Rheological and Mechanical Properties of Natural Rubber Reinforced with Agricultural Byproduct

J. E. Imanah,[1] F. E. Okieimen[2]

[1]*Department of Polymer Technology, Federal Polytechnic, Auchi, Edo State, Nigeria*
[2]*Department of Chemistry, University of Benin, Benin City*

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ABSTRACT: Cocoa pod powdered (CP) and Carbonized Cocoa pod powdered (CCP) sieved through 150 μm mesh were characterized in terms of loss on ignition, surface area, moisture content, and oil absorption and used as filler in compounding natural rubber and vulcanized using efficient vulcanization system. The processing and curing characteristics of the compound mixes were determined on a Monsanto Rheometer. Physical-mechanical properties of the vulcanizates were measured as a function of filler loading. It was found that vulcanizates with 40–50% filler loading showed maximum tensile strength of 8.4 MPa for CP, and 9.5 MPa for CCP. Hardness showed increased with increased filler loading for all the compounds. The reinforcing ability of the cocoa pod husk is not much inferior when compared to Carbon Black, N330. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3718–3722, 2003

INTRODUCTION

Besides Ghana, Nigeria is the second largest producer of Cocoa in West Africa. Most of the production take place in the Western part of the country. It has been estimated by previous workers that about 60% (wet basis) of cocoa pod is made up of husk; thus, annually, an estimated 8,000,000 tones of cocoa pod husks are discarded during harvesting;[1] these are made to rot away every year during the season. Several workers[2–7] made reasonable attempts at unraveling the numerous potentials inherent in the pod husk. Such attempts were, however, narrowed down to its applicability in feeding of livestock and serving as fertilizer.[7]

Bopaiah and Shanteram,[8] however, extend the scope of utilization of cocoa pod husk in the area of Biogas production.

Physico-chemical analysis of cocoa pod husk done by previous workers[1] showed the presence of Ca, P, K, Mg, Na, Zn, Fe, and Cu; with K relatively in abundance.

In the rubber industry, the dependence on carbon black as filler is still very much pronounced, with the attendant high cost and its production, which depends on complex technology that is not simple for all and sundry to manage, coupled with the increasing cost of petroleum, the source of carbon black. It was thought that the filler sourced from low-cost agricultural byproducts might be useful in reducing cost in certain natural rubber products.

It is known that reinforcement depend on the complex interaction of several filler-related parameters. These include particle size, particle shape, particles dispersion, surface area, surface reactivity, structure of the filler, and the bonding quality between fillers and the rubber matrix.[9,10]

Because previous studies have indicated a potential for the development of value added products from cocoa pod husk, this article presents the curing and mechanical properties of natural rubber reinforced with cocoa pod husk as filler.

EXPERIMENTAL

Materials

The cocoa pods used in this study were obtained from Cocoa Research Institute of Nigeria (CRIN) substation at Uhonmora, Ora, Nigeria, and were air dried, powdered, and sieved through a mesh size of 150 μm. Natural rubber was obtained from Pamol Nig. Ltd., Sapele, Nigeria, and was used as received.

Part of the sieved CP Powder was carbonized at 200–250°C using the procedure described by Ishak and Barker.[11] All the other rubber additive used in compounding were of industrial grade.

Characterization of cocoa pod powders

Cocoa pod powders were characterized in terms of loss on ignition,[12] moisture content, pH of slurry,[13] surface area,[14] and oil absorption.[9]

Correspondence to: J. E. Imanah (jeimanah@yahoo.com)

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TABLE I
Physical Properties of Cocoa Pod Powders and Carbon Black N330

Parameters	CP	CCP	N330 CB
Loss on ignition (875^{0c})	39.5	54.3	92.8
Moisture content (125^{0c})	5.2	3.6	2.4
p^H of slurry	8.0	8.5	6.5
Iodine number (g/kg)	41.0	62.6	81.24
Aggregate structure (kg)	44.13	50.1	55.05

TABLE II
Typical Formulations for CP and CCP-Filled Natural Rubber

Materials	% PPhr
NSR 10	100
Stearic acid	4.0
Zinc oxide	2.0
Filler	0–100
MBTS	2.0
Processing oil	2.0
Sulphur	1.5

Moisture content was determined gravimetrically by weighing 5 g of dried powder into a Petri dish. The samples were placed in an oven for 1 h at a temperature of 125 ± 1°C and then left to cool down in a desiccator. The change in weight was calculated as a percentage of the sample weight. Results of the cocoa pod powder characterization are given in Table I.

