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AN OVERVIEW OF BRAKE PAD PRODUCTION USING NON-HAZARDOUS REINFORCEMENT MATERIALS

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Abstract: An overview of brake pad production using non-hazardous reinforcement materials is carried out with assessment of various production methods and mechanical and tribological properties produced from these non-hazardous materials. Suggestion of new research directions with respect to the combination of these non-hazardous materials in different proportion is made. This paper concludes by advocating for commercial or industrial application of these brake pads that has been developed from these non-hazardous materials.

Keywords: material, mechanical properties, tribological properties, environment, friction

INTRODUCTION

Brake pad material is a heterogeneous substance composed of different elements. Each constituent element has its own functions which include improvement of frictional properties at low and high temperature, reduce noise, prolong life, increase strength and rigidity as well as reduce porosity. Changes in the weight percentage or types of elements in the formulation may result to the alteration of the chemical, mechanical and physical properties of the brake pad materials developed (Jang *et al.*, 2004; Cho *et al.*, 2005 and Mutlu *et al.*, 2005; Zaharudin *et al.*, 2012). Early researchers have concluded that no simple correlation exist between wear and friction properties of frictional materials with the mechanical and physical properties (Talib *et al.*, 2006; Todorovic, 1987 and Tanaka *et al.*, 1973).

As a result, each new formulation developed requires to be subjected to several tests to evaluate its wear and friction properties using on-road braking performance test as well as abrasion testing mechanism to ensure that the developed friction pad material meets the minimum requirements of its intended use (Talib *et al.*, 2006). Modern brake pad development has history spanning over the past 100 years. Herbert Froad was credited to be the first to invent brake pad materials in 1897. This pad was a cotton-based material that was used for wagon wheels as well as early automobiles and coupled with bitumen solution. This invention led to the formation of the manufacturing company known as Ferodo Company, a firm which still supplies frictional materials till date. Bertha Benz, the wife of Carl Benz was the first to invent patented automobile friction pads. This invention came during her first long and historic distance trip by a car in 1888 (Blau, 2001).

The earliest brake pad material was woven, but in the early 1920's, moulded materials which were made of crysotile asbestos fibres, a plentiful mineral were used to replace it. In the 1950's, metallic pads that were resin-bonded were introduced, and semi-metals which contain higher amount of metal additives were developed in the 1960s (Nicholson,

1995). Industrial brake pads usually contain many constituents such as ceramic particles and fibres, metallic chips, minerals solid lubricants and elastomers in a matrix material like phenolic resin. Also, Ole-Von *et al.* (2005) investigated the use of antimony in brake pads. The results show that the use antimony (Sb) in friction materials should be suspended as it posed a human cancer risk due to considerable concentrations of Sb in the material. Agricultural products are also emerging as inexpensive and new materials in the development of brake pad material with commercially viability and environmental acceptability (Bledzki and Gassan, 1999). Cyras *et al.* (2001) reported that among the different kinds of agricultural products investigated, lignocellulosic fillers are most times considered as attractive materials to be utilised as fillers of thermoplastic polymers due to its excellent properties.

It is possible to obtain composite materials with properties very similar to the existing synthetic-filler reinforced plastics with their superior properties such as low density, energy recovery, low cost, enhanced recyclability and biodegradability. Garcia *et al.* (2007), Bledzki and Gassan (1999) and Seki, (2006), also reported the use of rice husk that one of the agricultural products which can be potentially utilised as fillers in friction pad production is the. It was stated that rice is the most important food crop grown and planted in the world today and they can be grinded and burned at low temperature. This burning and grinding process produced white ashes which consist of about 80% silica. The rice straw comprises of 20% hemicelluloses, 30% cellulose and lignin, 10% water and about 15% mineral ash. This mineral ash is composed mainly of 95% silica, insoluble silicates of iron, aluminium, calcium and magnesium (Van-Hoest, 2006).

Concerted efforts have been channelled towards replacing asbestos and other carcinogenic materials in the production of brake pads. In the work of Nakagawa *et al.* (1986), metal fibres were used in the production of brake pads so as to counter the environmental pollution caused by asbestos.

During this study, a semi-metallic type of pad material was developed from chattered-machined metal fibres as it exhibits good properties in line with brake characteristics and also good wear resistance. This pad contained close to 60 % by weight of the steel fibres having 60 microns (μm) in diameter and length of 3mm. Dagwa and Ibhadode (2008) and Deepika *et al.* (2013), also developed a non-asbestos-containing friction pad material using an agro-waste material base, palm kernel shell (PKS) as a reinforcement material. It was reported in their work that palm kernel shell was selected because it exhibited more favourable properties than the other agro-waste they investigated. Aigbodion *et al.* (2010); Bashar *et al.* (2012) and Ruzaidi *et al.* (2011), also developed a non-asbestos brake pad by utilizing bagasse, coconut shell and palm ash respectively as reinforcement materials. The result of their study showed that the selected reinforcement materials were comparable with other commercially available brake pad materials. Similarly, Naemah (2011) reported that a good brake pad material must meet the following criteria:

- It must be environmentally acceptable and be safe for use.
- The contact materials must exhibit good resistance to wear effects
- The materials must have a good high heat capacity, thermal conductivity, and good thermal properties and also be able to withstand higher temperatures and high contact pressures
- The materials must exhibit a high frictional coefficient.
- The frictional value must be stable over a temperatures and pressures range.
- The materials must have a good resistant to environmental effects which arises from dust, pressure and moisture, and
- Must possess excellent shear strength of transferring frictional forces to structure.

Blau (2001) and Bashar *et al.* (2012) observed that brake pad additives serve different functions and a difference of two or three percent of additive can alter the performance of the friction material. Therefore, the control of the composition is of great important. Blau (2001) also stated that friction materials and additives based on their expected functions are categorised into the following:

- fillers and reinforcement,
- abrasives,
- friction modifiers, and
- binder materials.

NON-HAZARDOUS REINFORCEMENT MATERIALS

Medical research carried out has shown that asbestos fibres can lodge in the lungs thereby inducing adverse respiratory conditions. Environmental protection agency (EPA) in 1986, announced a proposed ban on asbestos. This proposed ban by EPA may have required all new automobile vehicles to possess non-asbestos brakes and clutches by 1993, and the aftermarket would have had until 1996 to convert to non-asbestos which is non-hazardous (Blau, 2001).

