Studies in the Utilization of Agricultural Waste Products as Filler in Natural Rubber Compounds

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ABSTRACT: Natural rubber samples were filled with agricultural waste products (cocoa pod husks and rubber-seed shell) at 50 phr, mixed on a two-roll mill, and cured using the semiefficient vulcanization system. The physicomechanical properties, tensile strength, modulus at 100% elongation, elongation at break, hardness, abrasion resistance, flex fatigue and compression set, of the agricultural waste products-filled natural rubber compounds were determined and compared with the values obtained for vulcanisates filled with commercial carbon black (HAF N330). The effect of blending the raw and carbonized agricultural waste products with the commercial grade N330 carbon black on the physicomechanical properties of the natural compounds was studied. It was found that the raw agricultural waste products were ineffective compared with N330 carbon black as reinforcing filler for natural rubber compound mixes and could be classified as semireinforcing fillers. Blends containing up to 40 wt % of the raw agricultural waste products and more than 60 wt % of the carbonized waste products gave natural rubber compounds with comparable physciomechanical properties with compound obtained with N330 carbon black. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2561–2564, 2006

Key words: cocoa pod husk; rubber-seed shell; fillers; natural rubber

INTRODUCTION

Particulate fillers are added to rubbers (synthetic and naturally occurring) either to extend and cheapen the rubber compound or to add desirable qualities to the final compound and enhance the products' service qualities. Carbon black is one of the most important raw materials, second to the polymer, used in the manufacture of rubber products. Commercially available carbon black falls into four categories: thermal blacks produced by the thermal decomposition or cracking of natural gas, channel blacks, acetylene blacks, and furnace black produced by the incomplete combustion of oil feed stock, usually petroleum refinery residues.[1] Therefore, there is a need to develop fillers from other sources, particularly from renewable resources, to replace some grades of carbon black. Agricultural waste products (maize cob, groundnut husk, cassava peel, cocoa pod husk, plantain peel, rubber-seed shell, etc.) represent a large stock of underutilized renewable resources, which can be used directly or converted by simple processes to high value-added materials.[2,3] Although significant progress has been made in the development and utilization of modified agricultural waste products in water and waste water treatment,[4–11] little information exists on the potential for the application of these waste products as extenders and/or fillers in the processing of polymers.[12,13] The objective of this study was to investigate the effect of cocoa pod husk and rubber-seed shell on the physicomechanical properties of natural rubber compounds.

EXPERIMENTAL

Materials

Natural rubber conforming to the Standard African Rubber grade 3 (SAR3) was obtained from the Rubber Research Institute of Nigeria, Benin City. Cocoa pod husk obtained from the Cocoa Research Institute, Uhonmora, was cut into small pieces, air-dried, milled, and sieved through a 150 mμ screen. The portion of the ground cocoa pod husk that passed through the 150 mμ screen was retained for use. Carbonized cocoa pod husk was prepared following the procedure described by Kadirvelu et al. with modifications.[9] Rubber-seed shell obtained from the Rubber Research Institute of Nigeria, Benin City, was processed in the powder and carbonized forms as described for cocoa pod husk. Some characteristics of the agricultural waste products are given in Table I.[14] The other compounding ingredients, such as zinc oxide,

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TABLE I
Some Physical Characteristics of Cocoa Pod Husk and Rubber-Seed Shell

Parameters	Cocoa pod husk	Rubber-seed shell	Carbon black (N330)
Loss on ignition at 875°C (%)	39.5	32.7	92.80
Moisture content (wt %)[a]	5.2	10.0	2.4
pH of slurry	8.0	8.5	6.5
Iodine adsorption number	41.0	50.1	81.24
Oil absorption (g/100 g)	44.1	50.9	55.05

[a] Sample heated to 125°C.

stearic acid, sulfur, processing oil, and mercaptobenzothiazole, were obtained from commercial sources and used as received.

Sample preparation

All the samples were prepared on the basis of formulations given in Table II. The compounds were mixed on a laboratory-size two-roll mill. After mixing, the compounds were molded in an electrically heated press to optimum cure using conditions that we previously determined from torque data using Monsanto rheometer.

