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Studies on the rheological properties of cashew nut shell powder (*anacardium accidentale*) and carbon black on natural rubber vulcanisates

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ABSTRACT

Cashew nut shell powder (CNSP) and carbon black were utilized as filler in Natural rubber vulcanizates. The CNSP was characterized in terms of pH and vulcanized using efficient vulcanization system and compared with commercial filler (NNPC carbon black). The cure characteristics revealed that samples filled with carbon black has a better and lower cure time than those filled with CNSP. The samples filled with carbon black needed higher torques than those filled with CNSP which is an indication of higher viscosity with compounds of carbon black than those with CNSP.

KEYWORDS

AnacardiumAccidentale;
Rheometer;
Vulcanizate;
Cure;
Scotch.

INTRODUCTION

The search for means and methods of improving the properties and processing of rubber dates back to over a century ago. One way of achieving this extension of service life of rubber is the incorporation of additives into the polymer matrix. Additives are materials when incorporated into a polymer base, help to ensure easy processing, reduce cost of product and enhance service properties. The different types of additives used in the processing of rubber into products include, vulcanizing agents acelerator, activator, antidegradants, fillers, softener, thickners, gel sensitizer, colorant e.t.c.

Fillers is one of the major additives used in natural rubber compound and has marked effect and influence on rubber materials. Filler functions to modify the physical and, to some extent, the chemical properties of vulcanizates.

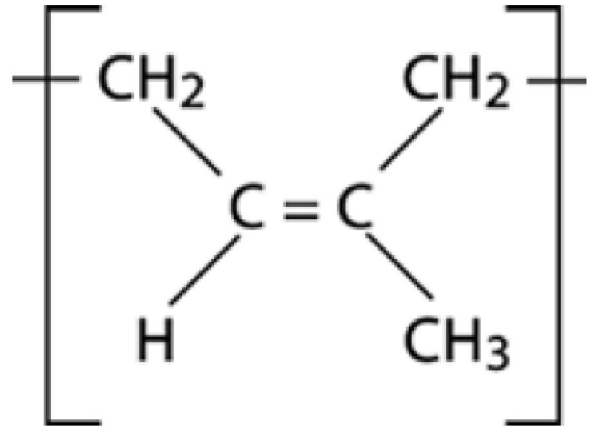
The mechanism of reinforcement of elastomers by fillers has been reviewed by several workers. They considered that the effect of filler is to increase the number of chains, which share the load of a broken polymer chain. It is known that in the case of filled vulcanizates, the efficiency of reinforcement depends on a complex interaction of several filler related parameters. There include particle size, particle shape, particle dispersion, surface area, surface reactivity, structure of the filler and the bonding quality between the filler and the rubber matrix.

In rubber industry, filters that are commonly in use are carbon black, china clay and calcium carbonate. Carbon black is derived from petro-chemical sources but the unstable price of crude oil has led to the search for filler that are derived from other sources. Agricultural by-products; maize cobs, cocoa pod husk, sugar cane chaff, rice husk, plantain peel etc. are low cost materials and readily available in large quantity for use everywhere, of which well over 300 million tones are produced annually. In previous reports, the use of cocoa pod husk, rubber seed shells, groundnut husk, plantain peels etc were examined. The results obtained from these studies indicated a potential for the utilization of agricultural residues as fillers in natural rubber compounds.

Rubber was known to the indigenous peoples of the Americas long before the arrival of European explorers. In 1525, Padre d'Anghieria reported that he had seen Mexican tribes people playing with elastic balls. The first scientific study of rubber was undertaken by Charles de la Condamine, when he encountered it during his trip to Peru in 1735. A French engineer that Condamine met in Guiana, Fresnau studied rubber on its home ground, reaching the conclusion that this was nothing more than a "type of condensed resinous oil".

The first use for rubber was an eraser. It was Magellan, a descendent of the famous Portuguese navigator, who suggested this use. In England, Priestley popularized it to the extent that it became known as India rubber. The word for rubber in Portuguese - borracha - originated from one of the first applications for this product, when it was used to make jars replacing the leather borrachas that the Portuguese used to ship wine.

