

Review

Ecological Transition in the Field of Brake Pad Manufacturing: An Overview of the Potential Green Constituents

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Abstract: Nowadays, the drive for green products has undergone a rapid increase following the global ecoawareness and the severe regulations aimed at preventing the environment from further damage. The use of ecosafe constituents in materials for harsh applications, such as brake pad systems, can be a possible solution for reducing health hazards arising from particle release during braking. Based on this, the present study provides a bibliographic review of green alternative constituents for friction material formulation, focusing the attention on their influence on the tribological properties of the final composites. The traditional materials still used in commercial brake pads are shortly described, with the aim to provide an overview of the current situation. In the final part of the review, following the trend of circular economy, works dealing with the use of waste as an ingredient of friction materials are also reported. The whole literature screening points out that much work is still required to obtain completely green friction materials. Indeed, few works dealing with the phenolic resin replacement, proposing inorganic ecosafe materials such as geopolymers, are present. On the contrary, the use of natural fibers is widely investigated: palm kernel, flax, agave and aloe can be identified as promising constituents based on the literature results and the generated patents.

Keywords: friction material; green constituents; tribology; natural fiber composites



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1. Introduction

1.1. Particulate Matter

Particulate matter (PM) consists of microscopic liquid and solid particles suspended in air whose dimension and chemical composition change continually [1,2]. Because of the extremely large dimension range, which varies from a few nanometers to ten microns, particle behavior in the human respiratory system changes. Particles with size below 10 μm can be a potential risk for the trachea-bronchial and alveolar regions [3]. They are subdivided into two groups: (i) coarse, having an aerodynamic diameter ranging from 2.5 to 10 μm ($\text{PM}_{10-2.5}$), and (ii) fine, with diameter below 2.5 μm ($\text{PM}_{2.5}$) [4], able to reach alveoli and terminal bronchioles [5]. PM toxicity depends on several factors such as geographic location, season, weather conditions and chemical composition of the different PM fractions [6]. Coarse ambient particles are typically of natural type, i.e., basically primary pollutants, while the finest ($\text{PM}_{2.5}$) originate from human activity and consequently are more toxic [7]. For this reason, $\text{PM}_{2.5}$ was advised by the World Health Organization (WHO) to be used as an air quality indicator. An epidemiologic study demonstrated that a 10 $\mu\text{g}\cdot\text{m}^{-3}$ increase in $\text{PM}_{2.5}$ is associated with a 1.04% intensification in the risk of death [8]. In order to safeguard citizens' health, air quality standards have been developed by governmental agencies. In 1987, the WHO developed quality guidelines, followed by updates in 1997 and in 2006, recommending maximum levels of several critical air pollutants that can have negative effects on human health. WHO guidelines, which formerly were addressed to Europe, have been globally extended and implemented, adding three interim targets (IT) [9] which provide a gradual approach to reach the targeted air

quality index value [10]. In 1971, the Environmental Protection Agency (EPA) established the criteria for PM: a maximum daily concentration of $260 \mu\text{g}/\text{m}^{-3}$ more than one day per year and an annual mean concentration lower than $75 \mu\text{g}/\text{m}^{-3}$ [11]. Later, the EPA introduced the first PM_{10} limit and, in 1997, the subdivision of PM_{10} and $\text{PM}_{2.5}$ [12]. Table 1 reports standard values of PM settled by the WHO and U.S. Environmental Protection Agency (EPA) which established the National Ambient Air Quality Standards (NAAQS).

Table 1. Standard values of PM defined by WHO and National Ambient Air Quality Standards (NAAQS) (USA/EPA).

Indicator	Averaging Period	Level	Primary/Secondary	Form	Agency
PM_{10}	24 h mean	$150 \mu\text{g}/\text{m}^3$	Primary and Secondary	Not to be exceeded on more than once per year on average over a 3-year period	NAAQS EPA ¹ [13]
$\text{PM}_{2.5}$	Annual mean	$12 \mu\text{g}/\text{m}^3$	Primary	Averaged over 3 years	
	Annual mean 24 h	$15 \mu\text{g}/\text{m}^3$ $35 \mu\text{g}/\text{m}^3$	Secondary Primary and secondary	Averaged over 3 years Annual arithmetic mean, averaged over 3 years	
PM_{10}	Annual	$20 \mu\text{g}/\text{m}^3$	-	-	WHO ² [13]
	24 h	$50 \mu\text{g}/\text{m}^3$	-	-	
$\text{PM}_{2.5}$	Annual	$10 \mu\text{g}/\text{m}^3$	-	-	
	24 h	$25 \mu\text{g}/\text{m}^3$	-	-	

¹ National Ambient Air Quality Standard (United State Environmental Protection Agency). ² World Health Organization.

Principal PM constituents usually include nitrates, sulphates, elemental and organic carbon, organic compounds (e.g., polycyclic aromatic hydrocarbons) and biological compounds [14,15].

1.2. Pollution from Brake Systems

The total $\sum \text{CO}_{\text{add}}$ emissions from the principal pollutants were computed using Equation (1), where R_t represents the relative toxicity of pollutants relative to carbon monoxide, $m(i)$ represents mass emissions of that pollutant and n represents the total number of kinds of pollutants considered.

$$\sum \text{CO}_{\text{add}} = \sum_{i=1}^n m(i) * R_t(i) \quad (1)$$

For petrol-powered passenger cars and electric vehicles (EVs), a $\sum \text{CO}_{\text{add}}$ of $133.9 \text{ g}/\text{km}$ was measured for Euro0, while 4.7 was the measurement for EVs. It is worth noting that a R_t of 150 was calculated for $\text{PM}_{2.5}$ originating from friction materials, ranking them in the first quartile among the 64 pollutants considered in the Klimenko's study [16]. Considering the total $\text{PM}_{2.5}$ emissions in urban areas, particles derived from traffic (automotive sector) (Figure 1) are responsible for up to 50% of them [17]. Exhaust emissions, which result from partial fuel combustion and lubricant evaporation during combustion, are usually separated from nonexhaust emissions, which are caused by tire, brake and road surface wear or by road dust resuspension [18]. Brake wear is one of the key factors, accounting for up to 21% of total traffic-related PM_{10} emissions [19].

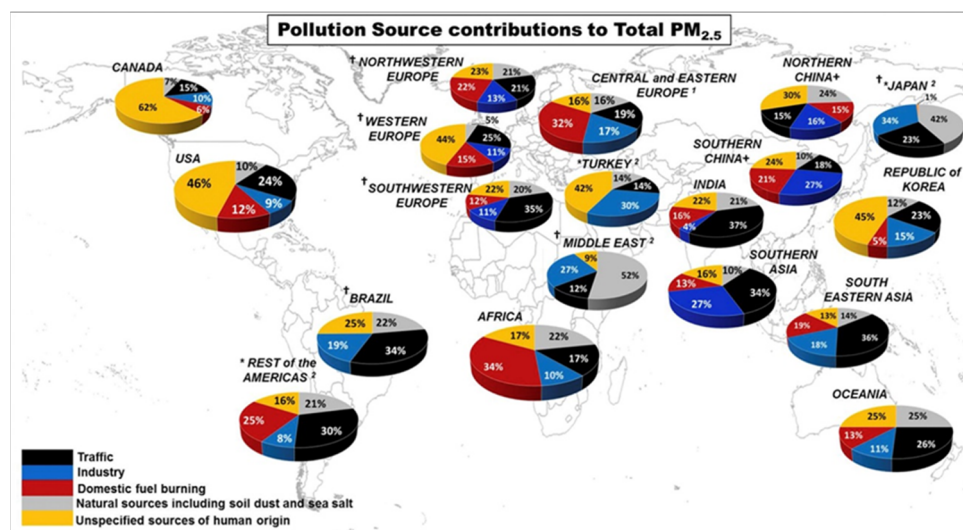


Figure 1. Pollution source contributions to total PM_{2.5} (courtesy of Karagulian et al. [20]).

Several papers studied the influence of brake system emissions on both the ecosystem and humans. Maiorana et al. evaluated the phytotoxicity of wear particles from both standard (phenolic matrix) and innovative (cement matrix) friction materials. They discovered that the brake pad wear debris (BPWD) produced by the two friction materials had comparable shape, but the traditional friction materials had higher phytotoxicity, resulting in significant root elongation and loss of plasma membrane integrity [21]. Similar phytotoxicity effects of BPWD were reported in lettuce and wheat but not in soybean roots [22]. A comparison between traditional, available-on-the-market brake systems and two innovative, more ecofriendly brake systems, in bench tests revealed that particles from traditional friction materials were not completely safe for edaphic and aquatic ecosystems [23].

Exposure to brake wear particles for human lung cell cultures showed an increase in oxidative stress and a proinflammatory response [24].

Several attempts to reduce the toxicity of particles produced during braking have been made over the years. The first concerns originated in the 1960s, when asbestos fibers were still widely used as important constituents of vehicle friction materials. Asbestos is a fibrous material generally classified into serpentine or amphibole [25]. Serpentine contains chrysotile asbestos, of which the fibers are quite long and flexible with good tensile strength, making them easily woven into fabric for friction materials [26]. Due to its unique characteristics, asbestos became an important component of vehicle friction materials from the beginning of 1900s to the end of 20th century. However, based on various epidemiological studies carried out since the 1960s, asbestos fibers were classified as having a carcinogenic nature by the International Agency for Research on Cancer (IARC). Therefore, since the end of 1980s, several countries world-wide have implemented a gradual asbestos ban. In 1983, Iceland was the first country who completely banned all types of asbestos [27], followed by fifty other countries, while others have developed programs aimed at exposure reduction and abatement of environmental contamination from asbestos. The EPA began taking steps to restrict the use of asbestos in the 1970s. However, friction materials and clutch facings containing asbestos are still currently authorized in the United States (EPA 2018), despite the fact that they are no longer produced and hence in extremely restricted circulation [28].

