Properties Characterization of Vulcanized Natural Rubber Filled with Uncarbonized Particulate Cow Bone

1Akinlabi Oyetunji, 2Isiaka O. Bakare, 3Reginald Umunakwe and 1Adetola O. Adeyemo

1Department of Metallurgical and Materials Engineering, Federal University of Technology, Akure, Ondo State Nigeria
2Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin City Edo State, Nigeria
3Department of Materials and Metallurgical Engineering, Federal University Oye- Ekiti, Ekiti State Nigeria

{akinlabioyetunji | iobakare@yahoo.com | reginald.umunakwe@fuoye.edu.ng | adeyemoadetola@ymail.com}

Abstract --- This work investigates the effects of addition of 63 µm uncarbonized particulate cow bone as fillers in vulcanized natural rubber on the tensile properties, hardness and abrasion resistance of the composites. Cow bones were procured from an abattoir, cleaned, crushed, pulverized, ball milled and sieved to obtain the particles that passed through the 63 µm mesh size. Natural rubber composites materials were prepared varying the filler loading as 5, 10, 15 and 20 pphr respectively. The compounded rubber samples were cured in a hot press using compression moulding technique. The control sample was produced using 20 pphr of carbon black. The cured rubber samples were conditioned at room temperature for two weeks before they were characterized. The tensile strength and elastic modulus of the samples filled with cow bone increased with filler loading up to 15 pphr before they started decreasing. Carbon black reinforced sample possessed higher tensile strength, modulus and hardness than the samples filled with uncarbonized particulate cow bone. The hardness for all samples maintained an increasing trend with increase in the filler loadings. Particulate cow bone reinforced natural rubber offered higher elongation than carbon black reinforced samples. At 10, 15 and 20 pphr, cow bone reinforced composites exhibited higher abrasion resistance than carbon black filled sample. The optimal filler loading of uncarbonized particulate cow bone reinforced natural rubber was 15 pphr. Cow bone reinforced natural rubber can find applications in areas where moderate strength, hardness, elongation and wear resistance are required such as in protective footwear, bouncing balls and cases of children toys.

Keywords --- carbon black, cow bone, fillers, natural rubber, composites

1 INTRODUCTION

Fillers are the most important additives in natural rubber added to improve strength and wear resistance needed to meet service requirements (Sobhy, et.al., 2003). Carbon black has been the main filler incorporated in natural rubber during vulcanization. The properties imparted in vulcanized rubber by fillers depend on factors such as particle sizes, structure, physico-chemical nature, surface area and porosity of the fillers (Igwe and Ejim, 2011). Arroyo, et.al. (2003) and Wang and Chen (2013) reported that the synthesis of carbon black from petroleum causes air pollution. Agricultural wastes are attractive for engineering applications due to their availability, low cost, renewability and the need to reduce pollution issues associated with their disposal. In order to replace carbon black as filler in vulcanized natural rubber, many researchers have investigated the use of various agricultural wastes as filler in vulcanized natural rubber.

The agricultural wastes that have been used and reported include milled coconut fibre (Egwaikhide, et.al., 2007), seed shells of cherry (Osabohien and Egboh, 2007), cocoa pod husk, rubber seed shell, rice husk and palm kernel shell (Ogiebefun, et.al., 2010), carbonized bagasse (Osarenmwinda and Abode, 2010), snail shells (Igwe and Ejim, 2011), carbonized ground nut shell (Ayo, et.al., 2011), carbonized cassava peel (Ugbesie, et.al., 2011), bamboo fibre (Onyeagoro, 2012), defatted rice bran (Moonchai, et.al., 2012), carbonized coir (Aguene and Madufofor, 2012), carbonized and uncarbonized dikanut shell pericap (Ekabafe, et.al., 2012), maize stalk (Chigondo, et.al., 2013), carbonized palm kernel shell husk (Egwaikhide, et.al., 2013).

Also, treated and non-treated oil palm ash (Ooi, et.al., 2013), guinea corn husk (Tenebe, et.al., 2013), hybrid carbon black and rice husk (Imoisili, et.al., 2013), chinin whiskers (Santulli, et.al., 2014), velvet tamarind seed shell (Okoh, et.al., 2014), carbonized coir and uncarbonized coir (Aguene, et.al., 2014) hybrid marble sludge and rice husk (Ahmed, et.al., 2014), sugarcane bagasse ash (dos Santos, et.al., 2014), Calamus deerratus powder (Osabohien, et.al., 2015), sugarcane bagasse (Okele, et.al., 2015), agricultural wastes (Oyetunji, et.al., 2017), and HCL/NH4F treated and untreated sugarcane bagasse ash (Huabcharoen, et.al., 2017). Findings from their reports showed that the optimum tensile strengths, tear strengths and abrasion resistance obtained in natural rubber filled with these agricultural wastes were below those obtained in carbon black and silica reinforced natural rubber (Oyetunji, et.al., 2017).