Returning to the works of Condamine, Macquer suggested that rubber could be used to produce flexible tubes. Since then, countless craftsmen have become involved with rubber; goldsmith Bernard, herbalist Winch, Grossart, Landolles and others. In 1820, British industrialist Nadier produced rubber threads and attempted to use them in clothing accessories. This was the time when America was seized by rubber fever, and the waterproof footwear used by the indigenous peoples became a success. Waterproof fabrics and snow-boots were produced in New England.



Structure of NR

In 1845, R.W. Thomson invented the pneumatic tire, the inner tube and even the textured tread. In 1850 rubber toys were being made, as well as solid and hollow balls for golf and tennis. The invention of the velocípede by Michaux in 1869 led to the invention of solid rubber, followed by hollow rubber and finally the re-invention of the tire, because Thomson's invention had been forgotten.

Natural rubber is a linear polymer of an unsaturated hydrocarbon called isoprene (2-methyl butadiene). There may be as many as 11,000 to 20,000 isoprene units in a polymer chain of natural rubber.

Charles Goodyear discovered the process of vulcanization in 1893 to modify the properties of natural rubber. Vulcanization is the addition of the right amount of sulphur to natural rubber to impart high elasticity, tensile strength and resistance to abrasion.

Rheology is the study of deformation and flow. In the Rubber Industry the effects of compound variations on curing characteristics are important in compound development studies or production control. In compound development, the composition of the ingredients can be varied until the desired vulcanization characteristics are achieved. For all this, the Computerized Rheometer with Micro-processor temperature controls is an equipment of vital importance. The Rubber Compounder feels handicapped without a Rheometer. The inventions of new Polymers & Rubber Chemicals leads the compounder to an embarrassing position regarding their choice & use.

The degree of vulcanization of a rubber compound has a big influence on the properties of the final product. Therefore, precisely defining the curing process including optimum cure time is important to ensure the production of final products having high performance. Typically, vulcanization is represented using vulcanization curves. The main types of equipment used for producing vulcanization curves are the oscillating disc rheometer (ODR) and the moving die rheometer (MDR).

The Rheometer is an only equipment in the Rubber Industry which helps the Compounder to choose the right material and its appropriate dose to meet the end requirements of the product. The Rheometer not only exhibits the curing characteristics of the Rubber Compound but it also monitors the processing characteristics as well as the physical properties of the material. The "Cure Curve" obtained with a Rheometer is a finger print of the compound's vulcanization and processing character.

MATERIALS AND METHODS

Natural rubber crumb was obtained from Alhson Lab Equipment consult, Zaria, the cashew nut shell powder were obtained from Auchi community in Edo state while othe compounding additives like TMQ, zinc oxide, stearic acid, MBTS, sulphur were obtained from Integrated rubber products Plc., Benin-city.

SAMPLE PREPARATION

The cashew nut shell powder was characterized. The pH and moisture content were determined using a Jenway pH meter and a hot air oven respectively.

The samples of recipes were prepared following the recipes in TABLE 1 & 2.

The compounding of the formulations was carried out on a standard laboratory roll mill in accordance with ASTM 3132 procedures. Sample were

TABLE 1 : Formulation table for carbon Black

		Formulations (PPHR) grams				
S/No	**Ingredients**	**1**	**2**	**3**	**4**	**5**
1	Natural rubber	100	100	100	100	100
2	Zinc oxide	5	5	5	5	5
3	Stearic acid	2	2	2	2	2
4	TMQ	1.5	1.5	1.5	1.5	1.5
5	MBTS	3	3	3	3	3
6	CNSP	--	--	--	--	--
7	Carbon black	10	20	30	40	50
8	Processing oil	2	2	2	2	2
9	Sulphur	3	3	3	3	3

TABLE 2 : Formulation table for cashew nut shell powder

		Formulations (PPHR) grams				
S/No	**Ingredients**	**1**	**2**	**3**	**4**	**5**
1	Natural rubber	100	100	100	100	100
2	Zinc oxide	5	5	5	5	5
3	Stearic acid	2	2	2	2	2
4	TMQ	1.5	1.5	1.5	1.5	1.5
5	MBTS	3	3	3	3	3
6	CNSP	10	20	30	40	50
7	Carbon black	--	--	--	--	--
8	Processing oil	2	2	2	2	2
9	Sulphur	3	3	3	3	3

sheeted out and the cure characteristics were analysed

ASSESMENT OF THE VULCANIZATES CURE CHARACTERISTICS

The cure characteristics of the vulcanizates was carried out using an Alpha Technology ODR 2000 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 150^{0}C. The rheographs, which contain the cross-link density against time plot for the compounded samples were analyzed for ts1, ts2, t10, t50 t90, scorch time, torque (minimum torque ML and maximum torque MH. Curing of the test pieces were done by moulding. This was carried out using steam heated hydraulically operated single daylight press.

