Perspectives on Developing Green Composite Friction Materials as a Sustainable, Safe and Eco-Friendly Pathway for Automotive Applications

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Abstract. Composite friction materials are in use since the inception of motor vehicles and they have undergone numerous cycles of evolution in order to fit to market scenarios, vehicle requirements and strict environmental regulations. Vehicles starting from simple two-wheelers to more complex multi-axled trucks need such friction materials to slow down and stop when required. Friction materials are made of various components, namely, binders, fillers, fibers, lubricants, abrasives and metals. Unfortunately, most of these components are seen as a threat to environment and hence search for newer routes to making eco-friendly materials is underway. Either the materials themselves are non-sustainable, or they are derived using non-sustainable pathways. For example, friction materials are prepared by employing one or more non-sustainable methods, resins used as binders are still derived from petrochemicals which are non-sustainable, and minerals used in friction material formulations are produced using non-sustainable processes. Alternatively, binders used in formulations could be made using plant derived material "lignin" as a starting material instead of the petrochemical 'phenol'. This short investigation looks into various aspects of a composite friction material and highlights different issues underlying them. Finally, it is felt that a huge research investment is required to feel and make greener composite friction materials for automotive applications, that are totally safe and completely eco-friendly and sustainable as a wholesome entity.

Keywords: Green Friction Materials, Eco-friendly Friction Materials, Brake Linings, Disc Pads.

1. Introduction

1.1. Composite Friction Materials

Composite friction materials for automotive / non-automotive / industrial applications are made up of six categories of materials, namely, (a) *binders* that act as a matrix wherein all other raw materials are embedded in and hold them together; they give hardness and rigidity to the product, (b) *fillers* that are cost-effective, easily available, inert towards friction and usually forms the major portion of friction materials, (c) *fibers* that act as a reinforcing agent and provides mechanical strength to the product that is subjected to severe conditions during service, (d) *lubricants* that provide required sliding force to stabilize friction and wear, and help to form tribological transfer films on surface of mating parts, (e) *abrasives* that provide the required wear resistance and friction for moving parts, and (f) *metals* that provide thermal conductivity and heat dissipation thus prolonging the life of friction material as well as mating parts. (d) and (e) together are categorized as friction modifiers. With increasing awareness on fate of many materials during service and strict regulations on environment restoration programs, green friction materials came into development.

1.2. Green Composite Friction Materials

Huge number of research groups around the world have started focusing on developing green friction materials as a sustainable, safe and eco-friendly pathway for automotive applications. More careful study is required to identify suitable alternates to replace "problem-posing" raw materials.

A friction material is said to be "*fully*" green if it fulfills four conditions: (a) shall be made up of raw materials derived from sustainable / renewable sources, (b) shall be made up of raw materials that pose NO harm to humans, plants, animals and aquatic lives, during both virgin state and product life cycle, (c) shall be processed / manufactured through completely sustainable processes, and (d) shall be made up of raw materials which in turn are manufactured / derived / processed through completely sustainable processes. Most of the current researches and developments focus on fulfilling the first two requirements, (a) and (b). The requirement (d) is completely concerned with raw material

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suppliers and it should be an extended responsibility for friction suppliers and core responsibility for raw material suppliers.

1.3. Author's Perspectives

Raw Materials. Raw materials are categorized into two broad classes, namely, renewable and non-renewable, based on types of resources (Fig. 1). Renewable sources of raw materials are sustainable and they provide carbon-balance to the environment, unlike non-renewable sources that are unsustainable and provide carbon-overload because their carbons are added to the environment over and above the amount already present.