Physicomechanical properties

The tensile stress–strain properties of the vulcanisates such as tensile strength, modulus, and elongation at break were measured using a Monsantotensometer model 110 and the ASTM D412 method. Dumb-bell-shaped test pieces ($45 \times 5 \times 2$ mm^3) were punched out from the cured rubber samples, clamped vertically at both ends on the tensometer, and stretched vertically to failure. The tensile properties were recorded automatically by the instrument. The flex fatigue, compression set, hardness, and abrasion resistance of the vulcanisates were measured using standard methods.[15–18]

TABLE II
Recipe for Compounding the Natural Rubber Mixes

Ingredients	Parts per hundred (phr)
Natural rubber	100
Filler	50
Zinc oxide	4.0
Stearic acid	2.0
Sulphur	1.5
Mecaptobenzothiazole	1.5
Processing oil	2.0

TABLE III
Physicomechanical Properties of Natural Rubber Compounds Filled with Cocoa Pod Husk and Rubber Seed Shell

Vulcanisate Properties	A	B	C	D
Tensile strength (Mpa)	4.3	6.1	5.1	39.0
Modulus at 100% elongation (Mpa)	0.89	1.5	1.1	5.6
Elongation at break (%)	853	413	460	275
Flex fatigue (De Mattia, kc)	nf	5.2	7.8	nf
Compression set (%)	35.2	14.2	13.5	8.7
Hardness (IRHD)	30	45	48	56
Abrasion resistance index	42	42	41	39

A, no filler; B, compound filled with cocoa pod husk; C, compound filler with rubber seed shell; D, compound filler with N330 carbon black; nf, no failure.

RESULTS AND DISCUSSION

The physicomechanical properties of natural rubber compounds filled with the agricultural waste products are given in Table III. The values obtained for tensile strength and modulus at 100% elongation of natural rubber compounds filled with agricultural by-product were markedly lower (by about five-fold) than the values obtained for compounds filled with N330 carbon black (Table III). The values of elongation at break suggest that the natural rubber compounds obtained with N330 carbon black were stiffer than the compounds with the agricultural waste products. Although the tensile properties of the agricultural waste products-filled natural rubber compounds appear poor compared with those of N330 carbon-filled compounds, the values are somewhat higher than those of the unfilled gum rubber and suggest reinforcing properties. High-tensile properties (high-tensile strength and modulus values) and low value of elongation at break are frequently attributed to chemical crosslinks produced in the vulcanisates and are indices of strong filler–rubber matrix interaction.[19] Tensile property measurements have been used to assess the distribution and dispersion of fillers in natural rubber mixes and the resistance of the compounds to thermal and chemical stress.[20,21] The distribution and dispersion of particulate fillers may be affected by the amount of associated water molecules. The amount of bound water molecules was markedly higher in the agricultural waste products than in the N330 carbon black (Table I). The poor distribution and/or dispersion of the agricultural waste products in the natural rubber matrix may account, in part, for the weak filler–rubber matrix interaction.[22] The hardness and abrasion resistance of the raw agricultural waste products-filled natural rubber compounds were comparable with the values obtained for N330 carbon black-filled com-

TABLE IV
Physicomechanical Properties of Natural Rubber Compounds Filled with Blends of Raw Cocoa Pod Husk and N330 Carbon Black

Composition of blends of filler [(%) agricultural waste product]	Tensile strength (MPa)	Modulus at 100% elongation MPa	Elongation at break (%)	Flex fatigue (kc to failure)	Compression set (%)	Hardness (IRHD)	Abrasion resistance index
0	39.0	5.6	275	nf	8.7	56	39
20	38.4 (36.1)	9.7 (6.7)	530 (654)	nf (nf)	12.0 (15.5)	55 (53)	38 (40)
40	34.0 (32.4)	6.1 (5.8)	496 (511)	nf (nf)	13.6 (14.9)	54 (53)	39 (41)
60	27.5 (28.4)	6.8 (5.1)	468 (498)	9.9 (11.0)	14.1 (14.4)	54 (51)	40 (41)
80	29.2 (27.1)	6.1 (4.8)	401 (409)	9.4 (9.4)	14.4 (14.3)	52 (49)	41 (43)
100	6.1 (5.1)	1.5 (1.0)	413 (460)	5.2 (7.8)	14.2 (13.5)	45 (48)	42 (41)

nf, No failure.
The values for blends of raw rubber seed shell and N330 carbon black are in parentheses.

