



## Mechanical and sorption properties of natural rubber reinforced with hybrid fillers

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### Abstract

Hybrid filler reinforcement is another fascinating technique used to combine properties of one or more fillers in the composite. In polymer composite, a symbiotic phenomenon due to the combination of different fillers, which is also known as the synergistic effect, can greatly enhance physical properties. Carbon black is always considered the most commonly consumed reinforcing filler in the rubber industry. Considering its problems such as its non-renewable petroleum origin, dark color, contamination and pollution, researchers are seeking an adequate alternative. The mechanical and sorption properties of natural rubber reinforced with hybrid fillers were investigated. The particle size of the fillers was 75  $\mu\text{m}$ . They were used in compounding natural rubber by varying hybrid filler loadings (0/60, 10/50, 20/40, 30/30, 40/20, 50/10 and 60/0) for carbon black/palm kernel and palm kernel shell/sandbox seed shell, using two roll mill. The results showed that incorporation of these hybrid fillers into the rubber matrix increased the tensile strength, tensile modulus, and hardness of the composites produced at hybrid filler loadings (0/60, 20/40, 30/30, 40/20, 50/10 and 60/0 for carbon black/palm kernel shell (CB/PKS) and 0/60, 20/40, 50/10 and 60/0 for carbon black/ sandbox shell (CB/SS) whereas the elongation at break, abrasion resistance and compression set decreased at these hybrid filler loadings. CB/PKS hybrid filled vulcanizates showed better mechanical properties than CB/SS hybrid filled vulcanizates. CB/SS hybrid filled vulcanizates had low swelling parameters (swelling ratios, swelling coefficients and mol% uptakes) than the CB/PKS hybrid filled vulcanizates. The CB/PKS hybrid filled vulcanizates, at 0/60, 10/50 and 60/0, the swelling parameters (swelling, swelling coefficient and mol% uptake) were low when immersed in diesel but at 20/40, 30/30, 50/10 and 60/0 when also immersed in fuel, the swelling parameters were also. The CB/SS hybrid filled composites at 20/40, 40/20, 50/10 and 60/0 the swelling parameters were also low when the samples were immersed in diesel and fuel. CB/PKS hybrid filled vulcanizates showed the better mechanical properties than CB/SS hybrid filled vulcanizates. CB/PKS hybrid filler could stand to be potential reinforcing filler for rubber compounds especially for articles requiring high mechanical strength while CB/SS hybrid filler for articles requiring less mechanical strength.

**Keywords:** hybrid, fillers, carbon black, diesel, vulcanizates

### Introduction

Filler is one of the major additives used in natural rubber compound and has marked effect and influence on rubber materials. Filler play a dominant role in modifying the physical properties of base polymer. (Thomas *et al.*, 2013) [12]. Fillers are materials which when added to rubber mix enhance the properties. These properties are physical in nature which include hardness, tensile strength, flex fatigue, stiffness and to some extent, the chemical properties. Fillers improve the processing characteristics, reduce cost and also act as auxiliary components necessary for vulcanisate. Fillers can either be reinforcing, semi-reinforcing or non-reinforcing. Reinforcing fillers enhance the physical properties of the cured article (Okieimen and Imanah, 2003) [10]. There are also non-reinforcing fillers, they reduce cost. Non-reinforcing fillers have little or no effect on the physical properties of the rubber. Examples of these include talc, barites, mica powder, whiting and china clay. Semi-reinforcing fillers are partially reinforcing. These include soft clay, calcium carbonate and antimony (Marut *et al.*, 2015; Okwele *et al.*, 2018) [8]. In rubber industry, fillers that are commonly in use are carbon black, China clay and calcium carbonate. The process of producing carbon black requires tremendous energy utilization, heavy infrastructure setup and constitutes a heavy source of environmental pollution and it is also carcinogenic (Okwele *et al.*, 2018).

Nowadays, there has been a growing interest in the use of individual and Agricultural waste such as rice husk (Attharansan *et al.*, 2012) [5]. Agricultural by-products as fillers has also been investigated, this included banana peel, rice husk, spent mango, bean seed skin and groundnut shell (Tenebe *et al.*, 2019) [11], melon and sawdust (Amoke *et al.*, 2017) [3]. Agricultural by-products are low cost materials and readily available in large quantity for use everywhere, of which well over 300 million tones are produced annually (Okwele *et al.*, 2018). One the major disadvantages of incorporating agricultural wastes as fillers into synthetic polymers is their incompatibility with the polymers (Iheoma *et al.*, 2015) [6].

The incorporation of various materials (additives as compounding ingredients) increases these aid characteristics to the level desired for NRs demands (Okieimen *et al.*, 2007). The additives which are added to enhance the processibility and properties of rubber vulcanizates are usually sourced from combinations of any of the followings: accelerators, activators, fillers, antioxidants, vulcanizing agents, softeners, plasticizers etc.

Hybrid composites offer a combination of advantages of constituent components to produce a material with determined properties. Imoisili *et al.*, 2013 [7] investigated the mechanical properties of rice husk/carbon black hybrid natural rubber composite. In the sample preparation, six

levels of filler loading were designed (100/0, 90/10, 80/20, 60/40, 50/50, 0/100) for carbon black/rice husk. They reported that the tensile strength, compression set, abrasion resistance, and hardness of the vulcanizate showed improvement with increase in carbon black, while elongation at break decreased and the flex fatigue showed great improvement. Amoke *et al*, 2021 [2] also investigated the comparison of mechanical properties of natural rubber vulcanizates filled with hybrid fillers (carbon black/palm kernel shell and palm kernel shell /sandbox seed shell), They reported that at the addition of the hybrid fillers at the ratio 0/60, 10/50, 20/40, 30/30, 50/10 and 0/60, the results showed an improvement in the tensile properties of the natural rubber.

### Objectives

1. To determine the effect of carbon black/sandbox shell and carbon black/palm kernel shell hybrid fillers on the mechanical properties of natural rubber vulcanizates.
2. Investigate the solvent absorption behaviour of the natural rubber vulcanizates in diesel and fuel.

