

DISSERTATION REFERENCE NO- 048/06/2019



QUALITY ASSESSMENT OF THE HIDES AND SKINS AT WET BLUE STAGE
AND ESTIMATING SOLID LEATHER WASTE TOWARDS VALUE ADDITION IN-
ITIATIVE IN ETHIOPIA

PhD DISSERTATION

BY

TEKLAY ASGEDOM TEFERI

ADDIS ABABA UNIVERSITY, COLLEGE OF VETERINARY MEDICINE AND
AGRICULTURE
DEPARTMENT OF ANIMAL PRODUCTION STUDIES
PHD PROGRAM IN ANIMAL PRODUCTION

June, 2019

Bishoftu, Ethiopia

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ITIATIVE IN ETHIOPIA

A dissertation submitted to the College of Veterinary Medicine and Agriculture of Addis
Ababa University in partial fulfillment of the requirements for the degree of Doctor of
Philosophy in Animal Production

By
Teklay Asgedom Teferi

June, 2019
Bishoftu, Ethiopia

Addis Ababa University
College Of Veterinary Medicine and Agriculture
Department of Animal Production Studies

As members of the examining board of the final PhD open defense, we certify that we have read and evaluated the dissertation prepared by **Teklay Asgedom Teferi** entitled: “**Quality Assessment of the Hides and Skins at Wet Blue Stage and Estimating Solid Leather Waste towards Value Addition Initiative in Ethiopia**” and recommend that it be accepted as fulfilling the dissertation requirement for the degree of Doctor of Philosophy in tropical animal production.

_____	_____	_____
Chairman (title and name)	Signature	Date

_____	_____	_____
Internal Examiner (title and name)	Signature	Date

_____	_____	_____
External Examiner (title and name)	Signature	Date

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_____	_____	_____
Dissertation advisor (title and name)	Signature	Date

_____	_____	_____
Co-advisor (title and name)	Signature	Date

_____	_____	_____
Department Chair (title and name)	Signature	Date

DEDICATION

This dissertation is dedicated to the Holy Spirit for blessing me with talents and opportunities in life. My mother Awetash Nerae, my father Asgedom Teferi, for the foundation they laid to my success. My wife Rigbe Kassahun and my children Eyob Teklay and Natnael Teklay for their patience during my absence and for providing me love and care all the time.

STATEMENT OF THE AUTHOR

First, I declare that this dissertation is my bona fide work and that all sources of materials used for this dissertation have been duly acknowledged. This dissertation has been submitted in partial fulfillment of the requirements for a PhD degree at Addis Ababa University College of Veterinary Medicine and Agriculture and is deposited at the University/College Library to be made available to borrowers under the rules of the Library. I solemnly declare that this dissertation is not submitted to any other institution anywhere for the award of any academic degree, diploma, or certificate.

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Name: Teklay Asgedom Teferi

Signature _____

Place: College Of Veterinary Medicine and Agriculture-Bishoftu

Date of submission _____

BIOGRAPHICAL SKETCH

The author was born in Almeda village Adwa central zone of Tigray Regional state in 1968. He attended Primary education in Betekihnet Primary School Adwa, Secondary Education in Queen Sheba Secondary School Adwa. After completion of high school education, He joined Haramay the then Alemaya University and awarded BSc Degree in Animal science in 1992. He worked for Ministry of Labour and Social Affairs (MOLSA) and went to the former Children's Amba in which he served for 10 years starting from junior expert up to department head, then moved to Agarfa Agricultural Technical and Vocational Education Training College (ATVETC) as fund raising coordination office head and worked for 10 months. He again moved to Bekonji ATVETC and worked as Vice dean for academic sector and taught different livestock courses for seven years. The author joined Addis Ababa University Faculty of Veterinary Medicine for post graduate study and awarded MSc degree in tropical animal production and health in the year 2008. He again worked for Engineering capacity building program (ecbp) as senior expert for leather sector, worked there for three years and then transferred to Ministry of Industry and assigned as a senior researcher in Ethiopian Leather Industry Development Institute (LIDI) and still working there. The author then joined Addis Ababa University, College of Veterinary Medicine and Agriculture (Department of Animal Production) for PhD study in Animal Production studies in 2014. He offered the course Hide and skin management for the under graduate students in the College. In his work experience the author awarded different national and international certificates.

ACKNOWLEDGMENTS

First of all, I would like to express my sincere gratitude and respect to my major advisor Dr. Gebeyehu G. and co-advisors Dr. T.P. Sastry, Dr. Getachew T., Dr. Yayneshet T. for their passionate and much desired support, supervision, friendly, humble treatment, critical remarks, encouragement and inspiration from problem identification to the final write-up of the Dissertation. They shared me their accumulated professional experiences and were cooperative from the beginning of proposal writing to the completion of this Dissertation work.

I would also like to express my solemn appreciation to Addis Ababa University, Leather Industry development Institute (LIDI) and Central Leather Research Institute (CSIR-CLRI) India for offering me every opportunity to pursue my PhD study at Addis Ababa University, College of Veterinary Medicine and Agriculture (AAU-CVMA), Bishoftu-Ethiopia and CSIR-CLRI-Chennai-India. I greatly acknowledge Professor Berhan Tamir head department of animal production studies and Professor Hagos Ashenafi Associate Dean for post graduate program (ADGP), for their administrative help, the management and staff members of LIDI for their assistance and encouragement, CVMA department of Animal production studies and every staff member for their modest treatment and making smooth my stay in the campus. Special thanks also goes to Dr. Chandrasekaran, Director, CSIR-Central Leather Research Institute, Adyar, Chennai-20, India, Dr. madhan, Principal Scientist, CSIR-CLRI, and Ato wondu Legesse, former General Director of LIDI for their kind administrative help. I thank Dr. Inbasekaran for his unreserved help during my experimental work at CLRI, Dr. Senthil R., Shekar J. and Dr. Sekar for their technical help and all Administrative and Scientific staff of CLRI for their help during my stay in CLRI.

I would also like to express my deepest appreciation to my beloved wife w/ro Regbe Kassahun and my Children Eyob Teklay and Natnael Teklay for their care and love, advice and selfless support in every aspect during the course of the study. My last but not least words of appreciation and respect are reserved to all my family members and friends.

ABBREVIATIONS

AA	Addis Ababa
AALF	All African Leather Fair
AAU	Addis Ababa University
AGP	Agricultural Growth Program
ATVET	Agricultural Technical Vocational Education Training
BBC	Bio-Fiber Derived Bio-Composites
BOD	Biological Oxygen Demand
C ₂ H ₆ O ₂	Ethylene Glycol
CLRI	Central Leather Research Institute
COD	Chemical Oxygen Demand
CSA	Central Statistics Authority Ethiopia
CSIR	Council For Scientific and Industrial Research
CVMA	College of Veterinary Medicine and Agriculture
DSC	Differential Scanning Calorimeter
Ecbp	Engineering Capacity Building Program
ECHA	European Chemical Agency
EIC	Ethiopian Investment Commission
ELICO	Ethiopian Leather Industry Corporation
EPA	Environnemental Protection Authority
ESGPIP	Ethiopia Sheep and Goat Productivity Improvement Program
ESQA	Ethiopian Quality and Standard Authority, Ethiopia
ETA	Ethiopian Tanners Association
ETFLGMA	Ethiopian Tanners, Footwear and Leather Goods Manufacturers Association
FAO	Food and Agriculture Organization
FDI	Foreign Direct Investment
FDRE	Federal Democratic Republic Of Ethiopia
FTIR	Fourier Transform Infrared
G.C	Gregorian Calendar
GDP	Gross Domestic Product

GOE	Government of Ethiopia
HCN	Hydrogen Cyanide
ILRI	International Livestock Research Institute
IT	Information Technology
IUE	International Union Environment Commission
JALCA	Journal of the American Leather Chemists Association
KPa	Kilopascal
LF	Leather Fiber
LIDI	Leather Industry Development Institute
LLPTI	Leather and Leather Products Technology Institute
M	Mole
MoA	Ministry of Agriculture
MoARD	Ministry of Agriculture and Rural Development
MOLSA	Ministry of Labour and Social Affairs
MOTI	Ministry of Trade and Industry
MPa	Mega Pascal
N/mm	Newton/Millimeter
NPC	National Productivity Center
NRL	Natural Rubber Latex
OM	Optical Microscopy
PEG	Polyethylene Glycol
PFs	Plant Fibers
ppm	Parts Per Million
PSI	Pounds Per Square Inch(Lb/In ²)
PUB	Polyurethane Binder
QSAE	Quality and Standard Authority of Ethiopia
R&D	Research and Development
RB	Resin Binder
RCL	Recycled Leather
SC	Scar
SDDC	Shoe Design and Development Center

SEM	Scanning Electron Microscope
SFF	Static Flaying Frame
SVHC	Substances of Very High Concern
SWMP	Solid Waste Management Program
Tcl	Crystallization Temperature
TDS	Total dissolved solids
Tg	Glass Transition Temperature
TGA	Thermo Gravimetric Analysis
Tm	Melting Temperature
TR	Table Rank
TS	Tensile Strength
UNCTAD	United Nation Conference on Trade and Development
UNIDO	United Nation Industrial Development Organization
USAID	United States Agency For International Development
UV	Ultra Violet
w/w	Weight By Weight

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Teklay Asgedom Teferi
PhD dissertation
Addis Ababa University (2019)

ABSTRACT

*This study was conducted to identify major defects of hide and skins and assess their impact on the quality of the products, estimate the solid wastes generated from the sector and identify possibilities for transforming such waste in to value added consumer products. The study was held in eight selected tanneries in and around Addis Ababa within a radius of 100 km. Observational survey was conducted in three potential shoe factories and two year data from Pitards garment & goods manufacturing industry were collected to estimate the volume of waste generated. composite leather boards were prepared using finished leather wastes and different plant fibers namely enset (*Ensete ventricosum*), hibiscus (*Hibiscus cannabinus*), jute (*Corchorus trilocularis L.*), palm (*Phoenix dactylifera*) and sisal (*Agave sisalana*) employing different binders like natural rubber latex (NRL), Resin binder (RB), and Poly urethane binder (PUB). These materials were incorporated in different proportions and their products were characterized for their mechanical and physicochemical properties. The Defects of hides and skins were categorized into pre-, peri- and post-slaughter problems. The overall prevalence of these defect categories were 81.80% in pre-slaughter, 59.90% in peri-slaughter and 27.80% in post-slaughter in hides. The corresponding values for sheepskin were 87.00%, 36.70%, 32.90%, respectively. About 70.00, 75.30, 27.20% of goatskins had defects at the pre, peri and post slaughter stages respectively. Grade values of hides and skins in this study showed that most grades fall in grade 5, 6 and rejects (7) showing that the quality of the raw materials is getting worse than ever due to the effect of defects occurred as pre slaughter mainly of (cockle, scratch, scar), peri slaughter (mainly flaying defects) and post slaughter (mainly putrefaction) that are taking greater share and responsible for the quality deterioration of the raw materials.*

Composite leather boards prepared using NRL as binder exhibited better mechanical properties compared to those of control boards. Composites prepared using resin binder (RB) and Poly urethane binder (PUB) have shown better tensile strength properties than their respective controls revealing the compatibility of the resin binder with plant and leather fibers. SEM pictures of the products in this study showed composite nature. In composite sheets prepared using RB having 10 % hibiscus, 20 % palm and 40 % sisal fibers showed better mechanical properties than their controls. In those composite sheets made using NRL having 30 % jute fiber exhibited better mechanical properties than its control and meet the required standards for insole/shank board, though has lower values of tensile strength in wet state than its control. Most of the plant fibers used in this study played a role in improving properties of the sheets though it is dependent on the ratio used and the nature of the binder. It was observed that all of the composite sheets prepared in this study can be used as raw material for the preparation of consumer products such as insoles, chapel-uppers, light hand bags, false roofing coverage, mouse pads, key chains, wallets, components of furniture and other interior decorations.

Key words: - *Ethiopia; Hide & skin; leather waste; composite; plant fibers; binders*

1. INTRODUCTION

The Ethiopian leather industry is a relatively older industry with more than 8 decades of involvement in processing leather and producing leather products (UNCTAD, 2018). The country is Africa's leading livestock producer and the 10th largest livestock producer in the world. It is not only about the supreme number of cattle, sheep and goats, but also that Ethiopian goat and sheepskins are preferable to other countries' products in terms of quality (Behailu, 2017). This enormous population of livestock and preferable quality provides ample opportunity for the development of the leather industry in the country. However, the livestock potential remains lagging behind in its role to hasten the country's economic development, and this might be due to lack of effective, efficient and coordinated support in terms of supply of raw hides, skins and other production inputs as well as other related problems are among the challenges faced to achieve the target (UNCTAD, 2018).

The leather sector is identified as one of the potential sectors that could play a crucial role in achieving long-run policy objectives and transforming the country's development status to a higher level by increasing the foreign currency earning of the country, expanding employment opportunities and attracting foreign direct investment (FDI) (Behailu, 2017). However the actual number of hides and skins collected in the country out of the total potential is 26% hide, 80% sheepskin and 65% goat skin that reach the different tanneries; the rest being either consumed locally or sold illegally through cross border illicit markets (ETA, 2004). Moreover, the quality of those hides and skins reaching tanneries is not up to the desired standard hence leading to down grading and rejections along the processing line with ultimate reduction in the volume exported to the world market (Teklay, 2010). The country loses millions of dollars annually from the large volume of rejected skins, which is reflected in decreased profits of millions of poor livestock keepers (Bekele and Ayele, 2008).

Poor animal husbandry practices expose the animals to skin diseases, scratches and wounds. Most of the hides and skins produced in the country are from backyard slaughter

which predisposes the raw materials to slaughter defects such as flaying defects (holes, gauge marks, poor patterns, ripping) and veinness due to poor bleeding. Absence of differential pricing for good quality raw materials has also discouraged good post-slaughter handling (Ahmed, 2001; Mohammad *et al.*, 2002); Tanning, a chain of processes of stabilizing the collagen fiber by the tanning agents, such that the skin/hide is no longer susceptible to putrefaction or rotting (HMIP, 1995), to convert it into useful end products called leather, that are used for the manufacture of fashion goods such as shoes, bags, caps, jackets, and other household products, is an age long art which has transcended generations (Thomason, 1985).

The leather industry generally uses hides and skins as raw materials, which are the by-products of meat and meat products industry. In this respect, the leather industry could have easily been distinguished as an environmentally friendly industry, since it processes waste products from meat production (Lang *et al.*, 1999). However, the leather industry has commonly been associated with high pollution due to the chemicals used, bad smell, organic wastes generated and high water consumption caused during manufacturing processes (Taylor *et al.*, 1998).

Different forms of biological wastes emerge during the transformation of hides and skins into leathers, in the leather industries all around the world; have negative impacts on the environment (Ozgunay *et al.*, 2007). Natural fibers in simple definition are fibers that are not synthetic or manmade. They can be sourced from plants or animals (Ticoalu *et al.*, 2010). These natural fibers have many remarkable advantages over synthetic fibers. Recently, due to the increase in population and very high competition on resource; natural resources are being exploited substantially as an alternative to synthetic materials. For this reason, utilization of natural fibers for the reinforcement of the composites has been receiving increasing attention. (Taj *et al.*, 2007).

The use of natural fiber from both resources, renewable and nonrenewable such as oil palm, sisal, flax, and jute to produce composite materials, gained considerable attention in the last decades. The plants, which produce cellulose fibers can be classified into bast fibers (jute, flax, ramie, hemp, and kenaf), seed fibers (cotton, coir, and kapok), leaf fi-

bers (sisal, pineapple, and abaca), grass and reed fibers (rice, corn, and wheat), and core fibers (hemp, kenaf, and jute) as well as all other kinds (wood and roots) (Faruk *et al.*, 2012). Composites are a versatile and valuable family of materials that can solve problems of different applications. They facilitate the introduction of new properties in the materials. Recycling and renewing natural resources are giving a new dimension in discovering new materials (Khan *et al.*, 2010).

The supply of quality raw materials (hides and skins) is highly deteriorating this time in Ethiopia due to different constraining elements. This deteriorated quality on the other hand imply the generation of huge volume of tannery wastes. However, even though there is ample tannery solid waste are available and have enormous utility to be exploited, the utilization effort of this solid waste in countries like Ethiopia is almost nil that needs due attention and mobilization to conduct in-depth scientific researches and utilize it for economic value.

The objectives of this study therefore are;

1. To assess the defects of hides and skins and their grade status;
2. To estimate solid leather waste generated from Ethiopian leather sector;
3. To develop models of value added consumer products from disregarded finished leather solid waste;
4. To identify the best binder and plant fiber in developing value added consumer products from the disregarded finished leather solid waste

2. LITERATURE REVIEW

2.1. Functional and Structure of Hides and Skins

Under this heading, function, chemical structure and anatomic structure of hides and skins are discussed as follow.

2.1.1. *Function of hides and skins*

The hide and skin commonly called as skin is the largest organ in the body and arguably the most complex. Its primary function is as a barrier from environmental factors (protection and cover), such as viruses, bacteria, chemicals and UV radiation (Rao *et al.*, 2002). It prevents rapid loss of water and is involved in thermoregulation (Walawsaka *et al.*, 2000). Furthermore, it resists physical stresses and continually repairs itself. The repair mechanisms vary depending on the type and the depth of injury (Cabeza *et al.*, 1998). Mammalian skin according to Varnali (2002) is an organ fulfilling many physiological functions such as regulation of body temperature, storage of body requirement, protection, elimination of waste products, sensory detection and communication, stress and state of health.

2.1.2. *Chemical components of hide and skin*

Though the relative proportions of these materials vary from skin to skin depending upon the species, age, breed, feeding and other habits of the animals, fresh raw hides or skins consist of water (64%), protein (33%), fatty materials (2%) mineral salts (0.5%) and other (0.5%). Of these, the most important for leather-making is protein. This protein may consist of many types. The important ones are collagen which, on tanning, gives leather and keratin which is the chief constituent of hair, wool, horn and the epidermal structures (Sharphouse, 1983) (Figure 1).

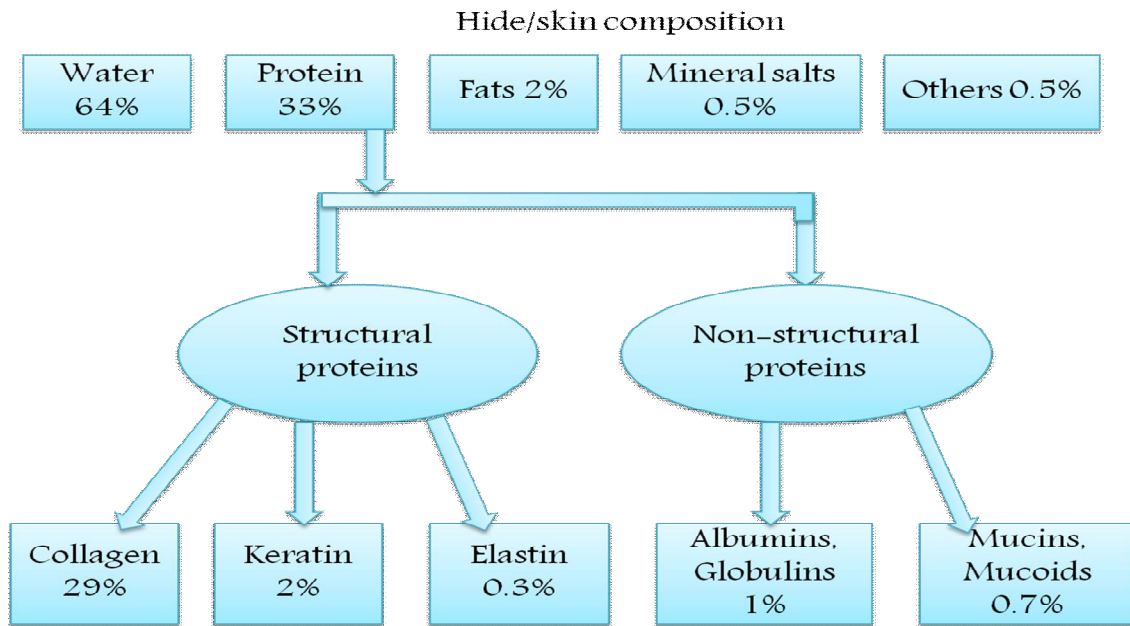


Figure 1: The approximate composition of animal hide/skin adapted from leather technicians hand book (Sharphouse, 1983)

2.1.3. Anatomic structure of hides and skins

Anatomically the hides and skins in their raw state have multilayered structure and mainly consist of three distinct layers, the grain (epidermis) or thin outside layer, a second thicker layer known as the corium or the central (dermal layer) and the inner subcutaneous tissue (hypodermal layer) of adipose tissue or flesh layers (Daniels, 2003).

2.2. Hides and skins production in Ethiopia

The hides and skins production systems in Ethiopia are outlined in the following sub sections;

2.2. 1. Traditional production system

90% and most 70% are slaughtered informally in homesteads for consumption by the owner or in a small community where no formal slaughtering facilities exist. Generally, these informal slaughtering activities are largely beyond the reach of government considerations (USAID, 2013). The rate of traditional production of hides and skins strongly

correlates with the homestead kill rates, one probable reason for informal slaughter as per this report could be due to the widespread dissatisfaction (informal interview) among butchers in Addis Ababa with the present system that the existing abattoirs are not efficient in their services, the slaughter fee is too high and there is improper take-out of meat cuts. In rural as well as urban areas, owing to traditional and religious customs, lack of slaughtering facilities and transportation and scattered settlement of the farmers, when the need for meat arises at different occasions, animals are slaughtered at home (MoARD, 2007).

