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Influence Of Eco – Friendly (Non- Asbestos) Based Bio-Composite Materials On The Physical, Mechanical And Tribological Properties Of Automobile Brake Pad - A Comprehensive Review

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ABSTRACT

Research into the use of eco-friendly materials, such as natural (lignocellulose/mineral) fibers for automobile brake pad application has gained momentum in the recent years. This can be attributed to the potentials of the natural fibers to replace traditional materials in automobile brake pad application. Natural fibers are abundant and have low harvesting costs with adequate mechanical properties. Asbestos, which is harmful and hazardous to human health, likewise the recycling issues, toxic byproducts and expensive nature of synthetic fibers are the main driving factors in the research and development of bio-composite brake pads. Bio-composites are degradable, renewable and non-toxic, with comparable properties to those of synthetic fiber composites. However, many efforts have been made by researchers to find other natural alternative materials for their replacement. Natural materials that have received much attention and research include banana peels, palm kernels, palm slag, bagasse, coconut fiber, wood powder, bamboo fiber, shell powder etc. This comprehensive review paper focuses on analyzing the main parameters that affect brake pad performance, a detailed analysis was also carried out to discuss developments in bio-composites which covers the structure and modifications of fiber, physical, mechanical and tribological properties, limitations of bio-composites and the need for hybrid composite development to balance component cost, production cost and technology cost without compromising the properties of the brake pad.

Keywords: Natural fibers; Biomass; Mineral Fibers; Hybridization; Alternative materials; Reinforcement; Characteristics; Friction Materials; Performance; Optimization.

INTRODUCTION

Eco – friendly (non- asbestos) based bio-composite materials such as biomass produced from agricultural activities (plant and animal waste products and agricultural residues) is a trending material for the brake pads manufacturing as they are commercially acceptable and environmentally friendly. Palm trees, Bamboo fiber, Corn stalks, Sugar cane bagasse, Banana peels, Snail shell, Periwinkle shell, Cocoa beans shell, Maize husk, Doum, Cashew nutshell, Coir (Coconut shell), Rice straw, Pineapple, Rice husk, Hazelnut powder, Sawdust, Palm kernel shell and Cow bone, Palm ash, Walnut shell powder, Coconut shell powder, Miscanthus, Groundnut shell, Canarium schweinfurthii shells, Costus Afer Waste and Kenaf fiber and plants (leaf, stem, fruit, seed, grass, stem) all contain Agricultural waste [1-8]. The braking system of a vehicle is a complex system that ensures the vehicle can be slowed down or stopped safely and efficiently by converting kinetic energy to thermal energy through friction. As shown in Plate 1, Kinetic energy is converted into heat energy during the brake system operation by friction between the rotor surface and the brake pads [9].

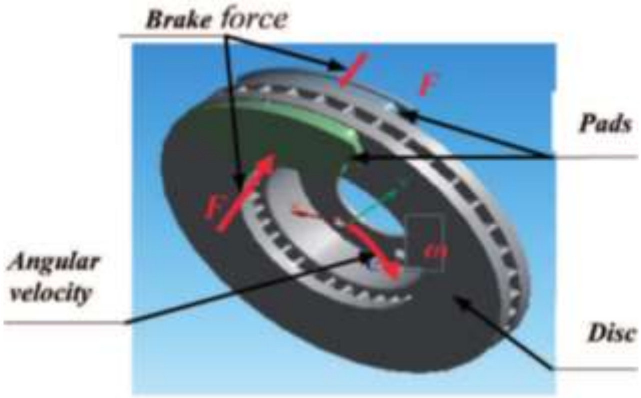
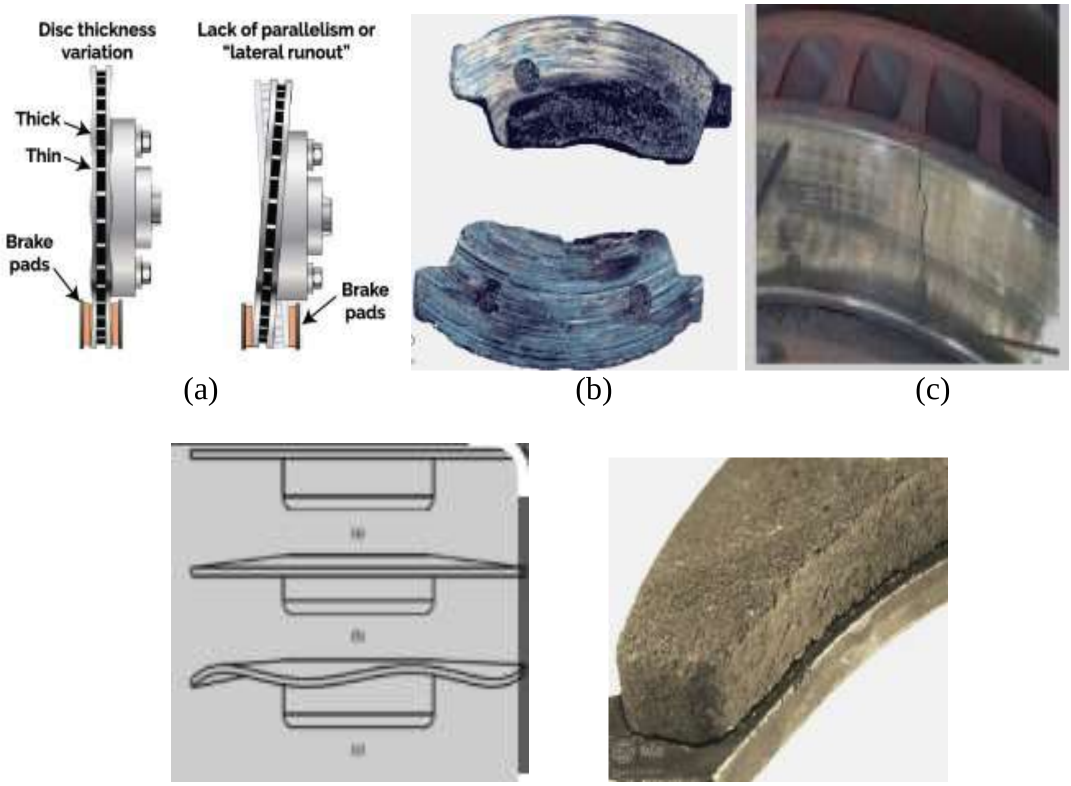


Plate 1.: Disc- pad assembly with forces applied to the disc

Conduction transfers the heat energy created to the components in contact. As seen in Plate 2a–e, excessive thermal loading can cause judder (disc thickness changes), severe wear on the contact surfaces, surface cracking, disc conning and friction lining coming loose from the base plate. In addition, high temperatures can also cause brake fluid, seals, and other components to overheat, resulting in malfunctions in the braking system [10,11].

For this reason, it is important for brake pads to have a high and stable Coefficient of friction [12,13]. This makes the selection of the appropriate friction material for brake pads of paramount importance and much research has been dedicated to the process of selecting and developing new friction materials.



(a) (b) (c)

(d) (e)

Plate 2.: Failure on brake pads caused by excessive thermal loading (a) disc thickness variations (b) wear (c) surface cracking (d) disc conning (e) Friction lining comes loose from the base plate

The use of natural fibers (agricultural-based and mineral based) as reinforcement materials has proven to have many advantages compared to synthetic fibers due to their low density, abundance, inexpensive, recyclable, biodegradable, renewable and relatively high strength, stiffness characteristics, eco-friendliness, affordability, abundance and sustainability [14,15]. Apart from their low cost and light weight, natural fiber reinforced composites are getting more attention because they are characterized with low energy consumption. Aside from these benefits, increasing environmental concerns and rising petroleum consumption levels are driving the entire world to use more sustainable natural resources such as natural fibers [16]. As a result of this, natural fibers are rising as reinforcing fibers for composite materials in the automotive, furniture, packaging and construction industries due to these advantages [17]. Due to carcinogenic health issues of asbestos from the findings of International Agency for Research on Cancer (IARC) and World Health Organization (WHO) which resulted in prohibition of its application in automotive and other industry as well as the need to enhance the emerging brake pad products' properties and quality, numerous researchers have employed a wide range of material selections, formulations / compositions, optimization and processing techniques in multiple research desire to replace asbestos with natural i.e (agricultural-based and mineral based) material in brake pad production [18,19].

Considering all these issues, this paper presents the overview of eco – friendly (non- asbestos) based bio-composite for automobile brake pad using various processing techniques i.e compression moulding, extrusion, hand lay-up, injection, hot pressing and protrusion as well as modification of the techniques to make the composites cost effective and achieve the desired properties. The physical, mechanical and tribological analysis of fabricated eco- friendly (non- asbestos) bio composites in terms of materials composition, the particle sizes, manufacturing parameters and types of binder have been extensively reviewed to find gap for further / future researches.

2. ECO – FRIENDLY MATERIALS FOR AUTOMOBILE BRAKE PAD

In the pursuit of more sustainable automobile components, researchers and manufacturers have been exploring eco-friendly materials to be used in brake pad production. Using eco-friendly materials has gained attention due to environmental concerns and health risks associated with traditional materials like asbestos. Thus, the use of Eco-friendly materials is aim to reduce environmental impact while maintaining or improving performance. Here are some examples of such materials:

2.1 Bio-Composite Materials

Bio-composites materials i.e composite materials made from natural fibers and a matrix in which the fibers can come from plants like the stem (Flax, Hemp, Jute, Ramie, Kenaf), the leaf (Sisal, Abaca, Pineapple leaf, Henequen), the fruit/seed (Coconut, Cotton), the stalk (Rice, Corn straws, Grass) or other natural sources, and the matrix which is typically a polymer that can be either biodegradable such as Polylactic Acid (PLA) or Polyhydroxyalkanoates (PHA) or non-biodegradable (like Polypropylene or Polyethylene), have become the center of attention due to their environmentally friendly and biodegradable nature [20]. A number of hazards and shortcomings are associated with Synthetic Composites i.e materials made by combining two or more distinct materials, where one acts as a reinforcement (such as fibers) and the other as a matrix (usually a polymer resin). Although, the goal is to produce a material with improved properties compared to the individual components alone. They have larger carbon footprints and need a large amount of energy for fabrication. A variety of inorganic fibers, including Nylon, Kevlar, Polypropylene and glass, are used in Synthetic composites [21]. Fossil fuel depletion also endangers the sustainability of these synthetic materials in the long term [22].