Though the use of asbestos in brake pads has not been fully banned, but most brake pad producing industries are moving away from the use of asbestos as reinforced material to using non-hazardous reinforced material in friction pad production. This is because of the concerns regarding airborne particles in the factories and disposal of asbestos containing wastes (Dagwa and Ibhadode, 2006). Several studies have been carried out using different reinforced materials to find a possible replacement for asbestos whose dust has been reported to be carcinogenic (cancer causing). Some of these studies are discussed in the following section.

— Palm Kernel Shell and Fibre

Ndoke (2006), reported that palm kernel shell as shown in Figure 1, has an average dry density of $0.65\text{mg}/\text{m}^3$, porosity of 28% and an impact value of 4.5%. The report suggested that the dry density, porosity and impact value of palm kernel shell place it in the same category as lightweight aggregate and a good substitute for asbestos.



Figure 1: Palm kernel Shell (Source: Mayowa *et al.*, 2015)

Fono-Tamo and Koya, (2013), developed brake pad materials for automobile using standard factory procedure from palm kernel shell. Mechanical properties of the material developed were studied. The results showed that the developed pad has an average hardness of 32.34 and average shear strength of 40.95 MPa. The coefficient of friction of the product was also tested and the result indicated that the pad possessed a frictional coefficient of 0.43. This result was in agreement with the work of Koya *et al.* (2004) in which it was stated that the coefficients of friction of palm kernel shell on metal surfaces are in the range of 0.37–0.52. In contrast, friction coefficient that falls within the range of 0.30–0.70 is desirable when using brake pad material (Roubicek *et al.*, 2008). The bonding of the material to the back plate was also tested and the result indicates a value of 3375 N/s. All the values of the responses though not as excellent as asbestos-based brake pads whose coefficient of friction falls within 0.37–0.41 as the recommended by SAE was reported to be good and can be applied as automotive friction material therefore making palm kernel shell a good substitute for asbestos and suitable for brake friction pads production.

Ikpambese *et al.* (2014) also developed asbestos-free automobile brake pads from palm kernel fibers together with epoxy resin as binder. The fibers (PKFs) were soaked in caustic soda solution (sodium hydroxide) for 24 hours to get rid of

the remnant of red oil in fiber. The fibers were then washed with water to remove the caustic soda and then dried under the sun for a period of one week. The binder used during the study was varied in formulations during production. The physical, morphological and mechanical properties of the composite were investigated to examine the effect of composition on the friction material.

The results obtained from the study indicated that the coefficient of friction, temperature, wear rate, stopping time and noise level of the pads increases with increasing speed. The results also show that moisture content, porosity, surface roughness, hardness, specific gravity, water and oil absorption rate remained stable with increasing speed. From the microstructure analysis it was observed that worn surfaces wear where the asperities ploughed were characterized by abrasion thereby exposing the white region of the fibers and increasing the smoothness of the composite material. The report showed that the brake pad sample with composition of 10% palm wastes, 40% epoxy-resin, 15% calcium carbonate, 6% Al_2O_3 , and 29% graphite gave optimum properties. Therefore, it was concluded that palm kernel fibers can be used effectively as a good replacement for asbestos in friction pad production.

Ibhadode and Dagwa, (2008), also studied the feasibility of using agro-waste material, palm kernel shell (PKS) as replacement for asbestos in brake pad production. The material was used along with other constituents. Taguchi optimization technique was utilised in achieving the optimal formulation and manufacturing variables. The value of experimental parameters selected includes moulding pressure (16.74–27.90 MPa), moulding temperature (150–170°C), curing time (6–10 minutes) and heat treatment time (1–3 hour). The composition used during their study includes 56% reinforcement, 24% binder, 14% abrasives and 6% friction modifier. The brake pads produced were tested on a test rig and on a car (Toyota Carina II) in order to examine its effectiveness and wear properties. The results of the test conducted on the produced brake pad samples indicates that the surface hardness falls within 64–89 Rockwell scale B while the coefficient of friction falls within 0.35–0.44 and wear values falls within 0.017–0.170. The results compared well with asbestos-based brake pad and also performed satisfactorily. However, it was also reported that more pad wear was observed on the PKS pad at high vehicular speeds beyond 80km/hour.

— Coconut Shell

Coconut shells shown in Figure 2 are agricultural wastes used in the preparation of various attractive articles (antiques) and also applied in the production of activated charcoal as well as reinforcement material in the production of composites. Salmah (2013) reported that coconut shell is a lignocellulosic filler which exhibits excellent properties compared to mineral fillers (kaolin, calcium carbonate, mica and talc). Some of the outstanding properties reported by Salmah (2013) include minimal health hazard, high-specific strength-to-weight

ratio, low cost, biodegradability, environmental friendly and renewability. Matthew (2012) reported that moisture desorption of coconut shells takes place between 25 and 150°C and at 150°C, degradation of sclerenchyma cells, which are responsible for holding water in the shell occurs. Further heating of the shells between 190°C to 260°C may result to the degradation of hemicellulose present in the shell and at 240°C to 350°C, degradation of cellulose take place. The final stage of thermal degradation involves the breakdown of lignin which occurs between 280°C and 500°C (Matthew, 2012).



Figure 2: Coconut shells

Bashar et al. (2012) conducted a study with the aim of finding a possible replacement for asbestos, used coconut shell powder to develop brake pad material. This material was mixed with other ingredients such as catalyst, epoxy resin, cast iron fillings, silica, and accelerator. The coconut shell was dried in the sun for some days in order to get rid of the shell moisture and then reduced into smaller sizes using anvil and hammer and then pounded using mortar and pestle. Finally, a grinding machine was used to ground it into powder and sieved with a mesh size of 710 μm . In the study, the weights of epoxy resin and the coconut shell powder were varied while the weight of the other ingredients remained unchanged. Mechanical (tensile, hardness, compressive, wear and impact) and corrosion tests were conducted to study the effect of process on the products. The results show that as the percentage of the coconut shell powder increases, the hardness, breaking strength, compressive and impact strength reduces. Therefore, it was reported that higher percentage of coconut powder results to brittleness and that brake pad samples with 50% matrix and 10% reinforcement as well as samples with 60% matrix and 10% reinforcement can be adopted in friction pad production since they are far lighter and possesses better properties when compared with the other compositions. The report also suggested that the coconut shell reinforced brake pad possessing this composition may be a better alternative to asbestos as it possesses lower wear resistance though; the presence of iron filings in the samples causes poor resistance to corrosion. Darlington *et al.* (2015) in their study also produced an asbestos-free brake pad from locally sourced raw materials using coconut shell powder and palm kernel shell as reinforcement materials, graphite as lubricant, polyester resin as binder material, carbides and metal chips as the abrasives.