pounds, but the compression set and flex fatigue properties of the latter were markedly higher than those for agricultural waste products-filled compounds (Table III). It appears that cocoa pod husk is relatively more effective than rubber-seed shell in enhancing the measured physicomechanical properties of the natural compounds. The factors that influence the reinforcing ability of particulate fillers include surface area and surface activity of the filler.[22] Ismail[23] examined the effect of short fiber wood cellulose on the mechanical properties of natural rubber compounds and reported that binding agents were required to markedly enhance the wood cellulose fiber–natural rubber interaction. Similar studies on the use of coconut fiber as filler for natural rubber compounds showed that only marginal improvements in tensile properties were obtained compared with the unfilled gum rubber.[12]

Tables IV and V give the effects of blending N330 carbon black with the raw and carbonized agricultural waste products, respectively, on the physicomechanical properties of natural rubber compounds. The results given in Table IV show that up to 40 wt % of the N330 carbon black can be substituted with the raw agricultural waste products without marked adverse effect on the measured properties. Although the values of modulus at 100% elongation of the natural rubber compounds with blends containing up to 80 wt % of the raw agricultural waste products are higher than those of N330 carbon black-filled compounds, the values of elongation at break and compression set suggest weak filler–rubber matrix interaction in the former. As with natural rubber compounds filled with raw agricultural waste products, the values of hardness and abrasion resistance of the compounds filled with the blends containing up to 80 wt % of the raw agricultural waste products are comparable with the values obtained for N330 carbon black-filled natural rubber compounds. Table V shows the effect of the substitution of N330 carbon black with the carbonized agricultural waste products on the physicomechanical properties of natural rubber compounds. Marked enhancement in the measured properties suggests that the carbonized agricultural waste products have higher reinforcing ability than the raw waste products. It can be seen that more than 60 wt % of the N330 carbon black can be substituted with the carbonized agricultural waste products without marked adverse effects on the measured properties.

TABLE V
Physicomechanical Properties of Natural Rubber Compounds Filled with Blends of Carbonized Cocoa Pod Husk and N330 Carbon Black

Composition of blends of filler [(%) carbonized agricultural waste product]	Tensile strength (MPa)	Modulus at 100% elongation (MPa)	Elongation at break (%)	Flex Fatigue (kc to failure)	Compression set (%)	Hardness (IRHD)	Abrasion resistance index
0	39.0	5.6	275	Nf	8.7	56	39
20	38.6 (36.0)	8.3 (8.0)	627 (641)	nf (nf)	5.11 (5.8)	60 (59)	41 (40)
40	35 (30.6)	6.5 (6.2)	533 (603)	nf (nf)	5.76 (7.9)	57 (54)	41 (38)
60	31 (34)	6.1 (5.1)	526 (512)	1.28 (11.99)	6.8 (7.8)	56 (55)	39 (38)
80	30 (28)	5.9 (5.1)	416 (510)	10.11 (11.57)	7.0 (8.1)	55 (53)	37 (41)
100	9.2 (8.7)	2.7 (2.1)	405 (415)	7.56 (6.3)	4.1 (8.6)	48 (51)	43 (41)

nf, No failure.
The values for blends of carbonized rubber seed shell and N330 carbon black are in parentheses.

CONCLUSIONS

Agricultural waste products constitute a large proportion of urban solid wastes in developing countries like Nigeria, represent persistent waste stream, and present disposal problems. The results from this study indicate a potential for the utilization of agricultural waste product carbon as filler for natural rubber compounds. The availability of large quantities of the waste products at little or no cost and the relative ease of conversion to the high value-added carbon are additional factors in favor of sourcing fillers to replace general purpose-grade petroleum derived carbon black from renewable resources.

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