load (1N) for a given period (24 h) at a given temperature (100°C).[17] The difference between the original thickness and the recovered thickness was expressed as a percentage of the original thickness. This was expressed mathematically as follows:

$$\text{Compression set (\%)} = \frac{(t_0 - t_r)100}{t_0} \qquad (1)$$

where $t_0$ is the initial thickness and $t_r$ is the recovered thickness.

### Hardness test

The hardness test of rubber is the relative resistance of a surface to indentation by an indicator of a specified dimension under a specified load. The hardness of the vulcanizate was determined by the adoption of the standard dead-load method described in BS 903 Part A26.[18] The standard dead-load method of measurement covers rubbers in the international rubber hardness degree (IRHD) range of 30–85.

### Abrasion resistance

A Wallace Akron abrasion tester was used in accordance with the BS method.[19] The angle between the test specimen and the wheel was adjusted to 15°. The abrasion was carried out for four sets of 1000 revolutions, and the material loss for each run was noted. The specimen was reweighed between each test run. From the mean of the five runs, the volume of rubber loss per 1000 revolutions of the abrasive wheel was calculated.

The results were expressed as follows:

$$\text{Abrasion resistance index} = \frac{[S]100}{T} \qquad (2)$$

where $S$ is the volume loss per 1000 revolutions of the abrasive wheel (calculated from the mean of five runs on standard rubber) and $T$ is the volume loss per 1000 revolutions of the abrasive wheel (calculated from the mean of five runs on the sample rubber).

### Crosslink density

The chemical crosslinking density ($\rho RT/M_c$, where $\rho$ is the density of the rubber hydrocarbon, $R$ is a constant (8.314 J/mol), $T$ is the temperature in Kelvin, and $M_c$ is the molecular mass between crosslinks) was calculated from the shear modulus ($G$), whereas $M_c$ was calculated with the Flory–Rehner equation:[20]

$$\ln(1 - V_2) + V_2 + \chi V_2^2 + \rho V_1 V_2^{1/3}/M_c = 0 \qquad (3)$$

$$\rho/M_c - G/RT \qquad (4)$$

where $V_1$ is the molar volume of the solvent, $V_2$ is the volume fraction of rubber in the swollen sample, $\chi$ is the polar solvent interaction parameter ($\chi = 0.44 + 0.18V_2$), and $\rho/M_c$ is the crosslinking density.

### Swelling and solubility experiments

The resistance of the vulcanizates to acetone, toluene, mineral oil, n-hexane, and cyclohexane were determined with the methods described in ASTM D 3610[21] with a slight modification, whereas the resistance of vulcanizates to mineral oil was determined with the method described by De et al.[22] Three different shapes of the cured samples (triangle, square, and rhombus) were cut from a 1-mm-thick mold and weighed before each sample was submerged in its respective solvent in airtight bottles maintained at 25°C for 72 h. The experiments were carried out in triplicate. At the end of the swelling, each sample was removed from the solvent and carefully blotted to remove excess liquid on the surface, and the weights were immediately taken. Thereafter, the sample was further dried to a constant weight. The percentage increase in weight of the sample was calculated as the swelling, whereas the percentage loss in weight after it dried to a constant weight was calculated as the solubility:

$$\text{Swelling (\%)} = \frac{W_2 - W_1}{W_2} \times 100 \qquad (5)$$

$$\text{Solubility (\%)} = \frac{W_1 - W_3}{W_1} \times 100 \qquad (6)$$

where $W_1$ is the initial weight of the sample, $W_2$ is the weight after swelling, and $W_3$ is the weight after drying to a constant weight.

## RESULTS AND DISCUSSION

The characteristics of CRSS are shown in Table II, the recipes for compounding blends of NR with TGA-ELMWNR using CRSS as a filler are shown in Table III, whereas the rheological characteristics of the vulcanizates are shown in Table IV.

