

## PHYSICO-MECHANICAL PROPERTIES OF NATURAL RUBBER VULCANIZATES FILLED WITH CARBONISED AGRICULTURAL RESIDUES

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### ABSTRACT

The reinforcement of rubber by fillers is of great practical and technical importance. Carbonised agricultural residues from cocoa pod husk, rubber seed shell, coconut fibre, rice husk, melon seed shell and palm kernel husk were evaluated as reinforcing fillers for natural rubber. The physico-mechanical properties such as tensile strength, stress at 100% strain, and elongation at break were measured and compared with those obtained for a vulcanizate filled with carbon black. It was found that carbonised agricultural residue filled vulcanizate compared favourably with carbon black filled vulcanizate in terms of hardness and abrasion resistance. Consequently the carbonised agricultural wastes can be a substitute for investigated and can replace carbon black for articles exposed only to compression.

### INTRODUCTION

In order to have useful properties, rubber must be reinforced with small filler particles which influence crosslinking reactions and consequently stiffness and compressive strength. They control shrinkages, thermal expansion as well as reduce the cost of the rubber goods (Byars & Jong, 2009).

Petroleum based carbon black is typically used as the reinforcing filler in the rubber industry.(Sadakne & White, 1973; Furtado *et al.*, 1999). Environmental impact, sustainability and life cycle analysis are new factors that must be considered alongside cost and technical performance when developing new materials, products and processes. The increasing desire by societies for products to be environmentally friendly has led to manufacturers exploring means of producing products entirely or mostly from renewable resources. The objective is

to replace materials from non-renewable feedstocks, by materials derived from renewable agricultural or biomass feedstocks. Recent examples in tyre manufacture include the use by Goodyear of starch as a filler (Goodyear tyres, 2001; Corvasce & Fottrgon, 2005) in their BioTRED technology, applied in the Goodyear GT3 tyre, and in the development by SRI Dunlop of an environmentally friendly tyre with only 30% petroleum based materials.(Sumitomo Corporate news, 2005).

Although a lot of work has been reported (Osabohien & Egboh, 2007; Helaly & El-Sabbagh, 2002; Ismail, Jaffi & Rozman, 2003) on the use of different agricultural residues as fillers for elastomers, a gap exist on the comparative studies of using different carbonised agricultural residues as fillers for rubber. The aim of the present work is to evaluate the effect of some carbonised

agricultural residues in comparison with commercial grade carbon black N330 as filler on the mechanical properties of natural rubber compounds.

### MATERIALS AND METHODS

Natural rubber crumb (NSR 10) was obtained from Iyayi rubber factory, Egba, Benin city and used as received. The industrial grade carbon black (N330) filler was obtained from the Nigerian National Petroleum Company (NNPC) Warri, Nigeria. All other rubber compounding ingredients were of industrial grade and were used without further treatment.

The agricultural residues (cocoa pod husk, rubber seed shell, coconut fibre, rice shell husk, melon seed husk and palm kernel husk) were obtained from different location within Benin-city. They were cut into smaller pieces, air dried and then milled to a fine powder. The powder obtained was sieved with a mesh size of 150 $\mu$ m and the portion retained by mesh 80  $\mu$ m was carbonised at 250-350 °C using the method

described by Ishak and Baker (1995).

The composition of the different carbonised agricultural waste products was done using standard procedures (Vogwl, 1962) and the results obtained are shown in Table 1.

The carbonised agricultural waste products were characterised in terms of weight loss on ignition which was determined by weighing 2g of dried powder in a 30 cm<sup>3</sup> porcelain crucible which has been placed in an electric furnace at a temperature of 875 °C  $\pm$  25 °C for 4 1/2 hours (ASTMD, 1983). The weight loss on ignition was calculated based on the amount of solid residue. Moisture content was determined by using the (ASTMD, 1983), and the pH of powder slurry was determined using a pH meter. The surface area and aggregate structure were determined by iodine absorption number (ASTMD, 1988), and oil absorption method (Hepburn, 1984) respectively. The result are presented in Table 2.