Bio-composites are eco-friendly, degradable, renewable, non-abrasive, non-toxic, and have low densities. These materials are used in cars to reduce the overall weight and to enhance fuel efficiency. Bio-composites are utilized to manufacture door panels, arm rests, seat backs and trays [23]. They are also used externally for trim parts and brake shoes. Bio-composite parts are better at sound absorbance and shatter resistance [24]. Fibers used in bio-composites are produced from agricultural products and by-products, which are subsequently inter-mixed with different polymer-based matrices [25]. Biodegradable and renewable polymer matrices are mixed with natural fibers known as lignocellulosic fibers [1]. It consists of cellulose, hemicellulose, lignin, pectin, waxes, extractive, and trace elements [26].

Cellulose is the most abundant form of living terrestrial organism. Purer forms of cellulose include cotton and hemp fibers, while in wood, stalks and leaves, cellulose is found in combination with lignin and hemicellulose. It provides strength and rigidity to the plant cell walls. Cellulose is hydrophilic, although it is insoluble in water; water absorption causes swelling. Cellulose properties are influenced by factors such as the type of plant, fiber modification, age of the plant, extraction methods, chemical composition, location of the plant, the maturity of the plant, and microscopic and molecular defects [27].

Hemicellulose is different from cellulose due to different sugar units. Hemicellulose is a branched non-crystalline or amorphous structure, different from a linear cellulosic structure. It has a degree of polymerization between 50 and 300, considerably less than cellulose. Hemicellulose acts as a compatibilizer to support microfibrils, cellulose, and lignin [28]. It is hydrophilic in nature, soluble in alkaline solution, and easy to hydrolyze in acids [29].

Lignin is a complex organic polymer that provides compressive strength and rigidity to plants, making them resistant to rotting and decay. Lignin fills the spaces between cellulose and hemicellulose in the cell walls [1].

Cellulose offers superior mechanical properties, while lignin reduces water absorption and enhances thermal stability [30]. Lignin serves to bind plant parts together, thereby acting as a cementing material. It also influences the structure and properties of plants [1]. The lumen is a hollow central cavity in a fiber cell, responsible for reducing the density, increasing thermal insulation, and noise-resistance properties [31]. Certain types of lignocellulosic fibers exhibit mechanical properties and overall strength comparable to that of synthetic fibers such as fiber glass [32].

Polymer matrix composites are made up of natural (PLA, PHA, PCL) or synthetic matrix materials (Thermoplastic, Thermosetting plastic), with one or more reinforcements such as carbon fibers, glass fibers or natural fibers in the case of bio-composites [33,34].

Thermoplastic polymer matrices, such as polypropylene and polyethylene, are hydrophobic and offer low compatibility with natural fibers. Surface treatments decrease the fibers' surface energy to optimize the strength and properties of the composite. Bio-composite performance is ultimately dependent on the fiber / matrix interphase. Adhesion between the matrix and fiber determines the final properties of the composite [35]. The mechanical properties of a composite depend on the amount and type of filler being used, how fiber adheres to the material, and the final fiber orientation in the matrix. The properties of these lignocellulosic fibers are also dependent on the origin of the plant species, fiber, location of the plant, environment around the plant, and methods to extract the fibers [1].

Polybutylene succinate (PBS), Polylactic acid (PLA), Poly-hydroxy alkanotes (PHA) and Poly (ε-caprolactone - PCL) are commonly used biodegradable matrices in bio-composites [36-38]. Synthetic matrix materials are not biodegradable. Some synthetic matrix materials are Polyethylene, Polypropylene, Polycarbonate, Polyvinylchloride, Nylon, Acrylics, and Carbon steel kevlar, Epoxy resins, etc. [39]. Out of these, due to its eco-friendly and degradable nature, PLA has attracted significant attention. However, it has mostly limited use due to the high cost [37].

Green bio-composites have pros and cons. Limitations of bio-composites include poor fire resistance, restricted processing temperature, low thermal resistance high hydrophilicity, low mechanical and thermo-physio properties and poor fiber–matrix adhesion [23,32,39,40]. Due to their hydrophilic nature, these composites tend to absorb water from the immediate environment causing the composite to swell [32]. Stem fiber, leaf fiber and seed fiber are the Three (3) main fibers [1]. Table 1 shows the Constituents of different natural (Lignocellulosic) fibers.

Table 1. Constituents of different Natural (Lignocellulosic) Fibers

Fiber	**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**	**Pectin (%)**	**Wax (%)**	**Reference**
Abaca	56–63	21–25	7–12	0.8	3	[29,33]
Alfa	45.4	38.5	14.9	-	2	[41]
Areca	57.35–58.21	13–15.42	23–24	-	0.12	[42]
Bagasse	32–44	19–24	22	10	-	[43]
Bamboo	26–43	20.5	21–31	-	-	[33]
Banana	62–64	12.5	5–10	4	-	[35,44]
Barley	31–45	27–38	14–19	-	2–7	[31]
Coir	45.6	20	45	4	-	[45,46]
Corn	38–40	28	7–21	-	3.6–7	[31]
Cotton	82.7–90	4	0.75	6	0.6	[45]
Curaua	70.7–73.6	9.9	7.5–11.1	-	-	[43]
Eucalyptus	41.7	32.56	25.4	8.2	0.22	[47]
Flax	62–72.5	14.5–20.6	2.5	0.9	-	[33]
Hemp	81	14–22	4–13	0.9	0.8	[48]
Henequen	60–77.6	28	8–13.1	-	0.5	.[45]
Hibiscus	28	25	22.7	-	-	[49]
Isora	74	-	23	-	1.1	[45]
Jute	59–71.5	12–20	9–13	0.2	0.5	[50,51]
Kenaf	53.5	21–33	17–21.5	2	-	.[52]
Phromium	67	30	11	-	-	[45]
Pineapple	80.5	17.5	8.3–12.7	4	-	.[45]
Ramie	72	5–16.7	0.6–0.8	2	-	[48]
Rice husk	28–36	23–28	12–14	-	14–20	[49]
Sisal	60–73	11.5–14	8–11	1.2	-	[53]
Sorghum	27	25	11	-	-	[31]
Wheat	33–38	26–32	17–19	-	6.8	[47]

Source**:** [8]

2.1.1 Fiber modification

Fiber modification helps to overcome various problems of natural fibers, such as poor fiber/matrix adhesion, moisture absorption, low fire resistance, inferior mechanical properties, low thermal resistance, and restrictive processing temperatures. A wide number of methods are used to overcome these problems [32,35,49-51].

2.1.1.1 Fiber/Matrix Adhesion

Fiber addition in a matrix significantly alters the properties of the matrix due to the dependency of bio-composites properties on the fiber/matrix interface. Strong interface bonds must be ensured to achieve the majority of desired mechanical properties. Many physical properties are considerably improved with strong fiber/matrix adhesion [35]. A poor fiber/matrix interface results in reduced mechanical and physical properties. The hydrophilic nature of fiber is one reason for poor interfaces, which leads to poor fiber dispersion in a matrix. Hydrophobic matrix material and hydrophilic fibers are incompatible, which reduces the composite's ability for stress transfer between the matrix and fiber. Fiber dimensional changes lead to micro cracking, thereby affecting fiber/matrix adhesion [44,51]. Many techniques (e.g., surface treatments) have been employed to enhance fiber/matrix adhesion. Surface treatments employ methods such as solvent extraction, physio-chemical treatments, corona discharge, plasma discharge, laser, gamma-ray, and UV bombardment, and chemical modifications by the condensation of coupling agents on a surface or their placement by free radical technique [1,52]. Others are Physical techniques, Corona discharge, Plasma treatment, Chemical methods, Silane treatment and Alkali treatment [33,53-

56].

2.1.1.2 Reducing Moisture Absorption by Natural (Lignocellulosic) Fiber

Strong polarized hydroxyl groups make natural fibers more hydrophilic. They absorb most of the moisture from the surrounding environment [57]. The fiber cell wall has many hydrogen bonds. As the water comes in contact with the fiber, old hydrogen bonds break, and new hydrogen bonds are formed between hydroxyl groups and water molecules which are responsible for water absorption [58]. Hemicelluloses are mainly responsible for moisture absorption in natural fibers [59]. Hydrophilic natural fiber absorbs moisture, affects mechanical properties, gives dimensional instability, and develops internal stresses [32]. Capillary action and water intake fills voids in the composite, giving dimensional instability to the composite [1]. Moisture absorption causes swelling and micro cracks [60]. The hydrophilic nature of fibers prevents the use of bio-composites in various potential applications [61].

Apart from water absorption, micro gaps and cracks can be a result of poor processing conditions, incompatibility between the fiber and matrix, and poor environmental and service conditions [62]. Water absorption in bio-composites is, somehow, a complex process due to the involvement of a hydrophobic matrix and hydrophilic fibers. Fiber must be modified physically and chemically to overcome moisture absorption issues. Compatibilizers and adhesion promotors showed promising results to reduce moisture absorption [64]. Hydro thermal treatment increases the crystallinity of cellulose in natural fiber and extracts hemicelluloses content, effectively reducing moisture intake. Others are Duralin process, esterification method, Benzoyl treatment, Peroxide treatment, sodium chlorite method [58,64-66].