The asbestos ban led to the production of several friction materials with compositions much more complex with respect to that of asbestos-based materials. Potassium titanate (KT) was considered a potential alternative to asbestos in non-asbestos organic (NAO) FMs [29]. However, due to potential health hazards of the acicular whiskers, use of potassium titanates in commercial friction materials was not promoted. In particular,

manufacturers of raw materials suggested platy potassium titanate as an alternative to the fibrous shape because it displayed similar wear and fade resistance to fibrous forms [30].

Among the several constituents of the current friction materials, Cu, Cd, Ni, Pb, Sb and Zn are now considered toxic materials necessary to be substituted [31]. Figure 2 shows the trend in the chemical compounds contained in automotive friction materials in the U.S.

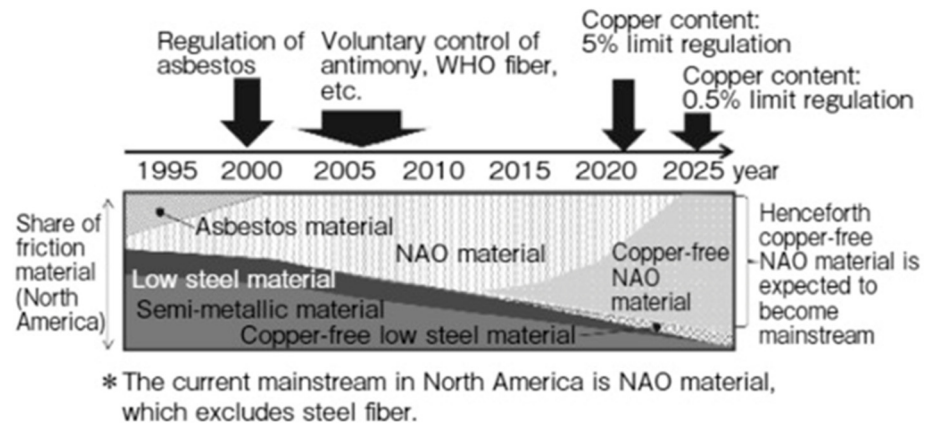


Figure 2. Transformation of chemical compounds in automotive friction materials in the U.S (courtesy of G. Straffelini et al. [32]).

Copper has been one of the most often used components in friction materials. However, it was recognized by the US Brake Pad Partnership that friction materials are the greatest contributors to environmental Cu pollution [33]. For this reason, U.S. legislation currently limits copper use. Beginning in 2021, friction materials shall include no more than 5% copper components (low levels), aiming at the amount of 0.5% by 2025 (no copper materials) [34]. However, the European Union has not enacted a precise regulation on this matter yet. At the moment, it is still possible to use nickel (Ni), antimony (Sb) and zinc (Zn) without restrictions, notwithstanding they are considered harmful elements [35]. In particular, Sb has attained much attention as a roadside contaminant because it may have hostile effects for humans and the environment [36], entering the human body by skin contact, the food chain and respiration, leading to cell hypoxia [37]. Because of high temperatures occurring during the braking process, some Sb_2S_3 may be oxidized to Sb_2O_3 , a potentially carcinogenic chemical [38].

Nowadays, ecological transition is a crucial issue in all production sectors, and friction materials cannot be an exception. The present review is attempting to provide an overview of the most common ecofriendly potential constituents in friction material formulation, raising awareness about the research efforts needed in this field for reducing the overall environmental impact of the automotive sector. In the following sections, a state-of-the-art review of the most widely used ingredients for friction material formulation is described, with a classification proposal of the constituents. Indeed, such classification is not unambiguous in research literature, since some materials can belong to different categories. The potential ecofriendly solutions for friction materials are then reported, based on a definition dating back to 1990 [39].

2. Friction Materials Overview

The brake pad, rotor and caliper are the three essential components of any braking system (Figure 3a). The role of friction material, that is, the part of the brake pad sliding against the disc (Figure 3b), is to slow and stop a vehicle by converting kinetic energy into heat at the friction material/disc contact in the air. During a braking action, the caliper acts mechanically on the brake pad, which rolls against the disc. Friction materials are subjected to huge frictional heat generation during sliding, resulting in wear of both friction materials and the rotor as well as the formation of particles of various sizes.

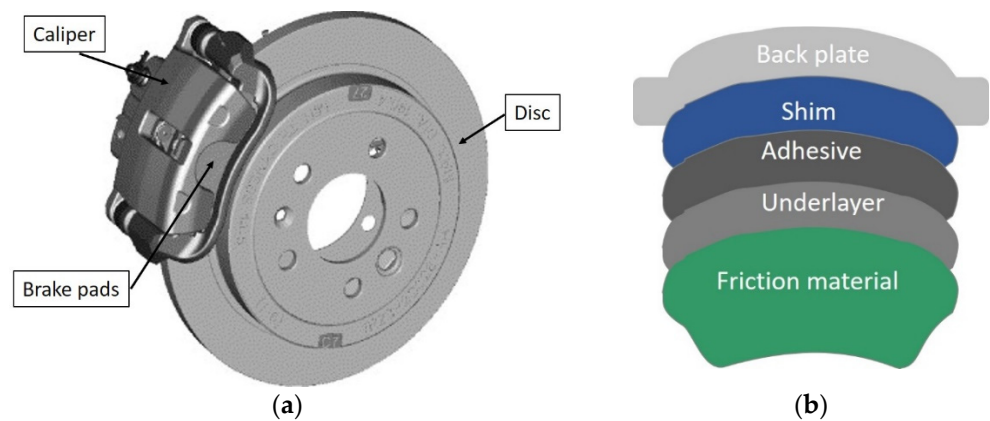


Figure 3. (a) Sliding disc brake (courtesy of Papinniemi et al. [40]); (b) Brake pad structure.

The most common disc material is grey cast iron, which has excellent thermal characteristics, wear resistance and mechanical strength. Moreover, it is a cheap material easy to machine [41]. There are alternative materials used for discs, such as aluminum-based metal matrix composites, titanium-based materials and ceramic matrix composites based on carbon fibers [42] and matrices of silicon carbide [43]. Disc materials still remain with simpler composition in comparison to friction materials.

The different materials constituting friction materials make their tribosystem very complex and variable. Friction materials are required to: (i) provide a constant coefficient of friction throughout a wide variety of braking situations and (ii) assure a low wear rate at various operating speeds, pressures, temperatures and climatic conditions [44]. Additionally, friction materials must be suitable for limiting vibration and noise while braking and must be resistant to both heat [45] and water [46].

The constituents of friction materials can be greater than one hundred and belong to all materials classes, i.e., metallic, ceramic and organic. Their constituents (Figure 4) are generally classified as binders, fibers, fillers (inert and functional) and friction modifiers (abrasives and lubricants), depending on the role they play in the friction materials: controlling the friction coefficient, improving fade resistance, reducing porosity and noise or increasing strength. Some compounds have various functions and can belong to more than one category.

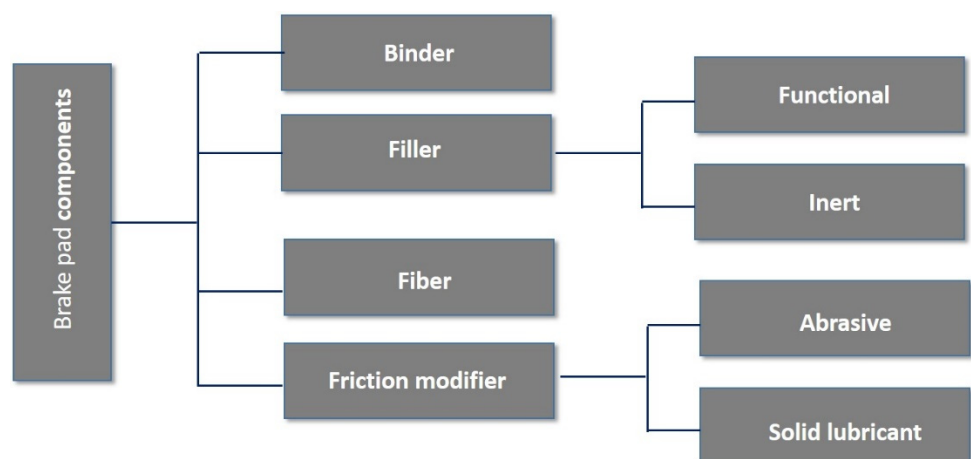


Figure 4. Friction material constituent classification.

Because of their cheap preparation procedure and good tribological qualities, most friction materials for light and commercial cars include an organic matrix (referred to as organic friction compounds). Organic friction materials belong to three groups, according to the different quantities of components [47]: low metallic (LM), semimetallic (SM) and

nonasbestos organic (NAO) friction materials [48]. Each group consists of many different formulations designed to match the requirements for specific brakes and vehicles.

Selection of the proper constituents and their combination is very problematic and fundamental because of the several requirements to be fulfilled by them [49]. A brief description of the different components of friction materials is provided in Table 2.

Table 2. Main components and main characteristics of friction materials [50–52].

Friction Materials Typologies	Common Content	Main Characteristics
Low metallic	Fe (10–50%), steel, copper and copper alloys and different abrasives	<ul style="list-style-type: none"> - Medium/high friction coefficient - High friction materials/rotor wear - At elevated temperature, shows good braking capacity - Good fade
Semimetallic	More than 50% Fe and steel fiber and alloy, porous iron powder, abrasives and graphite/coke lubricants	<ul style="list-style-type: none"> - Low/medium friction coefficient - At low temperatures, the wear rate is low - Good wear under heavy loads
NAO	50% metallic components, friction dust, phenolic resin, graphite and other reinforcements	<ul style="list-style-type: none"> - Low to medium-high friction coefficient - Excellent wear at lower temps, <200 °C

Basically, the friction material manufacturing process is divided into different steps as reported in Figure 5.