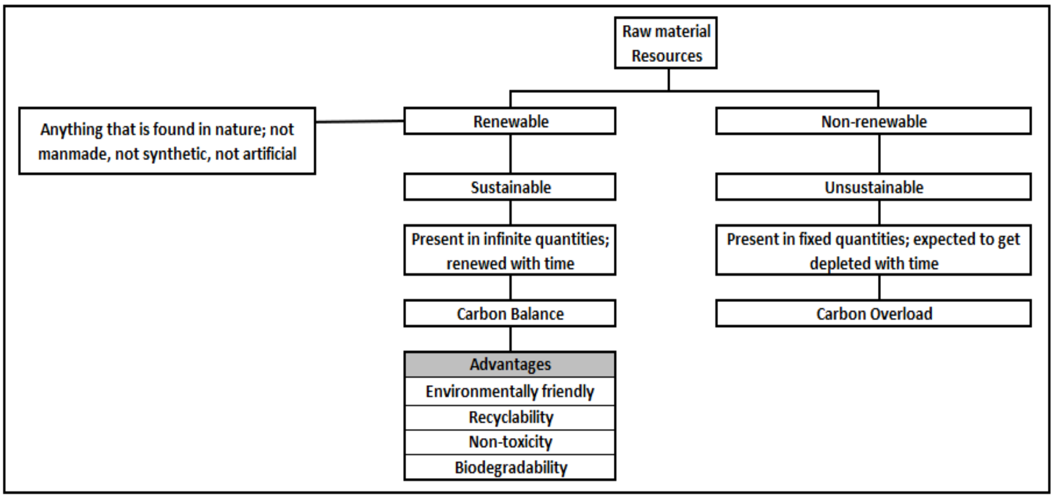

Fig. 1. Types of raw material resources.

Power. Electricity required for making products could be generated either through renewable means or through non-renewable route. Many studies have been carried out in renewable energy sector and have developed numerous alternate power sources, with their own advantages and disadvantages. Some of the examples are hydro, solar, tidal, wind, geothermal, nuclear and hydrogen. The last two still stand a debate considering safety and other handling issues. On the other hand, power through non-renewable sources is being generated using thermal route that uses coal. Non-renewable source, no doubt, still remain as unmatched fuel for various obvious advantages (cost, well-established processes, proven technology, etc.). Hence, their demand keeps exponentially increasing day-by-day. Very recently, Papua New Guinea, a small tropical country north to Australia experienced a severe fuel drought (National daily, 2024). A study indicated that the current reserves of coal, oil and gas would cater for the next ~140, ~55 and ~50 years respectively (Dale, 2021). So, after about 5 generations, there would not be any coal left behind for fuel applications. Alarmingly, just after 2 decades, there would not be any oil or gas left behind and all automobiles and other machineries that use them stand still, unless suitable downstream technologies are developed for using renewable sources, or a full-fledged electric mobility is sought to.

Demand on Friction Materials. Research carried out on the global market outlook for friction materials indicated that the composite friction materials (ground transportation includes all moving vehicles on road, off road and rails, aircraft & aerospace and industrial includes lifts, washing machines, etc.) keep growing and there is always a demand for them.

2. Friction Material Formulations and Raw Material Categories

Various formulations for various applications contain raw materials that could be classified as binders, fillers, fibers, friction modifiers (lubricants and abrasives) and metals.

2.1. Binders

A typical formulation for drum brake linings and disc brake pads contains respectively 10-15 wt.% and 4-6% of phenol formaldehyde novolak resin that are manufactured using non-renewable fossil-based resources. Binders are vital for a formulation because they form the base matrix and decide the integrity of friction materials, especially during severe vehicle drive conditions. A good strength of binders is expected from a good molecular weight distribution. Binders are polymers with high molecular weights and during service, friction materials experience high temperatures and result in gradual decomposition of polymers into small chain and carbonized fragments due to insufficient supply of oxygen under vehicle braking conditions. Usually, they are made up of phenol and formaldehyde (PF) and the crosslinking agent used is hexamethylenetetramine (HMTA). These three materials are petrochemicals derived from non-renewable crude oil sources. With modern vehicles, better roads and dedicated highspeed lanes on highways, high-performing fuels and electronic technologies, vehicles are now capable of reaching very high speeds within seconds and corresponding friction materials need thermally resistant binders. These are prepared by modifications using epoxy, aralkyl, silicon, boron and phosphorus. The key requirements of a binder are heat resistance to ≥250 °C and carbon formation at the surface that protects friction materials from degradation at even higher temperatures (>350 °C). Specific advantages of using PF resins are their easy availability, cost effectiveness, high resistance of cured resins to heat and chemical attacks, and good compatibility with many materials that are widely used in formulations.