### Experimental

#### Materials and Methods

The natural rubber (NSR-10) used for the research work was obtained from Rubber Research Institute of Nigeria (RRIN), Iyanomoh Benin-City. Diesel and fuel were obtained from NNPC Omega Filling Station, Auchi Edo State. The rubber compounding chemicals such as paraffin wax (processing oil) tetra methyl thiuram disulphate (TMTD), mercapto benzyl thiazole (MBT), zinc oxide, sulphur and stearic acid

were obtained from British Drug House, England. Sandbox Seed Shell (SSS) and Palm Kernel Shell (PKS) were obtained from Auchi, Edo State.

### Equipment

The equipment involved in this research work are: two roll mill, manufactured by British Company Limited, England, hydraulic press, Elektron Technology Series, UK, Monsanto Tensile Tester Model (1/m) manufactured by British Company Limited, England, Wallace Hardness Tester model C8007/25 for Hardness Test, Elektron Technology Series, UK, Taber Oscillating Abrasion Tester, Model: 6160-F735, manufactured by Taber Co. Ltd, Canada, was used for the Abrasion Properties, CTM-2P-200-2000KN (200Tons), manufactured by Interlaken Technologies Co. Ltd Thailand was used for the Compression Set.

### Method

#### Preparation of Hybrid Composites

The rubber was masticated and mixed with an additives (zinc oxide, stearic acid, TMTD, MBT sulphur and paraffin wax) using the two roll mill and adopting the standard method specified in the ASTM-D 3184-80 for all the hybrid composites. The filler hybrid loadings were varied at ratio of (0/60, 10/50, 20/40, 30/30, 40/20, 50/10, 60/0). Table 1 shows the formulations for the natural rubber hybrid composites. The rubber mixes were prepared on a laboratory size two roll mill. It was maintained at 70 °C to avoid cross-linking during mixing after which the rubber composite was stretched out. Mixing follows (ASTMD 3184-80, 1983).

**Table 1:** Formulations for Reinforced Natural Rubber Composites

Ingredients	(pph)
NR	100
Zinc oxide	5.0
MBT	1.5
TMTD	1.5
Fillers (CB/SS and CB/PKS)	0/60, 10/50, 20/40, 30/30, 40/20, 50/10, 60/0
Sulphur	3.0
Processing oil	5.0
Stearic acid	2.5

Pph = Part per hundred CB = Carbon black SS = Sandbox shell PKS = Palm kernel shell

### Hybrid Composite Curing

The curing of test pieces was done in a compression moulding machine at 140 °C and 2 bar for 10 mins.

### Mechanical Properties of the Hybrid Composites

#### Tensile Test

The test specimens were cut from the moulded dump-bell rubber sheets along the grain direction. The thickness and width of each test piece at the middle was maintained at 2.5 and 6 mm respectively. Each test piece was clamped into the grips of the tensometer. The stress applied, the load and elongation at break was recorded. The test samples were tested in the machine giving straight tensile pull, without any bending or twisting. The machine measures both the tensile stress and the tensile strain. The tensile stress is the strength of pull in the area between the notch marks; it is based on original cross sectional area. The tensile strain is a measure of how the test sample has been stretched by the pull.

#### Hardness Test

Test pieces from the moulded spherical rubber pieces were clamped onto a durometer (Instrol Wilson) and the penetration of the indenter measured. The standard dead method of measurement covers rubber in the range of 30 to 85 International Rubbers Hardness Degrees (IRHD). The test was carried out using the Shore "A" Wallace Hardness Tester.

#### Compression Set Test

The compression set is the difference between the original thickness of the sample and the thickness after the test expressed as a percentage of the original thickness. Compression set evaluate the extent by which the specimen fails to return to its original thickness when subjected to standard compression load for a given period of time at a given temperature. Stress of 2.8 MP was used and allowed for 24 hrs at 70 °C for 30 mins.

$$\text{Compression Set (\%)} = \frac{t_0 - t_r}{t_0} \times 100 \quad (1)$$

Where:  $t_0$  = Original Thickness and  $t_r$  = Recovered thickness of Sample.

### Abrasion Resistance Test

Wallace Akron abrasion tester was used. The angle between the test sample and the wheel was adjusted to an angle of 15°. The abrasion was carried out for 100 revolutions and the material loss for each run was noted. The specimen was re-weighed between each test run. The mean of the four revolutions of the abrasive wheel was calculated.

$$\text{Abrasion Resistance} = \frac{\text{Weight Loss of the Standard} \times 100}{\text{Weight Loss of the Sample}} \quad (2)$$

### Swelling Properties of Vulcanizate

Swelling behaviour was determined by change in mass using following swelling ratio, swelling coefficient and mol% uptake. For cured rubber vulcanizates; the test pieces of known weight was immersed in solvent (fuel and diesel) in diffusion test bottles and kept at room temperature for 24 hrs to allow the swelling to reach diffusion equilibrium. Samples were removed from the bottles and the wet surfaces were quickly dried using tissue paper and reweighed. The swelling behaviour of natural rubber vulcanizates were determined and calculated using the following swelling formulae.

### Swelling Ratio

This is a direct measurement of the degree of crosslinking. The swelling ratio was calculated as:

$$SR = \frac{M_2 - M_1}{M_1} \quad (3)$$

Where  $M_2$  = mass of the sample after swelling (g),  $M_1$  = mass of the dry sample (g)

### Swelling Coefficient

The swelling behavior of the composites was analyzed from the swelling coefficient value. It is an index of the ability with which the samples swell and is determined by the equation (Asore, 2000)

$$\text{Swelling Coefficient, SC} = \left( \frac{A_s}{m} \right) \times \left( \frac{1}{d} \right) \quad (4)$$

where 'As' is weight of the solvent absorbed at equilibrium swelling,

'm' is mass of the sample before swelling and 'd' is density of the solvent used.