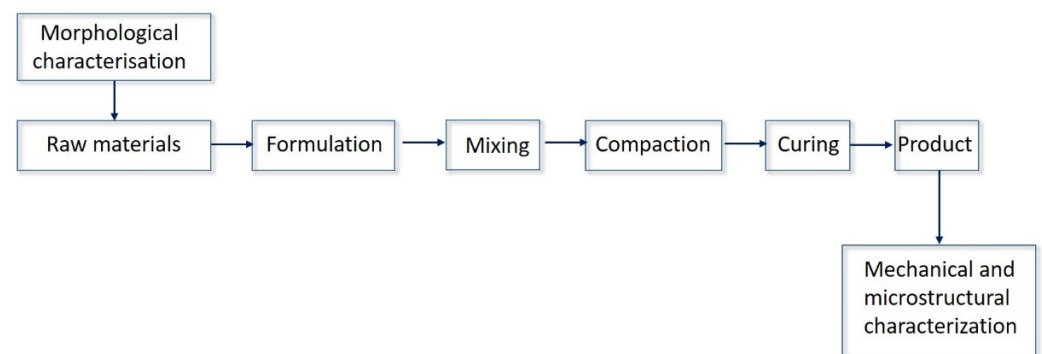


Figure 5. Brake pad manufacturing process.

Constituents are appropriately homogenized in a blend during the compression molding procedure. The molding and preliminary curing of the composite under heat and pressure is an essential phase in the production of friction materials. In most cases, the molding process is pressing a homogenous mixture of components into a shaped mold at 150–200 °C under pressure ranging from 30 to 70 MPa. Molding pressure, duration and temperature must be carefully set to fit the material formulation [53].

2.1. Binder

The role of the binder is to keep friction material components all together, guaranteeing their structural integrity under mechanical and thermal stresses without sacrificing other significant properties. The binder choice depends on the required performance of the brake pad, which in turn depends on the preparation process. The typical percentage of the binder in the friction material ranges between 20 and 40%. One of the most used binders is phenolic resin, or modified phenolic resin, formed by a condensation reaction between phenol and formaldehyde [54]. They are usually mixed with various rubbers [55]. Because of their affordability; high specific strength; good mix of thermal, mechanical and tribological qualities and ease of handling, phenolic resins have been almost universally employed as binders in friction materials for decades [56], notably after patents [57].

However, phenolic resins are sensitive to high temperature and humidity. The temperature reached during high-energy braking stress or an emergency stop can be high enough to degrade the resin. Above 450 °C, temperature of carbonization of phenolic resins, the decomposition process starts, decreasing the density of the friction material by increasing the porosity. This phenomenon can reduce structural integrity, resulting in a reduction in the friction coefficient, excessive wear and the release of noxious volatiles (NH₃ and HCHO) [58]. Lower temperatures (300–400 °C) can also result in serious concerns: when the resin glass transition temperature is exceeded, fade can occur, inducing a reduction in braking efficacy [50,59]. In order to obtain stable performance at high temperatures, phenolic resins are modified with a variety of compounds/processes to obtain, among others, condensed polynuclear aromatic (COPNA) resins, silicone-modified resins, cyanate ester resins, epoxy-modified resins, cashew-nut-shell-liquid (CNSL)-modified resins and rubber modified resins [44]. Bijwe et al. studied the properties of (i) straight phenolic resin, (ii) CNSL-modified resin, (iii) alkylbenzene-modified resin, (iv) NBR-modified resin and (v) linseed-oil-modified resin, finding that alkylbenzene-modified resin composites achieved the best performance in terms of strength, friction, fade and recovery, although wear resistance was low. Linseed-oil-based phenolic resin composites showed, instead, the opposite behavior [59]. Jang et al. (2000) investigated six different brake friction materials in terms of friction and wear behavior. Five constituents were used: phenolic resin (unmodified and modified resins in powder forms), aramid pulp, potassium titanate, barite and graphite. They found a good thermal stability for friction materials containing the modified resin. Furthermore, aramid-pulp-reinforced components had better friction stability than nonaramid-pulp-reinforced components. During the drag test, the wear rate was dependent on the friction level, porosity, heat resistance and mechanical strength of the binder resin [60]. Polybenzoxazine, a thermoset polymer, with mechanical, thermal and flame retarding properties similar to phenolic resin, was studied as possible friction material by Zeng et al. The addition of phenolic resin and rubber decreased the curing temperature and increased the glass transition temperature of polybenzoxazine resin. When braking temperatures were increased to 200 or 250 °C, there was a considerable rise in friction coefficients and wear rate values for all composites. As for polybenzoxazine, at 100 °C, the lowest friction coefficient was observed, while at 350 °C, the highest friction coefficient was observed. Concerning wear results, polybenzoxazine exhibited the lowest wear rate at 350 °C [61]. Although several works focused on a possible green alternative, phenolic/phenol-formaldehyde resin still remains the most studied and used.

2.2. Fiber

Fiber's role is to increase friction materials' mechanical properties and provide high thermal stability and structural integrity as well as adequate frictional value and stability. Fiber should also reduce shear and thermal stress, which can affect thermal fade and friction instability [31,62]. Fiber concentration and dimension are important for a good interaction with the matrix, since the lack of interfacial bonding between the constituent and the matrix can result in excessive wear. Fiber orientation also plays an important role, affecting wear resistance.

After the ban of asbestos, several types of other fibers were added to friction materials and their mechanical properties have been widely investigated. Commonly, commercial friction materials contain 5–25% (*v/v*) fiber ingredients [63] belonging to all the different materials classes (metallic, organic and inorganic) [64]. Addition of organic–inorganic and inorganic–inorganic fiber combinations appeared the most significant in enhancing various characteristics of brake friction materials [65]. Qu et al. studied the effect of steel fiber orientation with respect to sliding direction on frictional properties, observing a better wear resistance and a fair friction coefficient when parallel fibers were employed [66]. As for the fiber dimension, Oztürk et al. investigated the effects of resin type (phenolic resin, cashew-nut-shell-liquid-modified resin and melamine resin) and lapinus fiber length (150 ± 25, 300 ± 50 and 650 ± 150 μm) on mechanical and tribological properties. The

authors found a positive correlation between the fiber length and the wear resistance of the composites. Furthermore, the friction coefficient was strongly correlated with the composites' wear resistance [67]. Table 3 shows the main fibers utilized in friction materials and their principal features.

A mix of two or more different types of fibers is normally used, with the purpose of endowing friction materials with lower cost and higher mechanical and physical properties [68]. Using aramid pulps and potassium titanate whiskers as reinforcing fibers, for example, a synergistic behavior in wear resistance and friction stability was found [63]. Due to the carcinogenicity of titanate whiskers, granular and platelet shapes were also studied as potential substitutes, considering both potassium and potassium/magnesium as cations. Platelets of magnesium/potassium titanates were found promising as reinforcing materials, behaving as mild solid lubricants and increasing the hardness of the organic matrix [69].

Patnaik et al. measured the physical, mechanical and tribological properties of friction materials made of a ternary mix including potassium titanate whiskers, aluminosilicate ceramic fibers, and aramid fibers. Composites with higher content of ceramic whisker fiber (13.75% weight each) in conjunction with less aramid fiber (2.5 wt%) had promising friction coefficients and considerably lower fading propensities [70].

Wollastonite, a natural mineral, was used in the form of powder and fiber as a potential asbestos substitute, and a good performance in terms of wear and friction fluctuation was observed [71].

Because of their unique features and functions, such as friction stability, wear resistance, heat dissipation and noise dampening, copper and copper alloys have been widely employed as fiber materials. Moreover, copper has a fundamental role in friction materials since it helps in nanocrystalline tribofilm formation, which is responsible for smooth sliding conditions [32]. The need of substituting copper fibers due to environmental regulations has prompted efforts in finding alternative materials. Aranganathan and Bijwe, who categorized copper as a filler, substituted it with a patented special-grade graphite (C-Therm 011) in brake friction material formulation. An increase in thermal conductivity with increased graphite weight percentage was observed [72].

Table 3. Principal fibers employed in friction materials.

Fibrous Material		Advantage	Drawback
Metallic	Steel	<ul style="list-style-type: none"> - Gives good wear resistance - Maintains friction effectiveness at high temperatures (fade resistance with fast recovery) [73]. 	<ul style="list-style-type: none"> - Excessive brake disc/brake wear is possible [73]
	Copper and copper alloy	<ul style="list-style-type: none"> - Supports the level of the (COF) at elevated temperatures - High thermal conductivity - Stability in friction, i.e., a low sensibility of friction towards pressure and speed [74] 	<ul style="list-style-type: none"> - High environmental impact
	Brass	<ul style="list-style-type: none"> - Good plasticity - Enhances heat dissipation [50] 	<ul style="list-style-type: none"> - Poor wear performance [50]
Organic	Kevlar	<ul style="list-style-type: none"> - Good stiffness - High thermal stability, regular friction force and wear resistance [75] 	<ul style="list-style-type: none"> - High cost - COF reduction

Table 3. Cont.

Fibrous Material	Advantage	Drawback	
Inorganic	Wollastonite	- High thermal resilience - Stabilizes friction coefficient [76]	- Weak toxic [77]
	Potassium titanate	- Thermal stability at elevated temperatures due to higher melting point (1250–1310 °C) [63]	- Acicular whiskers could be classified as carcinogens [30]
	Glass	- Excellent heat and impact resistance - High melting point [78]	- Noise generation - Brittleness - Can cause for excessive wear of friction materials [50]
	Carbon fiber	- High strength - High elastic modulus - Stable chemical properties and resistance to carbonization [79]	- Costly [80]

2.3. Friction Modifiers

Friction modifiers are employed for inducing the proper friction coefficient and wear resistance. They are classified as abrasives and solid lubricants. The former improves wear resistance of friction material and increases the friction coefficient, while the latter reduces the friction coefficient level and stabilizes it over a wide range of temperatures, forming a friction film at the pad–disc interface. Lubricants can also protect the rotor surface by producing a thin coating at high temperatures, reducing noise and vibrations.