Alternatives to phenol are lignin (derived from lignocellulose), cellulose, tannin, resorcinol, guaiacol, tyrosol and cardanol. Rich literature information is available on their use in place of phenol during the manufacture of resin (Schutyser, 2018; Granado, 2019). Fig. 2 gives a structural comparison between tannin and phenol molecules. Lignocellulose is available in abundance and is also obtained as waste products from food industries. The main requirement is the presence of high aromatic content with comparably good reactivity features. On the other hand, alternatives used for formaldehyde are furfural and its derivatives (hydroxymethylfurfural, furfuryl alcohol, etc.), glyoxal and vanillin due to their structural similarities. Using these materials in place of formaldehyde, both resole and novolak resins were prepared and superior mechanical and rheological properties were achieved (Ballerini, 2005). Fig. 3 indicates the steps involved in converting biomass into furfural (Sarika 2020). However, bio-based alternatives (glyoxal and furfural) are classified as "*carcinogenic, mutagenic and reprotoxic*" (ECA, 2015). A research group has used a bio-based non-toxic alternative for formaldehyde, namely terephthalaldehyde which was found to exhibit good reactivity [4]. The resultant thermoset resin with self-curing resole properties exhibited high crosslink densities and elevated glass transition temperatures, probably suggesting superior tribological properties when used in friction materials. Using resole resins in friction materials is not common owing to disadvantages like self-curing of friction material mixes in industrial shopfloor temperatures (30~34 °C), self-curing and hardening of resins during storage and inferior thermal stabilities. Thermosets have long been in use for manufacturing friction materials, wherein a crosslinking agent like HMTA is needed; but bio alternatives to HMTA are unknown. The resin curing mechanism is complex in nature and hence developing suitable bio-substitutes need good research efforts.

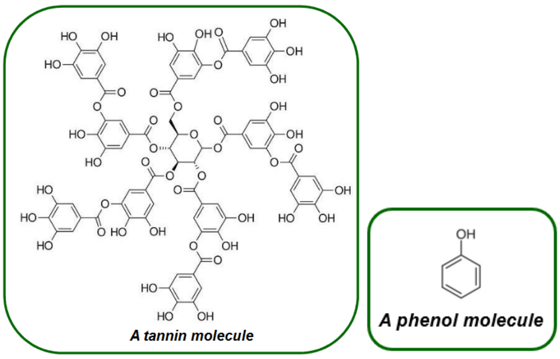

Fig. 2. Structural comparison between tannin and phenol molecules.

Recent studies have used geopolymers like metakaolin, calcined kaolinite, pozzolanic materials like lava and coal fly ash obtained from naturally occurring aluminosilicate powders with alkaline solutions of siliceous materials under moderate temperatures and pressures. The study concluded that the performance is on par with non-asbestos organic (NAO), semi-metallic and low-metallic friction materials (Xicola,2017). However, the products and processes are called *totally sustainable and green* only when all allied raw materials and processes are obtained and carried out from renewable sources.

