



ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF MULTIDISCIPLINARY ENGINEERING
CENTER FOR MATERIALS ENGINEERING

**Value added Consumer Product from Finished Leather Waste Incorporated
with Bamboo Fiber for better Strength Property**

By
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**A Thesis Submitted to Addis Ababa institute of Technology in Partial Fulfillment of the
Requirement for the Degree of Masters of Science in Materials Engineering.**

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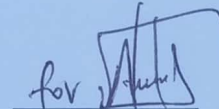
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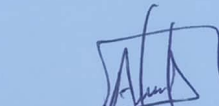
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DECLARATION

I declare that this thesis entitled “**Value Added Consumer Product from Finished Leather Waste Incorporated with Bamboo Fiber for better Strength Property**” has not been submitted in any form for another degree, diploma or an award at any university or other institution of the tertiary education. I confirm that appropriate credit has been given within this thesis where reference has been made to the work of others and has been duly acknowledged. The work was under the guidance of **Dr. Anteneh Wodaje**, instructor in Addis Ababa University, Addis Ababa institute of Technology, School of Materials Engineering.

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ABSTRACT

Finished leather waste is one of the most highly generated solid wastes. However, there is no proper utilization of these huge amounts of waste. So preparation of leather boards from finished leather waste is economical and helps in reducing environmental pollution, and also incorporating the plant fibers into leather board enhances its mechanical properties. In this research different treatment methods, such as water retaining, alkali treatment, and the combination of water and alkali treatment was used for the extraction of bamboo fiber. Then 5% alkali treatment was the optimum result for this research. After that fiberized finished leather waste mixed with the plant fibers in various proportions of 0, 1%, 5%, 10%, and 15% were used to prepare the composite leather board. Two different types of binders, mainly urea formaldehyde and fevicol synthetic in the proportion of 10%, 15%, 25%, 35%, and 45%, were used for the study. Here also 15% was optimum for both formaldehyde and favicon resin binder. The prepared leather board were characterized using the following techniques: Fourier transform infrared spectroscopy (FTIR), thermal stability (TGA), scanning electron microscope (SEM), tensile strength, water adsorption and desorption, flexing index, chromium six, and formaldehyde content. The results show that plant fibers improve the strength property of leather boards. Among the composite leather boards, composite board with 10% bamboo fiber with 15% urea formaldehyde, and fevicol synthetic resin show better strength property. However, the strength property of urea formaldehyde is better than that of fevicol binder. Therefore, this composite leather board can be used as a raw material for the preparation of leather goods (as a reinforcing material), false roofing, foot wear (insole board), mouse pads, interior decorations, and wall partitioning. The study also envisions the production of cost-effective composite, by converting the waste into wealth and thereby simultaneously reducing environmental pollution.

Keywords: *finished leather waste, plant fibers, binder, mechanical properties, chemical properties.*

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ABBREVIATIONS AND ACRONYMS

ASTU- Adama Science and Technology University

ATR - Attenuated total reflectance

BFRPE- Bamboo Fiber Reinforce Polyester

BOD- Biological Oxygen Demand

CAN- Chemical Assisted Natural

CETPS - Common Effluent Treatment Plants

COD- Chemical Oxygen Demand

CLRI- Central Leather Research Institute

CLRI-SDDC- Central Leather Research Institute-Shoe and Designing Development Desk

EU- European Union

FAO- Food and Agricultural Organization

FLS- Finished Leather Scrap

FTIR- Fourier Transform Infrared Spectroscopy

HPLC- High performance liquid chromatography

ISO- International Standard for Organization

LB- Leather Board

LF-BF-Leather Fiber - Bamboo Fiber

LF-C- Leather Fiber Composite

LF-E - Leather Fiber with Enset

LF-J - Leather Fiber with Jute.

LFS - Leather fiber with sisal

LLPIRDC- Leather and Leather Product Industry Research and Development Center

NC- Nitrocellulose

NF- Natural Fiber

SD - Standard Deviation

RB - Resin Binder

RSL- Restricted Substance List

SATRA- Shoe Allied and Trade Association

SEM- Scanning Electron Microscope

SLC- Society of Leather Technology and Chemist

SPE- Solid Phase Extraction

SS- Suspended Solid

TGA- Thermo gravimetric Analyzer

TS- Total Solid

Min- Minute

PEG- Poly Ethyl Glycol

PUB – Polyurethane Binder

QSTRDD- Quality Standard and Testing Research and Development Desk

UD- Unidirectional

UF- Urea Formaldehyde

UTM-Universal Tensile Machine

1. INTRODUCTION

1.1 Background of the Study

Leather Industry basically uses skins and hides as the by-product of the meat and meat items industry. So, these industries can effectively be classified as an environmentally friendly industry, because it processes the waste generated by meat production [1]. Even though, this industry is frequently exposed to high pollution due to obnoxious odors, natural waste and high water utilization during the leather making process [2].

During the processing of leather into leather products, the global leather industry generates various forms of solid waste. It has a negative impact on the environment[3]. Only 200 kg of 1 ton of salted hide is converted into finished leather and the rest is disposed of as a waste [1]. As the leather industry the solid waste generated during leather processing is significant. The raw material and the finished leather uses only 20-25 percent, where as 75-80 percent ends up as waste in the environment [4].

At the moment, not much is being done in Ethiopia to make use of this enormous volume of waste. Thus, together with other municipal solid waste, every tannery disposes of its solid waste straight to the ground. The improper handling of these leather wastes leads to degradation of the environment; therefore, the preparation of composite materials with better mechanical properties and suitable to use is a need of the time for the reason that it is eco-friendly [5].

In addition, research on the conversion of this waste into useful value-added composite products for consumer application can be considered as a means of generating income. Furthermore, it can be considered economically beneficial beside environmental reduction. So, more attention is being paid to the use of natural fibers to reinforce composites [6].

In Ethiopia natural fibers (NF) are available in abundance in plants, and animals form. It is most commonly extracted from bamboo [7], jute [8], oil palm [9], cotton [10], and sisal [11].

Among the various plant natural fibers, bamboo exhibits diverse properties, qualities, and is very appealing because of its enormous potential as a composite material for the production of polymer composites material [12,13].

Bamboo fiber exhibits better mechanical property upon the longitudinal alignment inside the polymer matrix [14].

Several studies summarized that bamboo fiber shows excellent potential for the use of reinforcement in thermoplastic composites [15,16,17, 18]. Also, researchers [19] estimated that about 16 million cars are manufactured in Western Europe each year using about 80,000–160,000 tons of natural fiber. In Ethiopia, attention is required to materials such as natural fibers, including bamboo, jute, sisal, banana stem, etc., in order to reduce the cost of structural components, for structural applications and regulate environmental degradation [20, 22].

So bamboo is one of the eco-friendly materials and has various properties such as, growing faster, being a renewable material, simple manufacturing process, having good mechanical strength, better specific strength, being able to not damage tools while machining, biodegradable, cheap, lightweight, etc. [23,24, 25] it can be used as reinforcement material for polymer composite.

1.2 Statement of the Problems

The Ethiopian government prioritizes tanning industries, and it is also one of a traditional technology that is not only fulfils people's needs but is also one of the fastest-growing economic sectors. However, this sector has been classified as extremely polluting since many chemicals are utilized in the tanning process, resulting in a variety of solid, gaseous, and highly liquid byproducts that are harmful to the environment [26].

In this sector, different chemicals have been used are salt for preservation of skin or hide which is responsible for pollution load of chloride in water and total dissolved solids. Other major polluting chemicals are ammonium sulphide ,sodium sulphide, lime, sulphuric acid, pigment, synthan ,ammonium chloride, non-ionic wetting agents, chromium sulphate, bactericides, resin, polyurethane, formic acid, binder, wax, and enzymes [26].

If they are not properly utilized or disposed of the solid waste generated during leather processing, which contains these hazardous chemicals, is likely to cause a number of problems for the environment. Especially due to the possibility of oxidation of chromium (III) into toxic chromium (VI), the disposal of chromium-containing solid waste in the land fill has a potential effect on public health [27].

Furthermore, insufficient work has been done in Ethiopia at the moment to make use of this enormous volume of waste.

Because there is no specific location for the disposal of hazardous waste, every tannery disposes of its solid waste straight onto the land, among other municipal solids. Some tanneries even dump their solid waste into a nearby river [28].

Moreover, inappropriate disposal of these leather wastes pollutes the environment, so properly utilizing these wastes by creating value-added end products will be a potential alternative [29]. Utilization of tanned leather solid waste for making leather board has been tried using different plant fibers, i.e., hibiscus, jute, sisal, etc. in this regard, the use of plant fibers that could induce better mechanical properties in leather has given greater attention.

Moreover, studies in recent years have shown that the rigidity of bamboo fiber can play a good supporting role in manufacturing, which can improve the physical properties of the composite [30].

On the other hand, on the premise of environmental friendliness, being biodegradable, cheap, and lightweight it will be very meaningful to seek a new way of the utilizing of bamboo fiber components [31].

Therefore, in this research, finished leather waste in combination with an appropriate proportion of bamboo fiber is used for making leather boards for better strength thereby reducing environmental pollution.

1.3 Objective

1.3.1 General Objective

The main aim of this study is to synthesis value added consumer products from finished leather waste incorporated with bamboo fibers for better strength property.

1.3.2 Specific Objectives

- To characterize the chemical and physical property of finished leather waste.
- To optimize strength properties of high land bamboo (*Yushania alpina*) fibers.
- To optimize the efficiency of various types of binders.
- To prepared leather board from finished leather incorporated with bamboo fiber.
- To characterize the mechanical, physical and chemical property of the leather board.

1.4 Scope of the Study

The scope of this study is the preparation of leather board with different contents of bamboo fiber and finished leather waste. Compare with individual components and identify the improved facilities of the composite.

Additionally, create a workable plan for the utilization of the finished leather waste generated in leather industry for applications of, leather goods, partitioning and false roofing in terms of waste management and income source for the industry itself as well as creating job opportunity for small enterprises. The scope is restricted to waste from finished leather.

1.5 Significance of the Study

In this research, finished leather waste was converted into useful products and it provides an alternative way to minimize and manage solid wastes which was dumped into the environment. Also, it provides a possible way to use the waste as a raw material for the preparation of leather board.

The recycling of solid waste from tanning industries, significantly lowers pollution levels in the environment and adds value to the industry by generating employment opportunities for small businesses, which has an impact on the national economy.

In addition, other researchers use the generated baseline data for additional research work.

2. LITERATURE REVIEW

2.1 Tannery Process

The tanning process turns animal hides and skins into leather, and also a stable and non-perishable commercial product. Not all tanneries utilize the same technologies, however there are key processes that are shared by all of them while producing leather. The raw cured skins and hides that are brought to the tannery are first trimmed to get rid of lengthy shanks and extraneous elements.

Mainly, there are four primary categories for the processes used in creating leather. This are beam house (pre-tanning), tanning, post-tanning, and finishing are the four primary subcategories of leather processing [32]. Each stage involves various unit operations utilizing various chemicals and mechanical operations.

1. **Beam house operations:** beam house operation are the first phase of the hide process and involve multiple chemical, mechanical, and biological unit operations. Its main aim is to remove dirt, hair, non-collagenous proteins, epidermis and grease from raw skin, and open up the collagen fibers to favor the subsequent tanning process. [32]
2. **Tanning process:** in the world tanning process is one of the oldest method, also currently this operations are based on chemical processes using several organic and inorganic compounds [32]. This step stabilizes the skin against, bacteria growth, wet and dry heat, mechanical stress, enzyme attack, and is the basis of leather production among other things. This stabilization is due to the formation of new chemical cross-links in the matrix proteins [33].

The tanning stages are divided into, mineral, synthetic and vegetable. When the leather is stabilized with a suitable inorganic salt, the process is called mineral tanning, and basic chromium sulfate ($\text{Cr}(\text{OH})\text{SO}_4$) is the most commonly used mineral tanning salt. When leather is tanned with chromium salt, we call it wet blue leather. Due to the quality they gave to skin and their high stabilizing capacity mostly chromium (III) salts are used as compounds, [34].

3. **Post-tanning process:** the post-tanning process is the third part of leather production, and these tanned leather is considered a commodity, i.e., many items can be made from it. Each post-tanning procedure is applied to finished product, such as shoe upper, clothing, and upholstery [35].

This post-tanning processes is to improve the aesthetic properties of the leather by coloring it and changing some of the mechanical and physical properties of the material during the storage, grease-staining stages, and dyeing [35].

4. **Finishing:** is final step of tanning gives and give the leather the necessary physical and mechanical properties, such as color, tensile strength, impermeability, softness, elasticity, and flexibility, with various binders, pigments, waxes and oils [36]. It consists of coating and changing the surface of the leather.

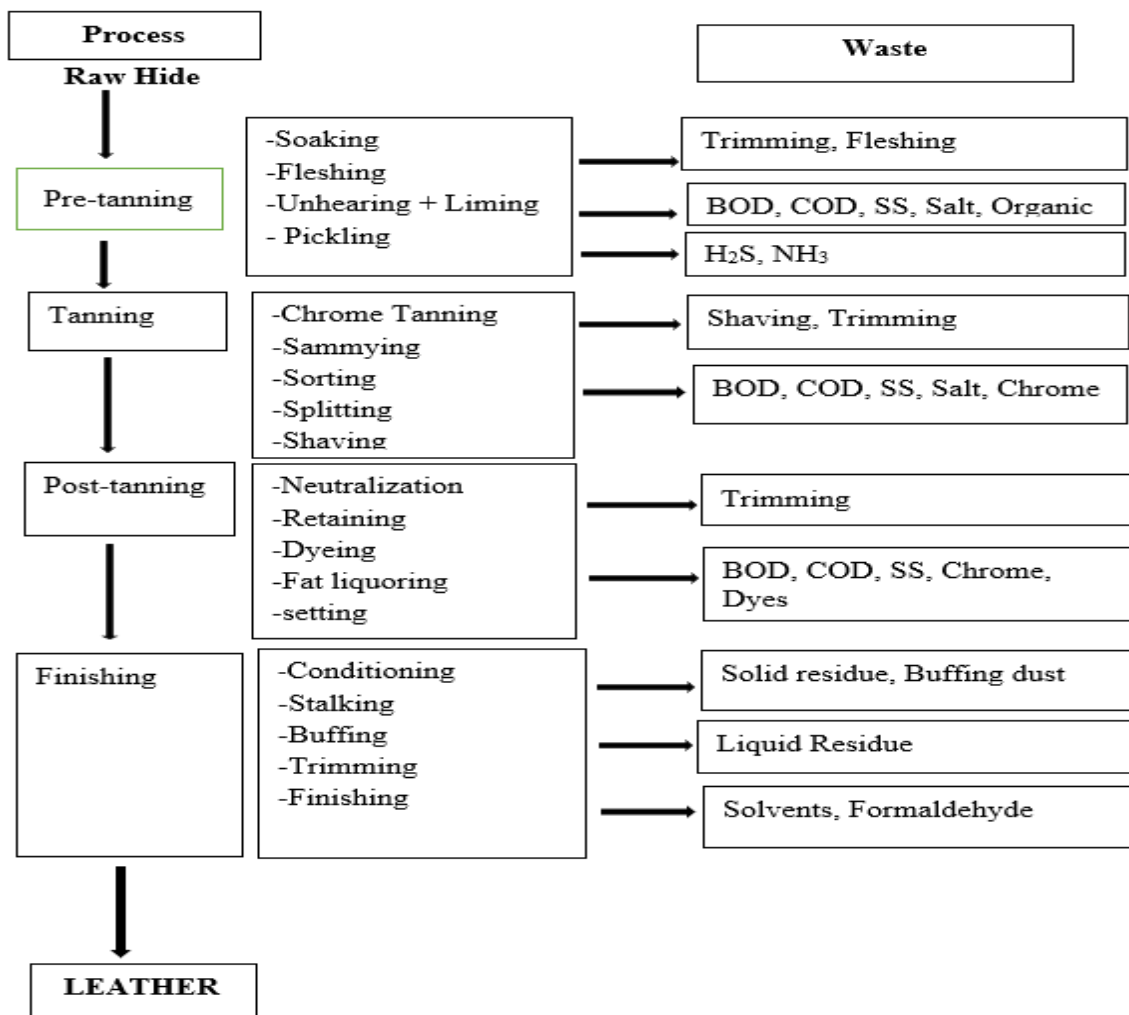


Figure 2-1 Leather Processing flow diagram and type of solid wastes generated [37]



Figure 2-2 Schematic diagram showing general leather processing [38]

2.2 Different types of Waste Produced during Leather-Processing

Worldwide, tanning industry produces an enormous amount of solid waste, and high environmental problems due to increasing emissions, which is also a problem for the industry. In addition, the overall assessment of their management options was based on several points [39].

