Chapter 2

Literature review

Chapter- 2 Literature review

The goal of this chapter is to offer contextual information on the themes that will be discussed in this thesis and to point out the significance of the current investigation. This section includes a variety of subjects related to NFRPC, with a focus on their physical, thermal, mechanical and tribological properties. This chapter contains reviews of research papers that are currently accessible on the following topics.

- **Natural fibers and natural fiber reinforced polymer composites (NFRPCs)**
- **Concerns of using natural cellulose fibers in composites**
- **Chemical treatment of fiber surface**
- **Physical, water absorption, mechanical and thermal properties of NFRPCs**
- **Tribological properties of NFRPCs**

2.1 Natural fibers and NFRPCs

Growing awareness of environmental issues has prompted researchers all around the world to design and use environmentally friendly materials. Natural fibers have evolved into viable substitute for typical manufactured (man-made) fibers, with the credential to be employed in better cost-effective, long-lasting, and environmentally sustainable composite materials. Animal or plant sources can be used to make natural organic fibers. With the exception of wool and silk, the bulk of valuable natural textile fibers are sourced from plants. Cellulose is the main ingredient of plant fibers, whereas protein is considered as major constituent of animal based fibers. Categorization of Natural fibers depends on their origin, and the categorization of plant-based fibers depends on the portion of the plant from which they were extracted. Fig. 2.1 depicts a broad picture of natural fibers.

Plant fibers are widely utilized as reinforcing elements in PMCs for a wide range of uses, that includes electronic devices, toys, pedestrian bridges, multi-purpose tables, roofs, door panels, and frames. Plant-based polymeric products offer various advantages over conventional materials, including ease of access, cheap cost, low weight, acceptable mechanical properties, and biological efficiency. Plant fibers are a sustainable resource that may also be recycled.

The fact that natural fibers can be generated at a cheaper cost than glass is the primary motivator for using them instead of glass. Glass fibre has a density of 2.5 g/cc and costs roughly Rs. 300.00/- per kg. Instead, natural fibers have relatively low density (around 1.1-1.6 g/cc) and they cost lesser than 1/10 th of glass fibers. The tensile strength of natural fibers is significantly lower than that of glass fiber. However, the plant based fiber exhibit poor tensile strength when compared to glass fibers as shown in Table 2.1 [12], despite the fact that these natural fibers have comparable tensile modulus. Table 2.1 also enlists the physical and mechanical properties of widely used natural fibers in PMCs [13,14]. Also, since the natural fibers have low density, therefore some of these fibers have equivalent or better specific modulus than glass fibers. Superior specific properties, cheap cost, ease of accessibility combined with the added benefit of not causing damage to the processing machines make natural fibers a suitable substitute for synthetic fibers.

2.1.1 Structure of plant fibers

Natural fibre qualities are mostly determined by the type of the plant, its age, the region in which it is cultivated, and the extraction process utilized. The strength of the fibre is influenced by physical qualities such as crystalline and amorphous composition, packing structure of fibers and cellulose and hemi-cellulose composition of the fibers [15]. Natural fibers are lignocelluloses, which are made up of helically wound cellulose microfibrils in a lignin and hemicellulose matrix [16]. Lignin helps to hold water in fibers, protects against wide range of pathogens, and stiffens the stem so that it can withstand gravity. Lignin and cellulose are connected to each other by a bonding agent known as hemicellulose. The characteristics of each fibre ingredient contribute to the fiber's overall properties. The cellular structure of natural fibre can be used to characterise it. Fig. 2.2 depicts the schymetic micro-structure of natural fibre. The cell walls of natural fibers are separated into two parts: the first section is the initial layer built during cell formation and is known as primary wall and this primary wall is surrounded by a second section, which is known as secondary wall. This secondary wall is further made up off three layers. S1 constitute the outer layer, S2 constitute the middle layer and S3 constitute the inner layer. The middle layer is the sturdiest of all the layers and most essential in determining the fiber's mechanical characteristics [13]. The intermediate layer comprises a sequence of spirally wrapped cellular microfibrils made of long chain cellulose molecules. These micro-fibrils having a diameter of 10-30 nm, are primarily responsible for providing strength to the fibers, usually consists of 25-110 cellulose molecules. Pectin works as a cement between fibres, makes up the majority of the middle lamella, which is the cell's outer layer [17]. When choosing a natural fibre for a certain purpose, fibre strength might be a significant consideration. Good aspect ratio is considered as an important criteria for acceptable strength properties in plant based NFRPCs.

