

Rheological and mechanical properties of natural rubber compounds filled with carbonized palm kernel husk and carbon black (N330)

Egwaikhide, A. P.¹, Okieimen, F. E.¹, Lawal. U.²

¹ Agricultural Waste Research Laboratory, Chemistry Department, University of Benin, Edo State, Nigeria

² Department of Chemical Sciences, Federal University, Wukari. Taraba State, Nigeria

Email address:

pegwaikhide@yahoo.com(Egwaikhide, A. P.), lawalusman2@gmail.com(Lawal U.)

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Abstract: Palm kernel husk carbon obtained from agricultural waste, were incorporated into natural rubber using a laboratory size two-roll mixing mill. For comparison purposes, commercial reinforcing filler, carbon black (N330) was also used. The effect of these fillers on cure characteristic and physico –mechanical properties of natural rubber materials at various filler loading, ranging from 0-80hpr, was investigated. Curing using a semi-efficient vulcanization was chosen and cure studies were carried out on a Monsanto Rheometer. The results indicated that carbonized palm kernel husk filler caused lower Mooney viscosity, shorter cure time, improved hardness, higher compression set values, but decreased tensile strength and tear strength, but show no significant change in abrasion resistance in comparison with the natural rubber materials. Overall results showed that palm kernel husk carbon can be used as cheaper filler for natural rubber materials where improved physical-mechanical properties are not critical.

Keywords: Palm Kernel Husk, Vulcanization, Tear Strength, Tensile Property, Hardness, Mooney Viscosity, Mechanical Properties, Natural Rubber

1. Introduction

In natural rubber compounding, fillers are major additives. Incorporation of fillers into natural rubber matrix enhances properties such as tensile strength, modulus, tear strength, abrasion resistance, stiffness and processibility. Also significantly reduced by the addition of additives is the cost of the manufactured rubber products [1, 2]. The mechanism of elastomeric reinforcement by fillers has been reviewed by several workers [3]. One of the mechanisms by which particulate fillers reinforces elastomers is that reported by Bueche and Flemmings(4). They considered that the effect of filler is to increase the number of chains, which shared the load of a broken polymer chain. Fillers used in rubber industries may be classified on the basis of sources, properties and colour. Those grouped on the basis of sources could be organic or inorganic fillers. Inorganic fillers are calcium carbonate, barytes, silica etc. while that of the organic fillers are phenolic resins, high styrene resins, cyclized natural rubber etc. They are categorized either as

reinforcing or non-reinforcing. While reinforcing filler on inclusion into a rubber mix increase the tensile strength, tear strength and abrasion resistance, the non-reinforcing only help to reduce cost of product and act as diluents. Examples of reinforcing fillers are carbon black, silica etc. while examples of non-reinforcing fillers are mica powder, barium sulphate etc. [5].

In the rubber industry, fillers that are commonly in use are carbon black, calcium carbonate and china clay. Calcium carbonate (CaCO_3) had attracted considerable interest in recent years due to its availability and low cost [3].

It is known that in the case of filled vulcanized, the efficiency of reinforcement depends on a complex interaction of several filler related parameters. These include particle size, particle shape, particle dispersion, surface areas, surface reactivity, structure of the filler and the bonding quality between the fillers and the rubber matrix [6]. Hepburn [7] has pointed out that good reinforcing fillers should possess a small particle size, that is $<1000\text{nm}$, a chemical active surface and a surface which

is both porous and very irregular in shape to maximize surface contact between rubber and filler [8]. This article presents results of assessment and utilization of cheaper and low cost carbonized palm kernel husk as filler for the production of rubber products.

2. Experimental

2.1. Material

Natural rubber (NSR10) was purchased from Iyayi rubber factory, Egba, Benin City. The palm kernel husk used in this study, were obtained from a local palm kernel mill in Ihievbe town, Edo State. The palm kernel husk were washed with KOH solution, air-dried and ground into fine powder, carbonized at 250°C using procedure described by Ishak and Baker[9]. finally were sieved through 80µm mesh size. Other materials such as zinc oxide, sulphur, stearic acid, MBTS, processing oil and carbon black were used as supplied.