The time for an increase of 1 unit of torque above the minimum torque ($M_L$), represented as $t_1$, decreased from mix A (vulcanizates with 100% CB) to mix I (vulcanizates with 100% CRSS). The highest value of 0.57 min was observed for mix A, whereas the shortest time of 0.40 min was observed for mix I; this showed a 29.8% reduction from mix A to mix I, signifying that as the ratio of CRSS increased, $t_1$ decreased. The scorch time (i.e., the time to an increase of 2 units of torque above $M_L$), denoted $t_2$, also decreased from mix A to mix I, with the highest time of 1.32 min for mix A and the shortest time of 1.03 min

**TABLE IV**
**Rheological Characteristics of the Vulcanizates**

| Mix | $t_1$ (min) | $t_2$ (min) | $t_{90}$ (min)[a] | $M_L$ (N m) | $M_H$ (N m) | ODRT (N m)[b] | Cure rate (%/min)[c] |
|---|---|---|---|---|---|---|---|
| A | 0.57 | 1.32 | 5.26 | 6.92 | 13.31 | 5.82 | 25.38 |
| B | 0.53 | 1.30 | 5.23 | 6.80 | 13.04 | 5.68 | 25.45 |
| C | 0.51 | 1.29 | 5.18 | 6.74 | 12.76 | 5.49 | 25.71 |
| D | 0.48 | 1.29 | 5.11 | 6.69 | 12.41 | 5.22 | 26.18 |
| E | 0.48 | 1.28 | 5.07 | 6.65 | 12.20 | 5.06 | 26.39 |
| F | 0.47 | 1.24 | 5.17 | 6.49 | 11.88 | 4.92 | 25.45 |
| G | 0.45 | 1.19 | 5.21 | 6.14 | 10.91 | 4.35 | 24.88 |
| H | 0.43 | 1.16 | 5.22 | 5.59 | 9.74 | 3.79 | 24.63 |
| I | 0.40 | 1.03 | 5.20 | 4.86 | 8.46 | 3.29 | 23.98 |

[a] Corresponds to the torque obtained.
[b] Calculated with the following formula: $[90(M_H - M_L) + M_L]/100$.
[c] Calculated with the following formula: $100/(t_{90} - t_2)$.

for mix I; this gave a 22.0% reduction in $t_2$. $t_{90}$, as shown in Table IV, was highest in mix A, with a value of 5.26 min, whereas the lowest $t_{90}$ value was observed for mix E, with a value of 5.07 min. The $t_{90}$ results showed that the substitution of CB with 20% CRSS reduced the cure time by about 3.6%. $t_2$ and $t_{90}$ are very important and useful parameters for rubber technologists. They give crucial processing information about the material. Materials of longer $t_2$ and shorter $t_{90}$ are generally preferred, in that if a material has a longer $t_2$, it does not scorch easily; this means that it gives room for better rearrangement and alignment of the rubber matrix before the setting of the vulcanizate commences. However, a shorter $t_{90}$ means that the material cures within a short time, thereby bringing efficiency through the reduction of the cure time and cost.

The results of $M_L$ and the maximum torque ($M_H$) for the vulcanizates showed mix I having the lowest $M_L$ and $M_H$ values of 4.86 and 8.46 N m, respectively whereas mix A had the highest $M_L$ and $M_H$ values of 6.92 and 13.31 N m, respectively. This gave a 29.77% reduction in $M_L$ from mix A to mix I and a 36.44% reduction in $M_H$ from mix A to mix I. This trend shows that as the ratio of CRSS increased, the $M_L$ and $M_H$ values also decreased. The results of the total oscillating disc rheometry torque (ODRT) followed a similar pattern of $M_L$ and $M_H$, with the highest value of 5.82 N m for mix A and the lowest value of 3.29 N m for mix I, giving a 43.47% reduction from a 100% CB filled vulcanizate to a 100% CRSS filled vulcanizate; this implies that CRSS has tendencies to reduce the torque required for a system, thereby leading to a reduction in the energy consumption and hence a reduction in the total processing cost.

