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The Physico-Mechanical Properties of Natural Rubber Filled With Cherry Seed Shell-carbon Black Blends

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Abstract

This study investigate the physico-mechanical properties of natural rubber (NR) filled with cherry seed shell (CSS) and cherry seed shell carbon (CSSC) separately and in blends with commercial carbon black, CB(N330) filler. The tensile strength and abrasion resistance of the NR vulcanizates increased to optimum values at 40 – 50 phr and then decreased thereafter with increasing filler content. This tendency of decreasing strength after a certain filler loading may be due to a phenomenon of "phase inversion", a condition that may result when the filler load becomes too much for the polymer matrix for optimum interaction. The decreasing reinforcement potential followed this order; CB(N330) > CSSC > CSS. The modulus (M100), specific gravity (S.G), hardness and thermal conductivity of the vulcanizates increased while elongation at break, resilience and equilibrium swelling (S_{eq}) decreased with increasing filler content. The NR vulcanizates filled with blends of CSS or CSSC with CB(N330) showed dilution effects on the vulcanizates properties.

Keywords: *carbonization, filler blending, natural rubber and reinforcement.*

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Introduction

In rubber compounding, the base polymer is the largest additive followed by filler. Fillers improve processibility, physico-mechanical properties of the polymer such as tensile properties, hardness, abrasion resistance, flex fatigue, tear strength, thermal conductivity, swelling resistance and may cheapen the final rubber article. The filler, which increases substantially the tensile strength, hardness, tear and abrasion resistance, is said to be reinforcing. Non-reinforcing fillers may cause reduction in strength properties but can increase hardness and modulus of the polymer product. They are usually applied as diluents or extenders to generally reduce cost (Whelan and Lee, 1979; Boonstra, 1982; Hepburn, 1984; Okieimen and Imanah, 2005; Osabohien and Egboh, 2007a).

Carbon black fillers which are petroleum derived and expensive are presently the most commonly used reinforcing fillers in the rubber industries. The rising cost of petroleum products especially in developing nations like Nigeria (WRPC, 2006) has necessitated the search for alternative fillers from locally available and renewable natural resources. Some of these materials such as limestones, eggshells, corn cobs, groundnut shell, rubber seed shell, cocoa pod husk, rice husk, cherry seed shell and red earth have been processed and utilized as fillers for natural rubber (Ogunniyi, 1989; Adeosun, 2000; Imanah and Okiemen, 2003; Osabohien and Egboh, 2007a, b; Osabohien *et al.*, 2007a, b).

The cherry plant (*Chrysophyllum albidum*) is a forest tree but can be grown in residential areas. It belongs to the sapotaceae family and its natural occurrences have been reported in diverse ecozones in Nigeria, Niger Republic, Uganda, Cameroon and Cote d'Ivoire (Keay, 1989). The fruit (African star apple) is a large berry containing about 4-5 flattened seeds. The tree fruits between December-April. The freshly sweet pulp is eaten but the seeds are usually thrown away as wastes, although the seed contains oil and sometimes can be used for local games. The fruit is a source of resin while the roots and leaves are used for medicinal purposes (Keay, 1989; Bada, 1997; Osabohien and Egboh, 2007b).

Earlier study of the cherry seed shell has revealed a carbonaceous content of about 85%, it is majorly an organic material with little mineral content. It is acidic with a pH of 6.41, density of 1.70 g/cm^3 and lead content of about 1%. The reinforcement potential of the cherry seed shell (CSS) as investigated is low (Osabohien and Egboh, 2007b). It is based on this premise that the present study was embarked upon. This work intends to further investigate the reinforcing potential of carbonized cherry seed shell and its blends with carbon black filler in natural rubber compounding.

Experimental

Materials

The cherry seeds used for this work were collected from Idumuesah; Ika-North-east local government area, Delta State, Nigeria. The carbon black (N330) was obtained from the carbon black production unit of the Warri Refinery and Petrochemical Company (WRPC), Warri, Delta State, Nigeria. The natural rubber grade 10, Standard Nigerian Rubber, (SNR_{10}), was obtained from Utagbuno Rubber Estate, Utagbuno, Delta State, Nigeria. Industrial grade chemicals and rubber ingredients were used for characterization and compounding. The standard rubber manufacturing equipment available at the Department of Polymer Technology, Auchi Polytechnic, Auchi, Edo State, Nigeria and Dunlop (Nigeria) Plc, Ikeja, Lagos were used. The atomic absorption spectrophotometer (AAS), Pye Unicam SP 2900 model, used for the metal analysis was obtained from Tudaka Environmental Consultants Ltd, Warri, Delta State, Nigeria.