Abrasive particles, along with solid lubricants, play a crucial role in brake performance. Indeed, the lubricant and abrasive amount are factors of paramount importance: a high lubricant quantity can weaken the composite, whereas an excess of abrasives may provoke abrasion (two-body and three-body), causing high friction coefficient variation. Usually, the amount of abrasives is up to 10%, while that of lubricants ranges between 5 and 29% [81].

Abrasives in commercial friction materials are hard particles which usually have a Mohs hardness ranging from 5 to 9, and the most commonly used are reported in Table 4.

Table 4. Principal friction modifiers employed in friction materials.

Abrasive	Zircon, zirconium silicate, quartz, alumina, zirconia, silicon carbide, chromium oxide, silica, mullite.	[82–85]
Lubricant	Antimony trisulphide, graphite, molybdenum disulphide, tin sulphide, petroleum coke, lead sulphide.	[86,87]

The abrasive choice depends on the other constituents and on the type of friction materials. They are selected based on shape, size, hardness and fracture toughness. Wear resistance and aggression against counter discs are other significant attributes [88]. Quartz and its polymorphs were generally used in friction materials as abrasives, but their use was limited because crystalline silica, inhaled in the form of quartz or cristobalite from occupational sources, was classified as carcinogenic to humans (Group 1) by the IARC [89]. Moreover, the IARC classified SiC in the form of fiber as a potentially cancerogenic material [90].

Lubricants protect the components from wear, creating a friction layer and providing a stable friction coefficient for a wide range of environmental conditions and stress conditions. Furthermore, lubricants must decrease noise and vibration at the friction contact caused by stick-slip. Because each lubricant has a distinct working temperature, friction materials frequently incorporate two or more solid lubricants to ensure friction stability across a broad temperature range [86].

The most extensively used solid lubricant is graphite, which is able to build a lubricant layer on the counterface, significantly reducing the friction coefficient. Kchaou et al. studied

the effect of graphite forms (thermally pure vein graphite, thermally pure flake graphite and purified expandable graphite) on friction material performance. The use of an expandable graphite composite resulted in enhanced thermal stability, superior fade resistance and decreased wear rate [91]. The lubricant effect of graphite and, in general, of carbon-based materials, was found to be affected by particle size, shape and density. Indeed, a study on six carbon materials, four of which consisted of graphite, showed that the lower the size and aspect ratio, the lower the friction coefficient. High density resulted in a stable and homogeneous tribolayer at the interface, reducing the COF. Finally, the graphite structure also played an important role: indeed, a higher number of overlapped aromatic planes appeared more prone to produce a thick and stable tribofilm, lowering the COF [48]. Rajan et al. compared tribological performance of graphene in phenolic-based friction composite with a sample filled with graphite. Results indicated that graphene gives high friction stability, friction-fade and friction-recovery performance [92].

Antimony oxide (Sb_2O_3) and stibnite (Sb_2S_3), both of which rapidly degrade to stable oxide forms during brake wear, are also utilized as lubricants in friction materials. Though antimony is considered a potential cancerogenic element, few alternatives can be found in literature. Tin sulphides are the most promising candidates for antimony substitution in friction material composition [93]. The effects of zirconium silicate ($ZrSiO_4$) and antimony trisulphide on the friction characteristics were investigated, finding that Sb_2S_3 improved the friction stability and $ZrSiO_4$ intensified the torque variation during brake applications [83].

2.4. Filler

Fillers are defined as materials with a minimum impact on friction performance. Two categories of fillers are used: inert and functional. The first is used to merely fill space and to lower manufacturing and product costs. The second type is principally used for a precise purpose, such as thermal resistance or to achieve homogeneous mixing. In terms of composition, fillers are subdivided into organic and inorganic. The type of friction material to be utilized as well as the other ingredients determine the filler to be used. Table 5 summarizes the principal organic and inorganic fillers.

Table 5. Main fillers used as constituents of friction materials.

Name	Role (Space/Functional)	Advantages	Drawback
INORGANIC			
Vermiculite	Functional	<ul style="list-style-type: none"> - Low density - Low hardness - Good thermal stability [94,95] 	<ul style="list-style-type: none"> - Low heat resistance (except when exfoliated)
Barium sulphate	Space	<ul style="list-style-type: none"> - Heat stability - Reduction in material cost [96] 	<ul style="list-style-type: none"> - Large frictional oscillations [95]
Mica	Functional	<ul style="list-style-type: none"> - Noise suppressors [97] 	-
Molybdenum trioxide	Functional	<ul style="list-style-type: none"> - Suppresses low-frequency brake noise - Gives heat stability for the material [98] 	-
Calcium carbonate	Space	<ul style="list-style-type: none"> - Low density [50] 	-
Hexagonal boron nitride (h-BN)	Functional	<ul style="list-style-type: none"> - At high temperatures, it is chemically and thermally stable - High thermal conductivity [99]. 	-
ORGANIC			
Cashew friction dust	Functional	<ul style="list-style-type: none"> - Reduces fluctuations in friction coefficients [100] 	-
Rubber	Functional	<ul style="list-style-type: none"> - Superior viscoelastic characteristics and brake noise reduction [101] 	<ul style="list-style-type: none"> - Affected by the vulcanization process [102]

2.4.1. Inorganic Filler

Vermiculite is made up of two silica tetrahedral sheets and has a lamellar structure. Due to its weak cohesive force between interlayers, homogeneous mixing is achieved [95]. Vermiculite can be exfoliated when heated rapidly to high temperatures. When exfoliated, vermiculite, a mineral filler with a stacked-layer morphology, can be utilized up to 30–50 wt% in friction composites and is known to improve friction material stability, durability and resilience to high temperatures [103,104].

Barium sulphate, considered a low-cost and nonhazardous raw material, turns into barium sulphide due to a reaction between carbon from phenolic resin with the formation of carbon dioxide. Kumar claimed that barium sulphide fills brake disc interstitial voids and creates a film on the disc surface, protecting the rotor surface from wear [50].

Calcium carbonate is a less expensive alternative to barium sulphate.

Mica is another frequent filler. Indeed, due to its plane-net-shape structure, it can suppress low-frequency noise. Nevertheless, because of low interlayer strength, mica can provoke friction materials' interlayer splitting [54].

Calcium sulphate (CaSO_4) whiskers can be also used as fillers due to their highly ordered crystal structure, endowing CaSO_4 with high thermal stability. Less wear was detected using CaSO_4 whiskers as a functional filler and a composite, with 10% CaSO_4 whiskers displaying the most stable COF, even at high sliding speeds [105].

Kosbe et al. studied the physical properties and friction performance of friction materials' varying weight percentages of hexagonal boron nitride (h-BN) as a functional filler while the wt% of barite was decreasing. Results showed an enhanced thermal conductivity from 0.86 W/mK to 1.40 W/mK with an increasing h-BN percentage. Furthermore, the composite with the most h-BN content showed the lowest friction fluctuations and a high coefficient of friction [99].

Many other fillers are incorporated into friction materials, such as alkali metal titanates, commonly used to stabilize the friction coefficient.

2.4.2. Organic Filler

Rubber is a common ingredient for friction materials. Among different rubbers, nitrile butadiene (NBR), a copolymer of synthetic rubber based on acrylonitrile (ACN) and butadiene, is used because of excellent chemical stability and vibration absorption [106]. The vulcanization process, which is commonly performed using sulphur- or peroxide-based solutions, is responsible for the majority of the physical qualities of rubber [107]. The principal role of rubber is the reduction in brake noises because of its superior viscoelastic characteristics.

Cashew dust, a substance formed by polymerizing cashew nut shell liquid with a curing agent, is also used for the same reason [108].

3. Green Constituents as Alternatives for Friction Materials

Over the years, many changes in the ingredients of friction material formulation have occurred. These changes arise from two major factors: improvement in brake performance and the need to meet legal requirements for environmental protection. In order to explore research trends on the study of constituent substitution for reducing environmental impact, a science mapping analysis was conducted.

The study was conducted using VOSviewer software version 1.6.16, consulting the SCOPUS database from the years 1980, the date of the asbestos ban, to 2021, using as a search option "all fields" with the following word combinations (the number of found publications is reported inside brackets): "brake pad (friction materials)"—"eco-friendly" (329); "brake pad (friction materials)"—"natural fiber" (316); "brake pads (friction materials)"—"green material" (33); "brake pads (friction materials)"—"agricultural waste" (50). Figure 6 reports a mapping visualization of the research of publications of "brake pad (friction materials)"—"natural fiber". The following parameters were used to create the map: minimum numbers of occurrence keywords: 10; clustering resolution: 1.