2.1.1. Characterization

Characterization of Carbonized Palm Kernel Husk and Carbon Black. Carbonized palm kernel husk and Carbon black were characterized in terms of loss on ignition, moisture content, pH, surface area and aggregate structure.

2.1.2. Compounding

The formulation shown in Table 1 was used with a batch factor of 4. The elastomer was placed in a water cooled laboratory two-roll mill. The mill was kept at maximum temperature of about 80°C so as to avoid the material cross-linking during mixing (scorching).

Table 1: Typical formulation for carbonized palm kernel husk and carbon black (N330)-filled natural rubber(NR)

Materials	%phr
NSR 10	100
Filler	0 – 80
Stearic acid	4.0
Zinc oxide	2.0
MBTS	2.0
Processing Oil	2.0
Sulphur	1.5

2.1.3. Mooney Viscosity

Mooney viscosity of the mixes was carried out using Negretti MK 111 Mooney viscometer. It measures the resisting torque exerted onto the rotor by rubber. It is expressed as ML 1+4 100°C. Where M = Mooney viscosity, L size of the head of rotor, 1 is the preheating time in minutes, 100°C is the temperature, and 4 is the reading time in minutes. It gives the flow behaviour of the material.

Table 2: Mooney Viscosity of filled NR natural rubber (ML 1+4 100°C)

Filler volume fraction	0	0.07	0.14	0.29	0.36	0.43	0.50
Mooney Viscosity CPKH	31	32	34	39	44	50	52
CB	31	35	41	48	63	76	70

2.1.4. Processing Characteristics

A Monsanto Rheometer model MDR 2000 was used to determine the processing characteristics of the compound mixed. The discs were set to an arc angle of 0.05 at a curing temperature of 185°C. The rheographs, which contain the cross-link density against time plot for the compounded samples were analyzed for t_{s1} , t_{s2} , t_{10} , t_{50} , t_{90} , scorch time, torque (minimum torque M_L and maximum torque M_H). Curing of the test pieces were done by moulding. This was carried out using steam heated hydraulically operated single daylight press.

2.1.5. Mechanical Properties Measurement

Tensile mechanical properties of the vulcanized were determined with instron tensile tester model $1^1/m$ at a cross speed of 500mm/min using dumb bell test pieces of dimension (45x5x2mm) as contained in ASTM 412 – 87 method A[10]. The hardness of the vulcanizates was measured with Wallance Hardness tester of model C8007/25 according to ASTM 1415 [11]. The procedures adapted for the measurement of abrasion resistance and compression set were based on DIN to 150, 4649 Akron to BS903 part 49 method C [12] and ASTM 385[13] respectively.

3. Results and Discussion

The values of some physico-chemical properties of the fillers are shown in table 2.

Results indicated that, weight loss on ignition at 825°C, are 42.38% and 92.8% for carbonized palm kernel husk and carbon black respectively.

Table 3: Physico –Chemical characteristics of the fillers, Palm kernel husk (CPKH): carbon black (CB)

Parameter	CPKH	CB
pH of slurry	6.30	6.50
Moisture content at 125°C%	6.8	2.4
Loss on ignition at 825°C%	42.38	92.8
Iodine absorption number (mg/g)	61.04	81.42
Aggregate structure kg	52.0	55.05

This shows that carbon black (N330) has the least resistance to thermal effect. The results obtained, indicates that carbon black is 93% carbon while a larger portion of the agricultural waste material is non-carbon elements.

Weight loss on ignition is a measure of the carbon content lost during burning. The larger the non- carbon elements of the agricultural by-product, the lower the reinforcing, as filler for elastomer. The pH shows that both fillers are slightly acidic. The pH of filler affects the cure rate of mix of elastomers. Iodine absorption number results, indicates that carbon black has a surface area of 81g/kg while carbonized palm kernel husk is 61.04g/kg respectively, implying that the surface area of carbon is higher. The higher the surface area values, the better reinforcing properties. This shows that carbon black could be more reinforcing than the agricultural by-product. The aggregate structures of both fillers are closely related and may produce similar effect.

3.1. Mooney Viscosity

Fig 1 Shows the dependence of Mooney viscosity measured at 100°C on filler loading.

