ABSTRACT

Periwinkle shell is an agricultural waste. The waste is produced in abundance globally and poses risks to human as well as environmental health. Thus their effective, conducive, and eco-friendly utilization has always been a challenge for scientific applications. This paper mainly deals with characterization of periwinkle shell as a potential material for asbestos-free brake pad materials using spectroscopic and wear analysis. The characterization of the periwinkle shell was investigated through X-ray diffractometer (XRD), thermogravimetric analysis (TGA/DTA), Fourier transform infrared spectrometry (FTIR), and X-ray Fluorescent spectrometry (XRF). Density, hardness values and wear rate of the periwinkle shell were also found. The various results obtained are comparable with asbestos commonly used in brake pad production. These results confirm that periwinkle shell can be used as a material for brake pad production.

(Keywords: Periwinkle shell, density, wear, thermal values, hardness values, material engineering)

INTRODUCTION

Brake pads are important parts of braking system for all types of vehicles that are equipped with disc brake. Brake pads are steel backing plates with friction material bound to the surface facing the brake disc. Different types of brake materials are used in different machines (Aigbodion et al., 2010).

The brake pads generally consist of asbestos fibers embedded in polymeric matrix along with several other ingredients. The use of asbestos fiber is now being avoided due to its carcinogenic nature. Therefore new asbestos-free friction materials and brake pads are been developed. It is envisioned that future developments in the trend of brake friction materials will closely mimic the current trends of the automotive industry. The shift towards environmentally friendly cars has already seen the release of hybrid cars such as Toyota Prius®, Honda Insight®, and Ford Escape® SUV (Dagwa and Ibhadode, 2006).

The brake pads were formally generally made from asbestos fibers. Because of its properties and risks, asbestos is being withdrawn from all the applications, where there is a possibility of alternate material for making non-carcinogenic materials (Aigbodion and Agunsoye, 2010).

There are two basic types of automobile brakes: drum brakes and disc brakes. In drum brakes, the brake shoes are located inside a drum. When the brakes are applied, the brake shoe is forced outward and presses against the drum. Disc brakes consist of two brake pads and a rotor. When the brakes are applied, the two pads squeeze against the rotor. One of the major differences between drum brakes and disc brakes is that drum brakes tend to be enclosed where disc brakes tend to be exposed to the environment (Bono and Dekyrger, 1990). Although use of asbestos for brake pads has not been banned, much of the brake pad industry is moving away from asbestos brake pads because of concerns regarding airborne particles in the factories and disposal of wastes containing asbestos. There are several patents for asbestos free organic friction materials (Dagwa, and Ibhadode, 2005).

A lot of research has been carried out in the area of development of asbestos-free brake pads. The use of coconut shell, palm kernel shell (PKS), etc. (Dagwa and Ibhadode, 2006) has been researched on over the years. Researches all over the world today are focusing on ways of utilizing either industrial or agricultural wastes as a source of raw materials in industry. Utilization of these wastes will not only be economically, but may also result in foreign exchange earnings and environmental controls. The purpose of this study...
is to characterize periwinkle shell particles as potential materials for asbestos-free brake materials; since periwinkle shell is readily available and very cheap to obtain.

MATERIALS AND METHOD

Materials / Equipment

The materials and equipment used during the course of this work are listed: Periwinkle shell was ground and sieved to a particle size of 255µm, Digital weighing balance, Sieve, Hardness tester, pin on disc machine, X-ray diffractometer (XRD), thermogravimetric analysis (TGA/DTA), Fourier transform Infar red spectrometry (FTIR) and X-ray Fluorescent spectrometry (XRF).

Method

Density measurements were carried out on the periwinkle shell particles sample using Archimedes’ principle. The buoyant force on a submerged object is equal to the weight of the fluid displaced. This principle is useful for determining the volume and therefore the density of an irregularly shaped object by measuring its mass in air and its effective mass when submerged in water (density = 1 gram/cc). This effective mass under water was its actual mass minus the mass of the fluid displaced. The difference between the real and effective mass therefore gives the mass of water displaced and allows the calculation of the volume of the irregularly shaped object. The mass divided by the volume thus determined gives a measure of the average density of the sample (Smalees, 1995).