Opportunities exist to further evaluate other agricultural wastes such as cow bone that have not been reported as filler in vulcanized rubber. Particulate cow bone has been used as filler in polypropylene and reported to distribute in the matrix to improve the impact energy, hardness, flexural, compressive and tensile strengths of the composites with filler loading up to 25 wt% (Asuke, et.al., 2012). The introduction of cow bone ash was also reported to decrease the wear rate in polypropylene/bone ash composite (Asuke, et.al., 2014). At 8 wt% filler loading, unsaturated polyester filled with particulate cow bone exhibited higher tensile strength than the unfilled sample at smaller (75 µm) particles sizes (Oladele, et.al., 2014), (Oladele and Adewole, 2013). This work therefore evaluates the suitability of particulate cow bone as filler in vulcanized natural rubber.
2 MATERIALS AND METHOD

2.1 FILLER PREPARATION

Fresh cow bones were obtained from Mimiko’s Ultra-Modern Abbattoir, Akure, Ondo State, Nigeria. The bones were properly boiled in water mixed with detergent to facilitate washing. They were properly washed to remove fats and dirt before they were sundried for four weeks. The bones were broken down with a sledge hammer and pulverizer before they were grinded with a laboratory ball milling machine. A set of sieves of mesh sizes 125, 103, 90, 63 µm were arranged respectively on a sieve shaker to sieve the grinded bones into various particle sizes. It has been reported that particulate cow bone in smaller particle sizes improves the mechanical properties of composites better than larger particles as fillers (Oladele, et.al, 2014), (Oladele and Adewole, 2013). Therefore, the particles passing through the 63 µm sieve mesh were collected and used as filler in the natural rubber/cow bone composites prepared.

2.2 FILLER CHARACTERIZATION

The fillers properties measured were moisture content, loss on ignition (LOI), filler pH and filler density following the procedures described by (Aguele, et.al, 2014).

2.3 COMPOUNDING AND Vulcanization of Rubber/Cow Bone Composites

Natural rubber crumb conforming to NSR10 used for this study was supplied by the Rubber Research Institute of Nigeria (RRIN), Iyanomo, Edo State, Nigeria. Sulphur, zinc oxide, stearic acid, 2-mercapto benzo thiazole (MBT), trimethylquinoline (TMQ) and carbon black used as compounding ingredients were also procured from RRIN. The formulations of the natural rubber/cow bone composites used for this study are shown in Table 1. Since most end-use applications of vulcanized rubber such as shoe soles are filled with 20-50 pphr carbon black (Arroyo, et. al. 2003), the control sample shown in Table 1 is filled with 20 pphr carbon black for comparison. The compounding operation was done on a laboratory size two-roll mill maintained at temperature below 70 oC with flowing water to avoid premature cross-linking as specified by ASTM-D 3184-89.

The compounded rubber composite samples were conditioned in the laboratory for twenty four hours before vulcanization. The different compounded rubber samples were Vulcanized in laboratory size compression moulding press using different moulds. The hot press was maintained at a temperature of 140 oC and pressure of 10 MPa was applied on the closed moulds and held for five minutes before the moulded samples were brought out. The cured rubber composites were conditioned at room temperature for fourteen days before testing.

2.4 TENSILE TESTING

Dumbbell shaped samples for tensile testing conforming to ASTM D 412-06a with the dimensions as shown in Figure 1 were cut from each sample of the vulcanized rubber with a cutting die. The tensile tests were performed at room temperature with a digital Universal Testing Machine at a cross head speed of 500 mm/min until the specimen ruptures in accordance with ASTM D 412-06a. Three tensile specimens of each sample were tested and the average results reported to ensure reliability. The parameters reported from the tensile test include tensile strength, elastic modulus and percentage elongation.

![Fig. 1: Dimensions in mm of the Tensile Specimens](image)

### Table 1: Formulations of the Natural Rubber/Cow Bone Composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Natural rubber</th>
<th>Zinc oxide</th>
<th>Stearic acid</th>
<th>TMQ</th>
<th>MBT</th>
<th>Sulphur (AB)</th>
<th>Cow bone (CB)</th>
<th>Carbon black (CB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>100</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>100</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>100</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>E</td>
<td>100</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>F (control)</td>
<td>100</td>
<td>5</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>20</td>
</tr>
</tbody>
</table>
2.6 Abrasion Resistance Testing

The abrasion resistance of each vulcanized rubber sample was determined with the aid of rotary drum abrader in terms of volume loss according to ISO 4649 – 2010 (E) standard. Four abrasion specimens of each sample with thickness 6.5 mm and internal diameter 16 mm were prepared with a drill. The samples were weighed and their densities determined following ISO 2781-1988 (E) description. Each specimen was mounted against the drum of the abrasion testing machine at applied force of 10 N. The machine was programmed to run and stop after 84 revolutions at 40 rev/min. The sample was reweighed at the completion of the run. The abrasion resistance of each sample was computed from equations (1) and (2). The average values for each sample was reported.

\[
\Delta V = \frac{\Delta m_{x,dm_{cont}}}{\bar{\rho} \times \Delta m_r} \quad \text{---- (1)}
\]

\[
\% \text{ARI} = \frac{\Delta m_{x,sp_k}}{\Delta m_{x,sp_r}} \times 100 \quad \text{---- (2)}
\]

Where \( \Delta V \) is relative volume loss of test specimen (in mg), \( \Delta m_{\text{cont}} \) is the mass loss of the test specimen (in mg), \( \Delta m_r \) is the mass loss of reference test piece (in mg), \( \bar{\rho} \) is the density of the reference compound (in g/cm³), \( \varphi_r \) is the density of the vulcanized rubber sample (g/cm³) and %ARI is the abrasive resistance index.