According to the report of their study, three different samples of brake pads were produced by varying mass compositions of coconut shell and palm kernel shell while the composition of the binder, lubricant and abrasive materials remained unchanged throughout the experiment. The tests results obtained shows that developed samples have density which falls between 2.55–2.78 g/cm³, wear rate of 0.2007–0.2733 g/min, percentage water absorption of 0.0399–0.0522% and hardness of 3.00 –3.41.

Samples of commercial brake pads were also tested and it was found that the commercial pads possesses a density of 3.36 g/cm³, wear rate of 0.1873 g/min, water absorption of 0.0327% and hardness of 2.53. These results indicate that the developed samples though could not meet up with properties of commercial brake pads due to its high density and wear rate but compared well with commercial brake pads and can serve as an alternative to commercial products. Therefore the study concluded that locally sourced palm kernel and coconut shell can be used as a replacement for commercial pad.

— Palm Ash

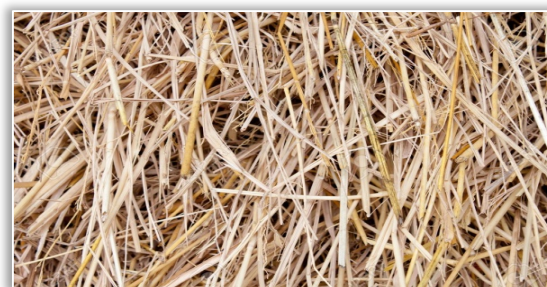
Ruzaidi *et al.* (2011) conducted a study to produce a non-asbestos brake pad at varying composition of palm ash and polychlorinated biphenyls (PCB) waste along with thermoset resin as a binder and metal filler as abrasive. Five samples were produced using moulding pressure, moulding temperature and curing time of 122 MPa, 150°C and 5 minutes respectively and were tested to examine its compression strength, water absorption rate, wear rate, and morphological properties.

The test results showed that the brake pads with higher percentage of palm ash gave the best mechanical and wears properties. This indicates that the wear properties of the produced brake pads are comparable with conventional brake pad. The study also concluded that brake pads can be developed by replacing asbestos with other reinforcement materials such as palm ash and PCB waste which could lower the cost of producing brake pad.

It was also suggested that compressive strength of the product can be increased if the percentage of palm ash in the composition is also increased while the samples with higher palm ash content may give optimum wear properties and water absorption rate which will lead to better properties of brake pad application (Ruzaidi *et al.*, 2011).

— Rice Husk and Rice Straw

Rice husks and rice straw are agricultural wastes which are abundantly available mostly in rice producing countries like Nigeria. Rice husk dust (RHD) and rice straw dust (RSD) shown in Figure 3 are known to have high silica and low lignin content which gives friction materials a ceramic-like behaviour (Ibrahim, 2009). These materials are used as filler or reinforcement materials in the development of composites like friction pads.



(a)



(b)

Figure 3: Rice straw (a) and Rice husk (b)

Acharya and Samantrai (2012) studied the wear and friction behaviour of rice husk using randomly oriented unmodified and modified rice husk as reinforcement in epoxy matrix (Araldite LY556 and hardener HY 951). A pin on-disc apparatus was used to study the wear behaviour of rice husk composites reinforced with 5–20 wt%. The pin of each sample was attached to a holder and then abraded under different loads of 5, 7.5, 10 and 15N. Each test was conducted for duration of 5 minutes.

The results of the coefficient of friction and wear rate of the composite were found to be the functions of sliding velocities, normal load and the filler volume fraction. Scanning electron microscope (SEM) was used to also study the morphology of the worn surface of the composites. According to the report of Acharya and Samantrai (2012), the test result shows that wear rates decreases with increase in the rice husk fibres addition under all testing conditions. It was then concluded that the addition of the rice husk fibres in epoxy is very effective in the improvement of the composite wear resistance and the optimum fibre fraction which gave the optimum wear resistance to the composite is found to be 10 w%.

The morphologies of scanning electron micrograph of worn surface for the untreated rice husk composite and the benzoyl chloride treated rice husk composite showed that surface damage and cracking of the matrix (longitudinal and transverse crack) are more pronounced for the untreated composite. Reverse is the case for the benzoyl chloride-treated composite as the surface damage seems to be minimal and only longitudinal cracks are observed on the surface of the material in the rolling direction. It was therefore concluded that the treatment of the surface of the fibre restricts the propagation of the cracks in the transverse direction thereby improving the wear resistance of the composite.

Mutlu (2009) also conducted a study with the aim of finding a possible replacement for asbestos whose dust is hazardous. Investigation was carried out using rice husk dust (RHD) and rice straw dust (RSD) to study the tribological properties of brake pads. The study was conducted for four different mixtures of brake pads which were coded RS₄, RS₂₀, RH₄ and RH₂₀. The materials in each brake pad were composed of rice husk dust (RHD), rice straw dust (RSD), copper particles, barite, brass, cashew, steel fibres, graphite and alumina and production of samples was done using moulding temperature, curing time and heat treatment time of 180 °C, 15 minutes and 4 hours respectively.

The newly formulated brake pads were tested and examined to study their performance and determine the coefficient of friction, wear rate and morphological properties. The results of the study shows a mean coefficient of friction of 0.315–0.381 which is very low to be applied in heavy duty automobiles brake pads as specified in the work of Dagwa and Ibadode (2008). The result of the wear rate varies from 0.000853–0.001041 g/mm². Therefore, considering the wear rate of all the samples, RS₄ has a little better wear rate than RH₄ which can be ignored. The coefficient of friction variations with test time are shown in Figure 4.

