

# **Physico-mechanical properties of rubber seed shell carbon – filled natural rubber compounds**

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## **Abstract**

Samples of rubber seed shells were carbonized at varying temperatures (100, 200, 300, 400, 500, 600, 700, & 800°C) for three hours each and sieved through 150µm screen. The portion of the rubber seed shell carbon that passed through the screen was characterized in terms of loss on ignition, surface area, moisture content, pH, bulk density, and metal content and used in compounding natural rubber. The characterization shows that the pH, conductivity, loss on ignition and the surface area increases as the heating temperature increases, unlike the bulk density which decreases. The compound mixes were cured using efficient vulcanization system. Cure characteristics and physico-mechanical properties of the vulcanisates were measured as a function of filler loading along with that of N330 carbon- black filled natural rubber vulcanisate. The results of the cure characteristics showed that the cure times, scorch times and the torque gradually increased, with increasing filler content for rubber seed shell carbon-filled natural rubber, with filler obtained at carbonizing temperature of 600°C tending to show optimum cure indices. The physico-mechanical properties of the vulcanisates increase with filler loading. The reinforcing potential of the carbonized rubber seed shell carbon was found to increase markedly for the filler obtained at the temperature range 500-600°C and then decrease with further increase in temperature.

**Keywords:** Rubber seed shell carbon, natural rubber, Physico-mechanical properties, Vulcanisates

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## **INTRODUCTION**

Fillers in rubber compounds play a major role in the physico-mechanical properties, and exercise control over cost of the products [1]. It is well established that carbon black is one of the most important classical reinforcing filler, especially for the rubber industry. However, carbon black is expensive and petroleum from which it is derived is non renewable [2]. Therefore, considerable research and developments efforts are being carried out to investigate the possibility of replacing this filler with renewable raw materials as fillers [3].

The use of carbon from agricultural by-products (maize cob groundnut husk, cassava peel, cocoa pod husk, plantain peel, rubber seed shell, etc) to produce vulcanisate materials that are competitive with synthetic composites is gaining attention over the last decade, because of availability of materials, easy processing, low cost, high volume applications and less abrasive to equipment [3-4].

Agricultural residues as by-products and co-products of agriculture and processing of agricultural products represent a large feedstock of underutilized resources which can be used directly or converted by fairly simple chemical processes into higher value added materials.

Rubber seed shell is an agricultural by-product of the rubber tree. The economic importance of the rubber tree has largely focused on the rubber latex with little or no attention paid to the potentials usefulness of its by-product. While significant progress has been made in the development and utilization of modified agricultural by-product in water and wastewater treatment, [5-6] little information exists on the potential for the application of these by-product as extender and/or filler in the processing of polymers [7-8].

Studies of previous works [5-8] reveal that the temperature at which carbonization of an agricultural by products is carried out could affect the characteristics of the carbon obtained and therefore, the physico-mechanical properties of the rubber vulcanisates. Against this background, the present research work was undertaken, with an objective to explore the influence of carbonizing temperature of rubber seed shell on the physico-mechanical properties of the carbon and on the rubber reinforcement potential of the carbon along with commercial grade N330 carbon. The N330 carbon black was chosen because of its availability and quality of end products.

## **MATERIALS AND METHODS**

Rubber seeds were obtained from the Rubber Research Institute of Nigeria, Iyanomon, Benin City, Nigeria. Natural Rubber used for the study was procured from the Famad Rubber Factory, Benin City, Nigeria. All the other reagents used were of commercial grade, while the industrial grade carbon black (N330) filler was obtained from the Warri Refinery and Petrochemical Company, Warri, Nigeria.

### **Preparation of the rubber seed shell carbon**

The rubber shells were separated from the seeds, air-dried and reduced to small sizes. Eight samples of 1kg each were weighed and heated to temperatures: 100, 200, 300, 400, 500, 600, 700, and 800°C and then three hours using the METM-525 Muffle furnace. The carbonized shells were then milled to fine powder, and sieved through a mesh size of 150µm. The carbon particles that passed through the screen were collected, characterized and used for compounding.