A huge amount of solid waste is generated in the various leather processing stages, and there is also no real approved procedure for how to use the solid waste. Therefore, processing is highly difficult for tanners. This solid wastes generated in trimming, fleshing, splitting, and shaving processes, and as well as sludge's discharge from the wastewater treatment plant, This all contributes to increasing the amount of the waste [40].

Usually, in the leather industry, almost 800 kilograms of solid waste is generated from 1000 kilograms of raw hide, and only 200 kilograms of raw materials are transformed into a usable product.

Table 1. Tannery solid wastes generated in leather processing [41]

From raw hides and skin processing , solid wastes generated - 1000 kg.	Quantity (kg)
Wet-blue trimmings	30
Crust trimmings	35
Raw trimmings	40
Lime sludge	60
Chrome splitting's	65
Buffing dusts	65
Conservation salts	80
Chrome shavings	95
Hair	100
Fleshing's	120
Dry sludge- cetps	125

Generally, the waste is generated either from beam house, tanning or after tanning. However, the difference can be untanned and tanned waste, respectively.

2.2.1 Untanned solid wastes

In the beam house solid waste is mainly generated, especially in meat production. One of the solid waste produced by a mechanical process is fleshing, that aims to remove meat residues or fat from the inner part of the skin [42]. Fleshing contain subcutaneous tissue, fat and flesh, which are composed of , fat (4–18%), protein (5–7%), lime (2–6%), sulfide (2–4%), etc. [42].

Trimming is cutting of unwanted parts of the hides immediately after the meat has been processed. Scraps can be collected and sent to adhesive manufacturers and also other by-product producers or sent to a landfill for disposal [43].

2.2.2 Chromium tanned solid wastes

Chromium tanned leather is called wet blue leather, and, also chromium tanning is based on the crosslinking of chromium ions with the free carboxyl groups of collagen, is characterized by the high hydrothermal stability, highest processing quality, versatility and user-specific properties [44].

The chromium (Cr_2O_3) remains in the collagen structure at the end of the chromium tanning process, almost it is 60-75%. In addition, in the wet blue skins small amounts of other chemicals and excipients such as acids and bases (in the form of soluble "reaction salts") remain. The main tannery solid waste environmental impact is the oxidation of Cr^{+3} to the Cr^{+6} form, which is highly toxic and has carcinogenic effects. The process of chromium tanning relies on the interaction between chromium ions and free carboxyl groups present in collagen. Wet-blue leather, also known as chrome-tanned leather, is distinguished by its exceptional hydrothermal stability, user-specific qualities, and adaptability [44].

60–75% of the chromium (Cr_2O_3) is still present in the collagen structure after the chrome-tanning procedure is complete. The wet-blue leathers also contain trace amounts of other auxiliaries and compounds, such as acids and bases (in the form of soluble "reaction salts"). The oxidation of Cr^{+3} to the Cr^{+6} form, which is extremely hazardous and has mutagenic and carcinogenic properties, is the primary environmental effect of tannery solid wastes.

Soil contamination and ground water pollution result from chromium-containing waste leaks into agricultural areas. Aquatic animals, which are frequently used as food sources, are impacted by water pollution, while soil contamination creates health risks for cattle and humans alike through the food chain and the absorption of poisonous dust [45].

2.3 Impact of Leather Solid waste on Health and Environment

Depending on the mechanical and chemical processes applied to the raw hides and skin, tannery solid wastes can cause many problems. Associated with inorganic matter, organic load, chromium, total organic, suspended solids, and ammonia, nitrogen, chloride, and sulfide. Moreover accumulation of these wastes leads to choking of treatment pipes, sludge problems and, ultimately results in a reduction efficiency of the treatment plant [46].

There are many solid waste problems currently facing leather industry. Also, these tanneries are closed for not fulfilling the standards of total dissolved solids (TDS) and biological oxygen demand (BOD) [47]. So it is very important to analyze the nature of these wastes in order to assure their application or a safe disposal to the environment. In terms of total dissolved solids and chlorides, salt, which is used to preserve hides or skin, discharges a huge amount of pollution and creates groundwater pollution [46].

Some of the biodegradable tannery solid wastes cause volatile organic compound emissions and, moreover, are sources of pathogenic bacteria. Trimmings, raw fleshing, limed fleshing and splitting waste can putrefy easily by producing noxious smells. Hair waste and lime sludge if discharged along with the effluents are likely to choke the drains [48].

Chromium contains shaving dust, a chemical that is not good for the environment. When it is discarded, it can easily find its way into the ground and surface waters, where it contaminates both. This heavy metal can cause serious health issues for aquatic life in the nearby rivers by leaching into the ground and causing surface water pollution. Due to this, drinking water for people and animals that live downstream of rivers is scarce due to surface and ground water pollution [49].

Comparing to other tannery solid waste, chromium- containing solid waste is more hazardous, makes up around 25% of the solid waste from tanneries [50]. Because of the chromium content, the waste produced from leather that has been tanned with chrome is poisonous and not biodegradable [51].

If untreated leather waste containing chromium is released into the environment, it is considered toxic and dangerous waste. There have been reports of increased risks for several malignancies, including testicular, bladder, pancreatic, lung, and soft tissue sarcoma [52]. In addition, chromium waste has been linked to tumors growth, birth abnormalities, infertility, respiratory issues, and a weakened immune system [53].

Solid trash that contains chromium seeps into the ground, contaminating soil and ground water. Aquatic creatures that are common food sources are impacted by water pollution, while soil contamination creates health risks for livestock and humans alike through the food chain and hazardous dust inhalation.

It can cause cancer, change genetic components, and harm fish gills [54]. Furthermore, the thermal burning of these wastes is linked to significant air pollution issues because it releases hazardous substances into the atmosphere, such as aromatic hydrocarbons [54].

2.4 Solid waste Management Techniques

There are various waste management techniques to ensure an appropriate and successful integrated solid waste management plan. The waste hierarchy is one of the most often utilized concepts.

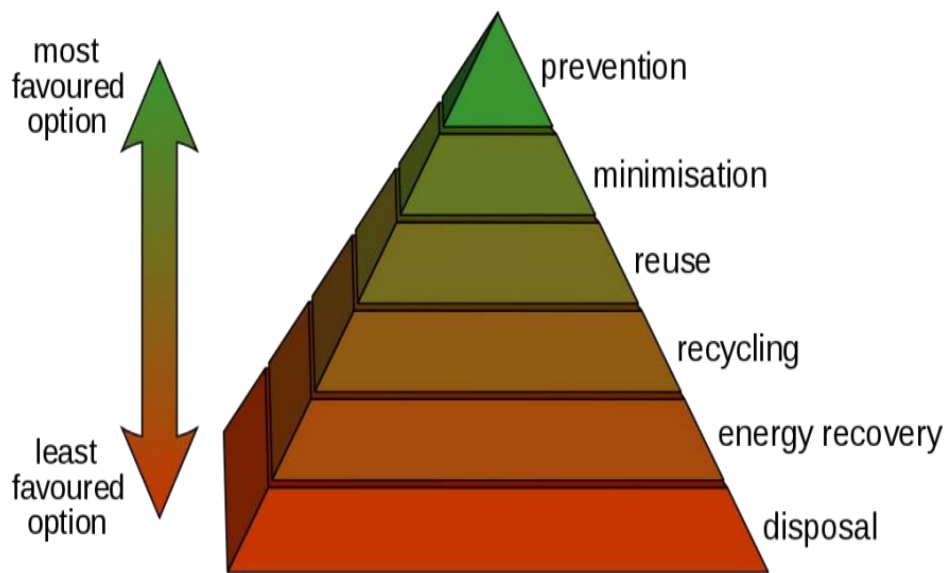


Figure 2-3 Waste management hierarchy [55]

Therefore, the waste management is based on this concept of hierarchy of options. In the first place not producing the waste is the most desirable alternative. If not, waste is increasingly being considered as a valuable resource to the industry and a major economic sector. So, managing the waste is not only has environmental positive effects but also economical, creating jobs, and business opportunities [48].

However, in Ethiopia current solid waste management practice is very weak or almost there is no significant work done on utilization of solid waste. Some have burned it with other dry solid trash, and others have dumped their solid waste in an open landfill alongside municipal solid waste.



Figure 2-4 Tannery solid waste disposal trend in Ethiopia [56]

Even though tanners mostly dispose tannery solid wastes in open dump area but there is few solid waste management practice in Ethiopia. This are:

A. Protein hydrolysate from chrome-bearing solid wastes

The main objective of the protein hydrolysate is to treat the leather shaving scraps to reuse it in the leather production as protein binder. As the concept of Reduce, Reuse, Recycling (3R), it is essential to reuse the waste generated from the industry in the industry. Benefits could reach broader aspects not only environmental aspect, but also economical aspect as well as social aspect. Thus, leather tanning industry could sustain and contribute to greener environment.

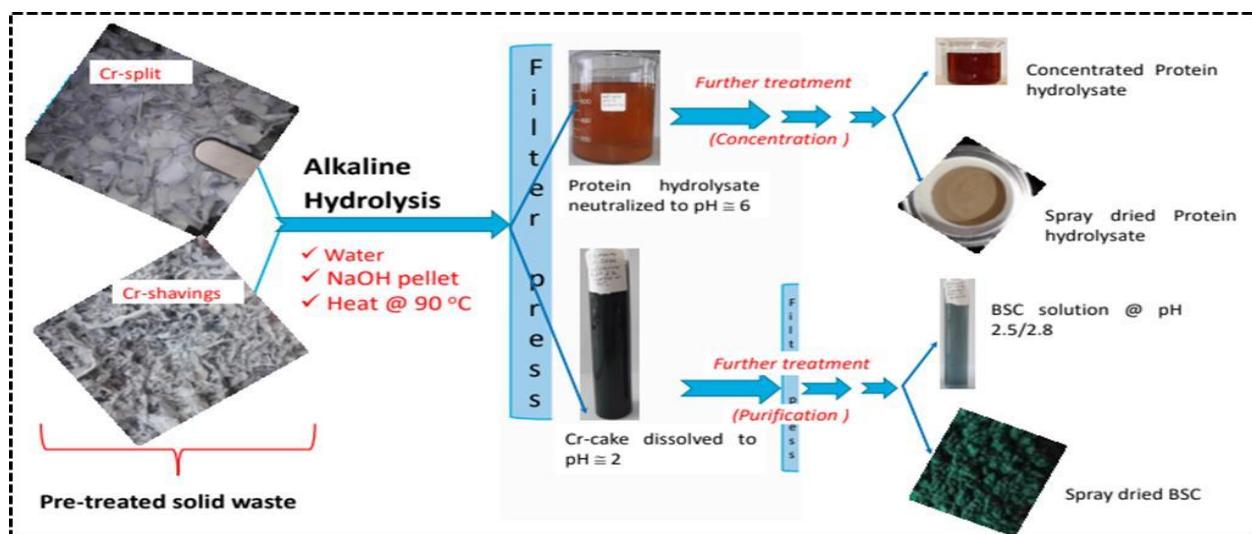


Figure 2-5 Protein hydrolysate preparation processes [57]

B. Preparation of organic compost from tannery fleshing waste

Composting has been used for the utilization of limed fleshing and it is a better option for solid waste management especially organic solid waste than all other options [58]. Various microorganisms break down organic matter into simpler nutrient-rich products, which are used as fertilizer. It is much better than chemical fertilizer because it is not associated with any kind of risk. So fleshing composting is one way of providing a solution for reducing solid waste volume by creating a valuable product and reducing the pollution load from tanneries.

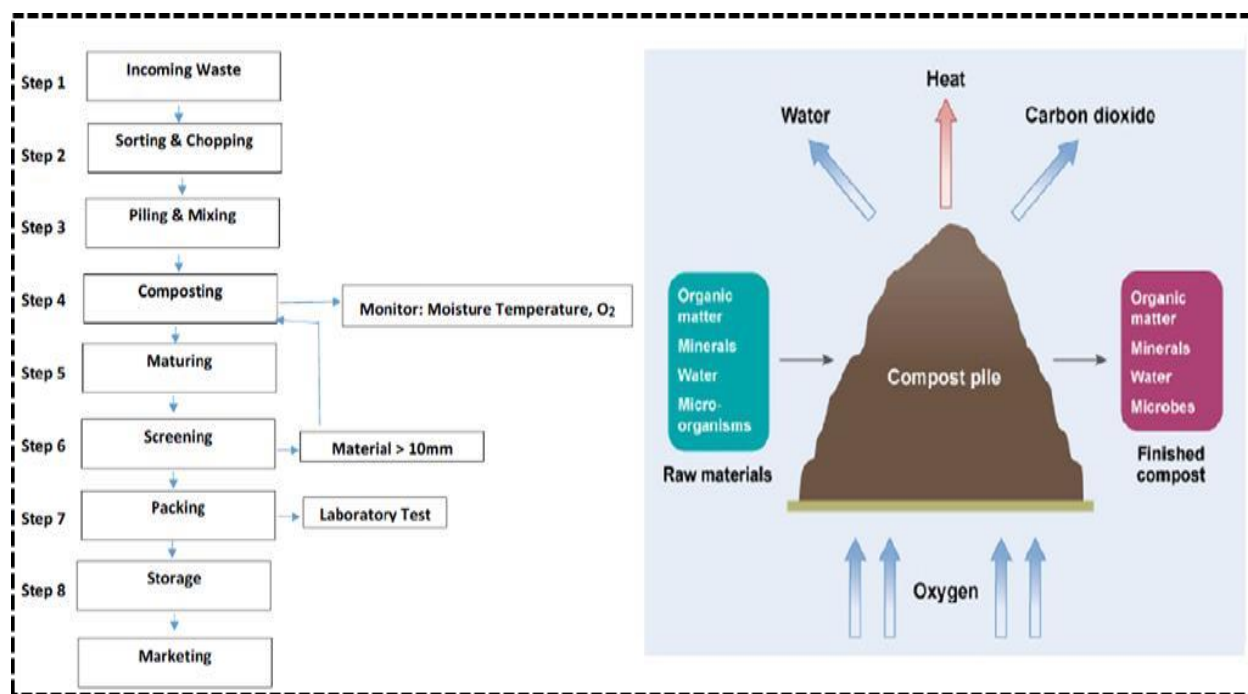


Figure 2-6 Composting Process from tannery fleshing waste [57]

C. Production of glue from hide lime trimmings

One of the well-known types of glue is animal glue. Animal glue could be bone glue, hide glue, fish glue, flesh glue, etc. Hide glue is the most important type of animal glue. Even though Ethiopia has plenty of raw materials from its tannery industries for the production of animal glue; it is still importing glue from abroad countries with high currency. Therefore, producing glue by studying its feasibility to replace the imported glue and saves foreign currency is not questionable rather than protecting the environment [59].

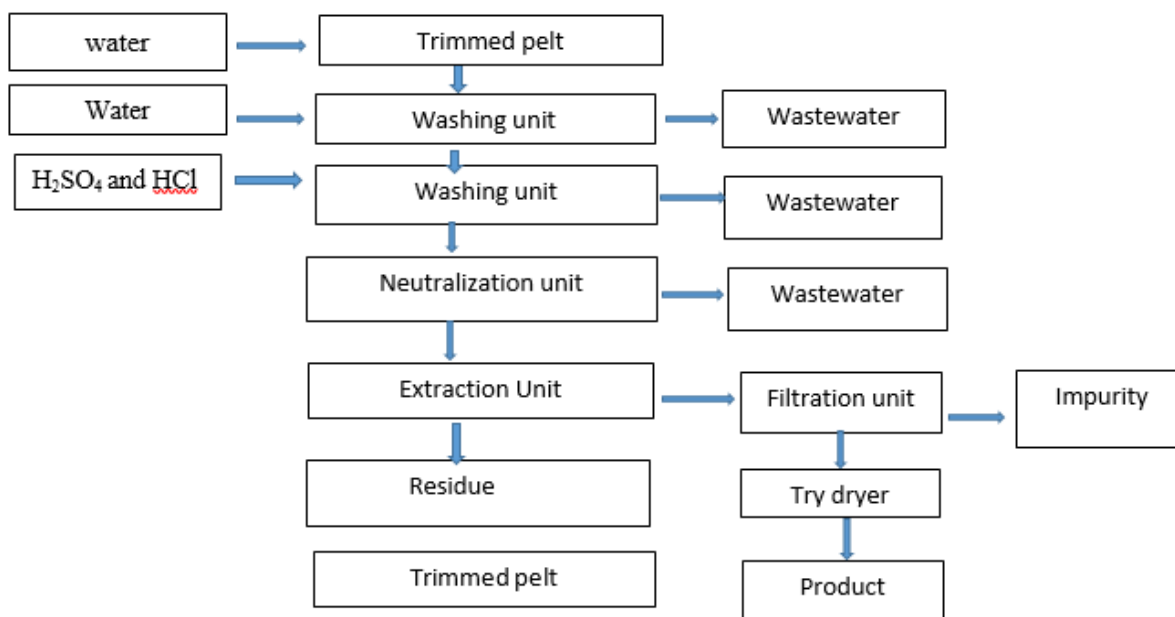


Figure 2-7 Process diagram of glue production from tannery solid waste [57]

D. Brick production from tannery effluent sludge and clay

The tannery solid waste in form of powder obtained by drying tannery sludge was used as additive to clay as the basic materials in the fired clay brick manufacturing. Some studies also have shown that tannery sludge can be stabilized in construction materials such as concrete, ceramic tiles and other engineering materials like clay and bricks from tannery effluent sludge.