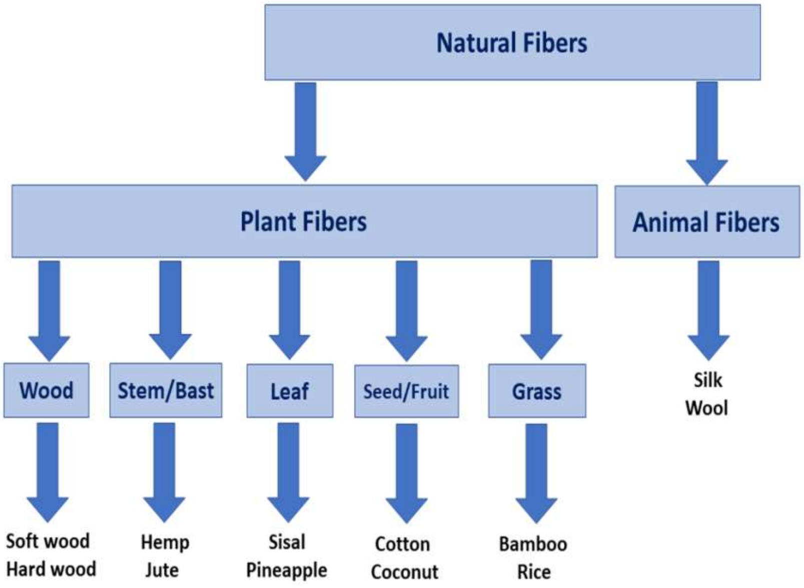

Figure 2.1. Classification of natural fibers [11]

Table 2.1. Comparison of properties of natural fibers with E-glass fibers [13-15]

Properties	Jute	Flax	Hemp	Sisal	Ramie	E-glass
Density (gm/cm^3)	1.45	1.41	1.47	1.32	1.51	2.26
Water absorption (%)	13	8	9	12	14	-
Tensile strength (MPa)	450-800	850-1550	600-950	650-750	520	2400
Modulus of elasticity (GPa)	15-35	65-85	71	40	44	73
Failure strain (%)	1.8	1.2-1.6	1.6	2-3	2	3
Specific modulus (GPa)	10-25	25-50	30-37	30	29	29

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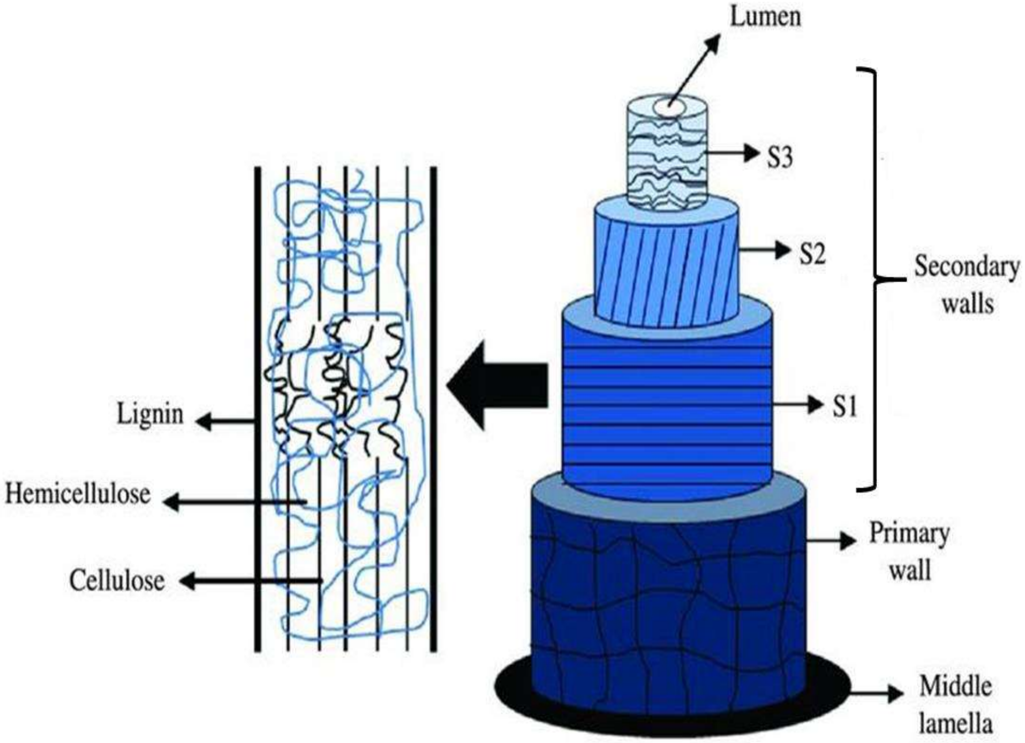

Figure 2.2. Schematic micro-structure of plant fiber [14]

2.1.2 Chemical constituents of natural fiber

The major constituents of a plant based fiber includes cellulose, hemicellulose, and lignin. They are also known as cellulosic or lignocellulosic fibres for this reason. The ratio of these elements in a fibre is influenced by the production region, plant variety, plant age, and the fiber extraction procedures. Average chemical content values for plant/vegetable fibre are represented in Table 2.2 [18].

Table 2.2. Chemical constitution of natural fibers [17,19]

Fibers	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ashes* (%)
Hemp	73	11	4	2.5
Jute	61	23	16	1
Kenaf	74	22	10	3
Sisal	75	12	7.8	0.5
Coir	47	15	39	-
Bamboo	40	31	24	-

*The ash content of natural fibers corresponds with their mineral content. The ash is obtained after burning of a defined amount of fibers in platinum crucibles over open flames or better in a muffle furnace and weighing out the residues quantitatively.