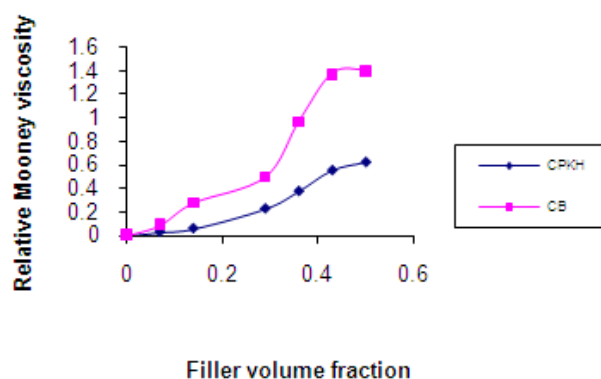


Fig 1: Plot of relative Mooney viscosity as a function of volume fraction for CPKH and CB

In order to illustrate the effect of the degree of filler loading, the relative viscosity, ML^R , was used for the plot. It is expressed as

$$ML^R = \frac{ML_F - 1}{ML_O}$$

Where ML_F is the Mooney viscosity of the filled compound, and ML_O is the Mooney viscosity of the gum. In both cases, the relative viscosity increases with filler loading per hundred of rubber [14]. At small concentrations of fillers, there is no significant difference in ML^R between the two fillers. However, at high loading, considerable increases in relative viscosity are observed for both fillers [15,16]. Mooney viscosity measures mainly the processing characteristics, that is, rheology of rubber compounds. The extent of variation of the relative viscosity in a mix caused by introduction of fillers is one way of determining whether fillers were reinforcing, active or inert [17]. It has earlier been reported that as the aggregate structure distribution broadens, the trend in processing characteristic is towards slightly lower Mooney Viscosity [18]. For fix filler content, the viscosity of a system with agglomerates is always higher than that of the well dispersed sample. Carbon black

have higher tendency to agglomerate in the rubber mix than carbonized palm kernel husk as indicated by the iodine absorption values obtained in Table 1.

3.1.1. Processing Characteristics

The rheological properties of natural rubber vulcanizates filled with carbonized palm kernel husk and carbon black as fillers at 185°C are given in Table 4. The table summarizes the values of t_{90} , scorch time, maximum torque and ODR of carbonized palm kernel husk and carbon black –filled vulcanizates. The t_{90} and scorch time of carbonized palm kernel husk-filled vulcanizates exhibit a slight retardation with increasing carbonized palm kernel husk; that is it shows slight enhancement in cure rate. The maximum torque increases with increasing filler content before a decline at 0.29 filler volume fraction. For carbon black-filled vulcanizates, the enhanced cure retardation may be due to two possible reasons. First, by virtue of having a smaller size, there is more surface area available for chemical interactions during vulcanization.

For carbon black cure retardation is directly proportional to the total surface area of fillers [19]. Secondly, the observed trend may also be due to the slower interaction between carbon black with the rubber compound during vulcanization. The different trend observed in the cure characteristics of the filled vulcanizates may be attributed to differences in the filler properties. The enhancement observed in the case of carbon black-filled vulcanizates can be associated to the filler related parameters such as surface area, surface reactivity, particle size, moisture content and metal oxide content. In general a faster cure rate is obtained with fillers having low surface area, high moisture content and high metal oxide content [20]. Butler and Freakley [21] reported that cure rate is directly related to the humidity and water content of the rubber compound. But however, in this present study, the main factors responsible for cure enhancement of carbon black fillers are surface area and particle size. Figure 2 gives a plot of ODR as a function of volume fraction for carbonized palm kernel husk and carbon black (N330) ODR gives the total energy or force to cure the rubber low ODR is recommended.