E. Preparation of leather board from chrome shavings or finished leather waste

Preparation of leather boards from chrome shavings waste or finished leather is economical and helps in reducing the environmental pollution. The process for the preparation of leather boards involves soaking chrome shavings/finished leather waste in mild alkali, processing in mincer, and mixer addition of rubber latex and other chemical required and diluted with water and passing through a nylon mesh and applying vacuum to get wet leather board. These wet boards are pressed in a hydraulic press to remove excess water and dried to get leather boards. These boards are ready for use or in other way the leather fibers are combined with latex and resin with the subsequent hot pressing of the mixture mass, and after coagulation, the mixture is de-watered, and pressed to create a board [54].

The unique feature is that the process provides an eco-friendly as well as economical option to utilize tannery chrome shavings or finished leather waste, which would otherwise add to disposal problems, into a value-added product, thereby creating value addition and utility for a byproduct of the tannery. So preparation of leather board and regenerated leather from chrome shaving waste and finished leather scrap is one of promising alternatives or solutions, to reduce the environmental pollution related to tannery solid waste [6].

Leather board Production

Leather board preparation and regenerated leather from chrome shaving waste and finished leather scrap is a promising solution [5]. But plant fibers are important as reinforcement material due to their good mechanical and physical characteristics, environmental friendly, availability and low cost. This reinforcement material can be natural or synthetic, as well as the matrix can be categorized as metal, ceramic, and polymer. In Ethiopia Natural fibers (NF) are available in abundance in plants, and animals form. It is most commonly extracted from bamboo [7], jute [8], oil palm [9], cotton [10], and sisal [11].

Fibers from plants such as bamboo [60], are lignocellulose based materials that are ecologically acceptable alternatives to other fibers that were formerly utilized [61, 62]. Natural fibers also have good toughness, renewability in the short term, biodegradability, low cost, better specific strength, lightweight, and availability, as well as easy to process [63].

Some studies are done composite from plant fiber such as palm, jute, hibiscus and Sisal in combination with leather waste from chrome shaving or finished leather scrap which was collected from tanneries or from different shoe industries [5], however the main aim of this study was composite were prepared from finished leather waste or scrap in combination with Ethiopian high land bamboo (*Yushania alpina*) which comes from Hagere-Selam to make the strength property better than other plant fibers. Which have not yet got on other plant fiber. i.e. enset, sisal, jute, palm and hibiscus [5].

In addition, Ethiopian have two indigenous bamboo species: lowland (*Oxytenanthera abyssinica*) and highland (*Yushania alpina*). Also this resources can be found in the highlands and lowlands of Assosa, Ambo, Injibara, Gimbi, Gurage, Bale, and Hagere-Selam [64]. The *Yushania alpina* bamboo species grow quickly and can be harvested at different ages of 3, 4, and 5 years [65].

Even though Ethiopia has more than one million hectares of land of bamboo, production, and consumption of bamboo products have been very limited, and minimum value addition. Due to a variety of factors, the use of Ethiopian bamboo as a composite material and improving its property is extremely limited. So because it is having high fiber content and is easier to extract fiber from hollow type highland bamboo (*Yushania alpina*), it is used most of the time for reinforcement as fiber in a polymer.

So this situation inspires a desire to concentrate on highland bamboo fiber and further investigation on its improvement of important property the fiber reinforcement that is the focus of this work. In addition, various researchers test the mechanical properties of various bamboo fibers species as a function of age, density, moisture content, and so on. They found that better strength occurs between the ages of 3 and 4 years [66]. So this all are into consideration.

2.5 Summary of the Literature Review

The leather industry in Ethiopia is one of the top-growing economic sectors and is set in the front position by the Ethiopian government. However, tanneries are generally pollution-intensive industrial complexes generating large volumes and high concentrations of liquid and solid waste. Tannery solid waste represents one of the burdensome environmental problems owing to the large quantities of discarded material. Tanneries in Ethiopia, in general, are characterized by their unpleasant smell and polluting behaviors, which is due to uncontrolled and desegregated disposal of tannery solid waste [67].

Lack of waste-to-wealth approaches and secured landfill makes the segregation and disposal of tannery solid waste much more difficult. Tannery wastes have historically been discharged into rivers, landfill waste sites, and the air with little, if any, purification. Even though it is evident that improper management of the waste from the tanning industry is full of risk to human and environmental health, presently almost all of the leftovers from leather product industries in Ethiopia and elsewhere are sent to the land as waste. Most of the factories do not possess well-established treatment plants for their waste and simply dump their waste into the rivers nearby [68].

This dumping into the river causes a serious pollution problem for the habitats near the tanneries. In addition to this, improper management of the industries solid waste is full of risk to the humans that live in the vicinity of the industry [5].

However, there are a few solid waste management practices in Ethiopia, like protein hydrolysate from chrome-bearing solid wastes, preparation of organic compost from tannery fleshing waste, production of fertilizer, production of glue from hide trimmings, and also leather board from chrome shavings or finished leather waste, etc. As stated in the above, it is insignificant compared to the huge amount of waste generated from tanneries.

Therefore, effective and optimized use of these wastes into more value-added end products will be a viable approach to prevent improper disposal of these leather wastes and protect against environmental contamination [29]. Utilization of tanned leather solid waste for making leather boards has been tried using different plant fibers i.e., hibiscus, sisal, enset and jute [69].

According to A. Tekelay et al. [69], a composite board of leather fiber with hibiscus, sisal, enset, and jute plant fiber was investigated with different concentrations 10%, 20%, 30% and 40% using two different binders, which were polyurethane binder (PU) and resin binder (RB). The optimum tensile strength values for hibiscus were 5.41 ± 0.30 MPa and 8.25 ± 1.48 with 40% and 10% plant fiber, respectively. The composite boards prepared using resin binder showed better tensile strength values than their respective controls, which means finished leather scrap and binder only. However, the composite boards prepared using polyurethane binder (PUB) showed lower tensile strength values than their respective control samples.

In the case of leather fiber with sisal (LF-S), the composite board prepared using the RB sample with 40 percent PF and sample with 30 percent PF had their respective values of 9.08 ± 0.91 MPa and 8.57 ± 0.85 MPa. However, in the case of composite board of leather fiber with Enset (LF-E) in all of the prepared board, the values of tensile strength are lower than their respective controls.

Leather fiber with Jute (LF-J) composite board is prepared using PUB and RB like the others, all the experimental samples have shown lower values of tensile strength than their respective controls, with the optimum value of being 5.17 ± 0.28 MPa for PUB and 5.98 ± 1.26 MPa in the sample of 20 percent PF.

Beside this, according to Sekar et al. [70], the tensile strength properties of regenerated leather boards from chrome shaving showed that 5.88 ± 0.09 MPa and that of Senthil et al. [69], from regenerated leather boards 5.88 ± 0.09 MPa.

Regarding other parameters, the composite has reasonable flexibility, water absorption, and desorption values. In conclusion, from the different composite boards, only composite with hibiscus and sisal have a lower strength property. Even composite with hibiscus and sisal also need improvement because products with good mechanical properties commercially viable on the market and last a long time.

Moreover, studies in recent years have shown that the rigidity of bamboo fiber can play a good supporting role in manufacturing, which can improve the physical properties of the composite [30]. On the other hand, on the premise of environmental friendliness, being biodegradable, cheap, and lightweight, it will be very meaningful to seek a new way of the utilizing of bamboo fiber components [31].

Therefore, in this research, finished leather waste in combination with an appropriate proportion of bamboo fiber is used for making leather boards for better strength thereby reducing environmental pollution. Hence, we can improve the strength properties of the finished leather waste composite material by incorporating the locally abundant and economical bamboo fiber as a reinforcement agent in the development of composite materials. So the above composite boards, which have a higher tensile strength value, suitable mechanical properties, an appealing surface, and reasonable flexibility, may be used as raw materials for the production of components of footwear preparation rather than protecting the environment.

Moreover, this composite can be used as a raw material for the preparation of leather goods as a reinforcement material, implying that the composite material for this study is suitable for consumer applications such as insole boards, mouse pads, components of small furniture, and interior decorations.

3. MATERIALS AND METHODS

The material and tools used in this section are categorized based on the way they are directly applied for the preparation of the composite, and these are directly used materials and that need further processing.

3.1 Sample Collection

Finished leather solid wastes were collected from the LLPI-RDC, specifically from the Quality, Standard, and Testing Laboratory- Research and Development Desk, and Ethiopian highland bamboo (*Yushania alpine*) from Hagere Selam, Southern Sidama Zone of Ethiopia.

3.2 Study Location

This research was performed at LLPI-RDC, mainly at the Quality, Standards, and Testing Laboratory - Research and Development Desk. The laboratories are equipped with Sophisticated analytical instruments, and mainly have instrumental, chemical, environmental, mechanical and physical tests for the leather sector among others. However, SEM and TGA analyses were conducted at Adama Science and Technology University (ASTU).

3.3 Materials

3.3.1 Bamboo fiber

Ethiopian bamboo is divided into two species: lowland (*Oxytenanthera abyssinica*) and highland (*Yushania alpina*). In this study, 3 to 4 years of highland (*Yushania alpina*) bamboo was utilized which comes from Hagere Selam, Southern region, Sidama zone of Ethiopia, and was cultivated in the farmyard.

3.3.2 Finished leather waste

Leather waste was taken from the Leather and Leather Product Research and Development Center (LLPI-RDC), Quality, Standard, and Testing Laboratory, Research and Development Desk.

3.3.3 Chemicals and reagents

The chemicals used for this studies for the characterization of finished leather waste were, Sulfuric acid (H_2SO_4) (98.0%) (SP.GR.1.84) AR, Oil of vitriol, Nitric acid (HNO_3) (69%) AR/ACS, from Loba Chemi P.L.C. Perchloric acid (HClO_4) (70%) extra pure AR, Orth phosphoric Acid (H_3PO_4) (85%) AR-from Loba Chem, Potassium Iodide (KI)-AR (99.8%).

Starch Indicator ($C_6H_{10}O_5$)-AR (90%), Sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) HPLC grade (99%) from Sigma Aldrich, di-Potassium hydrogen phosphate ($K_2HPO_4 \cdot 3H_2O$) (98%), Uni-Chem India, 1,5 Diphenyl Carbazide –DPC ($C_{13}H_{14}N_4O$) AR-HPLC grade (98%)-from Sigma Aldrich, Acetone ($CH_3)_2 CO$ for HPLC and Spectroscopy (99.8%) from Sigma Aldrich, Acetic acid Glacial (CH_3COOH) HPLC Grade (99.5%) from Sigma Aldrich, Potassium dichromate ($K_2Cr_2O_7$) extra pure (95.5%) from Sigma Aldrich, Methanol (CH_3OH) (99.8%) HPLC grade- from sigma Aldrich.

For characterization and optimization of bamboo fiber, control and composite board were Formaldehyde solution (CHHO)-AR (38%) Uni Chem India, Iodine (I_2)-AR (99.8%) Uni Chem. India, Sodium hydroxide pellets (NaOH) Extra Pure 98%, from Alpha Chemika, Polyethylene Glycol 400-LANCHEM IND., Dinitrophenyl hydrazine (2-4-diitrophenylhydrazine) DNPH- $C_6H_4N_4O_4$ (99%) Uni Chem- India, Acetonitrile -For HPLC and Spectroscopy (CH_3CN) (99.9%) from Sigma Aldrich, Urea Formaldehyde ($C_2H_6N_2O_2$), Fevicol SH –Synthetic Resin adhesive- (Pedilite Industries Limited-India). Aluminum sulphate purified ($Al_2(SO_4)_3$)-18- hydrated-(59%), from Sigma Aldrich, Potassium sulphate (K_2SO_4) HPLC grade (99.5%) from sigma Aldrich, Polyvinyl alcohol ($(CH_2CH(OH))_n$), Glycerol ($C_3H_8O_3$) and Hydrogen peroxide (H_2O_2) (30%). All the above chemicals are purchased from Addis Ababa Via their Agents.

3.3.4 Instruments and Apparatus

The following instruments were used for the chemical analysis and physical or mechanical testing of the raw material and the composite leather board. Thermal Analysis (TGA), (DTG - 60H - SHIMADZU Corporation -Japan), Fourier Transform Infrared - (FTIR), Shimadzu, Japan IR Affinity-1), Scanning Electron Microscope- (SEM), (JEOL manufactured JEOL- Labwrench.com JSM-IT300 LV, Japan), Double beam UV-Spectrometer (Agilent Technologies, Carry Series UV-Vis Spectrophotometer- Germany), Multi-functional Orbital Shaker (PSU-20i, Grant bio, England), Ultrasonic bath (IKAT25 digital Uitra Turrar Model T25 D), Hot plate magnetic Stirrer (CDL- JISLCO), Ultrapure Pure water system (FLOM-Model;FBL-3001-E UP-B) Germany, Universal Testing Machine (M350-20 AT-USA) ,Analytical balance (Model: E42S-B, GIBERTINI- Germany), PH meter (PHS-3C microprocessor, PH meter manufacturer Hanna instruments U.S.A), What man Filter Paper (No 40 ashless ϕ 125 mm), HPLC (Agilent technology -1260 Affinity).

Flexing Index (STRA-STM 129, UK) and Heating Oven (High performance oven, MOD.2100, model No: 2100F.LLI Giuliani, Italy). Muffle Furnace (INDECO-No. 21277), Solid phase extraction (SPE) WELCH -Model 2014-USA.



Figure 3-1 Fiberized finished leather waste Fiberized finished leather waste

3.4 Methods

3.4.1 Sample preparation

Finished leather waste was collected from LLPI-RDC-QSTRDD (Leather and Leather Product Industry and Development- Quality Standard and Testing Research and Development Desk) was cut into small pieces by using scissor and fiberized by leather grinding machine with mesh size of 6mm to convert it into leather fiber (LF).

3.4.1.1 Chemical characteristics of fiberized leather

To determine the chemical characteristics of chrome finished leather waste which were selected for the making of composite leather board the following parameters were performed. i.e. pH, moisture content, ash content, chromium trivalent, chromium six and formaldehyde content.

a) Determination of pH

In order to check the pH of the finished leather waste, 2 g of sample was soaked in 100 ml of distilled water and kept in orbital shaking device for 16-24 hour followed by direct measurement according to SLC 13 standard test method.

b) Determination of moisture content

The grinded finished leather waste moisture content was determined by gravimetric method, by placing 2 g of sample using crucible and by putting in an oven for 5–6 hour and finally the percent moisture content will be determined according to SLC 3 standard test method.

The percent moisture content can be calculated by:

$$\text{Moisture content \%} = \frac{(w_i - w_f)}{w_i} \times 100$$

Where: W_i - Sample weight before drying

W_f - Sample weight after drying

c) Determination of ash content

The grinded finished leather ash content was determined by measuring 2 g of the sample using the crucible and placed in a muffin furnace at 500 °C for 3 hours. The percent ash content was performed according to ISO 4047: 1977 standard test method.

d) Chromium trivalent content

To determine chromium trivalent according to SLC. 8. 2 g of fiberize finished leather scrap was measured; 5 ml of H_2SO_4 and, 15 ml of the mixture and 15 ml of nitric acid or 10 ml of per chloric acid were added. At moderate flame the sample was heated to boil on hot plate, and until the reaction mixture begins to turn to orange a small funnel was placed on the neck of the flask. until complete change of color, the flame was lowered, for extra two minutes further heated gently, cooled for a short time in air, then rapidly cold water finally diluted to approximately 200 ml. Further boiled to eliminate the chlorine interference the solution for approximately 10 min. Consequently, the solution cooled and 15 ml of orthophosphoric acid was added to mask if any iron is present and 20 ml of 10% potassium iodide leaved to the stand for 10 min in the dark place. The sample was titrated against 0.1 N Sodium thiosulphate until the solution in the flask turns to light green using 5 ml of 1% starch indicator (SLC, 1996).

$$Cr_2O_3\% = \frac{\text{Titration volume} \times 0.00253 \times 100 \times \text{Correction factor}}{\text{Sample weight}}$$

e) Chromium six content

In order to determine the fiberized leather, chromium six content was conducted using ISO 17075 by calorimetric technique.