RESULTS AND DISCUSSION

The pH of the filler slurry shows that cashew nut shell powder (CNSP) is acidic with pH of 4.97 while that of the carbon black is alkaline with pH value of 8.07. It is generally well known that acidic fillers retard cure rate or vulcanization (longer cure time) while alkaline fillers accelerate it (shorter cure time).

Rheological analysis results

DISCUSSION

The cure characteristics of the compound mixes were measured at 150^{o}C in an oscillatory disc rheometer (Alpha ODR 2000) in accordance with ISO 3417 method. The scorch time, cure time, torques, thermo-plasticity and reversion time were studied from the rheographs as shown in table for both compounds filled with carbon black and cashew nut shell powder.

In the rubber industries, the effects of compound variation on cure characteristics are important in compound development. The "cure curve" obtained with rheometer is a finger print of the compounds vulcanization and processing character. The rheology of a curing compound is determined by two factors, the degree of cure and the temperature. As the cure proceeds, the molecular size increases and so does the cross-linked density, which decreases the mobility and hence increases the viscosity of the resin.

All the compounds analyzed revealed curves that are in line with the standard methods. It is generally known that acidic fillers retards vulcanization/curing (increase the proper cure time) while alkaline fillers accelerates vulcanization (reduces the proper cure time). From the fillers used for this work which are carbon black and cashew nut shell powder happens to be alkaline and acidic in nature with carbon

TABLE 3: Rheological analysis

S/NO	SAMPLE	TEMP. (^{O}C)	tS1 (min)	tS2 (min)	t10 (min)	t50 (min)	t90 (min)	ML (Kg-cm)	MH (Kg-cm)	MI (Kg-cm)	CR	RT (min)	END TEMP. (^{O}C)	TR	R
1	100NR	150	0.05	0.08	0.07	5.09	5.51	06.80	26.11	06.0	18.42	6.8	149.2	R	P
2	CB 10	150	2.57	3.16	3.23	4.38	5.58	10.94	35.54	08.8	41.32	8.5	154.0	R	P
3	CB 20	150	0.04	0.05	0.07	4.22	5.31	08.55	36.62	08.0	19.01	6.4	152.0	R	P
4	CB 30	150	2.56	3.17	3.26	4.47	6.01	06.81	33.55	21.0	35.21	7.4	152.6	R	P
5	CB 40	150	2.35	2.53	3.05	4.37	6.16	10.11	38.86	10.0	27.55	9.1	155.4	R	P
6	CB 50	150	2.16	2.34	2.48	3.58	5.08	06.50	40.58	23.8	36.50	6.9	155.0	R	P
7	CNSP 10	150	3.49	4.22	4.11	5.21	6.30	07.13	23.25	06.8	48.08	9.2	149.1	R	P
8	CNSP 20	150	4.32	4.57	4.49	6.03	8.12	06.05	21.86	09.0	28.17	0.0	148.7	M	P
9	CNSP 30	150	3.22	3.45	3.33	4.29	5.19	08.02	21.80	10.6	57.47	6.3	148.2	R	P
10	CNSP 40	150	3.15	3.35	3.26	4.24	5.49	08.16	23.22	08.75	46.73	7.7	149.0	R	P
11	CNSP 50	150	2.59	3.14	2.59	3.47	4.46	06.28	16.60	09.0	75.76	6.6	146.2	R	P

LEGEND: CR- Cure rate, TR- Trends (R- Reversion, M- Marching, P- Plateau), RT-Reversion time, R- Results, P- Pass

