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Cure Characteristics and Physico-Mechanical Properties of Natural Rubber Filled with the Seed Shells of Cherry (Chrysophyllum albidum)

***OSABOHIEN, E; EGBOH, S H O**

Department of Chemistry, Delta State University, Abraka, Nigeria

ABSTRACT: The cure characteristics and the physico-mechanical properties of natural rubber, standard Nigerian rubber, SNR10 filled with cherry seed shell (CSS) and standard carbon black CB (N330) were determined. The results showed that the scorch, cure times and the maximum torque gradually increased with increasing filler content for CSS-filled natural rubber, 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. The tensile strength of both CSS and CB-filled vulcanizates increased to a maximum at 40 phr filler content before declining. The moduli (M100 and M300), specific gravity (S.G), hardness and abrasion resistance increased while the elongation at break and Dunlop resilience decreased with increasing filler content for both vulcanizates. The locally sourced CSS filler, had a lower reinforcement properties compared to the CB (N330) filler, probably due to its higher moisture content and larger particle size. @JASEM

Raw dry rubber is seldom, if ever used in its original state for any engineering application. Rubber manufacture involves the addition to rubber many ancillary materials called additives. This is to allow the rubber compounds to be satisfactorily processed and when vulcanized improve the application properties of the rubber articles. Additives in rubber include; vulcanizing agents, accelerators, activators/retarders, antidegradents, fillers, plasticizers and other ancillary ingredients. One of the most important additives and second largest following the base polymer in rubber compounding is the filler. Fillers improve processability, physico-mechanical properties such as tensile properties, hardness, flex fatigue, tear and abrasion resistances, and may cheapen the final product. They achieve performance enhancement by forming strong chemical bonds with the rubber, that is, strong filler-elastomer interactions. The fillers used in rubber compounding can be classified into reinforcing and non-reinforcing types. A reinforcing filler is one which increases the tensile strength, hardness and abrasion resistance of the rubber article. The finer the particle size the more reinforcing a filler is. Examples of reinforcing filler include; carbon black and silica. Non-reinforcing fillers cause reduction in strength properties but may increase hardness and modulus of the rubber product. They are usually applied as diluents or extenders to generally reduce cost, examples include the whitings ($CaCO_3$) and china clay (Blow et al, 1982; Bello, 2001; Whelan et al, 1979).

Carbon black is presently the most commonly used filler in the rubber industry, but it's petroleum derived and expensive commercially. Locally available materials such as limestones, eggshells, corn cobs, groundnut shells, rubber seed shells, rice husk, cocoa pod husk and Cherry (Chrysophyllum albidum) are amongst the underutilized renewable resources in our society today which can be used directly or converted by simple processes to valuable materials in polymer or related applications (Osabohien et al, 2004; Adeosun, 2000; Ishak et al, 1995; Ogunniyi, 1989; Jideonwo et al, 2000; Imanah, 2003; Adewisi, 1997).

The Cherry (Chrysophyllum albidum) is a forest tree belonging to the family, sapotaceae and its natural occurrences have been reported in diverse ecozones in Nigeria, Niger Republic, Uganda, Cameroon and Cote d'Ivoire. The fruit called the African star apple is a large berry containing about 4-5 flattened seeds. The tree can be grown in residential areas and fruits especially during the months of December to April. The freshly sweet pulp of the fruit is edible and has been found to contain high content of ascorbic acid (vitamin C) and iron. The seeds contain oil which is used for diverse purposes, and the seeds are sometimes used for local games. Also, the fruit is a source of resin while other components of the tree including the roots, and leaves are used for medicinal purposes (Keay, 1989; Bada, 1997; Adisa, 2000; CENRAD, 1999; Okafor et al, 1987; Umelo, 1997).

This research work is aimed at developing a filler for rubber compounds which can be an alternative to the commonly used commercial carbon black filler with a consequent reduction in cost. The seed shells of cherry are agro-wastes in Nigeria which have been applied here as filler for natural rubber in comparism with standard carbon black filler.