### Mole percentage (mol %) uptake, (Qt)

The mol% uptake of the solvent "Qt" for all the vulcanizates were determined by the following equation (Ahmed *et al*, 2004) [1]

$$\text{Mol \% uptake, } Q_t\% = \frac{(M_2 - M_1) / M_1}{M_s} \times 100 \quad (5)$$

Where  $M_s$  is the molar mass of solvent.  $M_2$  = mass of the sample after swelling (g),  $M_1$  = mass of the dry sample (g)

## Results and Discussions

**Table 2:** Mechanical Properties Test Results

Properties	Filler Loadings						
	0/60	10/50	20/40	30/30	40/20	50/10	60/0
Tensile Strength (N/mm <sup>2</sup> )	(36.16)	(29.02)	(35.24)	(36.89)	(38.54)	(39.09)	42.25
	{32.93}	{23.00}	{34.43}	{30.88}	{28.33}	{34.89}	
Tensile Modulus (N/mm <sup>2</sup> )	(21.01)	(15.27)	(19.77)	(22.30)	(23.17)	(24.00)	26.48
	{18.96}	{11.93}	{19.10}	{17.76}	{15.08}	{19.55}	
Elongation at Break (%)	(426.74)	(424.11)	(462.78)	(420.63)	(412.38)	(403.76)	379.14
	{486.03}	{577.35}	{473.30}	{515.04}	{529.22}	{465.07}	
Hardness (Shore A)	(61.31)	(47.38)	(62.46)	(64.28)	(66.24)	(68.09)	71.36
	{55.30}	{37.07}	{57.93}	{50.56}	{45.65}	{60.27}	
Abrasion Resistance (Mm <sup>3</sup> /rev.)	(16.78)	(29.13)	(24.29)	(21.69)	(18.05)	(15.82)	14.97
	{20.13}	{31.67}	{21.03}	{24.18}	{27.19}	{19.63}	
Compression Set (%)	(21.43)	(31.95)	(26.22)	(22.35)	(20.37)	(19.48)	17.69
	{25.59}	{36.87}	{26.37}	{28.59}	{31.11}	{22.40}	

**Table 3:** Swelling Properties in Solvents of Rubber Composites.

Filler Loadings (pph)	Diesel			Fuel		
	SR	SC	Qt	SR	SC	Qt
0/60	(0.60)	(0.72)	(0.34)	(3.30)	(4.29)	(2.89)
	{1.30}	{1.56}	{0.73}	{3.80}	{4.57}	{3.33}
10/50	(1.30)	(1.56)	(0.73)	(3.70)	(4.81)	(3.24)
	{1.50}	{1.80}	{0.84}	{3.50}	{4.21}	{3.06}
20/40	(1.30)	(1.56)	(0.73)	(2.30)	(2.99)	(2.01)
	{1.20}	{1.44}	{0.67}	{2.00}	{2.40}	{1.75}
30/30	(1.30)	(1.56)	(0.73)	(2.70)	(3.51)	(2.36)
	{1.50}	{1.80}	{0.84}	{3.00}	{3.61}	{2.63}
40/20	(1.40)	(1.68)	(0.78)	(3.10)	(4.01)	(2.71)

	{1.00}	{1.20}	{0.56}	{1.80}	{2.16}	{1.58}
50/10	(1.00)	(1.20)	(0.56)	(1.70)	(2.21)	(1.49)
	{0.80}	{0.96}	{0.45}	{2.20}	{2.64}	{1.93}
60/0	1.00	1.20	0.56	2.00	2.4	1.75

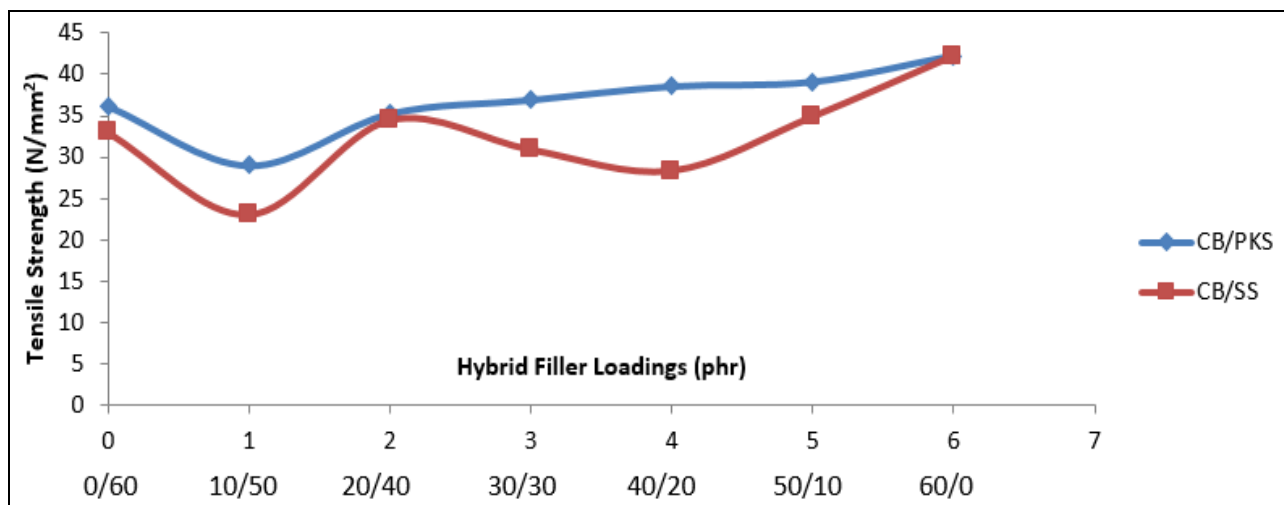


Fig 1: Effect of hybrid filler loadings on tensile strength of NR hybrid composites