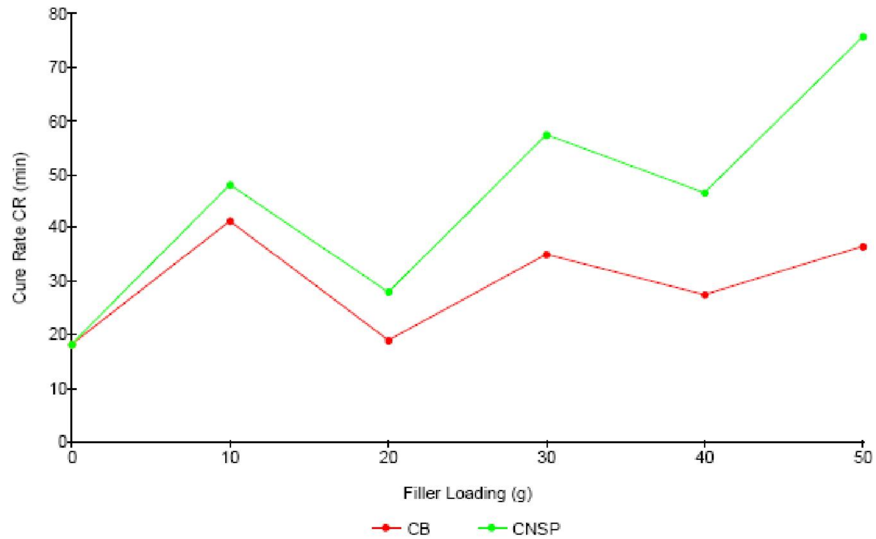


Figure 1 : Cure rate against filler loading

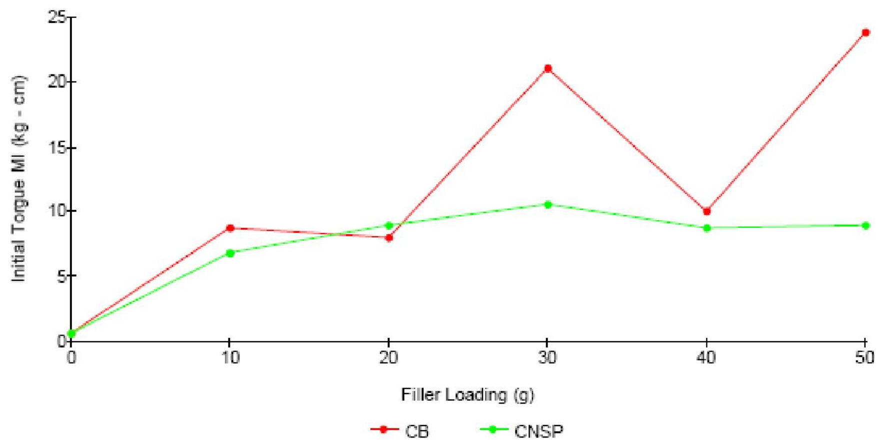


Figure 2 : Initial torque against filler loading

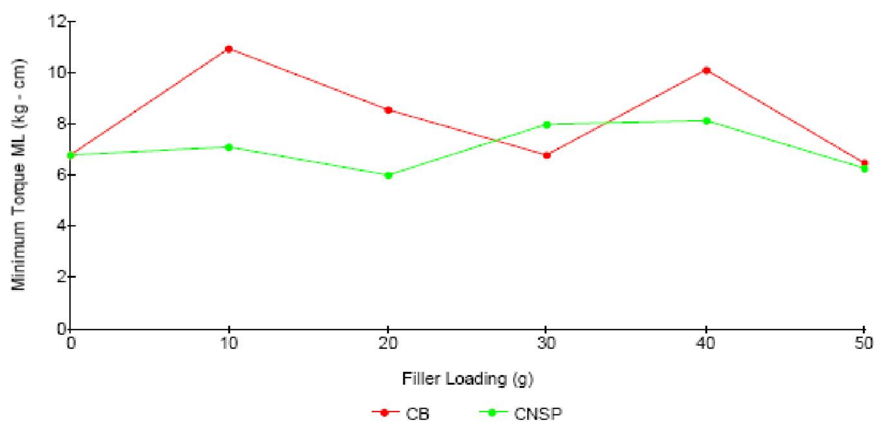


Figure 3 : Minimum torque against filler loading

black having acid value of 8.07 and cashew nut shell powder with acid value of 4.97 which is higher than that of the carbon black, hence have an effect on the cure rate of the compound mix where samples filled with carbon black had lower cure time than those filled with cashew nut shell powder at same filler loading, see Figure 1.