The elemental composition of the periwinkle shell particle was determined based on the X-Ray Fluorescence (XRF) analysis. Samples of the material were formed into pellets in a pelletizer with hydraulic press (Carver, Inc.). The pellets were then sealed into the chamber of the XRF (AmpTek, Inc.) and allow running for 1000 s at a voltage of 30 kV, and a current of 50μA. The resulting spectrum measured the elemental composition of the material. The observed properties of periwinkle shell particle were compared with those for asbestos to determine the needed variation in brake lining formulation when replacing asbestos with periwinkle shell.

XRD analysis of the periwinkle shell particles was carried to determine the various element and phases distribution in the periwinkle shell particles. The test was carried out on a Philips X-ray diffractometer. The X-ray diffractograms were taken using Cu Kα radiation at scan speed of 3°/min (Blau, 2001).

The Rockwell hardness values were obtained using a digital hardness tester. The hardness value periwinkle shell was determined according to the provisions in American Society of testing and materials(ASTM E18-79) using the Rockwell hardness tester on “C” scale (Frank Welltest Brinell Hardness Tester, model 38506) with 1.56mm steel ball indenter, minor load of 10kg, major load of 100kg (Aigbodion et al., 2010).

The wear rate for the periwinkle shell was measured using pin on disc machine by sliding it over a cast iron surface at a load of 20N, sliding speed of 5.02m/s and sliding distance of 5000m (Gudmand-Hoyer et al., 1999).

Thermal decomposition was observed in terms of global mass loss by using a DTA/TGA Instrument TGA Q50 thermogravimetric analyzer. This apparatus detects the mass loss with a resolution of 0.1 as a function of temperature. The periwinkle shell particles were evenly and loosely distributed in an open sample pan of 6.4 mm diameter and 3.2 mm deep with an initial sample amount of 8-10 mg. The temperature change was controlled from room temperature (25±3°C) to 900°C at a heating rate 10°C/min (Kim et al., 2003).

Fourier transform infrared spectrometry (FTIR) was carried out on periwinkle shell particles as well. IR spectra of the periwinkle shell particles were recorded using Perkin Elmer spectrum 100 FT–IR spectrometer in the frequency range 4000 to 400cm⁻¹, operating in ATR (attenuated total reflectance) mode.

RESULTS AND DISCUSSION

The periwinkle shell particle exhibited a density of 1.24g/cm³. The lower specific gravity shows that the periwinkle shell materials would be lighter than the asbestos. This means that periwinkle shell particles will be more suitable as filler material than asbestos on the account of the overall weight of the brake pad (Aigbodion and Agunsoye, 2010).
The XRD pattern (Figure, 1) obtained reveal that, the major diffraction peaks are 42.5, 16.15, 30.90, 34.47, and 54.08° and their inter-planar distance are: 2.13, 5.49, 2.89, 2.58, and 1.69Å and phases at these peaks are: magnesium manganese oxide, calcium silicate, quartz, and titanium oxide, while each of these phases have a score shown in Table 1 and Figure 2.

![Figure 1: XRD spectrum of Periwinkle Shell Particles.](image1)

![Figure 2: Plot of Identified Phases of Periwinkle Shell Particles.](image2)
Table 1: Identified Patterns List of Periwinkle Shell Particles.