Compounding and cure characteristics determination

The formulation shown in Table II was employed to evaluate the cure and mechano-physical properties of NR vulcanizates. An efficient vulcanization system was chosen. Mixing was carried out on a laboratory size (160 × 320 mm) two roll mixing mill maintained at a temperature below 80°C to avoid any crosslinking during mixing.

A Monsanto rheometer model 100S was used to determine the processing characteristics of the compound mixes. The discs were set to an arc angle of 0.50° at a curing temperature of 185°C. The scorch times, torques, and cure time of filled and unfilled natural rubber were determined from the rheometer rheograph are shown in Table III.

Measurement of physico-mechanical properties

The various rubber compounds were compression molded at 185°C using the cure time predicted by the reheometer into test specimen sheets using a steam heated hydraulically operated simple daylight press.

For tensile properties evaluation, a computerized Monsanto tensile tester model 1/m at a crosshead speed of 500 mm/min using dumbbell test pieces of dimension (45 × 5 × 2 mm) as contained in 512-87 method A.[15] The results produced by the computerized machine are given in Tables IV, V, and VI.

The test for hardness was carried out using the Wallace hardness tester of model c8007/25 according to ASTM 1415.[16]

Procedures adopted for the measurement of compression set was based on ASTM 385.[17] DIN to ISO 4649 Akron to BS 903 part 49 method C[18] was used to assess abrasion resistance.

RESULTS AND DISCUSSION

Some characteristics of cocoa pod husk (CP) and carbonized cocoa pod husk (CCP)

Table I shows the physical characteristics of Cocoa pod powders and that of N330 carbon black. Weight losses on ignition at 875°C are 39.5, 54, and 92.8% for CP, CCP, and CB, respectively. Weight loss an ignition is a measure of the carbon content loss during burning, and indicates the effectiveness of the filler. The higher the value the greater the reinforcing potential.

TABLE III
Processing Characteristics of the Compound Mixes Filled with Carbon Black N330, CP, and CCP

	Cure Time(s)			Scorch Time (s)			Change in Torque (àW,		
% Filler (phr)	N330	CP	CCP	N330	CP	CCP	N330	CP	CCP
0	40	40	40	27	27	27	4.62	4.62	4.62
10	41	57	53	29	30	34	4.98	4.91	7.23
20	40	54	59	30	28	29	5.10	6.24	7.11
30	38	57	64	81	29	38	4.68	7.09	8.68
40	60	61	71	42	31	25	5.39	6.56	10.98
50	57	55	84	40	25	35	6.95	10.67	13.15
60	52	51	60	38	22	32	7.86	−12.62	13.10
70	58	58	66	31	29	33	7.69	12.55	12.85
80	72	53	61	52	20	37	5.32	12.22	12.50
90	69	63	60	34	32	29	7.99	8.40	9.20
100	50	60	58	34	35	28	7.57	4.26	6.11

TABLE IV
Results of Physicomechanical Properties of Natural Rubber Filled with Cocoa Pod Husk

% Filler (phr)	0	10	20	30	40	50	60	70	80	90	100
Tensile strength (MPa)	4.8	4.9	5.2	5.8	8.0	8.4	7.5	7.3	7.1	6.3	6.2
M 300 (MPa)	1.10	1.12	1.82	1.87	2.11	2.41	2.19	2.18	2.01	1.82	1.78
M 100 (MPa)	0.61	0.64	0.81	0.91	1.09	1.21	1.11	1.11	0.97	0.91	0.89
Elongation at break (%)	853	711	652	454	440	428	385	315	295	270	255
Compression set (%)	35.2	32	28.1	21.6	9.61	7.20	5.4	4.60	4.2	4.0	3.3
Hardness	30	31	34	35	41	45	55	56	58	59	62
IRHD abrasion resistance	42	41	40	41	42	40	42	44	44	43	46

With carbonization; the percentage of carbon in CCP should have increased considerably. This was reflected in the results obtained with 54% loss on ignition. The results also indicate that CCP will be more reinforcing than CP but less reinforcing than CB.

The results of iodine adsorption numbers indicate that CCP and CP are 62.6 g/kg and 50.12 g/kg, respectively, and are lower then for CB (81.49 g/kg). The iodine adsorption of powders provide an estimate of its surface area. The value of iodine numbers obtained indicate that the surface area of CP and CCP are almost the same order of magnitude, and are markedly lower than the surface area of the CB sample. The higher the values, the larger the surface area, and the more reinforcing the filler becomes; hence, one can assert that carbonization of CP, which has enhanced its surfaces area, can improved its reinforcing potential.