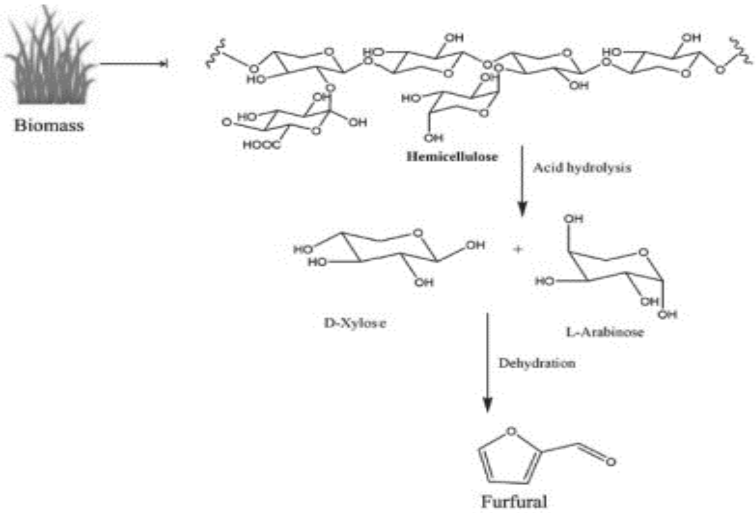

Fig. 3. Conversion of biomass to furfural (adapted from Sarika 2020).

2.2. Fibers

Organic, inorganic and metal fibers are widely used in friction materials. With increasing awareness on green economy and sustainability, researchers have focused their attention on developing fibers that are naturally available such as flax, hemp, jute, sisal and henequen (Li, 2007). Table 1 gives a list of fibers along with details on whether the fibers and production processes are sustainable. They possess certain special properties like low density and low cost that make them unique to be considered for the reinforcement role along with a polymeric matrix. Table 2 provides a few properties of natural fibers as compared to synthetic fibers.

Table 1. List of fibrous raw materials (natural and synthetic)

Class	Category	Name	Raw materials	Production Process	Remarks, if any
Organic	Synthetic	Aramid, PAN	Unsustainable	Unsustainable	Made from aromatic amine and carboxylic acid halide
Organic	Natural	Cellulose	Sustainable	Unsustainable	Cellulosic material of plant origin
Organic	Natural	Sisal	Sustainable	Unsustainable	Made up of cellulose and hemicellulose
Organic	Natural	Jute	Sustainable	Unsustainable	Made up of cellulose and hemicellulose
Organic	Natural	Hemp	Sustainable	Unsustainable	Made up of cellulose and hemicellulose
Organic	Natural	Palm kernel	Sustainable	Unsustainable	Contains higher percentages of cellulose
Organic	Natural	Coconut shell	Sustainable	Unsustainable	Contains higher percentages of cellulose
Inorganic	Synthetic	Glass	Sustainable	Unsustainable	Made from sand, soda ash and limestone
Inorganic	Synthetic	Rock	Sustainable	Unsustainable	Made from sand, alumina and limestone
Inorganic	Synthetic	Ceramic	Sustainable	Unsustainable	Made from silica and alumina
Inorganic	Natural	Asbestos	Sustainable	Unsustainable	Hydroxy magnesium silicate; carcinogenic, banned in many countries
Metal	Synthetic	Steel	Unsustainable	Unsustainable	An alloy made from iron and carbon
Metal	Natural	Copper	Sustainable	Unsustainable	Found in native state and mined as element

Table 2. Mechanical properties of fibers (natural and synthetic)

Fiber	Type	Cost indication	Density (g/cc)	Young's modulus (GPa)	Tensile strength (MPa)
Cotton	Natural	Relatively expensive	1.50 – 1.60	5.5 – 12.6	287 – 597
Flax	Natural	Cheap	1.40 – 1.50	27.6 – 80.0	345 – 1500
Hemp	Natural	Cheap	1.48	70.0	550 – 900
Jute	Natural	Cheap	1.30 – 1.46	10.0 – 30.0	393 – 800
Sisal	Natural	Cheap	1.33 – 1.50	9.0 – 38.0	400 – 700
E-glass	Synthetic	Expensive	2.50	70.0	2000 – 3500
Aramid	Synthetic	Very expensive	1.40	63.0 – 67.0	3000 – 3150
Carbon	Synthetic	Exorbitantly expensive	1.40	230.0 – 240.0	4000