### **Characterization of the rubber seed shell carbon and the N330 carbon black**

The rubber seed shell carbon (RSSC) and the N330 carbon black were characterized as follows; Loss of ignition was determined gravimetrically [9], moisture content was determined by method described in ASTM D 1509 [10], the bulk density was determined according to the method described in ASTM D [11], the pH was determined using ASTM D 1512 method [12], the method used for surface area measurement of the fillers is iodine adsorption number [13], conductivity was determined using the pH- conductivity meter. The calcium and magnesium contents of RSSC were determined by complexometric titration, while the sodium and potassium content were determined by flame photometry and are given in Table 1.

### **PREPARATION OF THE NATURAL RUBBER VULCANISATE**

Formulation of mixes is shown in Table 2. Natural rubber was masticated on the mill for five minutes followed by addition of the ingredients. An efficient vulcanization system was chosen. The Vulcanisate materials were prepared in a laboratory two-roll mill (160 x 320mm) maintained at a temperature below 80°C through an attached water cooling system.

## **CURE CHARACTERISTICS OF NATURAL RUBBER COMPOUNDS**

The cure characteristics were measured using the Mosanto Rheometer, MDR 2000 model. The cure times predicted by the Mosanto rheographs were used as guide to obtain vulcanisates for the test specimens.

### **DETERMINATION OF VULCANISATE PROPERTIES**

The curing of test pieces was done by compression molding. The curing was carried out at 140°C.

The tensile strength, modulus and elongation at break were measured using a Monsanto instron tensometer in accordance with ASTM D412-87 method A [14]. Dumbbell test pieces of dimension (45 x 5 x 2mm) were used.

Compression set of the Vulcanisates were determined using the method described in ASTM D385 [15]

The hardness of rubber Vulcanisate was determined using the Wallace hardness tester model C8007/25 in accordance with ASTM 1415 [16]. Abrasion resistance measurement was based on DIN to ISO 4649 Akron to BS 903 Part 49 method C [17]. The measurement of the flex fatigue was carried out in accordance to the procedure described in ASTM D430 [18], using the Du Pont model C82075.

## **RESULTS AND DISCUSSION**

### **Characteristics of the rubber seed shell**

The characteristics of the rubber seed shell carbon are given in Table 3, as well as the characteristics of N330 carbon black.

The trend of the pH of the rubber seed shell carbon as a function of the carbonizing temperature given in Table 3 varied over a range of 4.79 – 8.77. The results show a progressive increase in pH with increase carbonization temperature. The possible reason for the trend in the pH of carbon could be as a result of the metal content of the RSSC, whose effect or presence hitherto, was shielded by the influence of the inorganic volatiles present as the carbonization was being done at lower temperature, however, pH at acidity level tends to slow the cure rate, and hence reduce the cross link density which informs the choice of fast accelerator and

activators in the mixing formulation. From the table, the pH of the carbon black is 6.50, which is of close value to that of the rubber seed shell carbon at 600°C.

From the Table 3; the electrical conductivity of RSSC increases with the rising of temperature. When temperature reaches 600°C, the resistance in RSSC becomes very small, meaning good conductivity, while above 600°C the conductivity descended slightly. Probably, this is because the volatiles in RSSC released completely at that temperature. The Conductivity of the carbon black N330 from the table is quite superior to that of the rubber seed shell carbon, suggesting very low resistance and very good conductivity which could be as a result of the particle size and the conducting power of its ions in solution. High conductivity in N330 based elastomer composites is primarily due to its structure and N330's ability to retain that structure even when dispersed in elastomer matrix.