<table>
<thead>
<tr>
<th>Visible</th>
<th>Ref. Code</th>
<th>Score</th>
<th>Compound Name</th>
<th>Displacement [°2θ.]</th>
<th>Scale Factor</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>*</td>
<td>00-036-1377</td>
<td>53</td>
<td>Magnesium Manganese Oxide</td>
<td>-0.011</td>
<td>0.286</td>
<td>Mg$<em>{0.9}$Mn$</em>{0.1}$O</td>
</tr>
<tr>
<td>*</td>
<td>01-077-0420</td>
<td>41</td>
<td>Calcium Silicate</td>
<td>-0.148</td>
<td>0.334</td>
<td>Ca$_2$Si$_4$O$_4$</td>
</tr>
<tr>
<td>*</td>
<td>01-080-2148</td>
<td>43</td>
<td>Quartz</td>
<td>0.132</td>
<td>0.979</td>
<td>Si$_2$O$_3$</td>
</tr>
<tr>
<td>*</td>
<td>00-024-0234</td>
<td>30</td>
<td>Calcium Silicate</td>
<td>-0.242</td>
<td>0.132</td>
<td>Ca$_2$Si$_4$O$_4$</td>
</tr>
<tr>
<td>*</td>
<td>00-048-1278</td>
<td>31</td>
<td>Titanium Oxide</td>
<td>-0.327</td>
<td>0.329</td>
<td>Ti$_2$O$_3$</td>
</tr>
<tr>
<td>*</td>
<td>00-025-0843</td>
<td>33</td>
<td>Majorite</td>
<td>-0.223</td>
<td>0.245</td>
<td>Mg$_3$Fe$_2$(Si$_4$O$_9$)</td>
</tr>
</tbody>
</table>

Table 2: XRF Analysis of Periwinkle Shell Particles.

<table>
<thead>
<tr>
<th>Element</th>
<th>SO$_3$</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>K$_2$O</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>SiO$_2$</th>
<th>MnO</th>
<th>Cr$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>0.30</td>
<td>96.09</td>
<td>0.79</td>
<td>0.52</td>
<td>1.54</td>
<td>0.10</td>
<td>0.09</td>
<td>0.06</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Complete mineralogical analysis carried out by X-ray diffraction also revealed that the periwinkle shell particles contains each of these elements O, Na, Mg, Si, K, Ca, Ti, Cr, Mn, Fe, and none of these elements H, He, Li, Be, B, C, N, F, Ne, Al, P, S, Cl, Ar, Sc, V, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Fr, Ra, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr, D, T" which means that with the absence of all these other elements the periwinkle shell particles may not contain an abundance of radioactive and harmful materials. This is in par with the earlier of other researches (Aigbodion and Agunsoye, 2010, Blau, 2001)

The XRF chemical composition of the periwinkle shell particle is represented in Table 2. XRF analysis confirmed that SiO$_2$, CaO, MgO, Cr$_2$O$_3$, and Fe$_2$O$_3$ were found to be major constituents of the ash. Silicon dioxide, iron oxide, Cr$_2$O$_3$ and CaO are known to be among the hardest substances. Some other oxides viz. K$_2$O, Na$_2$O, and MnO were also found to be present in traces. The presence of hard elements like SiO$_2$, CaO, Cr$_2$O$_3$, and Fe$_2$O$_3$ suggested that, the periwinkle shell particles can be used as particulate material for brake pad production.

The results of XRF are in agreement with the results of XRD obtained. Therefore, the present work suggests the possibility of using periwinkle shell particles as brake pad materials since the chemical composition has close similarity with the XRF analysis of palm kernel shell, bagasse, and asbestos used in brake pad production (Aigbodion et al, 2010, Dagwa and Ibhadode, 2006).

Mainly, ten peaks were detected in the FTIR analysis of the periwinkle shell particles as shown in Figure 3 and Table 3. This results show that the presence of quartz in the sample gives rise in the IR spectrum to a series of bands located at 1384.94 and 700.18 cm$^{-1}$.

The presence of calcium oxide, in turn, is responsible for a series of bands at around 3399.65 - 2523.94 cm$^{-1}$. Quartz, mullite, and the calcium oxide overlap in the area between 1463.06 cm$^{-1}$ and 1598.08 cm$^{-1}$. Hence, quartz, mullite, and calcium oxide phases are confirmed to be present. This is in agreement with the earlier work of Gudmand-Hoyer et al., 1999)
The temperatures of destruction ($T_{des}$) of the periwinkle shell particles, subject to investigation, were determined from DTA curves. DTA data were recorded on "Derivatograph OD 102", at heating rate of $10^\circ C/min$ in argon. The results of the DTA/TGA scan of the periwinkle shell particles are shown in Figure 4. From the Figure 4, the TG/DTA curve shows three weight loss steps, while the thermal decomposition occurs in one stage.