2.2 Concerns of using natural cellulose fibers in composites

Natural fibers have numerous benefits over man-made fibers, which makes them appealing as reinforcements for polymer composites. These fibers are inexpensive, plentiful, and sustainable, with appreciable specific properties like strength and stiffness. Notwithstanding these benefits, unmodified NFRPCs have fared far beneath their capability and, as a result, their application is limited in the polymer industry for the following reasons.

- Interfacial or mechanical interaction between the plant based fibers and the polymer matrix is comparatively poor.
- Natural fibers have poor thermal stability.
- Cellulose fibers have high moisture absorption rate.

2.2.1 Interfacial bonding between the fiber and the polymer matrix

Because of the nature given chemical makeup of the plant based fibers, they are predominantly polar and as a result are hydrophilic in character. Hemicellulose, lignin, and pectin are non-cellulosic components found in plant fibers, with hemicellulose and pectin being the most hydrophilic. Many available hydroxyl (OH) and carboxylic acid groups are present in these constituents, which function as active sites for water uptake [19]. Although the cellulose component includes numerous OH groups, only a negligible amount of water can fit into the micro fibrils which are crystalline in nature. As a consequence, mainly un-bonded OH groups on the surfaces of micro fibrils are accessible for water uptake. Majority of the unmodified NFRPCs have poor mechanical properties owing to compatibility issues between the cellulose fibers which have strong affinity towards water and non-polar polymer matrix [20]. For proper utilization of NFRPCs in high end applications, the mechanical interlocking between the natural fibers and matrix must be improved. This could be accomplished by altering the outer layer of the fibers to make them highly amicable with the resin (polymer), or by altering the resin (polymer) by adding certain chemicals or fillers that reduces the voids and improves the affinity between the fibers and the matrix.

2.2.2 Thermal stability of natural fibers

Unlike many synthetic fibers (glass fiber, carbon fiber, etc) which remain thermodynamically stable upto 350°C, the thermal degradation of majority of cellulose fibers begins roughly at 200°C [21,23]. As a result, several production procedures are ruled out, and the composites' applications are limited to low-temperature uses. Yildiz et al. [21] contend that temperatures exceeding 150ºC may initiate irreversible modification of the physical and chemical characteristics of cellulose based fibers. They suggested that high-temperature modification of fibers may increase the ecological resilience of the fiber while reducing its strength and stiffness. Several researchers [22,23] have demonstrated that chemical treatment of the fiber surface can increase the high temperature performance of these modified fibers

2.2.3 Moisture absorption behaviour of plant fibers

High water retention is another issue with employing fibers derived from plant sources as reinforcement in composites [24]. The fiber cell wall can retain the water from the environment which results in swelling of the fiber, this results in poor interfacial performance of these NFRPCs [25]. The swelling of fibre swelling is responsible for poor affinity of natural fibers for the polymer matrix, this sparked of deterioration in the NFRPC's mechanical properties. Aside from dimensional stability, the hydrophilic character of the plant fibers has an impact on the composite's processability. Due to the ability of the plant fibers to retain moisture, water vapour gets trapped into the matrix material during the fabrication process, resulting in a composite with undesirable voids. According to Srinivasan et al. [26], these holes can operate as stress concentration locations, causing the composite to fail prematurely during loading. They've also suggested that by employing different surface modification techniques, water absorption in natural fibre composites can be significantly minimized.

2.3 Chemical modification of fiber surface

Unmodified NFRPCs are characterised by poor interaction of the fibers and the matrix, accompanied by unsatisfactory mechanical, thermal and tribological properties. The surface texture and the chemical structure of the natural fibers can be altered by different physical and chemical approaches to increase the affinity of these fibers with the polymer matrix. Chemical modification of the fiber surface can be carried out to attain some or all of the below mentioned goals:

- Elimination of unwanted fiber elements such as wax, grime, and other contaminants.
- Surface roughening of the fiber.
- Splitting of individual fibers from the fiber bundles.
- Alteration of the chemical structure of fiber.
- limiting the fibers' hydrophilic nature

Chemical modification of natural fiber does a crucial role in increasing the reinforcing capacities of these fibers in polymer matrices. These surface modification techniques involves the use of chemicals like coupling agents, compatibilizers, or dispersion agents. Various chemicals are used in pre-treatments to eliminate many unwanted impurities, hydrophilic agents like hemicellulose and non-strength generating chemical constituents such as pectin, and lignin. Compatibilizers are used to make the fiber surface less polar and hence more acceptable with polymer matrices by reducing the surface energy of the natural fiber. To enhance fiber dispersion in the matrix, dispersing agents are utilised. Coupling agents are primarily useful for raising the adherence of reinforcing fibers to matrix material, but they can also minimize fiber water absorption and aid in fiber dispersion [35] Effect of various chemical treatments on the the properties of natural fiber reinforced polymer composites are represented in Table 2.3.