Methods

Characterization of the Standard Nigerian Rubber (SNR_{10}) and the fillers

The natural rubber was characterized in terms of its dirt content, ash content, nitrogen content, volatile matter, plasticity retention index (PRI) and Mooney viscosity using standard techniques (Vogel, 1964; Palmer, 1965; Christian, 1980; RRIM, 1970). The cherry seed shell (CSS) was first air dried and ground using manually operated corona grinding machine for a period of 12 hours. 8.00 kg of the ground sample was screened with a sieve of mesh diameter 212 mm. A percentage yield of 81.25% was obtained after sieving. The cherry seed shell carbon (CSSC) was derived from CSS by carbonization at a temperature of 350°C ± 5°C in a Griffin muffle furnace for 2 hours with further grinding and screening using a sieve of 75 mm aperture and initial weight of 8.00 kg ground sample. The yield percent after screening was 68.75%. The fine particles obtained from these fillers were characterized in terms of moisture content, loss on ignition, silica content, iodine adsorption number, pH of aqueous slurry, density, metal contents and particle size, using standard methods (Vogel, 1964; Palmer, 1965; Christian, 1980; ASTM, 1983)., in comparison with the characteristics of standard carbon black (N330) filler.

Formulation, Compounding and Curing

The formulation given in Table 1, using efficient vulcanization system was employed in the rubber compounding. Mixing was done on a laboratory size (160x320 mm) two-roll mill maintained at 70°C using a standard mixing cycle of 14 min. The cure characteristics were measured using the Monsanto rheometer, MDR 2000 model. The curing of the test pieces was done by compression moulding in a steam heated, hydraulically operated press with a pressure of 150 kg/cm^2 at a temperature of 185°C for 20 mins – 30 mins. The cure times predicted by the Monsanto rheographs were used as guide to obtain vulcanizates for the test specimens (Morrell, 1982).

Table 1: Typical recipe of the natural rubber, Standard Nigerian Rubber compounds

Ingredient	Phr
Natural rubber (SNR_{10})	100.0
Zinc oxide (ZnO)	4.0
Stearic acid	2.0
**Filler	0.0-60.0*
Processing oil (Paraffinic)	2.0
N-Cyclohexylbenzthiazylsuphenamide (CBS)	2.0

Ingredient	**Phr**
Flectol H(TMQ)	1.5
Sulphur	1.5

**Filler loadings of 0, 10, 20, 30, 40, 50 and 60 phr were done using CSS, CSSC CB(N330) as fillers. The filler blends CSS/CB(N330) and CSSC/ CB(N330) were compounded at a total filler loading of 50 phr.*

Measurement of the Physico-Mechanical Properties

The tensile properties of the natural rubber vulcanizates obtained were determined using Instron 4301, tensile tester at a cross speed of 500 mm/min. Dumb-bell test specimens of dimension (45x5x2 mm) were used as described in ASTM D412. The specific gravity (S.G) and hardness of the test pieces were measured with the aid of Monsanto densitron 2000 and Monsanto duratron 20001 respectively. The rebound resilience, and abrasion resistance of the test specimens were determined using standard techniques (Morrell, 1982; BS, 1982).