The initial weight loss (~ 5%) observed between 400 and 500°C is attributed to the vaporization of the water from the sample, while degradation of the sample started at higher temperature, precisely after 600°C. Above this temperature, the thermal stability of periwinkle shell particles gradually decreased and degradation of the sample occurred.

DTA curve shows that the temperature of maximal decomposition/destruction was 756°C (Figure 4). The presences of endothermic effects in periwinkle shell particles sample are results of two processes: dehydrogenation and evaporation of some non-cellulosic materials. This conclusion was confirmed by the decreased mass of the sample. In an inert atmosphere, the final products of the degradation of periwinkle shell consist in carbonaceous residues and possible un-degraded fillers.

### Table 3: Identified Peaks of FTIR Analysis of the Periwinkle Shell Particles.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Intensity</th>
<th>Corr. Intensity</th>
<th>Base (H)</th>
<th>Base (L)</th>
<th>Area</th>
<th>Corr. Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>437.86</td>
<td>51.6935</td>
<td>8.6815</td>
<td>636.63</td>
<td>359.26</td>
<td>42.1791</td>
</tr>
<tr>
<td>2</td>
<td>700.18</td>
<td>62.4047</td>
<td>18.1163</td>
<td>757.09</td>
<td>636.53</td>
<td>16.8024</td>
</tr>
<tr>
<td>3</td>
<td>862.21</td>
<td>34.0381</td>
<td>38.4768</td>
<td>937.44</td>
<td>757.09</td>
<td>45.8030</td>
</tr>
<tr>
<td>4</td>
<td>1080.17</td>
<td>46.6073</td>
<td>7.9774</td>
<td>1134.16</td>
<td>938.4</td>
<td>54.0378</td>
</tr>
<tr>
<td>5</td>
<td>1384.94</td>
<td>20.1012</td>
<td>5.3391</td>
<td>1429.3</td>
<td>1135.15</td>
<td>144.0311</td>
</tr>
<tr>
<td>6</td>
<td>1463.05</td>
<td>20.3887</td>
<td>1.4612</td>
<td>1534.42</td>
<td>1430.26</td>
<td>69.5904</td>
</tr>
<tr>
<td>7</td>
<td>1598.08</td>
<td>19.5072</td>
<td>12.1487</td>
<td>1759.14</td>
<td>1535.39</td>
<td>123.038</td>
</tr>
<tr>
<td>8</td>
<td>2523.94</td>
<td>66.6503</td>
<td>23.3325</td>
<td>2683.07</td>
<td>2268.35</td>
<td>26.0452</td>
</tr>
<tr>
<td>9</td>
<td>2944.44</td>
<td>58.5355</td>
<td>10.9179</td>
<td>3030.27</td>
<td>2683.07</td>
<td>48.4753</td>
</tr>
<tr>
<td>10</td>
<td>3396.65</td>
<td>49.4291</td>
<td>25.6401</td>
<td>3796.04</td>
<td>3031.23</td>
<td>162.6997</td>
</tr>
</tbody>
</table>

Figure 3: FTIR Analysis of the Periwinkle Shell Particles.
On the analogy of these results it was assumed that the total burning/ degradation of the residual periwinkle shell particles took place in this temperature interval (700-800°C). In the last temperature interval the mass loss was minimal (accompanied by the evolution of CO₂ only) (Kim et al., 2003). The higher temperature of maximal decomposition of periwinkle shell than asbestos and many agro-wastes currently brake pad materials means that periwinkle shell can withstand higher temperature than asbestos.

The hardness values and wear rate of periwinkle shell particles are 75HRC and 0.2mg/m respectively. It was found that the hardness values and wear resistance of periwinkle shell particles are higher than that of asbestos (Aigbodion et al., 2010). This is probably due to the presence Fe₂O₃, CaO, and SiO₂ in the chemical made up of the particles.

CONCLUSIONS

Periwinkle shell was characterized by FTIR. Their thermal degradation behavior was fully investigated through TGA/DTA curves, chemical composition, and phases by XRF and XRD analysis, hardness values by Rockwell hardness tester, and wear by pin on disc machine. The various results obtained are comparable with asbestos commonly used in brake pad production. These results confirm that periwinkle shell can be used as a material for brake pad production.

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