Table 2.3 Effect of various chemical treatments on the properties of NFRPCs

Fibers used	Type of Chemical treatment	Effect	References
Bamboo	Alkaline treatment	An enhancement in tensile strength by adding 30% treated bamboo which is slightly higher than silane-treated composite	131
Pineapple leaf	Alkaline and acetic acid	Improvements in tensile strength, impact strength, and flexural strength.	132
Jute	Silane treatment	At 0.3%, silane-treated composites enhanced the tensile, flexural, and interlaminar shear strength by 40%, 30%, and 55%, respectively	134
Sisal	Silane treatment	silane treatment enhances the mechanical properties and moisture resistance	133
Sisal	Acetylation treatment	Improvement in tensile strength and shear strength by 14.08% and 435%, respectively. The acetic acid treatment followed by ethyl acetate with H_2SO_4 resulted in high levels of cellulose swelling or loosened cell wall structure	135
Flax	Permanganate treatment	Improvement in tensile and moisture resistance as compared to alkali and silane-treated fibers	136
Oil palm	Peroxide treatment	Improvement in flexural modulus as compared to other chemical treatments	137
Banana	Benzoylation treatment	The treatment significantly improved thermal conductivity and was found to have increase in tensile strength and modulus by 13% and 5%, respectively	138
Flax	Acrylation treatment	The treated fiber exhibited higher tensile strength and moisture resistance than those treated with silane, permanganate, and sodium chloride treatment. Higher smooth fiber surface was observed	139
Sisal	Acrylonitrile grafting	The treatment showed enhanced tensile and flexural strength as compared to other treatments. Least degradability of fibers was observed.	140
Hemp	PLA & PHB	Both the PHB and PLA coated composites exhibited appreciable	128

		improvement in tensile strength, tensile modulus, impact strength, and microhardness values in comparison to uncoated composites. Appreciable improvement in tribological properties were also observed.	
Hemp	Sodium carbonate and Hydrogen peroxide	Both the sodium carbonate treated (ST) and peroxide treated (PT) composites showed considerable enhancement in tensile properties (tensile strength and modulus). PT composites exhibited the maximum increase in tensile strength and modulus, followed by ST and UT composites.	126
Sisal	Glutamic acid	The water absorption resistance of the sisal fiber composites improved appreciably for the composites reinforced with glutamic acid treated fibers. Similar improvement was observed for mechanical properties of the treated composites.	123
Sisal	Stearic acid and sodium citrate	Both stearic acid (SA) and sodium citrate (SC) treatment improved the mechanical properties (tensile properties, flexural properties and ILSS strength) of the treated composites. However, SCT composites exhibited the best mechanical properties followed by SAT and untreated composites.	130
Jute	Sodium carbonate and sodium bicarbonate	Sodium carbonate (ST) composites showed the highest increase in both tensile strength and modulus. The impact strength of the composites also increases after the chemical treatments. ST composites showed the highest increase in both tensile strength and impact strength.	141

2.4 Mechanical, physical, water absorption and thermal properties of NFRPCs

Throughout their service lives, many NFRPCs are subjected to a variety of loads and stresses. Thus, it is vital to comprehend the mechanical behaviour of NFRPCs in order to ensure that the product manufactured from them does not malfunction over its life cycle. A thorough understanding of a material's mechanical characteristics aids in the identification of applications for it. The mechanical characteristics of NFRPCs include tensile properties, flexural properties, hardness, impact strength and inter-laminar shear strength. The mechanical properties of NFRPCs are controlled by variety of factors, including fibre orientation, fiber dispersion, fiber loading, aspect ratio, matrix-fiber bonding, etc [27]. As a result, suitable matrix and fiber characteristics aids in increasing composites' mechanical properties. The effect of numerous criteria on the mechanical behaviour of NFRPCs has already been studied extensively [28-30]. Since, the present thesis involves the surface modification of natural fibers, so majority of the literature review will be based on research articles involving the use of chemical treatment to change the texture and chemical constituents of the fiber surface to improve the affinity between the fiber and the matrix.

Bessa et al. [31] studied the influence of different chemical treatments (alkaline, silane and alkali + silane) on the thermal, dynamic and mechanical properties of Arundo donax L. fiber composites. Due to the substantial influence of alkaline solution on removing noncellulosic materials, dynamic mechanical examination of the manufactured composites demonstrated an improvement in storage and loss modulus values, notably for composites reinforced by alkali- or combined-treated fibres. Composites prepared with mixed NaOH-silane modified fibers have improved thermal stability. This improvement can be linked to surface modification, which provides a protective coating of matrix breakdown.

Han et al. [32] examined the interfacial UV ageing and silane modification of hemp fiber/polypropylene composites. Three silane agents with distinct functional groups of ester and vinyl groups, aniline groups, and primary amino were employed to change hemp fibre in this study. It is found that plant fiber polymer composites' interfacial adhesion and degradation are crucial for their exterior applications. The composites might have stronger initial mechanical qualities as well as high UV ageing resistance by using a specific silane or constructing a "appropriate" linking ageing structure. Furthermore, hemp fiber composites increases the ageing of the surrounding PP matrix while acting as a "barrier" to prevent additional UV radiation penetration into the composite core.

Jia et al. [33] investigated the tensile creep response of furfuryl alcohol treated unidirectional flax fiber/green epoxy composites. Composites made from furfuryl alcohol modified flax fibers had a 30% lower creep deformation than the unmodified flax fiber composites untreated at the same creep stress, demonstrating that modifying the flax fibers with furfuryl alcohol is an effective way to enhance creep resistance of NFRPCs.