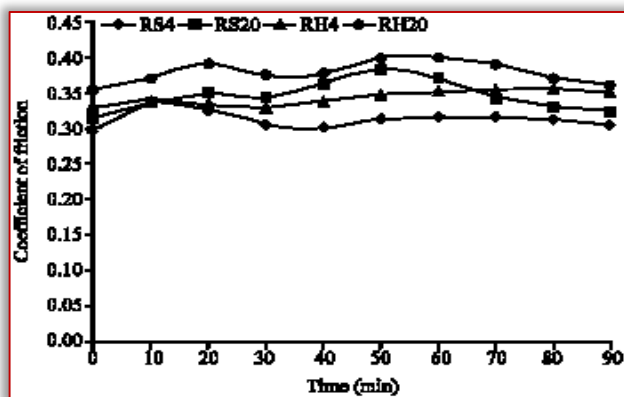


Figure 4: Change of coefficient of friction as a function of time for the four samples (Source: Mutlu, 2009)

From Figure 4, it was observed that the coded samples RH₄ and RS₄ showed a continuous initial rise in coefficient of friction (μ) between the 10th and 20th minutes of test. It was then concluded that such increase can often be attributed to the adhesion of metal chips in the brake pad to the friction surface of the cast iron disc. Also, the SEM micrographs of each coded samples was conducted and the results showed that there was homogenous distribution of the silica particles in the body (white points). It was also reported that the micro-voids on the surface of each sample were bigger and smaller in size which was reported to be due to the falling of the metal particles during friction. In addition to the micro-voids observed in the sample, it was also stated that there were some micro cracks on the surface which stayed as effective in the friction surface. The study then concluded that RHD and RSD can be used effectively in brake pad formulations when combined properly with other additives and that the use of RHD significantly improved the overall

performance of the formulated material. It was also established that the sample with 20 % rice husk (RH₂₀) will provide a better friction coefficient and wear rate when used in brake pad formulation.

— Banana Peels

Banana peels shown in Figure 5 are also known as banana skin. They are the outer covering of the banana fruit. It is a popular fruit consumed Worldwide with a yearly production of over 145 million tonnes. Once the peel is removed, the fruit can be eaten raw or cooked and the peel is generally discarded. Because of this removal of the banana peel, a significant amount of organic waste is generated (Babatunde, 1992).



Figure 5: Banana peel (Source: Idris *et al.*, 2013).

The coefficient of friction of banana peel on a linoleum (a tough washable floor covering) surface was measured at just 0.07. This is about half that of lubricated metal on metal surface. Several researchers have attributed this to the crushing of the natural polysaccharide follicular gel, releasing a homogenous sol (Kiyoshi *et al.*, 2012). It has been reported that at increased temperature, banana peel powder becomes more gelatinous and at much higher temperatures, the hardness increases. Therefore, because of these properties of banana peel, it is recommended for use in the formulation of new friction pad material as it increases the binding ability of resin at higher temperatures (Idris *et al.*, 2013).

Bashir *et al.* (2015), with the aim of establishing the general behaviour of a newly developed friction material to serve as light weight automotive friction pad material when subjected to high temperature and significant compression loads studied the wear and friction behaviour of disc brake pad material using banana peel powder. The newly formulated brake pad was composed of thirteen ingredients (phenolic resin, banana peel, CaCO₃, Ca(OH)₂, graphite, Sb₂S₃, MoS₂, Al₂O₃, MgO, SiC, Steel wool, PAN fiber and CaSiO₃). During the experiment, eleven of the ingredients were kept constant while two ingredients (phenolic resin and banana peel) were varied. To ensure homogeneity, an organic solvent, ethanol was utilised to mix the ingredients in a beaker using magnetic stirrer while samples were produced using moulding pressure (15MPa), moulding temperature (150°C), curing time (10 minutes) and heat treatment time (8 hours) as process parameters. A reciprocating friction monitor was used to study the wear and friction properties of the newly formulated brake pad. The machine is a digitally controlled versatile device used in the evaluation of wear and friction

properties of the material under lubricated and dry conditions. New set of disc of 14mm diameter was designed and fabricated to be suitable for area contact testing. The new disc was used as an upper specimen while the brake pad material serves as the lower specimen and the experimental results showed that at higher temperature, a breakdown of the efficiency of the brake occur which was termed as brake fade. Mutlu (2009) reported that the possible reason for brake fade is due to phenolic resin degradation.

Also, it was observed that with increase in temperature, the wear of the pads reduces. This was attributed to the binding ability of the resin used in the study which was retained because of the presence of the banana peel powder which led to the attainment of higher coefficient of friction. It was therefore concluded in the study that proper bonding can be achieved in brake pad formulation with the banana peel powder, which will result in increase in coefficient of friction. Idris *et al.* (2013) carried out a study with the aim of finding a possible replacement for asbestos and phenolic resin (phenol formaldehyde) binder, formulated a new brake pad using banana peels waste. The composition of the resin varied from 5 to 30 wt% with interval of 5 wt%. The banana peels used in the study was dried and ground into powder (uncarbonized, BUNCp). Analysis of the particle size of the peel particles was carried out in accordance with BS1377:1990.

Table 1: Summary of findings compared Asbestos based Brake Pads.

Properties	Asbestos based	New (Banana peel carbonized at 30% resin)	New (Banana peel uncarbonized at 25% resin)
Flame Resistance (%)	Charred ash 9%	Charred ash 12%	Charred ash 24.67%
Specific gravity (g/cm ³)	1.89	1.20	1.26
Coefficient of Friction	3.80	0.35	0.40
Thickness swells in water (%)	0.3–0.4	3.0	3.21
Wear rate (mg/m)	3.80	4.15	4.15
Hardness values (HRB)	101	71.6	98.8
Compressive strength (N/mm ²)	110	61.20	95.6

Source: Idris *et al.* (2013).