These traditional production systems consequences in a substantial amount of inferior quality grades and reject outputs. One of the major reasons is that preservations often start after celebrating a feast, when the hides and skins have started putrefaction (Tadesse, 2005). An unacceptable practice such as pecked drying methods of hides/skins, flaying cuts, drying by burning fire underneath are major defects practiced in some remote areas of the country. In particular, smoked hides and skins are graded as rejects as they are partially tanned with chemicals in the smoke and cannot produce good leathers (MoARD, 2007).

2.2.2. Modern production system

2.2.2. 1. Rural slaughter slabs

The livestock slaughter in rural slaughter slabs is done under poorly equipped slaughter points, where the infrastructure is sometimes a slab of concrete, under a shade or using poles for hoisting carcasses. These facilities are normally located in small towns adjacent to butcheries in various trading centers. More than 80 % of such facilities are established in Oromiya (54%) and Amhara Regional State (27%) (Table1). Such facilities are scattered in rural towns and often without adequate supervision. The tools used in these facilities are usually rudimentary and of inferior qualities causing damage to the hides and skins during flaying/slaughter. In many cases running water is not available and hides are not watered off after slaughter and most often, all operations are carried out on the floor.

The general situation, however, varies greatly from region to region depending on the capacity and availability of meat inspection services as well as the directives governing the operation of these facilities at the regional level (MoARD, 2007).

2.2. 2. 2. Municipal slaughter houses (bigger and medium abattoirs)

Cattle hides are recovered by hand from the carcass, causing extensive damage in the form of deep cuts and holes. The Static Flaying Frame (SFF) assists flaying and can produce, at very little cost, a perfectly machine flayed hide without holes or cuts. There are no special requirements, maintenance, nor power needed. The SFF could be introduced to slaughter houses and abattoirs. The greatest appeal of the SFF is that artisans without external supplies can produce it cheaply and locally. These facilities are better attended by local concerned officials, in particular meat inspectors, as there is continuous supervision and inspection of their activities. They are bigger in size and often located in medium to bigger towns. They are also relatively better equipped than rural slabs as far as water provision is considered (MoARD, 2007).

2.2. 2.3. Mechanized abattoirs (export abattoirs)

The hides and skin collection in these mechanized abattoirs is with 100 % recovery rate. The flaying methods in all mechanized abattoirs with the presence of skilled work force and appropriate tools along with the water availability, peri-slaughter damage are almost completely avoided. However, currently the abattoirs are mainly slaughtering lowland sheep as they are cheaper than the highland ones. Many concerned leather technologists have often complained that lowland sheepskins are inferior to the highland sheepskins mainly used for lining leathers. Therefore, although slaughter damage is overcome, this is of little economic benefit to tanners. These skins are still being salted before processing, for the convenience of the tanners (MoARD, 2007).

Table 1: Distribution of slaughtering facilities by regional states

Description Geographic area	Bigger Slaughter Houses(including commercial ones)	Medium Municipal Slaughter House	Rural Slaughter Slabs	Sub Total/ Grand Total
Tigray	4	15	6	25
Afar	-	1	-	1
Amhara	2	10	20	32
Oromiya	9	25	40	74
Somali	-	1	1	2
Benshangul Gumuz	-	-	6	6
S.N.N.P	14	15	-	29
Gambella	N.A	N.A	N.A	-
Harare	-	2	-	2
Addis Ababa	3	-	-	3
Dire dawa	1	-	-	1
Sub Total/Grand	33 (5 commercial)	69	73	175

-NA= no data available

Source: ([MoARD, 2007](#)) as computed from data base of MoARD 2004/2005 and personal communication

2.3. Marketing of hides and skins in Ethiopia

The marketing constraints and structures of hides and skins in Ethiopia are presented in following subheadings.

2.3.1. Constraints of hides and skins marketing in Ethiopia

([ESGPIP, 2009](#)) and ([Ahmed, 2000](#)) outlined the main constraints adversely affecting the production and marketing of skins as:-Shortage of raw material; quality deterioration; inadequate numbers of abattoirs and slaughter slabs; gap between demand and potential supply; and lack of incentive to suppliers motivating them to provide quality raw material and the failure of tanners and traders to implement procurement of raw hides and skins based on quality grades developed by the Quality and Standard Authority of Ethiopia (QSAE) discourages hide and skins suppliers.

2.3.2. Market structure

The marketing of hide and skin starts at the producer/consumer level and passes through a chain of middlemen until it reaches the tanneries (Figure 2). The market chain for raw hides and skins consists of the primary producers/consumers, who are the initial sources (individual meat consumers, rural slaughter slabs, municipal slaughter houses, abattoirs, meat processing plants), agents of traders, collectors, local tanners, regional medium/small traders, regional/Addis Ababa big traders and tanneries. The individual consumers who kill animals in their backyard sell the hides and skins either to agents, collectors, or directly to regional small/medium traders. After preservation by air-drying or wet salting, the hides and skins are passed on to big traders and then to the tanneries. The tanneries can be supplied directly from the slaughter premises, regional big traders or Addis Ababa big traders as well. The tanneries process the hides and skins received from their suppliers either in the green (fresh), air dried or wet salted states to semi-finished or finished stages for both local and export markets (Ahmed, 2000). The market structure for raw hides and skins is illustrated in Figure 2.

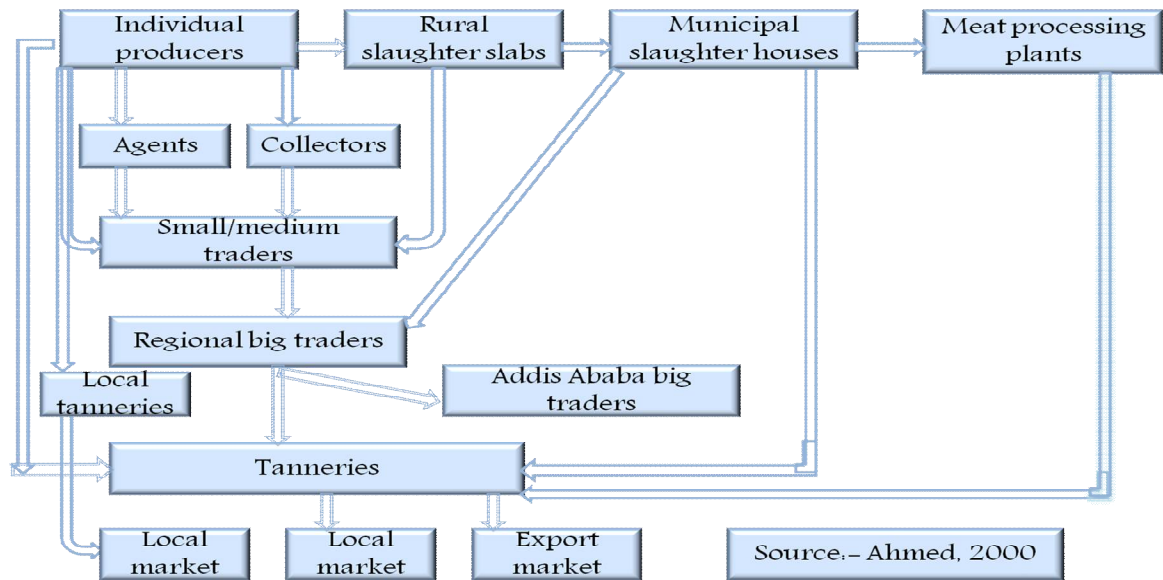


Figure 2: Ethiopian hides and skins market structure flow chart

2.3.4.2.1. Individual household producers

The major producers of hides and skins are individual householders residing in the different Kebeles across Ethiopia. About 90 to 95% of the skin production is derived from urban as well as rural backyard slaughters, while the remaining (5 to 10%) is produced from major urban slaughterhouses and export abattoirs (Ahmed, 2000)(Figure 3).

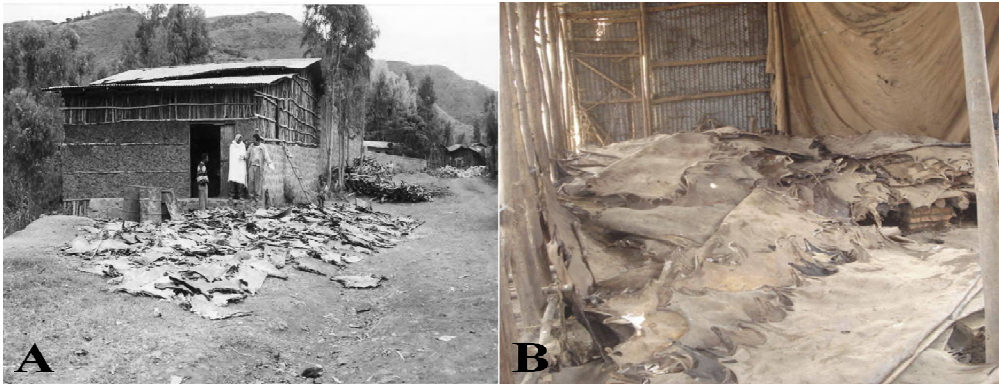


Figure 3: Hides and skins market and preservation

A) Hides and skins market in a rural area of Ethiopia (Photo by I. Leach) Source (FAO, 2009)

B) preserved hides in jimma slaughter house photo taken in 2010

2.2. 4.2.2. Rural and urban slaughter operators

The operators in rural slaughter slabs produce a substantial volume of hides and skins, second to the individual household. These operators use poorly equipped slaughter points, where the infrastructure is sometimes a slab of concrete, under a shade or using poles for hoisting carcasses. These operators are normally located in small towns adjacent to butcheries in various trading centers. The tools used in these facilities are usually rudimentary and of inferior qualities causing damage to the hides and skins during flaying/slaughter. Most often, all operations are carried out on the floor. In municipal slaughtering operation cattle hides are recovered by hand from the carcass, causing extensive damage in the form of deep cuts and holes. Cuts and holes reduce the value of a hide or skin. The difference between a machine-flayed hide, which presents no cuts or holes and a hand-flayed hide, with cuts and holes, can reach 20-30% of the hide's value (USAID, 2013).

2.4. Current situations, opportunities and challenges of Ethiopian leather sector

The current situation, opportunities and challenges of the Ethiopian leather sector is presented as follow.

2.4.1. Current situation of the Ethiopian leather sector

Ethiopian leather industry is one of the top growing economic sectors (MoARD, 2009). The country's leather and leather products industry has therefore reached an advanced stage of development when compared with other countries in the region (UNIDO & MOTI, 2005). In the country there are 28 tanneries, 16 medium and large scale footwear manufacturers, 15 garments and goods factories, 3 gloves factories and 368 Micro and small scale enterprises producing leather products (LIDI, 2013). These operational tanneries in the country have a soaking capacity for 153,650 shoat skins and 9,725 cattle hides per day (UNIDO, 2008). However, these tanneries are not working to their full capacity, for the reasons that the raw materials become available only when meat is needed (during festivals) and are not sustainably supplied to the leather processing industries (Bisrat, 2013). The hides and Skins as being the most valuable export item for the country next to coffee (Ecbp, 2009), with export earnings for the country ranging from US\$ 405 to US\$ 590 million between 1998 and 2004 (Tadesse, 2005).

2.4.2. Opportunities of the Ethiopian leather sector

Raw material availability

The recent livestock population of Ethiopia estimates that the country has about 57.83 million heads of cattle, 28.04 million sheep, 28.61 million goats (CSA, 2016). These huge livestock numbers provide a strong raw material base for the leather and leather products industry (FDRE, 2015). Export commodities of the country are mainly agricultural outputs like coffee, hides and skins, and oil seeds and nuts. As these are the main sources of foreign earnings, they automatically define the country's capacity to import other materials used in manufacturing. Hides and skins as important economic components contribute significant amount to the national economy by providing 14–18% of the

foreign exchange earnings (Bekele and Ayele, 2008) and 41.4% of the GDP (World Bank, 2006).

Hides and skins quality

The Ethiopian cattle hides are well known for their fine grain pattern and good fiber structure and are ideal internationally for making shoe upper. Correspondingly, Ethiopian highlands are estimated to comprise about 70 % of the national sheepskin production that have an international reputation for their unique combination of characteristics i.e. fine quality, thickness, flexibility, and strength and compact texture (UNIDO & MOTI, 2005) and these are given the name “*hair sheep/selale type*”. These sheepskins are excellent raw materials for high quality leather for dresses, gloves, sport gloves and other garments. This unique feature of the Ethiopian sheepskins enables them to fetch higher prices in the international leather market (FDRE, 2015).

Goat skins from the highlands are categorized as “*bati-genuine*” (the international name given for high quality goat skins) and those from the lowlands as “*bati-type*” in the international market. “*Bati-genuine*” is associated with highest quality class goatskins in the world. The particular characteristics of Ethiopian bati-genuine Goatskins are thicker, highly flexible and clean inner surface and are known world-wide for being excellent raw material for producing high quality suede leather (UNIDO and MoTI, 2004a). These skins are excellent for producing high quality leather products (Ahmed, 2000) and are equally acknowledged to be the finest and suitable for suede making for garments and footwear. In fact, the international leather market has coined special names for these two varieties of skins after two local places - *Selallie and Bati*. The sheepskins are referred to as *Selallie Genuine* (now commonly known as Ethiopian Hair Sheep Skin) and the goat skins *Bati Genuine* which are offered premium prices over all others (FDRE, 2015).

Enabling investment environment and incentives

The investment climate is improving, as is demonstrated by the total of 8,271 projects registered with the Ethiopian Investment Commission (formerly the Ethiopian Investment

Authority) with a total capital value of approximately US \$ 10.6 billion in 2003. As a result it is expected that some 960,000 new jobs will be created. A number of important measures, including tax incentives, have been introduced by the Government in order to improve the general business environment and promote an increase of activity within the business community (UNIDO & MOTI, 2005).

In Ethiopia investment incentives are provided with no discrimination between domestic and foreign investors with regard to the provision of incentives (AALF, 2013). According to (the same author), different investment incentives and schemes such as Customs duty exemption; Income tax exemption; Export Incentives; Duty Draw-back Scheme; Voucher Scheme; Bonded Manufacturing Warehouse Scheme: encouraging policy towards Leather garment are being designed.

Market opportunities

The leather and footwear industry of Ethiopia has significant international comparative advantages owing to its huge livestock population which implies to the availability of raw materials, highly disciplined and cheap trainable labor force, availability of big tanneries (soaking capacity), open access to Europe and U.S markets, that has potential to make the industry one of the most competitive industries if the existing local and international market opportunities are exploited and utilized in an efficient and effective manner, however, the reality gives a different picture (CSA, 2007; Birkinsh, 2012).

Institutional support

The Government of Ethiopia (GOE) has taken necessary legislative measures and has created support institutions to provide services required for industrial development. The challenge is to obtain a proper coordination and response from all these institutions. The major actors in the public sector are: The Ministry of Trade and Industry (MoTI), The Ministry of Agriculture and Rural Development (MoARD), The Quality and Standards Authority of Ethiopia (QSAE) the Ethiopian Investment Commission (EIC). For the

manufacturing sector these are: The Ethiopian Tanners, Footwear, and Leather Goods Manufacturers Association (ETFLGMA). For the R&D institutions: The Leather and Leather Products Technology Institute (LLPTI) (newly established). The Government of Ethiopia has established the Leather and Leather Products Technology Institute with principal function is forming the technical capabilities necessary for the improvement of the competitiveness of the LLPI. The activities of the LLPTI are to support the development of the sector by providing training in technical, managerial and marketing areas, direct services to industry as well as by promoting networking between the formal and the informal sector of the LLPI. An important role of the institute is to work closely with institutions such as QSAE (UNIDO & MOTI, 2005).

2.4.3. Challenges of the Ethiopian leather sector

Quality constraints of hides and skins

The production of quality hides and skins is constrained as a result of pre, peri and post slaughter factors (MOARD, 2007; Kahsay *et al.*, 2015). This sector therefore is losing large amount of money due to decline in quality and fall in export price (CSA, 2007). Flaying defects one among the other operational factors are very common and cause significant quality deterioration in Ethiopia because of lack of knowledge and experience of people who perform the job (Mwinyihija, 2010; Kagunyu *et al.*, 2011). Damerech (2014) also confirmed the previous reports mentioning that the major factor affecting the quality of hide and skin is poor hand flaying of farmers, which cause holes and cuts on the hides and skins and consequently resulting in lower price besides rejection by collection centers due to its inferior quality. Coordination failures arise in the raw hides and skins production and supply due to the strategic complementarities among various facets of production, distribution and trade are also mentioned as major demerit in the sector (Altenburg, 2010).

Effect of pre-slaughter factors on hides and skins quality

Quality deterioration in hides and skins can arise from the time an animal is born until the leather processing is completed (FAO, 2009). The quality of hides and skins is influenced

by factors throughout the production chain including animal husbandry practices and disease management. Most hide and skin are affected by pre slaughter defects accumulating during the life of the animal. Evidence indicates that sizable volumes of the raw material in the value chain substantially deteriorate due to animal husbandry factors that could be: - poor/inconsistent feed availability; Lack of efficient disease control and extension services; Absence of organized marketing system for livestock (MoA and ILRI, 2013).

The pre slaughter defects account for about 65 percent of the total defects which downgrade the quality of hides and skins in Ethiopia and these defects contribute to a huge national economic loss (MOARD, 2007).

Breed and climatic effects

Breed- Desirable or undesirable characteristics of hides and skins can be attributed to certain breeds. Cattle hides and sheepskins show more breed characteristics than goats and calf skins (NPC, 1981; Jean, 1992). E.g. bovine hides from North America and Europe normally yields flat hides of over 40 sq.ft in area. But the typical bovine hide from South America may yield a flat hide of only about 25 sq.ft areas and a Zebu cross-breed from Africa often provides a hide below 25 sq.ft Ovine skins such as that of wool bearing merino sheep in Australia can yield a larger skin often above 7 sq.ft area but will not be readily acceptable to the tanners due to the ribbings apparent on them (FAO, 1986).

Fine wool sheep breeds, such as Merino, produce skins that are thin, have pinhole grain and are extremely ribby. These skins produce only the cheapest type of leather. The skins of hairy sheep have a high proportion of fat in the upper part of the corium and on the flesh side of the skin. Skins from goats in the highlands are poor in substance, and open grained. The small size of skin yielded sheep of tropical and mountain area origin is not considered a drawback because of the skin's superior quality of high tensile strength, compact fiber structure and excellent grain. But small size skins that are downgraded due to poor quality are unwanted by tanneries (ESGPIP, 2009).

The breed of animal is of course important, the best hides for leather purposes usually coming from those animals which are bred for beef production, i.e. those which develop carcasses with a high proportion of lean meat in a reasonably short time under conditions of economic feeding. These hides, available from all the beef-producing countries of the world, are very tough and firm, fairly uniform in thickness and having a "square" form, since breeding programs are designed to produce a body conformation with minimal amounts of tissue in the neck, leg and belly regions ([Calcutta et al., 2008](#)).

Climate- The climate on which an animal is raised has an effect on substance of the skin and on the grain of the leather. Animals raised in warm climate have a short hair and leather produced has superior substance, smoother and finer grain patterns, whereas animal grown in cooler climate or higher altitude grow longer wool or hair, and the leather made from these hides/skins are of poorer substance and coarser grain patterns. These effects of climate, especially the effects on substance is more pronounced on sheep and goat skins than on cattle hides ([Tekle 2009](#); [Teklay, 2010](#)).

Poor nutrition- Poor nutrition causes an animal to be smaller, the skin to be thinner, poorer in substance and producing leather which lacks elasticity ([ESGPIP, 2009](#)). Poor nutrition predisposes the skin to low febrile condition where the weight and final quality of leather is affected irrespective of the subsequent efforts of other condition being optimized. The resulting condition is referred to as "papery leather" which is a common problem experienced in the areas where poor or unavailability of pastures and forbs is eminent. Hence animals in such areas are of dilapidated condition affecting subsequently the final quality of leather ([Mwinyihija, 2006](#)).



Figure 4: Underfed cow (photo taken during field visit in 2010 in Gondar & Tigray area)

Emaciation is the thinness and friability of hides and skins derived from animals suffering from prolonged and bitter starvation, leathers which are produced from such hides and skins are noted for their dryness and flabbiness (Figure 4). Cockles which are coarse wrinkles on shoulder portions of hides' increase considerably when animals are under fed. Diet plays an important role in the health of the animals and also in the quality of the raw material (ESGPIP 2009). Cattle that are undernourished produce thin hides. On the other hand, fat animals can cause too much fat content in the hide, which prevents curing agents from penetrating the hide. Intermediate body-conditioned animals produce the best quality hides (Wesley and Wright, 2002).

Age and sex- The skins from male goats and sheep will be heavy with a coarse grain. Female skins will have better tensile strength. The skin structure of young animals tends to be fine, compact and have tight grain patterns. As animals grow older, the grain surface becomes tougher and coarser grained. Also with age animals accumulate more scars from brands, diseases, parasites, scratches and other injuries (ESGPIP, 2009). In sheepskins the main difference is that the female skins have finer grains and always lighter but with greater tensile strength than the male one (Jean, 1992).

Mechanical damage

Mechanical damage is primarily the problem on cattle skin that is related to farming and handling practices. Most noticeable defects on hides and skins like brand marks, wounds (scars) and bruises scratches and horn rakes, are caused by mechanical means (Yacob, 2013).

Branding- Branding is widespread and indiscriminate practice of cattle with hot irons and it causes high losses in the hide and leather industry (Mohammad *et al.*, 2002). This practice is used to identify animals especially cattle due to the prevalence of cattle rustling. Unfortunately most of it is done in the areas of hides, like on the back and rumps, which have high value and spoils leather like wounds. 10-40 percent of the value of the hide is lost by the unsightly and irreparable damage caused by branding (Ahmed *et al.*, 2016). Defects on raw hides and skins are important in the domestic as well as in the export marketing of hides and skins, because they persist throughout the course of tanning and therefore affect the production and quality of marketed semi-processed and finished leather goods (Nyamrunda, 2007).