Sepe at al. [34] used both silane coupling agent and sodium hydroxide to modify the hemp fiber surface before using these fiber in the epoxy resin. They discovered that silane-modified fiber composites have better tensile modulus in-comparison to untreated and alkali-modified fiber composites, and that the properties acquired from silane treatment are far superior to those acquired from alkali treatment, while 1% silane modified fiber composites shown the best mechanical properties.

The effects of cyclohexane/ethanol, alkali, and silane treatments on waste hemp fibers/polybenzoxazine composites was investigated by Dayo et al. [35]. The findings of the flexural, tensile, and impact tests revealed that the silane-modified waste hemp fibers/polybenzoxazine composites exhibited the best properties related to the other surface modified fiber composites. Moreover, among the composites investigated, the silane treated fiber composites had the best stiffness and glass transition temperature. Furthermore, the silane treated composites exhibited superior thermal stability owing to the improved thermal stability of the silane treated fibers. The silane treated fiber composites also had the lowest water absorption. The silane-treated fiber composite had a stronger fiber/matrix adhesion contact, according to morphological analyses.

A new eco-friendly approach of using $NaHCO_3$ to modify the flax fiber surface was employed by Fiore et al. [36]. Their findings exhibited that this treatment promotes fiber–matrix adhesion, hence improving composite performance. When compared to un-modified fiber, treating them with a 10% $NaHCO_3$ solution improves the tensile properties (modulus and strength) of the composites by 45% and 20%. Additionally, raising the concentration resulted in minimal changes in the glass transition temperature and also slight scaling down of tanδ peak heights.

Mughal et al. [37] analyzed the performance of silane functionalized sisal fiber on the thermo-mechanical characteristics of sisal/epoxy composites. The sisal fiber functionalization with 3-aminpropyltriethoxy silane has a significant association with epoxy, leading to a homogeneous dispersion of the sisal fiber in the matrix. The thermal and mechanical characteristics of the composite have been greatly improved. By using 15% sisal fiber, the tensile strength of functionalized sisal epoxy composite was increased up to 23% relative to non-functionalized sisal epoxy composite.

Furthermore, the functionalized sisal epoxy composite outperforms the non-functionalized sisal epoxy composite in terms of thermal stability.

Liu et al. [38] altered the surface of jute fibers with alkali, ethylenediamine/alkali, and acid/alkali treatments to increase the interfacial compatibility of jute/polypropylene composites. Improved surface characteristics of the treated fibers prompted a considerable enhancement in interfacial compatibility of treated fiber composites. The surface energy of acid/alkali treated fibers was raised by 45.58% in comparison to untreated fibers due to the acidic hydrolysis of acid treatment. There is also a considerable enhancement in the bending and tensile strength of acid/alkali treated fiber composites by 22.53% and 34.80% , respectively.

Tita et al. [39] employed a novel approach of modifying the surface of sisal fibers and sugarcane bagasse with lignin for different time period (15, 30 and 60 mins). When sugarcane bagasse and sisal fibers were treated with hydroxymethylated lignin, morphologic alterations in their surfaces were detected, which enhanced the wettability of the phenolic prepolymer on the reinforcements. Water absorption was shown to be reduced in composites made from modified fibers. For the shortest reaction time (15 min) , the impact strength of composite materials prepared from modified sisal fibers also rose. As a consequence, the current findings support the possibility of chemical modification of vegetal fibers using hydroxymethylated lignin to improve their inter-facial adhesion with polymer matrix.

Vinod et al. [40] investigated the approach of alkali modification on the cellulosic fibers extracted from Ziziphus Mauritiana plants. Chemical examination and FTIR study show that the NaOH modification helps eliminate amorphous elements and enhances the crystalline index by 1.31 times, fibre strength by 1.44 times and thermal stability by 1.15 times. In alkali-treated Ziziphus Mauritiana fibers, the reduction in amorphous elements enhanced the surface roughness, which improved the bonding behaviour. The NaOH modification also leads to an enhancement of tensile and flexural properties of its composites.

Premnath [41] studied the over all performance of NaOH modified natural fiber/epoxy resin composites reinforced with sisal and jute. His findings indicates that flexural strength rises by 25%, tensile strength improves by 20%, hardness increases by 5% and impact strength increases by 27.3% for alkali modified fiber composites.

Zhan et al. [42] evaluated the adhesive property of the PLA matrix and the ramie fibre (RF) by adding the triglycidyl isocyanurate (TGIC) compatilizer and treating the fibres with NaOH, silane and NaOH + silane combined. They suggested that the chemical treatment and the TGIC mixing are equally responsible for promotion of the mechanical properties of the composites. The tensile and flexural strengths of PLA/RF/TGIC composites were raised by 49.8 % and 46.5 %, respectively, relative to pure PLA.

Chandekar et al. [43] investigated the impact of alkali, $KMnO_4$, and silane modification of jute fibers on the mechanical characteristics of jute/polypropylene composites. Relative to unmodified jute/PP composites, silane-modified jute/PP composites had the maximum enhancement in tensile strength, tensile modulus, and flexural modulus of roughly 6%, 22%, and 20%, respectively. Also, the silane-treated jute/PP composites exhibited the lowest water absorption rate.

