The influence of carbonization temperature on vulcanization behavior and cross-link density of filled NR compounds

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ABSTRACT

Investigation into the effect of carbonization on the rheological properties and crosslink density of natural rubber compounds using rubber seed shell carbon as filler was carried out. The samples of rubber seed shell carbonized at 100, 200, 300, 400, 500, 600,700,and 800°C were characterized in terms of pH, moisture content, bulk density, loss on ignition, conductivity, metal content and surface area. The rheological properties as well as the crosslink density of the vulcanizates were measured as a function of filler carbonization and loading and compared with the values obtained using commercial grade carbon black (N330). The rubber seed shell carbon showed good processing safety in terms of torques, and scorch. The results of the cure characteristics showed that the cure times, and the torque gradually increased, while scorch times decreases with increasing filler content for rubber seed shell carbon-filled natural rubber. The filler obtained at carbonizing temperature of 600°C tend to show optimum cure indices. Equilibrium swelling properties of the natural rubber vulcanizates in organic solvents; toluene, acetone, diesel and kerosene were determined and provided estimates of the dispersability of the particulate fillers derived from the rubber seed shell carbon in the natural rubber. *The crosslink density of the vulcanizates increased 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.*

INTRODUCTION

Polymeric materials have been replacing other conventional materials like metals, glass and wood in a number of applications. The use of various types of fillers incorporated into the polymer has become quite common as a means of reducing cost and to impart certain desirable mechanical, thermal, electrical and magnetic properties to the polymers[1]. Due to the energy crisis and high prices of petrochemicals, there has been a greater demand to use more and more fillers to cheapen the polymeric materials while maintaining and/or improving their properties. The advantages that filled polymer systems have to offer are normally offset to some extent by the increased complexity in the rheological behavior that is introduced by the inclusion of the fillers. Usually when the use of fillers is considered, a compromise has to be made between the improved mechanical properties in the solid state, the increased difficulty in processing, the problem of achieving uniform dispersion of the filler in the polymer matrix and the economics of the process due to the added step of compounding. It has been recognized that addition of filler to the polymer brings a change in processing behavior. The presence of the filler increases the viscosity leading to increases in the pressure drop across the die but gives rise to less die swell due to decreased elasticity. The decrease in elasticity can raise the critical shear rate at which fracture during extrusion starts to occur and hence one could often

consider increasing through put rate in the case of filled polymer processing.

A review of previous work on carbonization reveals that the temperature at which carbonization of an agricultural by products is carried out could affect the characteristics of the carbon[2] obtained and therefore, the rheological properties and crosslink density ofthe rubber vulcanizates. It is in view of this that the present research work was undertaken, with an objective to assess the effect of carbonization temperature of rubber seed shell on the rheological properties and crosslink density 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.

EXPERIMENTAL
Material
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 Compony, Warri, Nigeria.

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 for 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 Rubber seed shell carbon
The rubber seed shell carbon (RSSC) and the N330 carbon black were characterized as follows; Loss of ignition was determined ingredients. An efficient vulcanization system was chosen. The Vulcanizates 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.

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 vulcanizates for the test specimens.

Table 2: Formulation for Compounding Natural Rubber

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

Ingredients	Phr
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	1.0

Determination of the tensile properties of the vulcanisates
The curing of test pieces was done by compression molding. The curing was carried out at 145°C.

The tensile strength, modulus and elongation at break were measured using a Monsanto instron tensometer in accordance with ASTM

D412-87 method A[8]. Dumbbell test pieces of dimension (45 x 5 x 2mm) were used.

Determination of the Sorption properties and Crosslink Density of the vulcanizates

The equilibrium swelling of the vulcanizates in toluene, acetone, diesel, and kerosene were studied using the immersion – weight gain method[9] at room temperature. Square shaped samples of dimension (5 x 5 x 2mm) were cut and immersed in an air tight glass bottles containing the respective solvents. The samples were removed from the solvents after 48 hours; the samples are bottled after drying with filter paper to remove excess solvents from the surface of the sample and weighed. The equilibrium swelling was expressed as a percentage increase of the original sample.

The extent of crosslinking was determined from the reciprocal swelling values, $1/Q$, where Q is defined as the amount of solvent absorbed by 1g of rubber and is given as ;

Q = (Swollen wt. – Dried wt)/ Original wt. X 100/formula wt.

RESULTS AND DISCUSSION

Some of the characteristics of Rubber seed shell carbon

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 organic 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 bulk density of the RSSC samples given in the Table 3 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. 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[9]. Under higher

temperature (>600°C), the porosity reduces, 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.