From Table 2, it is very clear that many open challenges mentioned earlier are still applicable here: matching required properties (like good adhesion between fiber and the matrix, resistance to moisture, good thermal stability, good impact strength and high durability especially under stringent operations conditions), meeting the demands and manufacturing feasibility. Furthermore, natural fibers exhibit less uniform and rigid properties and further research in this aspect is required to improve fiber properties. Most of the values for natural fibers shown in Table 2 are in wide ranges and these in turn depend on growing conditions like climate, water and mineral intakes. Many natural fibers need surface preparation and treatment either with acid or base for a suitable modification (Gholampour, 2020), or to remove protons to make them compatible with friction matrices. Such chemical treatments are required to remove hydrogens of hydroxyl groups and make them hydrophobic, and thus achieve dimensional stability with enhanced mechanical properties. Treatments with sodium hydroxide, silane, acetic anhydride, benzoyl chloride, etc. have been used by different research groups for chemical modifications. Even physical treatments like use of plasma, corona, ultrasound and UV light have been described (Amiandamhen, 2020). This treatment is found to stimulate fiber surface, reduce surface contamination, increase surface roughness and hence compatibility, increase hydrophobicity, activate cellulosic content and increase thermal stability. Unfortunately, all natural fibers contain cellulose in varying percentages (50~70%); the abundant presence of hydroxyl groups (Fig. 4) make them highly hydrophilic and hence their reinforcement with a hydrophobic matrix is not sufficient.

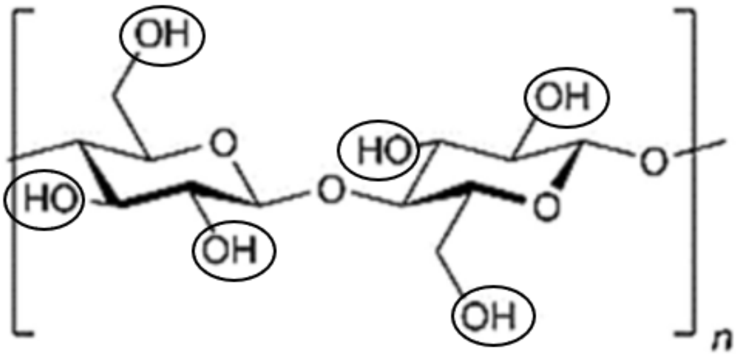

Fig. 4. Structure of cellulose (hydrophilic sites are circled).

2.3. Fillers

Fillers are mined as rocks from Earth and so they are considered as sustainable raw materials. Size reduction and refining processes are then carried out to make them suitable for use in friction material formulations (most of the materials are fine powders, -200 mesh with sizes <55 microns). These additional processes adopted, however, are mostly using unsustainable routes. For example, pulverization and industrial scale sieving of rocks and their broken-down aggregates make use of power resources that are derived from non-renewable sources. Examples of some widely used fillers are barites, calcite, dolomite, talc, mica, etc. Fillers like vermiculite that makes friction material matrix soft, needs an additional "*exfoliation*" step to open into porous, laminar and layer structures. It is to be noted that the replenishment rates of mineral resources are infinitesimally slow compared to their consumption rates and could be depleted in an imaginable timescale. On contrary, natural bio-derived fillers like coconut and palm kernel shell powders were used in composite friction materials, but higher wear of friction materials was observed (Egeonu, ,2015).

2.4. Friction Modifiers

Widely used example of an organic friction modifier is cashew friction particle and is manufactured from cashew nut shell liquid (CNSL), formaldehyde and HMTA through polymerization reactions. While CNSL is derived from sustainable sources through pressing of dried cashew nut shells under elevated temperatures, formaldehyde and HMTA are petrochemicals that are derived from non-renewable routes and materials. Suitable alternatives to formaldehyde are available as suggested earlier, but alternatives to HMTA are unknown. Pine cone dust was used as an organic friction modifier in friction materials and found to exhibit good friction and wear resistance (Sugozu,, 2019). Other inorganic friction modifiers are abrasives (zirconium silicate, alumina, silica, silicon carbide, ulexite, etc.) and lubricants (graphite, metal sulphides, etc.). Fortunately, many of them are naturally occurring and hence sustainable; unfortunately, still they are refined and particle-size-reduced using unsustainable process practices (reaction chamber, refiner, pulverizer and screening – all use non-renewable electrical power). Metal sulphide lubricants are both synthetic, employ relatively toxic (heavy) metals that also use non-renewable process conditions.