Rodrı´guez and Francucci [44] studied the effect of polyhydroxybutyrate (PHB) coating on jute fibers and reported that the PHB coating had remarkably improved the mechanical properties of PHB coated jute fiber reinforced polymer composites. After the fibre treatments, the dry composites' flexural strength and modulus were nearly unaltered. The impact strength of was observed to be higher in PHB-coated NaOH modified fiber composites, next by only NaOH modified fiber composites, and lastly un-modified fiber composites, with the lowest performance. Water absorption rate of composites manufactured with alkali-treated fibers covered with PHB was the lowest, followed by composites made with alkali-treated fibers.

Gupta and Singh [45] investigated the influence of polylactic acid (PLA) coated sisal fibers into the polyester resin. They found that PLA-coated sisal composites outperformed pure sisal and alkali-treated sisal composites. PLA-coated sisal composites showed improvement in tensile strength, water resistance, impact and flexural strength by 49% , 33%, 27%, and 48%, respectively, relative to pure sisal fiber reinforced polyester composites.

Gupta [46] studied the influence of NaOH modification and PLA coating on jute fibers and its polyester composites. The major objective of this study was to improve the overall performance of jute composites so that they might be employed in engineering applications. Biodegradable PLA coating of the fibers was able to achieve the above objective. However, NaOH modification in combination with PLA coating of fibers resulted in the superior mechanical properties of the composites.

2.5 Tribological properties of natural fiber reinforced polymer composites

Science and technology advanced at a breakneck pace throughout the 18th century. It was the age of the industrial revolution, which resulted in significant technological developments and the emergence of several monumental designs. As science and technology advanced without being noticed, the condition of the environment deteriorated to a dangerous level. Man trusted in his limitless ability to exploit Mother Nature's resources. Regrettably, this depleted important resources on the planet.

During this time, a world energy crisis occurred in the mid-1970s as a result of man's inefficient use of natural resources, resulting in rising greenhouse effects and high pollution levels [47]. The need of a new study age on preservation was generated when man realised the influence on the environment and the necessity for energy preservation and improvement in the quality of life. During the World Tribology Congress's presidential speech (1990), Dr. H. Peter Jost stepped in and introduced the new notion of 'green tribology.' It discusses the science and technology of tribological factors connected to environmental and biological consequences on the ecological balance. The major goal was to save energy and resources while preserving a healthy environment and a high standard of living [48].

Friction and wear are two essential tribological processes that occur when solid surfaces move relative to one another, and they generally lose energy and degrade materials [49]. There are several strategies to improve the tribological properties of neat polymer. Making composites by embedding fibers in polymers is a popular process [50]. Asbestos and copper were once chosen as friction materials because of their excellent heat dissipation capabilities, but they have now been proved to be hazardous to the environment. Because of its nontoxicity and biodegradability, nonhazardous natural fiber-based friction composite materials have recently piqued the interest of more researchers. Chemically treated natural fiber reinforced polymer composites like sugar palm fiber reinforced polymer composites can be used as friction material in the manufacturing of brake pads in automobiles. Rashid et al. [51] reported that the average coefficient of friction (COF) values of untreated, seawater treated, and alkali-treated sugar palm fiber polymer composites were approximately (0.47–0.58), (0.44–0.50), and (0.41–0.49), respectively, and that the COF values obtained are within the COF ranges for friction materials such as the brake pad materials used in automobiles.

Ramesh et al. [52] investigated the effect of alkali and $KMnO_4$ modification of Calotropis gigantea fibers (CGFs) on the friction and wear properties of CGF/epoxy composites. In relation to untreated and KMnO4 treated CGF composites, NaOH treated CGF samples exhibited the least wear rate. The change in COF is analogous to the change in frictional force over time. When compared to their counterparts, NaOH treated CGF composites had a lower COF, and the COF value rose with duration of wear for all three types of composites.

Rajeshkumar [53] evaluated the influence of different concentrations of NaOH treatment (5, 10, 15, and 20%) on the friction and wear characteristics of Phoenix sp. Fibre/epoxy composites. The results demonstrated that the concentration of sodium hydroxide treatment had a substantial impact on the produced composites' hardness, tribological characteristics, and surface roughness value. The composites reinforced with 15% NaOH treated fibre, in particular, demonstrated greater wear resistance under all operating circumstances and were recommended for producing friction composites for vehicle and machine tool applications.

Nayak and Mohanty [54] examined the erosion wear characteristics of randomly distributed benzoyl chloride modified short areca sheath (AS) fibre reinforced polyvinyl alcohol (PVA) composites. The influence of the erodent (silica sand)'s impact angle and velocity on erosion rate was investigated. Pure PVA had the highest erosion rate at 30 degrees, whereas PVA/AS composites have the highest rate of wear caused by erosion at 45 degrees, indicating partial-ductile behaviour. When compared to other produced composites, the least erosion was recorded at 10% fibre loading composites.

Sumesh et al. [55] studied the linear reciprocating wear properties of hybrid composites fabricated with Sisal fibre (SF), Pineapple fiber (PF), and Pineapple fly ash (PA) at varied weight percentage. The Taguchi optimization demonstrated that composites containing 5 wt.% PA and 30 wt.% hybrid fibers had the lowest specific wear rate. Furthermore, composites prepared with 1 wt. % PA and 30 wt. % hybrid fibres have the lowest COF.