2.1.1.3 Thermal Degradation and Flammability Properties of Natural (Lignocellulosic) Fiber

Natural fiber constituents such as cellulose, hemicellulose, lignin, pectin, and waxes are responsible for degradation and poor thermal properties. Both thermal stability and moisture absorption properties are temperature-dependent [67]. Poor thermal properties lead to the degradation of fibers with the release of various volatile products [1]. Cellulose degrades between 260℃ and 350℃, and hemicellulose between 200℃ and 260℃, while lignin starts to decompose at 160℃ and continues to degrade up to 400℃ [24]. Natural fiber-based composites decompose with the release of toxic byproducts and heat. Properties such as thermal stability, fire properties and water resistance are dependent on the constituents of lignocellulosic fibers. High cellulosic contents make natural fibers readily flammable [68]. Orientation and structural properties of fibers play a vital role in determining thermal and flammability properties. Flammability and thermal properties are improved with the addition of silica and ash [69].

Due to poor flammability, natural fibers have been limited to a few applications [68]. It is a challenge to find methods to overcome this issue, because few studies have been reported to address this problem. Flax fiber has the best fire resistance properties due to low lignin contents [69]. Thermal stability and the flammability of natural fibers is studied through various techniques, such as Thermogravimetric analysis (TGA), Vertical flame tests, Cone calorimetry techniques, etc. Some of the methods to minimize flammability and thermal issues are: the use of nanoparticles, fire retardant coatings, impregnation of natural fibers with fire retardants (e.g Ammonium, Halogens, Boron, Phosphorous compounds) before manufacturing, the use of non-flammable binders, resins, polymer matrices, and the insulation of composites to prevent possible damage from heat or flame [70]. Table 2 contains various research studies for bio-composites, fabrication techniques and surface modifications.

2.1.2 Mechanical properties of natural (lignocellulosic) fiber

Natural bio-composites exhibit reasonable mechanical properties such as stiffness, strength, flexibility and Young’s modulus [71]. Fiber type, fiber orientation, microfibril angle, treatment type, physical properties and adhesion between the fiber and the matrix are essential characteristics in composites to determine mechanical properties [72]. The microfibril angle determines the stiffness of the fiber [24]. Natural fibers act as reinforcements to improve mechanical properties [72]. Fiber/matrix adhesion is the most critical factor for the determination of mechanical properties. Better adhesion improves the stress /load transfer between fiber and matrix. Tensile strength is mostly dependent on matrix properties, while modulus is dependent on fiber properties [73]. Mechanical properties of different fibers are listed in Table 3 below:

2.1.3 Chemical composition of natural fiber

The following are some of the natural fiber (agro-wastes) recognized as potential reinforcing material:

2.1.3.1 Rice Husk Ash (RHA)

This agro-waste material is obtained from rice mills during the process of milling of the paddy. Usually, it is used as a fuel for generating electricity in the rice mills. However, it has been observed that about 25% of the total weight of rice husk forms ash during the steam generation process, thus not an efficient fuel [73]. Moreover, dumping it in an open land has resulted into a major impact on the environment. Therefore, researchers started utilizing this material most efficiently as reinforcement in high-performance polymer composite as it offers lower density (0.3–1.9 gm/cm^3) and ease of availability [75]. RHA consists of a higher percentage of SiO_2 along with other elements such as Al_2O_3, Fe_2O_3, and MgO [76]. Rice husk ash can be used as a filler material as it is rich in silica, which can enhance the frictional properties of brake pads. It provides good frictional properties i.e act as friction modifier and thermal stability.

Table 2. Different Research Studies for Bio-Composites and Modification Techniques.

S/n	Composite	Fabrication Method	Key Findings and Mechanical Properties	Effect of Surface Treatments	References
1.	Kenaf fibers/ sea urchin spike filler/neem oil/epoxy composite	Hand lay-up	Neem oil made epoxy eco-friendly while sea urchin spike filler and kenaf fibers increased the toughness of the composite. The addition of neem oil leads to the formation of an interpolymer-penetrating network and ketone groups, which decreased hardness and overall tensile strength of the composite.	Amino silane-treated particles dispersed well in matrix material without agglomeration, which improved wear resistance and thermal degradation. Treated fiber formed a layer at the fiber/matrix interface, and high temperature was required to break this layer. Modified fibers increased the moisture resistance in the composite.	[77]
2.	Hemp fibres/ polycaprolactone bio-composites	Twin screw extrusion	Flexural, tensile and impact properties of composite are improved. With the increase in aspect ratio of hemp fiber, water absorption increased. Flexural strength increased by 169% and flexural modulus increased by 285% for the aspect ratio of 26. Hemp fibers increased the stiffness of the composite.		[78]
3.	Jute fibers /clay / epoxy Bio-composite	Compression molding	The addition of 15 wt.% clay improved mechanical properties due to uniform dispersion in a composite. Clay can agglomerate, which increases composite porosity and decreases fiber/matrix adhesion.	Alkali treatment improved fiber/matrix adhesion with increased cellulose after removing pectin, lignin, and other impurities. An increase in cellulose content leads to better interfacial adhesion.	[79]
4.	Areca fibers/Pine resin composite	Solvent casting method	The tensile strength of the composite is affected by the adhesion of the fiber/matrix; 10 wt.% areca fibers and 90 wt.% pine resin exhibited better mechanical properties due to efficient stress transfer between fibers and matrix.	Alkali treatment increased fiber/matrix adhesion. Tensile strength increased by 25%, while impact strength increased up to 24% due to treatment.	[80]
5.	Sisal fibers/starch composite	Hot pressing	Compressive and tensile strength of the composite increased with the addition of sisal fibers. The addition of natural fibers increased the biodegradability properties of the composite.	Alkaline treatment increased fiber/matrix adhesion, which improved mechanical properties.	[81]
6.	Flax/epoxy composite	Vacuum infusion	Flax/epoxy composite is suspectable to water absorption due to high void content.	Sodium bicarbonate-treated fibers had less void content mainly due to the removal of impurities. With the increase in sodium bicarbonate	[82]

				concentration in fiber treatment, properties such as flexural, tensile strength and flexural moduli increased.	
7.	Banana fibers/PLA/Nanoclay composite	Melt blending	Nanoclay and PLA improved composite stability, flame resistance and thermal properties. Nanoclay formed a protective layer at the surface to prevent flame and acted as a thermal barrier to prevent degradation.	Silane treatment improved fiber/matrix adhesion by increasing the contact area of fibers.	[83]
8.	Ramie fibers/PLA composite	Hot compression molding	Low temperature and pressure in compression molding had led to poor fiber/matrix adhesion and wettability.	Alkali/silane-treated fibers composite had better tensile strength, modulus, and impact strength. Cellulose content increased due to the removal of impurities from fibers, which improved mechanical properties. Treated fibers had better stress transfer due to the formation of covalent bonds between fibers and matrix.	[84]
9.	Jute fibers/unsaturated polyester resin	Hand lay-up and compression molding	Jute fibers enhanced properties such as tensile, flexural strength, flexural modulus, and inter-laminar shear strength. Untreated fibers lead to low density and low volume fraction.	Alkali-treated fibers showed an increase in tensile, flexural strength, flexural modulus, and interlaminar shear strength due to better fiber/matrix adhesion. Alkali treatment removes hemicellulose and increases interlocking points in fibers for better adhesion and stress transfer.	[85]

Source: [8,86]

Table 3. Mechanical Properties of different Natural (Lignocellulosic) Fibers

Fiber	Density (g/cm^3)	Diameter (μm)	Micro fibrillar Angle $(^\circ)$	Moisture Content (%)	Tensile strength (Mpa)	Elongation at break (%)	References
Abaca	1.5	10–30	20–25	5–10	400–980	3–10	[87,88]
Areca	0.7–0.8	-	-	-	147–322	10.2–13.15	[89,90]
Bagasse	1.25	10–34	-	-	222–290	1.1	[33,91]
Bamboo	0.6–1.11	240–330	-	9.16	140–800	1.40	[33,92,93]
Banana	1.35	50–250	11–12	10.71	529–914	3	[48,94]
Coir	1.2–1.5	100–450	30–49	8–11.36	175–180	30	[95]
Cotton	1.5–1.6	12–35	-	7.85–8.5	287–597	7–8	[96]
Curaua	1.4	170	-	-	500–1150	3.7–4.3	[33]
Flax	1.5	5–38	5–10	1.2–8	345–1035	2.7–3.2	[97]
Hemp	1.48	-	2–6.2	6.2–12	690	1.6	[95]
Henequen	1.2	-	-	-	430–570	3.7–5.9	[45]
Isora	1.2–1.3	-	-	-	500–600	5–6	[98]
Jute	1.3–1.5	20–200	8	12.5–13.7	200–773	1.5–1.8	[99]
Kenaf	1.4	70–250	2–6.2	6.2–12	930	1.5	[96]
Nettle	1.51	20–80	-	11–17	650	1.7	[88]
Oil Palm	0.7–1.55	150–500	42–46	-	80–248	3.2	[96,100]
Palf	0.8–1.6	20–80	14	11.8	180–1627	1.6–14.5	[78]
Piassava	1.4	-	-	-	134–143	7.8–21.9	[101]
Pineapple	0.8–1.6	8–41	-	10–13	170–1627	2.4	[102]
Ramie	1.5	50	69–83		220–938	2–3.8	[95]
Sisal	1.5	50–300	-	11	511–635	3–7	[33,95,103]

Source: [8,86]

Khafidh, M. *et al.*, [75] studied the characteristics of Brake Pad Composite Materials by varying the composition of Epoxy, Rice Husk, Al_2O_3 and Fe_2O_3, the composites were then subjected to several characterization tests, including density, hardness, flexural strength, thermal analysis, Scanning Electron Microscopy (SEM), TGA/DSC, and wear testing. The test results showed that additional reinforcement materials to the epoxy resin matrix improved the mechanical properties of the composites.