The initial torque which is the torque recorded at time zero at the start of the test which reveals that as the filler loading is increasing, the initial torque needed to start the test also increases for both compounds filled with carbon black and cashew nut shell powder except for the sample filled with 40g for both fillers which shown a drop in the initial torque, see Figure 2.

The minimum torque (ML) which is a measure of the stiffness and viscosity of the un-vulcanized rubber compound reveals that for the compound filled with carbon and cashew nut shell powder where both not having a uniform flow as the filler loading were increasing from 10g pphr to 50g pphr. The highest minimum torque were recorded for carbon black at loadings of 30g and 40g pphr (06.81 & 10.11 kg-cm) respectively before dropping at 50g pphr loading with minimum torque of 06.50kg-cm.

There is a constant decrease of the minimum torque for compounds filled with cashew nut shell powder at 10g to 30g pphr before it eventually increased at 4og pphr then further decreased at 50g pphr, see Figure 3.

The maximum torque (MH) which increases proportionately as the curing starts, depending on the type of compound, the slope of rising torque varies. After a while the torque attains maximum value and it either plateau out, reverts or marched.

From the rheological plots obtained, it is revealed that all the samples subjected for this test reversed for both carbon black and cashew nut shell powder filled compound except for the compound filled with 20g pphr CNSP which experienced marching, i.e continuous rising trend during the period of record. See appendix.

From Figure 4, there is an increase in the maximum torque as the filler loading is increased from 10g pphr to 20g pphr before it further drops at 30g pphr from 36.62kg-cm to 33.55kg-cm and further increased from 40g pphr to 50g pphr (38.86-40.58kg-cm). That was not so as in the case of samples filled with cashew nut shell powder were there was a drop from 10g pphr to 20g pphr and then a little increase at 30g pphr to 40g pphr (21.80 – 23.22kg-cm) and further drops at 50g pphr (16.60kg-cm). Compounds