3 Results and Discussion

3.1 Filler Characteristics

The characteristics of particulate cow bone obtained from experiment and compared with the literature values (Aguele, et.al., 2014) of the characteristics of carbon black are shown in Table 2. Previous reports by (Aguele, et.al, 2014), (Aguele and Madufor, 2012), (Egwaikhide, et.al, 2013), (Egwaikhide, et.al, 2007) suggest that fillers with higher loss on ignition, lower moisture content and pH values that tend to alkalinity offer higher reinforcement in natural rubber. Higher loss on ignition as a result of higher loss of carbon during combustion indicates higher dispersion of the filler in the matrix. Fillers with pH values tending towards alkalinity improve the vulcanization rate better than those with lower pH. Comparing the filler characteristics of cow bone and carbon black, it can be deduced that carbon black offers higher reinforcement in natural rubber than cow bone.

3.2 Mechanical Properties

The tensile strengths, elastic moduli, elongations at break and hardness values of the vulcanized natural rubber samples filled with particulate cow bone, the unfilled sample and those of the control sample filled with carbon black are presented in Figures 2-5. The carbon black reinforced sample exhibited higher tensile strength, modulus and hardness compared to the samples filled with cow bone as shown in Figures 2, 4 and 5. This is because commercial carbon black has smaller particle sizes (in nm range), higher loss on ignition, lower moisture content and higher pH compared to uncarbonized 63 µm size particulate cow bone. The results followed the same trend as when carbon black was compared to other agricultural wastes reported as filler in vulcanized natural rubber. Particulate cow bone will be required to undergo further processing before it can compete effectively with carbon black in the rubber industry. Compared to the unfilled sample, cow bone filled natural rubber offered higher tensile strength, modulus and hardness at various filler loadings. The properties obtained in cow bone reinforced natural rubber depend on the filler loading and the best combination tensile strength, modulus of elasticity and hardness was 15 pphr filler loading. Further addition of cow bone to natural rubber beyond this 15 pphr leads to filler agglomeration and the strength and modulus of the composite start to reduce. Cow bone has shown a strong potential as reinforcing filler in natural rubber.

The modification of the surface properties of particulate cow bone such as surface area, surface reactivity, filler dispersion and filler-rubber interaction will further improve the strength and modulus of filled rubber vulcanizes. Cow bone reinforced natural rubber can be used in areas where moderate strength and wear resistance are required such as in children toys, protective footwear and bouncing balls. Particulate cow bone can also serve as extenders in carbon black filled natural rubber since they can reinforce to an extent. The percentage elongation of the cow bone filled rubber samples were lower than the unfilled samples as shown in Figure 3 due to the increase in modus. The same reason is attributed to the least elongation exhibited by the carbon black filled sample as it exhibited the highest elastic modulus. Fillers are reported to stiffen polymer chains and prevent the stretching of rubber (Egwaikhide, et.al, 2013).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Uncarbonized cow bone</th>
<th>Carbon black</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content at 120 °C (wt %)</td>
<td>3.9</td>
<td>2.40</td>
</tr>
<tr>
<td>Loss on ignition at 875 °C (wt %)</td>
<td>34</td>
<td>92.60</td>
</tr>
<tr>
<td>pH</td>
<td>5.28</td>
<td>6.50</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.6</td>
<td>--</td>
</tr>
</tbody>
</table>
The introduction of particulate cow bone in the matrix of natural rubber was observed to effectively improve the abrasion resistance at 10, 15 and 20 pphr filler loadings as shown in Figure 6. Compared to carbon black filled natural rubber, particulate animal bone offered a higher abrasion resistance than carbon black at 15 pphr of the filler in vulcanized natural rubber. Similar trends were reported when carbonized and uncarbonized coir (Aguele, et.al, 2014) and palm kernel husk (Egwaikhide, et.al, 2013) were used to reinforce vulcanized natural rubber and attributed to the smaller particle size of carbon black compared to agricultural fillers.

4 CONCLUSIONS
The main objective of this work is to evaluate the suitability of particulate cow bone as filler in vulcanized natural rubber. From the results, it can be concluded that the uncarbonized particulate cow bone can effectively serve as reinforcing filler in natural rubber at 15 pphr for applications requiring moderate strength, elongation and wear resistance such as shoe soles, children toys and bouncing balls. However, it will require further processing to further reduce the particle size and surface properties in order to effectively compete with carbon black as fillers in natural rubber for applications that require high strength such as in car tyre. The further processing of cow bone for application as filler in vulcanized rubber is recommended.

REFERENCES