2.5. Metals

Though copper, mined as element, is widely used in friction materials due to its unique properties (like low Mohs hardness, good lubricant at elevated temperatures, high thermal conductivity, primary contact site providers and low friction material wear), it is increasingly being restricted in many countries due to its threat to aquatic organisms and ecosystems (Baldwin, 2011). In most countries, copper is currently restricted to <5% in friction formulations and are designated as "B". From January 01, 2025, the same gets reduced to 0.5% and are designated as "N". Prior to January 01, 2021, there was no restrictions for use and it was >5% and were designated as "A". Other commonly used metals are aluminum, zinc and iron, and alloys are steel, brass and bronze, all in powder, chips or fiber forms. Zinc has already faced a threat in friction materials due to its danger associated with aqua systems. Currently zinc is under *declarable substances list* whose percentages have to be declared to customers. Many efforts are invested in developing copper-free and low-zinc formulations (Janarthanan, 2023). Aluminum is a non-toxic and safe metal, but it is mined as bauxite which makes use of a series of nonrenewable processes to extract aluminum. Moreover, this metal can't be used in higher percentages though it possesses a good thermal conductivity, because under vehicle operating conditions, the peak temperatures for brake linings and disc pads are ~400 and ~700 °C respectively, during which the metal transforms to alumina (Mohs hardness: ~9) whose abrasiveness is high and can cause a significant wear of mating parts (brake drum and disc castings). Iron and the three alloys (steel, brass and bronze) are extracted and made in industries using nonrenewable processes, thus questioning their sustainability in the true sense.

3. Advantages and Open Challenges in Using Bio-resources

3.1. Advantages

There are several advantages of using ubiquitous and environmentally benign bio resources: decreasing carbon foot print through circular economy, abundant natural feedstock availability, unique macromolecular chemical structures, possessing sterically hindered sites in structures that are less susceptible for attacks, and more resistant to chemical and physical degradations. Some of these are true only when treatments to natural materials are done.

3.2. Open Challenges

Many number of open challenges remain when using bio resources: scaling-up issues, plenty of functional sites in molecules, but less reactive, often activation of sites through chemical and physical modifications required, optimizing reaction conditions to increase yields, development of economical processes that suit current demand, meeting the current demand Vs supply, most of the biomolecules are solids and hence complex solid-solid or solid-liquid reactions are needed, multiple purification steps are required to get these bioresources to work, matching of properties (thermal, mechanical and chemical) with conventional raw materials and products, bio-based materials are generally polar, hydrophilic and brittle in nature, and their structures slightly vary from one another in terms of number of functional groups present, molecular weight and degree of crosslinking, depending on their origin.

4. C for "Carbon" and C for "Culprit"

The main reaction responsible for "climate change" and which encourages development of diversified sustainable materials is given in equation (1). Fig. 5 explains the reactions and thermodynamics of the oxidation reactions of carbon. If organics required for friction materials are derived from natural sources, then "circular economy" is maintained (Fig. 6).