Branding costs the leather industry large amounts of money due to the wasted portions of the hides (Alemnesh, 2015). However, the loss of value is dependent on the placement of the brand (Patterson and Loren, 2000). Pastoralists brand their livestock with hot irons for identification (as livestock rustling is a common practice among pastoral communities) and as cure for various diseases. Unfortunately, this is done indiscriminately and branding marks are made on the larger part of the body destroying the hide (Wayua and Kagunyu, 2012) (Figure 5).



Figure 5: Brand marks (Photo taken during field visit in 2010 around raya-Tigray and shashemene –Oromia)

Bruises and wounds

Bruises and wound commonly referred to as pre-slaughter defects. Most bruises and wounds are inflicted on animals due to severe beating especially for draught animals and during transportation on trucks for slaughter (Abainesh, 2014). Although wounds could be healed, they leave a permanent damage (scar) on hides and skins which remain visible in the final leather (Mwinyihija, 2010) (Figure 6).



Figure 6: Permanent damage due to wounds on the hide (Photo taken during field visit in 2010-raya)

Scratches and horn rakes

Scratches- Scratches are amongst the most common mechanical damages found on both hide and skins in Africa including Ethiopia and causing permanent marks (Mohammad *et al.*, 2002). Cause considerable loss of tear strength especially on skin, the quality also degraded as the tanners try to obscure the faults on the grains by embossing or printing (Jabbar *et al.*, 2002). Scratches are very common types of lesion caused mechanically by thorns, barbered wires and horns (Yacob, 2013).

Horn rakes- Horn rakes are a general problem as animal husbandry practices in the countries discourage dehorning and therefore cattle injure the hide mostly in crushes in fight or during transportation. In some case the damage is a quite serious as the wound is generally deep (Devassy and Argaw, 1989, Jabbar *et al.*; 2002) (Figure 7).



Figure 7: Scratch marks (Photo taken during field visit in 2010-Jimma)

Defects due to diseases

Many diseases can affect the quality of hide and skins. The commonly noticed ones can be (viral, fungal, and parasitic).

Viral

Lumpy Skin Disease- Lumpy Skin Disease is highly infectious skin disease of cattle caused by a herpes virus and is characterized by the sudden appearance of nodules on all parts of the skin. During the course of the disease, the affected portion of the skin becomes hard and dry, and separates from the surrounding normal tissue (FAO, 1986).

Smallpox - At first small red spots appears on the more tender parts of the skin such as the inner thigh, the abdomen and the sides. The red spots develop in to blisters from pin point to pea sized and turn in to sores. The animal is urged to scratches or rubs the sores on rough objects and secondary infection may develop. Mostly sheep and goats suffer from the small pox. Grain surface of skins damaged by the smallpox hollow resembling tiny dots (NPC, 1981).

Rinder-Pest- Rinder-Pest is an infectious disease of animals; the lesion on cattle may be in the form of malignant pustules (Jean, 1992). Hides of rinder-pest affected animals are thin and poor in quality (NPC, 1981).

Fungal

Ring Worm- is a fungus infection attacking the hair and its roots. It appears on the hair side in the form of circular patches varying from 0.5 to 4 cm in diameter. The patches are usually covered with scabby matters and are partly or completely bald. The scars are clearly visible to the tanner being shiny and circular in appearance (NPC, 1981).

Parasitic

In Ethiopia external parasites damage livestock skins, sheepskins by cockle an irritation caused by sheep ked (*melophagus ovis*) and sheep louse (*bovicola ovis*), goat skins by sarcoptic mange caused by mites (*sarcoptic scabies*) some are damaged during slaughter while relatively few are spoiled during preservation (FAO, 2009). One of the major caus-

es of down grading of hides and skins is attributed to tick-mark (Jabbar *et al*; 2002). A certain amount of the local damage occurs where the tick attaches itself by inserting the jaws and hypostome, the area become leather scarred and loose in texture at the site of damage (Kew, 1952). Ixodidae causes damage in skins (Damms, 1994). The damage caused by the mites was restricted to the epidermis and upper dermis causing scabs (Venkatesan *et al*; 1989). Demodex, Sarcotes and Corioptes mange cause a high rate of damage (Buchner *et al*; 1994). Bovine dermodecrosis and bacteria associated with it were reported in Sudan (Ibrahim, 1989).

Lice- Lesions made by lice, scar the grain surface of hide by the inflammation set up where the parasite has attached itself (Knew, 1952). Adult and nymph stages make inflamed area on skin, they were found on hide of slaughtered steers (Waston *et al.*, 1997). A sheep pelt defect was caused by *Bovicola ovis*, a sheep biting louse (Health *et al.*, 1996).

Grub/warble fly- this damage is usually seen along either side of backbone of the animal. It makes series of holes through the hide (Hamdin, 2006). The damage by holes in the hides of the animals has been the major economic loss that cattle grubs cause to the leather industry (Batte, 1972; Everett *et al.*, 1977).

Arthropods, Helminthes, and Protozoa- Dermatoses of cattle hides caused by arthropods, helminthes and protozoa have a severe effect on quality of leather and hide produced (Soulsby, 1977; Matthes and Hrep, 1987).The authors review the dermestids that are known to damage in warehouse or in ships is particular importance since holes make them useless and nullity the commercial value of this important export item. The injurious species was identified as dermestes maculates (Grillo *et al.*, 1980).

Mycotic- Mycotic dermatitis of cattle, or bovine streptothricosis it responsible for severe damage to the hides and considerable economics loss to the skins (Buxton and Frster, 1977). There is a skin defect known as rash associated with lice and mycotic dermatitis (Hamdin, 2006). (Habb *et al.*, 1995) reported that the visual examination of veal calves at

Zurich abattoir revealed the presence of ringworm defects to the leather. To prevent fungal growth on stored wet blue pelt fungicidal Busan72 was used (Cooper and Galloway, 1973).

Effect of peri- Slaughtering practices and improper facilities

Defects which occur at the moment of slaughtering or during and following flaying are like flaying defects (flay cuts, gouge marks, scores and corduroy), rubbed or dragged grain, bruises, poor Pattern, improper bleeding, Filth stains (fouling with blood, stomach contents and dung) (Teklay, 2010).

Flaying and flay cuts

Flaying is the process of removing the skin from the animal normally carried out by the butcher and the methods used generally give first priority to producing a good quality carcass if the animal is to be eaten. The value of the carcass is often ten times the value of the hide and this ratio will govern the degree of care given in flaying to the hide and to the carcass. The best flayed hides are a by-product of a well-developed meat industry (Sharphouse, 1983).

These flaying defects reduce considerably the value of hide or skin. These damages can all be avoided since they are caused by careless flaying, such as flaying by inexperienced people or use of poor or improper tools.

Flay cuts or butcher cuts are knife cuts and holes that pierce or go half way or more through the hide. Gouge marks are knife damage on the flesh side of the hide in which small portions of the corium are scooped out. Scores are knife cuts those don't penetrate half way through the hide but are deep enough to cause damage in the finished leather. "corduroy" is a series of fine parallel scores. This damage is caused by the careless use of the knife or by the use of unsuitable knives. Flay cuts constitute the most serious mechanical defects on hides and skins. Lack of proper tools like the rounded flaying

knives, lack of flaying skills and carelessness lead to loss of quality or outright rejection of raw hides and skins (Mohammad *et al.*, 2002).

Flaying damage can largely be avoided by using sharp knife which has curved convex edges with a rounded tip. This could be achieved by keeping the flat side of the knife blade against that part of the skin already removed and by giving sufficient care and time to the job, long steady strokes should be used in skinning because short strokes can cause corduroying (NPC, 1981) (Figure. 8).

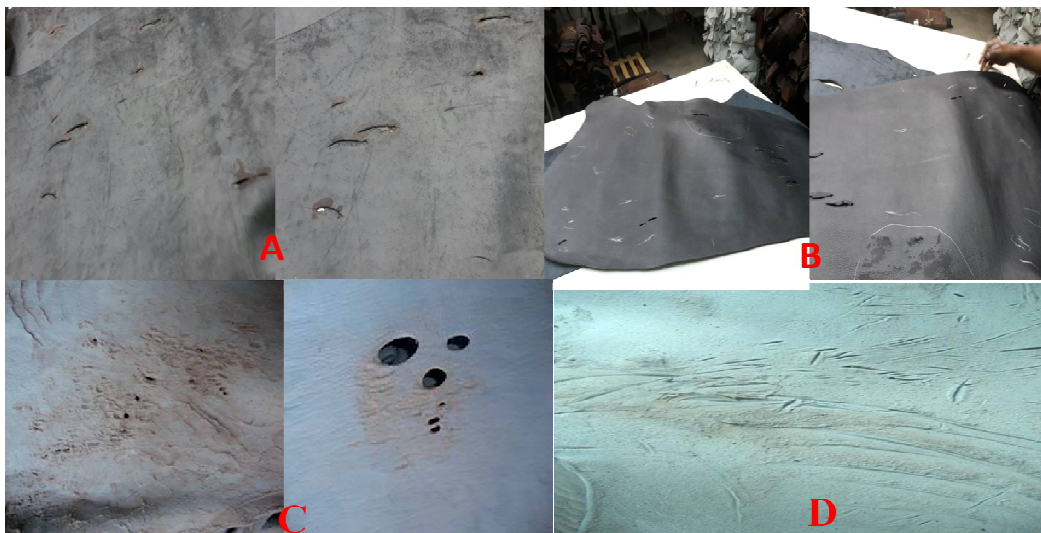


Figure 8: Defects of hides and skins during and after processing
A. Flay cut of tanned hide at peacock shoe factory from flesh side; B. Flay cut of tanned hide at peacock shoe factory from grain side (during study period); C. Flay cuts or scores; D. many knife incisions; source (Kahsay *et al.* 2015)

Rubbed grain

This damage is produced by dragging the un flayed carcass over rough and uneven ground and can even be caused by rough concrete. The grain is generally rubbed off or ‘frizzed’ and is a definite cause of loss in value to the tanner (Jabbar *et al.*; 2002). Preventative measures can be adopted in the field or slaughterhouses. In most cases poor flaying, lack of skills and absence of for instance hide pullers in modern abattoirs lead to production of low quality hides and skins (Mohammad *et al.*, 2002).

Bad pattern

This is caused by indiscriminate ripping. ‘Ripping’ being the initial opening cuts down the centre of the belly and the four legs. The correct method of ripping ensures a uniform pattern, with bellies of equal width, well opened shanks and dewlap, a round butt and adequate tails (Mohammad *et al.*, 2002). A regular pattern is very important to the tannery because it enable them to get the best cuts and the most useful part of the raw material (Terefe, 2004). If the hide or skin has been inexpertly flayed, it may not be symmetrical about the backbone. This may hinder the maximum use of its various parts, since these have differing thicknesses (ILO, 1981) (Figure 9).

Poor pattern that is asymmetric shape of the hide and skin is considered as a defect, as far as cuts or scores are concerned and this is commonly caused by incorrect line of ripping (Terefe, 2004). The bleeding cuts must be directly at the center of the throat. If the legs are not ripped and open properly, the proportion of the hide in the shoulder and belly section is not proper. Thus belly hide that should have been part of the belly may be on the shoulder area. “V” cut in the button either side of the tail downgrades the hide, according to the degree of damage to the pattern and it is very important that the bleeding cut, the belly cut, and the leg cut are made as straight (Selamawit, 2015).

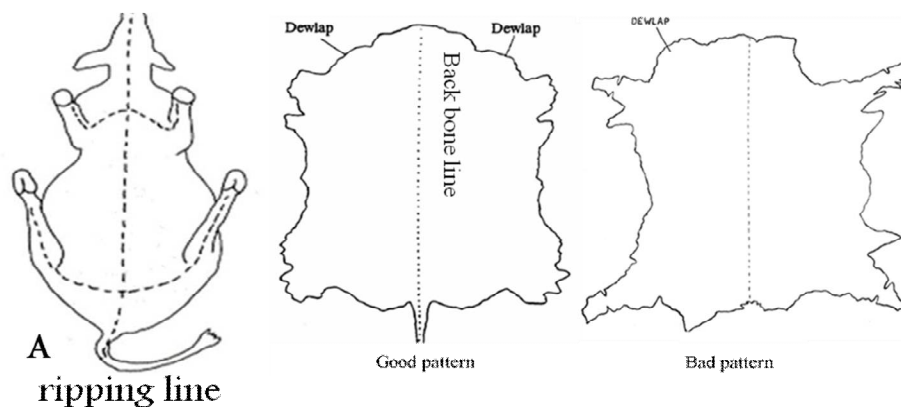


Figure 9: Skins pattern A. Ripping line. B. good pattern; C. bad pattern; Source (FAO, 1955)

Slaughtering facilities

Hides and skins coming to the tanning industry generally comes from two different sources, controlled slaughter house in designed establishment and slaughter as well as death elsewhere. The later includes significant quantities of hides and skins sometimes available from special festivals (Leach and Ijaz, 1993). Hides and skins from designed slaughtering operations may come from any one of a range of places including backyard activities, shambles (meat market), slaughter slabs, slaughter houses, and abattoirs. The facilities available at these establishments vary tremendously. At worst they may consist of no more than small space and a few small items of equipments such as knives. At best they may consist of purpose built structures with all main services (electricity, steam water, effluent treatment etc) and highly trained staff. Irrespective of the size of the establishment, the slaughter facilities should conform to certain minimum standard places (FAO, 1995).

Slaughtering equipment

Lairage fitted slaughter houses would generally contain a large assortment of equipment and plant to facilitate slaughtering operations. The basically required equipments according to (FAO, 1995) are:-1. *Protective clothing*:-boots, dust coat or overalls, hat, chain, mail gloves & scabbard for knives. These items are required to keep the staff clean, safe and minimize contamination of the products and provide safety. 2. *Ripping knife*: - a sharp pointed knife with straight blade about 150 mm long (Figure 10) should be used for cutting in to hides and skins and inserting ripping lines. It may also be used for bleeding animals. 3. *Flaying knife*:-a blunt tipped knife with a curved blade of about 150 mm long (Figure 10 A) used for cutting hides and skins off carcasses and fleshing. 4. *Mechanical hoist*: - a lifting device such as pulley or block and tackle (safety tested for at least one ton) capable of lifting carcasses to a point 3.5m above the floor level. A hoist helps in bleeding, flaying and butchery operations (Figure 10 C&D). 5. *Miscellaneous items*:-rope to restrain animals during slaughter, string to tie guts, a bucket to collect blood and carry water, and a wheel barrow to transport materials.

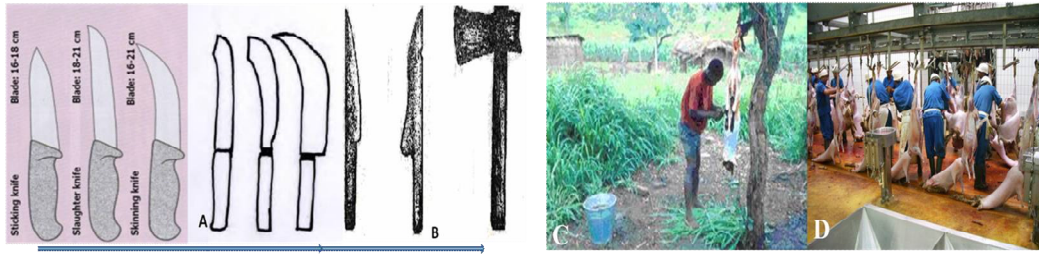


Figure 10: Flaying knives & hoists
 A) Proper ripping (FAO 2008) and flaying knives (Tekle, 2008); B) improper knives used in flaying; (Tekle, 2008). C) Traditional hoist; (FAO 2007); D) Modern hoist (Nippon and ProAnd 2009)

Slaughtering and flaying techniques

Good slaughtering techniques ensure proper restraint of animals before and during slaughter to limit struggling and bruising during the slaughter process. It also ensures proper bleeding that leads to better quality of hides and skins. Good flaying techniques involve use of proper flaying tools e.g. flaying knives which minimize defects arising from use of crude tools and kitchen knives. It also entails making of straight and accurate ripping lines resulting to good pattern (Elliot, 1985). Good flaying techniques also minimize use of tools and encourage tube flaying to minimize defects. Hides and skins produced in the pastoral areas is of low quality due to poor slaughter methods, poor flaying methods and poor curing methods among other short comings in the value chain. Pastoralists use sun drying methods of curing hides and skins leading to poor quality leather (Foxwell, 1999).

Effect of post-slaughter factors on hide and skin quality

The more serious damages encountered in hides and skins, in Ethiopia or other countries occur after killing the animals. These damages may be attributed to improper curing, handling the stock or to thorough carelessness and indifference in the work, some of such defects are (Grain crack and stretch marks, Bacterial damage, Pest infestation damage, Mechanical damage (flesh left over), Damage during curing, Storage and transportation) (NPC, 1981)

Grain crack and stretch marks

Grain crack- Hammer flaying is sometimes used. The hammer is round-nosed base or wooden mullet. This method produces flayed hides without the common flaying defects-cuts, scores, etc. but too heavy blows on the thin skins can cause breakage of the fibers and cracks in the grain surface. In case of small ruminants like calves, sheep, goats punching with fist or elbow is preferable method of removing the skin (NPC, 1981). Grain crack caused by dry in crumpled condition and by multi folding causes grain crack or any pressure and stain, combined with the low moisture content will in this trouble some damage folding and unfolding when the hides are dry will always be a danger and cracks are very frequently caused in this manner (Jabbar *et al.*, 2002).

Stretch marks-This defect results from too much tension on the skin at the time of flaying, drying or during the leather manufacturing process. Sheepskins are particularly susceptible to stretch marks. These grain layers split open as it can't withstand as much strain as the under laying collagen fibers. The skins are pulled or punched too strenuously (NPC, 1981). The leather produced from over stretched materials will have poor strength and fiber structure (FAO, 1986).

Bacterial damage

Green hide/skin that contains large quantities of proteins and moisture produces a favorable environment for the development of various micro-organisms (Lukin, 1967). All hides and skins carry great number of germs, while the hide is on the live animal, these germs unless there are very exceptional circumstances, don't damage the hide, and this is the result of the protective action of the hair and the horny nature of the epidermis. This protection is also due to the natural defense of the live animal. After death, these natural defenses no longer operate, hence under favorable conditions of temperature and moisture, bacterial multiplication and penetration in to the skin start. Enzymes (especially secreted by the bacteria) breakdown first the inter-fibrillary material i.e. soluble proteins, sebaceous and sweat glands and later the fiber components themselves, i.e. hide sub-

stance. As a rule, warmth and moisture favor a multiplication of bacteria, while on the contrary cold and dryness hinder it (NPC, 1981).

Generally bacteria require moisture and warmth for active growth but large differences may occur in their requirements. According to their air requirement they can be aerobes (those which require oxygen) and anaerobes (those which remain in dormant state, in dirt or excrement for a long time which can't multiply in the presence of air). These cause putrefactive change in the hide substance (NPC, 1981).

Putrefaction (Figure 11) is the result of bacterial growth which promptly starts once the animal is dead especially on the exposed flesh side of the flayed, unless it is properly cured. Often the first sign besides smell is hair slip which is evidence by spots where the hair is loose and can be easily rubbed off. Hair slip is always an indication that bacterial action is well started and will rot the hide if not checked promptly. Hair slip is accompanied by a dull grain, sensitive condition of the grain, so that the surface to rub away during normal processing. Slight rubbing gives "dull grain" and finishing is likely to be blotchy. Putrefaction causes, also, the general structure of the skin to be come loose and flabby. Bacteria can grow at any time before tanning. The Ph of these skins being either neutral or alkaline. When the skin is flayed off, soaked, limed, de-limed or batted, germs are very active (NPC, 1981).



Figure 11: Putrefaction damage: (Picture taken at colba tannery during the study period in February, 2018).

Pest infestation damage

Dirt cars or trucks and none cleaned store can become infested with pests which can do immeasurable damage to hides and skins (NPC, 1981; Jean, 1992).

Rodents- Even though their damage to hides and skins is not excessive, mites and rats are commonly seen. Nevertheless persistent attacks by gnawing rodents can reduce good hides and skins to an inferior quality. Precaution against this damage would include keeping stores clean, periodical rotation of stocks, and use of poison, traps and cats. Another objectionable contamination in this case is the defilement of the stock by rats, bats, and birds manure which does not really damage the hides and skins but they spoil the appearance of the stock (NPC, 1981).

Insect damage- By far the most serious damage to which hides and skins especially the bird ones, are exposed during storage and transport is that done by insects. Among the most common damages by insects are by (roaches, dermestes beetles, flies, moth, white ants) (NPC, 1981).

Roaches- Very little damage can be attributed to the common roaches but occasionally a superficial gnawing effect is seen where roaches have attacked the hide or skin. Roaches can cause damage to leather, also, if it contains oil or grease (Jean, 1992).

Dermestes beetles-Those of the beetle family are the most destructive of the insects damaging hides and skins. Dermestes, do more damage to stock than all other pests combined. It is the larvae of the *Dermestes maculate* (vulpinus) and *Dermestes lardarius* and not the beetle itself that cause the most damage. These dermestes beetles are 6 to 9 mm in length and they may be dark brown or black in color. They lay their eggs on hides and skins generally increase on fold and fatty parts of the flesh side (Jean, 1992).

