Chapter 03. Materials

3.1 Introduction

Environmental concerns have led to the development of sustainable products from waste and biomaterials. The materials preferred are natural waste such as natural fibers or materials derived from them such as biopolymers. The primary objective of the research is to produce CFF reinforced PLA composite filament for 3D printing. To achieve this objective first, the CFF is characterized for its properties and later it was prepared to be mixed with PLA granules. The mixture is passed through the indigenously prepared filament extruder to obtain the filaments.

The properties of CFF and PLA have been discussed in this section. The constituent material characteristics namely Physical properties, chemical properties, mechanical properties, and morphological properties were evaluated from the previous literature and are discussed in the subsequent sections. The pre-processing carried out on the materials before utilizing them to prepare the biocomposite has also been presented in the chapter.

3.2 Chicken Feather Fiber (CFF)

The annual consumption of poultry is around 900 metric kilotons (Hannah Ritchie and Roser, 2021). The feathers amount to an average of about 6-7 % of the total weight of the chicken (Solcova et al., 2021) forming about 63 metric kilotons of chicken. CFF is a bio-waste from the poultry industry. It is also a natural fiber that is being pursued as reinforcement in composites. The benefits of using CFF as reinforcement are:

- It is a waste material and is available in abundance (Khan et al., 2022).
- It is biodegradable (Aranberri et al., 2017; Das et al., 2018; Reddy et al., 2014).
- It has a higher strength to weight ratio compared to synthetic fiber reinforced composites (Lau and Cheung, 2017).
- They are hydrophobic, hydrophilic and hygroscopic at the same time because of the presence of various amino acids having similar natures (Khosa et al., 2013; Misra et al., 2001; Saucedo-Rivalcoba et al., 2011).
- The fiber structure of CFF exhibits good interlinking and helps retain matrix material to make stronger composites (Gassner III et al., 1998; Schmidt, 1998).
- It shows good acoustic properties because of its hollow internal structure (Huda and Yang, 2009).

- Long and Short fiber reinforced CFF composites exhibit better mechanical strength compared to particulate CFF (Baba and Özmen, 2017).

Four main types of feathers adorn a chicken's body: down feathers, contour feathers, semiplumes, and filoplumes. The feathers are highly ordered and have hierarchical branched structures. For maintaining the consistency of the size of the feather, the age of the broiler chicken was kept at 40-42 weeks. The average weight of the broiler chickens whose feathers were used in the study varied from 1.1 kg to 1.5 kg. Also, the barbs of the contour feathers from the wings of white broilers are used to maintain homogeneity in the properties of the fibres. The picture of the chicken feather is shown in Figure 3-1 Contour feather of a white broiler chicken.

Figure 3-1 Contour feather of a white broiler chicken.

3.2.1 Physical properties of Chicken feather

The physical properties of chicken feathers are presented in this section. Figure 3-2 Parts of the chicken feather with nomenclature. The properties include fiber length, diameter and density. The feathers were measured using the standard scale for length. The average length of the contour feather from chicken varied from 90 mm to 120 mm. The barbs cut from the feathers measured from 7-8 mm at the tip of the feather to 16-19 mm at the middle of the feather. The barbs were observed under the Nikon stereoscopic zoom microscope SMZ 800 for the diameter. The average diameter of the barbs varied from 23-44 µm. Sample photographs of measurement are shown in Figure 3-3 Diameter measured under Nikon stereoscopic zoom microscope SMZ 800