MATERIALS AND METHODS

The Cherry Seed Shells were collected from Idumuesah, Ika-North-East, Delta State, Nigeria,

**Correspondence, E-mail: osabohieneemma@yahoo.com.*

while the industrial grade carbon black (N330) filler was obtained from the Carbon Black Laboratory of the Nigerian National Petroleum Company (NNPC), Warri, Nigeria. The natural rubber, Standard Nigerian Rubber, (SNR10), used for this work was obtained from FAMAD (formerly BATA), Benin-City, Nigeria. All the rubber ingredients and chemicals used were industrial grades. The standardized compounding and test equipment used were got from the Department of Polymer Technology, Auchi Polytechnic, Auchi, Edo State, Nigeria and Dunlop, Nigeria PLC, Ikeja, Lagos. The atomic absorption spectrometer (AAS) used was the Pye Unicam SP 2900 model, which was got from Tudaka Environmental Consultants Ltd, Warri, Delta State, Nigeria.

Characterization of the SNR10, CSS and CB (N330): The natural rubber used was characterized in terms of the dirt content, this test was based on dissolution of the rubber in a high boiling solvent passing the solution through a sieve of 44mm aperture, the dirt retained was washed, dried and the weight recorded. The ash content of the rubber was determined by wrapping a test portion in an ashless filter paper and incinerated in a muffle furnace at about 600^{o}C. The weight of the test piece after incineration in percentage gave the ash content. The volatile matter present in the rubber sample was determined by taking known weight of a homogenized portion, milled and dried in an oven at 100^{o}C±3^{o}C for four hours. The weight difference taken after cooling in percentage was recorded as the volatile matter content. The Nitrogen content in the rubber was measured by a semi-micro kjeldah procedure. The plasticity retention index (PRI) of the natural rubber was obtained by measuring the plasticity of test portion before and after oven ageing for 30±0.25 min at 140^{o}C±0.5^{o}C using the parallel plate plastimeter with a platen 10mm in diameter. The ratio of aged plasticity number to that of unaged test piece in percentage was taken as the PRI of the rubber. The Mooney viscosity of the rubber was measured using the Mooney viscometer (Imanah, 2003; Anderson et al 1989; Linder et al 1942; Morton, 1973; Asore, 2000; Blow, et al 1982).

The CSS and CB (N330) fillers were characterized in terms of the following parameters; moisture content, here, known weight of the dried ground sample was put in an oven at 110^{o}C±15^{o}C for an hour. The difference in weight in percentage before and after oven drying was recorded as the amount of moisture in the sample. A known weight of the dried, pulverized and sieved filler sample was ignited in a muffle furnace at a temperature of 1000^{o}C for about an hour. The weight difference got after ignition in percentage was taken as the loss on ignition (Vogel, 1964; Palmer, 1965). The iodine adsorption number of the fillers were determined in accordance with standard method (ASTMD 1510,1983). The oil absorption, that is the amount of oil (linseed oil) required to produce a consistent putty-like paste of the fillers was measured (Hepburn, 1984). The pH of the aqueous slurries and the metallic compositions of the filler were determined using standard methods (ASTMD 1512, 1983; Christian, 1980).

Formulation, compounding and curing: The formulation given in Table 3, was used to compound the rubber, and efficient vulcanization system was employed. Mixing was done on a laboratory size (160 x 320mm) two-roll mill maintained below 80^{o}C. The cure characteristics were measured using the Mosanto 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 150kg/cm at a temperature of 185^{o}C. The cure times predicted by the Mosanto rheographs were used as guide to obtain vulcanizates for the test specimens (Blow et al, 1982).

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 500mm/min. Dumb-bell test specimens of dimension (45x5x2mm) were used as described in ASTMD412. The specific gravity (S.G) and hardness of the test pieces were measured with the aid of automatic machines, Mosanto Densitron 2000 and Mosanto Duratron 20001 respectively. The Dunlop resilience, and abrasion resistances of the test specimens were determined using the Wallace Croydon resiliometer 2A, and abrader, the DIN to ISO 4649 Akron to BS 903 part A9 method C respectively (Blow et al, 1982; BS, 1958).