The bulk density of the RSSC samples given in the Table3 varied from between 0.611 – 0.785 g/ml. Bulk density is principally influenced by the particle size and structure of the fiber and the lower the particle size the lower the bulk density and therefore better the interaction between the polymer matrix and the reinforcing fiber, it will thus enhance vulcanisate processing and improve the quality of the end product as the desirable properties for fibers include excellent tensile strength and modulus, high durability, low bulk density, good moldability and recyclability [19]. From the Table 3, it shows that at high temperature, the bulk density reduces showing that the interstitial spaces (micropores) in the carbon residue is opened and thus resulting in easy compaction and interaction with the polymer matrix.

The iodine adsorption number from the table reveals that as the filler carbonizing temperature increases the amount of iodine adsorbed per 100gram of the material increases. One important application of iodine adsorption number is that it elicits the surface area of the material and indicates the macrostructure of filler; reflects its reaction and adsorption abilities [19]. Like wood fiber, at high temperature, all kinds of porosities will form inside RSSC, which bring RSSC a certain specific surface area, reaction and adsorption capacity. The maximum iodine adsorption number (66.75mg/100g) represents the adsorbed iodine, which is formed when the carbonizing temperature reaches 600°C; eliciting the fact that maximum surface area occurs at this temperature; the surface area value is much smaller when carbonizing under low temperature

(200°C) due to the low porosity resulting from incomplete carbonization. Under higher temperature (>600°C), the porosity reduces too, the reason might be that some cavities have been burned and the surface area corresponding reduced. So when heating temperature reaches 800°C, the surface area value is small too.

It can be seen from the table that the loss on ignition percentage increases from 7.1% to 83.2% with the rising of the heating temperature of the rubber seed shell, the loss on ignition percentage increased rapidly with the rising of temperature up to 800°C, this might be caused by the almost completed volatilization of the volatile matter at the temperature above 600°C. The loss on ignition of N330 carbon black is 92.85% from the table which is higher than that of the rubber seed shell carbon suggesting high amount of carbon present and hence better reinforcement of natural rubber than RSSC.

#### **Cure characteristics**

The data on the processing characteristics of RSSC filled natural rubber systems being evaluated are given in Table 4. Analysis of the Monsanto rheograph facilitates the determination of the various cure related parameters. From the rheographs there is evidence of torque increase with increasing filler loading and filler type as with N330 carbon black. Torque values provide direct information on the extent of cross linking in the rubber compounds. The results showed that the scorch, cure times and the maximum torque gradually increased with increasing filler content for RSSC-filled natural rubber, but in the case of CB-filled natural rubber, the scorch and the cure times decreased while the maximum torque increased with increasing filler content. The trend observed in the cure characteristics may be attributed to differences in the filler properties. The cure enhancement of the vulcanisates can be associated with the filler related parameters such as surface area, surface reactivity, particle size, and moisture content. In general a faster cure rate is obtained with filler having a higher pH, and high moisture content [20]. There are many factors that affect the cure time of rubber compounds. Temperature, curing system and thickness are the most important factors that affect cure time. It has been reported that cure rate is directly related to the humidity and water content of the compound mix [21]. However, in the present study the most probable factors to account for the observed cure enhancement are surface area, moisture content, and

pH. The marked increment in the torques observed for the compound mix, shows that the presence of filler in the rubber matrix has reduced the mobility of the macromolecular chains of the rubbers.

### **Physico-mechanical properties of the natural rubber vulcanisates**

The mechanical properties of the RSSC-filled natural rubber vulcanisate and N330 carbon black are shown in Table 5.

A gradual increase in tensile strength as well as modulus with the weight fraction of filler is noticed up till 600°C. It clearly indicates that as the loading increases there is a progressive increase in tensile strength and the modulus for both the N330 carbon black and RSSC-filled natural rubber vulcanisates. It may be mentioned here that both tensile strength and modulus are important for recommending any vulcanisate as a candidate for structural applications.

In all filled systems, tensile strength and modulus at 100% increase with increasing filler type and content. The iodine adsorption value of carbon black N330 from the Table 3 shows that the N330 carbon black is higher in terms of surface area than the RSSC, suggesting more polymer-filler interaction and hence enhanced tensile properties for the CB-filled Vulcanisate than the RSSC-filled product.