The results for the cure rate in Table IV show that mix E had the highest value of 26.39%/min, which could have been caused by synergism of the filler admixtures; this was followed by mix D, with a value of 26.18%/min, whereas the lowest value of 23.98%/min was observed for mix I. Mix A gave a cure rate of

25.38%/min. These results showed that there was a 3.83% increase from mix A to mix E, whereas there was a 9.1% decrease from mix E to mix I, thereby showing that mix E had the best cure rate. It must be mentioned that materials with high cure rates have better crosslinking and polymer network formation in the rubber matrix. In NR processing, materials of low cure times ($t_{90}$) and high cure rates are preferred and considered because of processing advantages in time gained and cost reduction. Looking at all the rheological results in Table IV, we can infer that the gradual replacement of CB with CRSS to about 20% will not have any serious deleterious effect on the rheological properties of vulcanizates but instead lead to efficiency of the system as a result of a well-crosslinked vulcanizate within a shorter time, as indicated by the results for $t_{90}$ and the cure rate. Ismail and China[23] earlier documented that at a high vulcanization temperature in a semi-efficient vulcanization (EV) system, there is a possibility of having rubber-bound intermediates and their subsequent conversion to more crosslinks, thereby leading to a high cure rate of the vulcanizates. It was also shown by Akinlabi et al.[7] that the formation of strong rubber-bound intermediates and their conversion to crosslinks are largely enhanced by the cure time, cure rate, and total ODRT. This assertion was further explained by Baker et al.:[24] in semiefficient vulcanization systems, despite the predominantly polysulfidic crosslinks from the high-sulfur vulcanizates, which harden rapidly because of the byproducts containing sulfur, the rheological results always lead to an increase in the cure rate. This is a sign of a well-crosslinked material. It can therefore be inferred from the results in Table IV that replacing CB with about 20%CRSS will lead to a well-crosslinked material enjoying processing advantages in time, cost, and energy reductions.

Looking at the crosslinking properties of the vulcanizates, as shown in Table V, we found that the results for $G$ were highest for mix A, with a value of

**TABLE V**
**Crosslinking Properties of the Vulcanizates**

| Mix | $G$ (MN/m$^2$) | $(\rho/M_c) \times 10^{-4}$ | $M_c$ | $V_2$ |
|-----|------|------|------|------|
| A | 0.437 | 1.8 | 5.9 | 0.8 |
| B | 0.436 | 1.8 | 5.7 | 0.8 |
| C | 0.433 | 1.7 | 5.6 | 0.8 |
| D | 0.432 | 1.6 | 5.6 | 0.7 |
| E | 0.430 | 1.6 | 5.4 | 0.7 |
| F | 0.425 | 1.5 | 5.2 | 0.7 |
| G | 0.417 | 1.3 | 4.9 | 0.7 |
| H | 0.406 | 1.2 | 4.5 | 0.7 |
| I | 0.381 | 1.0 | 4.0 | 0.7 |

0.437 MN/m$^2$, whereas mix I had the lowest value of 0.381 MN/m$^2$. The crosslinking density was calculated from the volume fraction of the rubber in the swollen gel ($V_2$) with the Flory–Rehner equation [eq. (3)], and it was found to be decrease from mix A to mix I. $M_c$ was also found to decrease as the ratio of CRSS in the mix increased. The volume fraction of the rubber that took part in the reaction was determined through the calculation of $V_2$. The results in Table V show that the $V_2$ values observed for all the vulcanizates were very close, showing that the greater part of the rubber took part in the reaction, implying well-crosslinked and filled vulcanizates, and signifying the efficiency of the semi-EV method used and the compatibility of the two fillers. Technologically, a well-crosslinked polymer should contain at least two crosslinks per chain joining it to other chains to form a two- or three-dimensional molecular network as a result of the interaction between the chains and junction unit via a covalent bond. These crosslinking results were found to be in line with the above and also with Einstein's[25] theory on the increase in the crosslinking that fine particle fillers cause when incorporated into a polymer, which was derived from the increase in the viscosity of materials carrying rigid particles in suspension. This theory, after being successfully studied by Einstein, looked simple in conception but was applied to elastic behavior, with the modulus related to the viscosity and particle shape. Mullins[26] later