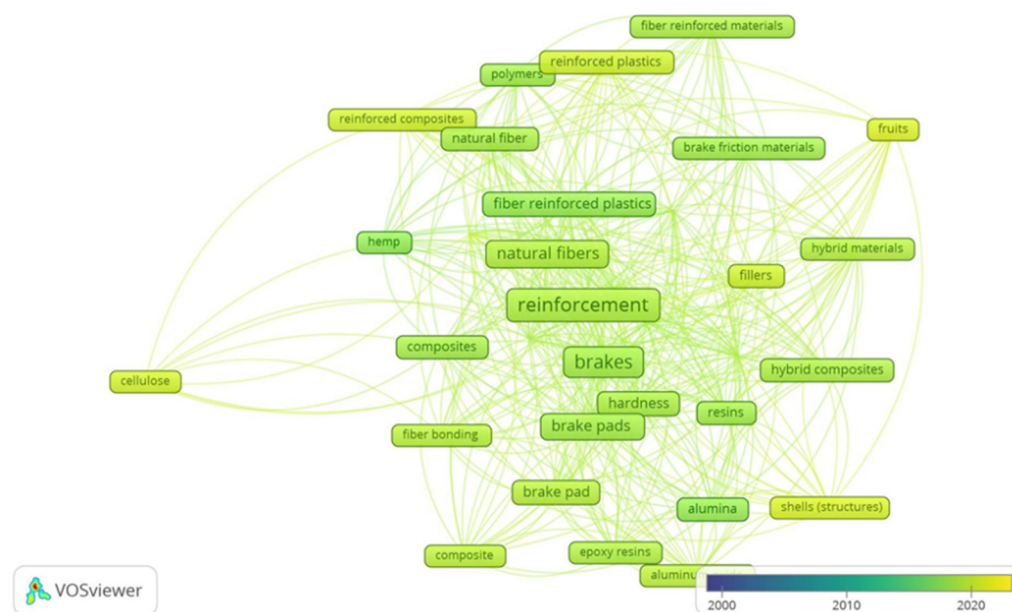


Figure 6. Representation of the relations between different keywords emerging from the analysis of the terms “brake pad (friction materials)” and “natural fiber”.

The VOSviewer results showed 2249 keywords. In order to make the connections clearer, the terms related to friction material characterization, for example, friction, wear and scanning electron microscopy, were eliminated and only the terms related to materials and friction materials were considered.

Each frame, marked with a different color, represents a term, whose size (diameter) indicates the number of publications where the term (title, abstract or keyword) occurred. The greater the frame, the higher the frequency of that keyword in the sample.

Furthermore, the closer the frames are to each other, the more often the terms occurred together, and the thicker the line connecting them, the more significant the co-occurrence.

Based on Figure 6, the most frequent keywords that occurred were “reinforcement” and, obviously, “friction materials (brake pads)”. Among the alternative materials, “natural fiber” showed the highest occurrence (67), while materials such as “cellulose” (11), “fruits” (10) and “hemp” (13) had a much lower occurrence.

Even though the analysis spanned the period 1980–2021, Figure 6 shows the trend from 2000 to present because in the previous period, very few works on this subject were found. It can be noticed that most of the works concerning natural fibers were published after 2010 and those related to cellulose and hemp are even more recent.

3.1. Green Binders

Few papers reporting about green or ecofriendly binders are present in literature. This fact can be related to the difficulties in finding good alternatives to phenolic resin in terms of mechanical and tribological properties.

Pizzi et al. (2016) studied the possibility of preparing friction materials using bio-based resin composed of tannins–furanic resin embedding inorganic abrasive particles. This green alternative showed excellent braking performance, comparable with commercial friction materials [109].

In the last decades of the 20th century, lignin was considered a promising alternative for phenol in phenol–formaldehyde (PF) resin synthesis, due to its structural similarity with PF.

Lignin is an integral part of the secondary cell walls of plants. Depending on wood type, isolation method and plant source, lignin structure can vary. Due to its properties, high amounts of lignin in wood can provide raw material with good durability [110]. Nehez (1997) proposed to apply organosolv lignin to friction materials in order to partially reduce

the amount of phenolic resins [111]. A friction material with a lignin–phenol resin as a binder was patented in 2012 [112].

Three different types of lignin (soda lignin and sulphuric acid lignin—SAL and heat-treated) were studied, using cashew nut shell liquid as a filler [113]. Moreover, lignin was also used as a filler in association with phenol–formaldehyde resin as a binder. When lignin was applied as a binder, only soda lignin showed a moderate advantage in terms of enhancing impact strength and regulating the friction coefficient. Instead, when lignin was used as a filler, heat-treated SAL lignin showed the best properties. The most suitable composition was with 10% lignin in the friction materials. Figure 7 shows friction coefficients, wear resistance, impact strength and thickness swelling in water of friction materials with lignin added as a binder [113].

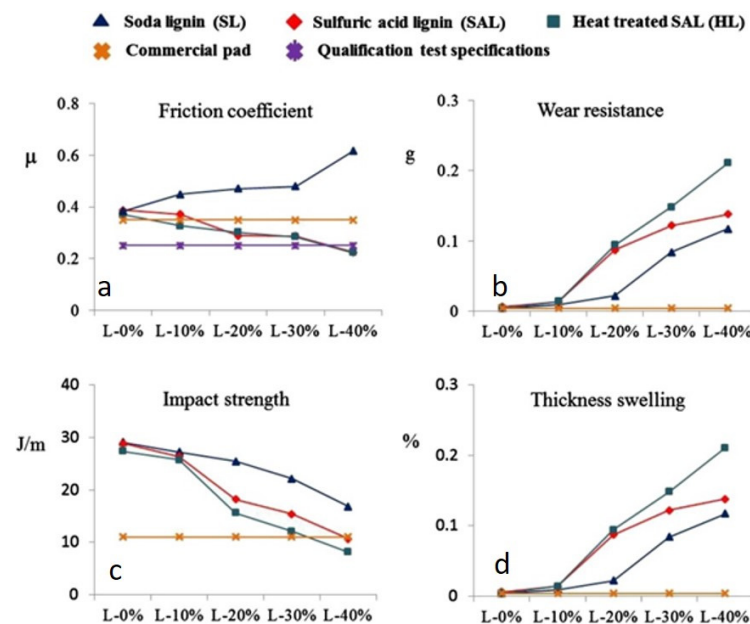


Figure 7. The effect of friction materials containing different amounts of lignin as a binder on: (a) friction coefficient, (b) wear resistance, (c) impact strength and (d) thickness swelling in water (courtesy of Park et al. [113]).

Another material that has showed interesting properties to potentially substitute nongreen binders is geopolymer. This inorganic compound has a chemical composition quite similar to zeolite, with an amount of amorphous content depending on precursor and synthesis conditions. The mechanical properties of the geopolymers are similar to those of cements and organic resins and they have a higher heat resistance than organic binders. Lee et al. investigated the wear and friction performance of a composite consisting of an environmentally friendly geopolymer and natural hemp fibers as a fraction replacement of phenolic resin and synthetic Kevlar fibers, respectively, with the goal of substituting Cu and Sb. Dyno analyses revealed a higher friction level of the Cu-free samples compared to the baseline material (formed with 9.5 wt% phenolic resin, 3.4 wt% Kevlar fiber, 8.0 wt% of copper and 3.6 wt% of antimony trisulfide). Similarly, a higher value was observed in terms of wear resistance for the modified samples. A stable third-body layer was formed on the unmodified composite, while the friction layer for the green formulation was insufficient [114].

It can be thus concluded that, at the moment, green substitutes for phenolic resins show promising results, as proved by literature and industrial patents. As for the last, in 2015, ITT ITALIA SRL, a company specializing in the production of brake pads, patented friction materials using geopolymer as a binder [115]. However, additional research is still needed to achieve a complete substitution of phenolic resins.

3.2. Fibers

Natural fibers are considered a prospective alternative to synthetic fibers in friction materials because of low cost, low environmental impact, full biodegradability, abundance and renewability. Moreover, using natural fiber, lightweight composites can be produced due to their lower density (1.2–1.6 g/cm³) compared to other materials, e.g., glass fiber (2.4 g/cm³) [116]. However, even though different natural fibers were tested, most of them presented flaws such as low wettability, lack of integration with certain polymeric matrices and excessive moisture absorption [117]. Moreover, fiber strength, modulus, fiber length, orientation and fiber–matrix interfacial bond strength may influence mechanical properties of composites. A good interfacial bond is required to transmit stress from matrix to fiber. For this reason, chemical treatments are necessary [118], and the most common are utilizing NaOH, benzoyl chloride, silane, HCl, plasma and KOH [119].

As an example, Figure 8 shows the effect of the chemical treatments (NaOH-treated fiber and NaOH+acrylic-acid-treated fiber) on bagasse fiber. It was found that both chemical treatments destroyed the cellular structure of the bagasse fiber, reducing its void content [120].