$$C_{(s)} + O_{2\ (g)} \rightarrow CO_{2\ (g)} \quad (1)$$

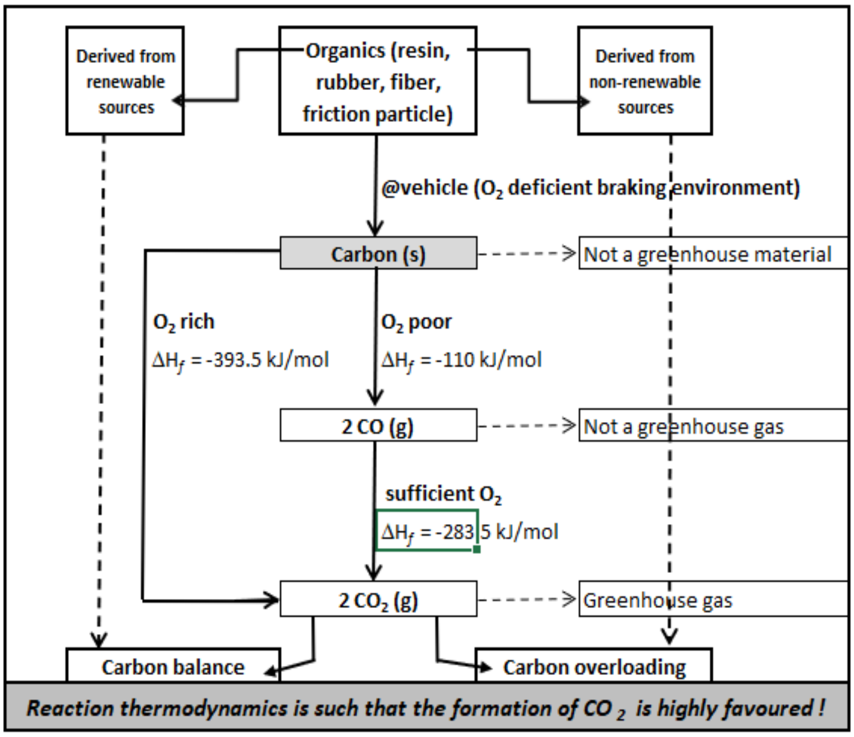

Fig. 5. Thermodynamics of the carbon oxidation reaction.

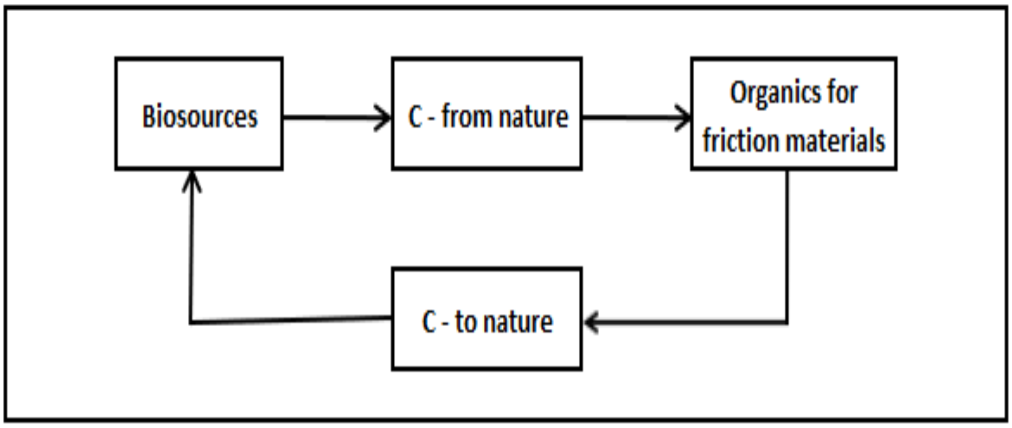

Fig. 6. "Circular economy" when natural bio sources are used.

Each phenolic resin molecule gives 8 moles of carbon dioxide as per equation (2), amounting to 72% of carbon per mole of phenolic resin, and gets decomposed and oxidized to carbon dioxide gas, a prominent greenhouse gas that is responsible for global warming and climate change. The ultimatum is, extended responsibility has to be exhibited by the producers / manufacturers at every stage of friction material manufacturing (Fig. 7). Though mineral resources are naturally available in Earth's crust, it is the mining of raw materials and subsequent operations that make the processes totally non-renewable and unsustainable, and two possibilities are given in Fig. 8.

$$\underset{mw\ 134n}{[\text{-}C_8H_6O_2\text{-}]_n} \rightarrow \underset{mw\ 352n}{8n\ CO_2} \qquad (2)$$