Measurement of the thermal conductivity (K)

The thermal conductivity of the natural rubber vulcanizates was determined using the Lee's disc method (Anomohanran and Emekeme, 1997; Halliday *et al.*, 1997). The quantity of heat, Q conducted through the rubber specimen is proportional to the time, t, the cross sectional area, A, the temperature difference ($\theta_1 - \theta_2$) and inversely proportional to the thickness, d of the specimen.

$$Q = \frac{KAt}{d}(\theta_1 - \theta_2) \quad \text{................}(1)$$

K is the constant of proportionality callped the thermal conductivity of the rubber specimen. In determining K by Lee's method using electrical heating system, the total heat emitted per second from the discs and specimen is equated to the heat supplied by the heating elements per second;

$$\frac{IV}{J} = ea_x\,\theta_x + ea_s\,(\theta_x - \theta_y) + ea_y\theta_y + ea_z\,\theta_z \quad \text{..............}\ (2)$$

V is the potential drop in volts, I is the current in amperes, J is the mechanical equivalent of heat whose value is 4.18J/cal, a_x, a_y, a_z and a_s are the cross sectional areas of discs X,Y,Z and the rubber specimen respectively. θ_x, θ_y and θ_z are the temperature increases in discs X,Y, and Z, 'e' is the rate of emission of heat from the exposed disc surfaces in calories per unit area per degree rise in temperature. When all measured parameters were substituted into equation (2), the value of 'e' was calculated and used to determine the value of 'K' from equation (3) below;

$$\frac{KA}{t}(\theta_y - \theta_x) = \tfrac{1}{2} e a_s (\theta_y - \theta_x) + e a_x \theta_x \quad \dots\dots\dots\dots\dots\dots (3)$$

Measurement of equilibrium swelling (S_{eq})

The equilibrium swelling (S_{eq}) of the natural rubber vulcanizates in toluene, kerosene and diesel solvents were determined by gravimetry (Tager, 1972; Valencia and Pierola, 2001). The rubber test pieces were cut into square shapes of known weights and immersed in air-tight plastic bottles containing the penetrant solvent in each case. The immersed test specimens in the bottles were monitored regularly for 3 days at room temperature (about 30°C) until equilibrium sorption was reached. They were removed from the bottles, surface dried with blotting paper and reweighed. The equilibrium sorption (S_{eq}) was calculated from the relationship;

$$S_{eq} = \frac{m_e - m_o}{m_o} \quad \dots\dots\dots\dots\dots\dots\dots\dots (4)$$

Where, m_o is initial weight of rubber test specimen
m_e is weight of swollen rubber test specimen at equilibrium

Results and Discussion

The experimental results are as shown in Tables 2-7 and figures 1-6. The values of the parameters measured for the CSS- and CSSC-filled vulcanizates were compared with that of standard carbon black(N330)-filled vulcanizates.

Table 2: Physico-chemical properties of the CSS, CSSC and CB(N300)

Test parameter	CSS	CSSC	CB(N330)
Moisture content at 110°C (%)	2.80	1.15	1.10
Loss on ignition at 1000°C (%)	85.35	92.20	94.10
Iodine adsorption number (mg/g)	55.01	68.51	80.01
Density (g/cm^3)	1.70	1.60	1.80
pH of aqueous shury	6.41	6.70	6.85
Silica, $Si0_2$ (%)	0.30	0.20	0.10
Calcium (%)	0.66	1.23	trace
Sodium (%)	3.14	4.16	trace
Potassium (%)	2.75	3.48	trace
Lead (%)	1.05	1.35	trace

Table 2 shows the physico-chemical properties of the CSS, CSSC and CB(N330) fillers. The moisture content decreased in the order, CSS>CSSC>CB(N330). Cherry Seed Shell (CSS) is majorly an organic (plant) material. This is presented in the high loss on ignition of 85.3%, though slightly less than that of CSSC and CB(N330) since loss on ignition is a measure of the carbonaceous content of a material. Iodine adsorption number decreased in the order; CB(N330)>CSSC>CSS. Carbonization of CSS decreased its density, increased the pH and metal contents of the filler. These results showed similar trend with that obtained by Imanah (2003), when cocoa pod husk and rubber seed shell were carbonized. Iodine adsorption number is a rough measure of the surface area of the filler. The higher the iodine adsorption number, the larger the surface area of the filler (Okieimen and Imanah; Osabohien and Egboh, 2007a).