During the study, two sets of samples were produced using the carbonised and uncarbonised banana peels particles. Physical, wear, morphology and mechanical properties of the formulated brake pads were investigated. During the tests, the samples contain 30 wt% carbonised (BCp) and 25 wt% in uncarbonised banana peels (BUNCp) gave the better properties in all. Table 1 shows the summary of the results findings compared with asbestos based friction pads.

From Table 1, it was observed that the results obtained are in close agreement with commercial brake pads. Therefore, it was concluded that taking into consideration all the desired dimensions of the brake pad, a prototype of Peugeot 504

brake pad of length 77 mm, width of 65 mm and depth of 12 mm asbestos-free brake pads can be produced with these formulations. Hence, banana peels particles can be used effectively as a replacement for asbestos in brake pad production.

— Bagasse

Bagasse as shown in Figure 6 is a fibrous residue that remains after crushing the stalks. It is composed of fibers, water and little amounts of soluble solute. The percentage contribution of each of these components in bagasse depends on the maturity, variety, efficiency of the crushing plant and the harvesting techniques. Bagasse contains about 30% hemicelluloses, 40% cellulose, and 15% lignin (Punyapriya, 2007).



Figure 6: Bagasse (Source: Punyapriya, 2007).

Aigbodion *et al.* (2010), with the conducted a study using bagasse to produce brake pads in the ratio of 30% resin and 70% bagasse using compression moulding machine. The bagasses used in the study were sieve into grades of 100, 150, 250, 350 and 710µm. The binder used during the study was phenolic resin (phenol formaldehyde). During the experiment, the compression moulding machine was set to a moulding temperature of 140°C, moulding pressure of 100 KN/cm² pressure and a curing time of 2 minutes and the final product was cured in an oven for 8 hours. The optimal values of the properties examined during the study include hardness (92 at 3000 kgf), density (1.65 g/cm³), microstructure analysis, compressive strength (103.5 MPa), flame resistance (charred with 46% ash), water and oil absorption (5.04 and 0.44 %). From the result obtained, it was reported that the compressive strengths of the produced samples followed similar trend with that of the values of the hardness as each of the properties increases with decreasing sieve sizes. The microstructure of each sample was reported and the results showed that as the particles size of the bagasse decreases, there was more uniform distribution of the resin with the bagasse which was attributed to the proper bonding between the resin and the bagasse as the sieve grade decreases. It was therefore concluded in the study that better properties of friction pad can be achieved using a lower sieve grade of 100µm of bagasse with a composition 70% and 30% of resin.

— Maize Husk

Maize husks as shown in Figure 7 are the outer covering of maize. For most applications, the husks need to be soaked in hot water to become flexible. This type of husk is commonly

used to encase foods for baking or steaming thereby imparting light maize flavour.



Figure 7: Maize husk

Ademoh and Adeyemi (2015) conducted a study using maize husks as reinforcement material to produce automotive brake pads. Three friction composite compositions were developed using the maize husks as strengthening material with varied epoxy resin binder. Maize husks were grounded and sieved to a mesh size of 300µm. Other ingredients used during the study include silica sand, epoxy resin, calcium carbonate, anhydrous iron oxide, talc as release agent and powdered graphite.

Three samples were produced using curing time of 80–120 minutes and varying percentage weight of maize husk and binder (epoxy resin and hardener at 1:2) while the weight of friction modifier (graphite powder), abrasives (silica and iron oxide), and fillers (calcium carbonate) were kept constant throughout the experiment. To ascertain suitability of the formulated composites for brake pad application, the samples were subjected to tests to determine its mechanical, physical and tribological properties. Some of the tests conducted include water and oil absorption, density, friction coefficient, wear resistance, thermal conductivity, hardness, compressive and tensile strengths. The optimal values of the developed brake pad compared with asbestos-based brake pads are shown in Table 2.

Table 2: Optimal values of developed brake pad compared with Asbestos-based Brake Pad

Properties	Newly Formulated Maize Husk Based	Asbestos based
Specific gravity (g/cm ³)	0.853	1.890
Wear rate (mg/m)	2.146	3.800
Friction Coefficient	0.37 – 0.40	0.30 – 0.40
Thickness swell in H ₂ O (%)	0.91	0.9
Thickness swells in SAE oil (%)	0.58	0.30
Hardness	127.8	101.0
Compressive strength (MPa)	103	110.0
Tensile strength (MPa)	20.22	7.00
Thermal conductivity (W/mK)	0.251 – 0.372	0.539

Source: Ademoh and Adeyemi, 2015.

As shown in Table 2, it can be observed that the newly formulated brake pads has slight higher thickness swell in water as well as SAE oil compare to asbestos based brake pads. The authors therefore concluded that maize husks are

suitable eco-friendly replacement for asbestos and other agro-biomass friction materials in automobile brake pads application.

— Periwinkle Shell

Periwinkles shown in Figure 8 are small marine snails belonging to the family *Littorinidae* (class Gastropoda, phylum Mollusca). They are widely distributed shore snails which are usually found on stones, rocks or pilings. Some are found on mud flats while some tropical forms are found on the prop roots or mangrove trees. The shell of periwinkles is the outer casing of the animal which is usually discarded after the flesh inside is consumed. They are usually considered as agricultural waste products in riverine area of southern Nigeria (Yawas *et al.*, 2013).



Figure 8: Periwinkle shells

Yawas *et al.*, (2013) developed an asbestos-free brake pad using periwinkle shell as reinforced material. The periwinkle shells used during the study was grounded and sieved into grain sizes of 125, 250, 335, 500 and 710 µm, and was mixed with 35% phenolic resin binder. Five test samples were produced using compression moulding machine at a pressure of 40 kg/cm², a moulding temperature (160°C) and a curing time (1.5 hours). All the samples were post cured in an oven of temperature 140 °C for 4 hours. The microstructure (surface morphology) of the developed friction materials was analysed using scanning electron microscope (SEM) and the results indicate that the microstructures of the developed samples showed a homogeneous distribution as the periwinkle shell particles sieve size decreases. Mechanical, physical and tribological properties of the periwinkle shell based brake pads were also investigated and compared with the properties of asbestos-based brake pads.