The larvae of these dermestes caused damage on the flesh side of the skin which devours the dermis, thus reducing the strength of the skin and altering the regularity of its thick-

ness. Skins infested in this way are frequently perforated. Moreover, in certain cases the dermestids can cause damage on the grain side of the skin, and even holes (ES, 2008). The larvae normally hatch out after three to twelve days period depending on the temperature and humidity. The larvae grow rapidly to about 13 mm in length and are brown and hairy in appearance, hence the term “woolly bear” is used by the trade. Before becoming fully grown the larvae molt six to seven times and evidence of this can very often be seen in any heavily infested hide. The damage is caused by the extremely ravenous appetite of the larvae. They first destroy the hair and then the grain, then burrows in to the hide making hollowed out space and perforation (Jean, 1992).

Flies- Numerous fly pests are attracted to hides and skins because of the presence of stale odors, blood and manure. Flies don't damage the hides and skins but, are annoying around hide cellars and tanneries because they bite and pester workers (Jean, 1992).

Moth- Various species of moth may be associated with dried skins and furs. The larvae of moth may cause considerable damage to the hair and grain surface. In serious cases numerous channels were found in the grain layer. Holes were found in sheepskins in the wool, which extended through the leather (Jean, 1992).

White ants-These can cause considerable damage forming their characteristic “lanes” throughout the bottom hides and gradually creep up through the pile. In less than two or three months, white ants can totally destroy at least 15 cm of the lowest part of the pile. Raw air dried stocks are sometimes affected (Jean, 1992).

Mechanical damage (flesh left over)

These mechanical damages (flesh leftovers) can be improper *after cleaning* and *trimming* defects:-

After cleaning- After cleaning is the operation of removing (trimming off) the fatty tissue and meat which is left over attached to hides/skins after flaying (Figure 12). Good flaying

should not need this cleaning, but many hides and skins do have adhered fat and meat (particularly around the tail area) and should be removed before curing to avoid some defects (NPC, 1981).



Fleshing beam

Fleshing using a fleshing knife

Figure 12: Fleshing instruments (ESGPIP, 2009)

During air drying, the grease is absorbed by the fibrous tissues on the corium and is most difficult to remove in leather manufacture causing greasy stains which do not take the dye and will show up on the finished. During salt curing, the fatty tissue and meat obstruct salt penetration and the curing may be delayed sufficiently to permit local putrefaction (NPC, 1981). The after cleaning should be applied only when necessary for the risk of gauging, scoring and cutting is very great. The cleaning of the flesh should be done on a flat smooth table (not when the hide is suspended in frames) with a very sharp and curve-edged knife. Care should be taken not to flesh the hide too closely, it is better to leave some superfluous tissue on the hide rather than to damage the flesh side by trying to remove every small piece (NPC, 1981).

Trimming- Properly cleaned hides/skins must be trimmed before curing. Dewclaws, tendons (sinews), cartilage, horns, skull bones and ears are usually removed on the slaughtering floor. If they are not, these and other parts such as switches, udders, tail bones, snouts, lips, cut heads, hammer holes and cuts shanks should be trimmed off the hide or skin before it is cured. These extraneous tissues will not make the leather and can be used to the best advantage before the hide is cured or put trough tannery process. If left on the hide these materials may prevent parts of the hide from receiving adequate amount of salt

in the curing operation. The “heel piece” or cartilage can damage the tannery machinery (Jean, 1992).

Damage during curing, storage, packing and transportation

These defects caused at the post slaughter include preservation, storage, packing and transportation damages and are presented as follow.

Preservations

Preservation is the name given to a variety of procedures, which can be applied to hides and skins in order to reduce, or stop spoilage (putrefaction). Preservation can only maintain quality. It follows that a bad preservation will allow deterioration of all a skin, irrespective of its original quality (Leach, 1995). Preservation is accomplished either by destroying active bacteria, by preventing bacterial activity or by preventing bacterial contamination. During preservation it is essential to avoid from usage of toxic materials as these materials are very dangerous for environment due to their chemical nature (Riga, 2015).

Raw hides and skin are associated in most occasions with aerobic and facultative anaerobic organisms. Different components of skin harbor large number of microorganism especially bacteria, depending on the body location and amount of skin moisture, the number of bacteria on the skin surface may range from only about 1000 organisms per square centimeter. The bacteria in the fresh skin are predominantly gram positive Micrococcus and Bacilli. But during storage skin harbor mainly gram negative Entero bacteriaeae and Alcaligens. Bacteria, molds and yeast can be isolated from raw skins and finished leather. The skin flora is predominantly aerobic and hemolytic organism like Staphylococcus pyogens, Staphylococcus aureus, Hemolytic sarcinacutis, Bacillus, Anthracoides, Bacillus mesenteries and Torula sp. (Samba *et al.*, 1977).

Preservation methods

Most hides and skins must be preserved to protect them from decay during storage and transport until they are converted into leather. Preservation should ideally begin immediately after slaughter and should never be delayed overnight. The most common methods of preservation are drying, salting, brining or the use of other chemicals (Table 2). Refrigeration, freezing and mechanical drying methods can also be used, but they are expensive and tend to be reserved for more valuable skins in particular situations (FAO, 2009). Flayed hides and skins are subject to rapid putrefaction particularly in hot climate (NPC, 1981). The water held in the tissues of hides and skins immediately after flaying amounts to about 60 percent of the total green weight. Removal of the greater of this can be brought about either by simply air drying or treatment with salt. Dehydration effectively reduces the risk of tissue break down when it is effectively performed because the residual water content is insufficient to sustain the preferred condition for bacteria or enzyme activity (FAO, 1986).

Table 2: Common methods of preservation of hides and skins

Drying	<i>Sun drying:</i> in direct sunlight and usually on the ground. <i>Frame drying:</i> in a large frame. <i>Shade drying:</i> in a roofed shelter and usually in a frame and is the recommended way. <i>Suspension drying:</i> in a large frame, over a pole or even on a porous wall.
Salting	<i>Pit salting:</i> using an excess of salt and preventing any loss of moisture by retention in a pit. <i>Stack/wet salting:</i> using an excess of salt and allowing excess moisture to drain away. <i>Dry salting:</i> using an excess of salt followed by drying.
Brining	<i>Static/pit brining:</i> by immersion in saturated brine with little or no agitation. <i>Raceway brining:</i> by immersion in saturated brine with considerable agitation.
Chemical	Chemicals (other than salt) provide preservation lasting days, weeks, months or years
Source:- (FAO, 2009)	

With the exception of sun drying, which has no real merits, most of the preservation procedures presented in (Table 2) can be used successfully almost everywhere. The final choice will depend on the availability of materials, chemicals and suitably trained staff and on the requirements of the customer. In practice, the most useful methods tend to be suspension drying on a frame in the shade (Figure 13) and stack salting (FAO, 2009).

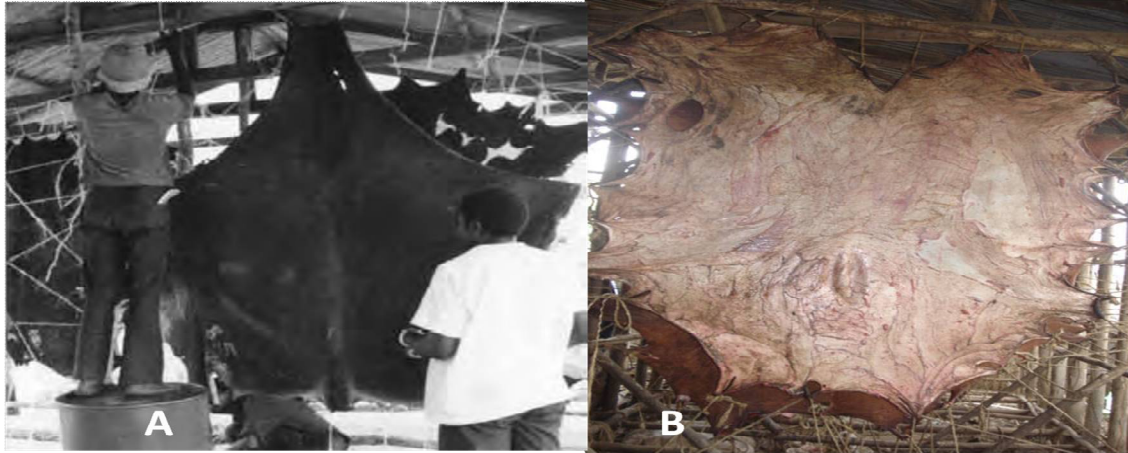


Figure 13: Suspension drying of hides Suspension drying of large cattle hides; A) (FAO 2009); B) photo at field visit in Jima slaughter house in 2010

Preservation is most effective when it is carried out quickly and thoroughly. Cattle hides, for example, should be dried to a moisture content of less than 15 percent within three days. Sheep and goat skins should be dried to a moisture content of less than 15 percent within one day. If drying takes longer, bacterial damage is likely to occur. Similarly, hides and skins preserved by salting or brining should be saturated with salt – sodium chloride – within one day. Properly preserved hides and skins should be free of post-slaughter defects related to preservation processes, such as bacterial decay, contamination and adulteration. Dried hides and skins should be flat, smooth and protected against insect damage during long term storage. Salted and brined hides and skins may be rolled, stacked or bagged to facilitate storage and transport. Preserved hides and skins may be stored for up to a year while waiting further processing (FAO, 2009).

Storage defects

To produce high quality hides and skins, storage conditions are as important as proper preparation and preservation. In Ethiopia, a large percentage of skins are damaged during storage and transportation, especially during the rainy season. Problems that occur in rural drying sheds are the major source of damage and loss of skins. Rural drying sheds are highly infested with skin damaging insects, have leaky roofs, and do not use slatted platforms. Skins become damaged and many are totally rejected. While the main portion of insect damage happens in rural drying sheds, insect damage also occurs in tanneries and warehouses of large traders (ESGPIP, 2009). Some of the common factors concerned with unwanted conditions responsible for stale hide substance defects during storage of salt cured stock are temperature, time, humidity, air circulation, drainage, length of hair, pressure in pack, and amount, size and re-use of salt (Jean, 1992). The preserved hides and skins may be collected and transported from remote parts of a country (Figure 14) and undergo grading, sorting and accumulation into large lots pending storage, sale and delivery. Storage usually involves costs such as rent, depreciation and interest charges (FAO, 2009).



Figure 14: Transport of hides and skins A) Dried hides from source to central collection in Ethiopia (FAO, 2009); B) wet salted skins transported from Mekelle to AA photo taken during field visit in 2010

Transportation damage

Careless handling of hides and skins at the time of transportation can result in damage of the leather. Among the damages include mechanical and delayed transit damages, excess heat and cold damages, sun and rain damages or water caused defects (Teklay, 2010).

Mechanical and delayed transit damages

In developing countries many forms of transport are used to convey hides and skins to more important markets. Motor lorry, bullock cart, and animal transport, bulls, camels and donkeys are used. Hides and skins are often loaded singly on to lorry transport and on tied in to loose bundles. Consequently any movement will make the surface rub together and cause considerable damage, especially to the grain, folded edges and corners. A lorry journey for instance of 400-500 km over rough road can result in deep abrasions in the goods and this cause irreparable damage, which could be reduced considerably by tighter baling and improved packing facilities. Cars and trucks should be cleaned to all loose objects and materials before being used for hides and skins (NPC, 1981). Nails, bolts, or other objects which can tear or puncture the stock cause damage in the leather. Metallic salts and rust picked up from car or truck will cause metallic stains. Such materials as metallic filings and coarse sand can become imbedded in the stock. These can cause grain abrasion and do much damage to the machinery at the tannery (Jean, 1992).

Excess heat and cold damages- Exposure of hides and skins to either heat or cold for prolonged time can result in dehydration of the stock. Later in the soaking operation, rewetting becomes difficult and result hard spots in the leather. These spots have raspy fibers because the stock will not tan properly (Jean, 1992).

Sun and rain damages- Sun shining directly on the hides and skins can cause over dehydration and hide separation. It causes the natural grease to migrate and coat the fibers of the stock (Jean, 1992).

Rain or water caused defects- Rain coming in contact with cured stock through leaking cars' or trucks' roofs can wash out salt and allow bacteria to grain entrance. Grain damages result and in extreme cases, areas become completely rotten (Jean, 1992). The importance of protecting against wetting by the rain, foods and contamination by sea water during shipment shouldn't be over emphasized. Hides or skins that has been cured or stored, if water or excess moisture accidentally comes in contact with, it result with defects such as grain damages and rotten spots, Water and moisture re-hydrate the stock, wash out the salt and allow autolysis and bacterial degradation to continue at rapid rate (Jean, 1992).

Such damage can considerably be reduced by ensuring that hide/skin stores are constructed with rain proof roofs and slopes to counteract any risk of flooding, that cured stocks are not subject to dripping water from pipes or steam lines etc. All piles of the hides and skins should also be kept clear of floor by stacking on rakes to raise the bottom hides or skins at least 10 cm from the ground. In many areas, simple shed will give sufficient protection (NPC, 1981). When hides/skins are allowed to get wet in shipment or in transit, bacterial action (putrefaction) will occur. Contamination in transit can cause varying degrees of damage, the worst being direct contact with sea water and iron decks. The resulting iron salt stains being permanent and a serious loss to the tanner (Sammy, 2012).

Grain cracks- Drying in a crumpled condition and by multi folding causes grain-cracks or any pressure and strain, combined with low moisture content will result in this troublesome damage. The theory that excessive strain, exerted by the tension of the strings when frame or "tent" drying, causing grain-cracks has now been disproved. Folding and unfolding when the hides are dry will always be a danger and cracks are very frequently caused in this manner. The initial fold along the ridge of the back after framing should always be done when the hide still retains some moisture. If the hide is dried out before folding it should be "conditioned" by leaving it over night and folding early in the morning (Mohammad *et al.*, 2002).

All the above mentioned factors deteriorating the quality of hides and skins means at the same time imply that they contributed to the increment of solid leather waste generation (authors view).

2.5. Solid Wastes

The solid waste means anything which is useless or discarded after its use for example yesterday's newspaper or empty bottle which is thrown after its use. In other words we can say that "matter in the wrong place". The term solid waste used internationally to describe non-liquid waste material arising out from domestic trade, commercial, industrial, agricultural and mining activities and from public services. Non liquid is a relative term because sludge of certain kind fall with the scope of solid waste management, which arises primarily from industrial and sewage treatment, plants (Kumar, 2013). Solid waste means anything that is neither liquid nor gas and is discarded as unwanted. In the modern age of development the increasing quantity of solid waste is one of the growing environmental problem in both developed and developing countries (FDRE-SWMP, 2007).

The solid waste generated from industrial sources contains a large number of chemicals, some of which are toxic. The waste is considered toxic, if the concentration of the ingredients exceeds a specified value (Nalawade and Kamble, 2009). The standard safe limit for chromium metal in the soil is 150 ppm (parts per million) (Singh, 2010). Tanning is the process of transforming the animal skin (a natural renewable resource) to leather (a market material used in the manufacture of a wide range of products). The increasing requirement of leather and its related products led to a global output that has risen by about 55 percent over the past 30 years, with a trade value estimated to be approximately US\$ 70 billion per year (Ramasami *et al.*, 1999). Its major expansion has taken place in developing and new industrialized countries rather than in other developed economies where solid waste and wastewater treatments are not state of the art (Rao *et al.*, 2003).

2.5.1. Factors contributing for solid waste generation and their solution

Solid waste generation is influenced by the quality of leather (with poor quality leather, the cutting rate can be five points higher than (normal); the type of leather (grain, split, side, belly), with split, the cutting rate can be ten points higher than normal; the size of the leather (lamb, bovine); the size of the item to produce and the combination (size, shape) of components to cut in the same piece of material; the ability of the operator in charge of the cutting: a good clicker can cut 3-5 percent below the allotted surface; the incentive given to the clicker, and the solutions to reduce the quantity of wastes are with good quality leather and recycling of the solid wastes (UNIDO, 2000).

2.5.2. Nature and estimated quantities of tannery solid wastes

Apart from liquid and gaseous wastes, a large amount of solid waste are also generated among all the tannery stages and, moreover, during effluent treatment. Although the characterization of solid wastes from the tanning industry is well documented, leather wastes generated from each type of leather and process have different characteristics. Thus, in order to find applications of these wastes in various fields it is essential to have accurate information about their nature. In addition, some of these solid wastes contain chromium and are categorized as hazardous wastes. Consequently, a safe disposal needs to be assured. The solid wastes are mainly generated during fleshing, trimming, splitting and shaving processes but also the sludge generated in the wastewater treatment plant contributes to increase the amount of these wastes (Cristina, 2018). The percentage of solid waste generated in every stage of leather processing from 1 ton of raw hides is represented in (Figure 15).

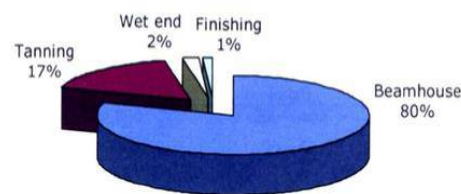


Figure 15: Solid waste percent generated in every stage of leather processing from 1 ton of raw hides (Onyuka, 2010)

According to the data analyzed in different studies, only 200 kg of leather (20% of the raw hide weight) is manufactured from 1 ton of wet-salted hide (FAO, 2015; Abebaw, 2015; Abebe, 2011). The main issues about waste generation are the volume used by the residue in landfills and the inadequate disposal, which lead to the contamination of the environment by the slow leaching of trivalent chrome. Furthermore, the cost of these deposits reaches up to US\$ 5.00/m³, increasing the manufacturing cost (Kindlein *et al.*, 2008).

The nature and quantity of solid wastes produced from processing one ton of raw skins/hides as presented in (table 3) and these tannery solid wastes among others include raw trimmings, fleshings, chrome shavings, buffing dusts and keratin wastes.

Table 3: Nature and quantity of solid wastes produced from processing a ton of raw skins/hides

S.No	Nature of solid waste	Quantity(kg)
1	Salt from handshaking	80
2	Salt from solar pans (not realized)	220
3	Hair (pasting ovine)	100
4	Raw trimmings	40
5	Lime sludge (mostly bovine)	60
6	Fleshing	120
7	Wet blue trimmings (grain splits)	30
8	Chrome splitting (bovine)	65
9	Chrome shaving (mostly bovine)	95
10	Buffing dust (including shaving bovine after crust)	65
11	Dyed trimmings	125

Source:(Thanikaivelan *et al.*, 2005; Kanagaraj *et al.*, 2006)

2.5.3. Characteristics of tannery solid wastes

The chemical composition of solid wastes generated from beam house operations (fleshings, trimmings, splits) depends mainly on a kind and quality of the raw material, treatment type and process conditions. The main components are proteins and fat, up to 10.5 percent (w/w) for both groups. Water content is high, moisture amounts up to 60 percent. These wastes contain small amounts of mineral substances, 2-6 percent (w/w). Chromium compounds are not present in the material. The tanned leather wastes are mainly useless

splits, shavings and trimmings. These waste groups differ mostly in size and shape, the chemical composition is comparable for each. They contain 3-6 percent (w/w) of fat and about 15 percent (w/w) of mineral components, including 3.5-4.5 percent (w/w) of chromium as Cr_2O_3 (Kanagraj *et al.*, 2006).

2.6. Classification of Tannery Solid Wastes

The solid wastes generated from leather industry can be broadly classified into tanned and untanned wastes (Tahiri and Dila Gurdia, 2009) (Figure 16).



Figure 16: Solid leather wastes A, B & H photos taken during study; C, D, E, F & G photos from (Cristina, 2018)

2.6.1. Un tanned tannery solid wastes

Trimming (raw hide/skin) - One of the early operations in a tannery is trimming of neck and tail pieces from hides/skins to provide a shape to the final leather. Non removal of these pieces may decrease the efficiency of machine operations. The head and belly rounds and other trimmings are estimated to be around 6 percent (Buljan *et al.*, 1997).

Green fleshing's- In some countries, the raw hides undergo fleshing operation yielding green fleshing's and fatty tissues. This operation is carried out before washing and soak-

ing. The yield is estimated to be 10 percent on the weight of the raw hide (IEU-2, 2008). The fleshing (50-60 percent of the total wastes generated in leather industry) has been explored for the possible utilization into useful end products (Kanagaraj *et al.*, 2001). Fleshing hydrolysates can also be used as a tanning agent by proper chemical modification. Fleshing wastes can also be used to develop glue, gelatin and poultry feed (Kanagaraj *et al.*, 2006).

Limed fleshings- Limed fleshings are obtained while scraping out the limed hides and skin either by hand or by machines. The fleshings are proteinaceous in nature comprising cutaneous muscle layers and sub cutaneous adhering tissues, which are undesirable in the subsequent operations of leather manufacture. The availability of limed fleshings is 35 percent on the wet weight of the raw hides (70 percent moisture). The composition of the limed fleshings is indicated as; 78 to 80 percent moisture content; 8.3 percent ash content and 15.2 percent total nitrogen. The fleshings obtained by employing machines in tanneries are potentially thermal denatured. The utilization of the same fleshings for glue manufacture is not economically viable. Similarly, fleshings obtained from hides treated with a high percent age of sodium sulfide are found to be unfit for the production of glue. They are at best disposed through landfill. Disposal of such fleshing's currently a serious problem (Fathima *et al.*, 2005).

Hair and wool- The hides and skins are treated with lime and sodium sulfide to remove hair/wool. Since hair and wool are valuable commodities, the goat and sheepskins are painted with lime and sulfide on the flesh side. After the treatment, which is known as hair saving process, hair and wool are removed mechanically or manually. Lime sulfide treatment of hides leads to pulping of hair; and as such, pulping leads to environmental problems if the pulping is not screened by using suitable mechanical means and prevented from entering the wastewater stream. Hair constitutes 10 to 12 percent on the weight of the animal, which is also dependent on the season of the year; for instance, it is higher in winter (Sarvanabhava *et al.*, 2005).