Sampling and preparation of samples

Leather sample was prepared according to the method by cutting it into small pieces. Test pieces that are wet (i.e., in excess of approximately 30% moisture) should be pre-dried at a temperature not exceeding 40 °C. Before grinding, the samples of leather should be reduced to small pieces of suitable dimensions, depending on the design of the cutter mill feed system.)

Preparation of analytical solution

The leather pieces of (2 ± 0.1) g were weighed and put into a 250 ml conical flask. A 100 ml solution was degassed. For 5 minutes, the solution was purging by allowing oxygen-free argon (or nitrogen) with a volume flow of 50 ± 10 ml/min. The aeration tube was removed, and the pieces of leather were added and the flask was closed with a stopper. As V_0 , the extract volume was weighed. On a mechanical orbital shaker, the conical flask, with the leather pieces was shaken for $180 \text{ min} \pm 5 \text{ min}$ to extract the chromium (VI). To keep the leather pieces from adhering to the wall of the flask the flask was shake in a smooth circular movement to avoid shaking faster than specified. Immediately after completing 3 hours of extraction, the contents of the conical flask are filtered through a membrane filter into a glass or plastic vessel with a lid. pH was checked, and it was between 7.0 and 8.0.

Determination of chromium (VI) by extraction solution

The extraction solution colorants were removed by passing the solution through a cartridge containing a suitable solid-phase extraction material. In the following way, Pre-treated the SPE cartridges:

- a) 5 ml methanol was flush with the cartridge
- b) Followed by 5 ml demineralized water
- c) With 10 ml of extraction solution, directly afterward

From the solution obtained, 10 ml (V_1) was taken and transfer quantitatively through the cartridge on an SPE system with a syringe or vacuum device. In 25ml volumetric flask the eluate was collected. The cartridge with 10 ml extraction solution into the 25 ml flask was flushed. The flask

was made up to volume (V_2) with extraction solution. This solution was as S_1 . After that 10 ml (V_3) of solution S_1 was poured into a 25 ml volumetric flask.

With the extraction solution, the solution was diluted 3/4 of the flask's volume. And 0.5 ml of phosphoric acid solution and afterwards 0.5 ml of diphenylcarbazide solution was added.

The flask was made up to volume (V_4) with extraction solution and mixed well. left for 15 min. The absorbance was measured in a 40 mm cell against the blank solution at 540 nm. Finally, the obtained absorbance was recorded as A_1 . For each run, pipette another 10 ml aliquot of solution S_1 into a 25 ml volumetric flask and treated it as described above, but without the addition of the diphenylcarbazide solution. the absorbance of this solution was measured in the same way as before and recorded it as A_2 .

Blank solution

The extraction solution was filled in a 25 ml volumetric flask three quarters, 0.5 ml of phosphoric acid and 0.5 ml of diphenylcarbazide solution was added and made up to the mark with extraction solution, and mix well. The solution was prepared daily and stored it in the dark place. The blank solution was treated in the same way as the analytical solution, excluding the solid phase extraction.

f) Formaldehyde content

Formaldehyde content was analyzed using the ISO 17226-1 and conducted using the High performance liquid chromatography (HPLC) technique. Leather-Chemical determination of formaldehyde content Part 1: Method using high performance liquid chromatography

Preparation of the formaldehyde stock solution

The formaldehyde stock solution was prepared in 1000 ml volumetric flask by taking 5 ml of the formaldehyde which contains approximately 100 ml water and then filled the flask with distilled water up to the mark.

Determination

10 ml formaldehyde solution was taken and poured into a 250 ml Erlenmeyer flask .and mix with 50 ml iodine solution. Then sodium hydroxide was added until it turns yellow.

Then the solution allows it to react for 15 min $\pm$ 1 min at 18 °C to 26 °C and then added 15 ml of sulfuric acid while swirling. After adding 2 ml of starch solution, the excess iodine was titrated with sodium thiosulfate until the color changes.

$$PFA = \frac{(V_0 - V_1) \times c_1 \times M_{FA}}{2}$$

Where

PFA is the concentration of the formaldehyde stock solution, in milligrams per 10 ml

V₀ is the titer of the thiosulfate solution for the blank solution, in milliliters (ml);

V₁ is the titer of the thiosulfate solution for the sample solution, in milliliters (ml);

M_{FA} is the relative molecular mass of formaldehyde, 30.02 g/mole;

C₁ is the concentration of the thiosulfate solution, in moles per liter (mole/l).

Sampling and preparation of samples

Leather sample was Prepared according to the method specified in ISO 4044:2017 by cutting into small pieces, Test pieces that are wet (i.e. in excess of approximately 30% moisture) should be pre-dried at a temperature not exceeding 40 °C.

Before grinding, the samples of leather should be reduced to small pieces of suitable dimensions depending on the design of the cutter mill feed system.

Extraction

2 g $\pm$ 0.1 g weighed leather sample was put into a suitable vessel. 50 ml of the detergent solution was pipetted and poured into a 100 ml erlenmeyer flask and warmed it to 40 °C. The leather was quantitatively transferred to the flask, and closed it with a glass stopper.

At 40 °C $\pm$ 0.5 °C in a water bath the content of the flask was shake smoothly for 60 min $\pm$ 2 min. Then the warm extract solution was filtered by vacuum through a glass fiber filter immediately into a flask. In the closed flask, the filtrate cooled down to room temperature (18 °C to 26 °C).

Reaction with DNPH

4.0 ml of acetonitrile, 5.0 ml aliquot of the filtered elute and 0.5 ml of DNPH solution was pipetted and poured into a 10 ml volumetric flask, then the flask was filled with demineralized water up to the mark and was shaking it by hand to mix the components. After 60 minute the solution filtered using a membrane filter and analyzed using HPLC.

HPLC conditions (recommendations)

The test was conducted at flow rate: 1.0 ml/min, Mobile phase: acetonitrile/water, 60:40, Separation column: C18 reversed phase column with pre column (1 cm, RP18), UV detection wavelength: 360 nm, Injection volume: 20 µl.

Calibration of HPLC

0.5 ml of the formaldehyde stock solution obtained with an exactly known formaldehyde content was peptide and poured into a 500 ml volumetric flask and pre-filled with 100 ml water. The solution was mixed and filled to the mark with water. For calibration purpose this solution is the standard solution, i.e. 2 µg formaldehyde/ml is the standard solution. In six 10 ml volumetric flasks a concentration series of 0.5 ml; 1.0 ml; 2.0 ml; 3.0 ml; 4.0 ml; 5.0 ml, 4 ml acetonitrile and 4 ml the standard solution was added. 0.5 ml DNPH solution was mixed in each flask immediately upon addition of the formaldehyde solution. The flasks filled up to the mark with demineralized water and mixed. After 60 minute the solution filtered through a membrane filter and analyzed the sample using HPLC.

The calibration plotting through a graph of the formaldehyde derivative peak area versus the concentration in micrograms per 10 ml.

Formaldehyde content calculation in the leather samples

$$w_F = \frac{P_S \times F}{m}$$

Where

w_F is the concentration of formaldehyde in the sample in milligrams per kilogram (mg/kg) rounded to 0.01 mg/kg;

ρ_S is the concentration of formaldehyde obtained from the calibration graph in micrograms per 10 ml ($\mu\text{g}/10\text{ ml}$)

F is the dilution factor in milliliters (ml);

m is the mass of leather weighed in grams (g)

Determination of recovery rate

Into a 10 ml volumetric flask 4 ml acetonitrile and an aliquot of 2.5 ml of the filtrate was added, then an accurately determined volume of the formaldehyde standard solution added to give an almost equal concentration to that found in the sample. In addition, the solution was treated following the procedure described. Finally determined ρ_{S_2} .

$$R_R = \frac{(PS_2 - 0.5 P_{S_2}) \times 100}{PFA1}$$

Where

ρ_{S_2} is the concentration of formaldehyde obtained from the calibration graph in micrograms per 10 ml

ρ_S is the concentration of formaldehyde in the non-spiked sample in micrograms per 10 ml

ρ_{FA1} is the spiked quantity of formaldehyde in micrograms per 10 ml ($\mu\text{g}/10\text{ ml}$);

RR is the recovery rate in percent, rounded off to 0.1%.

3.4.2 Preparation of plant fiber

In this study in order to extract the fibers from bamboo culm, first, the diaphragm and the node of the raw bamboo (2~4 years old) were first removed and the remaining parts were cleaved in the longitudinal direction into thin slabs with the length of 20-30 cm and with the thickness of 2-3 mm using the slicer (knife).

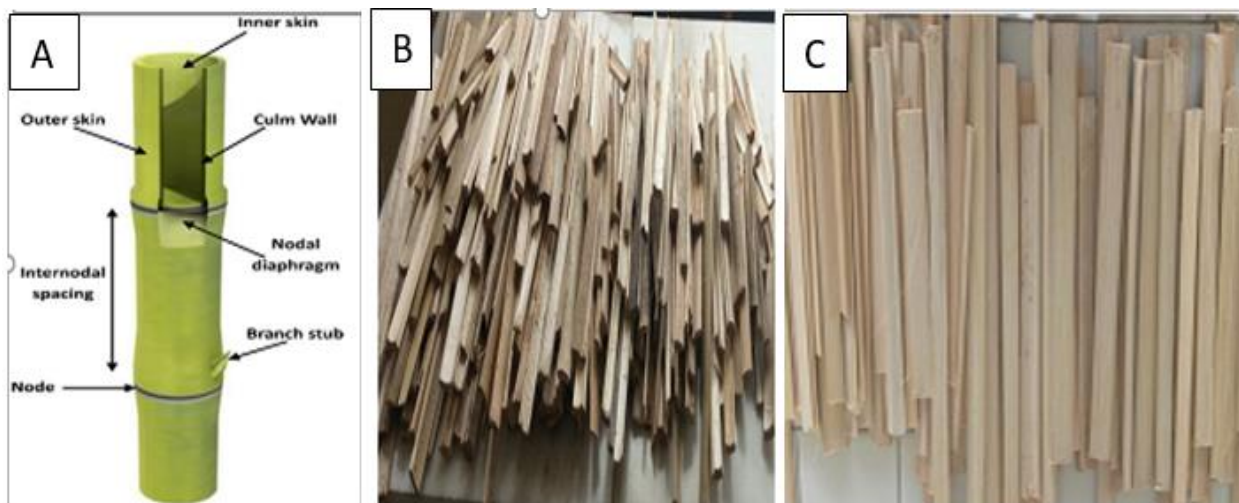


Figure 3-2 Preparation of bamboo culm [A. Bamboo Culm, B. 20 mm Length Bamboo Sample C. Bamboo Strip- for different extraction process]

Subsequently, three methods have been used to extract the bamboo fibers. These processes are chemical (Alkali treatment), mechanical process (water Retaining), and combined (mechanical and chemical) process.

3.4.2.1 Mechanical extraction (water retaining)

The bundled bamboo strips were soaked in distilled water for five days. The wet bamboo strips were beaten by hammer scraped with a sharp steel brush and left for 48 hours at room temperature.

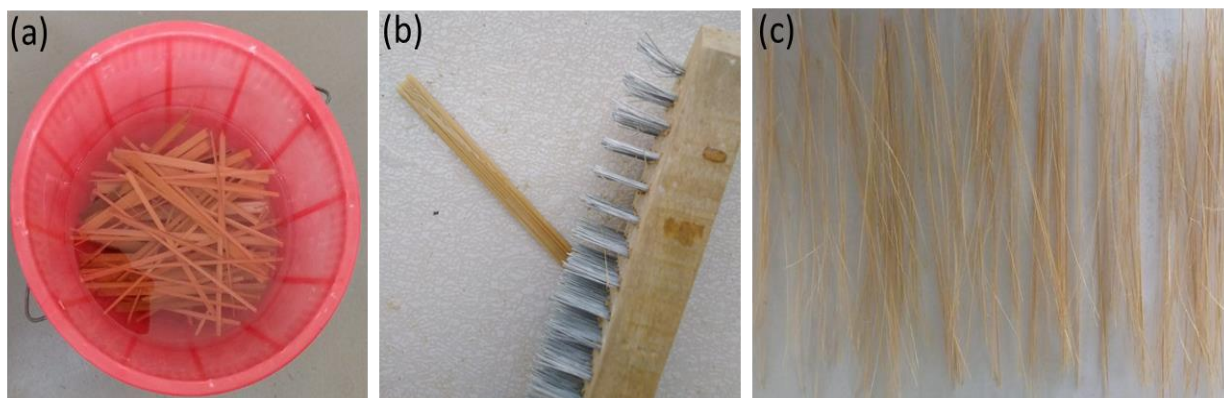


Figure 3-3 Mechanical Extraction [(a) Water Retaining (b) Steel Comb (c) Bamboo Fiber]

3.4.2.2 Chemical extraction (alkali retaining)

The bamboo strips were soaked in the Sodium Hydroxide (NaOH) solution for 72 hours at a mass volume of 4%, 5%, 6% and 7%, to influence the cellulosic as well as non-cellulosic components followed by washing with distilled water several times.

The strips rolled with roller, comb with steel brush, the fiber was left in room temperature for 48 hr. and measured the tensile strength to get the optimum result as a reference for the fiber.

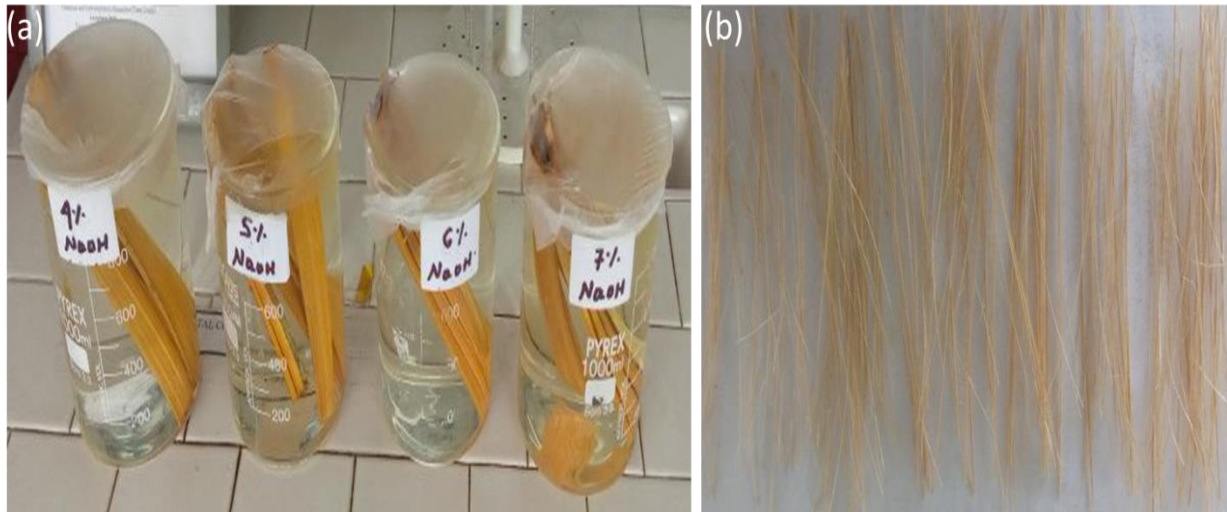


Figure 3- 4 Chemical extraction(Alkali Treatment) [(a) Different Concentration of the Alkali Treatments (b) 5% Alkali Treated Bamboo Fiber].

3.4.2.3 Combination of chemical and mechanical extraction

In this method commonly used mechanical process followed by chemical process. The only difference was alkali treatment took place for 24 hours.

3.5 Optimization of Bamboo Fiber

The treated bamboo fiber was performed using three dumbbell shaped specimens of 4mm wide and 20 mm length. Tensile strength (N/mm^2) and elongation at break (%) (ASTM 3379-75) were measured using the UTM (Universal Testing Machine M350-20 AT-USA) at an extension rate of 5 mm/min in order to now the optimum value of bamboo fiber.