**Table 1: Elemental composition of carbonised agricultural waste products**

Material	K %	Na %	Ca %	Mg %	Cl %
Carbonised cocoa pod husk (CCPH)	5.17	1.96	3.58	0.62	ND
Carbonised rubber seed shell (CRSS)	3.91	2.07	3.06	0.32	0.96
Carbonised coconut fibre (CCF)	2.56	1.92	2.71	0.05	1.29
Carbonised rice shell (CRS)	0.20	0.20	0.33	0.02	ND
Carbonised melon seed husk (CMSH)	0.04	0.10	0.03	0.01	ND
Carbonised palm kernel husk (CPKH)	4.22	2.34	3.26	0.46	0.98

**Table 2: Some characteristics of the fillers investigated**

Parameters	CCPH	CRSS	CCF	CRSH	CMSH	CPKH	CB(N330)
Loss on ignition at 875°C	54.34	59.18	76.40	48.60	47.08	62.88	92.80
Moisture content at 125°C	3.64	6.35	6.80	5.65	5.69	5.25	2.51
pH of slurry	8.50	8.50	6.95	6.77	6.64	6.60	6.50
Iodine number (g/kg)	62.63	57.31	66.21	54.05	63.00	68.58	81.00
Aggregate structure	50.15	44.11	52.06	46.70	48.00	62.63	55.10

**Table 3: Formulation for compounding natural rubber with the fillers**

Materials	phr (parts per hundred)
Natural rubber	100
Filler	40
Zinc Oxide	4.0
Stearic acid	2.0
Sulphur	1.5
Processing Oil	2.0
Mercaptobenzothiazole	2.0

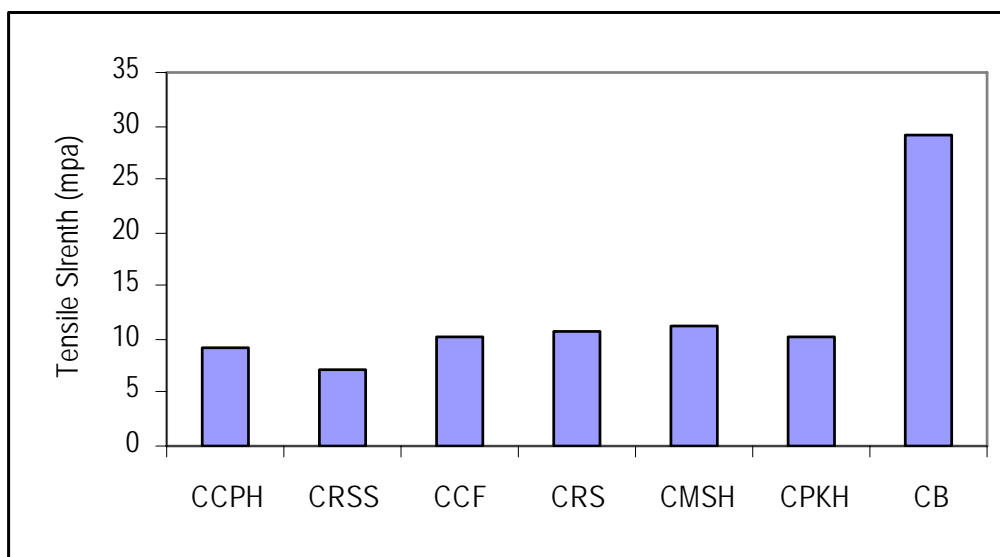
**Compounding**

Mixing was carried out on a convectional laboratory two- roll mill size (160 x 320mm) using the formulation shown in Table 3 with a batch factor of 4. The carbonised agricultural waste products and carbon black compounds were vulcanised at 185°C and their respective optimum cure time  $t_{90}$  as determined by a Monsanto Rheometer ,model MDR2000.