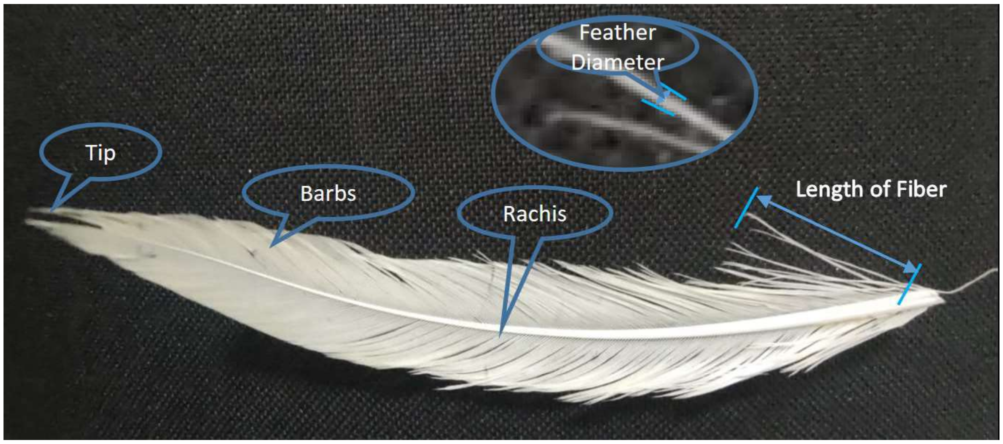


Figure 3-2 Parts of the chicken feather with nomenclature

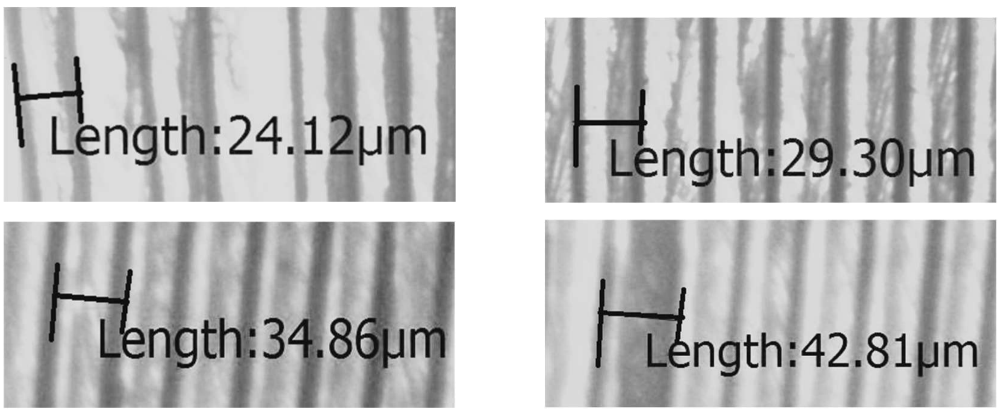


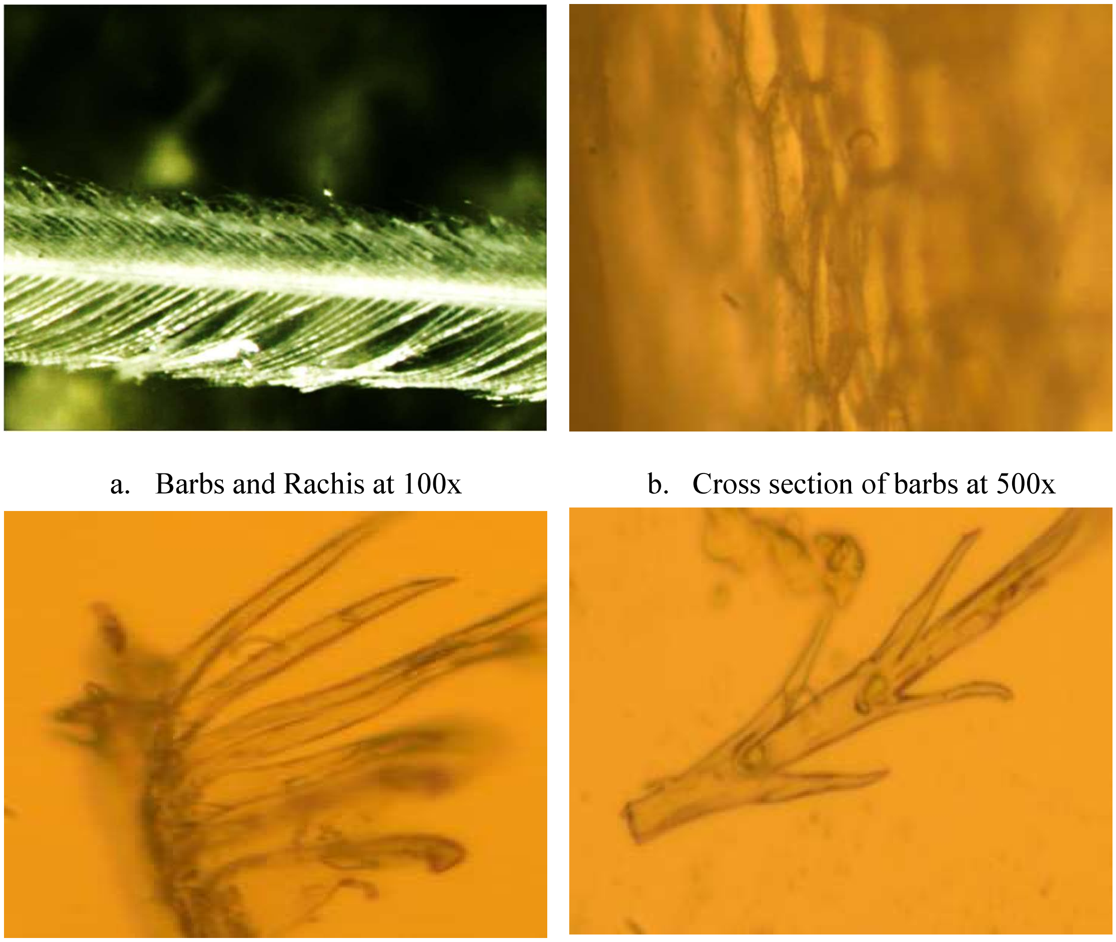
Figure 3-3 Diameter measured under Nikon stereoscopic zoom microscope SMZ 800 using MetaVue software.