Gang [56] employed an experimental approach to study the effect of silane modification of wood fiber on tensile and tribological properties of wood fiber/polyimide (PI) composites. His investigation verified that surface treatment with the coupling agent may significantly increase the fiber-matrix bonding. The coupling agent treated fiber composites demonstrated better interfacial adhesion than the untreated wood fiber/PI composites. Hence, the coupling agent treatment was critical in increasing the tensile and tribological parameters of the treated wood-polyimide composites.

Liu et al. [57] studied the influence of silane solution concentration on the mechanical, tribological, and morphological characteristics of Corn Stalk Fiber (CSF)/polymer composites. The experimental findings demonstrated that the silane-treated CSF reinforced polymer composite has a potential low density characteristic. Silane coupling agent treatments of the CSF might significantly minimise the polymer composite system's water absorption and perceived porosity. The silane modified CSF did not considerably improve the friction behaviour of the polymer composites, but it did greatly enhance the wear performance. The aggregate wear rate of the 5 percent silane-treated CSF reinforced composite dropped by 22.8 percent when compared to the raw CSF reinforced composite, indicating the best wear resistant behaviour.

An extensive literature review revealed that most of the researchers have employed several different chemical modification techniques to alter the fiber surface. However, some or majority of these chemicals used to modify the fiber surface are not environmental friendly and may also be harmful to the persons handling those chemicals. This will negate the very purpose of using pant based fibers as reinforcement for PMCs as these fibers are environmentally sustainable compared to synthetic fibers. The most popular chemical treatment method is mercerization, which involves immersing the fibers in a highly alkaline bath, such as sodium hydroxide solution. However, it is important to note that this strategy has significant downsides. It is particularly costly and detrimental to the environment because of the usage of toxic chemicals such as sodium hydroxide [58]. Furthermore, such a strongly alkaline treatment can degrade fiber mechanical characteristics, reducing their applicability as reinforcement in polymer composites. Potassium permanganate (KMnO4) is also frequently used to alter the surface of fibers. However, KMnO4 has several disadvantages. Direct contact with KMnO4 can cause serious skin and eye burn, as well as potential eye injury. Potassium permanganate can irritate the throat and nose when breathed in. Potassium permanganate may irritate the lungs, which can lead to coughing and/or shortness of breath when breathed in. So, researchers are more interested in using chemicals that are acceptable and sustainable to the environment [59,60]. The present research work involves the use of environmentally friendly chemicals like glutamic acid, $NaHCO_3$, Na_2CO_3 and hydrogen peroxide along with traditional chemicals like NaOH to modify the fiber surface. The present research work also offers an innovative approach to modify the fiber surface by coating the fiber surface with biodegradable natural polymers like PLA and PHB. The present work also investigated the effectiveness of a low-cost and environmentally friendly chemical modification of sisal fibers based on the usage of sodium citrate and stearic acid on the thermal, mechanical, tribological and morphological characteristics of sisal fiber reinforced epoxy composites.

2.6 Traditional and Eco-friendly chemicals used in the present study to modify the fiber surface

2.6.1 Sodium hydroxide treatment

Alkaline NaOH treatment is the most ancient and commonly employed chemical alteration procedure to modify the fiber surface prior to composite fabrication. The breaking of -OH in the fiber, which increases surface roughness, is the most significant alteration caused by alkaline treatment. This treatment eliminates a portion of the impurities, hemi-cellulose and lignin sticking to the fiber's exterior and also depolymerizes cellulose. The ionisation of the -OH present in the fiber to the alkoxide is promoted by introducing these fibers in NaOH solution. As a result, alkaline treatment has a significant implication on the cellulosic fibril, polymerization degree, and part elimination of lignin and hemicellulosic materials [61].

2.6.2 Glutamic acid

Glutamic acid is a type of non-essential amino acid usually found in both plants and animals and is produced through protein metabolism. It is comparatively more environmental friendly chemical than NaOH to modify the fiber surface. At 25°C, L-glutamic acid is water soluble with a solubility of 8.6mg/ml. Glutamic acid solution is also responsible for the removal of dirt and other impurities from the exterior part of the fiber and enhances the roughness of the fiber surface and thereby, improves the fiber’s adhesion with the polymer matrices [62].

2.6.3 Sodium hydrogen carbonate treatment

The monosodium salt of carbonic acid, sodium bicarbonate/sodium hydrogen carbonate or commonly known as baking soda, has alkalinizing and electrolyte replacement characteristics. Sodium bicarbonate can dissociates into sodium and bicarbonate ions. It is one of the most eco-friendly and cost effective replacement of NaOH for the fiber surface treatment. Selection of proper concentration and treatment time of fiber with the $NaHCO_3$ can produce the same result as NaOH treatment. However, the only drawback of using $NaHCO_3$ is its longer fiber surface treatment duration [63]. Most of the fibers have to be treated in excess of 24 h to obtain satisfactory results.