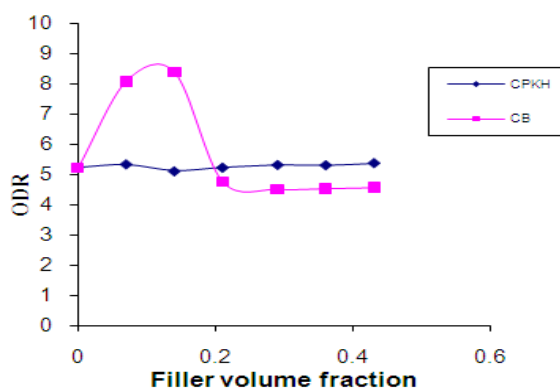
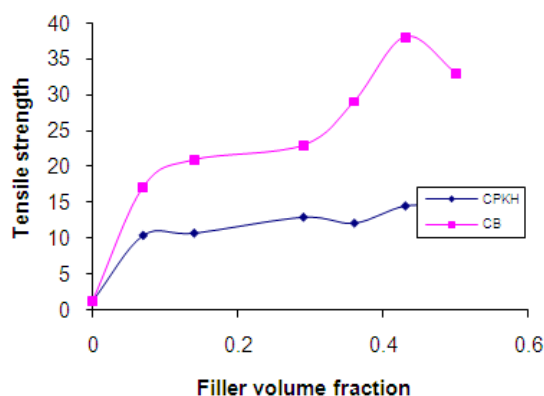


Fig. 2: ODR as a function volume fraction of fillers

Table 4: Rheological properties of NR vulcanizates filled with carbonized palm kernel husk and carbon black

Filler volume	Ts1	Ts2	Ts10	Ts50	T90	ML	MH
Fraction	Time(s)	Time(s)	Time(s)	Times(s)	Times(s)	Min Torque	Max Torque
0.07	0.31	0.4	0.27	0.43	0.98	1.40	5.58
0.07	0.29 (0.30)	0.33 (0.38)	0.23 (0.24)	0.40 (0.41)	0.61 (0.96)	1.62 (1.53)	6.90 7.25
0.14	0.28 (0.32)	0.32 (0.40)	0.22 (0.25)	0.41 (0.43)	0.61 (0.68)	1.67 (1.44)	6.65 8.03
0.29	0.29 (0.33)	0.35 (0.35)	0.22 (0.21)	0.41 (0.37)	0.64 (0.92)	1.70 (0.49)	6.78 6.60
0.36	0.29 (0.33)	0.36 (0.41)	0.22 (0.26)	0.40 (0.43)	0.63 (0.96)	1.74 (1.59)	6.87 8.25
0.43	0.29 (0.32)	0.36 (0.41)	0.25 (0.27)	0.40 (0.43)	0.64 (0.96)	1.67 (1.57)	6.85 7.86

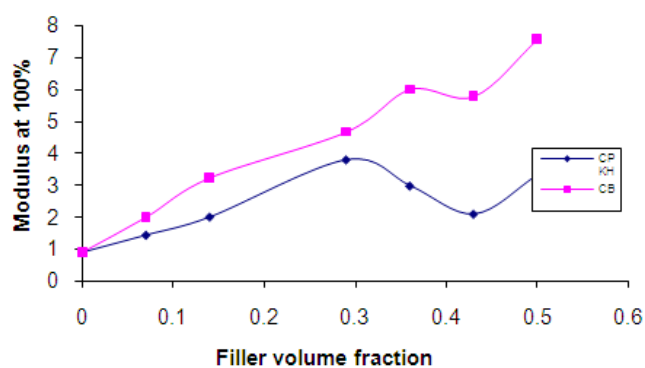
Examining Figure 3, with regard to tensile strength show great improvement in reinforcement of filled NR.

**Fig 3:** Tensile strength as a function of volume fraction for carbonized palm kernel husk (CPKH) and carbon black(CB)

It can be seen from the curve that the tensile strength of carbonized palm kernel husk-filled vulcanized is inferior than that of carbon black: it has been reported by several worker [22,23] that significant reinforcement is only attainable when the particle size of the filler is of the order of 0.02-0.05 μ m. Parkinson [24], found that decreasing the particle size of carbon black filler generally enhanced mechanical properties such as tensile and tear strength. According to Hepburn [7], filler with a particle size range of 1000-5000 μ m is classified as a moderate reinforcing filler. Carbonized palm kernel husk is moderate filler. Tear strength, like tensile strength is affected by particle size and surface area of the filler. The tear strength increases with increasing surface area or decreasing particle size of the filler [25]. In addition, it is also controlled by the nature of both the rubber and filler, as well as on the rate and

temperature of tearing [8]. Carbonized palm kernel husk-filled vulcanizate displays lower tear strength values as compared to the commercial one.