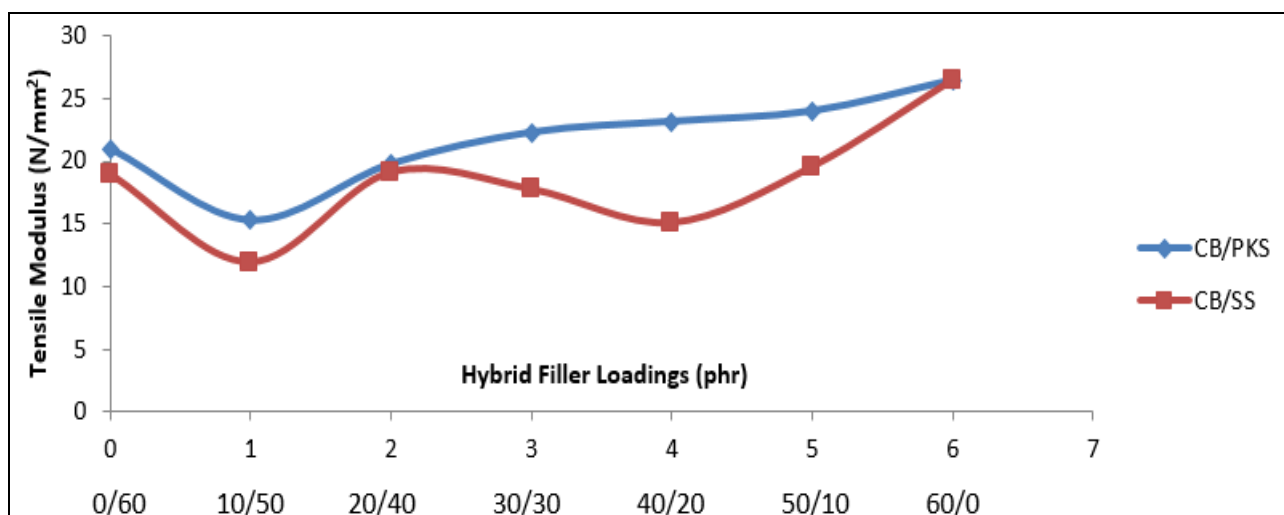


Fig 2: Effect of hybrid filler loadings on tensile modulus of NR hybrid composites

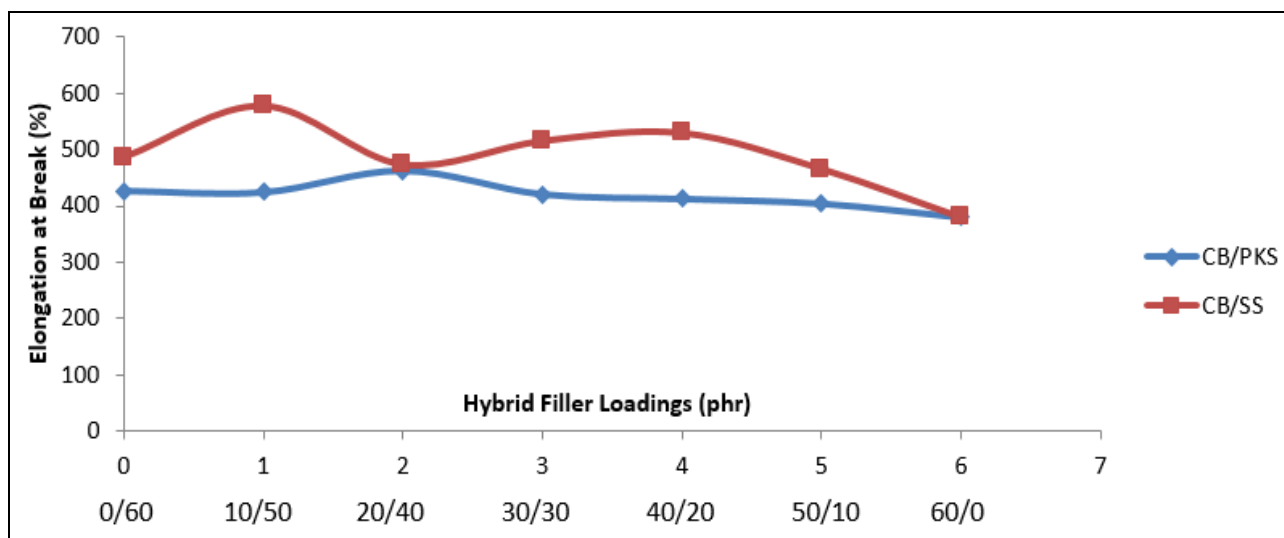
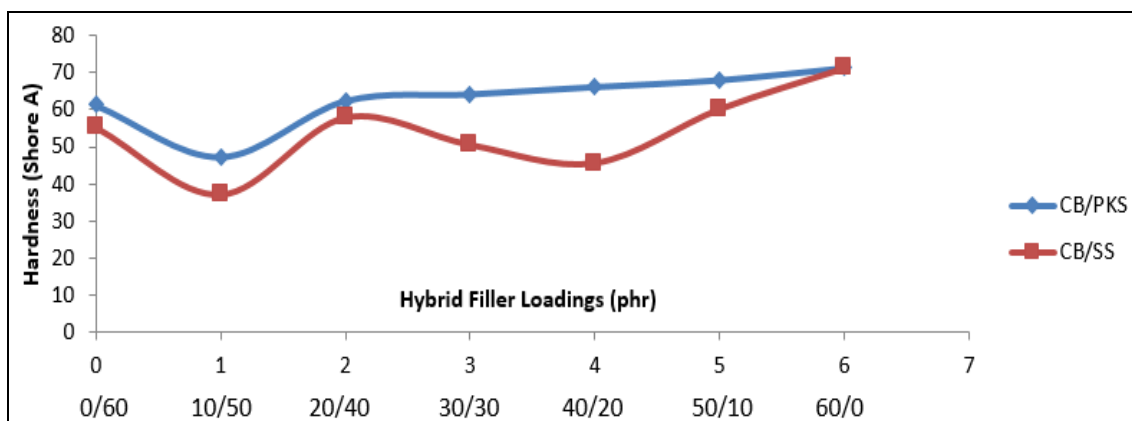
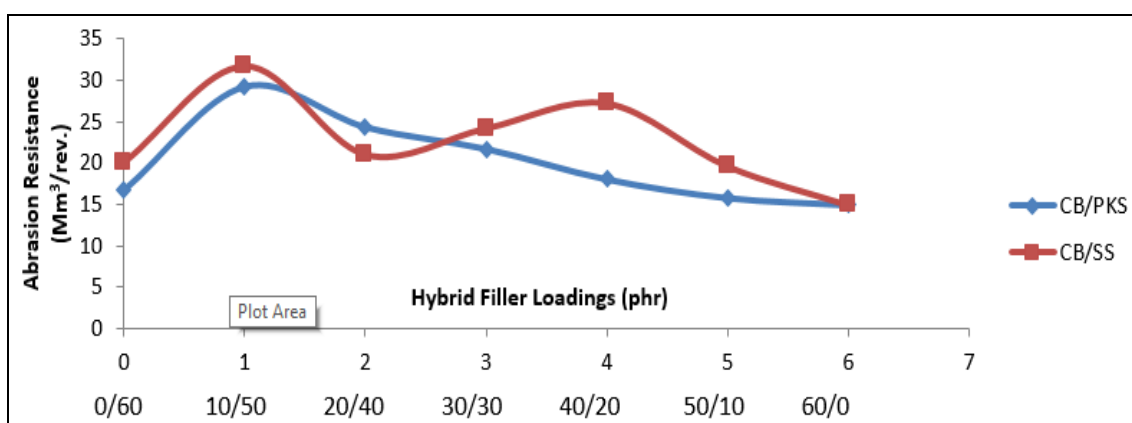