2.6.2. Tanned tannery solid wastes

Chrome trimmings- Excess water from chrome-tanned leather is removed before splitting and shaving. In this process, the hide develops pleats at the edges, which are trimmed out. If not, they may interfere in the forthcoming operations such as splitting and shaving operation. Sometimes, they may damage the hides and skins or sides in the machine operation. These trimmings (estimated at 5.5 to 6 percent of wet weight of hides) are collected from the tannery and utilized in the manufacture of leather boards and bricks production, using a low pressure and temperature process to avoid oxidation of Cr^{3+} (less toxic) to Cr^{6+} (more toxic). The use of chromed trimmings in fertilizer/leather meal applications is known. Chrome trimmings may also be de-chromed and processed into glue and commercial gelatin (Tylore *et al.*, 1999).

Chrome split-The splits obtained during the splitting operation are very thin in substance and cannot be utilized. As solid waste, chrome splits account for 4 to 6 percent of total solid waste. They are collected and used as raw material in the leather board industry. In most of the chrome wastes, the chrome content as Cr_2O_3 is found to be 2.0 to 2.5 percent (Rao *et al.*, 2002).

Chrome shavings-these are obtained as waste material when chrome-tanned leather undergoes the process of shaving operation. Chrome shavings in fibrous shredded form are available as 1 to 2 percent on the weight of the raw hide and present in trivalent state (Rao *et al.*, 2002).

Crust leather trimmings- Generally, crust leathers (leathers obtained after re-tanning, dyeing, and fat liquoring operations) are trimmed after staking, toggling, and nailing to remove the torn and ragged edges for aesthetic value and also for processing the leather in the subsequent machine without any damage (Zhang *et al.*, 2006).

Buffing dust- The crust leathers are buffed on the flesh side and sometimes on the grain side. The buffing (done on flesh side) and snuffing operation (done on the grain side to

produce specialty leathers such as nubuck) generates fine light weight leather fluffy mass (Zhang *et al.*, 2006).

Finished leather trimmings- After finishing, the leathers are trimmed at the edges uniformly. The purpose of trimming is aesthetic and also for easy measurement of the leather (Zhang *et al.*, 2006).

2.7. Challenges Associated With Tanning Industry

The challenges associated with the tanning industry are outlined as follow;

2.7.1. Its impacts on environment

Environmental impact of tannery wastes containing wastewater; hazardous chemicals such as chromium, synthetic tannins, oils, resins, biocides, detergents; careless disposal of solid wastes and gaseous emissions creates a negative image of leather industry, although it has significant economic influence (Islam *et al.*, 2014).

Solid wastes generated from tanning industries contain different chemicals which are used during leather manufacturing process. These tannery solid wastes have different characteristics as different chemical and mechanical processes are applied to the raw hides/skins. If these solid wastes generated during various tanning operations are not properly utilized or disposed they are likely to cause a number of problems on the environment (Singh *et al.*, 2010). Large quantities of solid wastes generated during leather processing and subsequently during effluent treatment. Although some of the wastes find limited applications, unsafe disposal of the bulk of the solid wastes has posed serious problems (Thanikaivelan *et al.*, 2005).

Salt dust or de-dusted salt, if stored in heaps outside the tanneries or dumped in open dumping area is likely to be washed away during raining and cause groundwater pollution. Hair waste and lime sludge, if discharged along with the effluents are likely to choke the drain. Raw and green fleshings, limed fleshings, splits (splitting waste) and

trimmings putrefy easily and give rise to noxious smells. In many tanneries, it is the foul odor which emanate from some of these putrescible solid wastes which accounts for much of the smell traditionally associated with tannery wastes. Some of the biodegradable tannery solid wastes are sources of pathogenic bacteria and volatile organic compounds emission. Vegetable and chrome tanned shavings and splits do not easily decompose. If they are not utilized, problems of disposal are encountered. Primary and secondary sludge obtained during the treatment of tannery wastes are also putrescible (Singh *et al.*, 2010). A great deal of sludge generated from the tannery plants (Ramasami and Prasad, 1991) render the solid waste management system highly inactive due to non-biodegradability of the tanned leather (Dhayalan *et al.*, 2007). Leather itself is slow biodegradable and treatment of different chemicals during tanning process makes it resistant towards chemical, thermal, and microbiological degradation (Han *et al.*, 2001). This in turn affects the agro based activities and degrades groundwater system (Mwinyihija *et al.*, 2012). These wastes are a threat to ecology and aquatic system in vicinity of tannery plants (Mwinyihija *et al.*, 2010). Adding of pesticides for hide conservation during transport also add to the problem (PPAHB, 1998).

Tanneries are distinguished for generating malodor. Rehydration of salted hides and skins generally emit odor of volatile fatty and amino acids evolved in the course of biological decomposition in presence of water. In addition, toxicity of hydrogen sulphide along with acids, fats, carbohydrates. In liming, de-liming and tanning processes is predominant within tanneries. The venting out of malodorous substances to ambient air and subsequent transports to further distance are responsible for atmospheric pollution. Hydrogen sulphide at 20 ppm (30 mg/m^3) in ambient air is lethal to human kind. Ammonia escaping from deliming operation to atmosphere is odorous and pungent. Maximum admissible level of ammonia in air is 50 mg/m^3 . Phenolics (monohydric, dihydric and trihydric) are emitted into air during processing of hides in the post-tanning and finishing operations. The permissible level of phenolics as phenol ($\text{C}_6\text{H}_5\text{OH}$) in water is 10.2 mg/l . The concentration shall not exceed 0.3 mg/l in drinking water. The toxicity of sulphide, ammonia, phenol and chromium that are found in tannery wastewater to freshwater fish has been reported (Mariappan, 1997). Though these solid wastes create a major problem for leather

industry in terms of both their variety and quantity, a high amount of reusable waste is generated in the leather industry. It is possible to recycle these products and even use them as raw materials for different industries (Colak *et al.* 2005). Another study which is congruent to this says proper optimized utilization of these wastes into valuable end products will be a promising solution (Assamoi and Lawryshyn, 2012).

2.7.2. Variation in legislation scenario for leather industries

The discharge limit parameters are different from one country to other. Some legislative authorities have a check on the quality of treated effluents; while others on the quality of the recipient water bodies; some define the permissible levels of impurities to be discharged per day into the recipient water body, whereas in some cases specifications are linked to the total amount of waste water discharged. In many countries, tannery effluents are subjected under overall legislation of industrial waste discharge rather than specific limits (Bosnic *et al.*, 2000).

Some countries have made regulations related to production, import and sale of leather products with regard to hazardous substances. Furthermore, in order to restrict the use of these chemicals, European Chemical Agency (ECHA) has prioritized few chemicals under Substances of Very High Concern (SVHC) which are considered to be hazardous not only to the environment but also to humans (UK REACH, 2009). It has been observed that out of these 30 SVHC substance list provided by ECHA, almost all of the chemicals are used in the leather industry (ECHA, 2010). Ethiopian government also took initiative and designed environmental impact assessment guideline for tanneries since 2005 (FDRE EPA, 2005).

2.8. Mitigating Options to Combat the Leather Industry Threats

Environmental concerns over leather industries have been growing for the past two decades. High industrial and human population density and the use of old technologies all cause increased levels of pollutant in the atmosphere (Maia, 1998). This situation has

highlighted the need for greener technologies (Krishnamoorthy *et al.*, 2012). The protection of the environment therefore has become a global issue throughout the world (Dixit *et al.*, 2015).

For reducing the negative environmental impact of hide/skin processing, there are two broad methods. The first method is generally termed as low waste or cleaner technologies that avoid the use of harmful chemicals and produce solid wastes which can be used as by-products. The second method is related to the treatment of wastewater and the environment-friendly handling and processing of solid waste. The methods applied in both groups can be used to prevent leather production with less negative impact on the environment (Dixit *et al.*, 2015).

2.8.1. Low waste or cleaner technologies

The cleaner processing options need to be cost-effective in order to be economically viable and the success of these technologies depends on: (a) reduction of pollution in terms of quantity and quality, (b) leather quality improvement and/or cost reduction, (c) reproducibility of the process, (d) cost effectiveness to be economically viable, and (e) wide market opportunities. A report by (Ludvik, 2000) shows some possible options of reduction of pollution load during processing of bovine hides into chrome tanned leathers by introducing advanced technologies based on low-waste processing methods (Fig 17).



Figure 17: Advanced technological options for leather processing (Dixit *et al.*, 2015)

The recycling and reuse of spent liquor after the removal of the pollutants in leather processing provides better water management (Parthasarathy, 1995). It has been suggested that ideally zero or near-zero discharge of waste liquors should be encouraged (Sykes, 1997). Common salt or sodium chloride emerges largely from the curing, pickling, and chrome tanning practices. Salt less or less-salt curing may be an alternative to wet salting (Kanagaraj *et al.*, 2005). Solar drying, freeze drying or microwave/dielectric drying should be considered (Komanowsky, 2000). Chemicals like potassium chloride, boraxphenol, boric acid, zinc chloride, silica gel and metal oxinates can be used in place of sodium chloride (Kanagaraj *et al.*, 2005). Processing green hides and skins, use of gamma and electron beam irradiation techniques and transportation in refrigerated condition are some other options for a better cleaner processing (Bailey *et al.*, 2001).

Soaking requires 25 percent of the total water consumption in conventional leather processing. But the chloride load is a hurdle in recycling process as salt is not eliminated during physical, chemical and biological treatment of wastewater. The industrially proven methods for reducing chloride load have been recommended by shaking the liquor in special drums (Dixit *et al.*, 2015); using wheel type desalting machines (Rao *et al.*, 2001) and counter-current soaking technique (Rao *et al.*, 2003). Addition of environmentally acceptable antiseptics or commercial chemical bactericides such as ethyl dithiocarbamate and isothiazolin (Buljan, 1995), use of sodium sulphate (Vankar and Dwivedi, 2009), processing green hides (Frendrup 1995) have also been suggested to decrease the salt load. The recycling of spent floats in liming and unhairing processes showed substantial decrease in sulphide (70 percent), $\text{Ca}(\text{OH})_2$ (90 percent), BOD (7 percent) and COD (26 percent) load (Frendrup, 1995). Sulphide-lime based unhairing and liming achieves a significant decrease in both total solids and dissolved solids (Frendrup, 1995). Enzymatic unhairing is an option for a clean beam house process (Valeika *et al.*, 2012). Enzyme-assisted unhairing followed by reliming with once used relimed liquor ensures complete reduction of water (Shrewsbury, 2002). An economically viable option based on enzymatic dehairing and pickle-less chrome tanning can lead to 67 percent and 78 percent decrease in COD and total solids (Aravindhhan *et al.*, 2007).

Lime splitted hides save chromium and other chemicals and the waste can be easily utilized as a by-product (Freundrup, 1995). Ultrasound not only decreases the waste but also yield better leather quality (Dettmer *et al.*, 2013). A 97 percent decrease in ammonia load in effluents may be obtained by using ammonia-free delimiting and bating with commercial products such as acids, esters of carboxylic acids, non-swelling aromatic acids (IUE-1, 2008). Carbon dioxide delimiting in place of ammonia decrease the pollution load of effluents to a significant extent (Manfred *et al.*, 2012).

Furthermore, it has been established that delimiting and bating can be effectively carried out as a float less operation without impairing any physical/chemical or grain characteristics (John *et al.*, 2001). The spent pickle liquor contains high concentrations of neutral salts (8-10 percent) and has an acidic pH (Chandrasekaran *et al.*, 1989). The options of salt less pickling pickle less chrome tanning and pickle recycle are some solutions to overcome the problem (Burrows, 2001). Conventional chrome tanning processes use only 40-70 percent of the material (Warrier *et al.*, 1995a, 1995b) and the remaining wastes disposal is a cause of concern (Fela *et al.*, 2010). Intrinsically modified chrome tanning salts (Thanikaivelan *et al.*, 2002), use of chromium syntan or oxazolidine (Sundarapandivan, 2011), high exhaustion tanning process (Covington, 1995), recycling/reuse techniques (Rao *et al.*, 2002) would invariably help in increasing the chrome utilization and decreases the chrome discharge. The reuse of pickle liquor for the subsequent batches as well as resorting to pickle free alumechrome combination for tanning result in reduction of significant levels of TDS (Sivakumar *et al.*, 2005). Use of *Sargassum* seaweeds to remove chromium from tannery effluent and make use of this seaweed in the manufacture of basic chromium salt as a reductant is another option (Aravindhan *et al.*, 2004).

A combination between the chemical precipitation and the biological removal of chromium from tanning wastewater may render the tanning process eco-sustainable and environment friendly (Abdullah *et al.*, 2010). Chromiumsilica-, chromium iron, aluminium-zinc-, chromiumzinc-, chromiumzincsilica-, zirconium oxychloride and aluminium tannic acid silica- based tanning agents have been developed (Krishnamoorthy *et al.*, 2012) for reducing the chromium emission. The controlled incineration of tannery wastes

in a starved air thermal incinerator and solidifying the calcined waste resulting in 99.1 percent metal ion fixation is another alternative to reduce the chromium burden on the environment (Sekaran *et al.*, 2007). The tannery wastes then can be used as fuel or nitrogenous source for leguminous plants (Famielec and Wieczorek-Ciurowa, 2011).

2.8.2. Solid leather waste treatment and management

The conventional disposal methods are not practicable for the disposal of tanned leather wastes due to leaching of Cr^{3+} from the tanned leather wastes to groundwater and conversion of Cr^{3+} to Cr^{6+} ; emissions of nitrogen oxide; generation of hydrogen cyanide (HCN); Cr^{3+} and NH_3 during incineration. Less toxic soluble Cr^{6+} can be produced at low incineration temperatures (300-600⁰C) (Rai *et al.*, 1989). Anaerobic digestion of solid waste produce biogas nutrient enriched effluents for agricultural purposes (Dhayalan *et al.*, 2007). Hydrolysate of keratin has been employed in chrome tanning, retanning and exhaustion without altering the physical strength of leather (Chakraborty and Sarkar, 1998). Fleshings have been explored for the possible utilization into useful end products such as soap, bio diesel and fat liquor (Ravindranath and Gopalakrishnan, 2010). Modified fleshing hydrolysate not only has better uptake capacity of chromium in chrome tanning and rechroming (Kanagaraj *et al.*, 2001a) but also, leather obtained has better physical and organoleptic properties than conventionally produced method (Kanagaraj *et al.*, 2001b). Fleshings hydrolysed by pancreatic enzymes could be used as feed ingredients for feed formulation by mixing with other feed ingredients (Kumaraguru *et al.*, 1998). A new parchment-like material from chrome shavings has been found to be useful in the manufacture of home furnishing products (Sastry *et al.*, 2005).

The wet blue shavings completely digested by alkali protease have been used for casein formulation in leather finishing (Crispim and Mota, 2003). Chrome collagen residues have been used for the production of regenerated leather and various articles (Cot *et al.*, 2003). Utilization of tannery waste as feed, fertilizer or cosmetic additive (Lima *et al.*, 2010) and Utilizing tannery waste as a protein source for poultry feed is a step for zero solid waste (Paul *et al.*, 2013).

2.9. The Concept of Value Chain and Value Addition

2.9.1. Value chain

A Value Chain “describes the full range of activities that are required to bring a product or service from conception, through the intermediary phases of production, delivery to final consumers, and final disposal after use (Kaplinsky, 2004). This includes activities such as design, production, marketing, distribution, and support services up to the final consumer (and often beyond, when recycling processes are taken into account). Value chains are part of Market Systems (ILO, 2011).

A value chain can be understood as a set of businesses, activities and relationships engaged in creating a final product (or service). It builds on the idea that a product is rarely consumed in its original form but becomes transformed, combined with other products, transported, packaged, marketed etc. until it reaches its final consumer. In this sense, the value chain describes how producers, processors, buyers, sellers, and consumers separated by time and space gradually add value to products as they pass from one link in the chain to the next. The value chain approach is becoming intensively used both by private sector agents as well as government and development agencies to both identify options for industrial development and implement development programs. Its particular attractiveness draws from, among other things; its capacity to deal with a new business environment prevalent in industrial development in the context of today’s globalized markets (UNIDO, 2009).

2.9.2. Leather value chain

The leather value chain has the full range of activities required to bring leather products (e.g. footwear, garments and goods) to the final consumers passing through the different phases of production, processing and delivery. A strong value chain exists when all the stakeholders in the chain operate in a way to maximize the generation of value along the chain. The weaker nodes of the value chain undermine economic optimization of the

chain. Issues such as weak governance, production of sub-standard products and exploitation of other value chain actors, have a far reaching negative impact to the sustainability of a value chain. The Leather Sector in Ethiopia has an immense potential to generate value addition, employment, exports and trigger other multiplier effects across the economy, because of its large livestock resource and competitively priced labour force (MOI, 2016).

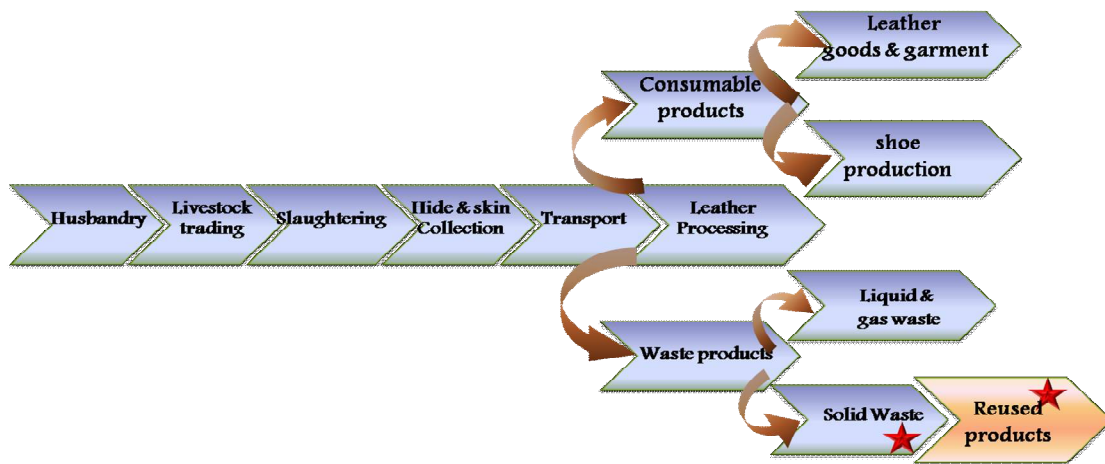


Figure 18: leather value chain

2.9.3. Value addition

Value-adding includes any process or service in the supply chain that adds to or enhances the value of products to customers. Value-adding may include supplying new products or different varieties, changing presentation to meet market requirements, providing expertise and/or services and promotion and marketing activities to differentiate products (CWDAFF, 1999). Value-added farming is defined any activity that allows producers to capture greater value than would normally be secured through conventional commodity channels. The additional value can come from production, marketing, and processing strategies that distinguish the products from standard agricultural commodities (PATS, 2005).

Value-added is a measure for the wealth created in the economy. According to the definition used in systems of national accounting, total value-added is equivalent to the total value of all services and products produced in the economy for consumption and investment (the gross domestic product - GDP), net of depreciation. To arrive at the value-added generated by a particular value chain, the cost of bought-in materials, components and services has to be deducted from the sales value (ILO, 2009). Adding Value – Process of changing or transforming a product from its original state to a more valuable state (Kaplinsky and Morris, 2001).

2.10. Waste Processing in the Tanning Industry

Different scholars reported that most tannery solid wastes now days are used for production of different useful end products and are considered as raw materials rather than simple wastes.

Some important benefits of solid leather wastes are explained in 2.8.1, 2.8.2 and their respective tables.

2.10.1. Solid leather wastes for preparation of different products

As indicated in (table 4 and 5) the solid leather wastes are used for the preparation of different economic value through value addition processes.

Table 4: Solid leather wastes for preparation of different products

Waste type	Benefit	source
Trimming	Raw hide	For glue/gelatin, animal feed, preparation of cosmetic, hair care formulations (shampoos, perming lotion, and bleaching aids). (IEU-2, 2008).
	Un tanned	Good source for production of collagen (Maffia <i>et al.</i> , 2002).
	tanned	Manufacturing of soles (Lacatus <i>et al.</i> , 2009).
Fleshings	Limed	Used for glue, technical gelatin, and animal feed, Tallow is good enough for cosmetic purposes. (Fathima <i>et al.</i> , 2005) (Buljan <i>et al.</i> , 1997)
	Green	Used for meat-cum-bone meal, to produce tallow-raw material for the cosmetic and cleaning products industry and is also added to different food items such as cookies, fuel for steamers (Fathima <i>et al.</i> , 2005)
Hair and wool	Carpet manufacturing, fertilizers.	(Yilmaz <i>et al.</i> , 2007)
Keratin	Hydrolyzed (concentrated NaOH or HCl) and used for chrome exhaustion of tanning bath and rechroming bath	(Chakraborty & Sarkar, 1998).
Chrome shaving	Gels, adhesives and films of high molecular weight, gelable protein fraction,	(Taylor <i>et al.</i> , 1999)
Chrome split	leather meal through steam treatment	(Rao <i>et al.</i> , 2002).
Crust leather trimmings	For making leather boards & production of bricks	(Zhang <i>et al.</i> , 2006)
Recovered chromium salts	used to tan hides, as pigment for glass making, for manufacture of heat-resistant bricks	(Cabeza <i>et al.</i> , 1999a)
Finished leather scrap and used leather wastes	insoles, chappel uppers, keychain holders, light hand bags, and wallets	(Sastry <i>et al.</i> , 2005)

2.10.2. Other benefits of solid wastes

Table 5: Other benefits of solid leather wastes

Waste type	Benefit	Sources
Chrome shavings and buffing dust	Remove motor oils and oily waste from demineralized water and seawater	(Fathima <i>et al.</i> , 2012).
Shavings	Remove vegetable tannins from mixed effluents	(Sreeram <i>et al.</i> , 2004).
Fleshings	Provide stability to the adsorbent, remove acid blue 113 dyes	(Fathima <i>et al.</i> , 2004b)
Iron-treated fleshings	Remove toxic Cr ⁶⁺	(Fathima <i>et al.</i> , 2005)

2.11. The Concept of Composites

2.11.1. Composites

A composite can be generally defined as a combination of two or more components differing in form or composition on a macro scale, having recognizable interfaces between its distinct phases (Herakovich, 1998). Composites usually consist of a reinforcing material embedded in a continuous phase, the matrix also called binder. The effective method to increase the strength and to improve overall properties is usually by incorporating dispersed phases into the matrix (Akovali and Uyanik, 2001).