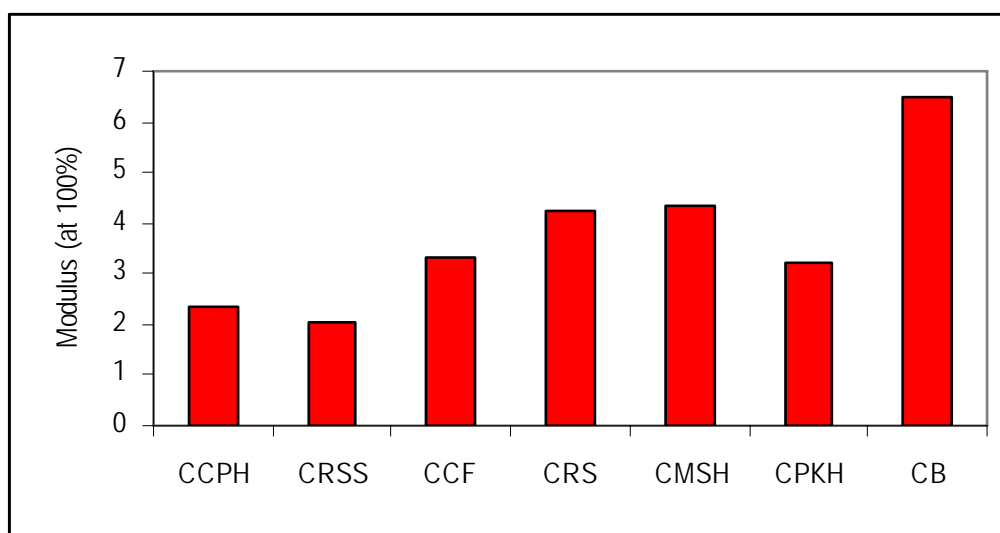
**RESULTS AND DISCUSSION**

Figure 1 shows the tensile strength of natural rubber vulcanizate filled with carbonised agricultural residues. The tensile strength of the vulcanizate filled with carbon black gave the highest value while that filled with different carbonised agricultural waste product gave lower values that varied depending on the filler .CRSS appears to have given the lowest tensile strength while

CMSH gave the highest tensile strength. The variation in the mechanical tensile strength may be due to the variation in the surface area, carbon content and aggregate structure (Table 2). These filler parameter influences the amount of cross-link in accelerated vulcanizates (Lawrence, 1974).



**Figure 1: Tensile strength of rubber vulcanizates**



**Figure 2: Modulus at 100% of rubber vulcanizates**

CCPH = Carbonised cocoa pod husk	CRSS = Carbonised rubber seed shell
CCF = Carbonised coconut fibre	CRS = Carbonised rice shell
CMSH = Carbonised melon seed husk	CPKH = Carbonised palm kernel husk

The modulus at 100% is highest for carbon black filled natural rubber (Figure 2).

Cohen and Spielman (1948) have argued that when tensile strength and modulus are used as criteria for reinforcement, it should be assumed that it is either the energy required to separate the elastomer chain from each other or the energy required to rupture a small fraction of the total chains that determine the tensile strength and modulus of materials. Hence the tensile strength and modulus may be a function of three forces, namely chemical cross-links produced by vulcanization or other means, adsorption cross-links produced by action of the surface pigment and forces produced by crystal formation along path of chain length. The fact that the carbonised agricultural residues have larger particle size and hence smaller surface area compared to N300 carbon black, can lead to poor filler-polymer interaction and may

account for the low modulus and tensile strength observed for the natural rubber filled carbonised agricultural waste.

The observed hardness for all the vulcanizates is shown in Figure 3. Apart from the vulcanizates filled with carbonised rubber seed shell, the values obtained for the others filled with carbonised agricultural residues varied within a narrow range (42-58) and the values compared favourably with that obtained for carbon black-filled vulcanizate. Therefore depending on the customized requirement of the vulcanizates, carbonised agricultural residue may compete favourably with carbon black.

The abrasion resistance index are shown in Figure 4. The result shows that CCF and CPKH vulcanizates abrades less than the vulcanizates of CCPH, CRS and CMSH and the value for the latter is close to the one for carbon black filled vulcanizate.