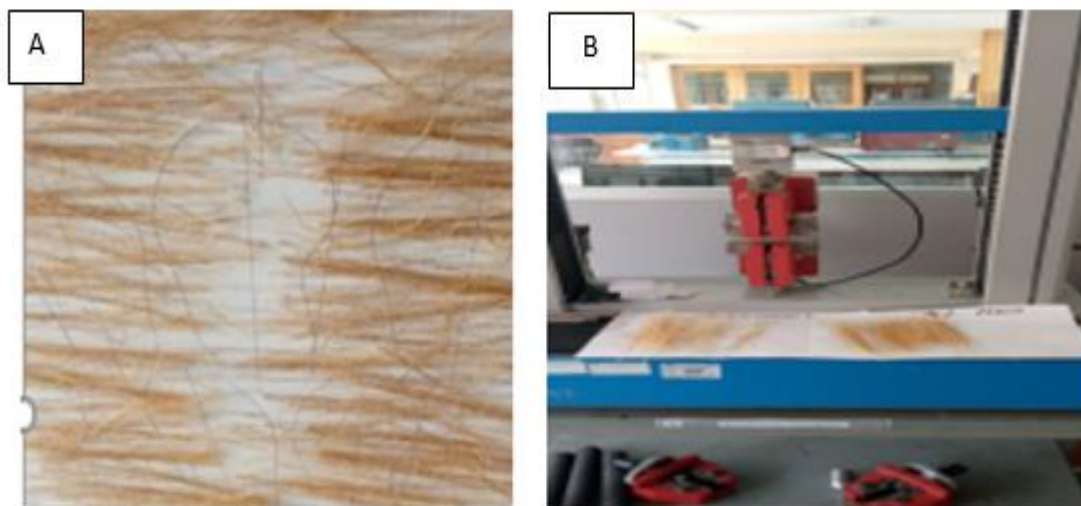


Figure 3-5 Tensile Strength of treated bamboo fiber (A) Treated bamboo fiber (b) Universal Tensile Machine (UTM)

3.6 Optimization of Binders

Leather board (LB) were prepared using leather fiber and two different binders namely Fevicol binder (synthetic resin) and Urea Formaldehyde (UF) at different levels of (10%, 15%, 25%, 35%, and 45%) and performed for their tensile strength to take the maximum result as reference for the binders.

3.6.1 Preparation of urea formaldehyde (UF) leather board (UF-LB)

The fiberized finished leather waste (162 g) was soaked in 1000 ml of water for 48 hours and mixed in the meat grinding machine (La Minerva C/E 680 N) two times to reduce the particle size and made a fine paste.

15% [24.3 ml] of UF, 3% of $\text{Al}_2(\text{SO}_4)_3$ and 5ml ethylene glycol was added and mixed thoroughly in the paste. Later, by adding 1:3 diluted Conc. H_2SO_4 , the pH was adjusted below 5. By adding 500 ml distilled water in to the mixture the slurry was formed.

Then into the board making mold (with the size of 30 cm x 30 cm) the sample was poured and in order to remove excess water wet board was pressed using the sheet plate. Finally, the board was air dried for 48 hours. and plated using the hydraulic press at a pressure of 50 bars and 50 °C for 2 second.

3.6.2 Leather board preparation using fevicol binder

The process was the same as the above (Urea Formaldehyde - LB preparation), the only difference is the binder; instead of UF in this case, the Fevicol synthetic resin was used.

3.6.3 Leather board preparation incorporated with plant fibers

Fiberized leather and already extracted PFs (plant fibers) were added in the proportions of 1%, 5%, 10%, 15% and mixed individually.

Composite board containing LF and PFs were prepared separately with the same procedure as that of control sheet. Finally, the details descriptions of the composite board prepared are noted as follows:

1. The composite board made from finished leather scrap and binders served as a control.
2. The composite board made from finished leather scraps (FLS) and bamboo fiber labeled as FLS-B

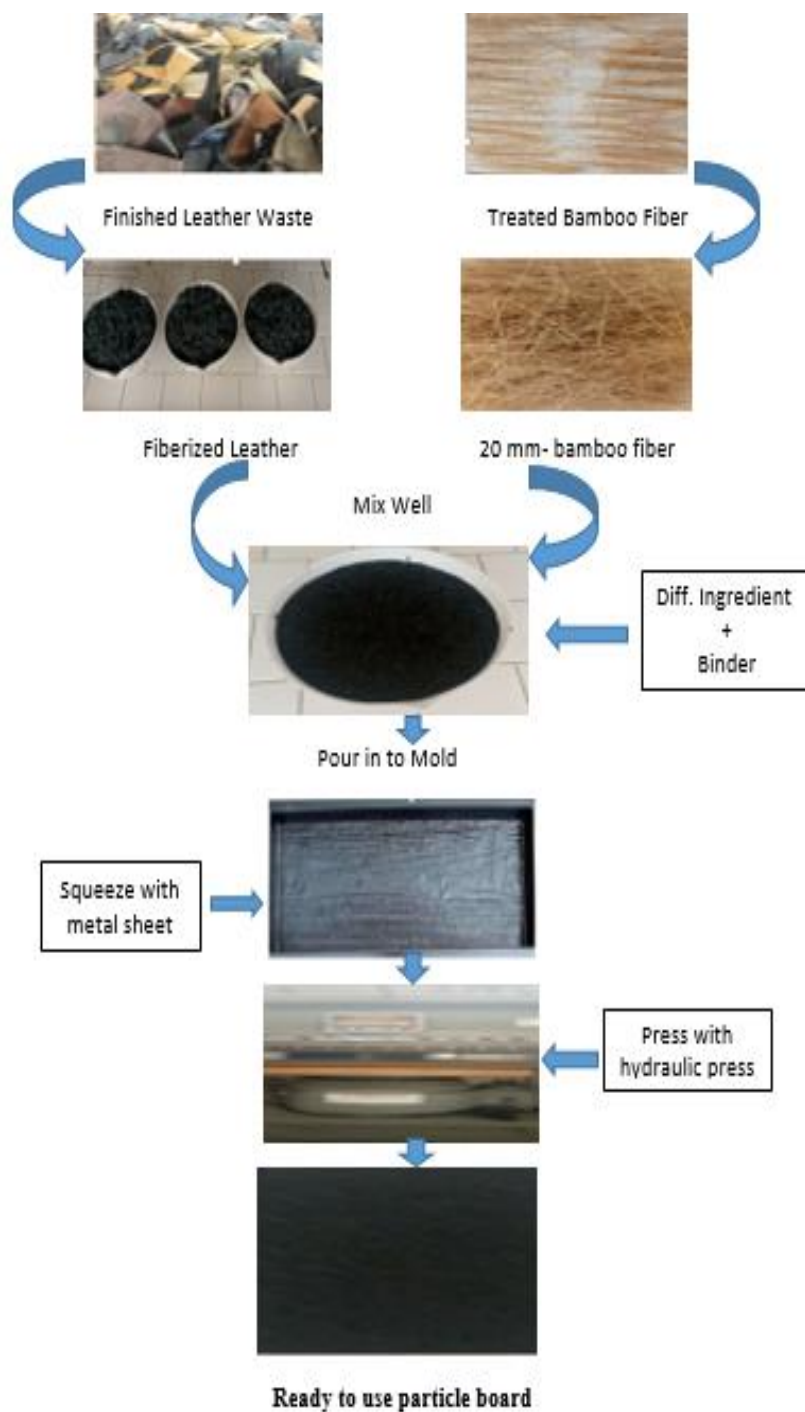


Figure 3-6 Leather board preparation process

3.7 Characterization of Control and Composite board

Finished leather scraps (FLS) and composite board were characterized for their physical and chemical characteristics such as mechanical studies, surface morphology (SEM) formation and changes in the functional groups (FTIR), and thermal stability (TGA).

3.7.1 Mechanical Properties

Mechanical properties were assessed using three dumbbell shaped specimens of 4 mm wide and 20 mm length. Tensile strength (N/mm²) and elongation at break (%) (ASTM 3379-75) were measured using the UTM (Universal Testing Machine M350-20 AT-USA) at an extension rate of 5 mm/min. The water absorption and desorption (%) capacities of the different control leather and composite board was determined according to SATRA TM6 [71]. Flexing Index was also assessed according to STM 129 test method and using SATRA-TRR 74 fiber board flexing machine.

3.7.2 Physical Analysis

✚ Thermal Stability (TGA) Analysis

TGA measurements were conducted using differential thermal gravimetric instrument (DTG - 60H -SHIMADZU Corporation (Japan). The test was carried out in a programmed temperature range of 30 °C- 800 °C, under nitrogen atmosphere, at a heating rate of 10 °C/min, and at a flow rate of 50 ml/min.

✚ Fourier transform infrared (FTIR) Analysis

FTIR measurements were done to see the formation and changes in the functional group. The spectra were measured at a resolution of 4.0 cm⁻¹ in the frequency range of 4000-400 cm⁻¹ using FTIR Shimadzu IR Affinity- IS spectrometer by ATR (Attenuated total reflectance) method.

✚ Scanning electrons microscope (SEM) Analysis

Specimen samples of approximately same dimensions from leather fibers, bamboo fibers, both experimental and control composite leather board were taken for morphology examination. Specimens/samples of interest were coated with gold using [Edwards E306] sputter coater after 24 hours drying in desiccator. Prior to drying in desiccator, the dried specimens/samples were mounted on a plate with double face adhesive tape. The micrographs for surface of the specimens were obtained using (SEM Model JSM-IT 300) Scanning Electron Microscope at high vacuum with accelerating voltage of 15Kv, and X600 magnifications.



Figure 3-7 Fiberized sample for physical analysis

(1) Bamboo Fiber (2), Urea Formaldehyde (UF), (3), Grind Leather, (4), UF- Control, (5), Fevicol Control, (6) Urea Formaldehyde (UF) Board, and (7) Fevicol -Board for TGA and FTIR samples.

3.7.3 Chemical characteristics of leather board

In order to determine whether the prepared board was environmentally friend or not, chromium six and Formaldehyde content was conducted using ISO 17075 by calorimetric technique and ISO 17226- using the HPLC technique respectively.

3.8 Data Analysis

- ✚ Measurements on the physical characteristics of the control and composite sheets were recorded, and mean values were compared between the leather and different concertation of plant fiber and binders. Excel Sheet was used for the mean and standard deviation of the three individual experiments ($n = 3$), and Origin 8.5 Software was also used for FTIR and TGA.
- ✚ For the tensile strength of bamboo fiber due to the natural behavior, the mean and standard deviation with nine unique tests ($n = 9$) were determined using an excel sheet after the outlier test could be performed.

4. RESULT AND DISS CUSION

4.1 Finished Leather Waste Chemical Analysis

The chemical analysis of the finished leather waste found in this study is shown in Table 2. The pH value of finished leather waste was found to be 6.2 ± 0.15 , which is within the range of (6-8), and the moisture content of the finished leather was $12.7\% \pm 1.2\%$, which results in the leather processing at the finished leather stage being undergone at the normal stage, which is 12-14%. Furthermore, in order to make the leather products environmental friendly and suitable for use, chromium trivalent (Cr^{+3}), chromium six (Cr^{+6}), and formaldehyde content are the basic parameters to be checked in leather processing.

Hence, in this study, it was found that $1.74 \pm 0.16\%$, $1.7 \pm 1.15 \text{ mg/kg}$, and $2.84 \pm 1.15 \text{ mg/kg}$, respectively, all meet the standard requirements of finished leather characteristics. The chemical characteristics of the finished leather waste were almost similar to the data reported in the SATRA Restricted Substance List European Union Regulation [SATRA RSL EU Regulation].

Table 2. Finished leather waste analysis

S/No	Parameters	Unit	Amount	SATRA RSL EU Regulation
1.	PH	-	6.2 ± 0.15	6-8
2	Moisture	%	12.7 ± 1.2	12-14
3	Chromium trivalent content	%	1.7 ± 0.16	< 2.0
4	Ash content	%	4.8 ± 1.15	2-6
5	Chromium Six (Cr^{+6})	mg/kg	1.7 ± 1.15	< 3.0
6	Formaldehyde Content	mg/kg	$2.8 \pm .15$	< 150

Different superscripts in the same column indicated that statistically significant difference ($P < 0.05$), Values are mean $\pm$ SD.

4.2 Bamboo fiber Tensile strength analysis

When natural fibers and matrix resins are not pretreated, there is insufficient interfacial adhesion in natural fiber composites. This frequently leads to the development of porous materials, environmental deterioration, and mechanical property deterioration [72].

Table 3. Tensile strength analysis of water retaining bamboo fiber (mechanical method)

S/no	Concentration	Tensile strength (N/mm ²)	Elongation at break (%)
1	-	266.74 ± 41.2	1.67 ± 0.5

Values are mean ± SD

Table 4. Tensile strength analysis of alkali retaining bamboo fiber

S/no	Concentration	Tensile strength (N/mm ²)	Elongation at break (%)
1	4% NaOH	355.33 ± 42.9	2.61 ± 0.9
2	5% NaOH	360.95 ± 87.4	1.89 ± 0.6
3	6% NaOH	303.15 ± 62.0	2.64 ± 2.6
4	7% NaOH	192.49 ± 22.1	1.21 ± 0.2

Values are mean ± SD

Table 5. Tensile strength analysis of combined (alkali and water retaining) bamboo fiber

S/no	Concentration	Tensile strength (N/mm ²)	Elongation at break (%)
1	4% NaOH	299.99 ± 87.6	2.88 ± 0.7
2	5% NaOH	306.46 ± 32.5	1.87 ± 0.6
3	6% NaOH	292.52 ± 30.0	1.81 ± 0.4
4	7% NaOH	233.59 ± 71.4	1.04 ± 0.1

Values are mean ± SD

As a result, a lot of work has been documented to enhance interfacial adhesion using chemical, physical, or other modification techniques. Alkali treatment, acetylation, cyanothylation, and coupling agent treatment are the most widely used techniques for surface modification. Alkali treatment was found to be one of the easiest and most efficient techniques [72].

Three methods were used to extract fibers from bamboo culms. These are mechanical treatment (water retention), alkaline treatment, and combined treatment (mechanical and chemical), as shown in Tables 3, 4, and 5 and Annex I.

In all methods, the extracted fibers have higher tensile strength values. However, 5% alkali treatment (NaOH-treated bamboo fibers) has been shown to be optimal [360.95 N/mm²] and suitable for manufacturing bamboo fiber composites. Alkali treatment is also widely used to improve the adhesion of various natural fibers in polymer-based composites [22]. Therefore, it fits well with other studies.

4.3 Tensile Strength Analysis of Binder

As shown in Tables 6 and 7, the maximum tensile strength (TS) values of the two binders (urea formaldehyde and fevicol resin binder) were obtained at 7.3 N/mm², and 6.1 N/mm² respectively, at a level of 15%, and it was taken as the maximum result and reference level for the making of controls as well as composite board materials.

Table 6. Tensile strength analysis of urea formaldehyde binder

S/no	Concentration (%)	Tensile strength (N/mm ²)	Elongation at break (%)
1	10	4.8 ± 0.10	2.9 ± 0.05
2	15	7.3 ± 0.06	3.4 ± 0.04
3	25	6.8 ± 0.10	4.2 ± 0.20
4	35	6.2 ± 0.10	4.1 ± 0.09
5	45	5.7 ± 0.06	3.1 ± 0.05

Different superscripts in the same column indicated that statistically significant difference ($P < 0.05$), Values are mean ± SD.

Table 7. Tensile strength analysis of fevicol binder

S/no	Concentration (%)	Tensile strength (N/mm ²)	Elongation at break (%)
1.	10	4.7 ± 0.10	2.9 ± 0.06
2.	15	6.1 ± 0.05	3.0 ± 0.20
3.	25	5.9 ± 0.06	3.8 ± 0.06
4.	35	4.4 ± 0.10	3.9 ± 0.06
5.	45	4.4 ± 0.06	2.0 ± 0.05

Different superscripts in the same column indicated that a statistically significant difference ($P < 0.05$). Values are mean $\pm$ SD.

4.4 Analysis of Control and Composites board

The mechanical properties of the waste leather scraps (WLS) and the corresponding composites (Cs) were measured and analyzed below.

4.4.1 Mechanical Analysis

A good mechanical property product lasts a long and is commercially viable in the market. Keeping the truth in mind, in this study, the mechanical properties of the composite board were examined.

Such as tensile strength and elongation at break, flexing index, water absorption, and desorption of the prepared control and composite.

As shown in Table 8 and Table 9, the prepared composite board (LF-C) using two different binders, namely UF and Fevicol binder, with their maximum respective tensile strength values of 12.9 ± 0.11 and 9.2 ± 0.98 N/mm². In the case of UF binder, as shown in Table 2, the tensile strength values of all the composite boards have higher values than their respective controls. The values of these composite boards meet the required standard set by CLRI-SDDC (7.0–4.0 MPa) [5], with optimum values in samples 3 and 4 (12.8 N/mm² $\pm$ 0.11 and 12.9 N/mm² $\pm$ 0.11), with a concentration of 5% and 10% plant fiber, respectively.

In the case of the composite board prepared using Fevicol resin binder as shown in Table 3, the strength properties of a composite at concentrations of 5% and 10% plant fiber (7.9 ± 0.09 and 9.2 ± 0.98 N/mm², respectively) are higher than their respective controls. But the value in sample 4 (10% plant fiber) with a strength property of 9.22 ± 0.98 N/mm² was optimum for this binder.