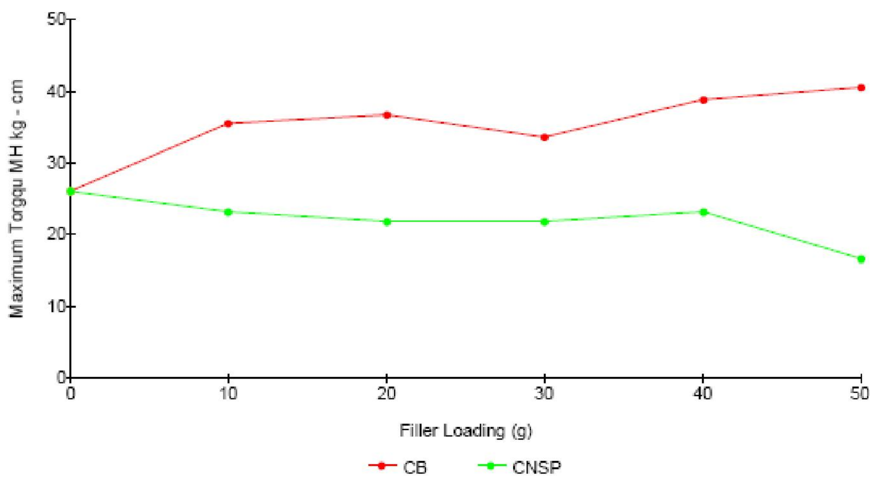


Figure 4 : Maximum torque against filler loading

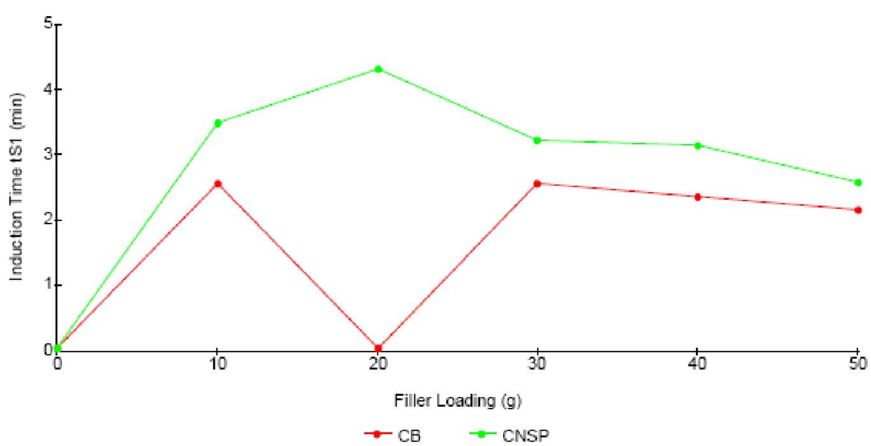


Figure 5 : Induction time against filler loading

filled with cashew nut shell powder generally showed lower maximum torque compared to those filled carbon black filler at all loadings, See Figure 4.

The induction time (tS1) which is the scorch time for viscosity to rise 1unit above minimum torque (ML) reveals that samples filled with carbon black have lower induction time compared to those filled with cashew nut shell powder. As filler loading was increased, the induction time also increased for samples filled with carbon black except for sample filled with 20g pphr which the induction time drastically dropped to 0.04s which gives the lowest induction time in all the compounds, this could be attributed to the in-homogeneity in the sample. This trend was not the same with samples filled with cashew nut shell powder as there were irregular increase and decrease in the samples as filler loading was increasing from 10g pphr to 50g pphr. See Figure 5.

The scorch time (tS2) which is the time for the viscosity torque to rise 2units above the minimum torque (ML) is a measure of processing safety of vulcanized compounds. Scorch being a premature vulcanization in which the stocks becomes partially vulcanized before the product is in its final form and ready for vulcanization. It reduces the plastic properties of the compound so that it can no longer be processed. Scorching is the result of both the temperature reached during processing and the time the compound is exposed to elevated temperature. Since scorching ruins the stock, it is of important that vulcanization does not start until processing is complete. The samples filled with cashew nut shell powder revealed better scorch time compared to those filled with carbon black filler, this is attributed to