Composites are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct within the finished structure. Basically, they can be categorized into two major types, i.e., structural composites with outstanding mechanical properties and functional composites with various outstanding physical, chemical or electrochemical properties. They have been widely used in a wide variety of products, e.g. ad-

vanced space craft and aircraft components, boat and scull hulls, sporting goods, sensor/actuator, catalysts and pollution processing materials, biomedical materials, and batteries (Ning, 2012).

2.11.2. Properties of composites made from collagen and plant fibers

Collagen constitutes the major portion of leather fiber, whereas cellulose, hemicelluloses and lignin constitutes the major portion of plant fibers. Due to the natural alignment of the carbon-carbon bonds within the structure of the plant fibers, it is expected that their linear chained polymers would possess significant strength and stiffness (Justiz *et al.*, 2008). Lignin provides plant tissue and individual cells with compressive strength and also stiffens the cell wall of the fiber. The presence of high amount of lignin contributes to increased tensile strength (Sun *et al.*, 2004).

Composites fabricated using plant fibers possessed enhanced mechanical properties (i.e. they exhibited significant values in terms of tensile strength, elongation at break, tearing strength, water desorption and flexibility). These smooth surfaced composites find potential applications not only in footwear and leather goods industry but also it could be exploited for other purposes such as roofing, wall partitions and components of furniture (Senthil *et al.*, 2014). According to Senthil *et al.*, (2014), preparations of composites envision production of cost-effective composites, by conversion of wastes into wealth and thereby simultaneously decreasing the environmental pollution.

2.11.3. Composites Classification

Composites can be classified based on the type of fibers or matrix used; based on the *type of fibers*; composites can be further classified as: *continuous fiber* reinforced composites and *short fiber* reinforced composites. Whereas based on the *type of matrix*, composites can be broadly classified into three categories: metal matrix composites, ceramic matrix composites, and polymer matrix composites (Clyne 1996). Out of the three, polymer matrix composites are widely used (Clyne, 1996).

Polymer matrix composites can be further sub-divided into two classes based on the type of matrix polymer i.e. thermoset or thermoplastic. A thermoplastic is a plastic that melts to a liquid when heated and freezes to a brittle, very glassy state when cooled sufficiently. Most thermoplastics are high molecular weight polymers whose chains associate through weak Van der Waals forces (polyethylene); stronger dipole-dipole interactions and hydrogen bonding (nylon); or even stacking of aromatic rings (polystyrene). Thermoplastic polymers differ from thermosetting polymers (Bakelite; vulcanized rubber) as they can, unlike thermosetting polymers, be re-melted and remolded. Many thermoplastic materials are addition polymers; e.g., vinyl chain-growth polymers such as polyethylene and polypropylene. The difference between thermoplastics and thermosetting plastics is that thermoplastics become soft, re-moldable and weldable when heat is added. Thermosetting plastics however cannot be welded or remolded when heated, simply burning instead. On the other hand, once a thermosetting is cured it tends to be stronger than a thermoplastic (Vigo and Kinzig, 1992).

Composites that are reinforced with continuous fibers provide the best mechanical properties. These types of composites are usually reinforced with high performance fibers like Carbon, Kevlar, PEEK, Which are expensive. Due to high cost these composites find applications in niche areas where performance outweighs the cost. Composites reinforced with short fibers are reinforced with staple fibers such as glass, cellulosic, or petroleum based fibers (De and White, 1996). They are well suited for low strength and stiffness applications like particleboard, automotive applications, construction, etc. The short fiber reinforced composites are finding ever increasing applications in engineering and in consumer goods, like door panel inserts in cars, as they can offer a unique combination of properties and also because they are more economical than competing materials (De and White, 1996).

Bio composites from renewable resources gained much importance universally, because of their biodegradable nature. Bio-composites are most suitable materials insightful in nature for their use in various fields due to their eco-friendly advantages. Bio-composites are manufactured using biopolymer as binder and natural fiber as the reinforcement ma-

terial. Depending on the origin, natural fibers are classified as leaf, seed, and bast or fruit fiber. Natural bio-fiber derived bio-composites (BBC) are renewable, light weight, energy proficient, biodegradable, environmental friendly and bio compatible as compared to other binder fabric composites ([Asokan *et al.*, 2012](#)).

BBC is the challenging issue among researchers all over the world because of the necessity of biodegradable composites at large scale. The major sources of natural fibers are hemp, flax, sisal, jute, coir, banana, bamboo, sun hemp, and pineapple. However, other fibers viz rice, wheat-straw, soybean, sugarcane, and other agricultural residues may also prove to be proficient for use as bio-fiber. BBC has immense applications in the field of biomedical, agriculture, packaging and other allied engineering fields. The only limitation of BBC is hydrophilicity ([Asokan *et al.*, 2012](#)).

3. MATERIALS AND METHODS

3.1. Description of Study Area

The study was conducted in eight purposively selected tanneries (namely Colba tannery (Mojo), Ethiopia Leather Industry Corporation(ELICO) tannery (AA-Saris), Ethio tannery (Awash- Ejersa), Mojo tannery (Mojo), Addis Ababa tannery (AA-Asko), Abiyssinia tannery (AA-Saris), Dire tannery (AA-winget) and Debre Berhan tannery (Debreberhan)); shoe factories (Anbesa shoe factory (AA-Lideta), peacock shoe factory ((AA-Saris), Tikur Abay shoe factory (AA-Asko)), garment and leather goods manufacturing industries (Pitards) the branch or sister company of Ethio tannery (AA-Saris) in Ethiopia and in the laboratory of CSIR- CLRI (Council of Scientific Industrial Research - Central Leather Research Institute) in Chennai- India.

3.2. Materials Used

The different materials used in this study are outlined in the next sections.

3.2.1. Defect assessment study of hides/ skins and solid leather waste estimation

Hides and skins from the eight sampled potential tanneries at wet blue stage were used to know the prevalence of each defect and the grade status of the raw materials (hides & skins). Finished leather (of hides and skins) from three shoe factories and one garment and goods industries were chosen as raw materials; dyes of different models were used to cut the leather and estimate waste generation.

3.2.2. Materials used to prepare composites boards/sheets

Finished leather scrap (finished leather waste material) was collected from ELICO (Ethiopian Leather Industry Corporation) and from Central Leather Research Institute in Chennai-India used as source of leather fiber for composite leather board and sheet making. Natural rubber latex (NRL), ethylene glycol (C₂H₆O₂), sulfuric acid (H₂SO₄) for the first trial, Resin binder (RB), polyurethane binder (PUB), Polyethylene glycol (PEG), Al₂

(SO₄) and sulfuric acid (H₂SO₄) for the second trial and Resin binder (RB), Natural rubber latex (NRL), Polyethylene glycol (PEG), Al₂(SO₄) and sulfuric acid (H₂SO₄) for the third trial, purchased from Sastha PLC Chennai India were used as adhesive mixes. Plant fibers such as jute (*Corchorus trilocularis L.*), hibiscus (*Hibiscus cannabinus*), sisal (*Agave sisalana*), palm (*Phoenix dactylifera*) and enset or Ethiopian banana (*Ensete ventricosum*) were collected from the Ethiopian market places (Addis Ababa- Merkato) and India (Chennai and Andhra Pradesh) and used as sources of reinforcement fibers commonly in all trials.

3.3. Sampling Methods

3.3.1. Defect assessment study of hides and skins

Overall, 1620 hides and skins (N=648 hides; 648 sheepskin; N=324 goatskin) were collected from eight purposively selected tanneries (Table 6) located in and around Addis Ababa in 100 km radius to identify the defects potentially affecting hides and skin quality in different categories like defects observed before killing (pre slaughter), those occurred during the killing operation process (peri slaughter defects) and defects observed after killing of the animals (post slaughter defects) and assign grades to each one of them according to the quality standards described by (ESQA, 2001a; Juhani, 2007). The raw materials are sourced from different areas throughout the country.

Table 6: Number of hide and skins assessed for defects and quality status (grades) from different tanneries

No	Tannery Name	Hide	Sheepskin	Goatskin
1	Colba tannery	108	108	108
2	ELICO tannery	108	108	0
3	Ethio tannery	108	108	0
4	Mojo tannery	108	108	108
5	Addis Ababa tannery	108	108	0
6	Abiyssinia tannery	0	0	108
7	Dire tannery	108	108	0
8	Debre Brhan tannery	0	108	0
	Total	648	648	324

The hide and skin samples included in this study were taken in such a way that the materials were evaluated one by one indiscriminately in a continuous manner from the heaps of hides or skins at wet blue stage until the desired number is obtained from each tannery. Defect types and grades were identified and listed out for each hide and skin by experienced selection and grading experts of the tanneries and records registered immediately by the researcher (ESQA, 2001).

3.3.2. Estimating solid leather waste generation

Secondary data from Sheba tannery was taken and computed to know the solid waste generation of hide and shoat skins. Questionnaires on the volume of hide/skin used, grade of green hide/skin, pieces of product produced, consumption of hide/skin per product produced and total consumption were collected from three potential volunteer shoe companies located in Addis Ababa. Four year (2014 to 2017 G.C) data on raw hides and skin used from all tanneries was collected to know the actual performance of tanneries and estimate amount of waste generated annually (Table 9). Observational measurement study was conducted by taking two hides from table rank (TR) and two from scar (SC) ranked samples from the three potential volunteer shoe companies. Each respondent was asked to explain the model type of the final product, number of products obtained from each raw material used (we used the total sample in ft² used for shoe making, amount of shoe prepared (indicates cutting value) and then by difference we computed the amount of waste generated).

The study also considered garment and goods manufacturing companies located in Addis Ababa. Out of these only one factory having well organized four year data and volunteer to provide information (i.e. Pitards) was included in the survey purposely where as others are excluded for lack of accurately recorded data and for the reason that they are not volunteer to be included in the study/ are even not interested to provide information .

3.3.3. Preparation of leather and plant fibers

Finished leather scrap (LFS) was cut into small pieces of convenient size to use in the pulverizing machine (length 5-10 cm and width 2-3 cm) using Swing ARM Clicker (Porielli S.20, VIGEVANO-ITALIA) ([Appendix 1A](#)) and converted into leather fiber (LF) ([Appendix 1D](#)) with the help of Hinged Hammer Pulverizing machine (Sturtevant, SDL868, USA) ([Appendix 1B](#)). Similarly, all long uneven plant fibers (PF) were cut into small pieces to convert them into smooth and short fibers ([Appendix 1E](#)). The average fiber size ranged between 1.5 and 2.5 cm in length and 0.2 - 0.7 mm in width according to the procedure of ([Satyanarayana et al., 1990](#)).

3.3.3.1. Optimization of binder

For standardizing of the latex utilization different ratios of natural rubber latex (NRL) composition were taken and different boards made. Since among the four ratios the 400:300 is with better tensile strength as indicated in ([Table 23](#)) it was taken as control for further composite making and the characteristics of the boards evaluated.

3.3.3. 2. Preparation of recycled leather (RCL) boards

About 300 g of fiberized LF was soaked in water for 24 hours and then squeezed manually using mesh, after which 400 ml natural rubber latex, 5 ml of ethylene glycol was added and mixed thoroughly. The final pH was adjusted to be below 5 using diluted 1M H₂SO₄, the prepared paste was then poured into steel plate size (62 x 62 cm), pressed gently using hand roller to make leveling, and covered by another steel plate. The wet sheet was again pressed using hydraulic press (Polyhydron 4DL10SGS-10) at a pressure of 1,000 PSI (pounds per square inch) for 10 seconds. The pressed sheet was dried in open air for 2-3 days and plated using hydraulic press at a pressure of 1,500 -2,000 PSI at 60-80 °C for 10 seconds([Appendix-1H](#)).

3.3.3. 3. Preparation of leather composite boards

The extracted and fiberized PFs were added to the LF individually in various proportions (10, 20, 30, and 40 percent) and then mixed in the industrial mixer. Composite boards containing LF and different species of PFs were then prepared separately following the same procedure as that of control board. The detail is presented as follows:-

1. RCL- composite board made from RCL + NRL - as a control;
2. RCL-J- composite board made from RCL + jute fiber +NRL
3. RCL-H- composite board made from RCL + hibiscus fiber +NRL
4. RCL-S- composite board made from RCL + sisal fiber +NRL
5. RCL-P- composite board made from RCL +palm fiber +NRL
6. RCL-E- composite board made from RCL + enset fiber +NRL

3.3.4. Preparation of leather fiber (LF) and plant fibers (PFs)

Finished leather scrap was cut into small pieces (length 5-10 cm and width 2-3 cm) using Swing ARM Clicker machine (Porielli S. 20, VIGEVANO-ITALIA) and converted into leather fiber (LF) with the help of Hinged Hammer Pulverizing machine (Sturtevant, SDL868, USA). Similarly, all long uneven plant fibers were cut into small pieces to convert them into smooth and short fibers. The average fiber size ranged between 1.5 and 2.5 cm in length and 0.2- 0.7 mm ([Satyanarayana et al., 1990](#)).

3.3.4. 1. Optimization of binders

Composite sheets were prepared using the leather fiber and two different synthetic binders namely resin binder (RB) and Poly urethane binder (PUB) at different levels of (30, 60, 90, 120 and 150 ml (weight of the leather fiber) and tested for their tensile strength to take the optimum result as reference for the binders.

3.3.4. 2. Preparation of leather sheets using resin binder

About 130 g of fiberized leather fiber was soaked in 1000 ml of water for 12 hours, minced in meat mincing machine (La Minerva C/E 680N) (Appendix 1F) (Minced three times to reduce the particle size) and made into fine paste. To this paste, 90 ml of RB, 10 ml of PEG and 4 percent of $\text{Al}_2(\text{SO}_4)_3$ was added and mixed thoroughly. Later, 10 ml of 1:3 ratio diluted H_2SO_4 is added and pH adjusted to below 5 by thorough mixing, the mixture was diluted using 4000 ml water so that slurry was formed. Then the sample was poured in to the sheet making machine of (30 cm x 30 cm) or vacuum tab (Appendix 1G) and wet sheet was pressed using hydraulic press (polyhydron 4DL10SGS-10) at a pressure of 1500 PSI for 10 seconds. The pressed sheet was air dried for at least three days and plated using hydraulic press at a pressure of 2,000 PSI at 80 °C for 10 seconds.

3.3.4.3. Preparation of leather sheets using polyurethane binder

The process was same as above (RB-LS preparation) the change is only binder, Instead of RB, PUB was used.

3.3.4. 4. Preparation of plant fiber incorporated leather composite sheets

To the prepared LF, already extracted and fiberized PFs were added individually in the proportions of 10 percent, 20 percent, 30 percent and 40 percent (weight of the leather fiber) and then fiberized in the Hinged Hammer Pulverizing machine (SDL868, USA). Composite sheets containing LF and different species of PFs were then prepared separately following the same procedure as that of control sheet. The details of the composite sheets prepared are noted as follows:-

1. LF-CS- Composite sheet made from leather fiber + PUB served as control
2. LF-ES- Composite sheet made from leather fiber + enset + PUB
3. LF-HS -Composite sheet made from leather fiber + hibiscus + PUB labeled
4. LF-JS -Composite sheet made from leather fiber + jute+ PUB labeled
5. LF-PS -Composite sheet made from leather fiber + palm + PUB labeled
6. LF-SS -Composite sheet made from leather fiber + sisal + PUB labeled

3.3.5. Preparation of leather fiber (LF) and plant fibers (PFs)

Finished leather scrap was cut into small pieces of convenient size to use in the pulverizing machine (length 5-10 cm and width 2-3 cm) using Swing ARM Clicker (Porielli S. 20, VIGEVANO-ITALIA) and converted into leather fiber (LF) with the help of Hinged Hammer Pulverizing machine (Sturtevant, SDL868, USA). Similarly, all long uneven plant fibers were cut into small pieces to convert them into smooth and short fibers. The average fiber size ranged between 1.5 and 2.5 cm in length and 0.2- 0.7 mm in width according to the procedure of (Satyanarayana *et al.*, 1990).

3.3.5.1. Optimization of binders

Leather sheets (LS) were prepared using leather fiber and two different binders namely natural rubber latex (NRL) and resin binder (RB) at different levels of (30, 60, 90, 120 and 150 ml) and tested for their tensile strength to take the optimum result as reference for the binders.

3.3.5.2. Preparation of natural rubber latex leather sheets (NRL-LS)

About 130 g of fiberized leather fiber was soaked in 1000 ml of water for 12 hours, minced in the food mincing machine (La Minerva C/E 680N) (three times minced to reduce the particle size) and made into fine paste. To this paste 120 ml of NRL, 10 ml of PEG and 4 percent of $\text{Al}_2(\text{SO}_4)_3$ was added and mixed thoroughly. Later, 10 ml of 1:3 ratio diluted H_2SO_4 is added and pH adjusted to below 5 by thorough mixing, the mixture was diluted using 4000 ml water so that slurry was formed. Then the sample was poured in to the sheet making machine of (30 cm × 30 cm) and wet sheet was pressed using hydraulic press (polyhydron 4DL10SGS-10) at a pressure of 1500 PSI (10342 KPa) for 10 seconds. The pressed sheet was air dried and plated using hydraulic press at a pressure of 2,000 PSI at 80 °C for 10 seconds.

3.3.5.3. Preparation of resin binder leather sheet

The process was same as above (NRL-LS preparation) the change is only binder, Instead of NRL, RB was used.

3.3.5.4. Preparation of plant fiber incorporated leather composite sheets

To the prepared LF, already extracted and fiberized PFs were added individually in the proportions of 10 percent, 20 percent, 30 percent and 40 percent), mixed with the LF, and then fiberized in the fiberizer machine (SDL868, USA). Composite sheets containing LF and different species of PFs were then prepared separately following the same procedure as that of control sheet. The details of the composite sheets prepared are noted as follows:-

1. FLS-composite sheets made from finished leather scraps + binders served as control
2. FLS-E -composite sheet made from FLS + enset fiber
3. FLS-H -composite sheet made from FLS + hibiscus fiber
4. FLS-J- composite sheet made from FLS + jute fiber
5. FLS-P -composite sheet made from FLS + palm fiber
6. FLS-S -composite sheet made from FLS + sisal fiber

3.4. Data Processing and Analysis

All data collected were entered in to Microsoft Excel spreadsheet, coded and analyzed using Chi square test for defect and grade values comparison, SPSS (Statistical Package for the Social Sciences) software version 20 was used for all data analysis. Descriptive statistics such as mean, standard deviation, frequency and percentages was applied. Figures were drawn using Microsoft excel; Origin 8 software was also used to draw FTIR, TGA and DSC graphs.

4. RESULTS

4.1. Defect Assessment in Hides and Skins

Generally the defect categories of hides and skin were, classified as defects observed before killing (pre slaughter), those occurred during the killing operation process (peri slaughter defects) and defects observed after killing of the animals (post slaughter defects).

4.1.1. Defect prevalence and grades of hides and skins

This study has revealed 13 different types of defects which can be categorized under pre, peri and post-slaughter problems (Table 7). Cockle, scratch, wound (scar), flaying defect (flay cuts, scores, gouges, holes, poor pattern) and putrefaction appeared in the majority of the hides and skins whereas prevalence of veinness caused by poor bleeding was more common in sheep and goat skins than in cattle hides. Although there were hides and skins affected by only one defect type, the majority of them had multiple types of defects originating from one or more of the defect categories. Cockle was much more prevalent in sheepskins followed by hides and goatskins ($P < 0.0001$). Similarly more hides and goatskins were recorded than sheepskins for presence of scratches ($P = 0.003$) whereas scars from wounds were more important in cattle hides than in shoaat skins. Cattle hides and goat skins were found to be much more vulnerable to slaughter/flaying defects ($P < 0.0001$) and putrefaction ($P < 0.05$) than sheepskins.

Table 7: Over all prevalence (percent) of hides and skin defects observed at wet-blue stage

No	Defect types	Hide (N=648)	Sheepskin (N=648)	Goatskin (N=324)
<i>Pre-slaughter defects</i>				
1	Cockle(ekek)	41.98 ^a	60.00 ^b	28.40 ^c
2	Scratch	44.60 ^a	31.00 ^b	40.74 ^c
3	Brand marks	8.02	3.50	3.40
4	Pox lesions	2.16	4.63	3.09
5	Scar from wounds	17.59 ^a	9.72 ^b	9.88 ^b
6	Tick mark	2.31	0.46	0.00
7	Shrinkage	0.15	0.46	0.93
8	Poor substance	2.62	10.49	4.32
<i>Peri-slaughter defects</i>				
9	Flaying defect	59.88 ^a	35.20 ^b	69.44 ^c
10	Veinniness	0.93 ^a	14.20 ^b	26.85 ^c
11	Ripping defect	0.93	3.24	1.54
<i>Post-slaughter defects</i>				
12	Putrefaction	24.38 ^a	20.20 ^b	25.31 ^a
13	Processing defect	2.62	0.31	0.31

* ^{a, b, c} Proportions in a row with different superscripts are statistically different (P<0.05) among the three products (using χ^2 test)

As presented in [Table 8](#), the majority of hides and skins were categorized under the low grades five and six (62.65 percent for hides and sheepskin, and 69.75 percent for goatskin) followed by reject category 31.48 percent, 27.31 percent, &19.75 percent) in hide, sheepskin and goatskin, respectively. Surprisingly, there was no single hide or skin with grade one or two category whereas the proportions of hides and skins falling in grade 3 & 4 were very minimal (ranging between 5.87 percent and 10.49 percent). Significantly higher number of hides (31.48 percent) and sheepskins (27.31 percent) were rejected compared to goatskin (19.75 percent) (P<0.05).