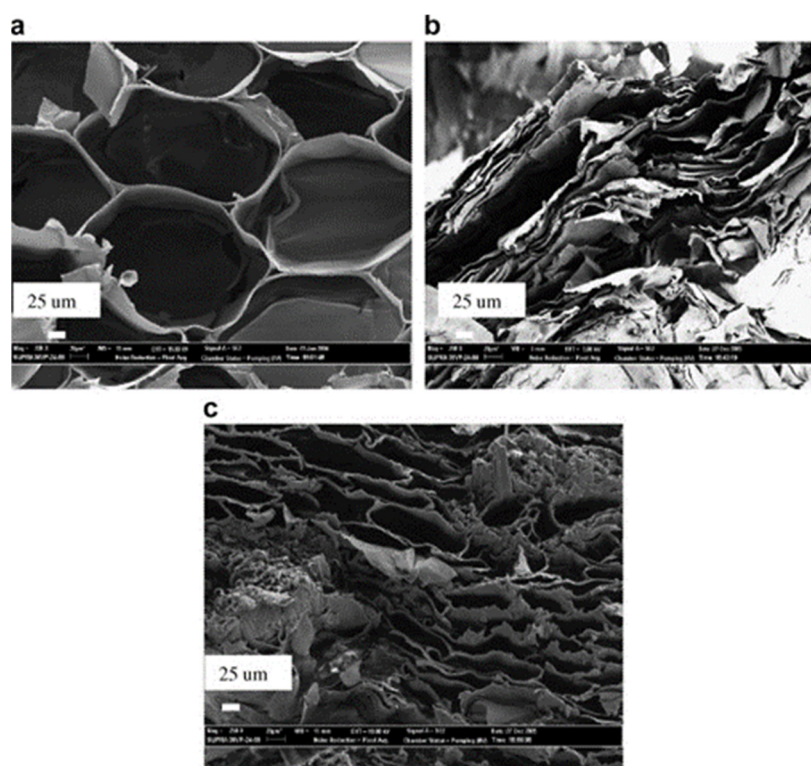


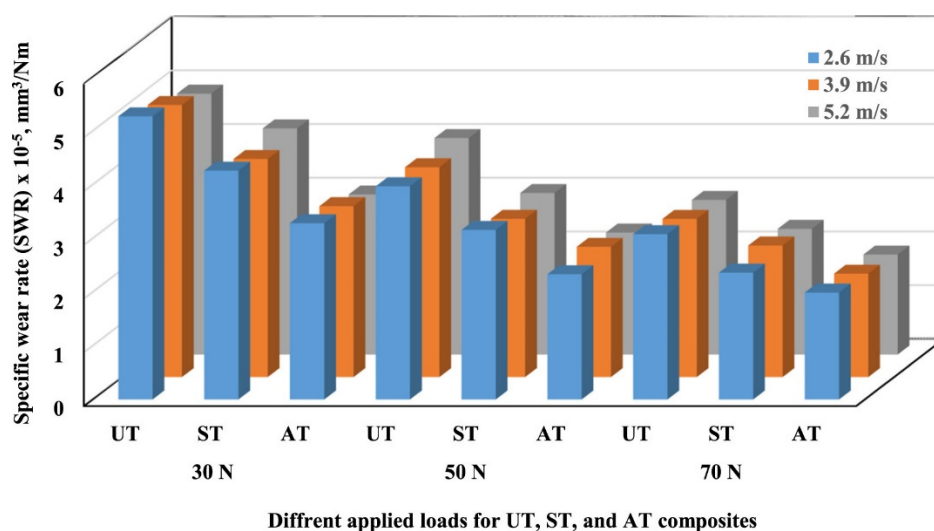
Figure 8. Effect of the fiber treatment on the structure of bagasse fibers: (a) bare bagasse fiber, (b) NaOH-treated fiber and (c) NaOH+acrylic-acid-treated bagasse fiber (courtesy of Vilay et al. [120]).

Another crucial aspect that can influence natural fiber properties is thermal stability. Indeed, degradation of natural fibers leads to a deterioration of their mechanical properties. Fibers show different temperatures of decomposition. For example, sisal thermal degradation range temperature is between 290 and 490 °C, kenaf fibers degrade at 297–434 °C, while bamboo fibers degrade at 250–420 °C [121–123]. Table 6 highlights mechanical properties and chemical treatments utilized for fiber optimization.

Table 6. Mechanical properties and chemical treatments of ecofriendly fibers from plants.

Plant	Elongation (%)	Density (g/cm ³)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Most Used Chemical Treatment	References
Sugar palm	12.8	1.48	276	3.85	Alkaline treatment	[124]
Palm kernel	-	-	-	-	Sodium hydroxide	[125]
Areca	1.47–1.48	1.05–1.25	35.68	-	Alkaline treatment	[118,126,127]
Banana	10.35	1.35	529–914	-	Alkaline	[128–131]
Bagasse	1	1.3	222–290	-	Alkaline + Acrylic acid (AA)	[120,132,133]
Corn stalks	1.90–2.30	0.21–0.38	33.40–34.80	-	Alkaline treatment	[134,135]
Jute	1.5–1.8	1.3	393–773	10–30	Alkaline + HCl; HCHO and C ₆ H ₆ + NaOH + H ₂ SO ₄	[133,136,137]
Bamboo	1.4	1.1	500	-	Alkaline	[136]
Kenaf	2.5–3.5	1.2	223–930	40	Alkaline	[138,139]
Abaca	2.9	1.5	430–813	-	NaOH + H ₂ SO ₄	[131,140]
Flax	2.7–3.2	1.5	345–1035	-	NaOH + HCl	[131,136,141,142]
Coconut	15–51.4	1.15–1.46	95–230	-	-	[133]
Pineapple	14.5	0.8–1.6	400–627	-	Alkaline	[143,144]
Sisal	2.0–7.0	1.33–1.5	363–700	9.8–38	NaOH–Ammonia base liquor+ H ₂ SiO ₃ , Na ₂ B ₄ O ₇ –HCHO–NaHSiO ₃	[78,139]

Rashid et al. studied the influence of sugar palm fiber as a reinforcement. Wear and friction tests were conducted on bare, alkali-treated and seawater-treated composites. Fiber–matrix interface bonding was enhanced as a consequence of alkali treatment, resulting in a higher wear performance. Reduction in the friction coefficient was also observed. Figure 9 shows specific wear rate (SWR) of bare and treated sugar palm fiber, while Figure 10 represents SEM images of untreated (UT), seawater-treated (ST) and alkali-treated (AT) composites at 30 and 70 N loads at 2.6 m/s sliding speed and 5000 m sliding distance. SEM micrographs show the good matrix–fiber bonding promoted by alkali treatment, resulting in the observed higher wear resistance [124].

**Figure 9.** Specific wear rate (SWR) of bare and treated sugar palm fiber (courtesy of Rashid [124]).

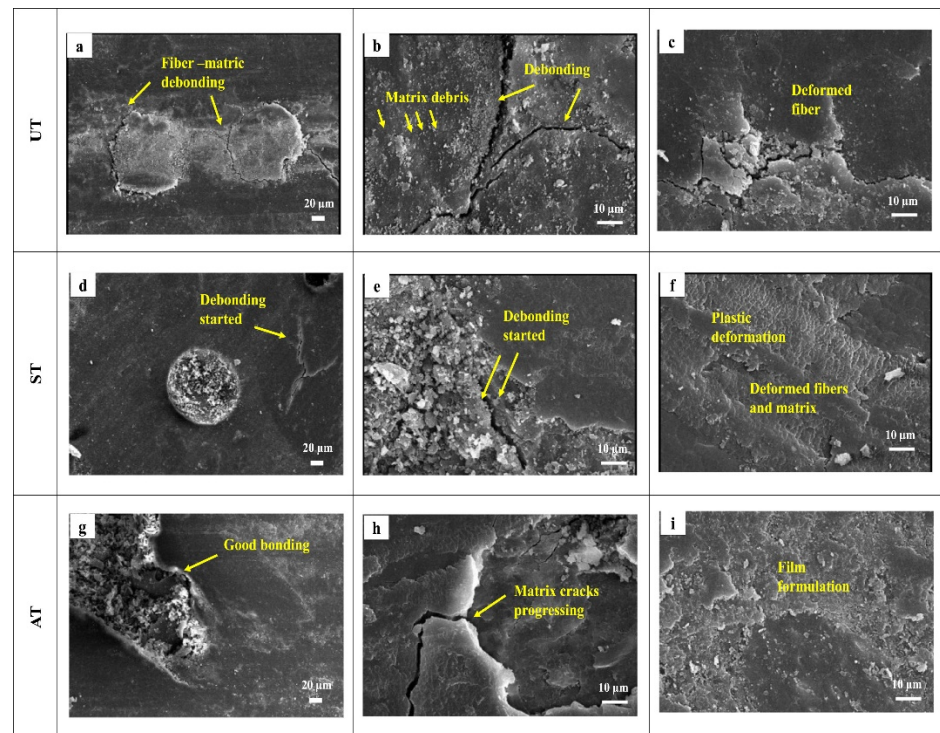


Figure 10. SEM micrographs of (a–c) UT; (d–f) ST and (g–i) AT composites at 30 and 70 N loads at 2.6 m/s sliding speed and 5000 m sliding distance (courtesy of Rashid [124]).

Berdard et al. (2018) investigated the impact of palm fiber on the tribological performance of composite materials. It was found that an increase in palm fiber content led to high hardness and 8% of palm fiber content in friction materials resulted in good tribological performances [145]. Different composites including palm kernel fibers as reinforcement resulted in a hardness decrease with increasing palm fiber content as a consequence of the porosity induced in the composites. Moreover, the palm fiber content decreased the friction coefficient [146].

Palm kernel fibers were also studied by Ikpambese et al. Fibers treated with a caustic soda solution and incorporated in an epoxy resin binder exhibited encouraging results and were considered a viable alternative in friction material manufacturing [125]. A composite incorporating palm kernel shell fibers in epoxy resin using a compression molding technique and adding aluminum oxide, calcium carbonate and carbon showed that with increasing fiber content, hardness and compression strength decreased, probably due to the weak bonding between fiber and resin. In addition, flame resistance dropped as the amount of palm kernel shell fiber increased. However, an increase in wear resistance was observed with increasing fiber content [147].

Other fibers potentially alternative to synthetic fibers are obtained from areca palms and kenaf.

Areca as a friction material constituent was studied by Krishnan et al., who found that a fiber content of 5%w/w was optimal for wear resistance [148].

Employing a weighted decision matrix (WDM) technique, Abdollah et al. investigated the feasibility of using kenaf fiber as a friction material ingredient. The method, which considered the impact on the environment and human health, indicated kenaf fiber as the most suitable material because it passed all the design requirements [149]. However, a friction material made of phenol–formaldehyde resin with three different amounts of kenaf fiber induced decreases in density and hardness when increasing kenaf content [150].

Banana is also considered a valid fiber substitute. Different phenolic resin samples reinforced with lignocellulosic banana fiber at varying resin and banana percentages showed the best tribological results when 7% of banana fiber and 28% of phenolic resin were

mixed [128]. Banana fiber together with coconut fiber, rice husk, graphite powder and aluminum oxide were embedded in epoxy resin, resulting in a wear rate lower than that of common commercial friction materials at a speed of 350 rpm [151]. Aigbodion et al. investigated morphological, physical, mechanical and wear properties of friction materials with uncarbonized and carbonized banana peel particles embedded in phenolic resin. Interestingly, suitable bonding was obtained with uncarbonized banana peel particles. Moreover, after increasing resin quantity, compressive strength, hardness and specific gravity increased, while wear rate decreased [152]. The mechanical and thermal characteristics of banana and ramie fibers treated with Na_2CO_3 were the best for a composite reinforced with 10% banana fiber [153].