On oil adsorption, it is clear from Table I that the amount of oil required to wet 45.5 kg of CCP is greater than that require for CP but a little less than that required for CB. It is well known that CB consists of irregular chain-like branched aggregates of nodular subunits, which are called particles in the ASTM classification.[19] The results also indicate that CCP form aggregates that are similar to CB, and further suggest that CCP, and to some extent CP, have structures that may be closely related to CB in the sense considered above, and therefore may produce similar effect.

Rheological properties

The data on the rheological properties of compound mixes from the Monsanto rheograph are given in Table III. Analysis of the torque time facilitates the determination of the various cure-related parameters.

The optimum cure time and scorch time of CCP-filled vulcanizations exhibit a retardation with increasing CCP content, i.e.. shows enhancement in cure rate with the torques at maximum higher than CP and CB.

There appears to be an increase in torque with increasing filler loading up to 60% for CP and CB and 70% for CCP, above which the torques experience a decline. This shows that filler loading may be a function of torque value, especially for CP and CCP. The cure enhancement observed in the case of CCP-filled vulcanizates over that of CP may be associated with the filler-related parameters, such as surface area, surface reactivity, and moisture content.[20] Butter and Freakley[21] reported that cure rate is directly related to the humidity and metal content of the rubber compound. However, in the present study, the most probable factors to account for the observed cure enhancement of CCP filler over CP and CB are surface area, pH, and aggregate structure.

The marked increment in the maximum torque with increasing filler loading up to certain filler loading indicates that the presence of filler in the rubber matrix has reduced the mobility of the macromolecular chains of the rubber. The higher maximum torque registered in the case of CCP-filled vulcanizates may be attributed to the nature of CCP filler—the presence of high alkaline, as indicated in Table I.

TABLE V
Results of Physical–mechanical Properties of Natural Rubber Filled with Carbonized Cocoa Pod Husk

% Filler (phr)	0	10	20	30	40	50	60	70	80	90	100
Tensile strength (MPa)	4.8	5.6	5.9	6.8	9.2	9.5	8.3	7.1	5.8	5.1	4.0
M 300 (MPa)	1.10	1.3	1.88	1.91	2.14	2.65	2.23	2.21	1.97	1.92	1.56
M 100 (MPa)	0.61	0.70	0.89	1.01	1.16	1.81	1.09	0.98	0.93	0.90	0.78
Elongation at break (%)	853	5.33	501	486	465	430	401	315	301	259	233
Compression set (%)	35.2	21.01	15.7	7.2	5.8	4.1	3.3	3.0	2.7	2.7	2.8
Hardness	30	41	45	50	57	58	61	61	63	65	66
IRHD abrasion resistance	42	39	39	41	40	40	43	41	42	41	40

TABLE VI
Results of Physical–Mechanical Properties of Natural Rubber Filled with Carbon Black (N330)

% Filler (phr)	10	20	30	40	50	60	70	80	90	100
Tensile strength (MPa)	17.1	23	25	31	40	35	34	32	31	28
M 300 (MPa)	1.5	2.3	2.5	3.7	5.61	5.13	5.01	4.50	4.00	3.10
M 100 (MPa)	0.88	1.02	1.10	1.6	3.02	2.56	2.48	2.23	1.9	1.30
Elongation at break (%)	659	557	496	301	285	245	221	210	190	106
Compression set (%)	20.95	15.0	13.86	9.57	8.66	6.17	5.62	4.78	4.56	4.09
Hardness	41	43	45	50	56	61	62	68	69	73
IRHD abrasion resistance	38	39	40	38	39	40	40	41	42	45

Physico-mechanical properties of vulcanizates

Some of the physico-mechanical properties of CP, CCP, and CB-filled NR vulcanizates are given in Table IV, V, and VI. In all filled systems, the tensile strength increased with increasing filler content until a maximum level is reached, as shown in Figure 1. A further increase in filler loadings reduces this property. As the filler loading is increased, eventually a level is reached where by the filler particles or aggregate are no longer adequately separated or wetted by rubber phase. This reduction in strength may be due to agglomeration of the filler particles to form a domain that acts like a foreign body. The CCP-filled NR vulcanizates exhibit a higher tensile strength at any particular loading of filler than CP-filled vulcanizates. The superior tensile strength of the CCP-filled vulcanizates implies that there are other factors besides particle size that determine the properties of the filler in terms of reinforcement. These factors may include filler dispersion, surface reactivity and bonding quality between the fillers and NR matrix. The optimum filler loading is 40 and 50% phr for CCP and CP, respectively. From modulus data, an appreciable increase in modulus was observed between 40–50% filler loading. Even though the increase was minimal, the increase in modulus suggests that the fillers are reinforcing. The modulus of 300% for CCP-filled vulcanizates are relatively higher than those of CP. They, however, gave lower value when compared with the CB-filled system. In reinforced systems, strong carbon–polymer bonds are formed. This results in the filler becoming part of the polymer network and no longer free to move independently. The net results of this difference bring about some increase in modulus of elasticity. Also from Tables, IV, V, and VI, elongation at break decreases with increasing filler loading for all the filler used. Generally, addition of fillers results in decrease in elongation at break. The results obtained are in agreement with expected results. Decrease in Eb with increasing % filler loading may be due to the 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.[22,23]