Even though all results meet the required standard value ($4.9 \pm 0.98 - 7.9 \pm 0.09$ N/mm²), with its maximum in sample 4 (10% PF) (9.22 ± 0.98 N/mm²) with Fevicol binder, the strength property of urea formaldehyde binder is better than that of Fevicol binder which is 12.9 N/mm² $\pm$ 0.11.

Among the two binders (urea formaldehyde and fevicol binder), the tensile strength difference might be due to the nature and quality of the binder or the compatibility of the binder with the leather fiber.

All composite boards were prepared using the binder UF and Fevicol; the water absorption value did not meet the required standard, which means it will not be applicable for the insole board as it can't absorb water to the required level. Also, it creates more moisture inside the shoe; hence, it requires some improvement.

All the composite boards prepared by both binders with water desorption values according to SATA TM2:1995 are capable of producing the required product. In addition, the flexing index according to the SATRA TM 3:1995 test method for both composite boards prepared using UF and Fevicol meets the required standard set for the insole board by CLRI-SDDC, as presented in Table 8.

Table 8. Mechanical properties of the LF-BF composite board -UF

Sample ID	LF/BF (%)	Tensile Strength (N/mm²)	Elongation at Break (%)	WA (%)	WD (%)	Flexing Index (%)
1	100:0	7.5 ± 0.10	4.7 ± 0.98	55.13 ± 2.01	57.16 ± 1.18	3.90 ± 1.10
2	99:1	8.7 ± 0.11	4.9 ± 0.98	57.10 ± 2.01	61.00 ± 1.18	3.75 ± 1.10
3	95:5	12.8 ± 0.11	5.5 ± 0.98	61.18 ± 2.01	70.26 ± 1.18	3.80 ± 1.10
4	90:10	12.9 ± 0.11	3.8 ± 0.11	68.33 ± 2.01	74.30 ± 1.18	3.90 ± 1.10
5	85:15	10.6 ± 0.09	4.6 ± 0.10	72.00 ± 2.01	79.18 ± 1.18	2.00 ± 1.10

Different superscripts in the same column indicated that statistically significant difference ($P < 0.05$), Values are mean ± SD.

Table 9. Mechanical properties of LF-BF composite board- Fevicol

Mechanical properties of LF-BF composite board- Fevicol

Sample ID	LF/BF (%)	Tensile Strength (N/mm ²)	Elongation at Break (%)	WA (%)	WD (%)	Flexing Index (%)
1.	100:0	5.7 ± 0.08	6.2 ± 0.04	57.2 ± 1.08	79.5 ± 2.98	2.9 ± 0.18
2	99:1	4.9 ± 0.98	5.2 ± 0.02	61.1 ± 1.18	55.6 ± 2.98	2.9 ± 0.05
3	95:5	7.9 ± 0.09	4.4 ± 0.03	75.0 ± 2.00	80.6 ± 2.98	3.1 ± 0.04
4	90:10	9.2 ± 0.98	4.0 ± 0.03	81.4 ± 2.18	74.4 ± 2.98	2.0 ± 0.03
5	85:15	5.2 ± 0.03	3.2 ± 0.01	85.0 ± 1.98	79.8 ± 2.98	1.9 ± 0.09

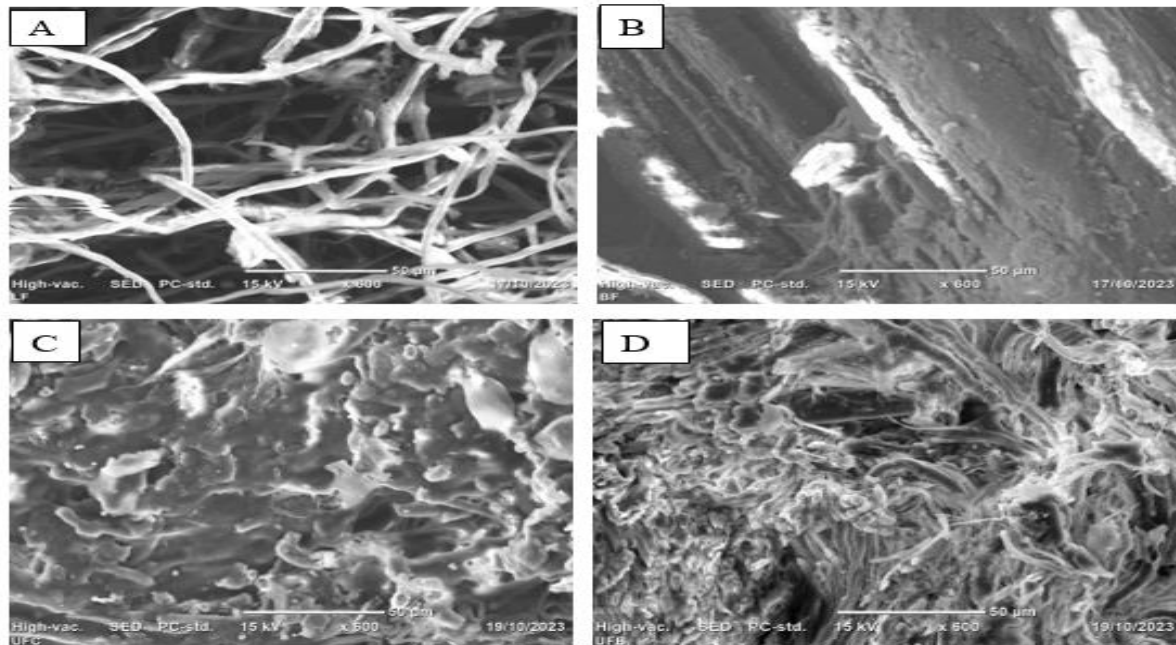
NOTE: WA-Water absorption; WD-Water desorption

Different superscripts in the same column indicated that statistically significant difference ($P < 0.05$), Values are mean ± SD.

4.4.2 Physical Analysis

4.4.2.1 SEM Image

The SEM image of the control and composite sample were taken using Scanning electron microscope at 1.5 kv and X600 at ASTU as shown in the Figure 4-1.



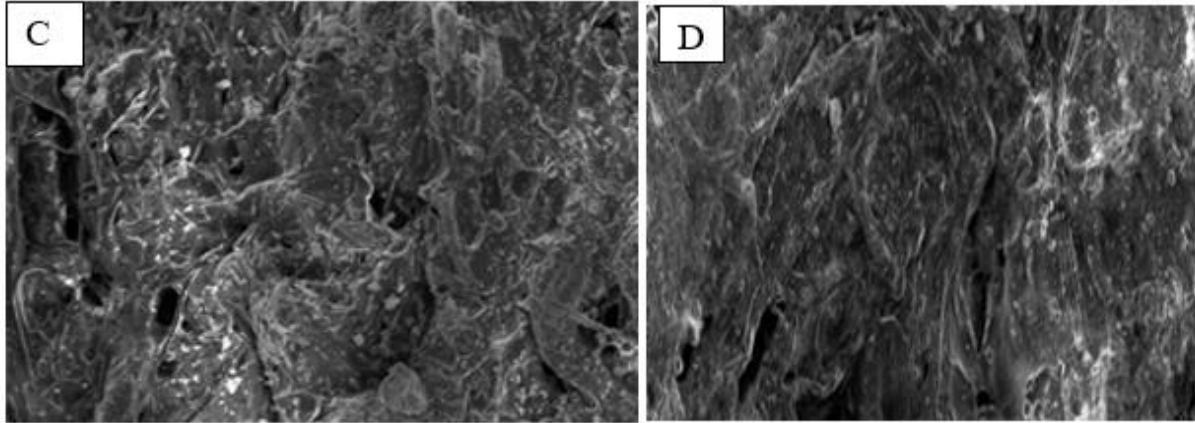


Figure 4-1 Surface morphology image at X600 [A. Grind finished leather waste B.5% treated bamboo fiber C. UF control board D. UF composite board E. Fevicol control board F. Fevicol composite board].

SEM images of the finished leather fiber in Figure 4.1 [A] at the magnification of X600 shows that individual collagen fibers were clearly observed. In Sample [B] surface morphology of Bamboo fiber consists of long and thick fibers was Observed.

In Figure 4.1 [C] and [D], the SEM image of the control and Experimental sample with leather fiber along with the UF adhesive. Figure 4.1 [C] the fiber is well embedded with the binder and it seems less porosity. Where as in Figure 4.1 [D] shows an assortment of fibers along with the binder having no significant difference among the samples. So this SEM images revealing that they have composite nature.

In Figure 4-1 [E] and Figure [F] show the control and experimental sample of with the fevicol binder, respectively. Figure 4-1 [E], the control sample of the fevicol network of leather fibers is observed to be adhered to the binding material. The porosity of experimental sample 4-1 [F] was observed to be more homogenous than the control one. So the composite nature of the experimental sample was clearly seen. In addition, the fiber composite of fibers (leather and bamboo) is apparently bonded with fevicol, as seen in the SEM-Micrograph.

In this study, the SEM images are comparable to those of composite boards made in the previous study [5, 73]. The porosity of the experimental sample seems to be more homogenous than its counterpart (the control sample). This reveals that they have a composite nature.

4.4.2.2 TGA Analysis

Figure 4-2 shows that samples of the control and composite boards were subjected to TGA from 30 °C to 800 °C, mainly weight loss of materials with increasing in temperature.

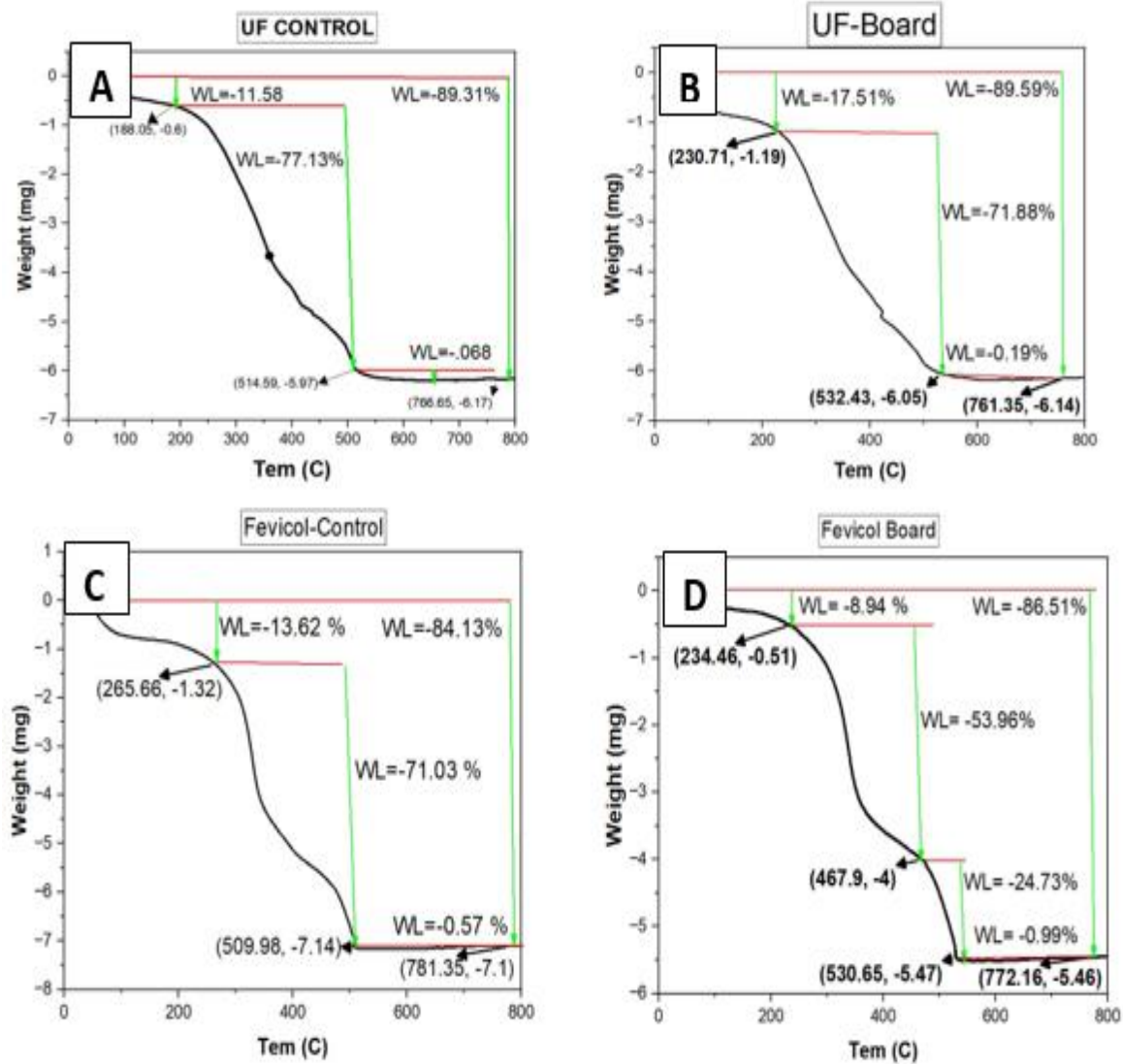


Figure 4-2 TGA Analysis [A. UF Control sheet B. UF Composite sheet C. Fevicol Control sheet D. Fevicol Composite sheet].

As shown in Figure 4-2 [A] and [B], the TGA analysis revealed that the weight loss of the materials increased with temperature. For this analysis of the UF control samples and the composite board, the working temperature was set from 30 °C to 800 °C. As shown in Figure 4-2 [A], the control board revealed a three-step weight loss. The initial weight loss (11%) was due to the loss of free and bound water from 30 °C up to 265 °C. The second major weight loss from (77%) 265 °C to 509 °C was due to collagen degradation in the samples. The third weight loss (0.68%) was due to the decomposition of degraded products. And around 10.7% residue was observed at about 800 °C.

Figure 4-2 [B], UF Composite board, showed that the three-step weight loss. The initial weight loss (17%) from 30 °C up to 230 °C is due to the loss of water molecules in the sample. The second major weight loss (71%) that has occurred from 230 °C up to 532 °C is due to protein and cellulose degradation. The third weight loss (0.19%) which occurred from 532 °C up to 761 °C may be due to the decomposition of the degraded products. A residue of 10.5% was also registered in this sample.

Whereas Figure 4-2 [C] shows that the leather control board with Fevicol binder has a three-step weight loss, the initial weight loss (13.6%) was observed at 30 °C up to 265 °C and this is due to the evaporation of free or bonded water molecules in the sample. The second major weight loss of 71% occurred from 265 °C up to 509 °C is due to protein and cellulose degradation. The third 0.57% weight loss is observed up to 800 °C with a final residue of 16.0%, this is due to the decomposition of degraded products.

In leather composite with bamboo fiber (LF/BF) Figure 4-2 [D] had a three-step weight loss. The first weight loss of 8.9% was observed from 30 °C up to 234 °C; this is due to the loss of water in the sample: and the second and major weight loss of 54% was observed from 234 °C and the third step was from 500 °C up to 800 °C, this is due to the degradation of protein, cellulose, hemicelluloses, and lignin with a final residue of 10% [74].

No sudden degradation was observed compared to the leather control board. This might also be due to the presence of hemicelluloses, cellulose, and lignin in the fiber reviles composite nature of the board.

4.4.2.3 FTIR Analysis

FTIR is an easy way to identify the presence of certain functional groups in a molecule. In this steady UF-Composite and Fevicol resin Composite are shown in Figure 4-3 and Figure 4-4.