It was reported that the hardness, compressive strength and density of the formulated brake pads increases as the particle size of periwinkle shell decreases from 710 to 125 µm while the oil absorption, wear rate and water absorption rate decreases as the particle size of the periwinkle shell decreases. Therefore, the results obtained for the sieve size of 125 µm of periwinkle shell particles compared well with that of commercial brake pad. The optimal values of the test results reported include specific gravity (1.01 g/cm³), coefficient of friction (0.41), hardness (116.7 HRB), Compressive strength (147 N/mm²), and thickness swell in water (0.39 %) and thickness swell in SEA oil (0.37 %). It was therefore concluded that periwinkle shell particles can

effectively serve as a replacement for asbestos in the production of brake pads.

—Cow bone

Due to large number of cows being slaughtered daily in the Nigeria, cow bones as shown in Figure 9 are abundantly available. These natural fibers are obtained from cow wastes which causes environmental pollution. Isiaka and Temitope (2013) reported that cow bone exhibit excellent structural compatibility in addition to the surface compatibility requirements as biomaterials. Mayowa *et al.* (2015) also reported that cow bone consists of living cells which are renewed constantly in the bone and widely scattered within a non-living material known as the matrix formed by osteoblasts cells. It was also reported that this osteoblasts in the bone secrete and makes protein collagen, which gives the bones elastic property which help it withstand stresses generated by lifting, walking, and other related activities.



Figure 9: Cow Bones (Source: Mayowa *et al.*, 2015).

Isiaka and Temitope (2013) investigated the influence of particle size distribution of cow bone powder on the mechanical properties of polyester matrix composites with the aim of considering how suitable it is to be applied as biomaterials. During the study, the cow bone used was thoroughly washed to get rid of unwanted materials and then crushed into smaller particles sizes using hammer. Sieve size analysis was conducted on the crushed bones and was sieved into three sieve sizes of 300, 106 and 75 μ m.

Other materials used during the experiment include unsaturated polyester resin which serves as the binder, a catalyst known as methyl ethyl ketone peroxide (MEKP), polyvinyl acetate which serves as the mould releasing agent, 2% cobalt solution (accelerator) and a cleaning agent known as ethanol.

During the production of the composite, 120 g of the polyester resin was mixed with 1.5 g each of catalyst and accelerator while the particulate of the cow bone was varied in 2, 4, 6, and 8 wt% predetermined proportion. The developed composites were tested using standard testing methods to determine its mechanical properties.

The test results indicate that the sample reinforced with 8 wt% from sieve size of 75 μ m gave a better tensile strength than others polyester matrix while hardness results show that the 300 μ m particle size gave the optimal result as the 300 μ m particle reinforcement increases the hardness as the fibre content rises from 2 to 8 wt%. Also, the flexural strength

results specify a peak improvement with the addition of cow bone particles.

The study further concluded that the optimal reinforcement can be obtained by the addition of 6 % of cow bone powder from 106 μ m particle size. Though, from the results obtained, the authors reported that cow bones can serves as a reinforcement material in polyester matrix as well as a good replacement for asbestos but tribological properties such as wear resistance and friction coefficient which majorly affect the frictional behaviour of a brake pad was not investigated. Mayowa *et al.* (2015) also formulated a new friction material using cow bone and palm kernel shell (PKS) as reinforced materials. Both the cow bone and the palm kernel shell were washed, dried, grounded into fine powder and subjected to sieve analysis. The retained fractions which were below the 100 μ m, on 100 μ m and 120 μ m, were used in the production of the friction material. About 60% epoxy resin and 10% hardener along with 30% of different grade sizes of amount retained on 120, 100 and grading below 100 (-100%) was used for the production.

The manufacturing parameters used during the study include a preform pressure which was varied between 0.40 MPa and 0.60 MPa for a period of 2–4 seconds. A hot pressing pressure of 0.27 MPa at a temperature of 200°C and breathing at 30 and 45 second after a minute of hot pressing. After which the curing is continued at 0.90 MPa for another 10 minutes. Post curing of the samples was done for 2 hours in an electric oven at a temperature of 200°C. The formulated friction materials were characterized based on the requirements for its application in automobile vehicles. The experimental test results obtained during the study showed that density of the palm kernel shell and cow bone reinforced composites falls between 1.03–1.2 g/cm³ and 1.3–1.5 g/cm³ respectively while the impact energy ranges between 0.5–1.0 J and 0.8–1.5 J correspondingly and the tensile strength for the two composites ranges between 9–23 J/mm² and 12–24 J/mm² respectively.

The study also reported that as the particle size increases, the density decreases. This was due to fact that smaller particle size occupies higher surface area (Isiaka and Temitope, 2013). Also, the result of the impact energy showed that samples with higher sieve size gave a relative increase in impact strength when compared to samples with finer particle sizes and that cow bone composition tends to absorb more water than palm kernel shell composition. Mayowa *et al.* (2015) reported that this was due to the closer packing in palm kernel shell as compare to cow bone. This close packing makes it difficult for water to pass through as a result of the stronger binding properties.

Finally, thermogravimetric analysis (TGA) was conducted and a rise in weight loss with increasing temperature in the range of 200–500°C was observed. The percentage weight loss rises as the sieve size rises. The study therefore concluded that palm kernel shell and cow bone reinforced material can serve as a good replacement for asbestos in the production of

friction materials. Though tribological properties such as wear resistance and friction coefficient which majorly affect the frictional behaviour of friction materials were not investigated.

— Fly Ash

Fly ash shown in Figure 10 is the finely divided residue obtained from the combustion of pulverized coal and is transported from the combustion chamber by exhaust gases. It is generally captured by a particle filtration equipment such electrostatic precipitators before the flue gases reach the chimneys of coal fired power plants. This waste generated by thermal power plants poses a great environmental concern (Anushree & Alka, 2009).



Figure 10: Fly ash (Source: Natarajan *et al.*, 2012)

Natarajan *et al.* (2012) conducted a study on the effect of ingredients on the tribological and mechanical properties of different brake pad materials. A non-asbestos organic based friction material was utilized in developing brake pads which was applied in automobile brake system. Two different types of frictional materials having different combinations were developed. The first consist of fly ash range (10–60%) and the second was developed without fly ash. Fly ash according to the study is composed of substantial amounts of silica, calcium sulphate, alumina, and un-burnt carbon. These two materials were studied to investigate the effect of ingredients on the tribological (wear) and mechanical properties of different brake pad materials.