Table 8: Grade categories of hides and skins regardless of the defects observed

Hide and skin quality (grade)	Hide(N=648)		Sheepskin(N=648)		Goatskin(N=324)	
	<u>Frequency</u>	<u>percent</u>	<u>Frequency</u>	<u>percent</u>	<u>Frequency</u>	<u>percent</u>
Grade three	2	0.31	6	0.93	8	2.47
Grade four	36	5.56	59	9.10	26	8.02
Grade five	148	22.84	172	26.54	111	34.26
Grade six	258	39.81	234	36.11	115	35.49
Reject	204	31.48	177	27.31	64	19.75
Total	648	100.0	648	100.0	324	100.0

4.1.2. Association between cattle hides quality and defect category

About 82 percent, 60 percent, and 28 percent of hides examined had pre-slaughter, Peri-slaughter and post-slaughter defects, respectively. Among these, hides with pre-slaughter defects only (N=185), Peri-slaughter defects only (N=60) and post-slaughter defects only (N=27) were filtered out and their grades assessed to know the impact of each defect categories on quality of the products. Best quality grades (Grade 1 & 2) were absent in all of the defect categories (Figure 19). Although it is relatively small proportion, peri-slaughter defects such as ripping, flaying and bleeding problems caused relatively less quality deterioration than pre- and post-slaughter defects (P=0.005). On the other hand, post slaughter problems (mainly putrefaction), when they occur, really caused the greatest damage to quality leading to rejection of 66.7 percent of the products compared to the other two stages of hide production (P<0.0001).

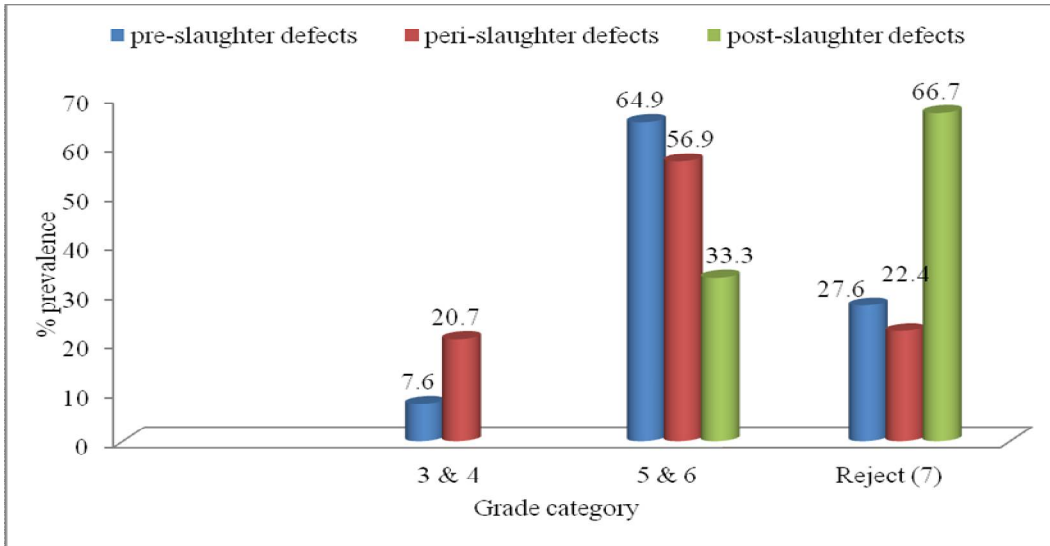


Figure 19: Quality grades of hides with single defect category (Pre-slaughter, peri-slaughter or post-slaughter)

4.1.3. Association between sheepskin quality and defect category

When all the sampled sheepskin defects were grouped into three as pre, peri and post-slaughter, the highest defect was observed at the pre-slaughter stage (87 percent), followed by peri-slaughter (36.7 percent), and post-slaughter (32.9 percent). Among these, sheepskins with pre-slaughter defects only (N=306), Peri-slaughter defects only (N=24) and post-slaughter defects only (N=32) were filtered out and their grades assessed to know the impact of defect categories on quality of the products. The majority of the skins fall under low grade (5 and 6) in all cases whereas significant proportion of skins also got rejected in almost similar proportion ($P>0.05$) regardless of the stages at which the defects were created (Figure 20). The best quality grade (grade 1 & 2) sheepskins were absent in all of the defect categories.

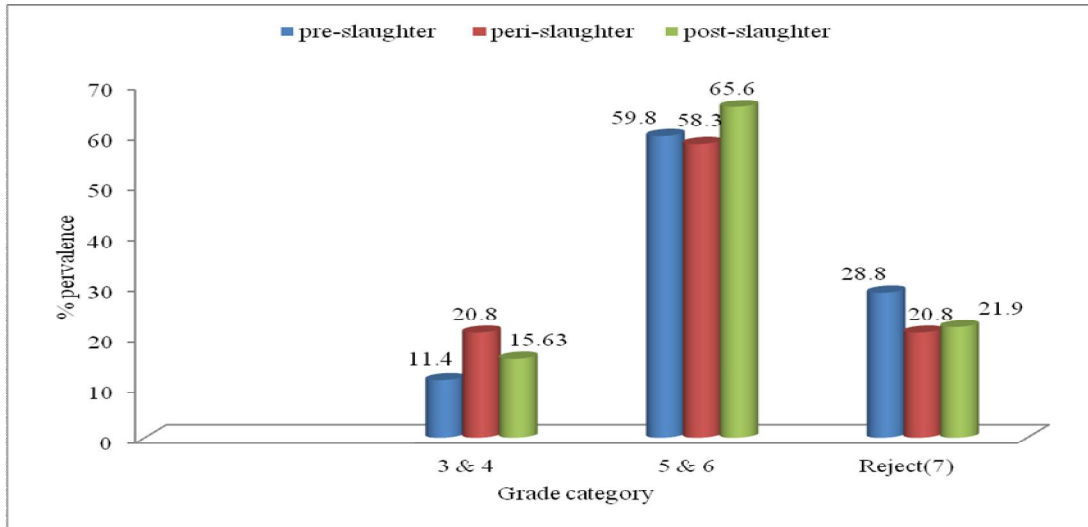


Figure 20: Quality grades of sheepskins with single defect category (Pre-slaughter, peri-slaughter or post-slaughter)

4.1.4. Association between goatskin quality and defect category

Pooled goatskin defects revealed 70 percent, 75.3 percent, and 27.2 percent for pre-slaughter, peri-slaughter and post-slaughter defect categories respectively. Among these, goatskins with pre-slaughter defects only (N=46), peri-slaughter defects only (N=46) and post-slaughter defects only (N=12) were filtered out and their grades assessed to know the impact of each defect categories on quality of the products (Figure 21). As usual, best quality grades (grade 1 & 2) were absent in all the three categories. Majority of the goatskins fall under low grade (5 and 6) in pre-slaughter and peri-slaughter categories whereas most of the goatskins categorized under post-slaughter defect only were rejected compared to those in the other two groups ($P < 0.001$).

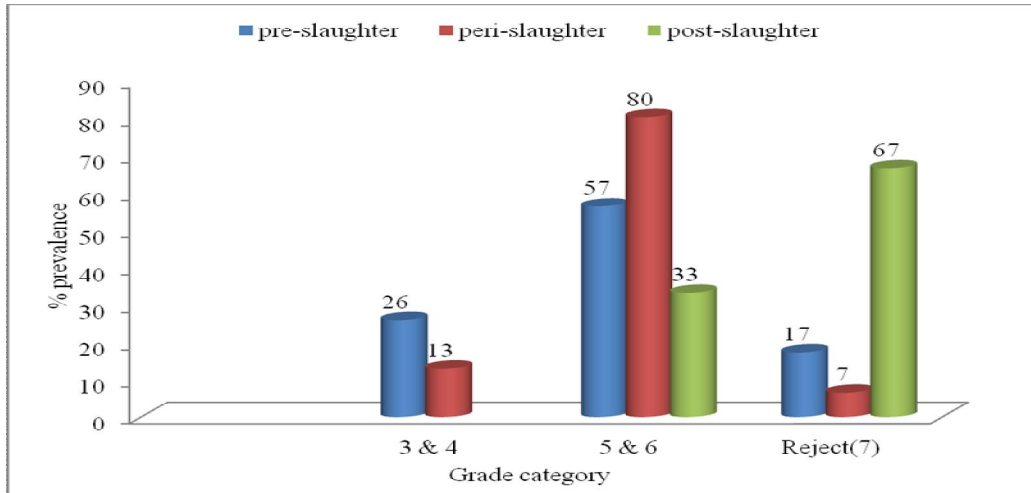


Figure 21: Quality grades of goatskins with single defect category (Pre-slaughter, peri-slaughter or post-slaughter)

4.1.5. Individual effects of major defects on the quality/grades of hide and skins

Among the various defects observed during this study, cockle (ekek), scratch and wound (scar) from pre-slaughter defects, flaying defect from peri-slaughter and putrefaction from post-slaughter defects were problems observed with high frequency. Accordingly, the impact of each of these major defects on quality (specifically on grade values of the hides) when they occur singly was evaluated.

4.1.5.1. Cockle

Cockle is small hard nodule, which form in the skin following ectoparasite infestations such as by sheep ked and lice. Twenty nine cattle hides, 115 sheepskins and 11 goatskins were found to harbor defects due to cockle only. Here also, there was no hide or skin falling under grades one and two (Figure 22). Cockle was responsible for 17-18 percent of the hides and skins rejected in the absence of all other defects affecting quality. Moreover, most of the hides and skins affected by this problem received low grade (5 and 6). Hence, no significant difference was observed on the effect of cockle among grades of hides, sheepskin and goatskin ($P > 0.05$).

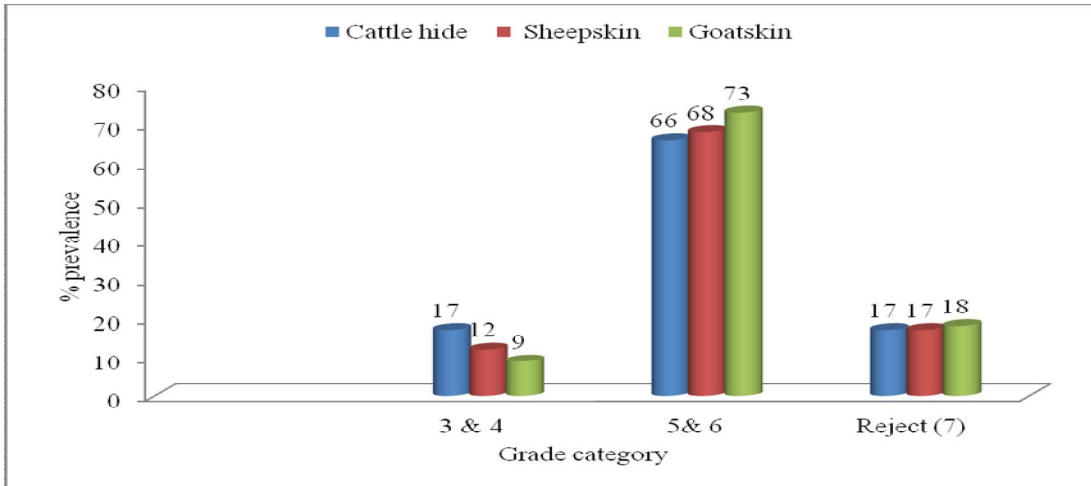


Figure 22: Quality grades of hides and skins as affected by cockle only

Scratch

Forty four cattle hides, 24 sheepskins and 22 goatskins were found to harbor defects due to scratch only. Scratch was responsible for only 5-13 percent of the hides and skins rejected in the absence all of other defects affecting quality (Figure 23). Moreover, most of the hides and skins affected by this problem received low grade (5 and 6). This defect is significantly less damaging in goat skin than others ($P < 0.05$) as witnessed by large proportion of goatskins falling in the grade categories of moderate quality (grades 3 to 4).

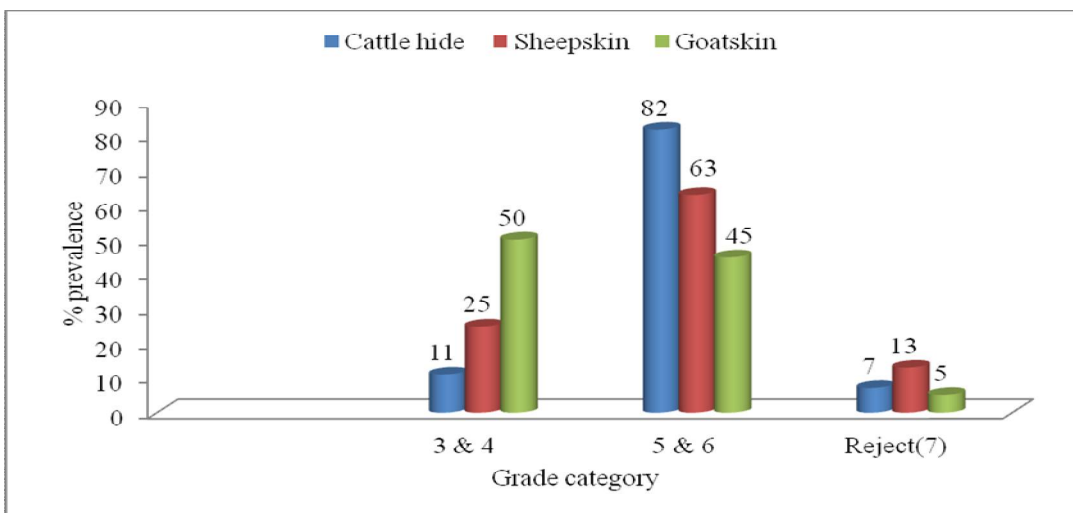


Figure 23: Quality grades of hides and skins as affected by scratch only

4.1.5.2. Scar/wound

Scars and wounds were also one of the major problems affecting especially cattle hides and sheepskins. Fifteen hides, 16 sheepskins and one goatskin were found to harbor defects due to scars/wounds only. The problem was responsible for 24-44 percent of the hides and sheepskins rejected in the absence of all other defects affecting quality although rejection was not observed in goatskins affected solely by this problem. In the same way as described for other major defects, most of the hides and skins affected by this problem received low grades (5 and 6) whereas hides and skins receiving grades 3 and 4 were very low in number (Figure 24). No significant difference was observed on the effect of scars/wounds among hide, sheepskin and goatskin grades ($P>0.05$).

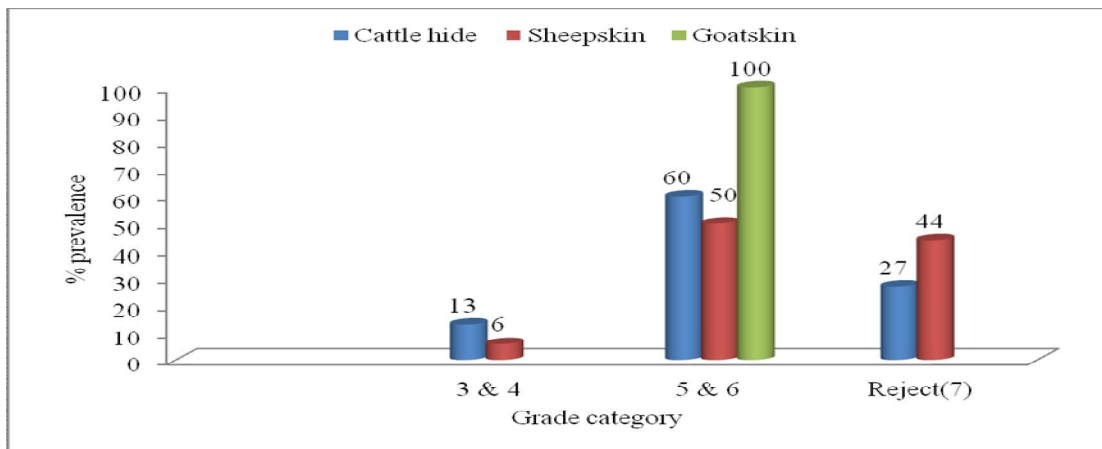


Figure 24: Quality grades of hides and skins as affected by wounds/scar only

4.1.5.3. Flaying/slaughter defect

Among peri-slaughter defects, flaying defect was one of the most prevalent man made problem affecting hide and skin quality. Sixty hides, 25 sheepskins and 32 goatskins were found to harbor defects due to improper slaughter and flaying only. The problem was responsible for 22-24 percent of the hides and sheepskins rejected in the absence of all other defects affecting quality (Figure 25) which is much higher compared to the 3 percent rejected in goatskins ($P=0.017$). However, significantly higher proportions of goatskins with flaying defects only received low grades (5 and 6) than cattle hides and sheepskins with similar defects ($P=0.003$).

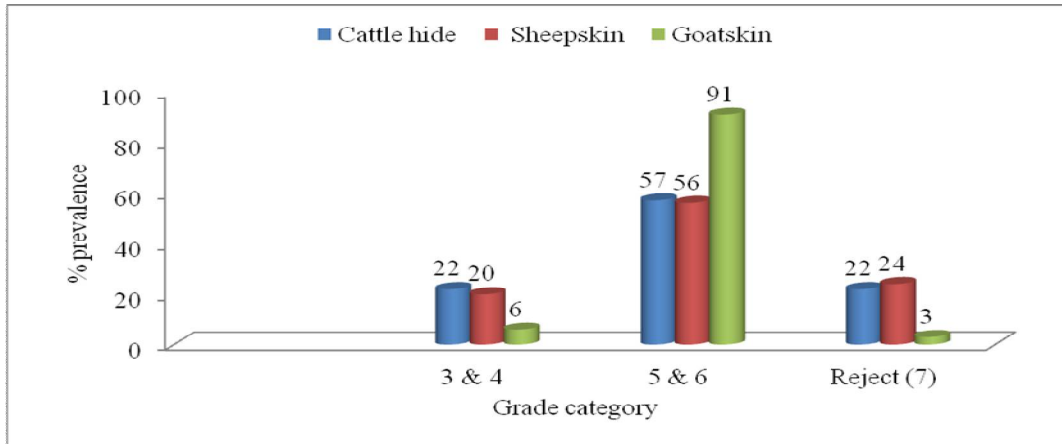


Figure 25: Quality grades of hides and skins affected by flaying defect only

4.1.5.4. Putrefaction

Post-slaughter defects are caused as a result of handling, storage, transportation and processing problems. Among post-slaughter defects, putrefaction was one of the most prevalent problems affecting hide and skin quality. Eighteen hides, 31 sheepskins and 13 goatskins were found to harbor defects due to putrefaction only. The problem was responsible for 62-83 percent rejection rate of the hides and goatskins in the absence of all other defects affecting quality which is much higher compared to the 19 percent rejected in sheepskins ($P < 0.05$). Although rejection was low in sheepskin affected by putrefaction, most of these skins fall under low grade category (Figure 26).

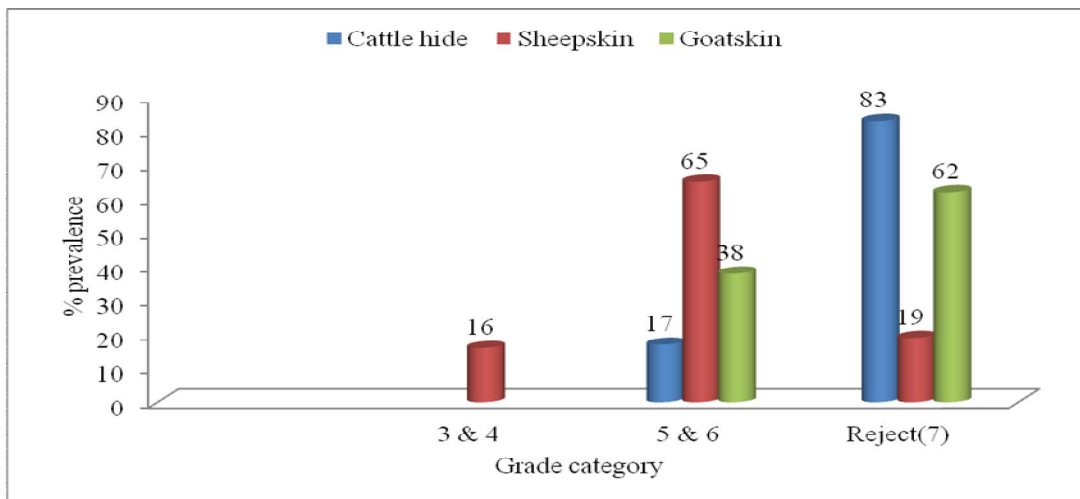


Figure 26: Quality grades of hides and skins as affected by putrefaction only

4.2. Estimation of Solid Leather Waste

4.2.1. Installed capacity and performance of Ethiopian tanneries

Table 9: Installed soaking capacities and performance of Ethiopian tanneries

Year	No of tanneries in each year	Installed daily and annual soaking of tanneries				Performance			
		Installed daily soaking (23.3 working days in a month)		Installed annual soaking (280 working days)		hide		skin	
		Hide	skin	hide	skin	per-cent	hide	percent	skin
2014	30	9,050	141,500	2,534,000	39,620,000	60	1,520,400	53	20,998,600
2015	29	10,500	162,380	2,940,000	45,466,400	69	2,028,600	42	19,095,888
2016	28	10,500	162,380	2,940,000	45,466,400	83	2,440,200	52	23,642,528
2017	28	10,500	162,380	2,940,000	45,466,400	56	1,646,400	54	24,551,856
total		40,550	628640	11,354,000	176,019,200		7,607,180		88,449,648
Annual average				2,838,500	44,004,800	67	1,901,795	50.25	22,112,412

4.2.1.1. Tanneries

Table 9 showed that during the study period (2014-2018) 28 tanneries were in operation and almost all of these tanneries were performing half of their installed capacities (67 percent for hide and 52.25 percent for skin). The data collected from the tanning industries confirmed that the solid wastes generated during the tanning process were as follows: salt from hand shaking, fleshing, raw trimming (green trimming), hair (from hair shaving process), pelt trimming, wet blue split, dry sludge, chrome shaving and trimming, buffing dust, crust and finished leather scraps, The major reasons mentioned by the respondent companies for their low performance among others are absolute shortage of supply and deteriorated quality of hide and skins, power failure, and shortage of spare parts. Furthermore, it has been observed that considerable amount of hides and skins are left aside uncollected at every backyard (**Figure 27**) as a result of which the country is losing huge amount of foreign currency (personal observation).