Lower wear was achieved using 25% of candlenut shells and 15% of coconut shells in friction materials [154].

Among fibers derived from common crops, bagasse provided better properties with finer sieve size and using 30% bagasse [155].

Friction materials reinforced with corn stalk fiber (CF) embedded in NBR-modified phenolic resin prepared by wet granulation improved tribological and morphological properties, giving the possibility of reducing resin content [156]. Adding corn stalk fibers to friction composites improved the friction coefficients and wear rates [134]. Fu et al. developed an ecofriendly friction material using flax fibers together with mineral basalt and wollastonite as reinforcements embedded in cardanol-based benzoxazine-toughened phenolic resin, with natural graphite as a solid lubricant, zircon as an abrasive and vermiculite and barite as functional and space fillers. Flax fibers helped to stabilize friction coefficients and improve wear rates at high temperatures [142].

Bijwe et al. evaluated the influence of aramid, PAN (poly-acrylo-nitrile), carbon and cellulose on the fade and recovery of friction composites. Higher fade resistance was observed with adding carbon fiber, while composite based on cellulose fiber showed the lowest fade resistance, probably due to its low degradation temperature. Moreover, composites containing aramid and cellulose showed the highest and the lowest wear resistances, respectively [157].

Pineapple fiber, widely used also in different industrial sectors, can be a sustainable alternative for the automotive industry. Friction composites with increasing amounts of pineapple and Kevlar (5–10 wt%) lowered composite density, hardness and ash content. As for wear behavior, it was observed that increasing the amount of pineapple fibers in the composites increased the specific wear rate, while increasing the amount of Kevlar fibers enhanced it. The introduction of fewer fibers changed the nature of the transfer film and its adhesion to the counterface [143].

Embedding jute fibers with different (5 mm, 10 mm, 15 mm and 20 mm) dumbbell-shaped spacing in friction materials made of NBR induced strong physical and mechanical properties. Higher fluctuation in friction coefficients was observed using dumbbell-shaped jute fibers compared with straight fibers. As for wear resistance, friction material with dumbbell-shaped spacing of 15 mm was the highest except at 200–250 °C [137]. When epoxy composites were reinforced with different percentages of short jute fiber, it was demonstrated that fiber loading, sliding velocity, applied load and abrasive size affected wear rate. Composites with a fiber loading of 36 wt% displayed the lowest specific wear rate [158].

Lui et al. investigated abaca fibers, which are often used in a variety of applications due to their high tensile strength. Changing the length of an abaca fiber had no effect on density or hardness, but it influenced impact strength. An improvement in wear resistance was obtained with abaca short fibers (lengths of 5 mm and 10 mm) [140].

Both air plasma surface treatment of bamboo fiber and graphite had a positive impact on friction and wear of bamboo/polyimide composites [159].

Due to its good mechanical properties, sisal fiber is commonly used in different fields [116]. Xu et al. (2007) studied the wear and friction parameters of brake composites

with various sisal fiber contents. The best friction and wear properties were obtained using resin and sisal fiber in the proportion of 3:4 [78].

Microcellulose modified with 3-aminopropyltriethoxy-silane was embedded in phenolic resin together with barium sulphate, aluminum oxide and graphite, with the aim to study mechanical and tribological properties. The researchers discovered that friction material containing 10wt% of microcellulose fiber performed similarly to a commercial friction material [160]. Similar tribological behavior was observed when comparing the physical and mechanical performance of cellulose fiber and thermographite and friction material with copper fiber. However, friction material with Cu exhibited higher thermal stability [161].

Several other natural fibers from uncommon plants have been tested in order to replace synthetic fibers. Krishnan et al. compared friction materials with embedded bare and silane-treated *Demostachya bipinnata*, a perennial grass, obtaining better tribological results using the treated fiber [162]. Embedded fibers of *Cyperus pangorei*, a sedge species native to Asia, treated with benzoyl chloride into friction material showed good friction and higher wear resistance with respect to a similar composite containing the untreated fibers [163]. Bajpai et al. incorporated nettle, *Grewia optiva* and sisal into PLA polymer, which resulted in an improvement of the composite wear resistance [164]. Fibers of *Coccinia indica*, a tropical vine, embedded in epoxy resin as potential reinforcement for friction materials induced good wear when treated with silane in comparison to sodium hydroxide surface treatments [165]. Akıncioğlu et al. used boron oxide and hazelnut shell powders as ecofriendly alternatives to chalcopyrite and petroleum coke. Friction materials made of phenol resin with embedded hazelnut shells and boron oxide showed similar hardness with respect to a commercial sample. Moreover, hazelnut dust induced the highest friction coefficient, probably due to the observed enhancement in hardness of friction materials [166].

Because of comparable features, including heat resistance, hardness and good adhesive nature with the binder, basalt was considered as a potential fiber for friction materials. Basalt fibers are made from basalt rocks that have been melted. Basalt rocks can be finely split into little particles to the point where they can be made into fibers [167]. Moses et al. studied physical properties and wear behavior of basalt-fiber-reinforced friction materials, obtaining promising results [168]. Zhao et al. evaluated physicomachanical and tribological performance of the friction composites with different basalt fiber contents. The mechanical and tribological characteristics were enhanced by adding 15% basalt fiber [169]. The wear mechanism of phenolic resin with embedded flax and basalt fiber was studied using a pin-on-disc wear tester. Higher wear resistance was obtained using 6% of basalt fiber, probably due to good thermal characteristics and the bonding nature of basalt fibers [170]. When basalt fibers were used with alumina and shellfish powder, hardness of friction materials and wear resistance was higher than that of asbestos-based ones [171].

Grey relational analysis, a system theory based on an orthogonal array, and a fuzzy-based Taguchi approach for optimizing the multiresponse process were used to evaluate seashell embedded in epoxy resin with graphite as a friction modifier and aluminum oxide as an abrasive. Results indicated that curing time has a limited effect on the mechanical properties, while it significantly affected friction coefficients and wear rate [172].

Maleque et al. examined five different laboratory formulations made of different coir fiber contents together with silicon carbide as abrasive material, graphite as solid lubricant, zirconium oxide as a friction modifier. Adding 5% of coir fiber to the mix resulted in increased density, which was seen as encouraging in terms of physical and mechanical qualities [173].

As a result of the increasing drive to reduce environmental impact, some brake pads reinforced with natural fibers have been patented, mainly in China; examples of these are listed in Table 7.

Table 7. List of some brake pad patents with natural fiber.

Code	Title	Inventor	Reference
CN103436236A	Palm-fiber-reinforced environmentally friendly type brake pad and preparation method thereof	LI MEIFENG	[174]
CN103361031A	Brake pad for flax-fiber-reinforced environmentally friendly car and preparation method thereof	LI MEIFENG	[175]
CN104976258A	Environmentally friendly brake pad	HUANG XIAOSHUANG	[176]
CN103423345A	Automobile brake pad mixing with bamboo fibers	LI MEIFENG	[177]
CN106015400A	Hibiscus-Manihot-fiber-reinforced environmentally friendly brake pad and preparation method thereof	JIANG YIKUAN	[178]
CN106641049A	Method for preparing brake pad from basalt fiber	LI XIAOCHUAN	[179]

This literature overview demonstrates the potential of natural fibers, both plants and minerals (basalt) as green constituents of friction materials. In order to promote their wide diffusion, some issues still need to be faced. For example, the bonding strength between the fibers and the matrix in absence of treatments using chemicals with high environmental impact should be improved.

3.3. Friction Modifier

In the automotive industry, replacement of friction modifiers with environmentally friendly compounds should endow the final material with a stable friction coefficient and a decreased wear rate at diverse operating speeds, pressures, temperatures and climatic conditions. As mentioned in the previous section, the most common materials used as friction modifiers are: quartz, silica, alumina, silicon carbide, mullite, zircon, zirconium silicate, zirconia and chromium oxide as abrasives and tin sulphide, antimony trisulphide and graphite in different forms, such as natural, flake, synthetic and polarized, as solid lubricants [88]. Although some concerns about potential risks of copper and antimony lead to environmental regulations for limiting their use, most of the friction modifiers are considered safe. This is probably the reason why few works about ecofriendly substitutes can be found in literature. Some researchers studied colemanite and ulexite, two boron minerals, as friction composites. Boron is a fundamental element widely used in different sectors such as production of fiberglass and detergents. Boron minerals are not considered green substances like natural fibers, but they are utilized as sources for crop fertilization, and the WHO organization assumed boron safe for human health [180]. Indeed, a positive effect of borax, colemanite and ulexite was observed on human health through an oxidant effect and reducing the genotoxic effects induced by low quantity of heavy metals [181].

Physical and frictional characteristics of composites containing *Pinus brutia* cone dust and colemanite indicated they can be promising green constituents [182].

Adding ulexite to a composite improved tribological properties and braking performance: in particular, when ulexite amount increased, an increase in the friction coefficient was noticed, although wear enhancement was observed where ulexite was in the form of dust [183].

Ahlawat et al. utilized white ark shell powder, a natural sea waste, as an abrasive component and compared its performance with that of two commercial abrasives: quartz sand and CNSL powder. Grey cast iron volume loss was ranked as follows: quartz sand > CNSL powder > white ark shell powder [184]. Seashell was used also by Bretotean and coworkers, even though they categorized this material as a filler. Different composites

with embedded shell, metals, silicon carbide, graphite and hexamethylenetetramine in phenolic resin were compared. An increase in seashell quantity led to an increase in density, hardness, compressive strength and Young modulus. Values of friction coefficients were inside the recommended standard for small and medium automotive friction materials [185]. Walnut was used as a friction modifier by Akincioğlu et al. and the performance compared with a commercial Clio brake tip: different contents of walnut (3.5 and 7%) in the friction materials exhibited performance similar to commercial materials [186].