The results show that the filler loading at which maximum values of the tensile strength and modulus at 100% obtained were less at above filler type F600. The factors that affect the reinforcing potential of fillers include filler dispersions, surface area, surface reactivity, particle size, bonding quality between the filled and elastomers matrix. The modulus data showed decrease as filler loading increase above F600. From the table, the values of the tensile strength and modulus at 100% for N330 carbon black shows that as the filler loading increases the tensile strength and modulus also increases suggesting that these could be as a result of the high surface area and loss on ignition of the N330 carbon black

The values of Elongation at break (EB) decreases with increase in filler type and content of the mixes for all the fillers below F600 and also for N330 carbon black. Decrease in elongation at break 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, 7].

From the results in Table 5 it may be observed that an increase in filler loading of the vulcanisates, its hardness value increases. However, above 600°C the trend took a different direction as a result of the filler characteristics. 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 vulcanisate. Hardness increases as the filler loading increases for N330 carbon black vulcanisate.

The compression set results in Table 5 show that as the filler type and loading increases the compression of filled vulcanisates decreases for both the RSSC-filled and the N330 carbon black (CB) –filled vulcanisates. The observation may not be unconnected with the amount of filler incorporated into the matrix, the degree of dispersion of the filler and its particles size; which may have enhanced the CB-filled vulcanisates.

The abrasions resistance of a solid body is defined as its ability to withstand the progressive removal of material from its surface as the result of mechanical action of a rubbing, scrapping or erosive nature. The trend of abrasion resistance with loading is presented in Table 5; It shows a regular pattern of increase with increasing filler type and loading for both the RSSC – filled and CB-filled vulcanisates. This indicates that filler loading is a function of the measured parameter. This observation may therefore be attributed to the degree of dispersion of the fillers.

The values of flex fatigue decreases with increase in filler type and content of the mixes for all the fillers below F600. 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.

## **CONCLUSION**

The main aim of this work is to examine how the filler carbonizing temperature of the rubber seed shell may influence its characteristics properties and hence the mechanical properties of natural rubber vulcanisates and the possibility of comparative study of the mechanical properties of the vulcanisates with that of carbon black. The preliminary results show that carbonized rubber seed shell is potential reinforcing filler for natural rubber compounds.

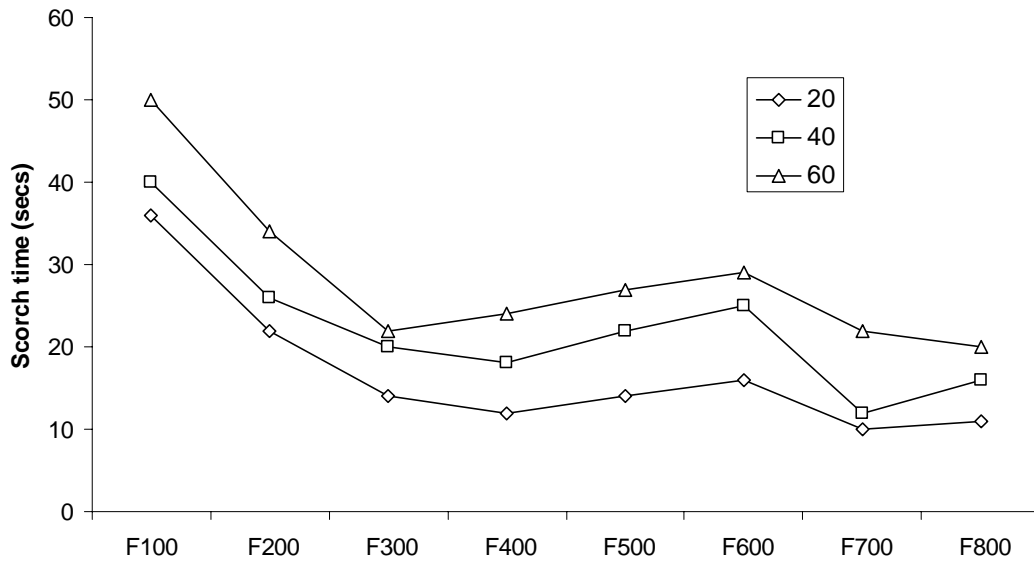
The results indicate that mechanical properties of vulcanisates are greatly influenced by filler carbonizing temperature and loading; and are therefore significant factors in determining the application in rubber compounding.