The average density of whole chicken feathers has been observed to be between 0.67 gm/cm^3 to 0.68 gm/cm^3. The average density of only the barbs is 0.5 gm/cm^3 to 0.8 gm/cm^3 (Bharathi and Raj, 2021; Rijke, 2016; Tesfaye, Sithole, Ramjugernath, Chunilall, et al., 2017).

3.2.2 Morphology of Chicken feather

The morphology of the barbs of the chicken feather is unique and has been observed using a stereoscopic microscope. The observations are shown in Figure 3-4.

The barbs and rachis show a hollow honeycomb structure at 500x magnification. This results in a lower density of chicken feathers. The micrograph of the feather shows the secondary and tertiary structure of barbs and barbules. At 100x the hooklet structure of barbules is visible. The intertwining of hooklets gives the feather bulk strength.



a. Barbs and Rachis at 100x

b. Cross section of barbs at 500x

c. Barbules at 500x

d. Hooklets at 1000x

Figure 3-4 Morphology of barbs and barbules observed under stereo microscope.

3.2.3 Chemical structure of Chicken feather

The chemical composition indicated in the proximate analysis of chicken feathers is 82- 91% protein (Keratin), 1% lipids, crude fiber 2-2.5%, and 8-12% water (Arai et al., 1986; Lau and Cheung, 2017; Martínez-Hernández et al., 2005; Tesfaye, Sithole, Ramjugernath, and Chunilall, 2017). The composition obtained with ultimate analysis is Carbon 62-65% Nitrogen 16-17% and Sulphur 2-3%. The keratin in chicken feathers is a mixture of various proteins. The chemical structure of keratin in chicken feathers is shown in Figure 3-5.

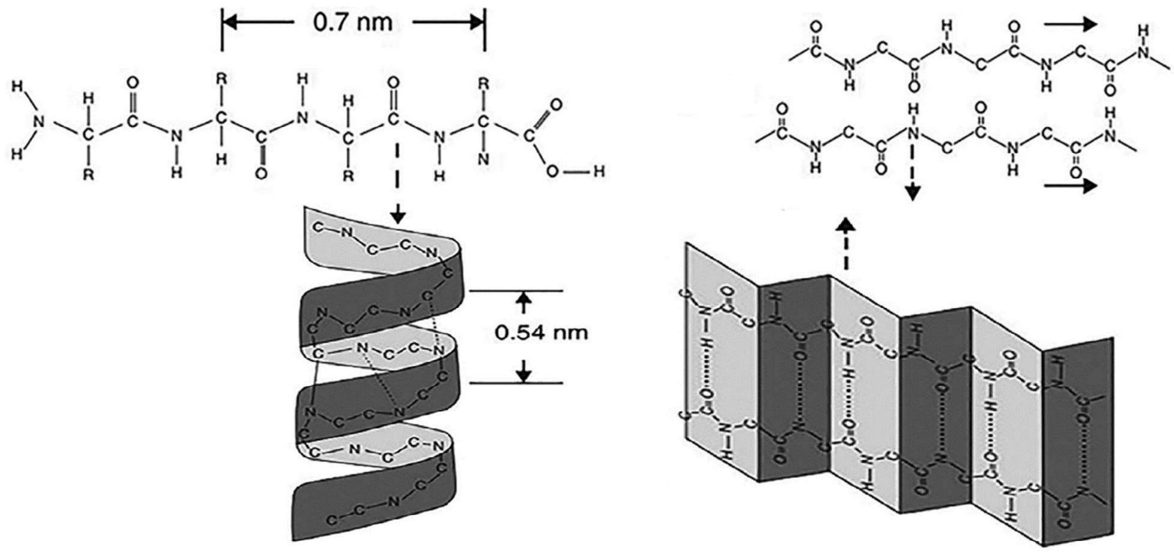


Figure 3-5 Chemical structure of keratin from Chicken feather α-keratin (α-helix) and β-keratin (β-pleated sheet) (Acda, 2010a; Chilakamarry et al., 2021).