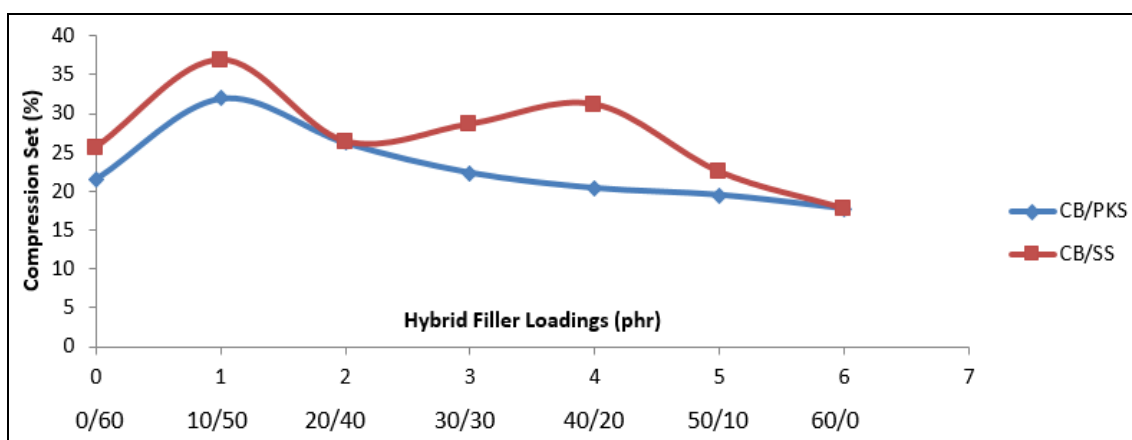
Fig 3: Effect of hybrid filler loadings on elongation at break (%) of NR hybrid composites



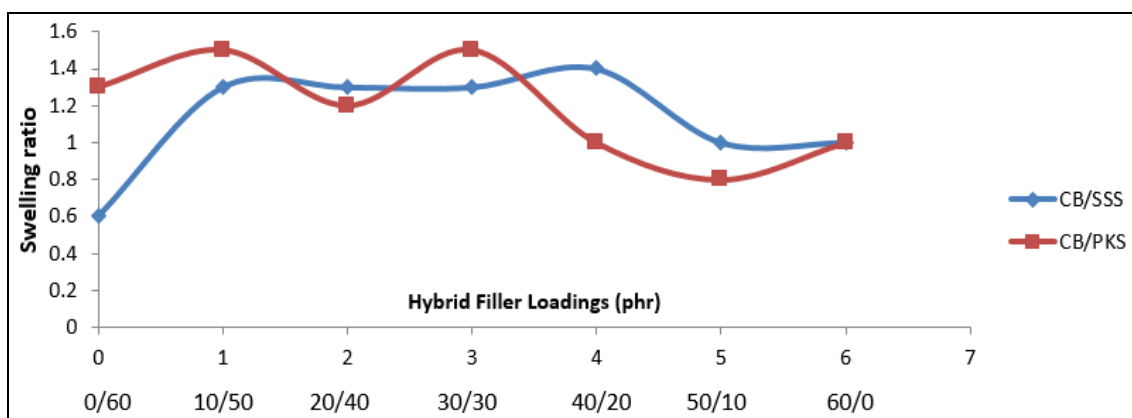
**Fig 4:** Effect of hybrid filler loadings on hardness of NR hybrid composites



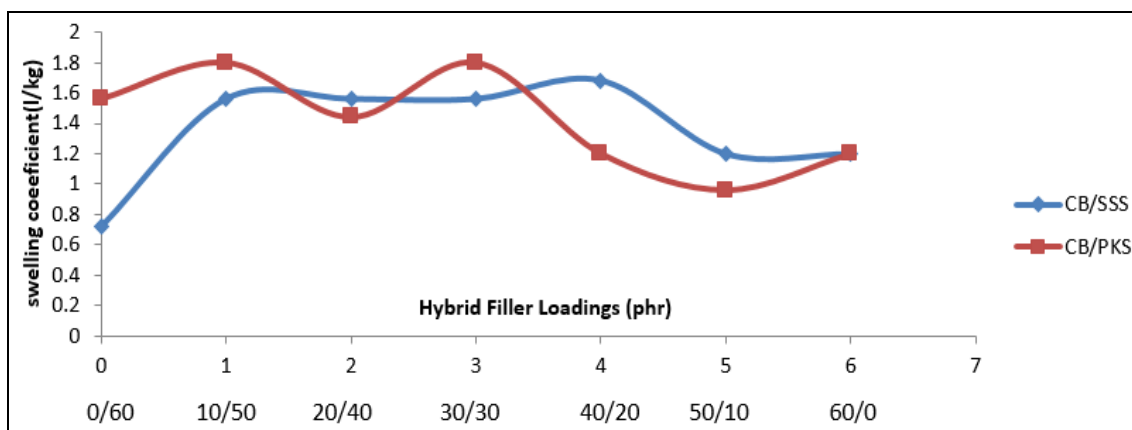
**Fig 5:** Effect of hybrid filler loadings on abrasion resistance of NR hybrid composites