Periwinkle shell particles as abrasives were tested by Obot et al., showing that increasing concentration from 4 to 12 wt%. provoked a progressive increase in hardness and compressive strength while decreasing wear rate [187].

Periwinkle shell particles were also studied for their physical, mechanical and tribological properties within five sets of friction materials with varying periwinkle shell sieve size (710–125 µm). When particle size decreased, good interfacial bonding was observed, while the best overall properties were obtained adding periwinkle shell with particle size of 125 microns [188].

In conclusion, the addition of seashell in phenolic-resin-based composites results in friction materials with proper friction coefficients and enhanced mechanical properties. In addition, walnut appears as a promising green constituent because its addition in friction materials does not reduce overall performance. Periwinkle shell, too, can be considered as valuable additive when proper size is employed.

3.4. Fillers

Few works are found in literature in the case of fillers. A filler based on ground nut shells resulted in reducing friction material cost, but high friction coefficients compared with the traditional values were found [189].

The addition of 10% (wt) zeolite led to a constant and higher frictional coefficient and lower wear rate [190].

Chandradass et al. (2021) fabricated friction materials using agrowaste sugar cane bagasse ash as a filler in different proportions (0%, 5% and 10% weight), utilizing epoxy resin as a binder. Results indicated that the sample with 10% agro waste had high tensile and flexural strength. From a tribological standpoint, a higher friction coefficient was obtained adding 5% agro waste, while the sample containing 10% sugar cane bagasse ash showed the highest wear rate [191].

Rice husk, an agroindustrial waste product obtained from the outer shell of rice grains, induced better wear resistance than asbestos friction materials when a 20% filler carbonized in 100 mesh size particles was utilized [192]. Embedding 80 and 100 rice husk dust mesh in a friction material and evaluating hardness and impact resistance properties indicated that composites with smaller particle size and higher filler percentages resulted in better properties [193]. Multiwall carbon nanotube (MWCNT) increased friction and fade performance while decreasing wear performance. As far as nanoclay, an improvement of wear properties and a drop in friction performance was observed [194].

As concluding remarks, zeolite and rice husk seem the most promising green fillers, since they induce higher wear resistance in friction materials.

4. Friction Materials from Industrial Waste

Researchers have been prompted to produce new solutions utilizing waste resources as a result of increasing environmental concern and circular economy. Slags, fly ashes, dusts and sludge are only some of the by-products and wastes created by the metallurgical industry. In the automotive sector, one of the main waste materials is tire. Tire rubber waste particles have been explored as useful additives to nonasbestos organic friction material compounds. Limited tire waste rubber led to a high and constant coefficient of friction, low fade, low frictional variability and the minimum variations during sliding, while, when employing a high content of tire, the most recovery, the least wear and the lowest disc temperature rise were found [195].

Basalt and aramid recycled fibers, used as reinforcements, enhanced mechanical and thermal properties when increasing content from 5 to 25 wt% [196].

Singh et al. investigated the physical, mechanical and tribological characteristics of cement kiln dust, a significant waste product in the cement industry, when it was filled with various resins (straight phenolic, cashew-nut-shell-liquid-modified, linseed-oil-modified and alkyl-benzene-modified). Results showed that a combination of cement kiln dust and cashew-nut-shell-liquid/linseed-oil-modified resin enhanced both recovery and wear performance and reduced variability in friction [197].

Fly ash, produced during the combustion of coal for energy production, is an industrial by-product considered an environmental pollutant. Most fly ashes are made of silica, alumina, calcium sulphate and unburnt carbon [198]. Friction material composites containing various mixtures of zinc borate and fly ash (i.e., 0–5 wt% zinc borate and 65–60 wt% fly ash) had superior friction stability. Decreased wear rate was obtained by increasing zinc borate and decreasing fly ash contents [199]. Satapathy et al. studied mechanical and tribological behavior of composites made by different combinations of fly ash and mineral rock fiber. Better mechanical properties were obtained for composites with low fly ash and high lapinus fiber, while higher wear resistance was obtained with high fly ash and low lapinus fiber [200].

Slag fibers of 0.5–5.5 microns in diameter were produced by fiber blowing equipment from water-quenched slags. Slag fiber, embedded in phenol–formaldehyde resin, led to an increase in friction coefficients and reduction in wear [201].

Slate, a metamorphic rock mineral, was used as a friction material component with the aim to reduce the environmental impact caused by its inadequate disposal. Varying slate percentage, the authors found that friction materials with 40% of slate and 35% of phenolic resin offered better performance compared to commercial friction materials [57].

Cenosphere, a fraction of coal fly ash, and barium sulphate as fillers were compared. Figure 11 shows the spherical morphology of cenosphere, which presented a hollow nature. Lower densities, higher wear resistance, enhanced recovery, lower disc temperature increase and fluctuation in the friction coefficient were observed with respect to the friction material composite with barium sulphate [202].

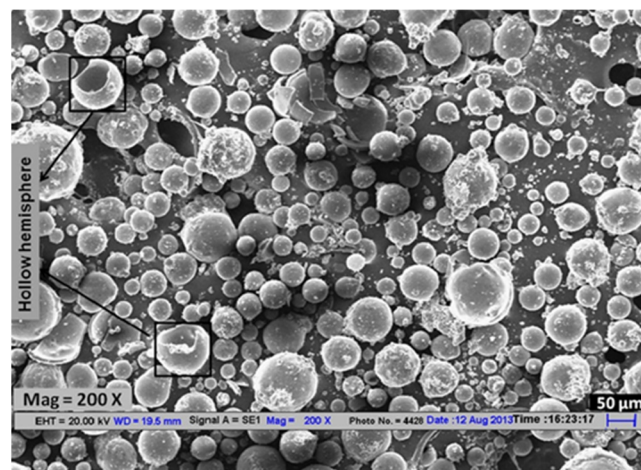


Figure 11. Cenosphere particles (courtesy of Tiwari et al. [202]).

In summary, some promising examples of waste from industry as constituents of brake pads have been individuated. Indeed, tire rubber, kiln dust, fly ash, slag fibers, slate and cenosphere were found suitable additives for friction materials, allowing for the preparation of composites fulfilling the proper requirements.

Finally, friction material waste could be also taken into consideration in view of a circular economy, as they cannot be degraded naturally, causing environmental pollution. It should be underlined that before they become completely worn out, rotor and friction

materials are usually exchanged with new ones: an automobile requires 16 spare sets of brake pads and four rotors throughout the course of its lifetime [203].

To address this issue, in recent years, many researchers have attempted to use friction material waste as mineral fillers in asphalt [204] or to add them to geopolymers [205].

5. Conclusions

The new environmental regulations have increased the demand for brake systems producing low-polluting compounds. Indeed, particulate matter in the nonexhaust category is mainly emitted by friction materials. With the aim to reduce toxic substances enclosed in brake pads, several attempts to replace them with natural fibers have been made in the last ten years. The main outcomes for each category of friction material constituents can be summarized as follows.

5.1. A: Binder

Phenolic resin is the most widely utilized form of the friction material matrix, owing to its inexpensive cost. Volatile organic compounds, such as formaldehyde, may be released during the manufacture of friction materials. Furthermore, high-temperature organic-based hazardous compounds can be produced during braking events.

Little research concerning the elimination of phenolic resin is present in literature. Most of the works are related to the improvement of phenolic resin mechanical properties and friction performance in fade and recovery conditions. As a possible substitute to phenolic resin, researchers try to use lignin, a phenolic polymer forming the plant cell wall. The advantages of using lignin as a binder are related to a more stable friction coefficient.

Geopolymers and bioresins are also considered. A comparable mechanical strength with traditional friction materials has been achieved using bioresin, while promising results in terms of general performance were obtained with geopolymers.

5.2. B: Fibers

Various natural fibers were evaluated and the majority of the studies demonstrated that environmentally benign materials had the potential to replace asbestos in friction material manufacturing. However, the intrinsic properties of natural fibers limit their use to certain applications. Indeed, they are less regular and uniform than the man-made fibers and present poor wettability and incompatibility with some polymeric matrices. Chemical treatments are necessary to improve mechanical properties, providing promising opportunities in the friction material market. Moreover, many studies have found a strong dependence of mechanical properties on both fiber orientation and fiber length.

It is difficult to establish which fibers could be the best candidates to be used for friction materials, as it is often difficult to compare properties among different published works. It could be inferred from the present literature study that the most promising natural fibers have been patented. From research on the EU Patent Office site, fibers of palm kernel, flax, agave and aloe can be identified as the most promising.

5.3. C: Friction Modifier

As for the binder, few papers on friction modifiers can be found in literature. Although some of the main friction modifiers used in friction material formulation cannot be considered completely green materials, they are nontoxic for humans and the environment. Some interesting papers dealing with two boron compounds, such as ulexite and colemanite, report promising results.

5.4. D: Filler

Rice husk, ground nut shell, periwinkle shell along with maize husk can be valid alternatives to conventional fillers. Moreover, it also emerged that unlike fibers, a chemical treatment is not necessary. Along with the use of natural products to replace synthetic products, there has been also an increase in the use of waste as a substitute. Indeed, tire

rubber, aramid recycled fibers and cement from the cement industry have been the subject of some research papers.

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Abbreviation

PM	Particulate matter
WHO	World Health Organization
IT	Interim targets
EPA	Environmental Protection Agency
USA-EPA	National Ambient Air Quality Standards (NAAQS)
BPWD	Brake pad wear debris
US EPA	United States Environmental Protection Agency
IARC	International Agency for Research on Cancer
LM	Low Metallic
SM	Semimetallic
NAO	Nonasbestos organic
PF	Phenolic resin
CVD	Cardiovascular diseases
BFM	Brake friction materials
BPW	Brake pads waste
CNSL	Cashew nut shell liquid
NBR	Nitrile butadiene
EPO	European Patent Office

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