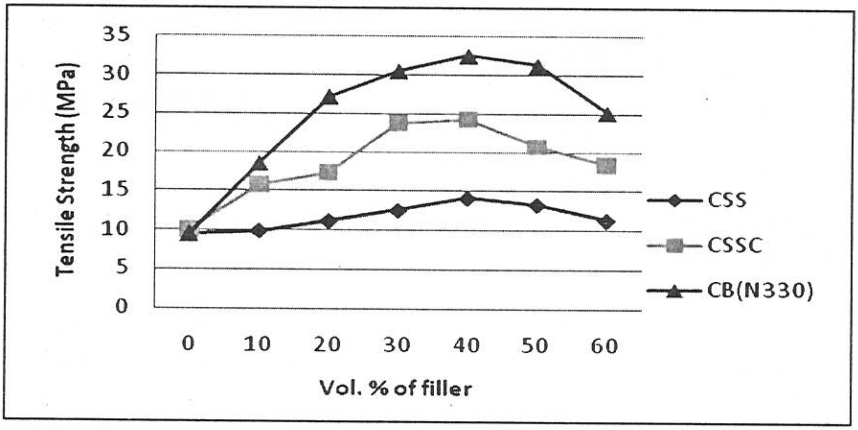

Fig. 1. Tensile strength of rubber/filler composites as function of volume fraction of fillers

Table 3: Physico-mechanical and equilibrium swelling properties of natural rubber filled with Cherry seed shell (CSS)

Filler(phr)	0	10	20	30	40	50	60
Specific gravity (S.G)	1.006	1.006	1.018	1.042	1.053	1.066	1.081
Abrasion resistance (%)	40.1	41.0	41.7	42.2	42.8	43.8	43.4
Thermal conductivity. (W/m k)	0.170	0.174	0.176	0.178	0.180	0.185	0.191
Equilibrium swelling, Seq T (%)	345.54	297.23	278.10	259.76	251.50	237.41	215.28
Equilibrium swelling, Seq K (%)	329.13	284.44	258.23	248.91	238.75	230.50	198.24
Equilibrium swelling, Seq D (%)	253.24	240.63	224.63	180.51	175.18	160.39	153.91

Tables 3-7 and figures 1-6 summarize the physico-mechanical and equilibrium swelling properties of the natural rubber vulcanizates. The tensile strength (Fig. 1) and abrasion resistance of the natural rubber vulcanizates increased to optimum value at 40 phr and 50 phr filler loading respectively and thereafter showed gradual decrease as filler content increased. This decreasing tendencies of the vulcanizates in the above mentioned properties after a certain optimum value may be due to the phenomenon of "phase inversion". Phase inversion may set in when too much filler particles are present which can inhibit effective crosslinking with the rubber molecules thereby reducing strength properties (Morton, 1973; Boonstra, 1982; Osabohien and Egboh, 2007a).

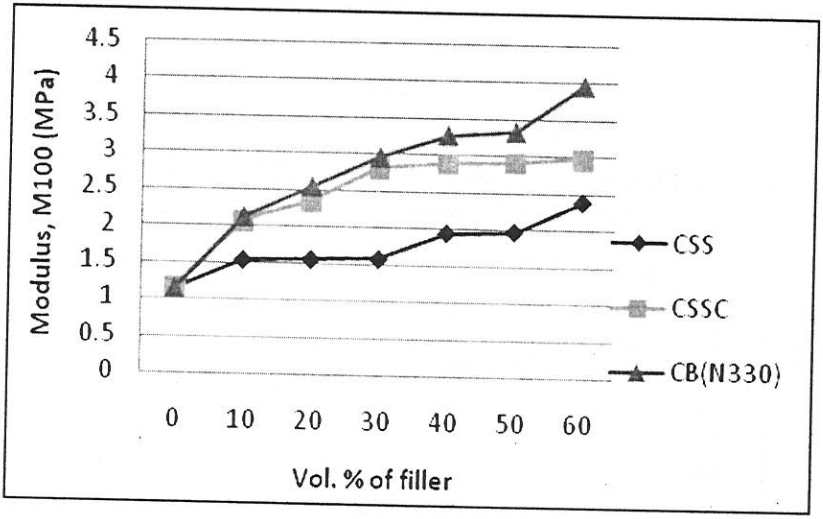

Fig. 2. Modulus of rubber/filler composites as function of volume fraction of fillers

The modulus which is a relative measure of stiffness increased steadily with increasing filler loading in all the vulcanizates tested (Fig. 2). The tensile strength and modulus of filled polymer can be enhanced by improving the surface area, dispersion and filler-polymer interactions (Boonstra, 1982; Osabohien and Egboh, 2007a). In this work, the order of increasing tensile strength and modulus is CSS-NR < CSSC-NR < CB(N330)-NR corresponding to the order of increasing surface area or iodine adsorption number (Table 2).