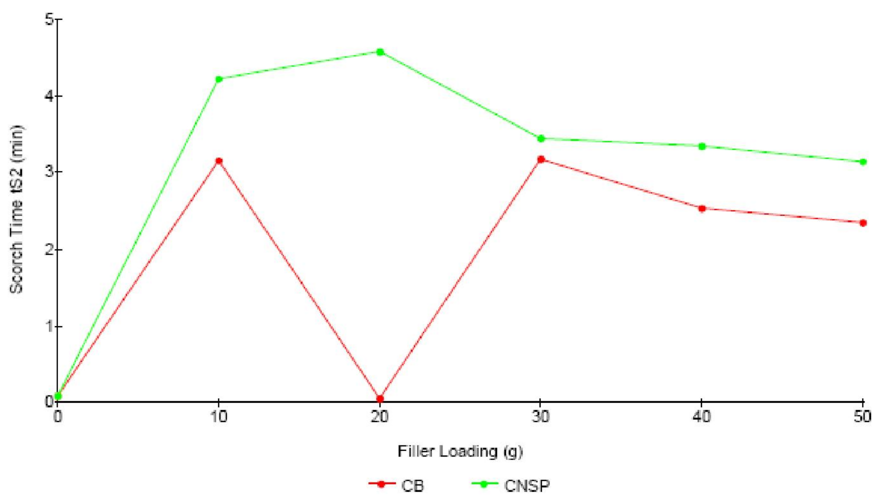


Figure 6 : Scorch time against filler loading

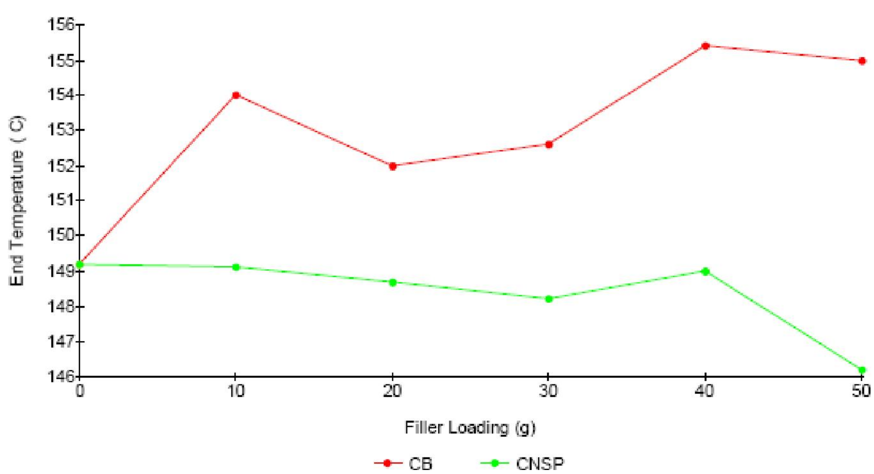


Figure 7 : End temperature against filler loading

the chemical nature of the filler as the acidic content in the CNSP help to prolong the cure time and scorch time and hence reduced deterioration of the compound. See Figure 6.

The processing/rheological end temperature is a reflection of the amount of heat a specimen can be subjected to or withstand before deterioration will start setting in above that temperature, From the rheological analysis carried out, carbon black revealed a better end temperature compared to compounds filled with cashew nut shell powder at the same filler loading.

The end temperatures were not stable for both samples filled with carbon black and cashew nut shell powder. At the beginning of the analysis, the end temperature increased from the control sample to the sample filled with 10g pphr of carbon black (149.2°C to 154°C) which was not so at the beginning for compounds filled with cashew nut shell powder as there was a decrease in the end temperature from the control sample to sample filled with 10g pphr of cashew nut shell powder, this were generally attributed to the chemical nature and surface area of the fillers, see Figure 7.

Reversion is the time to reach 98% maximum torque, and is recorded in minutes. It gives an indication of the quality of the compound as to how long it retains its physical properties when subjected to heat ageing. Reversion occurs with over cure leading to a decrease in the modulus and tensile strength. All the samples subjected for this analysis reversed except that filled with 20g of cashew nut shell powder which marched and revealed in indication of better process safety of the physical properties when subjected to heat at higher temperature without adversely affecting the compound. Although samples filled with carbon black revealed better reversion time compared with those filled with cashew nut

