Chapter 3

Materials & Methods

Materials and Methods

The materials and techniques utilised to fabricate and characterize various types of NFRPCs under research are described in this chapter. It provides information on the tests conducted to characterize different varieties of natural fibers and NFRECs' physical,thermal, mechanical and tribological properties.

3.1 Matrix material

This study involves the use of a thermoset polymer, i.e. Bisphenol-A ($C_{18}H_{21}ClO_3$), which is also considered as an industrial epoxy resin [69]. Epoxy (Bisphenol-A) is primarily chosen for the fabrication of natural fiber composites because it has outstanding chemical and humidity resistivity with greater thermal resilience. In addition to the above advantages, epoxy (LY 556) also has good mechanical properties [70]. The density of the epoxy varies between 1.1 and 1.3 gm/cm^3 and its tensile strength varies from 40 to 60 MPa. Bisphenol-A-Diglycidyl-Ether (BADGE) is a chemical compound that belongs to the 'epoxide' family. This BADGE remain in liquid state but when combined with tri-ethylene-tetramine (HY-951) it gets solidify with or without the application of temperature. LY 556 epoxy resin and the associated hardener HY-951 are supplied by Herenba Instruments and Engineers (Ambattur, Chennai, Tamil Nadu, India).

3.2 Natural fibers employed in the present study

3.2.1 Fiber material - 1: (Hemp fiber)

Hemp is a perennial flora indigenous to Asian continent that has been planted for many centuries. This plant is largely planted in China, the European Union, Central Asia, Philippines, and India. The fibers from the plant is obtained from the bast region, which serve to keep the plant upright. The tree gains strength and rigidity as a result of these fibers. Hemp fiber's exceptional stiffness and tensile strength render them an excellent property to be used as reinforcement in NFRPCs. In recent years, the utilisation of hemp for diverse purposes has increased at an exponential rate. The tensile strength and modulus of elasticity of hemp fiber are about 300–800 MPa and 20–41 GPa, respectively, which is relatively higher than the tensile strength and modulus of commonly used natural fibers such as jute, sisal, cotton, banana, bamboo, and so on [71]. Higher tensile strength and modulus of elasticity of hemp fibers compared with other natural fibers make hemp fiber one of the best natural fiber alternatives to synthetic fiber and therefore has tremendous potential as a reinforcement for polymer composites [72]. Hemp fibers have also been used in the manufacturing of carpets, ropes, gunny sacks, and so on. The hemp fiber usually consists of cellulose (74%), hemicellulose (14%), lignin (5%), pectin (1%), and other impurities like waxes (6%) [71]. However, hemp fiber like all other natural fibers has some undesired properties like a high water retention rate, which results in poor - interfacial adhesion with polymer matrix due to improper bonding between hydrophilic fiber and hydrophobic polymer. Bidirectional hemp fiber mats (density = 1.47 gm/cm^3) used in this study were obtained from Go green products (Chennai, India).

3.2.2 Fiber material - 2: (Sisal fiber)

Agave sisalana plant is the source for the sisal fiber, which is collected from its leaves. Though originally from tropical and subtropical North and South America, the sisal plant is now commonly produced throughout tropical Africa, Asia and West Indies. One of the most widely used natural fibers is sisal and it's also one of the easiest to grow. It has a quick renewal cycle and widely grown in field and railway track hedges. The world wide production of sisal fiber is around 4.5 million tonnes per annum. The bulk of this production came from Tanzania and Brazil. A typical sisal plant produces around 200-250 leaves, each of which includes 1000-1200 fiber bundles, each of which is made up of 4% fibre, 8% dry matter, 87.3 % water and 0.75 % cuticle [73]. So, on average, a 600 g leaf yields roughly 3% of its weight in fibre, with each leaf comprising about 1000 fibers. Sisal fiber consisting primarily of 65% cellulose, 12% hemicellulose, 9.9% lignin, and 2% wax [73]. Sisal fiber properties like fiber length and tensile strength vary depending on the field of cultivation, fiber extraction process, and the age of the plant. The average tensile strength of the sisal fiber varies from 100 to 600 MPa and the average fiber length ranged from 1.5 to 1.78 m. Sisal fibers are widely used in making ropes, mats, handcrafted articles, etc. Sisal fibers are also used as reinforcement in polymer composites. Automotive manufactures have also used sisal fiber-reinforced polymer composites in making various automotive parts. Sisal fiber (density = 1.33 gm/cm^3) mats used in this study was supplied by Go Green Products (Chennai, Tamil Nadu, India).