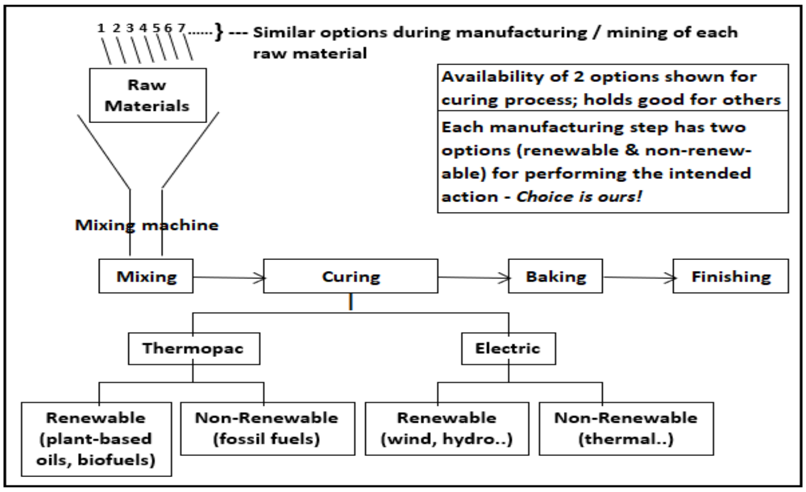

Fig. 7. Possibilities of using power at every stage of operation in industries.

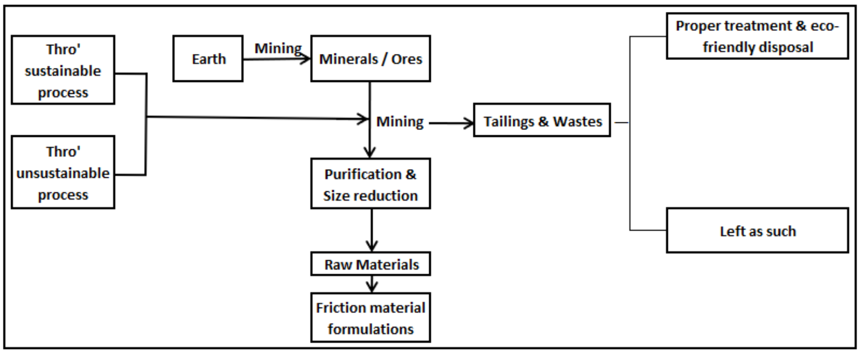

Fig. 8. Mineral resources – manufacturing of raw materials.

5. Carbon Dumping

Since no promising alternatives could fulfill the global demand, still carbon finds a primary place in all processes. This led to Government Regulatory bodies to develop carbon footprint calculations (EPA, 2024). Based on values, "*carbon taxes*" are imposed to industries and these extra costs are being borne by end users / consumers.

6. Greener, Safer and Sustainable

When using natural resources, the products are expected to be greener, safer, non-toxic and fully sustainable wherein renewable resources and materials are used. Each and every single step in making a product should be through sustainable routes and all players involved in producing a product need to practice this *mantra*. To envisage and realize this, a Sustainability Management System and a Team could be setup in all organizations to monitor the carbon figures, to take up new projects, to carryout trials and review results, and to implement results.

7. Conclusions and Future Research

Huge challenges have to be overcome to make sustainable friction materials. Extended responsibility lies on global regulatory bodies for carefully designing appropriate protocols. Most of the naturally occurring materials have poor reactivity and non-uniformity in properties, amidst others. Bio alternatives to materials like HMTA are still not available. A friction material could be considered as fully sustainable if all materials and all sub-materials are produced and processed through purely green, renewable and sustainable routes. Conventional friction materials do leave considerable amounts of carbon footprints. Decarbonization techniques could be used, but feasibility and viability remain questioned. Many countries have started imposing carbon taxes for dumping carbon into the environment; this extra cost is being absorbed through the product cost and common people get burdened.

The trifold focus on developing future composite friction materials lies in designing "smart" formulations that target on eco-friendly, safe, green and sustainable approaches. Some of the materials using which intense research efforts are directed are carbon-carbon composites, ceramic and sintered materials, metal matrix composites with emphasis on lightweighting.

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