modified Einstein's theory with particular reference to filled-elastomer behavior, from which it was concluded that a uniform distribution and dispersion of fillers in a rubber matrix will give rise to a well-crosslinked material of good physicomechanical properties. The crosslinking properties of all the vulcanizates used in this study were observed to be in line with the aforementioned assertions, signifying good compatibility between CB and CRSS with a well-crosslinked rubber network.

The mechanical properties obtained from the vulcanizates are shown in Table VI. As the ratio of CRSS increased from mix A to mix I, the measured parameters [tensile strength, modulus at 50% elongation (M50), modulus at 100% elongation (M100), modulus at 300% elongation (M300), and elongation at break] were decreased. The tensile values ranged from 16.1 MPa for 100% CB to 7.8 MPa for 100% CRSS. It was initially thought that the substitution of CB with CRSS might produce a drastic reduction in the tensile strength, but the results showed that there was about a 51.55% reduction from mix A to mix I, an 18.0% reduction from mix A to mix F, and a 13.67% reduction from mix A to mix E. This observation suggests that even if 25% CB is replaced with CRSS, there will be only an 18.0% reduction in the tensile strength, and if 20% CB is replaced, there will be a 13.67% reduction; this shows an effective way of converting an agricultural waste into a useful material, provided that a high-tensile-strength product is not compulsorily anticipated or desired. Technologically, the standard accepted tensile-strength level for an NR mix is between 27.5 and 6.5 MPa. Looking at the tensile strengths obtained for all the mixes, we can see that the results are still within the accepted technologically permitted level. Hence, it can be inferred that if parts of CB are replaced with CRSS, the vulcanizates will still have tensile strengths that can provide technological advantages in some applications.

The values of M50, M100, and M300 decreased with an increase in the ratio of CRSS. The results in Table VI show that the highest M50 value of 2.6 MPa was

**TABLE VI**
**Mechanical Properties of the Vulcanizates**

| Mix | Tensile strength (MPa) | Modulus (MPa) | | | Elongation at break of the original length (%) |
|-----|------|------|------|------|------|
| | | 50% elongation | 100% elongation | 300% elongation | |
| A | 16.1 | 2.6 | 6.6 | 10.1 | 912 |
| B | 15.6 | 2.5 | 6.3 | 9.6 | 893 |
| C | 15.0 | 2.3 | 6.2 | 9.4 | 877 |
| D | 14.5 | 2.2 | 5.8 | 8.9 | 868 |
| E | 13.9 | 2.0 | 5.6 | 8.5 | 849 |
| F | 13.2 | 1.9 | 5.3 | 7.9 | 814 |
| G | 12.1 | 1.5 | 4.9 | 7.1 | 785 |
| H | 10.2 | 1.3 | 4.2 | 6.4 | 733 |
| I | 7.8 | 1.2 | 3.4 | 5.7 | 671 |

**TABLE VII**
**Physical Properties of the Vulcanizates**

| Mix | IRHD | Compression set (%) | Abrasion resistance (%) | Mooney viscosity[a] |
|-----|------|---------------------|--------------------------|---------------------|
| A | 55 | 45 | 59 | 80 |
| B | 54 | 45 | 57 | 77 |
| C | 52 | 44 | 57 | 73 |
| D | 52 | 43 | 56 | 71 |
| E | 49 | 43 | 54 | 69 |
| F | 46 | 43 | 53 | 66 |
| G | 44 | 42 | 50 | 62 |
| H | 40 | 40 | 47 | 59 |
| I | 35 | 40 | 41 | 53 |