2.6.4 Sodium carbonate treatment

Sodium carbonate (Na_2CO_3) is a potent alkali and can be compared with the effectiveness of NaOH in terms of the alteration induced on the surface of the fibers. One of the most significant benefits of Na_2CO_3 over NaOH is that it has a lower degradation rate toward the fibers [64]. Na_2CO_3 also has several advantages over $NaHCO_3$, such as being more environmentally friendly and reduction in fiber treatment time.

2.6.5 Hydrogen peroxide treatment

Hydrogen peroxide (H_2O_2) treatment alters the surface of natural fibers in the same way as alkali treatment alters the surface of natural fibers by eliminating the noncellulosic components of the fibers [65]. H_2O_2 induces fiber discoloration as an oxidative bleaching agent. By including bleached fiber into the polymeric composite, superior mechanical properties, as well as improved physical appearance of the composites, can be achieved.

2.6.6 Polylactic acid (PLA) and polyhydroxybutyrate (PHB) coating

Majority of the research work in last decade has been based on the use of chemicals to treat the fiber surface to obtain the desired results of enhancing the fiber-matrix adhesion. The present thesis work involves the application of plant derived polymers like PLA and PHB to coat the surface of fiber. Both PLA and PHB are easily soluble in chloroform and simple dip coating method was used to coat the fiber surface [44,45]. This biodegradable polymer coating of the fiber can reduce the hydrophilic nature of the fibers and therefore, can enhance the fiber-matrix bonding.

2.6.7 Sodium citrate treatment

Sodium citrate is a mildly alkaline chemical with sodium cations can be used to treat the fiber surface to increase their compatibility with epoxy resin. Sodium citrate is an inexpensive, widely available and non-toxic salt of citric acid, which is also used in medicine as a source of sodium ions in locking solutions alternative to unfractionated heparin for dialysis catheters. Due to its antibacterial effects against many food-borne pathogens, sodium citrate is also employed as a food additive to improve the sensory qualities of fish and meat [66]. Furthermore, sodium citrate does not have an adverse impact on the skin and its smoke is not considered severely toxic and it is also easily soluble in water. All these properties make sodium citrate an effective, cheap and eco-friendly alternative to other chemical treatments [67].

2.6.8 Stearic acid treatment

Stearic acid is a fatty acid with a long alkyl chain that can be utilized to reduce the hydrophilic nature of natural fibers. Stearic acid is found in higher concentrations in animal fat (up to 30%) than in vegetable fat (usually 5%). Stearic acid dissolves quickly in ethanol and water (upon heating). Stearic acid, as a fatty acid, has the least environmental impact. Stearic acid has several niche uses due to its low cost, nontoxicity, and inertness. Stearic acid is primarily utilized in the manufacture of detergents, soaps, and cosmetics such as shampoos and shaving cream. All of these features combine to make stearic acid an effective, low-cost, and environmentally friendly alternative to traditional chemical treatments [68]. The carboxyl group of stearic acid reacts with the hydroxyl groups of the fiber through an esterification reaction during the treatment of natural fibers with the stearic acid. This reaction decreases the amount of hydroxyl groups that are accessible to form bonds with water molecules. Stearic acid treatment also has the benefit of making natural fiber/polymer composites resistant to oxidation when processed at high temperatures.

2.7 The research gap from the literature reviews

Despite the numerous experimental and numerical studies that have been published in the past, there remains a significant ambiguous understanding that requires an extensive and methodological investigations in the field of NFRPCs. According to the wide-ranging literature review discussed above :

- The potential application of NFRPCs in structural and thermal insulation applications, where machine-made fibers are frequently utilised, is limited, despite the fact that they have numerous low-end uses including housing, packaging, furniture, and transportation.

- In the last two decades, many researchers have employed several different chemical modification techniques to alter the fiber surface. However, some or majority of these chemicals used to modify the fiber surface are not environmental friendly and may also be harmful to the persons handling those chemicals. This will negate the very purpose of using natural fibers as reinforcement for polymer composites.
- Majority of the previous research works were based on the application of chemical treatment to modify the fiber surface. However, very few research was done on modifying the fiber with biodegradable polymer coatings of PLA, PHB etc.
- Majority of the previous research works were based on understanding the tribological behaviour of NFRPCs by various means, incorporating fiber hybridization, fiber content modification, matrix material modification, and more. However, there are very few reports in the literature about the tribological analyses of composite materials reinforced with chemically treated and polymer coated natural fibers.

2.8 Research plan and objectives of the present work

The research gap in the available literature, as mentioned above, has aided in establishing the aims of this study endeavour, these are discussed as below:

- Surface modification of the natural fibers (hemp, sisal and jute) with various eco-friendly chemicals.
- Bio-degradable polymer (PLA & PHB) coating of natural fibers.
- Physical (SEM, FTIR, XRD) and thermal characterization (TGA) of natural fibers.

- Fabrication of various natural fiber reinforced epoxy composites (NFRECs) (both unmodified and modified).
- Investigation of water absorption and mechanical characteristics of the NFRECs
- Investigation of tribological behaviour of the NFRECs.
- The main objective of the eco-friendly surface modification employed in this research work is to develop a new generation of natural fiber composites with improved fibre/matrix interface resulting in enhanced mechanical and tribological properties.