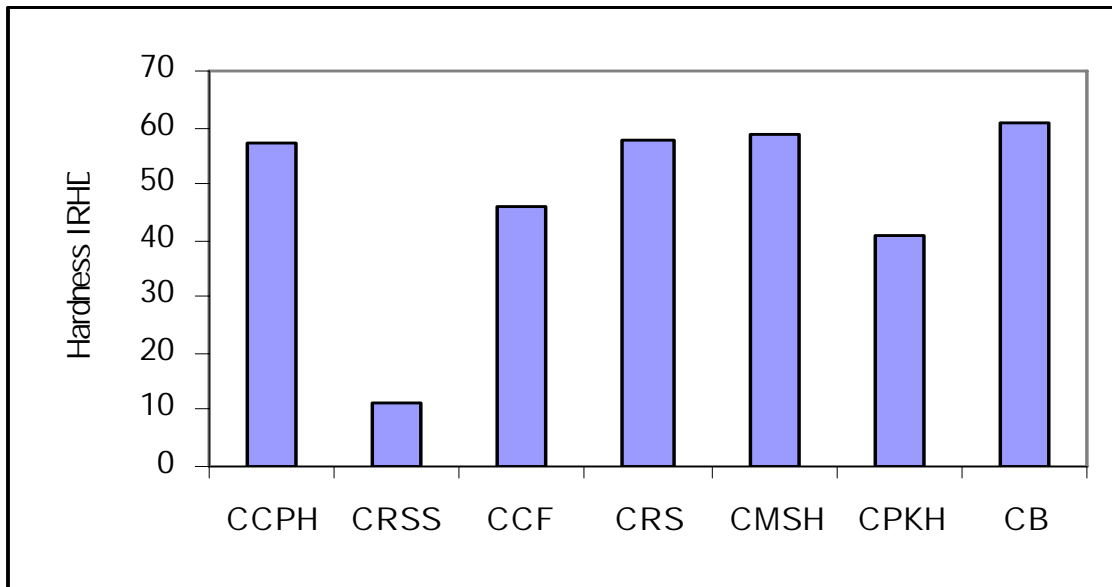


Figure 3: Hardness of the rubber vulcanizates

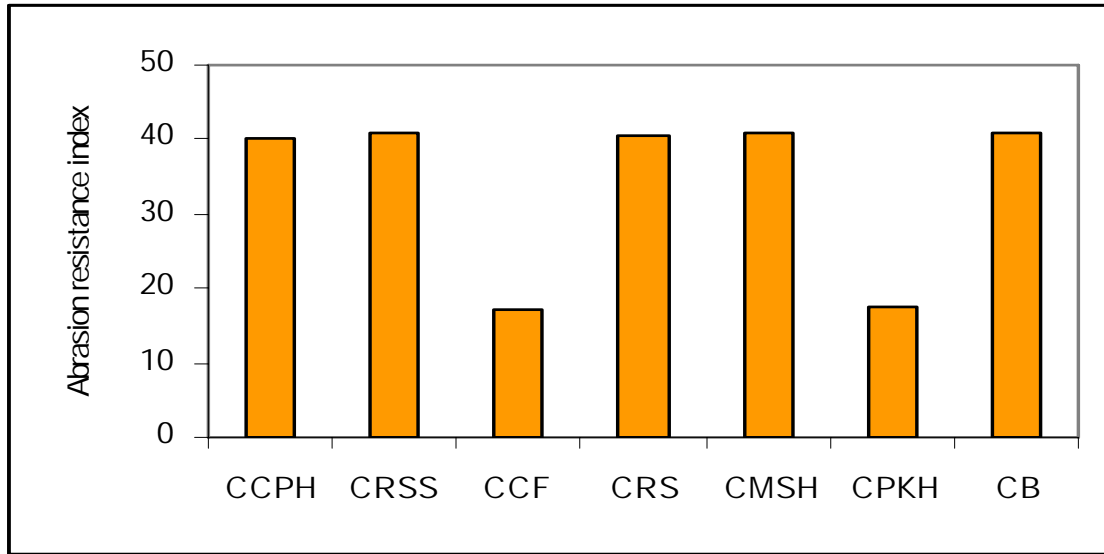


Figure 4: Abrasion resistance rubber vulcanizates

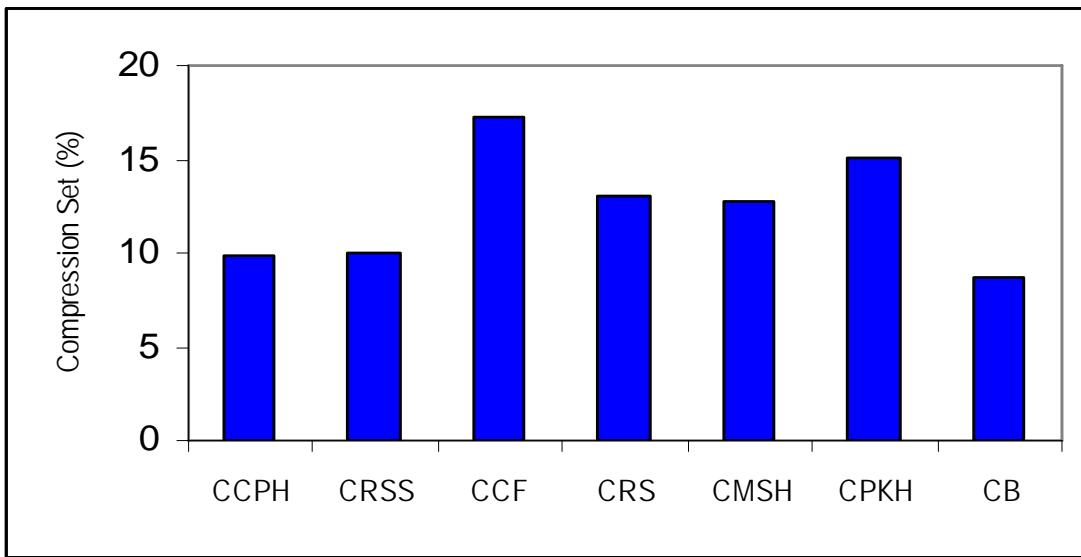


Figure 5: Compression set of rubber vulcanizates

The results of compression set of carbonised agricultural waste product and carbon black filled natural rubber are shown in Figure 5. Compression set is an estimation of prediction of the service performance of rubber articles. The level of compression determines the area of

application and service life of the composite. The value obtained for carbon black-filled vulcanizate is lower than those obtained for carbonised agricultural residue filled vulcanizate. Carbonised agricultural residue may therefore substitute for carbon black in vulcanizates that may be exposed to

**Table 4: Flex fatigue and elongation at break for rubber vulcanizates**

materials	Elongation at break %	Flex fatigue Kc x 10 <sup>3</sup>
Carbonised cocoa pod husk (CCPH)	47.01	8.77
Carbonised rubber seed shell (CRSS)	47.60	8.22
Carbonised cocoanut fibre (CCF)	37.60	8.00
Carbonised rice shell (CRS)	35.00	8.12
Carbonised melon seed husk (CMSH)	36.40	8.50
Carbonised palm kernel husk (CPKH)	37.15	8.40
Carbon Black (N330)	34.40	nf

Table 4 shows the values obtained for flex fatigue and elongation at break .

The flex values are almost the same for all the vulcanizates filled with carbonised agricultural wastes . The difference in values of flex between the carbonised agricultural waste vulcanizate and that of carbon black may be due to the smaller surface area of the former.

As stiffness is related to flex fatigue ,it may be expected that during cyclic deformation, such inhomogeneity resulting from the smaller surface area will initiate crack with attendant failure Nie *et al.* (2010).

### CONCLUSION

The result from this study showed that carbonised rubber seed shell (CRSS) filled vulcanizate had the poorest mechanical properties while carbonised melon seed shell (CMSH) vulcanizate had the best mechanical properties apart from

compression set where coconut fibre carbonised showed better property.

Carbonised agricultural waste products can be used as fillers for natural rubber in the manufacture of moulded article which require low stress during service application and may serve as semi- reinforcing fillers impacting little improvement in tensile properties and at the same time increasing the bulk of the polymer product with cost reduction.

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