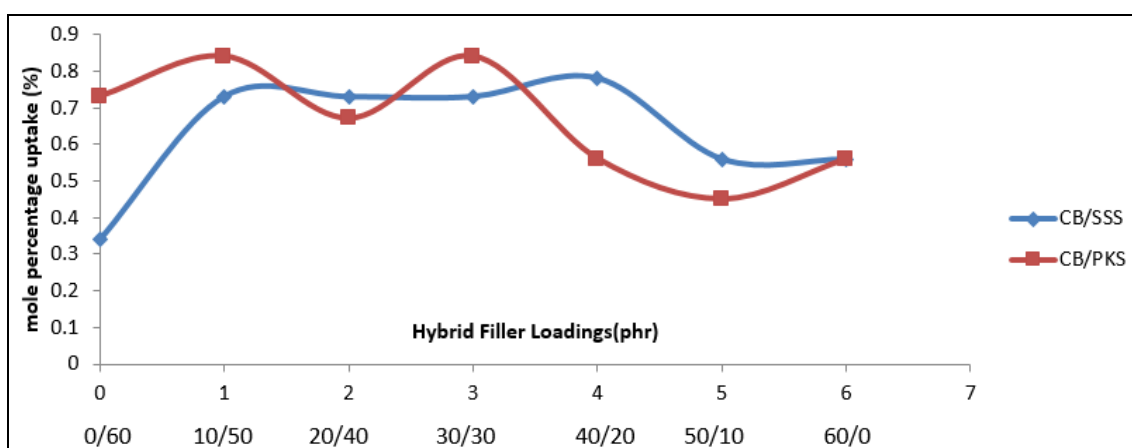
**Fig 6:** Effect of Hybrid Filler Loadings on Compression Set of NR hybrid composites



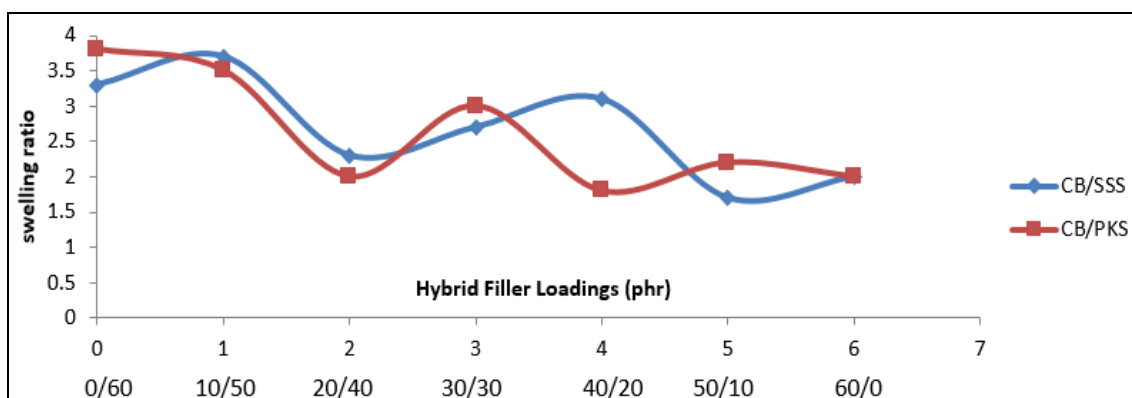
**Fig 7:** Effect of hybrid filler loadings on swelling ratio of NR hybrid composites in diesel



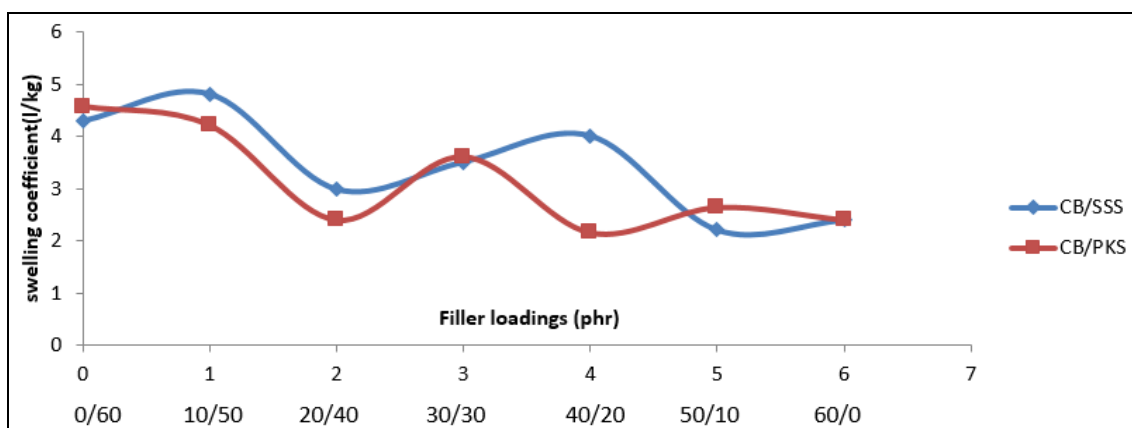
**Fig 8:** Effect of hybrid filler loadings on swelling coefficient of NR hybrid composites in diesel