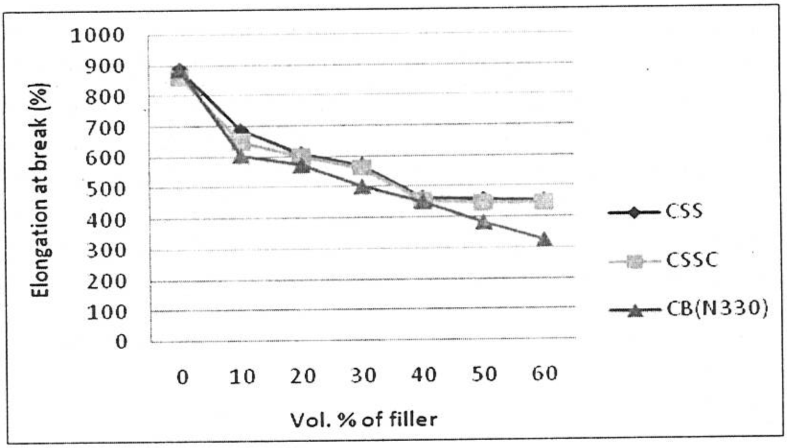

Fig. 3. Elongation at break of rubber/filler composites as function of volume fraction of fillers

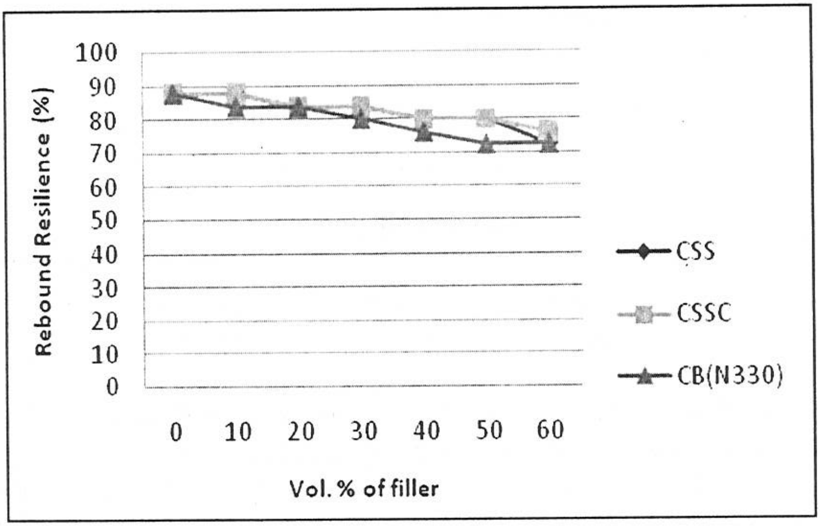

Fig. 4. Rebound resilience of rubber/filler composites as function of volume fraction of fillers

Table 4: Physico-mechanical and equilibrium swelling properties of natural rubber filled with Cherry seed shell carbon (CSSC)

Filler(phr)	0	10	20	30	40	50	60
Specific gravity (S.G)	1.001	1.001	1.003	1.031	1.034	1.048	1.050
Abrasion resistance (%)	40.1	41.5	42.0	43.3	43.8	44.2	43.1
Thermal conductivity. (W/m k)	0.170	0.175	0.177	0.179	0.182	0.187	0.193
Equilibrium swelling, S_{eq} T (%)	345.5	289.4	258.9	245.0	237.6	226.1	195.1
Equilibrium swelling, S_{eq} K (%)	329.1	274.3	251.2	240.9	228.7	219.8	181.5
Equilibrium swelling, S_{eq} D (%)	253.2	232.0	217.4	171.5	158.6	145.5	126.1

S_{eq} T, S_{eq} K and S_{eq} D were the equilibrium swelling values in toluene, kerosene and diesel respectively calculated after 72 hours in the solvents.