As for the modulus properties, carbonized palm kernel husk –filled vulcanized have lower modulus than carbon black filled vulcanized. This is due to differences in filler properties. Parkinson(6) and Wagner(20) reported that the stiffness of modulus for filled vulcanized figure (5) can be enhanced by improving the surface area and surface reactivity of fillers.

**Fig.4:** Modulus at 100% as a function of volume fraction for carbonized palm kernel husk(CPKH) and carbon black(CB)

The stiffness or modulus of CPKH – filled vulcanized may be accounted by two main factors. First, the fact that these fillers have a larger particle size, hence a smaller surface area than carbon black filler. Secondly, CPKH-fillers show a greater tendency towards filler agglomeration. Apart from CPKA-filler possessing a larger particle size and broad particle size distribution, their dispersion in a rubber matrix is not uniform if compared to carbon black. This poor filler dispersion will reduce the filler-rubber

interactions and consequently decrease the ability of the fillers to restrain gross deformation of the rubber matrix. Figure 6 shows the hardness enhancement that can be attributed to better wetting and dispersion of the fillers.

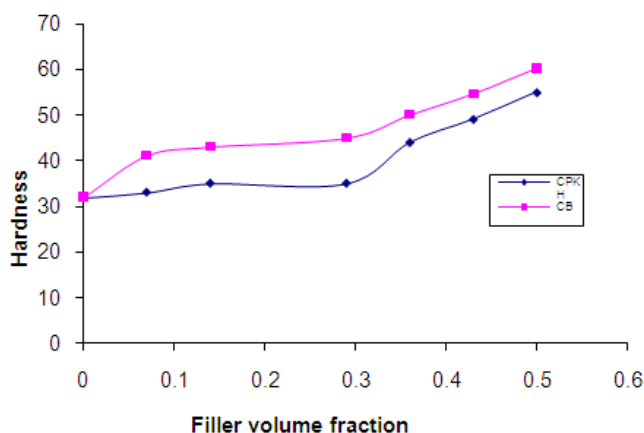


Fig. 5: Hardness as a function of volume fraction for carbonized palm kernel husk (CPKH) and carbon black (CB)

Figure 6 shows that elongation at break decreases with increasing filler loading for both fillers. Decrease elongation at break with increasing filler loading may be due to the stiffening of the polymer chain and hence resistance to stretch when strain is applied [26,27].

The compressibility is shown in figure 7, the curve showed that unfilled stock have the largest compressibility of 35.00. As filler content increases, the % compression of filled vulcanizates decreases. At 0.43 filler loading, the % compressibility seems to be the same for both fillers. Compressibility therefore could be dependent on the amount of filler incorporated into the rubber.

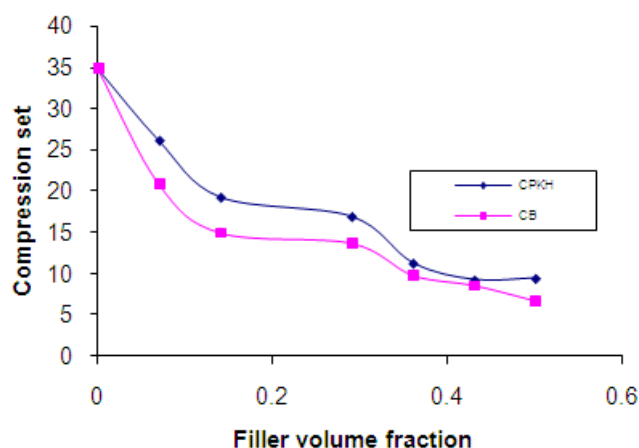


Fig. 6: Compression set as a function of volume fraction for carbonized palm kernel husk and carbon black

The results of the abrasion resistance of the vulcanizates, are given in Figure 9. The percentage abrasion resistances for carbonized palm kernel husk filled vulcanizates appear to be higher than carbon black filled vulcanizates. This reason for this could be due to the smaller particle size or larger surface area of carbon black filler used.