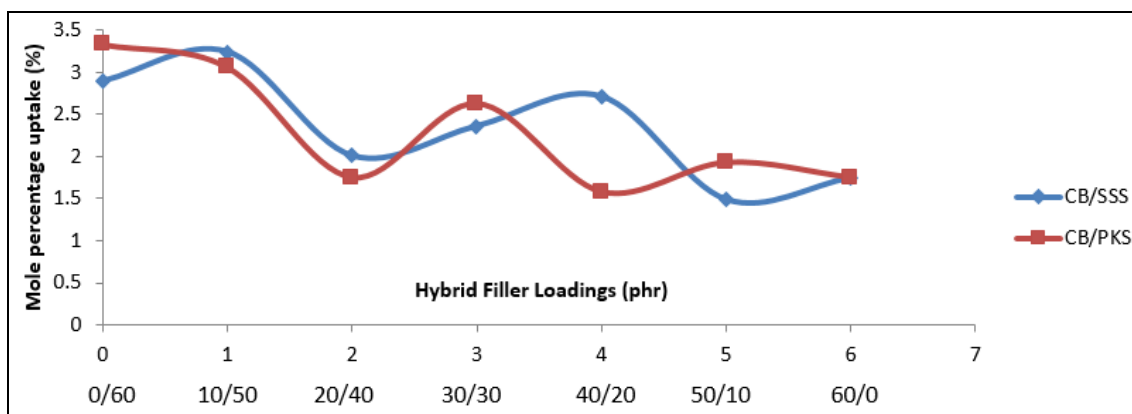
**Fig 9:** Effect of hybrid filler loadings on mol% uptake of NR hybrid composites in diesel



**Fig 10:** Effect of hybrid filler loadings on swelling ratio of NR hybrid composites in fuel



**Fig 11:** Effect of hybrid filler loadings on swelling coefficient of NR hybrid composites in fuel



**Fig 12:** Effect of hybrid filler loadings on mol% uptake of NR hybrid composites in fuel

### Mechanical Properties

The tensile strength of various hybrid composites is shown on Table 1 and Figure 1. The CB/PKS hybrid composites showed higher tensile strength than the CB/SS hybrid filled NR vulcanizates in all the filler ratios. Figure 1 showed that as the addition of CB increase in the hybrid with PKS and SS, results in the improvement in the tensile properties, because of higher carbon content in the hybrid filler of CB/PKS and CB/SS in accordance with Amoke *et al*, 2021 [2] and Imoisili *et al*, 2013 [7]. The effectiveness of filler may be measured by its carbon content hence fillers with higher carbon content, provide greater reinforcement than those with lower carbon content because carbon itself is very good reinforcing filler (Okieimen and Imanah, 2003) [10]. At 0/60 of filler loading, the tensile strength had high values for CB/PKS and CB/SS (36.16 N/mm<sup>2</sup> and 32.93 N/mm<sup>2</sup> respectively), indicating that PKS and SS are good filler reinforce. At 10/50 for CB/PKS composites, the tensile strength decreased (29.02 N/mm<sup>2</sup>). The decreased in the tensile strength may be as a result of poor adhesion, uneven distribution or agglomeration of PKS within the polymer matrix but the tensile strength increased progressively at filler loadings 20/40, 30/30, 40/20 and 50/20, indicating that there was a better filler-polymer matrix interaction and possibilities of even distribution of the filler within the polymer matrix. There was a decrease in tensile strength for CB/SS hybrid filled NR vulcanizates at filler loadings 10/50, 30/30 and 40/20. This decrease may be as a result of poor blending of the two filler which could have results to poor adhesion or uneven distribution of the filler within the polymer matrix but there was a significant increase in the tensile strength at 20/40 and 50/10. At 60/0, which had the pure carbon black, had the highest value of tensile strength (42.25 N/mm<sup>2</sup>) showing that carbon black is a very good reinforcing material than the PKS and SS.

The effect of loading of CB/PKS and CB/SS hybrid filled NR vulcanizates on tensile modulus is summarized in Table 2 and Figure 2. It can be seen that tensile modulus was high at the loading 0/60 for CB/PKS and CB/SS hybrid filled NR vulcanizates. Although the increase in carbon black in the mass ratio of CB/PKS and CB/SS hybrid, at 20/40, 30/30, 40/20 and 50/10 for CB/PKS and at 20/40 and 50/10 for CB/SS enhance the stiffness, which may have cause increase in the tensile modulus of the concerned composites. The tensile modulus decreased at the hybrid filler loading 10/60 for CB/PKS hybrid filled NR vulcanizates and 10/50, 30/30 and 40/20 for CB/SS hybrid filled NR vulcanizates. PKS and SS being an agro-waste may form agglomeration

within the rubber matrix, which may have led to decrease in tensile modulus. At similar loadings of CB/PKS and CB/SS hybrid filler content, it is clearly that the tensile modulus of CB/PKS hybrid filled NR vulcanizates are considerably higher than that of CB/SS hybrid filled NR vulcanizates. The pure carbon black filled NR vulcanizates had the highest tensile modulus.

The results of percentage elongation at break are shown in Table 2 and Figure 3. CB/PKS hybrid filled NR vulcanizates had lower percentage elongation than CB/SS hybrid filled NR vulcanizates because of its excellent filler-polymer matrix interaction. It can be seen that percentage elongation at break decreased with increasing the loading of CB hybrid filler content in PKS (from 30/30 to 50/10). It is expected because the interfacial adhesion between CB/PKS hybrid and NR matrix is better than CB/SS hybrid. At 0/60 and 20/40 of CB/PKS hybrid, percentage elongation at break was high, due poor adhesion or even distribution of the filler into the polymer matrix, but decreased at 10/50. For CB/SS hybrid filled NR vulcanizates, at 10/50, 30/30 and 40/20 the percentage elongation at break increased, this maybe as result of poor interfacial adhesion between CB/SS and NR matrix, but at 20/40 and 50/10 there was a decrease, showing a better filler-polymer matrix interaction. The pure CB (at 60/0) filled NR matrix had the lowest values.

The results of hardness are shown in Table 2 and Figure 4. The hardness of CB/PKS hybrid filled NR vulcanizates increased progressively from hybrid filler loadings 20/40 to 50/10, but for CB/SS hybrid filled NR vulcanizates, the hardness were high at 20/40 and 50/10 and low at 30/30 and 40/20. Both hybrid NR composites had the lowest values of hardness at 10/50, may be as a result of poor interaction between the hybrid fillers and the polymer matrix. At 0/60 for both hybrid fillers, the hardness was high, indicating better hardness properties. The 60/0 (purely CB filled NR vulcanizate) had the highest hardness of 71.36 Shore A. The CB/PKS hybrid filled NR vulcanizates had better hardness properties than the CB/SS hybrid filled NR vulcanizates. The highest values of hardness for CB/PKS and CB/SS hybrid filled NR vulcanizates is seen at filler loading of 50/10 (68.09 Shore A and 60.27 Shore A respectively).