Tables 3-5 and Figures 3-6 showed that specific gravity and hardness of the natural rubber vulcanizates increased with increasing filler content while the elongation at break, rebound resilience, compression set and equilibrium swelling (S_{eq}) in toluene, kerosene and diesel solvents decreased with increasing filler content. Similar observations have been made by earlier workers (Ishak and Bakar, 1995; Imanah and Okieimen, 2003; Osabohien *et al.*, 2007a, b). This behaviour may be due to increased crosslinking of the vulcanizates resulting from increased filler-elastomer matrix interactions (Boonstra, 1982; Osabohien and Egboh, 2007a).

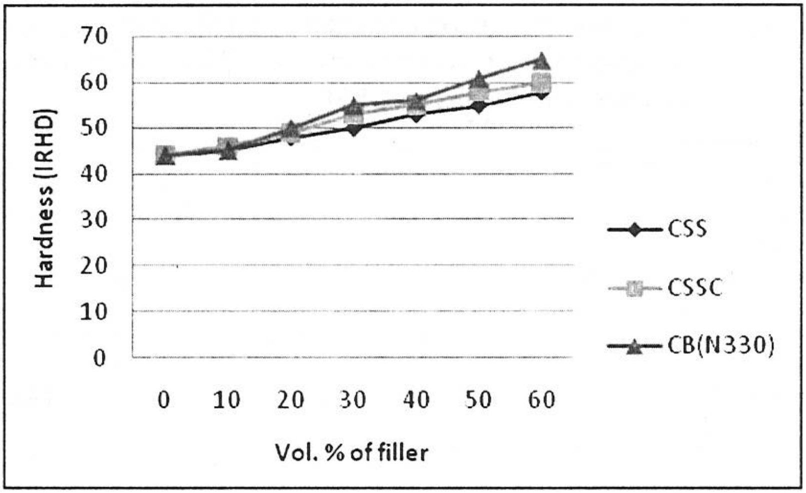

Fig. 5. Hardness of rubber/filler composites as function of volume fraction of fillers

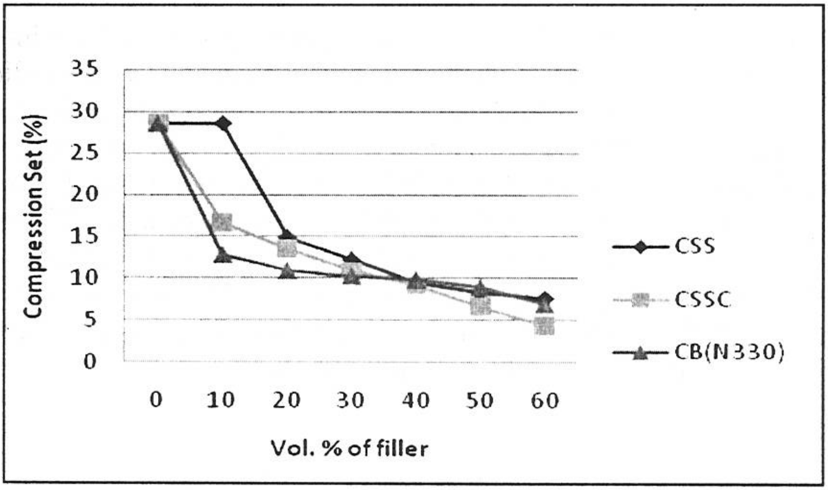

Fig. 6. Compression set of rubber/filler composites as function of volume fraction of fillers

Table 5: Physico-mechanical and equilibrium swelling properties of natural rubber filled with carbon black, CB(N330)

Filler(phr)	0	10	20	30	40	50	60
Specific gravity (S.G)	1.006	1.015	1.046	1.069	1.089	1.104	1.119
Abrasion resistance (%)	40.1	41.2	42.1	43.8	44.6	46.5	45.6
Thermal conductivity (W/m k)	0.170	0.172	0.175	0.176	0.178	0.180	0.185
Equilibrium swelling, S_{eq} T (%)	245.54	287.08	251.69	239.30	235.24	217.91	189.64
Equilibrium swelling, S_{eq} K (%)	329.13	269.78	248.57	237.20	225.54	215.33	178.70
Equilibrium swelling, S_{eq} D (%)	253.24	226.95	203.21	160.30	153.16	140.44	120.10