RESULTS AND DISCUSSION

The results of the aforementioned tests, are shown in Tables 1-7. The CSS filled vulcanizates were compared with the standard carbon black filled systems. The characteristics of the natural rubber, Standard Nigerian Rubber, SNR10 (Table 1), followed similar trends with other standard natural rubbers such as the Standard Malasian Rubber (SMR) and Standard African Rubber (SAR) (Blow et al,1982; Morton, 1973; Imanah et al, 2004). The high PRI, and Mooney viscosity of the rubber are indications of good ageing resistances and rigidity of the resulting vulcanizates. Table 2 compares the physico-chemical properties of the CSS with the CB (N330) fillers. There were appreciable differences in the values of the loss on ignition, iodine adsorption number, moisture content, metal contents and particle size. The loss on ignition is a measure of the carbon content or organic materials present in a sample. Also, the amount of carbon in a filler has been associated with the reinforcing potential (Imanah et al, 2004). That is, the higher the carbon content of a filler, the higher the reinforcement of the rubber because carbon itself is a very good reinforcing filler. The iodine adsorption number is a measure of the surface area of the filler, the higher it is, the finer or smaller the particle size of filler and the more the reinforcement potential (Blow et al, 1982; Hepbum, 1984). The oil absorption is a measure of the aggregate structure of the filler, and the results indicate similar structure for both fillers. The presence of lead metal in appreciable quantity (approx. 22ppm) may make the cherry seeds pollutive and poisonous (Ademoroti 1996; Bockx 1986).

Table 1: The characteristics of SNR10, standard Africa rubber SAR10 and standard Malaysian rubber SMR5

Test parameter	SNR10	SAR10	SMR5
Dirt content (%)	0.01	0.02	0.05
Ash content (%)	0.25	0.32	0.5
Nitrogen content (%)	0.2	0.23	0.7
Volatile matter (%)	0.25	0.4	1.0
Plasticity retention Index (PRI)	71.05	67.0	-
Mooney viscosity ML (1+4) 100^{o}C	76.0	70.0	60.0

Table 2: Physico-chemical properties of the CSS and CB(N330)

Test parameter	CSS	CB(N330)
Moisture content @110^{o}C(%)	6.8	2.10
Loss on ignition@100^{o}C (%)	84.5	94.05
Density (g/cm^3)	1.70	1.80
Iodine adsorption umber (mg/g)	55.01	79.92
Oil absorption (g/100g)	51.12	54.50
pH of aqueous slurry	6.41	6.65
Sodium (ppm)	55.09	-
Potassium (ppm)	15.65	-
Calcium (ppm)	16.76	-
Magnesium (ppm)	54.27	-
Iron (ppm)	22.42	-
Lead (ppm)	77.70	30.0 – 32.0
Particle size range (nm)	15.0-212.0	30.0-32.0

Table 3: Typical formulation of the natural rubber compound Ingredient

Natural rubber (SNR10)	100
Zinc oxide (ZnO)	4.0
Stearic acid	2.0
*Filler Processing oil	0.0 – 70.0**
N-Cyclohexylbenzthiazylsuphenamide (CBS)	2.0
Flectol H (TMQ)	1.5
Sulphur	1.5

Filler: Red earth and carbon black (N330); ** Filler loading: 0, 10, 20, 30, 40, 50, 60, and 70 Phr.

Tables 4 and 5 summarise the processing cure characteristics at different filler loadings for both fillers (CSS and CB (N330). They showed interestingly fast curing when compared to other similar works (Imanah et al, 2004; Gelling, 1985; Iyasele 2004). This result has been attributed to the accelerator used. N-Cyclohexylbenzthiazylsulphenamide(CBS) accelerator is inactive at processing temperatures and very active at curing temperatures for best safety requirements (Blow et al, 1982). The scorch and cure times were generally increasing for the CSS-filled SNR10, while they were decreasing in the case of CB (N330)-filled SNR10. This observation may be attributed to the differences in pH, carbon, metal and moisture contents. The lower surface area and pH may have contributed to the increasing scorch and cure times for the CSS- filled SNR10 compounds as opposed to the CB(N330) filled types. Furthermore, the cure retardation experienced by CSS -filled vulcanizates as against cure enhancement of the CB-vulcnizates may be due to the existence of the metal components having different particle sizes, surface areas and surface reactivities. Here, the metals or their oxides present in the CSS filler can cause the retardation of the accelerator activity, which in turn can slow down the sulphur reaction leading to increased scorch and cure times (Ishak et al, 1995). The maximum torques reached (T_{max}) generally increased with increasing filler loading, though the increases were higher for the CB-filled vulcanizates. This result may be due to the higher surface area, then higher rubber-filler interactions and consequently higher retardation in the mobility of the macromolecular chains in the rubber matrix in the case of CB-filled systems (Wolff et al, 1993; Tan et al, 1993).