[a] $ML(1 + 4)$ at 100°C.

observed in mix A, whereas the lowest M50 value of 1.2 MPa was observed in mix I, showing a 53.9% reduction in M50 from mix A to mix I. For M100, there was a 48.48% reduction from mix A to mix I, whereas M300 gave a 43.56% reduction from mix A to mix I. It was also observed that as the elongation percentage increased (from M50 to M100 to M300), the reduction percentage decreased (M50, 53.9%; M100, 48.48%; and M300, 43.56%). This trend also influenced the elongation at break: mix A had the highest value of 912%

and mix I had the lowest value of 671%; this gave a reduction of 26.4% from mix A to mix I. The results for the modulus and elongation at break suggested that CRSS acted as a low reinforcing filler in comparison with CB, a high reinforcing filler. When a filler is used to enhance certain mechanical properties, it is essential that such a filler must be uniformly distributed within the rubber. Some fillers have been found to impart high stiffness or hardness to rubber products. This result has shown that mixes with a higher

**TABLE VIII**
**Swelling Results for the Vulcanizates**

| Solvent | Mix | $W_1$[a] | $W_2$[b] | $W_3$[c] | Swelling (%) | Solubility (%) |
|---------|-----|------|------|------|--------------|----------------|
| Toluene | A | 0.57894 | 0.77305 | 0.52197 | 25.11 | 9.84 |
| | B | 0.59879 | 0.79711 | 0.54065 | 24.88 | 9.71 |
| | C | 0.60002 | 0.79610 | 0.54266 | 24.63 | 9.56 |
| | D | 0.58945 | 0.77867 | 0.53457 | 24.30 | 9.31 |
| | E | 0.58847 | 0.77471 | 0.53474 | 24.04 | 9.13 |
| | F | 0.57982 | 0.76012 | 0.52740 | 23.72 | 9.04 |
| | G | 0.57699 | 0.75384 | 0.52737 | 23.46 | 8.60 |
| | H | 0.57775 | 0.75159 | 0.52951 | 23.13 | 8.35 |
| | I | 0.59816 | 0.77522 | 0.54971 | 22.84 | 8.10 |
| Acetone | A | 0.58114 | 0.71262 | 0.53843 | 18.45 | 7.35 |
| | B | 0.59312 | 0.72668 | 0.54988 | 18.38 | 7.29 |
| | C | 0.57831 | 0.70819 | 0.53667 | 18.34 | 7.20 |
| | D | 0.57923 | 0.70880 | 0.53816 | 18.28 | 7.09 |
| | E | 0.58523 | 0.71553 | 0.54497 | 18.21 | 6.88 |
| | F | 0.56952 | 0.69454 | 0.53131 | 18.00 | 6.71 |
| | G | 0.59163 | 0.71896 | 0.55317 | 17.71 | 6.50 |
| | H | 0.58883 | 0.71443 | 0.55162 | 17.58 | 6.32 |
| | I | 0.57391 | 0.69413 | 0.53896 | 17.32 | 6.09 |
| n-Hexane | A | 0.59913 | 0.71021 | 0.55773 | 15.64 | 6.91 |
| | B | 0.58972 | 0.69781 | 0.54997 | 15.49 | 6.74 |
| | C | 0.58769 | 0.69352 | 0.54902 | 15.26 | 6.58 |
| | D | 0.57981 | 0.68229 | 0.54264 | 15.02 | 6.41 |
| | E | 0.60008 | 0.70424 | 0.56294 | 14.79 | 6.19 |
| | F | 0.59002 | 0.69032 | 0.55503 | 14.53 | 5.93 |
| | G | 0.57823 | 0.67471 | 0.54533 | 14.30 | 5.69 |
| | H | 0.58888 | 0.68466 | 0.55702 | 13.99 | 5.41 |
| | I | 0.60004 | 0.69546 | 0.56932 | 13.72 | 5.12 |