The vulcanisates exhibit high quality characteristics at filler type F600 (that is at filler carbonized at 600°C) and with 60phr loading. It is concluded that for high quality vulcanisate using Rubber seed shell as the reinforcing filler, carbonization should be done at 600°C for 3 hours.

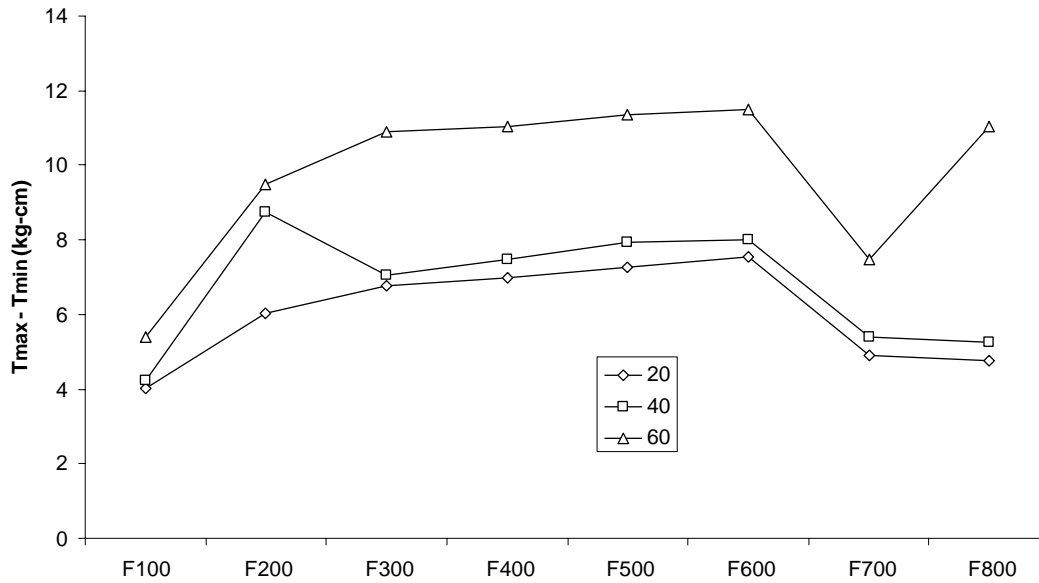
It also shows that the mechanical properties of the RSSC vulcanisates are quite comparable to that of CB vulcanisates particularly in terms of hardness, compression set and abrasion resistance.

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**Fig 2: Variation of scorch time with filler loading and filler type**



**Fig 3: Variation of change in torque (T<sub>max</sub> - T<sub>min</sub>) with filler loading and filler type**

**Table 1: Mineral content of rubber seed shell carbon**

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Magnesium (%)	0.673
Sodium (%)	0.014
Potassium (%)	0.01
Calcium (%)	0.32

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**Table 2: Formulation for Compounding Natural Rubber**

The recipe for compounding of the natural rubber (NSR 5) with RSSC for each sample:

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<b>Ingredients</b>	<b>Phr</b>
Natural Rubber	100
Filler (RSSC/CB)	20/40/60
Stearic acid	4.0
Zinc Oxide	2.0
ZMBT	3.5
Processing oil	2.0
Sulphur	0.5

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Table 3: Characterization of the rubber seed shell carbon