The feather contains aspartic acid (~5%), glutamic acid (~7%), arginine (~5%), proline (~12%), glycine (~11%), alanines (~8%), cysteine (~7%), valine (~9%), leucines (~11%), and serine (~4%) as the major constituents (Arai et al., 1986; Martínez-Hernández et al., 2005; Tesfaye, Sithole, Ramjugernath, and Chunilall, 2017). There are 20 amino acids, and tree like structure in central carbon linked to functional groups of amine, amides, and carboxylic acid along with the hydrogen atoms and the sulfur molecules (Martínez-Hernández and Velasco-Santos, 2012).

3.2.4 Mechanical properties of Chicken feather

The tensile strength of chicken feathers is 23.9 g/tex, breaking extension 1 to 6%, and density is 0.8 to 1.12 g/cc. (Pradhan et al., 2020; Saravanan and Prakash, 2020). The mean tenacity of the chicken feather was observed at 16.93 cN/tex, while the mean elongation at maximum load was 0.48mm (Tesfaye et al., 2018).

The young modulus of the feather is around 1.78 GPa. (Bonser and Purslow, 1995; Cameron et al., 2003). The tensile modulus of CFF is 3.59 ± 1.09 GPa, and the average tensile strength was 203±74 MPa. The failure follows the Weibull distribution with a scale parameter value of 178.7 MPa and a shape parameter value of 2.32 (Zhan and Wool, 2011).

3.2.5 Thermal properties of Chicken feather

It is important to understand the thermal properties of chicken feathers before processing them for manufacturing the samples. The thermal stability and thermal resistivity of the chicken feather can be understood by understanding the DSC thermograms of its various parts.

Figure 3-6 shows the DSC thermograms of various parts of chicken feathers. From the DSC it can be seen that the chicken feather undergoes three different stages when subjected to heat.

Stage 1: Between 43-145 °C, Moisture is removed.

Stage 2: Between 230-275 °C, The feather shows signs of blackening, which can be interpreted as melting (W. F. Schmidt and Line, 1996).

Stage 3 It is observed from 280 °C to 340 °C. In this stage, the total decomposition of the chicken feather occurs

The glass transition temperature of the chicken feather is observed in the second stage, i.e., between 230-275 °C. It indicates that the drying temperature for CFF should be above 100 °C and below 125 °C.

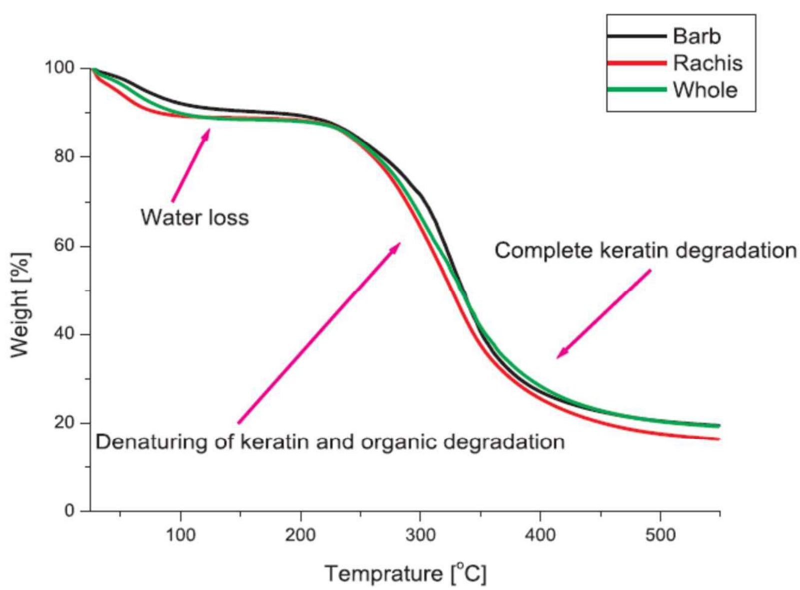


Figure 3-6 DSC of various parts of the chicken feather (Webb et al., 2013).

The processing of chicken feathers should be carried out at temperatures below 230 °C to avoid deterioration during processing (Martínez-Hernández et al., 2005; W. F. Schmidt and Line, 1996; Tesfaye et al., 2018).

The properties of the chicken feather are summarized below in Table 3-1.

Table 3-1 Summary of Properties of Chicken Feathers.