[a] Weight after extraction.
[b] Weight after swelling at 25°C for about 6 h.
[c] Weight after drying in a vacuum to a constant mass.

ratio of CB are more flexible and elastic. It was initially thought that the presence of sulfur in thioglycolic acid might increase the tensile strength of vulcanizates (because sulfur enhances crosslinking), but this was not the case, possibly because of the acid present in TGA-ELMWNR, which might have militated against the extent of crosslinking in the system by forming weaker bonds, which resulted from the weak power of the acid.

The physical properties of the vulcanizates, as shown in Table VII, depict the softening effect of CRSS on the vulcanizates. The hardness, compression, abrasion, and Mooney viscosity were decreased as the ratio of CRSS increased. The hardness result decreased from mix A to mix I with a 36.36% reduction, the compression set result decreased 11.11%, and the abrasion resistance decreased 30.51%, whereas the Mooney viscosity decreased 33.75%. This trend confirmed the softening influence of CRSS on the vulcanizates even more so, in that vulcanizates with a higher loading of CB gave higher values. Some workers[4,9,26] have previously shown the successful usage and influence of fillers (clays, silicas, CB, and coca pod husks) on the physical properties of vulcanizates. Hary and John[27] stated that the addition of any particulate filler can reduce some of the physical parameters of a polymer more or less in proportion to the volume present. The only exception to this is CB in rubbers, which have hydrocarbons in the main-chain structure and fibrous fillers. Fibrous fillers behave exceptionally whenever their volume loading is sufficiently high, the length-to-diameter ratios are sufficiently large, and the fibers themselves are strong. All these will influence the tensile strength, stiffness, hardness, and flexural strength because they will be determined almost wholly by the fiber or filament. The results of the physical properties still confirm CRSS not to be a reinforcing filler as CB is. However, the substitution of some parts of CB with CRSS will lead to some processing advantages without any deleterious effect on the vulcanizate.

The swelling and solubility results are shown in Table VIII. The vulcanizates from mix A generally showed better resistance in all the solvents, which signified well-crosslinked vulcanizates and conformed to the results for the crosslinking properties. Basically, a well-crosslinked polymer will show resistance to solvents because of the difficulty of the solvent power in penetrating the well-crosslinked matrix of the rubber network. The resistance of vulcanizates to solvents is also enhanced by the uniform distribution and dispersion of fillers in the rubber matrix. The swelling of NR has been documented to be influenced by various factors, such as the solvent type, crosslink density, amount and type of filler, and type of elastomer.[13] The swelling results in Table VIII follow the aforementioned assertion because the results from each of the solvents are different. The vulcanizates were generally found to be easily penetrated by toluene, followed by acetone, then n-hexane, and cyclohexane, whereas mineral oil was the least. The observed solvent penetration sequence was a result of the penetrating power and molecular mass of the solvents used. Moreover, the swelling of the vulcanizates for longer periods (≥96 h) in acetone and toluene showed the vulcanizates from all the mixes turning into a slurry, which could have been due to the prolonged penetrating power of the solvents into the vulcanizates by the weakening of the resistance of the vulcanizates through their segmental packing and crosslinked network matrix. Generally, this result still shows CB to be a better filler because vulcanizates with a higher loading of CB were found to be more solvent resistant, and this signified a well-crosslinked material.

## CONCLUSIONS

Vulcanizates with higher ratios of CRSS exhibited lower tensile strengths and lower elongations at break. The replacement of CB with 15% CRSS as a filler in blends of NR and TGA-ELMWNR led to processing advantages in time gain, cost reduction, and energy conservation without any serious deleterious side effects on the vulcanizates. CRSS also was found to be compatible with CB as a filler in NR compounds; hence, the use of admixtures of CRSS with CB is recommended whenever a material of high tensile strength is not anticipated or desired. Toluene was also found to penetrate all the vulcanizates more than acetone, more than n-hexane, more than cyclohexane, and more than mineral oil. The set of data presented in this study has opened up a new area and challenges in the technology of NR because the data represent a new set of information.