Rheological characteristics

The results showed that the cure times and the maximum torque gradually increased (Figure 2&3), while scorch times (Figure 1) decreased with increasing filler content for RSSC-filled natural rubber, This is due to the restriction of mobility and deformability of the matrix with the introduction of mechanical restraint, 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.
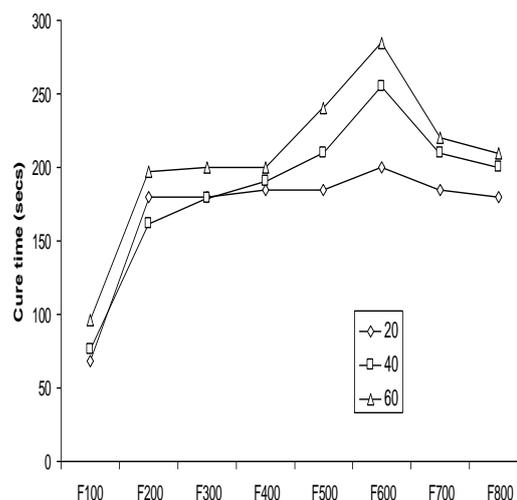

Fig 1: Variation of cure time with filler loading and filler type

The minimum torque gives an indication of the filler content in the rubber while the maximum torque in the rheograph is a measure of crosslink density and stiffness in the rubber. In general, for all the mixes the torque initially decreases, then increase and finally levels off. The initial decrease in torque to a minimum value is due to the softening of the rubber matrix while the increase in torque is due to the crosslinking of rubber.
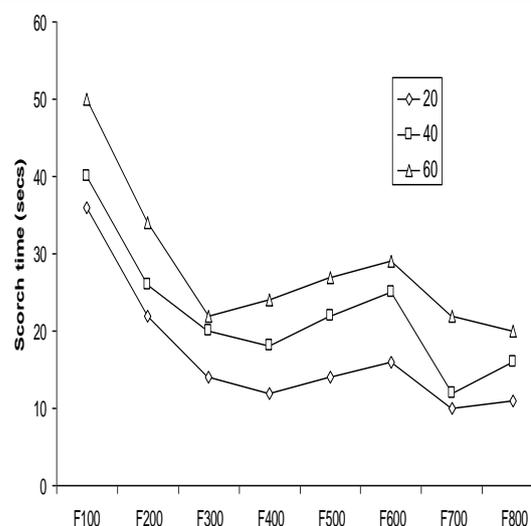

Fig 2: Variation of scorch time with filler loading and filler type
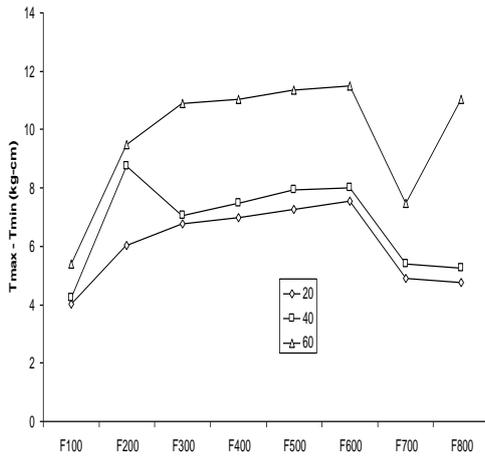
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Fig 3: Variation of change in torque (Tmax - Tmin) with filler loading and filler type

The leveling off is an indication of the completion of curing. It is found that generally the presence of fibers increases the maximum torque.

The trend observed in the cure characteristics may be attributed to differences in the filler properties. With increasing concentration of the filler, the interparticle interactions increase weakly at first and then rather strongly as the concentration becomes higher and higher. The concentration at which particle-particle interactions begin depends on the geometry and surface activity of the filler particles[10].

It has been reported that cure rate is directly related to the humidity and water content of the compound mix[11]. 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.

Tensile properties of vulcanisates
The tensile properties of the RSSC-filled natural rubber vulcanisate and N330 carbon black are shown in Table 4.

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[1,2,]

Table 3: Characterization of the rubber seed shell carbon

Temperature (°C)	100	200	300	400	500	600	700	800	CB (N330)
Yield (%)	92.9	70.9	40.7	25.9	23.0	22.4	17.5	16.8	NA
pH of slurry at 28°C	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
Conductivity ($\Omega^{-1}m^{-1}$)	31.90	43.40	181.40	173.50	135.80	261.0	226.0	245.0	288.50
Bulkdensity (g/ml)	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
Iodine adsorp. number (mg/100g)	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
Loss on ignition (%)	7.1	29.1	59.3	74.1	77.0	77.6	82.5	83.2	92.85

Table 4: Tensile properties of the natural rubber vulcanisates

Properties	Filler Loading	F100	F200	F300	F400	F500	F600	F700	F800	CB (N330)
Tensile Strength (MPa)	20phr	25.41	26.13	26.50	27.01	27.65	27.98	27.77	26.19	41.60
	40	26.14	27.22	27.33	27.89	29.11	30.82	30.00	28.26	49.00
	60	26.90	28.80	29.32	30.40	31.23	34.55	33.98	30.40	52.08
Modulus at 100%	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
Elongation at break (%)	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

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.