2.1.3.2 Coconut Shell Ash (CSA)

This agro-waste material is mostly available in tropical regions in abundance and often used as fuel in boilers and furnaces [104]. But the combustion of CSA results in the release of CO_2 and methane in large quantities and hence, leads to significant environmental pollution [105]. It is preferred to use them as reinforcement in the production of composites taking these considerations. The density of CSA was found to be 2.05 gm/cm^3 and its constituents of elements are like SiO_2, MgO, Al_2O_3, and Fe_2O_3 as mentioned in Table 4. Blending coconut shell powder with epoxy gum upgrades its properties and makes a wide scope of uses [106]. Egeonu and Okolo [107] produced coconut shells based brake pad. The formulation included ground coconut shells (filler), Epoxy resin (binder –matrix), Iron chips (reinforcement), methyl ethyl ketone peroxide (catalyst), cobalt nephthanate (accelerator), iron and silica (abrasives), and brass (friction modifier). Sieve of 710μm aperture was used to sieve the pulverized filler. It was concluded that higher percentage of ground coconut powder induces brittleness and high tensile strength.

2.1.3.3 Banana Peel

Banana peel is a waste material with rich of starch. This characteristic makes them potential to produce biopolymer thin film which is more environmentally friendly due to its biodegradable abilities compared to the conventional synthetic petroleum-polymer. In addition, banana peels are agricultural waste that are discarded as useless material. This waste contributed to waste management problems although they have some compost and cosmetics potentiality [108]. Banana peels are readily available, low cost and environmental friendly bio-material. This agriculture waste is also inexhaustible, cheap, non-hazardous and specifically selective for heavy metals and able to dispose easily by incineration [109]. For this reason, applications of waste natural fiber of bio-polymer are being investigated as good alternative resources.

2.1.3.4 Egg Shell

Eggshells are litter and kitchen waste that can be collected in a large amount from many places such as housing areas, restaurants, hotels, food industries and even from the hatcheries and farm [110]. Eggshell consists of 95% Calcium carbonate ($CaCO_3$) as its main component and it is in the form of calcite. In the form of Calcium carbonate, Calcite is the most stable which forms elongated structures called columns, crystallite or palisade [111]. Besides that, there are remaining 5% of others inorganic material in the eggshell which are Calcium phosphate, Magnesium carbonate, soluble proteins and insoluble proteins. Calcium carbonate is a compound that brittle white stuff that limestone, chalk, sea shells, coral and pearls are made of [112]. Egg shell containing Calcium carbonate (94%), calcium phosphate (1%), organic compounds (4%), and magnesium carbonate (1%). The high contains of calcium in eggshells can be converted as a CaO catalyst by calcinations process at temperature around 800 ºC for 2 hours where the reaction takes place as exothermic reaction.

Table 4. Chemical Composition of Natural Fiber (Agro-Based Reinforcements)

Agro Waste	**Composition**							
	SiO_2 (wt %)	Al_2O_3 (wt %)	MgO (wt %)	Fe_2O_3 (wt %)	CaO (wt %)	K_2O (wt %)	SO_3 (wt %)	P_2O_5 (wt %)
Bamboo Leaf Ash [BLA][113,114]	75.9	4.13	1.85	1.22	7.47	5.62	-	-
Coconut Shell Ash [CSA][115]	45.05	15.6	16.2	12.4	-	-	-	-
Palm Oil Clinkers [POC][116]	81.8	3.5	1.24	5.18	2.3	4.66	-	0.76
Palm Oil Fuel Ash [POFA] [117]	49.20	35.45	3.93	-	7.5	5.3	1.73	6.41
Rice husk ash [RHA] [118,119]	97.09	1.135	0.825	0.31	-	-	-	-

2.1.3.5 Palm Kernel Ash (PKA)

Palm kernel ash (PKA) is the residue obtained after the combustion of palm kernel shells, which are the by-products of palm oil production. The ash contains various minerals and chemical compounds, making it useful in several applications, such as soil amendment**,** construction material**,** waste management**,** industrial uses and animal feed. Palm Kernel shell are suitable for use as a brake pad material due to its large content of environmentally friendly minerals such as graphite (C) (12.55%), Fe (8.3%), Si (22.3%), Al (10.6%), Ca (20.9%), Mg (0.4%), S (12.8%), N (0.4%), K (11%) etc. They are also seen as frictional modifiers in a purely or semi metallic brake pad manufacture [120]. Adeyemi *et al.* [121] revealed in their work that Palm Kernel Shells (PKS) can be used to make brake pad and friction material as it showed good potentials based on results obtained from evaluation. PKS is cheap to obtain and available in large quantity. It has the characteristics of Influencing adhesion and dispersion of polymer composite fabrication.

2.1.3.6 Bamboo Leaf Ash (BLA)

The bamboo trees are found in abundance in various sections of the world. These trees often litter their leaves in these regions; however, these can be used as BLA for economic purposes. It mainly constituents of ceramic oxides like SiO_2, CaO, Al_2O_3, and Fe_2O_3 and K_2O as shown in Table 4; thus, it was used as reinforcements in the AMC's [122,123]. Aleneme *et al.* [124] reinforced BLA in Al alloy and observed an improvement in the wear behavior of the resultant composites. Bodunrin *et al.* [125] carried out the influence of Igbokoda Silica sand and Bamboo Leaf Ash (BLA) on the porosity and wear performance of Al6063 hybrid composites. The results showed that the composites became less dense with increasing BLA content. Porosity increased as the quantity of BLA exceeds 2.5 wt. %, while the hardness reduced. Single reinforced Al6063-10 wt. % silica sand composite had superior wear resistance when compared to all the composites containing more than 2.5 wt. % BLA. However, hybrid Al6063-7.5 wt. % silica sand / 2.5 wt. % BLA has slightly improved wear resistance in comparison with single reinforced Al6063-10 wt. % silica sand composite.

2.1.3.7 Palm Oil Fuel Ash (POFA)

This is agricultural waste abundantly found in Nigeria. It contains a higher content of siliceous material. It is obtained on the combustion of Oil palm fiber, Mesocarp and empty fruit brunch as boiler fuel to produce steam for palm oil mill, and the end product remaining after combustion is POFA [126]. This can be later used as reinforcing material [127]. Silica or Silicon dioxide (SiO_2) is the main constituent found in POFA, mostly up to 40%, besides Silica, other chemical components found in POFA are Potassium oxide, Magnesium oxide, Calcium oxide, Aluminum oxide, and Iron oxide. The composition is shown in Table 4. The study of the effect of POFA on the mechanical and tribological properties revealed that addition of POFA improved the hardness, tensile strength, wear and coefficient of friction of the resultant composites [127].

2.1.3.8 Palm Oil Clinkers (POC)

The production of Palm oil in Nigeria reached 1.4 million metric tons. Between 2009 and 2023, the production quantity generally increased, registering the highest growth in 2010, when it grew by roughly 14 percent. From 2014 onwards, the output from Palm oil production followed a rising trend. Nigeria is one of the leading producers of palm oil worldwide [128]. The extraction process of this palm soil results in the production of waste in large quantities in the form of POC [129]. The disposal of these can be hazardous for the environment. Thus, it found its usage as reinforcements in composites production [130]. Table 4 shows the chemical compositions of POC.

2.1.3.9 Sugarcane Bagasse Ash (SCBA)

Bagasse is the waste product obtained after processing of sugarcane for extraction of juice. It is one of the largest agricultural wastes in the world. Many researchers have used this residue due to its versatility but not limited to feedstock, biofuel (ethanol) and paper [131]. The main elements of SCB are hemicellulose, cellulose, wax, lignin, and ash [132]. Their presence makes SCB an ultimate material as a reinforcement fiber in the development of new material with exceptional physical and chemical properties [133,134]. Chandla *et al.* [135] reinforced varying content of bagasse ash in Al6061 / 5 wt% Al_2O_3 based composites via stir casting technique and observed an increase in hardness as well as the tensile strength of the composites with increasing bagasse ash content.

2.2 Recycled Materials

2.2.1 Recycled rubber: It is sourced from old tires or other rubber products, helps in reducing waste and offers good friction characteristics in brake pads. Recycled rubber can help in noise reduction, used as an additive to enhance friction properties and can be used to improve the flexibility and durability of brake pads.

2.2.2 Recycled metals: Iron, Steel and other metals can be recycled and reused in brake pads, reducing the demand for raw materials and energy consumption.

2.2.3 Recycled carbon fibers: Offers high strength and lightweight properties.

2.2.4 Recycled Fiberglass: Incorporating recycled fiberglass can reinforce and enhance the strength, heat resistance and durability of brake pads, while reducing the environmental impact.

2.3 Mineral-Based Materials (Fibers):

2.3.1 Basalt fibers: Made from volcanic rock, offering high strength and heat resistance i.e. they offer good mechanical and thermal properties while being environmentally friendly.

2.3.2 Zeolites: Naturally occurring minerals that can improve thermal stability and friction properties.

2.3.3 Wollastonite: A naturally occurring mineral that enhances mechanical strength, thermal stability and frictional properties of brake pads.

2.3.4 Diatomaceous Earth: A naturally occurring, soft, siliceous sedimentary rock that is easily crumbled into a fine white to off-white powder.

2.3.5 Vermiculite: A hydrous phyllosilicate mineral that undergoes significant expansion when heated. It is known for its thermal resistance and lightweight properties.

2.3.6 Mica: Mica can improve thermal stability and reduce wear in brake pads.

2.3.7 Clay: Various types of clay can be used to improve the mechanical properties and thermal stability of brake pads.

2.4 Organic Resins Material: Phenolic resins derived from renewable sources like cashew nut shell liquid can be used as binders.

2.5 Bio-Based Resins Materials

2.5.1 Soy-based resins: Derived from soybeans, these resins are biodegradable Used as a binder, reducing reliance on petroleum-based products.