The result of the experiment showed that the presence of fibers in the phenolic matrix improved the tensile strength and hardness of the friction material. It was reported that this result was expected because soft resin matrix is reinforced by the hard fibers.

The results of the study also indicated that the coefficient of friction of the fly-ash was in the range of 0.35 to 0.48. It was reported that these results were better when compared barites based (without fly-ash) and asbestos based brake pads. Also, the results showed that wear resistance of the friction material was greatly influenced by the amounts of rockwool, ceramic wool, zirconium silicate (zircon) and calcium hydroxide in the samples and the presence of friction dust powder, potassium titanate (terracas) and wollastonite (CaSiO_3) strongly influence the friction coefficient of the product. Similarly, the increasing strength of the friction material was achieved by the presence of para-aramid fiber and glass fiber. It was therefore concluded in the

report that the presence of ingredients posed a great impact on the properties of frictional materials. Though, according to National Precast Concrete Association (NPCA) of 2010, some fly ash, especially those produced in power plant are usually compatible with engineering material, while some other needs to be beneficiated and few other types cannot actually be improved for use in engineering application. Thus, the use of fly ash in friction material may pose some negative effects on the properties of friction material.

— Cocoa Beans Shells

Cocoa bean shells as shown in Figure 11 also called cocoa bean mulch or cocoa bean hull mulch are shells of cocoa bean which come off the beans during roasting process and are separated from the beans by strong air action, therefore insuring a dry weed-free product. Oliver, (2013) reported that the waste shells of cocoa bean are rich in anti-oxidants and fiber which constitute a great potential as brake pad ingredients.



Figure 11: Cocoa beans shells (Source: Foodbev Media, 2015)

Adeyemi *et al.* (2016) developed asbestos-free brake pad materials using cocoa bean shells (CBS). The materials used for the production of the samples include calcium carbonate, silica sand, anhydrous iron oxide, epoxy resin and graphite. The base material, coco bean shells were prepared by washing, sun-drying, grinding into a fine powder and sieving of grinded powder using a sieve of aperture 300 μm . Three samples were produced by varying the epoxy resin (50–60%) and Cocoa beans shells powder (21–31%) while keeping the calcium carbonate (CaCO_3), silica, iron oxide and graphite constant at 4, 7, 3 and 5% respectively.

Experimental tests were conducted on the samples to determine the physical, mechanical and tribological properties of the material and to ascertain the feasibility of applying the product on automobile brake pad. The experimental results shows that the specimen labelled as sample 3 (60% epoxy resin and 21% Cocoa beans shells powder) gave the optimum performance compared to other experimental samples. The responses obtained were compared with asbestos-based brake pad as shown in Table 4.

From Table 4, it can be observed that the optimal values of the experimental results compared favourably with that of commercial brake pad (asbestos based). Though the samples performed well as reported by the authors but the presence of iron in the composition may result to poor corrosion

resistance which was not investigated by the researchers. Lawal *et al.* (2016) reported that poor corrosion resistance of brake pads may lead to poor braking performance.

Table 4: Experimental Test Results Compared with Existing Ones

Properties	Newly formulated (CBS at 325 μm)	Asbestos based (Commercial)
Specific gravity (g/cm ³)	1.010	1.890
Wear rate (mg/m)	3.934	3.800
Friction Coefficient	0.32 – 0.35	0.30 – 0.40
Thickness swells in water (%)	1.19	0.9
Thickness swells in SAE oil (%)	0.28	0.30
Hardness Values (MPa)	120.3	101.0
Compressive strength (MPa)	23.2+	110.0
Tensile strength (MPa)	16.88	7.00
Thermal conductivity (W/mK)	0.239 – 0.338	0.539

Source: Adeyemi *et al.* (2016)

— Cow Hooves

Cow hooves shown in Figure 12 are the horny covering protecting and encasing the foot of a cow.



Figure 12: Cow Hooves (Bala *et al.*, 2016)).

Bala *et al.* (2016) conducted a study using cow hooves with the aim of replacing asbestos whose presence in brake pad was reported to be carcinogenic. The cow hooves used during the experiment were washed thoroughly to remove impurities and then properly dried in the sun. Other processes involved in preparing the pulverised hooves powder include drying it in an electric vacuum oven for 180 minutes at 250°C in order to remove contaminating oil, crushing using pestle and mortar, grinding into powder using a milling machine and finally sieving the powder using sieve size of 710 μm. Other materials used along with the pulverized hooves powder include graphite, aluminium oxide, barium sulphate and epoxy resin.

Seven different samples were produced by varying the epoxy resin (10–40 %) and pulverized cow hooves (10–40 %) while keeping the barium sulphate, alumina and graphite constant at 30, 10, and 10 % respectively. The production of the samples was done using a moulding temperature of 70 °C, a moulding pressure of 30 MPa and a curing time of 10 minutes. The produced samples were post-cured in an electric oven for one hour at a temperature of 180°C.

Tests were conducted on the products to determine the mechanical, tribological and physical properties of the developed friction materials. The test results obtained shows that sample composed of 15 % pulverized cow hooves, 35% epoxy resin and sample 7 with 10% pulverized cow hooves, 7% epoxy resin gave the optimum results and were compared with commercially available brake pads as shown in Table 5.

Table 5: Comparison of developed brake pads with Asbestos based Brake pads

Property	Commercial (Asbestos based)	Sample 6 (Pulverized cow hooves)
Oil absorption (%)	0.30	1.30
Hardness (Shore D)	–	71
Relative density	1.89	1.66
Coefficient of friction	0.3 – 0.4	0.41
Water absorption (%)	0.90	2.00
Wear rate (mg/m)	0.38	0.176
Compressive strength (MPa)	110	75.53

Source: Bala *et al.* (2016)

From the summary of the results presented in Table 5, it was concluded that pulverized pulverised cow hooves is a suitable reinforcement material for brake pad production. Though, some of the results obtained during the study compared well with commercially available brake pads but the use of a design of experiment technique instead of trial and error method of design may have given a better comparable result as trial and error method are sometimes characterised by repeated, varied attempts which are continued until success is achieved.