3.2.3 Fiber material - 3: (Jute fiber)

Jute is the most affordable plant based bast fiber, and it is abundant in India and Bangladesh. Jute fiber is traditionally used to manufacture shopping bags, floor mats,

hessian clothing, and ropes, among other things [74]. Jute fibers offer a number of advantages, including low cost, environmental friendliness, and moderate mechanical qualities, making them a better substitute for synthetic fiber to be used as reinforcement in composite industries. It is collected after 2 to 3 months of cultivation and stands 2-4 meter in height. The jute blast fibers develop longitudinally around the jute stick called pith. Retting is the process of separating jute blast fiber from pith. Cut jute stalks are retted by soaking them in ponds for a few weeks. The pond's microbial activity loosen the fibre and breaks the connections uniting the fibre and the jute stick. After that, the fibre stands are removed off the jute stick and dried in the atmosphere. It was discovered that jute plants absorb 15 tonnes of carbon dioxide from the environment and release 11 tonnes of oxygen throughout their 120-day life span. The decomposing roots and leaves of jute plants boost soil fertility while lowering fertilizer costs. This demonstrates that jute is probably the most eco-friendly plant based bast fiber. Bidirectional jute fiber mat having a density of 1.46 gm/cm^3 used in this study was procured from Go green products, India.

3.3 Surface treatment of hemp fiber

Just before the chemical modification, hemp fiber mats were thoroughly cleaned with regular tap water and then left to dry in the sun for 10 h.

3.3.1 Sodium carbonate treatment

The hemp fiber mat was subjected to sodium carbonate surface treatment, which required the dipping of the hemp fiber mat in a 5 wt% solution of sodium carbonate for a time period of 6 h. The fibers were then thoroughly cleaned with deionized water for 5–6 times to remove the sodium carbonate solution sticking to its surface,

followed by air drying for 24 h at 60°C in an oven [64]. The Na_2CO_3 modified fiber is represented as sodium carbonate treated (ST) hemp fiber.

3.3.2 Hydrogen peroxide treatment

The hemp fiber mat was subjected to surface alteration procedure by dipping it in 5 vol% H_2O_2 solution for a time period of 80 min, while pH 11 was maintained by using 0.5 M NaOH in a 75°C water bath. After the hydrogen peroxide treatment was over, the hemp fiber mat was properly washed with deionized water until a neutral pH was achieved and then oven dried at 60°C for 25h [65,92]. The hydrogen peroxide-modified hemp fiber is denoted as peroxide treated (PT) hemp fiber. Sodium carbonate and hydrogen peroxide were obtained from Sigma Aldrich, India.

3.4 Biodegradable polymer coating of hemp fiber

Prior to the fiber coating process, the hemp fibers were subjected to sodium hydrogen carbonate treatment by submerging the hemp fibers in 5 wt% solution of $NaHCO_3$ at room temperature for time period of 24 h. The $NaHCO_3$ treated fibers were then properly washed with distilled water for 4-5 times and oven dried for 24 h at 62°C [77].

3.4.1 PHB coating of fibers

PHB solvent was prepared by submerging 2% w/v of PHB pallets in a chloroform solution. Uniform dispersion of PHB was achieved by heating the solution to 60°C with constant stirring. $NaHCO_3$ treated hemp fibers were then coated with PHB by dipping the hemp fibers in the solution for 5 mins [44]. Finally, the PHB coated hemp fibers were dried at room temperature for 30 h.

3.4.2 PLA coating of fibers

PLA solvent was prepared by submerging 2% w/v of PLA pallets in a chloroform solution. Uniform dispersion of PLA was achieved by heating the solution to 60°C with constant stirring. $NaHCO_3$ treated hemp fibers were then coated with PLA by dipping the hemp fibers in the solution for 5 mins. Finally, the PLA coated hemp fibers were dried at room temperature for 30 h [45,46]. Sodium hydrogen carbonate was obtained from SRL chemicals (Mumbai, India). PHB and PLA pallets were provided by Eshwari Chemtech (Bangalore, India).