The degree of enhancement of tensile strength, modulus at 100% strain, hardness and abrasion resistance is in the order of CB(N330)>CSSC>CSS-filled vulcanizates. This order was also followed in the degree of resistance to swelling by the natural rubber vulcanizates. The densities of the fillers used were found to be proportional to the specific gravities of the resultant natural rubber vulcanizates (Tables 2 - 5). The properties of the fillers such as moisture content, surface area (determined by the iodine adsorption number) and metal contents are factors which may be responsible for the degree of performance of the fillers in the rubber reinforcement. Rubber reinforcement is favoured by high surface area and low moisture content of filler. The higher the surface area, the smaller the particle size of filler and the higher the reinforcement (Boonstra, 1982; Hepburn, 1984; Ishak and Bakar, 1995).

Carbonization is a process of removing free moisture and volatile matter from solid carbonaceous materials by application of heat in the absence of air. Carbonization improves the surface area of an organic filler and increase its carbon content, which may be significant in its reinforcement potential (Imanah, 2003; Okieimen and Imanah, 2005). The metal contents of CSSC were slightly higher than the CSS derived fillers. This may be due to the further grinding and screening to obtain CSSC using metallic grinding and sieving equipments. The higher the metal contents of the fillers (Table 2), the higher the thermal conductivity of the natural rubber vulcanizates. Hence, the thermal conductivity is in the order of CSSC>CSS>CB(N330)-filled vulcanizates (Tables 3-5). This may be due to conducting effect of metals on the vulcanizates (Osabohien *et al.*, 2007b).

Generally, as filler loading increases, there is an increase in the number of crosslinks between the filler and rubber matrix. This could result in the increase in tensile strength, modulus at 100% strain, hardness and abrasion resistance of the rubber vulcanizates with an attendant reduction in elongation at break due to the restriction of the mobility of the polymer chains leading to resistance to stretching upon application of stress (Morrell, 1982; Tan *et al.*, 1993). The results showed that the rebound resilience is in the order of, CSSC^{3}CSS^{3}CB(N330)-filled vulcanizates. The higher the resilience, the lower the hysteresis and heat build-up in the rubber product (Osabohien and Egboh, 2007a). This is advantageous in tyre and belt products coupled with superior conducting properties of the CSSC-filled vulcanizates which could improve the service life of the product.

The results also showed that the equilibrium swelling (S_{eq}) is in the order of the CB(N330)-<CSSC-<CSS-filled natural rubber vulcanizates. This may be due to the higher surface area arising from the higher iodine adsorption number and lower moisture content of the CB(N330) filler (Table 2). The higher the surface area of the filler, the higher the dispersion in the rubber matrix, the higher the crosslinking and interaction between filler-rubber matrix. This improved filler-rubber matrix interaction can lead to lowered solvent diffusion into the rubber matrix and hence the higher the resistance to swelling by the filled vulcanizates (Tan *et al.*, 1993; Wolff *et al.*, 1993; George and Thomas, 2001; Imanah, 2003, Osabohien, 2008). A filler particle acts as an obstruction to the diffusion of solvent molecules into the rubber matrix, thereby reducing the amount of penetrant solvent into the rubber (Wolff *et al.*, 1993; George and Thomas, 2001; Osabohien *et al.*, 2007b). The higher the filler content, the smaller the amount of solvent that can diffuse into the polymer

matrix and hence the higher the resistance to swelling by the filled rubber. In addition to this, the molecular size and diffusion coefficient of the solvent could affect the penetration of the solvent into the rubber matrix (Wolff *et al.*, 1993; George and Thomas, 2001; Osabohien *et al.*, 2007b). The higher the molecular size of solvent, the slower the diffusion into the polymer matrix. This could be the reason why the rate of diffusion of toluene solvent was highest followed by kerosene and then diesel (Osabohien *et al.*, 2007b).