2.5.2 Lignin-based resins: Lignin, a by-product of the paper industry, can be used as a resin in brake pads, providing a sustainable alternative to petroleum-based resins. Derived from wood, providing a renewable and sustainable option

2.6 Natural Resins Materials

2.6.1 Cashew Nut Shell Liquid (CNSL): A renewable resource, CNSL can be used as a binder in brake pads due to its good thermal and mechanical properties.

2.6.2 Rosin: Derived from pine trees, rosin is a natural resin that can be used as a binder or filler.

2.7 Nano-Composite / Other Sustainable Materials:

2.7.1 Graphite: Natural or synthetic, used for its lubricating properties.

2.7.2 Graphene Oxide: A single layer of carbon atoms with excellent mechanical properties and high surface area.

2.7.3 Nano-clay: A nanoparticle of layered mineral silicates that improves mechanical strength and thermal stability of brake pads while being eco-friendly.

2.7.4 Nano-silica: Enhances the wear resistance and durability of brake pads.

2.8 Eco-friendly Friction Modifiers Materials:

2.8.1 Graphite: While not new, graphite is an eco-friendly option that can help reduce wear and improve frictional properties.

Incorporating these eco-friendly materials into brake pad production can reduce the environmental footprint of automobile components, promote sustainability and potentially improve the performance and safety standard of the brake pads [136-140].

3. FACTORS AFFECTING THE PERFORMANCE OF BRAKE PAD

Different components and the proportion of the components in the brake pad formulation are reported in the literature that may affect the physical and mechanical properties of the brake pads to be developed [141, 142].

Selection of components' types for the manufacture of brake pad samples is a difficult task because it affects the properties of brake pad samples. There are limited reports in the literature about the investigations of the effects of the manufacturing processes and components of brake pad materials to the mechanical and physical properties of brake pad materials. The physical and mechanical properties of brake pad materials also depend on manufacturing process parameters and the characteristics of the components used in production of brake pad [143].

3.1 Composition of Eco-Friendly Materials and Manufacturing Processes

Brake pad lining materials mostly made of five ingredients such as, reinforcement, lubricant, abrasive, binding agent and filler components (Figure 1). Each component has a specific function in composite structure such as, to adjust the balance friction and wear properties, increase strength, improve lifetime, porosity and noise.

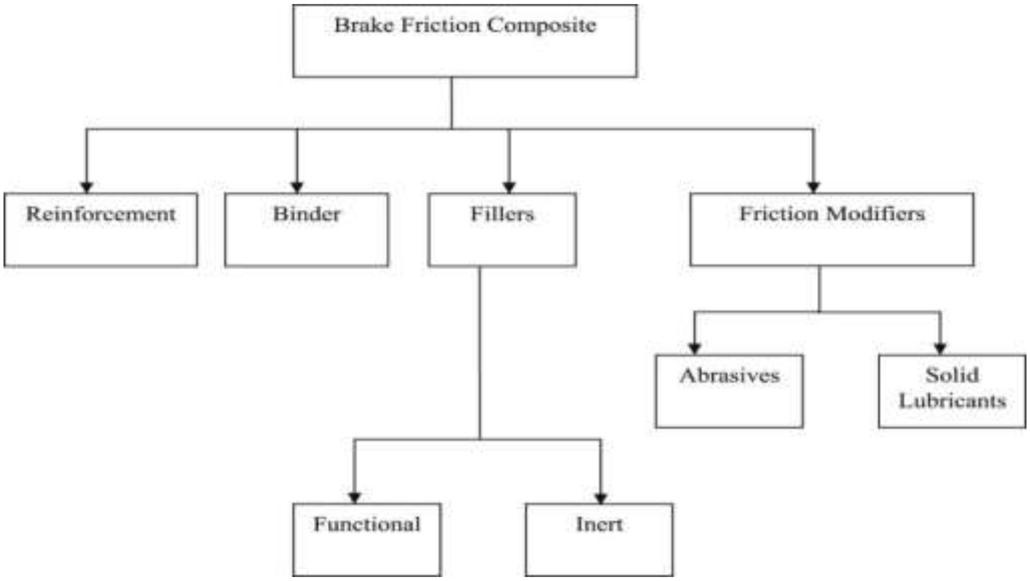


Figure 1: Composition of Brake Pad

Brake pads are made up of several layers Plate 3. The adhesive that holds the friction material to the other layers is provided by the under layer, which is placed in between the friction material and the back plate. The under layer's primary function is to reduce vibrations caused by friction materials contacting the disc. The back plate gives the brake pads the required rigidity and enables them to keep moving along on the caliper guides. To minimize the amount of unnecessary noise throughout braking, some industries utilize specific interference shims. The friction material that is in direct contact with the disc during the braking process is the essential layer on the brake pads. This material is made of various ingredients that are each developed for specific applications [144-146].

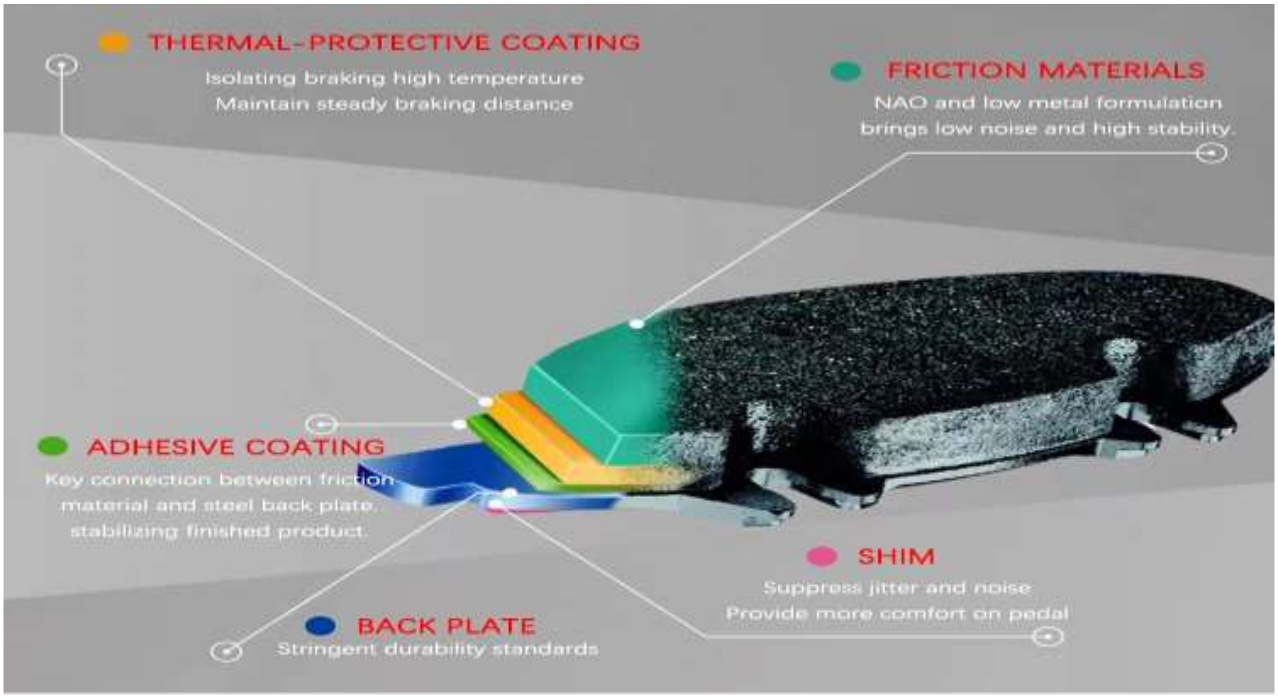


Plate 3: Layers of Brake Pad

Binders are the materials that keep all of the pads' components together. This material must have a stable and high friction coefficient, be resistant to high temperatures and fast temperature changes, and be light in weight. Reinforcement is a fibrous material that is added to the binder to increase its mechanical qualities. The brake pads' durability is greatly influenced by the types of reinforcing materials used. Asbestos is an excellent reinforcing fiber. However, due to its dangerous nature, a replacement material is required. Fillers are utilized to fill the gaps between the brake pads' other components, while abrasive ingredients are used to modify the coefficient of friction. Steel, refractory oxides, cast iron, quartz, or silicates, for instance, are employed as additives to improve the friction coefficient between the disc and the brake pads due to their hardness. The brake pads' service life is increased by increasing the friction coefficient [144-146].

Mahmut Unaldi and Recai Kus [142] used Taguchi method in order to determine how the compositions of brake pad components in the range of 5-20 wt. % would have effect on the properties of the brake pads. In the study, brake pad components in powder form such as miscanthus, cashew, alumina, phenolic resin and calcite were used to manufacture ecological brake pads. The result had it that the characteristics such as density, hardness, porosity and wear rate of the brake pad samples were more affected by the proportions of Miscanthus and phenolic resin in the mixture.

Aleksendrić and Senatore [147] investigated the effects of the manufacturing process such as moulding temperature, time and pressure values, heat-treatment temperature, and heat treatment time to wear behaviour of the brake friction materials. They used artificial neural networks as an appropriate modelling technique for development of a model representing the effects of the manufacturing process on wear behaviour of the friction materials. In the article, moulding pressure was determined the most influential factor on wear behaviour of the brake friction materials and it is expressed that wear behaviour of friction materials were strongly affected by the manufacturing processes.

The effect of brake pad samples produced with different periwinkle shell particle size on the wear behaviour has been investigated by [148]. Pin on disk machine used to perform the wear tests under different test conditions such as periwinkle shell particle size, sliding speed, applied load and temperature. The results of the study showed that the wear rate increased with increasing the periwinkle particle size, sliding speed, load and temperature.

Idris *et al.* [149] studied the influence of banana peels waste on the physical and mechanical properties of Phenolic based friction composites. They concluded that water absorption decreased as the wt. % resin increases which can eventually be attributed to the decreased pores because of the close interface packing achieved.