The hardness of both CCP and CP increased with increasing filler content as shown in Figure 2, up to 70% for CP and 80% for CCP, above which the increase becomes insignificant. This result is expected for filler loading up to 80%. However, the unexpected result recorded after 80% filler loading may be thus explained. As more filler particles get into the rubber, the elasticity of the rubber chain is reduced, resulting in more rigid vulcanizates, and beyond certain filler

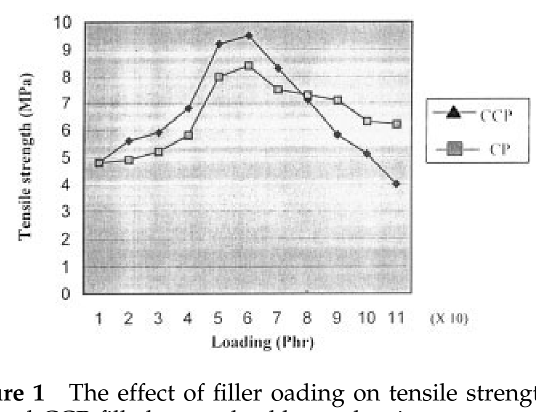

Figure 1 The effect of filler oading on tensile strengths of CP and CCP-filled natural rubber vulcanizates.

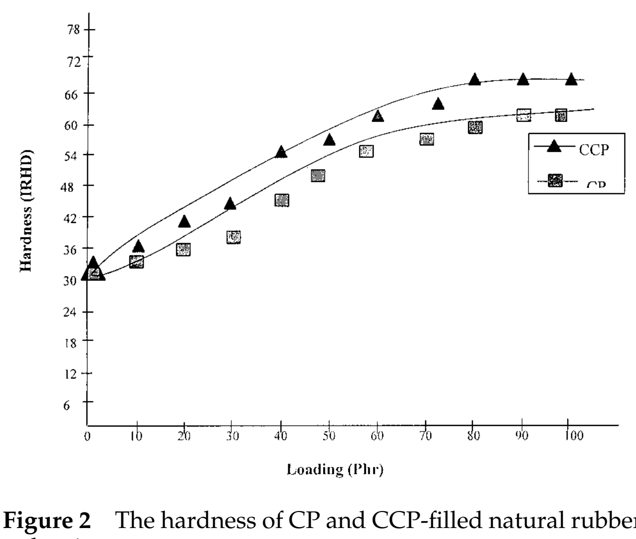

Figure 2 The hardness of CP and CCP-filled natural rubber vulcanizates.

loading, there is a phenomenon of phase inversion, which usually result to loose attachment of the filler-to-rubber phase without improvement in the physico-mechanical properties.

The percentage of the compression set result showed that unfilled stock had the largest percentage compression of 35. As filler loading increases, the percentage compression of filled vulcanizates decreases. However, vulcanizates filled with CB have the least percentage compression. This property could therefore be dependent on the amount of filler incorporated into the rubber and particle size of filler.

The abrasion resistance results showed an irregular increase with increasing filler loading; however, the values are higher for CP products than CCP and much superior with CB-filled systems. This attests to the widely acclaimed fact that abrasion resistance is a function of the particle size of fillers.

CONCLUSION

This article is a preliminary work that describes the rheological and physico-mechanical properties of NR filled with cocoa pod husk. The results show that CP and CCP are potential reinforcing filler for natural rubber compounds. In all, CCP exhibits relatively better physical properties than CP products, and their vulcnizates properties are not much inferior when compared to N330 carbon black. The results also predict potential application of cocoa pod husk as low-cost filler in natural rubber products. The differences in vulcanizate properties of the filled and unfilled systems in all the parameters measured indicate that cocoa pod husk is reinforcing, and the close resemblance of CCP to CB in the measured parameters may be due to surface area and filler reactivity.

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