A. FTIR analysis of UF Composite

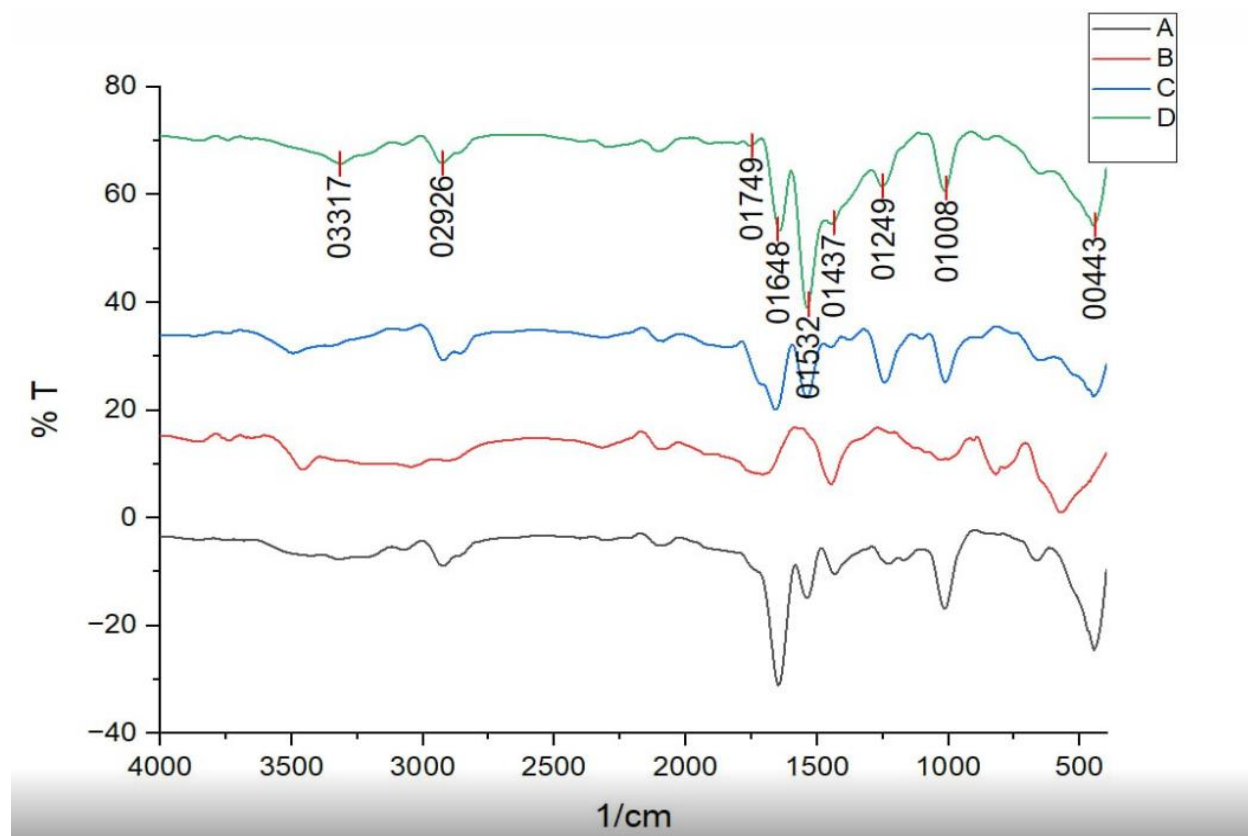


Figure 4-3 FTIR Analysis of overlap image of UF [**B**-UF Control, **C**-Bamboo Fiber, **D**-Leather Fiber on **A**-UF Composite]

Figure 4-3 presents the FTIR vibrational spectrum of wave number 4000-400 cm^{-1} of Urea formaldehyde composite. Due to the inter- and intra-molecular hydrogen bonding of cellulose and lignin compounds The FTIR spectroscopic analysis showed a broad band peak at 3570-3250 cm^{-1} assigned to the stretching of the O-H group. Which might be from bamboo fiber.

The peak at 1648 cm^{-1} is due to -C-N and -C-H overtone bending [74]. Most prominent peak at 1532 cm^{-1} represents C=O stretching peak in amide and 1249 cm^{-1} is due to C-N stretching. This proves the presence of amide group in UF resin.

The absorption band at 1158 cm^{-1} is C-O stretching of aliphatic ether and 1008 is due to C-O-C stretching [75] The shift in peaks of C-H stretching to around $2915\text{--}2820$ in composites from 2926 cm^{-1} in pure UF resin suggests some chemical interaction between matrix and reinforcement to some extent also it might be from the finished leather waste

Since it originates from skin or hides, it possesses the characteristic peaks corresponding to collagen fiber. Since there is no significant peak shift in the FTIR spectra of the constituents in the composites, it can be concluded that no strong chemical interaction or strong chemical bonding occurred at the matrix-filler interface [69,70].

B. FTIR analysis of Fevicol resin composite

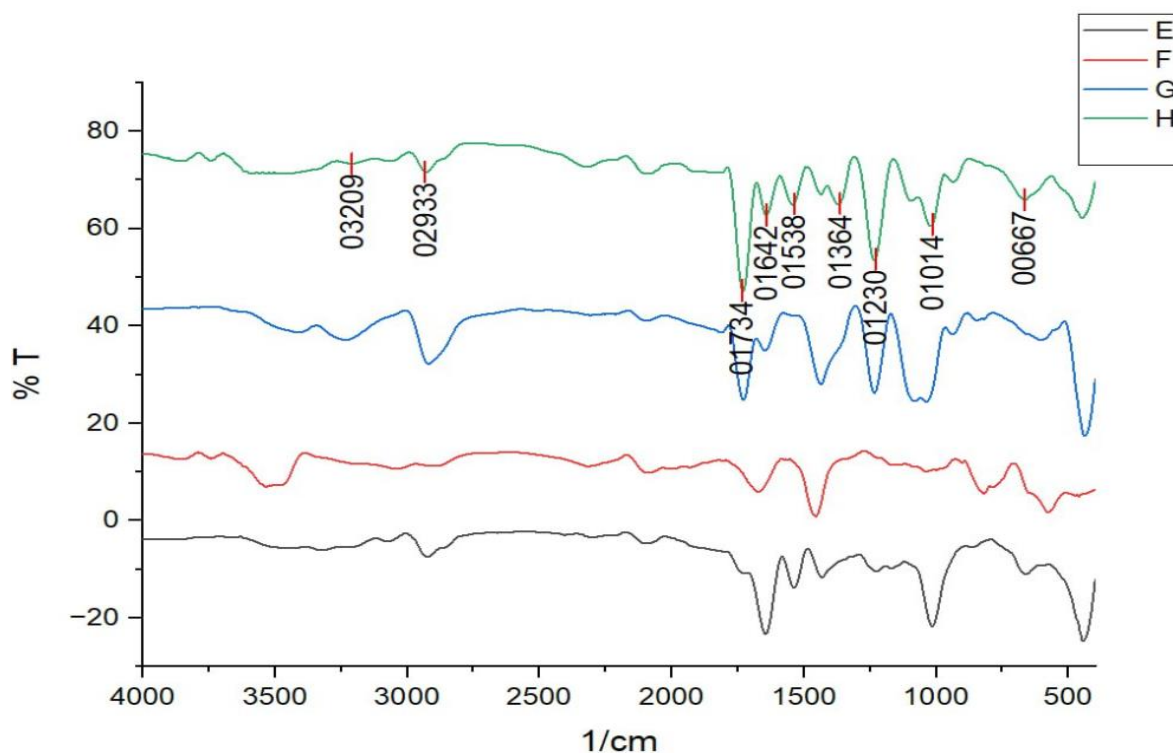


Figure 4- 4 FTIR Analysis of overlap image of Fevicol Resin [**F**-Fevicol Control, **G**-Bamboo Fiber, **H**-Leather Fiber on **E**-Fevicol Composite]

Figure 4-4 present the FTIR analysis showed the O-H stretching vibrations occur at 3209 cm^{-1} indicating the presence of free hydroxyl groups and bonded O-H bands of lignin.

The weak peaks at $2923\text{--}2854\text{ cm}^{-1}$ (control and after composite) could be attributed to C-H stretching vibrations. resulting from the finished leather waste.

The FTIR spectra of the composite sample show a broad peak from 1030 to 1635 cm^{-1} representing C-O-C and C-O stretch (primary and secondary hydroxide. groups) and, bonds are belong to the glucoside linkage , possibly due to lignin [78]. A sharp pick is observed at 2933 cm^{-1} representing the C-H of the fevicol synthetic binder.

4.5 Chromium Six (Cr^{+6}) and Formaldehyde Content of the Leather Board

It is vital to investigate the effect of certain parameters, such as Cr^{+6} and the formaldehyde content of the leather board. It should meet the EU REACH regulations that is, (chromium six < 3 mg/kg and formaldehyde content < 150 mg/kg). In this research, the control and the composite (LF/PF) using UF and Fevicol resin both meet the standard requirements.

Table 10. Chromium six and formaldehyde content of the leather board composite

S/no	Parameters	Unit	Amount	EU Reach Regulation
Urea Formaldehyde Composite Board				
1.	Chromium Six (Cr^{+6})	mg/kg	1.9 $\pm$ 1.1	< 3.0
2.	Formaldehyde content	mg/kg	9.41 $\pm$ 1.7	< 150
Fevicol Composite Board				
1.	Chromium Six (Cr^{+6})	mg/kg	2.1 $\pm$ 1.1	< 3.0
2.	Formaldehyde content	mg/kg	3.1 $\pm$ 1.1	< 150

Values are mean $\pm$ SD, different superscripts in the same column represent statistically significant difference (P < 0.05)

5. CONCLUSION, RECOMMENDATIONS, AND FUTURE WORK

5.1 Conclusion

In Ethiopia now a day, with the actual soaking capacity of the tanneries is 8216.7 ton per year of different leather processing waste (i.e., finished leather waste) disposed of in the environment. Only 200 kg of 1 ton of salted hide is converted into finished leather, and the rest is disposed as a waste [60].

This high amount of waste utilization into useful products is a promising process. Therefore, in this research, the prepared sample was fabricated at a different weight ratio of randomly oriented short bamboo fiber with finished leather waste fiber - reinforced polymer.

The mechanical properties such as tensile strength, flexing index, and physical properties (water absorption and desorption), thermal stability (TGA), Fourier transform infrared (FTIR), and surface morphology (SEM), of the manufactured sample are characterized. The bamboo fiber content shows a significant effect on the composites' mechanical and physical characteristics. Among the tested composite samples, the urea formaldehyde composite exhibited the highest tensile strength properties among other plant fiber [5].

The results revealed that composites with finished leather waste weights of 90% and bamboo fibers of 10% showed the maximum ultimate tensile strength on both resins with a value of 12.9 ± 0.11 N/mm² and 9.2 ± 0.98 N/mm², which was improved by 72% and 44%, respectively, when compared to the control one. In addition, UF binder composite exhibited better tensile strength values than the Fevicol binder composite. This might be the compatibility of the UF binder with leather fibers and plant fibers. Also, SEM, FTIR and TGA studies have confirmed that the composite nature of the board.

Hence, we can improve the strength properties of the finished leather waste composite material by incorporating the locally abundant and economical bamboo fiber as a reinforcement agent in the development of composite materials. So the above composite board, having suitable mechanical properties, an appealing surface, a higher tensile strength value, and reasonable flexibility, values might be used as a raw material for the production of footwear components.

Therefore, this composite can be used as a raw material for the preparation of leather goods as a reinforcement material, implying that the composite material for this study is suitable for the consumer applications such as insole boards, mouse pads, components of small furniture, and interior decorations.

5.2 Recommendations

- ✚ The recommendation from this thesis paper is that the composite made up of the bamboo fiber reinforced composite board with resin binders (Urea formaldehyde and Fevicol) showed better tensile strength properties and can be used as a raw material for the making of leather goods or as a supporting tool, mouse pads, foot wear (insole), false roofing, wall partitioning, and interior decorations.

5.3 Future Work

- ✚ Regarding the bamboo fiber reinforced polymer composites, there are several issue to be improved that were not addressed in this research. Some of them are explained below:
- ✚ The preparation of the composite specimen with different contents of bamboo fiber is unidirectional 0° (using the hand layup method) instead of randomly oriented.
- ✚ Additional mechanical and physical properties of the control and the composite board.

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ANNEXES

I. Bamboo Fiber Tensile Strength properties [V=AXL]

1. Water Retting

No	Treatment	Density (g/cm ³)	Density (g/mm ³)	Mass (gm)	Length (mm)	Volume (mm ³)	Area (mm ²)	Force (N)	Tensile Strength (N/mm ²)	Elongat ion at break
Mechanical Extraction (Water Retting)										
1	Water	0.800	0.0008	0.02	125	30	0.24	76	316.7	1.8
2	Water	0.800	0.0008	0.02	125	30	0.24	76	316.7	1.8
3	Water	0.800	0.0008	0.02	125	30	0.24	61	254.7	2.2
4	Water	0.800	0.0008	0.02	125	30	0.24	55	229.2	2.7
5	Water	0.800	0.0008	0.02	125	30	0.24	72	300.0	1.1
6	Water	0.800	0.0008	0.02	125	30	0.24	58	241.7	1.3
7	Water	0.800	0.0008	0.02	125	30	0.24	60	250.0	1.1
8	Water	0.800	0.0008	0.02	125	30	0.24	48	200.0	1.3
9	Water	0.800	0.0008	0.02	125	30	0.24	70	291.7	1.2
Mean Average							0.24	61.6	266.74	1.6
STDEV							-	9.4	41.20	0.5

2. Alkali Treatment [4%]

No	Treatment	Density (g/cm ³)	Density (g/mm ³)	Mass (gm)	Length (mm)	Volume (mm ³)	Area (mm ²)	Force (N)	Tensile Strength (N/mm ²)	Elongation at break (%)
Chemical Extraction [Alkali Treatment]										
1	4% NaOH	0.999	0.000999	0.02	125	19	0.152	60.6	398.6	3.5
2	4% NaOH	0.999	0.000999	0.02	125	19	0.152	56.1	369.0	3.4
3	4% NaOH	0.999	0.000999	0.02	125	19	0.152	55.6	265.7	3.4
4	4% NaOH	0.999	0.000999	0.02	125	19	0.152	60.5	398.0	3.5
5	4% NaOH	0.999	0.000999	0.02	125	19	0.152	50.3	330.9	1.9
6	4% NaOH	0.999	0.000999	0.02	125	19	0.152	54.0	355.2	2.7
7	4% NaOH	0.999	0.000999	0.02	125	19	0.152	60.0	394.7	1.5
8	4% NaOH	0.999	0.000999	0.02	125	19	0.152	50.0	328.9	1.7
9	4% NaOH	0.999	0.000999	0.02	125	19	0.152	54.2	356.5	1.5
Mean Average							0.152	55.7	355.3	2.6
STDEV							-	4.1	42.95	0.89

3. Alkali Treatment [5%]

No	Treatment	Density (g/cm ³)	Density (g/mm ³)	Mass (gm)	Length (mm)	Volume (mm ³)	Area (mm ²)	Force (N)	Tensile Strength (N/mm ²)	Elongation at break (%)
Chemical Extraction [Alkali Treatment]										
1	5% NaOH	0.947	0.000947	0.02	125	24	0.192	55.6	289.5	1.4
2	5% NaOH	0.947	0.000947	0.02	125	24	0.192	58.6	385.5	2.2
3	5% NaOH	0.947	0.000947	0.02	125	24	0.192	48.3	317.7	1.3
4	5% NaOH	0.947	0.000947	0.02	125	24	0.192	73.3	482.2	2.3
5	5% NaOH	0.947	0.000947	0.02	125	24	0.192	36.0	236.8	1.2
6	5% NaOH	0.947	0.000947	0.02	125	24	0.192	70.1	461.1	2.3
7	5% NaOH	0.947	0.000947	0.02	125	24	0.192	57.9	380.9	2.9
8	5% NaOH	0.947	0.000947	0.02	125	24	0.192	68.4	450.0	2.2
9	5% NaOH	0.947	0.000947	0.02	125	24	0.192	50.4	331.5	1.3
10	5% NaOH	0.947	0.000947	0.02	125	24	0.192	39.2	251.8	1.1
Mean Average							0.192	55.0	358.7	1.8
STDEV							-	11.9	87.4	0.6

4. Alkali Treatment [6%]

No	Treatment	Density (g/cm ³)	Density (g/mm ³)	Mass (gm)	Length (mm)	Volume (mm ³)	Area (mm ²)	Force (N)	Tensile Strength (N/mm ²)	Elongation at break (%)
Chemical Extraction [Alkali Treatment]										
1	6% NaOH	0.999	0.000999	0.02	125	23	0.184	55.6	302.1	1.6
2	6% NaOH	0.999	0.000999	0.02	125	23	0.184	58.6	318.4	1.8
3	6% NaOH	0.999	0.000999	0.02	125	23	0.184	48.3	262.5	1.3
4	6% NaOH	0.999	0.000999	0.02	125	23	0.184	73.3	398.3	2.3
5	6% NaOH	0.999	0.000999	0.02	125	23	0.184	36.0	195.6	1.2
6	6% NaOH	0.999	0.000999	0.02	125	23	0.184	70.1	380.9	2.5
7	6% NaOH	0.999	0.000999	0.02	125	23	0.184	57.9	314.6	1.2
8	6% NaOH	0.999	0.000999	0.02	125	23	0.184	68.4	371.7	2.9
9	6% NaOH	0.999	0.000999	0.02	125	23	0.184	50.4	273.9	1.4
10	6% NaOH	0.999	0.000999	0.02	125	23	0.184	39.2	213.0	1.9
Mean Average							0.184	55.0	303.1	1.8
STDEV							-	12.6	62.0	0.6