Dagwa and Ibhadode [150] determined the Optimum Manufacturing Conditions for Asbestos-free Brake Pad using Taguchi Method, a non – asbestos friction material was developed using an agro-waste material base – Palm Kernel Shell (PKS) along with other constituents. The results suggest that Palm Kernel Shell could be a possible replacement for asbestos in friction lining materials

Ruzaidia *et al.* [151] produced an asbestos free brake pad composites using different fillers (Palm Slag, Calcium Carbonate and dolomite) with phenolic as binder, metal fiber as reinforcement, graphite as lubricant and Alumina as abrasive. The result showed that the wear rate of Palm Slag composite was comparable with the conventional asbestos-based brake pad. The result was also supported by SEM micrograph. Palm slag and calcium carbonate $(CaCO_3)$ brake pad composite shown better wear properties than dolomite and comparable with the conventional asbestos-based brake pads.

Onyeneke *et al.* [152] developed new composite brake pad using Periwinkle and Coconut Shell. The disc brake friction lining with the geometrical specifications of Audi 90 model was produced using periwinkle and coconut shell powder as base materials, araldite and epoxy resin as binder materials and carbon as fibre reinforcement. Aluminum, Copper, Zinc and Cashew nut shell were used as abrasives and rubber dusts from shoe as filler. It was revealed that the Coefficient of friction of the pad material ranged from 0.4-0.65, scratch hardness of 80-85, bonding strength of 25-27kg/cm^2 and wear rate of 0.025 mm/min to 0.06 mm/min as compared to the conventional brake pad material that has hardness of 80-85, bonding strength of 25-27 kg/cm^2 and wear rate of 0.03-0.08 mm/min.

Nuhu and Adeyemi [153] developed a brake pad using maize husks to replace the asbestos material of the brake pad, they reported that there was a reduction in the wear rate and the brake pad is environmentally stable.

Swamidoss and Prasanth [154] worked on the fabrication and characterization of brake pad using pineapple leaf fiber (PALF). They fabricated brake pad by using pineapple leaf fiber as a reinforcement/filler. The result obtained in the work is compared with asbestos brake pad.

Adeyemi *et al.* [121] worked on development and assessment of composite brake pad using pulverized cocoa beans shells filler, the development of asbestos-free friction material from an agro-waste (cocoa beans shells - CBS) as filler element. The results showed that reducing the filler content, an increase in the wear rate, tensile strength, compressive strength were observed, while hardness, density, water absorption, oil absorption and thermal conductivity varied differently. Coefficient of friction increased with increase in the filler wt %.

Bala *et al.* [155] worked on the development of automobile brake lining using pulverized cow hooves. The results obtained showed that proper bonding was achieved as the percentage by weight of epoxy resin increased and percentage by weight of pulverized cow hooves decreased. The hardness, compressive strength, coefficient of friction, water and oil absorption, relative density and wear rate of the brake linings were determined and compared with existing brake lining properties. The result indicates that pulverized cow hooves can be used as brake lining material for automobiles.

Wisdom and Adeleke [156] worked on the development of brake pad using corn husks. The result obtained showed that the brake pad produced with the corn husk having the finer 100 μm screen gave better compressive strength, higher hardness, lower porosity and lower rate of wear, consequent on the finer distribution of the corn husks particles in the matrix.

Yi and Yan [157] studied the effect of three friction modifiers (0-25 vol.-%) calcined petroleum coke (CPC), talcum powder (TP) and hexagonal boron nitride (h-BN) on the mechanical properties of phenolic based friction composites. It is seen that the bending strength and hardness of the phenolic resin-based friction composite increased with increasing CPC content.

Mutlu *et al.* [158] studied effect of boric acid modification in phenolic friction composites. They show that hardness increases whereas density decreases due to modification.

Kim *et al.* [159] studied performance of friction composite based on phenolic resin, potassium titanate and cashew nut-shell liquid (CNSL). They suggested that the friction composites having a low hardness, high porosity and compressibility tended to reduce noise propensity.

Kim *et al.* [160] have investigated the synergistic effect of Aramid pulp and Potassium Titanate ($K_2O.6TiO_2$) on the physical properties of friction materials. They show that a composite having Potassium Titanate exhibit high porosity and less hardness as compared composites having Kevlar or both the fibers.

Abutu *et al.* [161] produced brake pads from locally sourced non-hazardous raw materials using grey relational analysis. The materials used for production include seashell, epoxy resin (binder), graphite (friction modifier) and aluminum oxide (abrasive). The results indicated that optimum performance could be achieved with 14 MPa molding pressure, 160℃ molding temperature, 12 min curing time and 1 hr heat treatment time. Analysis of variance shows that curing time has the least significant effect on the mechanical properties, while curing time of 24.26% and 55.23% has the most significant effect on Coefficient of friction and wear rate respectively on the brake pad developed.

Friday, G.P. [143] carried out the Physico-mechanical properties of Basalt-based Brake Pad as Alternative to Ceramics Brake pad, a basalt-based automobile brake pad was developed through optimization of the volume fractions and manufacturing parameters, a mathematical model was developed based on rule of mixture for the optimization of the volume fraction and solution obtained using excel solver; the result showed that the physical and mechanical properties of the basalt-based brake pad are good when compared to ceramics brake pad, however, the compressive strength and coefficient of friction are lower than that of ceramics brake pad.

Sanjay *et al.* [162] investigated the effect of hybridization on the mechanical performance of hybrid composites. Polypropylene/bamboo fibre - reinforced composites (BFRP) and polypropylene-bamboo/glass fibre based hybrid composites (BGRP) were compared using an intermeshing counter-rotating twin-screw extruder followed by injection moulding in which maleic anhydride grafted polypropylene (MAPP) was used as a compatibilizer. It was observed that replacement of 15 wt.% of bamboo fibre by 15 wt.% of glass fibre with 2 wt.% of MAPP on a total amount of 30 wt.% of fibre content showed optimum mechanical performance. The water uptake of the hybrid composites was also found to be less than that of their unhybridized counterpart. The crystallization, melting behaviour and thermal stability of the hybrid composites were investigated employing differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA*)*. TGA thermograms showed an increase in thermal stability of the matrix polymer after incorporation of bamboo and glass fibers, confirming the effect of hybridization and efficient fiber matrix interfacial adhesion. The fiber-matrix interfacial morphology of the tensile fractured specimens was studied using scanning electron microscopy (SEM) which showed less fiber pullout and fewer gaps between the fiber and the base matrix in case of MAPP-treated hybrid composites.

Fiore *et al.* [163] looked into the effects of hydrothermal stress and UV light on the ageing of composites made from jute and basalt. Every sample is examined for 14, 28, 56 and 84 days. The results showed that the hybrid composite outperforms its parent jute in impact resistance, flexural strength and aging resistance.

Kholil A. *et al*. [164] investigated brake pads made from sawdust, coconut fiber and cow bones. The polyester resin was used as matrix, with a constant composition of 50%. To obtain a fine material, the coconut fiber, sawdust and cow bones were ground and filtered through a 40-m mesh sieve before use. Wear testing is carried out to obtain wear data after testing braking at speeds of 10, 15, and 20 km/h. The brake pads before and after the test were weighed to determine the mass loss. Furthermore, the coefficient of friction of each test object is determined with the help of an inclined plane (90°). Specimen C, which was made up of 50% polyester resin, 20% wood powder, 20% coconut fiber, and 10% cow bone, had hardness characteristics and braking time that was similar to commercial products. Furthermore, specimen C has a rougher surface than the other specimens, improving braking performance and wear resistance.

Paramasivam, K. *et al.* [165] carried out evaluation of natural fibers for the production of automotive brake pads replacement for asbestos brake pad. In the research, the natural fibers used were Banana fiber (5 & 10%), Coconut fiber (2 & 5%), Rice husk (3 & 5%) with additives like graphite powder (30% & 35%)and Aluminium oxide (15%) to improve the abrasiveness, Epoxy resin (35% & 40%) which is used as binder material. The rice husk is used in order to reduce rate of wear. The wear properties and hardness of the composite material were investigated further and thus, recommended to be used as an effective replacement of asbestos in the brake pad production.

Anaidhuno, U. P. *et al*. [166] developed vehicle brake pad using local materials. The disc brake friction lining with the geometrical specifications of a Toyota Camry 2000 model was produced using palm kernel and coconut shells powder as base materials, epoxy resin (Araldite) as binder materials and carbon as fibre reinforcement, Aluminum, Copper, Zinc and cashew nut shell were used as abrasives rubber dust from shoe as filler. The experiment conducted, it was revealed that the co-efficient of friction of the pad material ranged from 0.4-0.65, scratch hardness of 80 - 85, bonding strength of 25-27 kg/cm^2 and wear rate of 0.025mm/min to 0.06mm/min as compared to the conventional brake pad material that has hardness of 80-85, bonding strength of 25 - 27 kg/cm^2 and wear rate of 0.03-0.08 mm/min.

Ilanko and Vijayaraghavan, [167] investigated wear mechanism of flax/basalt fiber-reinforced eco-friendly brake friction materials. Three different fibers (flax fiber, basalt fiber, and flax/basalt composite fiber) reinforced hybrid phenolic composites were produced and compared. The results indicated that basalt fiber had good thermal characteristics and bonding nature, which greatly improved the wear resistance of basalt fiber/phenolic resin composites, and the wear resistance.