The results of abrasion resistance are shown in Table 2 and Figure 5, for CB/PKS hybrid filler loadings, abrasion resistance showed decreasing values as carbon black increase in the hybrid CB and PKS at 20/40 (24.29 mm<sup>3</sup>/rev.), 30/30 (21.69 mm<sup>3</sup>/rev.), 40/20 (918.05 mm<sup>3</sup>/rev.) and 50/10 (915.82 mm<sup>3</sup>/rev.), because there is a existence of strong bond or interaction between the hybrid

filler and the rubber matrix. At hybrid filler loading 0/60, that is pure PKS filled NR vulcanizate, the abrasion resistance is low (16.78 mm<sup>3</sup>/rev.), showing that the pure PKS filled NR has a good abrasion resistance but at 10/60 of CB/PKS loading, the abrasion resistance is higher, this maybe as a result of poor interaction or weak bond between the hybrid filler and the rubber matrix. For CB/SS hybrid filler loadings, there is a decrease in abrasion resistance as the CB content increased at filler loading 20/40 (21.03 mm<sup>3</sup>/rev.) and 50/10 (19.63 mm<sup>3</sup>/rev.) because of better interaction between the CB/SS and the rubber matrix. At pure SS filled NR vulcanizate (0/60), showed a better abrasion resistance (20.13 mm<sup>3</sup>/rev.) than when compared with hybrid filler loading of CB/SS at 10/50, 30/30 and 40/20 which have high abrasion resistance values, showing weak bond between the hybrid filler and the rubber matrix. The pure CB (60/0) filled NR vulcanizate has the lowest value of abrasion resistance, showing the best abrasion resistance when compared with CB/PKS and CB/SS hybrid filled NR vulcanizates while the CB/PKS hybrid filled NR vulcanizates have better abrasion resistance than the CB/SS hybrid filled NR vulcanizates.

Compression set is useful in prediction of the service performance of rubber articles. The level of compression determines the service life and area of application of the rubber composites. The results of compression set in Table 2 and Figure 6 showed that for CB/PKS hybrid filler loadings 20/40, 30/30, 40/20 and 50/10, the compression set of the NR composites progressively decreased while for CB/SS hybrid filler loadings 20/40 and 50/10 there was a decrease in the compression set. Both hybrid NR composites had highest values of compression set at 10/50phr, 31.95% for CB/PKS hybrid and 36.87% for CB/SS hybrid. This high value of compression set may be as a result of poor filler-polymer matrix interaction, this also is applicable to CB/SS hybrid filled NR vulcanizates at filler loading 30/30 and 40/20 the compression set increased from 28.59% to 31.11% respectively. The 60/0 hybrid filler loading (purely CB) had the lowest compression set 17.69%, indicating a better compression set than the CB/PKS and CB/SS hybrid filled NR vulcanizates. The CB/PKS hybrid filled NR vulcanizate has better compression set than CB/SS hybrid filled NR vulcanizates at hybrid filler loading of 50/10 for both (19.48% for CB/PKS and 22.40% for CB/SS). The purely PKS and SS filled NR vulcanizate (0/60) had better compression set than some of the hybrid filled NR vulcanizates.

### Swelling Properties of Vulcanizates

The factors which can influence the equilibrium sorption in organic solvent of filled vulcanizates are nature of solvent and filler, level of crosslink and filler dispersion in the polymer matrix. The equilibrium behavior of an elastomer when exposed to fluid is very important in many applications (Okieimem *et al*, 2003).

For the two hybrid fillers investigated, Table 3 and Figures 7-12, show the effects of various swelling parameters where the samples (hybrid composites) were under observation for 24 hours in diesel and fuel. It was observed that the swelling ratios, swelling coefficients and mole% uptakes of the hybrid composites in fuel had higher values of swelling parameters than that in diesel this may be as a result of fuel (molecular weight = 114.232g/mol) having a low molecular weight than diesel (molecular weight = 178.6g/mol),

indication that solvents of lower molecular weight are absorbed more compared to those of higher molecular weight when filled vulcanizates are immersed in them (Ahmed *et al*, 2004) <sup>[1]</sup>.

### Conclusion

This research work showed that incorporation of CB/PKS and CB/SS into rubber vulcanizates increased the tensile strength, tensile modulus and hardness at hybrid loadings of 0/60, 20/40, 30/30, 40/20, 50/10 and 60/0 for CB/PKS and 0/60, 20/40, 50/10 and 60/0 for CB/SS whereas the elongation at break, abrasion resistance and compression set decreased at these hybrid filler loadings mentioned early. The hybrid fillers under investigation (CB/PKS and CB/SS) have shown their effects on the vulcanizates produced at different hybrid filler loadings. Hence, the mechanical properties of the hybrid composites produced are found to be a function of matrix filler adhesion, dispersion of fillers within the matrix and particle size. CB/PKS hybrid filled vulcanizates showed the better mechanical properties than CB/SS hybrid filled vulcanizates. CB/PKS hybrid filler could stand to be potential reinforcing filler for rubber compounds especially for articles requiring high mechanical strength while CB/SS hybrid filler for articles requiring less mechanical strength. CB/SS hybrid filled vulcanizates had low swelling parameters (swelling ratios, swelling coefficients and mol% uptakes) than the CB/PKS hybrid filled vulcanizates in the relevant solvents used. For CB/PKS hybrid filled vulcanizates, at 0/60, 10/50 and 60/0, the swelling parameters were low when immersed in diesel and at 20/40, 30/30, 50/10 and 60/0 when also immersed in fuel. The reasons for this, is as result of good dispersion of filler within the rubber matrix and better adhesion of the hybrid filler to the rubber matrix which increased the crosslink of the vulcanizates limiting the penetration of the solvents in the rubber matrix. These reasons are also applicable when CB/SS hybrid filled composites at 20/40, 40/20, 50/10 and 60/0 the swelling parameters were also low when immersed in diesel and fuel.

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