Table 4: Cure characteristics of SNR10 filled with CSS

Filler (phr)	0	10	20	30	40	50	60	70
Scorch time(s)	28.8	26.4	26.8	27.0	28.0	28.2	28.8	29.0
Cure time(s)	41.4	38.4	40.4	42.0	43.0	43.8	45.0	48.0
*T_{max} (Ib-in)	6.47	7.20	7.89	8.49	9.20	9.87	10.49	11.67

T_{max} is the maximum torque recorded

Table 5: Cure characteristics of SNR10 filled with CB(N330)

Filler (phr)	0	10	20	30	40	50	60	70
Scorch time(s)	28.8	32.4	28.2	26.4	25.8	24.8	24.2	24.0
Cure time(s)	41.4	49.2	46.2	43.8	43.2	47.2	41.2	40.2
T_{max} (Ib-in)	6.47	7.57	8.93	11.07	11.13	11.26	11.87	13.18

Tables 6 and 7 summarise the physico-mechanical properties of the CSS and CB(N330)- filled natural rubber vulcanizates. There were general increases in tensile strength, modulus, specific gravity (S.G), hardness and abrasion resistance with increasing filler loading. The tensile strength increased up to a maximum at 50phr for CSS-filled and 40phr for CB-filled vulcanizates before declining. That is, the vulcanizates achieved optimum strength between 40-50phr filler loadings. The CB-filled vulcanizates gave higher tensile strength, modulus, S.G, hardness and abrasion resistance increases, but slight differences in hardness and abrasion resistance. The CSS-filled SNR10 showed higher S.G. due to higher specific weight (density) of the CB over CSS filler (Table 2). The elongation at break and Dunlop resilience generally decreased with increasing filler loading. The CSS-filled vulcanizates showed higher elongation at break and showed higher Dunlop resilience at all filler loadings. This observation implied better resilience for the CSS-filled vulcanizates and consequently lower heat build-up and hysterisis for the rubber articles made with the filler. The decrease in elongation at break with filler loading can be due to the adherence of the filler particles to rubber matrix causing stiffening effects on the polymer chain and decreasing stretching (blow et al, 1982). The gradation in the physico-mechanical properties of the vulcanizates follow closely the works of Okieimen and Imanah (Okieimen et al, 2005; Imanah et al, 2003).

Table 6: Physico-mechanical properties of SNR10 filled with CSS

Filler (phr)	0	10	20	30	40	50	60	70
Tensile strength (Mpa)	9.48	9.88	11.15	12.54	14.13	13.69	12.30	11.12
Modulus, M100(Mpa)	1.13	1.53	1.55	1.57	1.94	1.97	2.39	2.59
Modulu, M300(Mpa)	3.04	3.25	3.33	3.48	3.66	3.82	4.44	4.60
Elongation at break (%)	836	686	608	569	462	456	452	448
Specific gravity (S.G.)	1.006	1.006	1.018	1.032	1.053	1.066	1.081	1.097
Dunlop resilience (%)	88	88	87	84	82	80	79	78
Hardness (IRHD)	44	45	48	50	53	55	58	61
Abrasion resistance index	40	40	41	42	42	42	43	43

Table 7: Physico-mechanical properties of SNR10 filled with CB(N330)

Filler (phr)	0	10	20	30	40	50	60	70
Tensile strength (Mpa)	9.48	18.52	21.24	30.53	35.55	30.24	25.15	20.48
Modulus, M100 (Mpa)	1.13	2.12	2.55	2.96	3.28	3.34	3.98	4.54
Modulu, M300 (Mpa)	3.04	1.78	12.30	14.10	14.59	14.76	14.20	15.76
Elongation at break (%)	836	664	582	500	450	382	325	308
Specific gravity (S.G.)	1.006	1.015	1.046	1.069	1.089	1.104	1.119	1.139
Dunlop resilience (%)	88	84	83	82	80	73	71	69
Hardness (IRHD)	44	45	50	55	56	58	61	67
Abrasion resistance index	40	41	41	42	42	43	43	44

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Conclusion: This research work has revealed the potentials of CSS as filler in natural rubber compounds. The cure characteristics and the physico-mechanical properties investigated showed comparable results with that of reinforcing standard carbon black (N330) filler. Though significant inferiorities of the CSS filled systems were noticed in cure and tensile properties, these could be improved by employing modern methods of grinding and size separation to obtain finer particle size CSS filler similar to that of carbon black (N330). This could stand to be a potential reinforcing filler for rubber compounds especially for articles requiring less mechanical strength.

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**Correspondence, E-mail: osabohieneemma@yahoo.com.*

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