Yilma, W. M. *et al.* [168] investigated Taguchi Method Optimization of Water Absorption Behavior by Wheat Straw-Basalt Hybrid Brake Pad Composite. The study aimed to optimize the water absorption capacity of biomass-based, wheat straw fiber-basalt hybrid composite brake pad using the Taguchi method by considering the particle size and volume % of the composite compositions. All composites were molded using a compression molding process at compressive pressure of 6 MPa for 2 h curing in a forced convection oven at 100 °C. Water absorption capacity was determined. The wheat straw fiber was chemically treated with 5 wt.% of sodium hydroxide (NaOH) to remove the impurities, lignin, and hemicellulose and increase the surface area of the fiber, resulting in a larger area of contact between the fiber and the matrix. The maximum compressive strength and minimum and maximum water absorption capacity of composites were obtained as 77 MPa, 3.55%, and 26.86%, respectively. From the optimum setting of the confirmation experiment, the optimal water absorption value of 5.718% has been obtained. The optimum particle size of the composite compositions was 1 mm basalt particle, 0.5 mm wheat straw fiber, 1 mm steel particle, 1 mm river sand, 0.5 mm graphite dust particle, and 30 vol% epoxy resin by Taguchi method. The parameter impact of Taguchi ranking on water absorption capacity presented the maximum improvement of water absorption, 10.47%, with river sand particle size.

Bandaru, A. K. *et al.* [169] investigated the Mechanical Behavior of Kevlar / Basalt Reinforced Polypropylene Composites. In this study, mechanical behavior of thermoplastic composites reinforced with two-dimensional plain woven homogeneous and hybrid fabrics of Kevlar/basalt yarns was studied. Five types (two homogeneous and three hybrids) of composite laminates were manufactured using compression molding technique with polypropylene (PP) resin. Static tensile and in-plane compression tests were carried out to evaluate the mechanical properties of the laminates. The tension and in-plane compression tests shown that the composites with the combination of Kevlar and basalt yarns present better tensile and in-plane compressive behavior as compared to their base composites. Improvement in the properties such as elastic modulus, strength and failure strain in both tension and in-plane compression was observed due to the hybridization.

Kumar, J.A.A. *et al.* [170] investigated the tribological analysis on basalt/aramid hybrid fiber reinforced polyimide composites for an alternative brake pad material. In the study, three frictional composite materials namely Basalt Fiber Reinforced Composite (BFRC), Aramid Fiber Reinforced Composite (AFRC) and Hybrid of these fibers reinforced Composite (HFRC) were prepared with polyimide matrix using hot compression molding machine. In the result, HFRC is found to be a better choice as an alternative for brake pad, since it showed higher wear resistance, higher fusion of the fibers and the matrix, less frictional heat at contact surface and better thermal stability compared to BFRC and AFRC.

Zhao, X.G. *et al.* [171] investigated the enhancement of the mechanical properties of basalt fiber/nylon 6 composites by surface roughening and hydrogen bonding interaction. basalt fibers (BFs) were modified with polydopamine and then composited with nylon 6. The effect of polydopamine content on the interfacial interactions and mechanical properties of the composites was investigated. In addition, silica nanoparticles were grown on the surface of polydopamine-modified BFs to investigate the synergistic effect. The study revealed that the mechanical properties of the composites based on polydopamine-modified BF were gradually enhanced with the increase of the dopamine coverage concentration, and gradually decreased after reaching the peak. 0.5 g/L concentration of dopamine solution modified BFs showed the best enhancement effect on nylon 6, and its tensile strength could reach 133.1 MPa, which was 28.5% higher than that of the unmodified composites. The tensile strength of the composites modified with both dopamine and silica nanoparticles reached 157 MPa, which was 51.7% higher than that of the unmodified composites.

Eslami-Farsani, R. *et al.* [172] investigated the Influence of thermal conditions on the tensile properties of basalt fiber reinforced polypropylene–clay nanocomposites. The tensile properties of clay reinforced polypropylene (PP) nanocomposites (PPCN) and chopped basalt fiber reinforced PP–clay nanocomposites (PPCN-B) were compared. The ultimate tensile strength, yield strength, Young's modulus and toughness are measured at various temperature conditions. It was stated in the result that addition of nanoclay improves the yield strength and Young's modulus of PPCN and PPCN-B; however, it reduces the ultimate tensile strength. Furthermore, the addition of chopped basalt fibers to PPCN improves the Young's modulus of the composites.

Moses, A.J. *et al.* [173] produced a novel brake pad using basalt fiber and glass fiber to replace asbestos. The main aim of the work was to study the physical properties and wear behavior of basalt fiber reinforced brake pad. The authors formulated basalt brake pad materials samples with ten different ingredients using conventional methods. In the experiment study the change of friction co-efficient, porosity, hardness, specific gravity, water swell and Heat swell were measured. The results were compared with commercial brake pad available in the market. It was finally concluded that basalt and glass fibers are suitable reinforcement and can be used as replacement asbestos for brake pad production.

Kishore and Amirta [174] investigated the mechanical characteristics of jute-basalt hybrid composites with graphene nanofillers of different concentrations. Both the hybridization of various fibers and the impact of graphene on mechanical properties were examined. Based on the findings, a hybrid composite with 0.4 wt.% graphene had 17% higher impact strength than a hybrid composite without graphene.

Kumar, I.A. *et al.,* [175] investigated the thermal characterization of Flax / Basalt fiber reinforced Phenol Resin brake pad material for effective replacement of asbestos i.e. Flax fiber reinforced phenolic resin composites (FRPCs) and Basalt fiber reinforced phenolic resin composites (BRPCs). FRPCs and BRPCs with different volume percentages of 2, 4, 6, and 8 of chemically treated flax and basalt fiber are fabricated by diffusion bonding technique. The thermal behavior was investigated by the use of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques. DSC results revealed that FRPC and BRPC samples reinforced with 6% volume fraction (V_f) of the respective fibers are having better thermal stability than other volume percentage, since the glass transition temperature (T_g) is relatively high. TGA analysis also shows that FRPC and BRPC specimens reinforced with 6% V_f of flax and basalt fibers have good thermal stability when compared to other volume fractions.

3.2 The Particle Size of Eco-Friendly Materials

Asep B.D.N. *et al.* [176] investigated the effects of rice husk particle size on resin-based brake pad performance. In the experiment, rice husk with a specific particle size (i.e., 250, 500 and 1000 μm) was added to the resin. Rice husk was said to have received considerable interest due to its lignin, cellulose and silica content, making it suitable as friction material due to its ceramic-like behavior. The experimental results showed small rice husk particles improved compressive strength, puncture strength, and bulk density. Particle size affected interpacking distances, interfacial bonding, and thermal softening of rice husk particle-resin matrix. Small particles improved the compressive strength of the brake pad. Decreases in particle size also resulted in fewer pores formation, less mass loss, better wear rate, high friction coefficient, and the brake pad's coarser surface. Comparison between the prepared resin-based and commercial brake pad was also done, confirming the utilization of agro-waste as a potential alternative for friction material in the brake pad.

Primaningtyas *et al.,* [177] determined the effect of particle size of rice husk powders and structural mechanisms on non-asbestos brake composites. The ratio of reinforcement and matrix as follows 20:80; 30:70; 40:60 with carbonized and un-carbonized condition, the result from the Rice Husk composite's wear resistance value showed that rice husk powder can be used for filler element in polymer epoxy composites. It provided better wear resistance value than asbestos brake pad in 20% filler carbonized in 100 mesh size particle, means it can replace the asbestos contained brake pad. Carbonized process gives slight increasing of wear resistance value for the composite.

Stephen *et al.* [179] investigated the development of non-asbestos brake pads using sawdust. Sawdust from hardwood is sieved into 100 μm and 250 μm grades for the brake pads production. The smaller sawdust particle size gave the highest density, hardness, and compressive strength values and improved the brake pad specimen's wear properties.

Elakhame *et al.* [179] studied and produced new brake pads by employing varying particle sizes of Palm Kernel Shell (PKS), according to the conclusions of this investigation, for all material compositions, the sample with 100 μm of palm shell had better properties than other samples with particle sizes of 1 mm, 710 μm, and 355 μm. The research's findings suggest that palm shells could be a viable alternative to asbestos in brake pad manufacturing.

Fono-Tamo and Koya, [180] studied the influence of Palm Kernel Shell (PKS) particle size on the wear and brake pads' fade resistance. In the study, the PKS used had particle sizes of 0.212 mm, 0.300 mm, 0.425 mm, 0.600 mm, and 0.850 mm. PKS (12.5%wt.) is mixed with other materials and processed using cold pressing, hot pressing, and post-curing methods to produce brake linings. Compared to other specimens, the best density, fading resistance, and wear were achieved utilizing PKS with a particle size of 0.300 mm.

3.3 Types of the Binder for Brake Pad

The binder resin is assumed to serve as a key influence in brake performance since it keeps components together as a matrix in a composite [15,181]. The kind of binder and its proportion in the brake pad material composition are crucial to meeting the standard requirements for friction materials [182]. Phenolic resins are thought to be the first production of commercial polymeric products made from simple low-molecular-weight compounds. Table 5 shows the physical and mechanical properties of the phenolic resin. Phenolic resins are suited for high-temperature applications that require parts to be fire-safe. Phenolic resins are used in various applications, including ballistics, electronics, offshore water pipe systems, mine ventilation, aircraft, mass transit, and rail. Low thermal conductivity, excellent corrosion, low density (weight-efficient), chemical resistance, enhanced design flexibility, outstanding fatigue and impact properties, cost-effective production of complex three dimensional (3D) structures, radar/sonar transparency, enhanced acoustic performance and low maintenance are just some of their primary elements [183,184]. The phenolic resin has already been utilized in brake pads due to its superior heat resistance and inexpensive manufacturing cost. Nevertheless, recent high expectations for brake performance have compelled enhanced friction stability and wear resistance at higher temperatures, necessitating various chemical modifications to the binder resin to fulfill the needs for a short stopping distance and lowered pad wear in brake applications at higher temperatures [182]. High thermal stability brake pad friction materials result in safer braking performance and better resistance to thermal decay. The friction material of the brake pads has increased thermal stability, resulting in an improved ability to withstand compressive forces during the braking process and a stable friction coefficient. As a result, the amount of weight loss and the rate of wear on the brake pads are reduced. In general, brake pads with a high coefficient of friction provide better braking with less effort on the brake pedal [185].