<b>Temperature (°C)</b>	100	200	300	400	500	600	700	800	CB (N330)
<b>Yield (%)</b>	92.9	70.9	40.7	25.9	23.0	22.4	17.5	16.8	NA
<b>pH of slurry at 28°C</b>	4.79 ±0.021	5.17 ±0.020	5.30 ±0.022	5.75 ±0.030	6.16 ±0.021	6.36 ±0.020	7.68 ±0.023	8.77 ±0.0225	6.50
<b>Conductivity (<math>\Omega^{-1}\text{m}^{-1}</math>)</b>	31.90	43.40	181.40	173.50	135.80	261.0	226.0	245.0	288.50
<b>Bulk density (g/ml)</b>	0.755 ±0.0214	0.646 ±0.020	0.785 ±0.015	0.678 ±0.012	0.635 ±0.010	0.691 ±0.0214	0.667 ±0.001	0.611 ±0.056	ND
<b>Iodine adsorp. number (mg/100g)</b>	20.12 ±0.060	36.32 ±0.057	47.20 ±0.058	50.34 ±0.060	61.24 ±0.062	66.75 ±0.063	65.11 ±0.062	57.24 ±0.060	80.78
<b>Loss on ignition (%)</b>	7.1	29.1	59.3	74.1	77.0	77.6	82.5	83.2	92.85

**Table 4 Mechanical properties of the natural rubber Vulcanisates**

<b>Properties</b>	<b>Filler Loading</b>	<b>F100</b>	<b>F200</b>	<b>F300</b>	<b>F400</b>	<b>F500</b>	<b>F600</b>	<b>F700</b>	<b>F800</b>	<b>CB (N330)</b>
<b>Tensile Strength (MPa)</b>	20phr	5.41	6.13	6.50	7.01	7.65	7.98	7.77	6.19	21.60
	40	6.14	7.22	7.33	7.89	9.11	10.82	10.00	8.26	29.00
	60	6.90	8.80	9.32	10.40	11.23	14.55	13.98	10.40	32.08
<b>Modulus at 100%</b>	20phr	1.40	1.40	1.94	2.38	2.81	3.27	3.20	2.39	4.33
	40	1.44	2.03	1.72	2.64	2.89	3.60	3.41	3.00	6.30
	60	1.62	2.22	2.44	3.27	4.33	5.96	5.11	3.28	8.43
<b>Elongation at break (%)</b>	20phr	560.02	513.20	513.10	510.19	410.10	362.01	375.12	458.13	525.02
	40	481.04	476.07	448.10	490.11	381.07	301.04	366.08	490.11	324.07
	60	430.05	381.01	349.03	354.14	311.10	263.05	275.11	476.07	251.10
<b>Flex Fatigue (Kc x 103)</b>	20phr	nf	nf	nf	nf	nf	nf	3.11	3.36	-
	40	nf	nf	nf	8.70	7.86	6.31	7.00	7.22	-
	60	8.72	7.36	6.67	6.33	5.86	3.36	4.72	6.89	-
<b>Hardness IRHD</b>	20	35.22	37.30	32.00	34.24	37.22	41.10	41.30	38.56	45.20
	40	41.00	41.02	49.00	50.00	50.10	55.60	55.50	42.40	58.60
	60	43.01	53.00	56.50	57.89	59.11	61.33	60.02	51.05	60.50
<b>Abrasion resistance</b>	20phr	17.02	20.03	21.17	24.09	27.18	35.24	35.11	31.21	39.54
	40	19.22	20.12	23.41	27.01	33.00	42.70	39.10	34.68	40.60
	60	21.01	25.21	27.01	39.08	40.96	44.41	40.45	38.50	41.22
<b>Compression Set (%)</b>	20phr	27.10	23.41	19.20	17.11	15.22	13.02	13.75	15.10	16.34
	40	19.20	15.22	13.02	11.55	10.02	8.64	8.98	10.42	8.61
	60	16.10	12.76	10.25	9.61	8.66	6.30	7.34	10.21	6.25