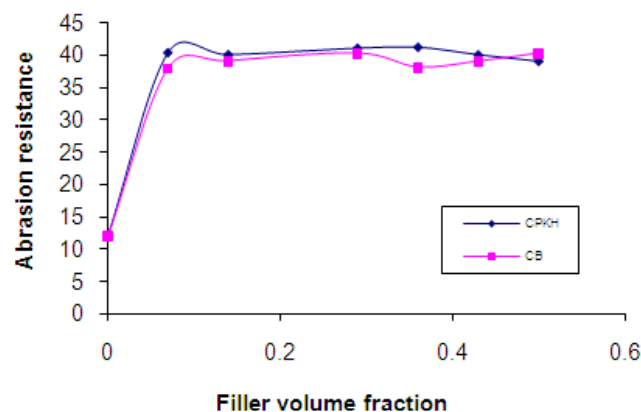


Fig. 7: Abrasion resistance as a function of volume fraction for carbonized palm kernel husk (CPKH) and carbon black (CB)

4. Conclusion

The main objective of this study is to gauge the possibility of utilizing the low-cost agricultural by-products as alternative filler materials. The degree of reinforcement of carbon black and carbonized palm kernel husk filler in natural rubber depends on particle size, aggregate structure, surface area, and level of filler loading and other physical nature of the fillers. This indicates that the agricultural by-products are reinforcing but carbon black is more reinforcing than carbonized palm kernel husk.

References

- [1] H.F. Mark (2001). Encyclopedia of Polymer Science and Technology, Interscience, New York Vol. 12:42
- [2] F. E. Okieimen and J.E. Imanah (2003); The characterization of agricultural waste products as fillers in NR formulation Nig. J. Polym Sci and Tech. Vol. 3 No 1 210-216.
- [3] E.M. Danneberg (1981); Proceeding of international Rubber conference, Loughborough.
- [4] G. Fleminert and C. Bueche (1957); "Light Reinforcement filler" A paper presented before the Swedish institute of Rubber Technology.
- [5] C. Blow and C. Hepburn (1971); Rubber Technol and Manufacture, Butter Worth Publishers London 3rd Ed. 188.
- [6] D. Parkinson (1957); Reinforcement of Rubber Lakeman and Co. London. 12
- [7] C. Hepburn (1984); Filler Reinforcement of Rubber Plastic and Rubber international No. 9 11-15.
- [8] M. Morton (1987); Rubber Technology, 3rd Edn. Van Nostrand, New York; 74.
- [9] Z.A. Ishak and A.A. Bakar (1995) An investigation on the potential of rice husk as fillers for expoxidized Natural Rubber, Euro Polym. J. Vol. 31 No 3 259–269.
- [10] ASTM 1510 (1983); American Society for Testing and Materials.

- [11] ASTM 1415 (1983); Method for Testing Hardness of Rubber.
- [12] ISO 4649 (1948); Abrasion Resistance Measurement.
- [13] ASTM 385 (1980); Method for Testing Compression set of Rubber
- [14] S. Wolff and M.J. Wang (1992) Filler –Elastomer Interaction part IV.
- [15] Egwaikhide, P.A; Okieimen F. E and Ohikhen S.O (2007). An investigation on the potential of palm kernel husk as fillers in rubber reinforcement. Middle East Jurnal of Scientific Research 2(1) 28-32.
- [16] B.L. Lee (1979); The Effect of the Surface Energies of Fillers on Elastomer Reinforcement. Rubb. Chem. and Technol. Vo. 65 No 2: 331
- [17] A. K. Sircar (1987); Rubb. World 197(2), 30.
- [18] R.F. Fendors (1979); Rubb. World 56, 285.
- [19] M.Q. Patterman (1986); Rubb. World 194, 38
- [20] M.P. Wagner (1976); Rubb. Chem. Tech. 49,704
- [21] J. Butler and P.K. Freakley (1991); Rubb. Chem. Tech. 65,374
- [22] M. Nasir and C.H. Choo (1987); Eur. Polym J. 25, 355
- [23] P.K. Mehta and N. Pitt (1974);Rice by-Products conference, Valencia, 76
- [24] D. Parkinson (1957); Reinforcement of Rubber, Lakeman and Co London, 12
- [25] L. Holiday (1966); Composite Material 313 Elsevier New York.
- [26] D. Rivin (1963); Rubb Chem & Tech 36, 729
- [27] C. Hepburn and C.M. Blow (1971); Rubber Technology andManufacture 3rd Edition, Butter Worth Publishing 188.