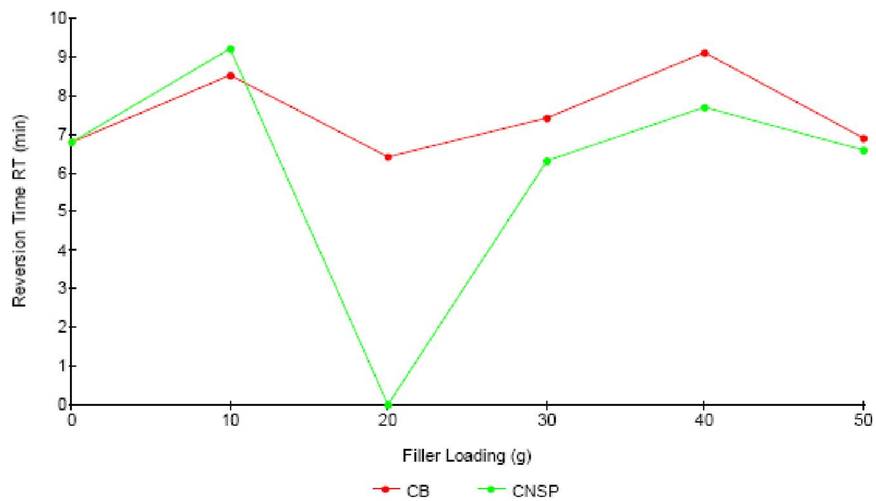


Figure 8 : Reversion time against filler loading

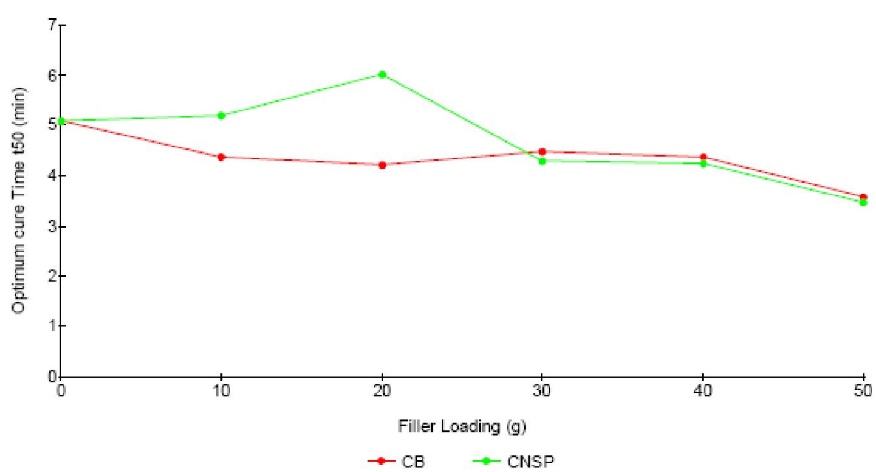


Figure 9 : Optimum cure time, t50 against filler loading

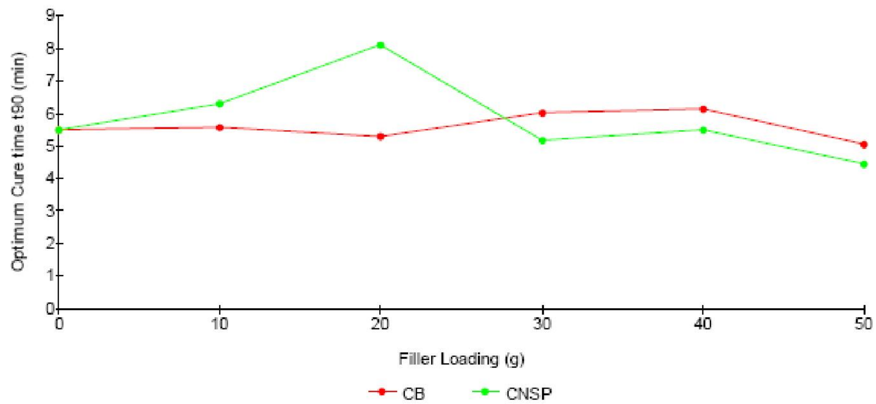


Figure 10 : Optimum cure time, t90 against filler loading

shell powder at the same filler loading except for sample filled with 10g of cashew nut shell powder which only revealed a better reversion time over its counterpart filled with 10g pphr of carbon black. See Figure 8.

The t50 and t90 time values which are the time the compound reaches 50% and 90% cure respectively revealed similar cure trends for both carbon black and cashew nut shell powder. At filler loading 10g and 20g, the optimum cure time of CNSP were higher than those of the carbon black (indication of lower optimum cure rate) and there was an overlap at both t50 and t90 at 30g pphr loading showing a lower optimum cure time for CNSP than carbon black up to 50g pphr filler loading (indication of a higher optimum cure time), see Figure 9 and 10 respectively. It has already been established in rubber curing that if an elastomer is processed with filler of high acid content, it tends to prolong vulcanization or cure time. This result is in accordance because acid content of carbon black is higher than that of cashew nut shell powder. All the samples analyzed for rheology passed the test.

CONCLUSION

The degree of rheology of carbon black and cashew nut shell powder (CNSP) filler in natural rubber depends on particle size, aggregate structure, surface area, level of filler loading and other physical nature of the fillers. This indicates that agricultural by-product like cashew nut shell powder (CNSP) is comparable to carbon black filler in terms of rheology. The cure characteristics revealed that samples filed with carbon black has a better and lower cure time than those filled with CNSP, this was as a result of the acidic nature of CNSP. The samples filled with carbon black needed higher torques than those filled with CNSP which is an indication of higher viscosity with compounds of carbon black than those with CNSP.

RECOMMENDATIONS

i This research work reveals certain outstanding properties of the cashew nut shell powder (CNSP). In order to modify and establish these findings, the following recommendation has been put forward from some of the problems encountered:

ii The cashew nut shell powder can perfectly serve as an extenders or diluents i.e. to increase the bulk of the polymer product with reduction in cost.

iii Efforts should be made to improve the surface area of cashew nut shell powder and more particle sizes and filler loading should be tried in future work

iv Measures should be taken to neutralize the filler because of its acid nature.

v Compactabilizer could be used in compounding cashew nut shell powder with natural rubber compound to improve to improve on its miscibility.

vi A wide ranges of particle sizes should be varied to know how particle size will affect the properties of the vulcanizates.

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