## References

1. UNIDO—Development of the Applications of Liquid Natural Rubber; UNIDO Project Final Report; 1989.
2. Akinlabi, A. K.; Okieimen, F. E.; Aigbodion, A. I. Polym Adv Technol 2005, 16, 318.
3. Okieimen, F. E.; Akinlabi, A. K. J Appl Polym Sci 2002, 85, 1070.
4. Akinlabi, A. K.; Farid, A. F.; Fasina, A. B.; Okieimen, F. E. Nigerian J Appl Sci 2000, 18, 63.
5. Perera, M. C. S.; Elix, J. A.; Bradbury, J. H. J Polym Sci 1988, 26, 637.
6. Okieimen, F. E.; Akinlabi, A. K.; Aigbodion, A. I.; Bakare, I. O. J Polym Mater 2003, 20, 403.

7. Akinlabi, A. K.; Okieimen, F. E.; Egharevba, F.; Malomo, D. Mater Des 2006, 27, 783.
8. Studebaker, M. Rubber Chem Technol 1957, 30, 1400.
9. Boonstra, B. B.; Taylor, G. L. Rubber Chem Technol 1965, 38, 943.
10. Imanah, J. E.; Okieimen, F. E. J Appl Polym Sci 2003, 90, 3718.
11. Ishak, Z. A. M.; Baker, A. A. Eur Polym J 1995, 31, 259.
12. Okieimen, F. E.; Akinlabi, A. K.; Aigbodion, A. I.; Bakare, I. O.; Oladoja, N. A. Nigerian J Appl Sci 2001, 19, 11.
13. Akinlabi, A. K.; Okieimen, F. E.; Aigbodion, A. I. J Appl Polym Sci 2005, 98, 1733.
14. Standard African Rubber Manual No 2: Determination of Cure Characteristics with the Rheometer; ISO-3417; International Organization for Standardization: 1998.
15. Standard African Rubber Manual No 2: Determination of Mooney Viscosity of Natural Rubbers; Professional Association of Natural Rubber in Africa (ANRA), Abidjan, Côte d'Ivoire. ISO-289; International Organization for Standardization: 1998.
16. Determination of Mechanical Properties of Rubber Compounds; ASTM D 412-87; American Society for Testing and Materials: West Conshohocken, PA, 1992.
17. Method for Determination of Compression Set at Ambient, Elevated or Low Temperatures; HW Wallace & Co., Ltd., Croydon: UK. BS 903 Part A6; 1992.
18. Method for Determination of Hardness; HW Wallace & Co., Ltd., Croydon: UK. BS 903 Part A26; 1995.
19. Method for Determination of Abrasion Resistance; HW Wallace & Co., Ltd., Croydon: UK. BS 903 Part A9; 1988.
20. Flory, P.; Rhener, J. J Chem Phys 1943, 11, 521.
21. Swelling and Solubility Procedures; ASTM D 3610; American Society for Testing and Materials: West Conshohocken, PA, 1992.
22. De, P. P.; De, S. K.; Alex, K. J Polym Sci Part C: Polym Lett 1989, 27, 361.
23. Ismail, H.; China, H. H. Eur Polym J 1998, 34, 1857.
24. Baker, H. C.; Barker, L. R.; Farlie, E. D.; Greensmith, H. W. Transactions 1966, 42, 210.
25. Einstein, A. Anal Phys 1906, 19, 289.
26. Mullins, L. In The Chemistry and Physics of Rubber-Like Substances; Bateman, L., Ed.; Maclaren: London, 1963.
27. Hary, S. K.; John, V. M. Handbook of Fillers for Plastics; Van Nostrand Reinhold: New York, 1987.