3.5 Surface modification of sisal fiber

Sisal fiber mats were thoroughly washed with distilled water in order to remove dirt and other impurities sticking to its surface. The untreated (UT) fiber mat was then left for drying at room temperature.

3.5.1 NaOH treatment

The sisal fiber mat was dipped in a 5 wt. % solution of NaOH at room temperature for a time period of 5h. After that the alkali treated (AT) fiber mat was thoroughly washed with distilled water and then with acetone until the pH becomes 7. The AT fiber mat was put in an oven at 70°C for 24h for drying [53].

3.5.2 Glutamic acid treatment

10 wt. % (total weight of the fiber to be treated) solution of glutamic acid was prepared. The sisal fiber mat was dipped into the glutamic acid solution and allowed at room temperature for a period of 24h. The glutamic acid treated (GT) fiber mat was

then washed 5 to 6 times using deionized water and was placed in an oven for drying at a temperature of 65℃ for 24h [62].

3.5.3 Combination treatment

Combination treatment means that the sisal fiber mat was first treated with sodium hydroxide and then modified with glutamic acid treatment. In combination treatment, the sisal fiber mat was first modified by 5 wt. % solution of NaOH as mentioned above. After that, the sisal fiber mat was immersed for a time period of 24h in a 10 wt. % (total weight of the fiber to be treated) solution of glutamic acid. Then the sisal fiber mat was removed from the solution, thoroughly cleaned using deionized water, and put in an oven for 24h at a temperature of 65℃ for drying. This fiber mat was represented as Alkali + Glutamic acid treated (AGT) fiber mat [62]. Sodium hydroxide and glutamic acid were supplied by Sisco Research Laboratories Pvt Ltd. Hydrochloric acid and Acetone were supplied by Sigma Aldrich. Hydrochloric acid was used as a pH regulator and acetone was used as a cleaning agent.

3.5.4 Stearic acid treatment

A homogeneous solution of stearic acid was prepared by adding 4 wt% stearic acid in the deionized water with continuous heating. After that, the untreated (UT) sisal fiber mats were treated for 1 h in an ultrasonication bath with the prepared stearic acid solution [68]. The stearic acid treated (SAT) sisal fiber mats were thoroughly washed with distilled water to remove the excess stearic acid attached to the fiber surface and then oven dried for 24 h at 80^{o}C.

3.5.5 Sodium citrate treatment

Sodium citrate surface modification of sisal fiber was performed by soaking the sisal fiber mats in a solution prepared by adding 4 wt% sodium citrate in deionized water for 120 h at room temperature. After that, the sodium citrate treated (SCT) sisal fiber mats were dried at ambient temperature for 24 h before being oven dried for another 24 h at 85°C [67]. Stearic acid and sodium citrate used in this research work was supplied by SRL chemicals (Mumbai, India).

3.6 Jute fiber surface treatment

Prior to any chemical treatment, jute fiber mats were thoroughly cleaned with normal tap water and were then left at room temperature for drying.

3.6.1 Sodium hydroxide treatment

The untreated jute fiber (UT) mat was dipped in a 5 wt% sodium hydroxide solution with constant stirring for a time period of 5 h at room temperature [53]. The alkali treated jute fibre (AT) mats were then cleaned with distilled water for multiple times until the pH was 7. After that the AT fibre mat was placed in a drying oven at 60°C for 30 h.

3.6.2 Sodium carbonate treatment

Sodium carbonate modification of jute fiber mat was done by submerging the jute fiber mat in 5 wt% solution of Na_2CO_3 for 6 h at ambient atmosphere [64]. The sodium carbonate treated (ST) fibers were the properly washed with distilled for multiple times and put in an oven for 24 h at 60°C.