Table 6: Physico-mechanical and equilibrium swelling properties of natural rubber filled with blends of cherry seed shell (CSS)and carbon black (N330)

***Filler blend (%CSS)**	**0**	**20**	**40**	**60**	**80**	**100**
Tensile strength (Mpa)	31.28	23.36	20.57	18.03	16.76	13.29
Modulus, M100 (Mpa)	3.24	2.72	2.35	2.31	229	2.27
Elongation at break (%)	383	390	392	399	406	456
Specific gravity (S.G)	1.104	1.102	1.100	1.096	1.081	1.066
Rebound resilience (%)	72.4	76.1	79.9	79.9	79.9	79.9
Hardness (IRHD)	61	61	58	58	56	55
Abrasion resistance (%)	46.5	45.1	44.8	44.2	43.9	43.8
Compression set (%)	8.98	8.91	8.83	8.55	8.47	8.31
Thermal conductivity (W/m k)	0.180	0.181	0.182	0.183	0.184	0.185
Equilibrium swelling, S_{eq} T (%)	217.91	221.08	226.70	230.14	235.68	237.41
Equilibrium swelling, S_{eq} K (%)	215.33	219.29	223.45	227.51	228.80	230.50
Equilibrium swelling, S_{eq} D (%)	140.44	152.32	155.90	158.46	160.98	160.39

**Filler blends [CSS + CB(N330)] were compounded at a total filler loading of 50 phr.*

Table 7: Physico-mechanical and equilibrium swelling properties of Natural Rubber filled with blends of cherry seed shell carbon (CSSC) and carbon black(N330)

*Filler blend (%CSSC)	0	20	40	60	80	100
Tensile strength (Mpa)	31.28	30.72	28.66	27.90	26.58	20.79
Modulus, M100 (Mpa)	3.24	3.34	2.96	2.63	2.59	2.32
Elongation at break (%)	383	389	392	408	420	447
Specific gravity (S.G)	1.104	1.101	1.097	1.083	1.066	1.048
Rebound resilience (%)	72.4	76.1	76.1	76.1	79.9	79.9
Hardness (IRHD)	61	61	61	58	58	58
Abrasion resistance (%)	46.5	46.2	46.0	45.5	44.8	44.2
Compression set (%)	8.98	8.91	8.03	7.85	7.14	6.62
Thermal conductivity (W/m k)	0.180	0.182	0.183	0.184	0.185	0.187
Equilibrium swelling, S_{eq} T (%)	217.91	218.16	220.74	222.05	224.50	226.1
Equilibrium swelling, S_{eq} K (%)	215.33	215.89	216.37	217.08	218.11	219.8
Equilibrium swelling, S_{eq} D (%)	140.44	140.96	141.67	143.01	143.84	145.5

**Filler blends [CSSC + CB(N330)] were compounded at a total filler loading of 50 phr.*

The results of the filler blends, that is, CSSC or CSS mixed with CB(N330) at a total filler loading of 50phr showed dilution effects of the fillers, CSSC and CSS on the CB(N330) filler in all measured properties with the exception of the rebound resilience and thermal conductivity where CB(N330) showed slightly lower performance (Tables 6 - 7). This means that the reinforcing ability of CB(N330) was reduced by the incorporation of CSSC and CSS in the NR compounds. This was evidenced in the reduction of tensile strength and modulus in the CSSC-CB(N330) and CSS-CB(N330)-filled vulcanizates as compared to the CB(N330)-filled types. The dilution effects were less with CSSC filler compared to the uncarbonized CSS filler.

Conclusion

This investigation has shown the effects of carbonization and filler blending on the reinforcing potentials of cherry seed shell as filler in natural rubber compounding. The results showed that the carbonized cherry seed shell performed better than the uncarbonized type in all measured properties. The reinforcing potentials of cherry seed shell was enhanced by carbonization. The properties of the natural rubber vulcanizates were improved further by blending the local fillers, CSSC and CSS with the standard commercial carbon black(N330) filler. However, the deficiencies of the CSS and CSSC fillers could be reduced by further reduction of particle size and screening to match with that of commercial CB(N330). So, while CSS could be used as a diluent filler, the carbonized variety could be used as a reinforcing filler for natural rubber compounds. The blend of CSSC with CB(N330) fillers could produce satisfactory reinforcement for natural rubber vulcanizates.

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