Table 5: Physical and Mechanical Properties of Phenolic resin [15,186,187].

Properties	**Values**
Specific gravity	1.12–1.16
Flash point(°C)	72.5
Boiling point(°C	181.8
Melting point (°C)	100–115
Elongation at break (%)	2
Density (g/cm^3)	1.2 – 1.4
No tamped volumetric weight (g/dm^3)	350–550
pH	7–8.5
Solubility	Acetone, Ethyl alcohol, Ethylacetate
Thermal-decomposition temperature (°C)	300 (starting)
Tensile Modulus (GPa)	2.76–4.8
Tensile strength (MPa)	34.5–62.1
Tamped volumetric weigh (g/dm^3)	600–800
Total weight losses (%) during the thermal degradation process (room temperature to 800 °C)	55.2

Phenolic resin contributes to the friction performance of brake pads. The amount of phenolic resin with cashew nut shell liquid (CNSL) and potassium titanate enhances the hardness and friction coefficient at temperatures around 100 °C [188].

Binda *et al.* [189] described a unique friction element made of slate particles used as a tribological reinforcement in a phenolic resin-based composite matrix. In the study, fiberglass, aluminum oxide, and graphite were used at a constant mass percentage. At the same time, slate particulates and phenolic resins are used in varied compositions. The composites' friction coefficients were found to be regular and stable, averaging 0.44 between samples. When compared to commercial friction materials currently in use, the optimized formulation of 40% slate and 35% phenolic resin (specimen A3) had the most desirable characteristics. This specimen employs slate with the lowest composition and the highest resin composition. This formulation resulted in a composite that performed admirably in friction testing and even better in wear tests.

Nawangsari *et al.* [190] investigated the effect of phenolic resin as a binder in a non - asbestos organic brake pad with varying volume fractions of 25 wt.%, 20 wt.%, 15 wt.%, and 10 wt.%. Phenolic resin, $BaSO_4$, friction dust, Al_2O_3, SiO_2, MgO, Copper, MoS_2, graphite, and hBN were used in the study. As the volume percentage of phenolic resin grew, porosity reduced, but hardness increased. The composite samples' thermal stability reduces as the phenolic resin volume fraction grows. Thermal stability is better in the composite sample with 10% phenolic resin than in the other specimens. With an increase in the volume percentage of phenolic resin, the friction coefficient will decrease, and the volume wear rate will rise. Moreover, while having superior thermal stability than the other specimens, composite samples comprising 10% and 15% phenolic resins were not recommended for use in the production of this brake pad since they have a poorer resistance to mechanical stress throughout friction performance tests.

In addition to the amount of resin used, the type of resin used can have an impact on the brake pads' performance. The amount and type of binder are both critical for modifying the required performance properties of the friction material on the brake pads. The wear resistance, friction coefficient, and thermal resistance of the friction specimen are all influenced by the binder matrix. Furthermore, during brake application, the polymer matrix limits noise propensity. Interestingly, the binder resin has a big influence on the friction material fabrication design parameters [191,192].

Joo *et al.* [181] looked at the tribological behavior of brake linings and found that different binder resins had distinct effects. The brake lining specimens in this investigation were made using a variety of binder resins. This experiment used alkyl-modified phenolic resin, straight phenolic resin, acrylic 30% modified phenolic resin, silicon-modified phenolic resin, and aromatic ring-modified phenolic resin. Table 4 shows the thermal characteristics of the resins employed. The brake linings were created using a combination of mixing, performing, compression molding, and heat treatment. The tribotester findings demonstrate that at high temperatures, the decomposition of the binder resin has a substantial impact on the friction coefficient, wear rate and brake linings' brake emission. The use of heat-resistant resins in brake linings resulted in a considerable reduction in particulate matter with a diameter of less than 2.5 m (PM 2.5) at high temperatures, demonstrating that heat-resistant binder resins can reduce brake lining wear rate and particle emission. Despite having a low high-temperature wear rate, the heat-resistant alkyl-modified resin brake lining generated a substantial amount of brake emission, showing that the unanticipated volatile vapors released by the modified resin can boost brake emission. A high-temperature wear test's activation energy is much higher than a low-temperature wear test. The binding resin's activation energy used to create brake lining specimens at high temperatures varies greatly, implying that the heat resistance resin has a major effect on the brake lining's wear rate.

Table 6: The Thermal-Decomposition Temperatures of the Binder Resins [15,181,193,194]

The Binder Resins	**Thermal Decomposition Temperature(°C)**
Aromatic Ring-Modified Phenolic Resin	488.0
Straight Phenolic Resin	418.5–550
Alkyl-Modified Phenolic Resin	461.5
Silicon-Modified Phenolic Resin	378.8
Acrylic 30% -Modified Phenolic Resin	373.9
Cashew Nut Shell Liquid Modified Resin	431
Melamine Resin	408
Alkyl Benzene modified resin	420

The higher the thermal breakdown / degradation temperature in resin-based brake pad materials, the lower the oxidation and decomposition. The brake pads' friction qualities will be stable as a result. Various modified phenolic resins (modified with cashew nut shell oil, melamine, nitrile rubber, and so on) can be used to raise the resin's decomposition temperature. In addition, the fade and wear of the friction materials were linked to the binder resin's heat degradation. The percentage of fade was significantly reduced in friction materials with changed resin. High-thermal-stability friction materials showed resistance to fading [195].

Öztürk and Öztürk, [193] investigated the fiber length effect and resin type on the mechanical properties and friction characteristics of brake friction materials. Straight phenolic resin (SR), melamine resin (MR), and cashew nut shell liquid modified resin (CR) were used as matrix materials in their study. As an inorganic fiber, several lengths of Lapinus were employed. Both fiber length and resin type influenced the friction materials' mechanical and tribological properties, according to the findings. The SR and MR composites had the highest and lowest coefficients of friction, accordingly. MR and CR composites have the highest and lowest wear resistance, correspondingly. On the other side, increasing the fiber length raised the wear resistance of the composite.

4. DISCUSSION

Various Bio-Composite materials were researched and employed as asbestos substitutes in brake pads in this review. Thus, it was found that brake pads developed with eco – friendly (non- asbestos) based bio-composite materials perform almost the same as or better than the brake pads developed with asbestos or synthetic (ceramic) materials in terms of their physical mechanical and tribological properties. Furthermore, it was confirmed that the use of eco – friendly (non- asbestos) based bio-composite materials on brake pads can reduce environmental pollution and health risks. It was also confirmed that a better wear rate is influenced by the proportion of materials and the right bonding properties. The strong adhesion of natural fibers with resin provides good wear resistance for composites [196-198]. Reducing the level of wear on the brake pads can be done by reducing the particle size of the filler because smaller particle size will increase the bond between the binder and the filler [199-201]. The wear resistance, friction coefficient, and thermal resistance of the friction specimen are all influenced by the binder matrix [191,192]. The brake pad's wear rate and particle emission can be reduced using heat-resistant binder resins. The greater the heat resistance of the resin, the higher the thermal decomposition temperature, thereby reducing decomposition and oxidation. As a result, the friction properties of the brake pads will be stable [194,195].

Moreover, small particle size of reinforcement creates stronger structural interfacial bonds and allows the particles to withstand more force or pressure before breaking. Small particles (rice husk ash) resulted in fewer pores formation (porosity), less mass loss, better wear rate, high friction coefficient and improve the compressive strength and hardness of the resulting brake pad samples.

It has been confirmed that the amount and the type of resin used can have an impact on the brake pad's performance. The amount and type of binder are both critical for modifying the required performance properties of the friction material on the brake pads. The use of phenolic resins for brake pads based on natural fiber has improved physical, mechanical and tribological properties over polyester resins.

Despite the advantages of natural fibers mentioned in this comprehensive review, the use of agricultural waste (lignocellulosic) has not been extensive due to their limited thermal stability (i.e thermal instability), the high moisture absorption of the fibers, low degree of dispersion and poor interfacial adhesion between the hydrophilic lignocellulosic fiber and the hydrophobic polymer matrix, so, investigation has proven that chemical treatment of the agricultural waste (lignocellulosic) fiber or development of hybrid composites of lignocellulosic/synthetic fibers or lignocellulosic/mineral fibers give a synergistic effect with performance optimization and behavour enhancement, hence the need for hybrid composite brake pad.

5. CONCLUSION

From this comprehensive review, it can be concluded that:

I. Asbestos can cause lung cancer from the dust produced leading to its product ban in brake pad production by Environmental Protection Agency (EPA) and the Occupation Safety and Health Administration (OSHA) not withstanding it stands as a good friction lining material.
II. Conventional synthetic material (ceramic) which is equally good and being used for brake pad production is costly, not readily available and being imported into the country.
III. The use of natural biodegradable materials as reinforcement components in the production of brake pads shows that the materials have potential to substitute inorganic material content for brake pads.
IV. Hybridization brings about enhanced interfacial fiber / matrix bonding.
V. It is observed that performance of brake pad constituent materials can be optimized and the behavior enhanced using hybrid composites.
VI. Hybrid composite outperforms its parent composite in all ramifications.
VII. Recently, Basalt fiber gained attention as possible alternative for asbestos and ceramic due to some of its increased advantages in terms of its physical, mechanical, tribological properties and environmental cost, however, its application in brake pad production has not been extensive due to its deficiencies such as such as high void content, low compressive strength and low coefficient of friction compare to ceramic brake pad
VIII. Finally, future development of friction materials for brake pad should be explored in the areas of hybridizing basalt with natural fiber reinforcement that has the potential to serve as hybrid reinforcement for brake pad besides those already used in the literature so as to compensate for basalt fiber deficiencies for its extensive application in brake pad production.

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