Sorption Properties and Crosslink Density of the vulcanizates

The results in Table 6 show that the equilibrium sorption decreases with increase in filler loading and filler carbonization temperature.

Table 5: Equilibrium sorption in organic solvents of natural rubber vulcanizates filled with RSSC

Parameters Solvents	Filler loading	F100	F200	F300	F400	F500	F600	F700	F800	N330
Acetone	20	101.11	90.24	86.72	80.15	72.86	68.42	70.35	69.10	70.60
	40	80.25	75.98	70.12	66.45	62.30	57.82	52.24	50.82	80.55
	60	55.82	48.35	42.68	39.40	36.12	33.86	29.34	25.50	34.90
Diesel	20	293.15	264.10	240.45	224.16	208.34	196.44	193.68	191.42	65.62
	40	210.74	182.83	176.44	170.10	164.05	157.21	149.09	160.32	35.48
	60	150.89	137.28	100.77	94.02	89.11	82.95	80.26	92.56	31.70
Kerosene	20	348.24	320.85	295.10	291.55	285.40	277.62	270.30	280.29	41.64
	40	287.75	270.56	256.79	225.28	200.18	187.03	181.40	191.35	40.10
	60	228.46	200.15	192.67	180.25	172.65	163.02	148.20	170.46	18.25
Toluene	20	396.50	380.28	356.75	340.10	328.08	306.75	295.40	288.05	146.20
	40	345.65	316.84	308.28	290.42	272.11	265.05	262.15	270.66	210.11
	60	310.55	295.78	270.45	258.12	240.30	222.21	200.11	235.93	178.45

Table 6: Apparent Crosslink density of natural rubber vulcanizates filled with RSSC

Parameters Solvents	Filler loading	F100	F200	F300	F400	F500	F600	F700	F800	N330
Acetone	20	0.7481	0.7809	0.7493	0.8101	0.8912	0.9491	1.0752	0.9397	1.0714
	40	0.9426	0.9275	0.9950	1.0472	1.0423	1.2613	1.4480	1.2777	0.9390
	60	1.3551	1.4575	1.5224	1.6481	1.7978	1.9178	1.5781	1.5465	2.1674

The decreasing sorption values with increasing filler loading and filler carbonization show that the Rubber seed shell carbon had reinforcing effect. Several factors can influence the equilibrium sorption in organic solvent of filled vulcanisates; notable among them are the cross link density and filler dispersion in the polymer matrix besides nature of filler and solvent. As for the higher uptake also decreases.

When a cross-linked polymer is brought in contact with a solvent, the network absorbs a sorption values observed for kerosene over that of diesel, the explanation by Gent and Lui, 1991 may suffice[12].

The diffusion mechanism in rubbers is essentially connected with the ability of the polymer to provide pathways for the solvent to progress in the form of randomly generated voids. As the void formation decreases with fiber addition, the solvent certain amount of liquid to an extent determined by the molecular weight of the liquid. Kerosene being a mixture of

hydrocarbon C_{10}- C_{14} with a lower molecular weight than diesel C_{14}-C_{19} may be expected to diffuse faster and be accommodated in the rubber matrix with less hindrance. The decrease in sorption with increasing filler concentration and filler carbonization temperature may be that each filler particle behaves as an obstacle to the diffusing molecule. As concentration of filler increase and temperature at which the filler was carbonized increases; in the rubber matrix, more and more obstacles are created to the diffusing molecule and thus reduce the amount of penetrant solvent.

With carbonization, higher agglomerates of filler particles content are produced and these aggregates sorption, and lower the diffusion of solvent into the elastomer matrix.

The results in Table 6 show that the apparent crosslink density increases with increase in filler loading and filler carbonization temperature. The decreasing sorption values in Table 5 for acetone with increasing filler loading and filler carbonization show the extent of crosslinking of the vulcanizates and therefore the crosslink density. The cross link density influence the equilibrium sorption in organic solvent of filled vulcanisates; and the extent of filler dispersion in the polymer matrix.

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, the rheological properties and crosslink density of natural rubber vulcanisates, the possibility of comparative study of the tensile 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 rheological 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 crosslink density at filler type F600 – F700 (that is at filler carbonized at 600°C – 700°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.

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