3.6.3 Sodium hydrogen carbonate treatment

The jute fiber mats were dipped in 5 wt% solution of sodium hydrogen carbonate at room temperature for a time period of 120 h. The sodium hydrogen carbonate treated (SHT) fibers were then washed with distilled water for 4-5 times and placed in an oven for one day at 60^{o}C [77]. Sodium hydroxide, sodium carbonate and sodium hydrogen carbonate were supplied by Sisco Research Laboratories Pvt Ltd, India.

3.7 Physical and thermal characterization of natural fibers

3.7.1 Scanning electron microscopy (SEM)

The surface morphology of untreated, chemically modified and surface coated fibers were performed employing a scanning electron microscope (EVO-Scanning Electron Microscope MA15/18 by Carl Zeiss Microscopy Ltd).

3.7.2 Fourier transform infrared spectroscopy (FTIR)

FTIR was carried out to study the functional group of both treated and untreated fibesr. Infrared spectrum of both raw and modified fibers were recorded in Nicolet iS5 spectrophotometer (THERMO Electron Scientific Instruments LLC) with a scanning range of 4500 cm^{-1} to 550 cm^{-1} and a resolution of 4 cm^{-1}. The dried natural fibers were analyzed in an attenuated total reflectance (ATR) mode.

3.7.3 X-Ray diffraction (XRD)

X-Ray diffraction test was conducted to evaluate the crystallinity of both the chemically modified and untreated fiber. The XRD test was performed on a Rigaku miniflex 600 desktop X-Ray diffraction system (Rigaku Corporation) with a Cu Kα

radiation (1.54 Å set at 40 kV voltage and 40 mA current. Crystallinity index is a quantitative indicator of crystallinity. The crystallinity index has been used to describe the relative amount of crystalline material in cellulose. The traditional two-phase cellulose model describes cellulose chains as containing both crystalline (ordered) and amorphous (less ordered) regions. The following equation was employed to obtain the crystallinity index (I_C) of the fiber.

$$I_C = \frac{I_{002} - I_{am}}{I_{002}} \quad (1)$$

Where, I_{002} = Highest diffraction intensity of the crystalline material.

I_{am} = Lowest diffraction intensity of the amorphous material.

3.7.4 Thermogravimetric analysis (TGA)

TGA curves for the investigation of the thermal stability of UT and treated sisal fibers, as well as their composites, were generated using a TGA-50 instrument (M/S Shimadzu Asia Pacific Pvt Ltd). TGA tests were conducted in an inert atmosphere containing nitrogen gas. Samples weighing 4.7 gm to 6.9 gm were heated at a rate of 10°C/min from 21°C to 600°C in this method. To ensure reproducibility, the measurement was carried out twice.

3.7.5 Differential scanning calorimetry (DSC)

A model DSC-60 Plus modulated differential scanning calorimeter (M/s Shimadzu (Asia Pacific) Pvt Ltd) was used for the DSC analysis of the fibers and composites. Each scan was carried out in an open aluminum pan with a heating rate of 10°C/min from ambient temperature to 550°C in the presence of nitrogen gas. To ensure reproducibility, the measurement was carried out twice.

3.8 Composite fabrication

3.8.1 Composite fabrication - 1: (Hemp fiber reinforced epoxy composites)

Both untreated hemp fiber reinforced epoxy composites (HFREC) and treated HFREC was fabricated by simple hand layup technique. A steel mould having a measurement of 200 mm × 200 mm × 6 mm was utilized for the fabrication of the HFREC samples. Five layers (19 percent) of bidirectional hemp fiber mats having fiber orientation of 0^o and 90^0 were used and the fiber mats were arranged one layer over the other layer in similar direction. Five layers of similarly arranged bidirectional hemp fiber mats were then placed in the steel mould and a combination of epoxy and its hardener was streamed into the mould at a weight ratio of 10:1. A uniform weight of 20 kg was placed over the mould for a time period of 24 h for curing. Hemp fiber composite samples were cured for another 12 h following separation from the steel mould. : Fiber concentration in the composite greatly affects its properties. Majority of the Natural fiber-based polymer composites give their optimum performance in terms of mechanical, water absorption tribological properties when the fiber content in the composite is $\leq$ 25%. It has been observed that on further increase in fiber content there was decrease in the strength. This is due to insufficient amount of matrix needed to wet the fibers, thus leading to debonding and premature failure of the composite material due to shear stress developed between the lamina. This is the reason for choosing fiber content less that 25%. Fiber orientation in the composite is also responsible for determining its mechanical properties. In this research work 0^o /90^o fiber orientation was chosen so that the composite can give optimum mechanical performance in both longitudinal (0^o) and transverse direction (90^o).