5. Alkali Treatment [7%]

No	Treatment	Density (g/cm ³)	Density (g/mm ³)	Mass (gm)	Length (mm)	Volume (mm ³)	Area (mm ²)	Force (N)	Tensile Strength (N/mm ²)	Elongation at break (%)
Chemical Extraction [Alkali Treatment]										
1	7% NaOH	0.999	0.000999	0.02	125	24	0.192	35.9	186.9	1.2
2	7% NaOH	0.999	0.000999	0.02	125	24	0.192	37.6	195.8	1.2
3	7% NaOH	0.999	0.000999	0.02	125	24	0.192	31.2	162.5	1.7
4	7% NaOH	0.999	0.000999	0.02	125	24	0.192	44.9	233.8	1.2
5	7% NaOH	0.999	0.000999	0.02	125	24	0.192	42.8	222.9	0.9
6	7% NaOH	0.999	0.000999	0.02	125	24	0.192	34.4	179.1	1.4
7	7% NaOH	0.999	0.000999	0.02	125	24	0.192	33.2	172.9	1.3
8	7% NaOH	0.999	0.000999	0.02	125	24	0.192	40.7	211.9	1.2
9	7% NaOH	0.999	0.000999	0.02	125	24	0.192	37.4	194.7	1.1
Mean Average							0.192	36.9	195.6	1.2
STDEV							-	4.26	22.1	0.2

6. Combined (Mechanical Extraction & Chemical Extraction [4%])

No	Treatment	Density (g/cm ³)	Density (g/mm ³)	Mass (gm)	Length (mm)	Volume (mm ³)	Area (mm ²)	Force (N)	Tensile Strength (N/mm ²)	Elongation at break (%)
Combined (Mechanical Extraction & Chemical Extraction [4%])										
1	4% NaOH	0.944	0.000944	0.02	125	23	0.184	58.9	320.1	3.5
2	4% NaOH	0.944	0.000944	0.02	125	23	0.184	57.4	311.9	3.4
3	4% NaOH	0.944	0.000944	0.02	125	23	0.184	60.5	328.8	1.4
4	4% NaOH	0.944	0.000944	0.02	125	23	0.184	60.5	60.5	1.9
5	4% NaOH	0.944	0.000944	0.02	125	23	0.184	47.8	328.8	1.8
6	4% NaOH	0.944	0.000944	0.02	125	23	0.184	53.0	288.0	1.8
7	4% NaOH	0.944	0.000944	0.02	125	23	0.184	61.0	331.5	2.6
8	4% NaOH	0.944	0.000944	0.02	125	23	0.184	44.0	239.1	2.4
9	4% NaOH	0.944	0.000944	0.02	125	23	0.184	54.7	297.2	2.3
Mean Average							0.184	55.3	299.9	2.8
STDEV							-	5.71	87.6	0.7

7. Combined (Mechanical Extraction & Chemical Extraction [5%])

No	Treatment	Density (g/cm ³)	Density (g/mm ³)	Mass (gm)	Length (mm)	Volume (mm ³)	Area (mm ²)	Force (N)	Tensile Strength (N/mm ²)	Elongation at break (%)
Combined (Mechanical Extraction & Chemical Extraction [5%])										
1	5% NaOH	0.944	0.000944	0.02	125	23	0.184	60.1	326.6	1.0
2	5% NaOH	0.944	0.000944	0.02	125	23	0.184	59.4	322.8	1.4
3	5% NaOH	0.944	0.000944	0.02	125	23	0.184	61.7	335.3	1.8
4	5% NaOH	0.944	0.000944	0.02	125	23	0.184	62.4	339.1	1.4
5	5% NaOH	0.944	0.000944	0.02	125	23	0.184	48.0	260.8	1.0
6	5% NaOH	0.944	0.000944	0.02	125	23	0.184	53.0	288.0	1.4
7	5% NaOH	0.944	0.000944	0.02	125	23	0.184	61.0	331.5	2.0
8	5% NaOH	0.944	0.000944	0.02	125	23	0.184	47.0	255.4	2.0
9	5% NaOH	0.944	0.000944	0.02	125	23	0.184	54.9	298.3	2.7
Mean Average							0.184	56.3	306.4	1.8
STDEV							-	5.58	32.2	0.5

8. Combined (Mechanical Extraction & Chemical Extraction [6%])

No	Treatment	Density (g/cm ³)	Density (g/mm ³)	Mass (gm)	Length (mm)	Volume (mm ³)	Area (mm ²)	Force (N)	Tensile Strength (N/mm ²)	Elongation at break (%)
Combined (Mechanical Extraction & Chemical Extraction [6%])										
1	6% NaOH	1.066	0.001066	0.02	125	19	0.152	49.2	323.6	1.2
2	6% NaOH	1.066	0.001066	0.02	125	19	0.152	44.8	294.7	1.7
3	6% NaOH	1.066	0.001066	0.02	125	19	0.152	49.1	323.0	1.4
4	6% NaOH	1.066	0.001066	0.02	125	19	0.152	40.4	265.7	1.0
5	6% NaOH	1.066	0.001066	0.02	125	19	0.152	49.7	326.9	2.1
6	6% NaOH	1.066	0.001066	0.02	125	19	0.152	37.4	246.0	1.4
7	6% NaOH	1.066	0.001066	0.02	125	19	0.152	41.9	275.6	1.9
8	6% NaOH	1.066	0.001066	0.02	125	19	0.152	43.2	284.	1.7
Mean Average							0.152	44.463	292.5	1.8
STDEV							-	4.56	30.0	0.4

9. Combined (Mechanical Extraction & Chemical Extraction [7%])

No	Treatment	Density (g/cm ³)	Density (g/mm ³)	Mass (gm)	Length (mm)	Volume (mm ³)	Area (mm ²)	Force (N)	Tensile Strength (N/mm ²)	Elongation at break (%)
Combined (Mechanical Extraction & Chemical Extraction [7%])										
1	7% NaOH	1.00	0.001	0.02	125	16	0.152	34.0	223.68	0.9
2	7% NaOH	1.00	0.001	0.02	125	16	0.152	23.0	151.31	1.1
3	7% NaOH	1.00	0.001	0.02	125	16	0.152	31.0	203.95	1.2
4	7% NaOH	1.00	0.001	0.02	125	16	0.152	27.5	180.92	0.9
5	7% NaOH	1.00	0.001	0.02	125	16	0.152	56.3	370.39	1.3
6	7% NaOH	1.00	0.001	0.02	125	16	0.152	33.5	220.39	0.9
7	7% NaOH	1.00	0.001	0.02	125	16	0.152	42.1	276.97	1.1
8	7% NaOH	1.00	0.001	0.02	125	16	0.152	24.5	161.18	0.9
Mean Average							0.152	33.99	223.598	1.0
STDEV							-	10.86	71.4	0.1

II. Outlier checking using 1.5 IQR Rule

1. Water Retaining – Diameter = 0.31 mm

Data	76	76	61	55	72	58	60	48	70
Ascending order	48	55	58	60	61	70	72	76	76
Median = 61 $Q_1 = 58 + 60 = 59$ $Q_3 = 70 + 72 = 71$ $IQR = Q_3 - Q_1 = 12$ $Q_1 = \text{Quartile one}$ $Q_3 = \text{Quartile three}$ $IQR = \text{Interquartile Range}$									

✚ Calculating outlier using 1.5 IQR rule

$Q_1 - 1.5 \times IQR \leq \text{Acceptance range} \leq Q_3 + 1.5 \times IQR$; Q_1 Quartile one,

$$[59 - [1.5 \times 12] \leq \text{Acceptance range} \leq [71 + [1.5 \times 12]]$$

$$41 \leq \text{Acceptance range} \leq 89$$

✚ This means that anyone outside this is an outlier, however all the data are within the limit [41-89]. So in this data there is no outlier.

2. Alkali Treatment [4% NaOH]- Diameter = 0.24 mm

Data	60.6	56.1	55.6	60.5	50.3	54.0	60.0	50.0	54.2
Acc. order	50.0	50.3	54.0	54.2	55.6	56.1	60.0	60.5	60.6
Median = 55.6 $Q_1 = 54 + 54.2 = 54.1$ $Q_3 = 56.1 + 60 = 58.05$ $IQR = Q_3 - Q_1 = 3.95$ $Q_1 = \text{Quartile one}$ $Q_3 = \text{Quartile three}$ $IQR = \text{Interquartile Range}$									

✚ Calculating outlier using 1.5 IQR rule

$Q_1 - 1.5 \times IQR \leq \text{Acceptance range} \leq Q_3 + 1.5 \times IQR$; Q_1 Quartile one,

$$[54.1 - [1.5 \times 3.95] \leq \text{Acceptance range} \leq [58.05 + [1.5 \times 3.95]]$$

$$48.2 \leq \text{Acceptance range} \leq 63.97$$

✚ This means that anyone outside this is an outlier, however all the data are within the limit [48.2-63.97]. So in this data there is no outlier.

3. Alkali Treatment [5% NaOH]- Diameter = 0.27 mm

Data	55.6	58.6	48.3	73.3	36.0	70.1	57.9	68.4	50.4	39.2
Ascending order	36.0	39.2	48.3	50.4	55.6	57.9	58.6	68.4	70.1	73.3
Median = 56.75 $Q_1 = 48.3 + 50.4 = 49.35$ $Q_3 = 58.6 + 68.4 = 63.5$ $IQR = Q_3 - Q_1 = 14.15$ $Q_1 = \text{Quartile one}$ $Q_3 = \text{Quartile three}$ $IQR = \text{Interquartile Range}$										

✚ Calculating outlier using 1.5 IQR rule

$Q_1 - 1.5 \times IQR \leq \text{Acceptance range} \leq Q_3 + 1.5 \times IQR$; Q_1 Quartile one,

$[49.35 - [1.5 \times 14.15] \leq \text{Acceptance range} \leq [63.5 + [1.5 \times 14.15]$

$28.12 \leq \text{Acceptance range} \leq 85.25$

✚ This means that anyone outside this is an outlier, however all the data are within the limit [28 -85]. So in this data there is no outlier.

4. Alkali Treatment [6% NaOH] – Diameter = 0.27 mm

Data	55.6	58.6	48.3	73.3	36.0	70.1	57.9	68.4	50.4	39.2
Acc. order	36.0	39.2	48.3	50.4	55.6	57.9	58.6	68.4	70.1	73.3
Median = 56.75 $Q_1 = 48.3 + 50.4 = 49.35$ $Q_3 = 58.6 + 68.4 = 63.5$ $IQR = Q_3 - Q_1 = 14.15$ $Q_1 = \text{Quartile one}$ $Q_3 = \text{Quartile three}$ $IQR = \text{Interquartile Range}$										

✚ Calculating outlier using 1.5 IQR rule

$Q_1 - 1.5 \times IQR \leq \text{Acceptance range} \leq Q_3 + 1.5 \times IQR$; Q_1 Quartile one,

$$[49.35 - [1.5 \times 14.15] \leq \text{Acceptance range} \leq [63.5 + [1.5 \times 14.15]$$

$$28.13 \leq \text{Acceptance range} \leq 84.7$$

✚ This means that anyone outside this is an outlier, however all the data are within the limit [28.1-84.7]. So in this data there is no outlier.

5. Alkali Treatment [7% NaOH] – Diameter = 0.27 mm

Data	35.9	37.6	31.2	44.9	42.8	34.4	33.2	40.7	37.4
Ascending order	31.2	32.2	34.4	35.9	37.4	37.6	40.7	42.8	44.9
Median = 37.4 $Q_1 = 34.4 + 35.9 = 35.15$ $Q_3 = 37.6 + 40.7 = 39.15$ $IQR = Q_3 - Q_1 = 4$ $Q_1 = \text{Quartile one}$ $Q_3 = \text{Quartile three}$ $IQR = \text{Interquartile Range}$									

✚ Calculating outlier using 1.5 IQR rule

$$Q_1 - 1.5 \times IQR \leq \text{Acceptance range} \leq Q_3 + 1.5 \times IQR; Q_1 \text{ Quartile one,}$$

$$[35.15 - [1.5 \times 4] \leq \text{Acceptance range} \leq [39.15 + [1.5 \times 4]$$

$$29.2 \leq \text{Acceptance range} \leq 45.2$$

✚ This means that anyone outside this is an outlier, however all the data are within the limit [29.2-45.2]. That means there is no outlier.

6. Combined [Chemical and water retaining] [4%] – Diameter = 0.27 mm

Data	58.9	57.4	60.5	60.5	47.8	53.0	61.0	44.0	54.7
Acc. order	44.0	47.8	53.0	54.7	57.4	58.9	60.5	60.5	61.0
Median = 57.4 $Q_1 = 53 + 54.7 = 53.9$ $Q_3 = 58.9 + 60.5 = 59.7$ $IQR = Q_3 - Q_1 = 5.9$ $Q_1 = \text{Quartile one}$ $Q_3 = \text{Quartile three}$ $IQR = \text{Interquartile Range}$									

✚ Calculating outlier using 1.5 IQR rule

$$Q_1 - 1.5 \times IQR \leq \text{Acceptance range} \leq Q_3 + 1.5 \times IQR; Q_1 \text{ Quartile one,}$$

$$[53.8 - [1.5 \times 5.9] \leq \text{Acceptance range} \leq [59.7 + [1.5 \times 5.9]$$

$$44.9 < \text{Acceptance range} \leq 68.1$$

✚ This means that anyone outside this is an outlier, however all the data are within the limit [44.9-68.1]. So in this data there is no outlier.

7. Combined [Chemical and water retaining] [5%] – Diameter = 0.27 mm

Data	60.1	59.4	61.7	62.4	48.0	53.0	61.0	47.0	54.9
Ascending order	47.0	48.0	53.0	54.9	59.4	60.1	61.0	61.7	62.4
Median = 59.4 $Q_1 = 53 + 54.9 = 53.95$ $Q_3 = 60.1 + 61.0 = 60.55$ $IQR = Q_3 - Q_1 = 6.6$ $Q_1 = \text{Quartile one}$ $Q_3 = \text{Quartile three}$ $IQR = \text{Interquartile Range}$									

✚ Calculating outlier using 1.5 IQR rule

$$Q_1 - 1.5 \times IQR \leq \text{Acceptance range} \leq Q_3 + 1.5 \times IQR; Q_1 \text{ Quartile one,}$$

$$[53.95 - [1.5 \times 6.6] \leq \text{Acceptance range} \leq [60.55 + [1.5 \times 6.6]$$

$$44.05 \leq \text{Acceptance range} \leq 70.45$$

✚ This means that anyone outside this is an outlier, however all the data are within the limit [44-05- 70.45]. So in this data there is no outlier.

8. Combined [Chemical and water retaining] [6%] – Diameter = 0.24 mm

Data	49.2	44.8	49.1	40.4	49.7	37.4	41.9	43.2	
Acc. order	37.4	40.4	41.9	43.2	44.8	49.1	49.2	49.1	
Median = 44 $Q_1 = 40.4 + 41.9 = 41.15$ $Q_3 = 49.1 + 49.2 = 49.15$ $IQR = Q_3 - Q_1 = 8.0$ $Q_1 = \text{Quartile one}$ $Q_3 = \text{Quartile three}$ $IQR = \text{Interquartile Range}$									

✚ Calculating outlier using 1.5 IQR rule

$Q1 - 1.5 \times IQR \leq \text{Acceptance range} \leq Q3 + 1.5 \times IQR$; Q1 Quartile one,

$$[41.15 - [1.5 \times 8.0] \leq \text{Acceptance range} \leq [49.15 + [1.5 \times 8.0]$$

$$29.15 < \text{Acceptance range} \leq 61.2$$

✚ This means that anyone outside this is an outlier, however all the data are within the limit [29.15 -61.2]. So in this data there is no outlier.

9. Combined [Chemical and water retaining] [7%] – Diameter = 0.24 mm

Data	34.0	23.0	31.0	27.5	56.3	33.5	42.1	24.5	
Ascending order	23.0	24.5	27.5	31.0	33.5	34.2	42.1	56.3	
Median = 32.3  $Q_1 = 24.5 + 27.5 = 26.0$ $Q_3 = 34.2 + 42.1 = 38.15$ $IQR = Q_3 - Q_1 = 12.15$ $Q_1 = \text{Quartile one}$ $Q_3 = \text{Quartile three}$ $IQR = \text{Interquartile Range}$									

✚ Calculating outlier using 1.5 IQR rule

$Q1 - 1.5 \times IQR \leq \text{Acceptance range} \leq Q3 + 1.5 \times IQR$; Q1 Quartile one,

$$[26 - [1.5 \times 12.15] \leq \text{Acceptance range} \leq [38.05 + [1.5 \times 12.15]$$

$$7.8 < \text{Acceptance range} \leq 56.3$$

✚ This means that anyone outside this is an outlier, however all the data are within the limit [7.8-56.3]. So in this data there is no outlier.