— Seashell

Natural materials such as seashell (exoskeletons of mollusks) is made up of three distinct layers which include the smooth inner layer composed mainly of calcium carbonate, intermediate layer (calcite) and the outer layer of horny substance known as conchiolin (Schaeffer, 2014). Norazlina *et al.* (2015) reported that seashell as shown in Figure 13 primarily consist of calcium carbonate (CaCO₃), been naturally above 80% CaCO₃ by weight with only about 2 % protein content and no complex extraction process is needed to use it for composite production.



Figure 13: Seashells (Norazlina *et al.*, 2015)

Seashells exhibit significant combinations of low weight, toughness, stiffness and strength which are in some cases

unrivaled by mineral fillers (Vignesh *et al.*, 2015). Table 6 shows the chemical composition of a commercial calcium carbonate and calcium carbonate obtained from seashell as reported by Michele *et al.* (2012). The seashell powder used in the study was utilised as filler by the authors to produce a composite using polyester binder. The test results indicate that the commercial CaCO₃ based composite possesses an impact and tensile strength of 918 MPa and 3.2 kJm⁻² respectively while seashell based composite exhibit an impact and tensile strength of 904 MPa and 3.4 kJm⁻² correspondingly.

The authors therefore concluded that seashell can be used in place of commercial CaCO₃ to produce composites since commercial CaCO₃ and seashell (mussel or oyster shells) produces similar results regardless of their variation in distribution of particle size and particle sizes.

Table 6: Chemical composition of seashell and commercial CaCO₃

Oxides	CaCO ₃ from seashell (%)	Commercial CaCO ₃ (%)
CaO	95.7	99.1
SO ₃	0.7	–
SiO ₂	0.9	–
K ₂ O	0.5	0.4
Fe ₂ O ₃	0.7	–
Al ₂ O ₃	0.4	–
MgO	0.6	–
SrO	0.4	–

Source: Michele *et al.*, (2012)

Albert *et al.* (2006) conducted a comparative study on the mechanical properties and structure of haliotis rufescens, tridacna gigas and strombus gigas sea shells. The study shows that seashells are made of crystals of CaCO₃ interwoven with viscoelastic proteins layers as well as dense-tailored structures that produce tremendous mechanical properties. The mechanical test conducted include compressive and flexural (three-point bending) strength test. The test results indicate that the red abalone (haliotis rufescens), conch (strombus gigas) and giant clam (tridacna gigas) has compressive strength values of 233–540 MPa, 166–218 MPa and 87–123 MPa respectively.

The authors reported that the differences in the compressive strength of the shells was attributed to an optimisation of microstructural design form of 2-D laminates which enables the development of higher stresses before fracture as well as improving the toughness of the shell material. The flexural test results also show that the red abalone seashell exhibited the highest value. Therefore, it was concluded that the macro and microstructure of seashells play an important role in increasing the toughness of a brittle-based material like CaCO₃.

Abiodun *et al.* (2014) also evaluated the properties of seashell reinforced unsaturated polyester composite using seashell particle size of 250 μm at varying percentage composition together with unsaturated polyester resin. Tensile, hardness,

impact, flexural and water absorption tests were conducted to determine the properties of the material.

The test results show that bending strength varies from 0.077–30.85 MPa, tensile strength, 90.70 –262.05 MPa, impact strength, 3.54–4.76, Brinell hardness, 20.10–24.87 and percentage water absorption, 0.908 –1.211%. Also, it was concluded that the seashell-reinforced sample of 10 % seashell powder provided that optimal properties thereby making seashell suitable for production of seashell reinforced unsaturated polyester composite.

Vignesh *et al.* (2015) carried out an experimental analysis of the mechanical properties of seashell particles– polymer matrix composite. The particles of the seashell were separated into five sieve sizes (75, 150, 300, 425 and 600 μm) and used to produce a composite. Mechanical test was conducted to evaluate the properties (hardness, impact, flexural and tensile strength) of the material.

The experimental results showed that particle size of 75μm seashell exhibit better properties compared to other particle sizes and can act as a reinforcement material in polymer matrix composites.

— Lemon Peel Powder

Ramanathan *et al.* (2017) investigated the use of lemon peel powder as a filler material in brake pad production. Two samples composed of lemon peel particles (10–20%), epoxy resin (40 %), aluminium oxide (7.5–12.5 %), graphite (15%), iron oxide (7.5–12.5%) and calcium hydroxide (10 %) were produced by varying the composition of lemon peel powder, iron oxide and aluminium oxide. The process parameters reported by the authors shows a curing time of 24 hours while other production parameters were not reported. Samples produced were also tested to study the wear rate, hardness, density, water and oil absorption.

The test results showed that the brake pad samples possess a density of 1.55–2.00 g/cm³, hardness of 26–32 (barcol hardness), percentage wear loss, water and oil absorption of 13.45–19.14%, 0.96 –1.38% and 0.01– 0.02% respectively. The authors therefore concluded that the sample composed of 10% lemon peel powder, 15% graphite, 12.5% Aluminium oxide, 12.5 % iron oxide and 40% epoxy resin, 10% calcium hydroxide gave the optimum properties and can be applied in brake pad applications.

Though some of the results compared well with asbestos based brake pads but the high rate of wear (13.45–19.14%) experienced by the samples represent a limitation and also, in reality, conclusion cannot be drawn by producing only two samples for automobile application and subjecting them to testing.

CHALLENGES AND FUTURE RESEARCH DIRECTION

Production of brake pad from non-hazardous materials to replace asbestos is receiving serious attention in the laboratory and a lot have been achieved, but these achievements have not been translated into commercial application.

Again, there is need for utilisation of these combinations of non-hazardous materials (hybrid) in different ratios to further study their effect on mechanical, physical and tribological properties of brake pad produce from such hybrid.

CONCLUSION

A comprehensive review of application of non-hazardous reinforcement materials as possible replacement for asbestos has been highlighted in this study. The physical, mechanical and tribological properties of these brake pads compared favorably with the commercial brake pad.

The need for results obtained from these research works to evolve from laboratory will address the current gap in making available eco-friendly and low-cost brake pads for commercial consumption.

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