Simple hand layup technique was also employed to manufacture the uncoated and PLA and PHB coated hemp fiber reinforced epoxy composites (HFREC). A silicon mold having a dimension of 180 mm × 180 mm × 4 mm was utilized for the purpose of composite preparation. Four layers (about 20%) of both uncoated and coated hemp fiber mats were placed in the silicon mold, and a 10:1 weight ratio of epoxy and its hardener was fed into the mold. The curing was done for a time period of 24 h by placing a uniform load of 5 kg over the mold and a further curing of 12 h was also done for HFREC sample after removal from the mold.

3.8.2 Composite fabrication - 2: (Sisal fiber reinforced epoxy composites)

Sisal fiber mats were used as the reinforcement and epoxy and its hardener were used as the matrix of the composite. Simple hand layup technique was used to prepare the composites. Untreated, NaOH treated, GT and GAT sisal fiber mats were used as reinforcement to fabricate the composites. A wooden mould having a dimension of 250 mm × 250 mm × 6 mm was used for the preparation of the composites. Three layers of sisal fiber mats were put in the wooden mould and a mixture of epoxy and its hardener in the weight ratio of 10:1 was poured into the mould. For even distribution of epoxy and its hardener, a roller was used. To improve the epoxy flow through the sisal fiber mats, a uniform load of 20kg was applied to the mould. The composites were kept under the load for a time period of 24h for curing. After removal from the mould, the composites were post cured for another 12h. Teflon sheets and silicon spray were used for the smooth removal of the composites from the wooden mould. Finally, the prepared composites were cut into the required sizes for various testing.

Vacuum assisted resin infusion process was used to produce square size (280 mm × 280 mm × 5 mm) composite plates reinforced with untreated, stearic acid and sodium citrate treated sisal fibers. Six sisal fiber mats (25 %) were utilized as reinforcement for each composite plate, and epoxy resin in combination with the hardener at a ratio 10:1 was used as the matrix. All of the composite plates were cured at room temperature for 24 h before being post-cured for another 15 h. Samples for mechanical and tribological tests were cut from the fabricated composite plates to their required dimensions with the help of a diamond cutter.

3.8.3 Composite fabrication - 3: (Jute fiber reinforced epoxy composites)

Jute fiber reinforced epoxy composite (JFREC) specimens were prepared with simple hand layup technique. An aluminium mould with a dimension of 260 mm × 260 mm × 5.5 mm was employed for the manufacturing of the composite samples. In the aluminium mould, four layers (17%) of jute fibre mats were placed and a mixture of epoxy and its hardener was poured into the mould at a weight ratio of 10:1 and was left at an ambient atmosphere for 24 h under a uniform load of 25 Kg for curing. Composite specimens were further post cured for 12 h after removal from the aluminium mould. Teflon sheets and silicon spray were employed for the easy separation of the JFREC specimens from the aluminium mould. The fabricated composite specimens were then cut in to desired shapes and sizes for various mechanical and tribological testings.

3.9 Water absorption, mechanical and tribological tests of the composites

3.9.1 Water absorption test

The water absorption experiment of the HFREC samples was performed according to ASTM D570-98 standard by submerging the composite samples from 24 h to 192 h and the changes in the mass of the composites were measured every 24 h. The percentage water absorption for the HFREC samples was calculated by employing the following formula.

$$\% \text{ water absorption} = \frac{W_F - W_I}{W_I} \times 100 \quad (2)$$

Where, W_F = Weight of the composite specimen after immersion.

W_I = Initial weight of the composite specimen before immersion.

3.9.2 Tensile test

Tensile tests of the composite specimens were carried out using an Instron universal testing machine with a 100 kN load cell that was computer controlled. Tensile tests were performed on test specimens according to the ASTM D-3039 standard, using a cross-head speed of 2 mm/min.