Property	Parameter value
Physical properties	
Average length	90 – 120 mm
Average Diameter of Barbs	23 - 44 µm
Density	0.5 -0.8 gm/cm^3
Mechanical Properties	
Mean tenacity	16.93 cN/tex
Maximum Elongation	0.48 mm
Young's Modulus	1.78 GPa
Tensile strength	203 ± 74MPa
Thermal Property	
Glass Transition Temperature	230 – 275 °C
Chemical Composition	
Keratin	82 - 91 %
Lipids	1 %
Crude Fiber	2-2.5 %
Water	8 – 12 %

3.2.6 Pre-processing of Chicken feather

The chicken feathers are collected from the local supplier - Kadariya Chicken Shop in Vadodara, Gujarat, India. The feathers are removed from the skin and washed with soap to degrease and clean them of all dirt and bloodstains. The clean and rinsed chicken feathers are dried for 24 hours at room temperature. The feathers are put in the NaCl solution for 15 minutes. They are then washed with tap water for three cycles to remove any residue remaining of blood, dirt, NaCl, or soap. The chicken feathers are sun-dried for 72 hours to remove all the unbonded water. The dried chicken feathers are trimmed using a pair of scissors to remove the fibres (barbs) from the rachis part of the feathers

3.3 Poly-Lactic Acid (PLA)

Poly-Lactic Acid (PLA) is a non-petroleum derived bioplastic. PLA is a thermoplastic polymer derived from monomer lactic acid which is obtained from cellulose produced from biomass such as corn, sugarcane, sugar beet, cassava, and other agricultural wastes. PLA is produced in similar methods as those plastics produced from fossil fuels. PLA has many shortcomings as the polymer chain is entirely dependent on the biomass it is derived from.

Poly-lactic Acid (PLA) is an aliphatic polyester obtained by polymerization of the lactide $[C(CH_3)HC(=O)O–]_2$ molecules. The chemical composition of PLA is $(C_3H_4O_2)_n$ or $[C(CH_3)HC(=O)O–]_n$. Figure 3-7 Chemical structure of Poly-Lactic Acid.

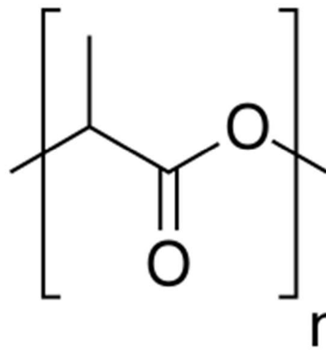


Figure 3-7 Chemical structure of Poly-Lactic Acid.

Raw material with parameter value as shown in Table 3-2 Properties of PLAwere received from PLA supplier - CHEM TECH PRO, Vadodara.

Table 3-2 Properties of PLA.

Property	**Parameter value**
Flexural modulus	3600 - 3650 MPa
Flexural Strength	108 MPa
Tensile strength	45 - 60 MPa
Melting Temperature	153 – 155 °C
Glass Transition temperature	57.5 – 60 °C
Density	1.24 gm/cm^3

The thermal properties mentioned in Table 3-2 are also visible in the DSC curve of PLA shown in Figure 3-8.

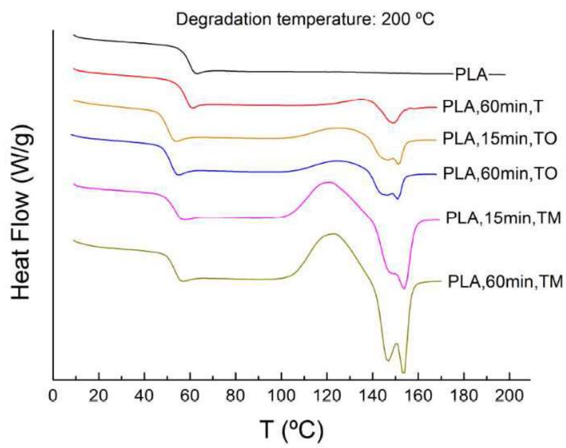


Figure 3-8 DSC curves of PLA (Cuadri and Martín-Alfonso, 2018; Cuiffo et al., 2017).

Polylactic gets easily hydrolyzed in the presence of moisture (Yew et al., 2005). This makes them brittle over a period of time. PLA is a hydrophobic polyester (Cuadri and Martín-Alfonso, 2018), which is responsible for the formation of pinholes when used without pre-processing.

3.3.1 Pre-processing of Poly-Lactic Acid

For preventing the moisture to form pinholes during filament processing, PLA granules are to be preprocessed. In the present study, the granules were baked at 90 °C for 6 hours in a hot air oven before utilizing them for manufacturing the filaments. The granules were placed on a Borosil Petri plate and then placed in the hot air oven as shown in.

Figure 3-9 Hot air oven HAO DM -101 Make DM – instruments.