3.9.3 Flexural test

A computer-controlled Instron universal testing equipment was used to conduct the flexural tests of the composite specimens according to ASTM D-790 standard. The flexural characteristics of the composite specimens were evaluated at a cross-head speed of 2 mm/min and span length of 80 mm. The below mentioned formula is employed to calculate the flexural strength of the NFRPC specimen.

$$\text{Flexural strength} = \frac{3PL}{2bt^2} \quad (3)$$

Maximum load is denoted by symbol P (N), the length of the span is denoted by symbol L (mm), and width and thickness of the NFRPC specimens are denoted by b and t, respectively (both in mm).

The below mentioned formula can calculate the value of Flexural modulus

$$\text{Flexural modulus} = \frac{mL^3}{4bt^3} \quad (4)$$

Where, m is the slope of the tangent of the load deflection curve (N/mm).

3.9.4 Impact test

Impact energy is the amount of energy necessary to cause a material to fracture under an impact load. The composite specimens are put through instrumented low-velocity impact testing. The Resil impactor impact testing machine was used to perform the charpy impact tests in accordance with ASTM standard D 6110-10. A hammer in the form of a pendulum is used to break the specimen and the energy utilised is measured which is co-related to cross-section area of the sample. The dial indicator directly records the impact energy that was used to break the composite specimens.

3.9.5 Short beam shear test

Interlaminar shear strength (ILSS) of the composite specimens (width $=$ 7 mm and length $=$ 27 mm) were determined by short beam shear test using Instron universal testing machine according to ASTM D-2344 standard at a cross-head speed of 2 mm/min. All the mechanical tests were performed for at-least three

times for each type of sample. ILSS of the composite samples are calculated from the following equation

$$\text{ILSS} = \frac{3P}{4bt} \quad (5)$$

3.9.6 Vickers microhardness test

ASTM E384 standard was used to study the microhardness properties of the natural fiber epoxy composites with the help of Microindentation Tester:MHT3 (Anton Paar). When a load (F) is applied, a diamond indenter with a right pyramid shape, square base, and 136° angle between opposing faces is pressed into the material. After the load has been removed, the two diagonals X and Y of the indentation still visible on the material's surface are calculated, and their arithmetic mean H is determined. Microhardness tests were performed at six different locations of the composite specimen and the average value was taken. Vickers microhardness (H_V) is calculated from the following equation.

$$H_V = 0.1889 \frac{F}{H^2} \quad (6)$$

Where, $H = \frac{X+Y}{2}$

3.9.7 Dry sliding wear tests

Sliding wear tests of the natural fiber reinforced epoxy composite specimens were performed in a ball-on-block test setup provided by Ducom Instruments, India under dry environment. A 5.5 mm diameter of steel ball was used as a counter surface and was held stationary against the rotating specimens. The composite specimens were

tested under different applied loads and at various sliding speeds. The normal load is applied through a lever mechanism and the friction forces are calculated by a friction sensor. An electronic balance having an accuracy of 10^{-4} gm was used for the purpose of measuring the weight loss of specimens after the tribological tests. Specific wear rate (SWR) of the specimens were calculated with the help of following Equation

$$\text{SWR} = \frac{\Delta M}{\rho \times P \times L} \tag{7}$$

Where, SWR = specific wear rate (mm^3/Nm), ΔM = mass loss (gm), ρ= density of the composite sample (gm/cm^3), P = applied load (N) and L = sliding distance (m).

3.10 Surface morphology tests

Investigation of the surface morphology of tensile, flexural and wear surfaces of the composites were done by scanning electron microscope (EVO-Scanning Electron Microscope MA15/18 by Carl Zeiss Microscopy Ltd).

Chapter summary

The following topics are discussed in this chapter:

- The details of the fibers and matrix materials used in this study.
- The descriptions of the various chemical treatment and surface coating techniques employed to modify the fiber surface.
- The technicalities of manufacturing process of the various NFRECs.
- The details of different experimental methods employed for evaluating the physical, thermal, water absorption, mechanical and tribological behaviour of the fibers and NFRECs.

The next chapter presents the results and discussion of the physical and thermal characterization of the fibers under this study.