Figure 27: Uncollected Hides (From the backyard slaughter around Akaki-Addis Ababa)

The annual processing performance was 7,607,180 pieces of hides and 88,449,648 skins. According to the information obtained from the tanneries during the questionnaire survey, the average weight of the Ethiopian cattle hide is 12 kg and that of skin 1.2 kg. Using the above conversion, 91,286,160 kg (100,625.77 ton) of hide and 106,139,577.60 kg (116,998.86 ton) of skin is processed annually in all of the Ethiopian tanneries. The finding of [Zulfikar \(2012\)](#) showed that from processing of both raw hide and skin 55.8 percent solid waste was generated. Taking this finding as a reference plus the current performance of the Ethiopian tanneries, and using conversion factor, the total solid waste generated from the tanneries is estimated to be 78,506,097.6 kg (86,538.16 ton) from hide and 26,363.95 kg (29.06 ton) from skin of solid waste or a total of 86,567.22 ton of solid waste is generated annually and disposed to environment without due care ([Figure 28](#)).



Figure 28: Solid waste disposed in tannery and shoe factory compounds
 (A) Picture at wukro tannery-Tigray (B) picture at Tikur abay shoe factory Asko-Addis Ababa.

4.2.2. Solid waste generated in the leather industries

The data presented in the tables (17-20) show the daily solid waste generation of hides and skins at Sheba tannery only.

4.2.3. Annual solid waste generated from Sheba tannery

Table 10: Solid waste generated per day for 600 pieces of raw hide

S/N	Type of waste	Weight (kg)	Generation (kg / kg of wet salted hide)	Generation (kg/ton of wet salted hide)
1	Shacked salt	57.60	0.0043	0.43
2	Fleshings & Trimmings	1512.00	0.1120	11.20
3	Unusable splits	586.72	0.0435	4.35
4	Wet trimmings(after sammy-ing)	300.00	0.0222	2.22
5	Shavings	918.94	0.0681	6.81
6	Trimmings(Dry)	22.32	0.0017	0.17
7	Sludge	1702.08	0.1261	12.61
	sub total	5099.66	0.3778	37.78
8	Fleshings& Trimmings	2268.00	0.1680	16.80
9	Unusable splits	879.41	0.0651	6.51
10	Wet trimmings(after sammy-ing)	450.00	0.0333	3.33
11	Shavings	1378.44	0.1021	10.21
12	Trimmings(Dry)	33.84	0.0025	0.25
13	Sludge	1134.00	0.0840	8.40
	Sub total	6143.69	0.4551	45.51
	Grand Total	10324.41	0.8328	83.28

As presented in [Table 10](#), processing one ton of wet salted hide can generate 83.28 kg of solid wastes in Sheba tannery. The daily hide soaking capacity in Sheba tannery is 9,000 kg and, as the factory has 275 working days per year, the annual soaking capacity is 2,475 tons of hide. Consequently, 206.19 ton of solid waste is generated annually during the overall tannery hide operations (from beam house to finishing processes).

Table 11: Solid waste generated per day for 4000 pieces of sheep skin

S/N	Type of waste	Weight(kg)	Generation (kg / kg of wet salted hide)	Generation (kg/ton of wet salted hide)
1	Raw Trimmings	550	0.0688	68.75
2	Shacked salt	78	0.0098	9.75
3	De-wooled hair	1,916	0.2395	239.5
5	Fleshings	2,320	0.2900	290
6	Wet Trimmings	300	0.0375	37.5
7	Trimmings(Dry)	26.6	0.0033	3.325
8	Buffing dust	2.25	0.0003	0.28125
9	Trimmings(Dry)	2.45	0.0003	0.30625
10	Buffing dust	0.18	0.0000	0.0225
11	Trimmings(Dry)	3.45	0.0004	0.43125
12	Buffing dust	8.1	0.0010	1.0125
13	Shavings	76.5	0.0096	9.5625
14	Buffing dust	4.45	0.0006	0.55625
15	Off-cuts	17.77	0.0022	2.22125
16	Buffing dust	2.08	0.0003	0.26
17	Off-cuts	8.29	0.0010	1.03625
	Total	5,316.12	0.6645	664.515

Regarding sheepskins as seen in (Table 11), processing one ton of sheep skin can generate 664.515 kg of solid wastes. The daily sheepskin soaking capacity of the tannery is 3,000 kg, and the annual soaking capacity is 825 tons of skin. Accordingly, 548.224 ton of solid waste is generated annually during the overall tannery sheep skin operations.

Table 12: Solid waste generated per day for 1200 pieces of goat skin

S/N	Type of waste	Weight(kg)	Generation (kg / kg of wet salted hide)	Generation (kg/ton of wet salted hide)
1	Raw Trimmings	234	0.0975	97.5000
2	Shacked salt	7.8	0.0033	3.2500
4	Fleshings	600	0.2500	250.0000
5	Wet Trimmings	32.51	0.0135	13.5458
6	Trimmings(Dry)	0.98	0.0004	0.4083
7	Buffing dust	0.072	0.0000	0.0300
8	Trimmings(Dry)	4.45	0.0019	1.8542
9	Buffing dust	1.1	0.0005	0.4583
10	Shavings	110.5	0.0460	46.0417
11	Trimmings(Dry)	1.915	0.0008	0.7979
12	Buffing dust	4.5	0.0019	1.8750
13	Shavings	42.5	0.0177	17.7083
	Sub Total	1,040.33	0.4335	433.4696

Table 13: Solid waste generated per day for 800 pieces of air--dried goat skin

S/N	Type of waste	Weight(kg)	Waste generation (kg / kg of wet salted hide)	Waste generation (kg/ton of wet salted hide)
1	Raw Trimmings	14	0.0088	8.75
2	Shacked salt	-	-	-
4	Fleshings	480	0.3000	300
5	Wet Trimmings	21.68	0.0136	13.55
	Sub Total	515.68	0.3223	322.3

Tables 12 & 13 show the case of goatskins in which processing one ton of goatskin can generate $(433.46.96+322.30) = 755.77$ kg of solid wastes. Since the daily goatskin soaking capacity of the tannery is 5,600 kg, and then the annual soaking capacity is 1,540 tons of skin. Therefore, 1,163.886 ton of solid waste is generated annually during the overall tannery goatskin operations. A total of 1,918.228 tons of solid waste was generated annually by the company. At that point in time, the overall solid wastes generated are disposed to an open dumping area on the surrounding of the industry without any treatment.

Table 14: Solid waste generation for hide

Company code	Name of Raw material	No of samples taken	Grade of the sample		Model & shoe no		Size of the sample taken (ft2)	Pair of shoe obtained/hide	Consumption/shoe(ft ²)	Total consumption	Difference	Waste (percent)	TR	SC
			TR	SC										
A	Cattle hide	1	√		E	39	14.5	5	2.68	13.4	1.10	7.59	7.59	
A	Cattle hide	1	√		E	42	15.25	4.5	3.19	14.36	0.90	5.87	5.87	
A	Cattle hide	1		√	E	39	9.25	2.5	2.68	6.70	2.55	27.57		27.57
A	Cattle hide	1		√	E	42	12.25	3.0	3.19	9.75	2.68	21.88		21.88
B	Cattle hide	1	√		927	42	12.75	2.5	4.17	11.78	0.98	7.65	7.65	
B	Cattle hide	1	√		927	42	13.00	2.5	4.71	11.78	1.23	9.42	9.42	
B	Cattle hide	1		√	927	42	12.50	2.0	4.71	9.42	3.08	24.64		24.64
B	Cattle hide	1		√	927	42	11.75	1.75	4.71	8.24	3.51	29.85		29.85
C	Cattle hide	1	√		M66	41	11.75	2.0	5.50	11.00	0.75	6.38	6.38	
C	Cattle hide	1	√		M66	41	12.00	2.0	5.50	11.00	1.00	8.33	8.33	
C	Cattle hide	1		√	M66	41	11.25	1.5	5.50	8.25	3.00	26.67		26.67
C	Cattle hide	1		√	M66	41	11.5	1.5	5.50	8.25	3.25	28.26		28.26
Average												17.01	7.54	26.48

E=Elgin (Model) C, TR= Table rank (Grade I, II, III, IV); SC=Scar (Grade V, VI, VII); TR and Scar is the name given by the shoe factories to measure the leather quality (Grade level).i.e. TR= leather having cutting value of greater than 50 percent but SC= leather having cutting value of less than 50 percent .

Table 15: Solid waste generation for skin

Company code	Name of Raw material	No of sample taken	Grade of the sample		Model & shoe no		Size of the sample taken(ft2)	Pair of shoe obtained/hide	Consumption/shoe(ft ²)	Total consumption	Difference	Waste (percent)	TR	SC
			TR	SC										
A	skin	1	√		ETHY	36	5.15	2.00	2.35	4.70	0.45	8.74	8.74	
A	skin	1	√		ETHY	36	5.25	2.00	2.35	4.70	0.55	10.48	10.48	
A	skin	1		√	ETHY	37	4.50	1.50	2.44	3.66	0.84	18.67		18.67
A	skin	1		√	ETHY	37	4.55	1.50	2.44	3.66	0.89	19.56		19.56
B	skin	1	√		6202	42	3.25	1.25	2.30	2.88	0.38	11.54	11.54	
B	skin	1	√		6202	42	3.30	1.25	2.30	2.88	0.43	12.88	12.88	
B	skin	1		√	6202	42	3.00	1.00	2.30	2.30	0.70	23.33		23.33
B	skin	1		√	6202	42	3.15	1.00	2.30	2.30	0.85	26.9 8		26.9 8
C	skin	1	√		1577	42	6.00	2.00	2.70	5.40	0.60	10.00	10.00	
C	skin	1	√		1577	42	6.25	2.00	2.70	5.40	0.75	12.20	12.20	
C	skin	1		√	1577	42	5.50	5.50	2.70	4.05	1.45	26.36		26.36
C	skin	1		√	1577	42	5.25	5.25	2.70	4.05	1.2	22.86		22.86
Average												16.97	10.97	22.96

E=Elgin (Model) C, TR= Table rank (Grade I, II, III, IV); SC=Scar (Grade V, VI, VII)

4.2.1.2. Shoe factories

The average solid waste generated for hide was 7.54 percent in the table rank (TR) (those having cutting value of greater than 50 percent that include materials having Grades I, II, III and IV). In case of scars (SC) those having cutting value of less than 50 percent and having grade values of V, VI and VII, gave generation rate of 26.48 percent. The average solid waste generation (taking both ranks) was 17.01 percent. The sampled Ethiopian shoe factories used 4,677,065.06 square feet (ft²) (434,513.56 m²) of hide and 6,565,885.61 square feet (ft²) (609,990.73 m²) of skin. Since the average area of Ethiopian skin is 5ft² (0.46m²) and that of hide is 22ft² (2.04 m²), then 4,126.94 ton of hide and skin is used annually in the sampled shoe factories. This is then translated to solid waste generation which is equivalent to 705.71 ton per annum (Tables 14 and 15).

4.2.1.3. Garment and goods manufacturing factories

In the case of garment and goods manufacturing factories, though it was difficult to estimate the waste generation because of lack of properly recorded data and diversity of products produced by the companies, estimation was done based on the available data from Pitards (Sister company of Ethio-tannery). To estimate solid waste amount, we therefore depended on only one factory which has kept proper data. The average annual solid waste disposed from this factory was therefore estimated to be 82.68 tons of finished leather waste.

4.3. Preparation of Composite Boards Using Natural Rubber Latex

The different evaluation methods in the composite preparation are outlined as follow;

4.3.1. Mechanical properties of composite boards

Table 16: Tensile strength of leather fiber with different natural rubber latex ratios

Sample No	Latex (ml):Leather fiber (g)	Tensile strength(MPa)
1	200:300	0.64
2	300:300	0.85
3	400:300	0.34
4	500:300	0.48

For standardizing of the latex utilization different ratios of NRL (natural rubber latex) composition was taken and different boards made. Since among the four ratios the 400:300 was with better in tensile strength as indicated in Table 16 and was taken as control for further composite making and evaluated the characteristics of the boards.

Table 17: Mechanical properties of recycled leather Jute (RCL-J) composite boards

Sample no	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
1	100:00	1.85 ± 0.34	12.01±2.61	45.21±11.33	62.41±6.97	83.29±15.27	2.35±0.40
2	90:10	2.08±0.22	14.31±2.65	22.52±3.68	57.86±2.67	60.03±9.86	2.39±0.06
3	80:20	2.20±0.27	12.20±3.46	16.54±3.97	25.84±10.87	78.8±8.63	2.64±0.32
4	70:30	2.05±0.33	8.75±1.43	21.82±3.25	21.90±0.88	61.30±13.17	0.69±0.01
5	60:40	2.17±0.72	8.08±1.43	22.57±1.30	40.74±1.49	85.94±2.15	2.62±0.05

N=4

Table 17, shows that all RCL-J fiber composites had better tensile strength than the control board (1.85 ± 0.34). Among the four different samples, sample 3 (20 percent PF) RCL-J composite boards have optimum tensile strength (2.20±0.27 MPa) and Flexing index (2.64±0.32). Elongation at break (14.31±2.65) and water absorption (57.86±2.67) results were higher in sample 2 (10 percent PF) whereas of Stitch tear strength values (22.57±1.30) and water desorption (85.94±2.15) were greater in sample 5 (40 percent PF).

Water absorption values of sample 3 (20 percent PF compositions) (25.84 ± 10.87) and sample 4 (30 percent) (21.90 ± 0.88) did not meet the minimum standard value set by CLRI-SDDC (i.e. minimum 35 percent; as per the SATRA test method: TM 9:1993).

Table 18: Mechanical properties of recycled leather-hibiscus (RCL-H) composite boards

Sample no	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
1	100:00	1.85 ± 0.34	12.01 ± 2.61	45.21 ± 11.33	62.41 ± 6.97	83.29 ± 15.27	2.35 ± 0.40
2	90:10	2.35 ± 0.22	12.03 ± 2.15	25.29 ± 2.98	25.80 ± 5.06	68.29 ± 7.05	1.93 ± 0.01
3	80:20	1.90 ± 0.16	12.00 ± 1.70	31.55 ± 2.40	37.23 ± 8.53	57.05 ± 3.32	2.44 ± 0.02
4	70:30	2.09 ± 0.26	10.89 ± 2.06	31.76 ± 4.81	49.27 ± 1.91	62.48 ± 17.18	2.24 ± 0.14
5	60:40	2.00 ± 0.45	6.61 ± 0.49	20.05 ± 5.35	35.52 ± 1.14	82.46 ± 8.35	0.93 ± 0.06

N=4

The tensile strength of the RCL-H fiber composite boards as indicated in (Table 18) was better than the control board (1.85 ± 0.34 MPa). The optimum result in tensile strength (2.35 ± 0.22 MPa) and elongation at break (12.03 ± 2.15) was obtained in sample 2 (10 percent PF) of RCL-H composite but stitch tear strength of the control board had better value (45.21 ± 11.33) than all the RCL-H composites. Sample 3 (20 percent PF) and sample 4 (30 percent PF) had better flexing values of (2.44 ± 0.02 and 2.24 ± 0.14 respectively) which is greater than the value of the control. Except Sample 2 (10 percent PF) all samples meet water absorption requirement for industrial use (i.e. minimum 35 percent; SATRA: TM 9:1993).

Table 19: Mechanical properties of recycled leather-sisal (RCL-S) composite boards

Sample no	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
1	100:0	1.85 ± 0.34	12.01 ± 2.61	45.21 ± 11.33	62.41 ± 6.97	83.29 ± 15.27	2.35 ± 0.40
2	90:10	3.39 ± 0.49	14.36 ± 5.20	21.33 ± 0.88	10.74 ± 3.75	78.30 ± 4.68	2.40 ± 0.47
3	80:20	2.63 ± 0.13	10.89 ± 3.51	39.46 ± 3.37	17.02 ± 1.06	76.72 ± 0.16	2.76 ± 0.62
4	70:30	2.37 ± 0.56	11.00 ± 4.92	33.54 ± 1.65	13.5 ± 2.77	83.07 ± 1.97	2.66 ± 0.72
5	60:40	2.87 ± 0.25	16.28 ± 1.00	32.01 ± 4.92	29.24 ± 6.46	74.02 ± 3.39	2.88 ± 0.02

N=4

All of the composite boards of RCL-S mixtures had better tensile strength than that of control board (1.85 ± 0.34 MPa). Among the four different ratios of RCL-S composite

boards, optimum result of tensile strength (3.39 ± 0.49 MPa) was obtained in sample 2 (10 percent PF ratio mixture) whereas elongation at break (16.28 ± 1.00) in sample 5 (40 percent PF). The stitch tear strength of all the composite mixtures, however, was lower than the control board. The water absorption values of the composites were lower even than the standard value for light use footwear (i.e. minimum 35 percent; SATRA: TM 9:1993) (Table 19) It should be noted that, these products can be used for other services like auto interior covers and mouse pads.

Table 20: Mechanical properties of recycled leather-palm (RCL-P) composite boards

Sample No	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
1	100:0	1.85 ± 0.34	12.01 ± 2.61	45.21 ± 11.33	62.41 ± 6.97	83.29 ± 15.27	2.35 ± 0.40
2	90:10	2.60 ± 0.36	14.45 ± 3.61	26.52 ± 3.80	30.90 ± 2.96	77.71 ± 0.22	2.80 ± 0.14
3	80:20	2.66 ± 0.09	17.75 ± 1.50	32.50 ± 3.55	29.65 ± 8.24	75.19 ± 0.98	2.35 ± 0.28
4	70:30	2.74 ± 0.22	9.50 ± 0.80	23.83 ± 1.75	24.45 ± 4.32	82.13 ± 3.08	2.35 ± 0.33
5	60:40	1.99 ± 0.31	11.53 ± 1.62	30.62 ± 2.84	31.00 ± 1.32	77.54 ± 5.28	2.70 ± 0.37

N=4

Table 20 showed that the tensile strength values of all RCL-P composite boards exhibited better results when compared to the control board (1.85 ± 0.34 MPa). From the four proportions of RCL-P composites, sample 4 (30 percent PF) RCL-P composite possessed optimum tensile strength value (2.74 ± 0.22 MPa), whereas the elongation at break value (17.75 ± 1.50) was higher in sample 3 (20 percent PF) ratio. Samples 2 (10 percent PF) and 5 (40 percent PF) composites showed better flexing indexes (2.80 ± 0.14 and 2.70 ± 0.37 respectively) and comparatively better water absorption values (30.90 ± 2.96 and 31.00 ± 1.32 respectively) than those of other composites.

Table 21: Mechanical properties of recycled leather –enset (RCL-E) composite boards

Sample No	LF/P F (percent)	Tensile strength (MPa)	Elongation at break (percent)	stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
1	100:0	$1.85 \pm .34$	12.01 ± 2.61	45.21 ± 11.33	62.41 ± 6.97	83.29 ± 15.27	2.35 ± 0.40
2	90:10	2.91 ± 0.06	27.84 ± 0.82	78.03 ± 18.46	13.70 ± 1.78	68.43 ± 8.95	3.36 ± 0.17
3	80:20	2.65 ± 0.21	17.75 ± 3.38	70.15 ± 8.68	15.79 ± 2.55	70.24 ± 1.63	3.61 ± 0.16
4	70:30	2.78 ± 0.24	19.12 ± 2.07	39.35 ± 5.73	28.96 ± 13.89	66.51 ± 8.74	3.05 ± 0.00
5	60:40	1.91 ± 0.13	14.98 ± 0.83	35.07 ± 6.11	20.18 ± 2.21	55.74 ± 7.49	1.85 ± 0.49

N=4

All RCL-E composite boards have better tensile strength values than RCL control board (Table 21). Out of the four different RCL-E composites, sample 2 (10 percent PF mix) exhibited optimum tensile strength (2.91 ± 0.06 MPa), elongation at break (27.84 ± 0.82) and stitch tear strength (78.03 ± 18.46) followed by sample 3 (20 percent PF) (70.15 ± 8.68 percent). All except sample 5 (40 percent PF mix) of the RCL-E composite boards have better flexing index than the control board.

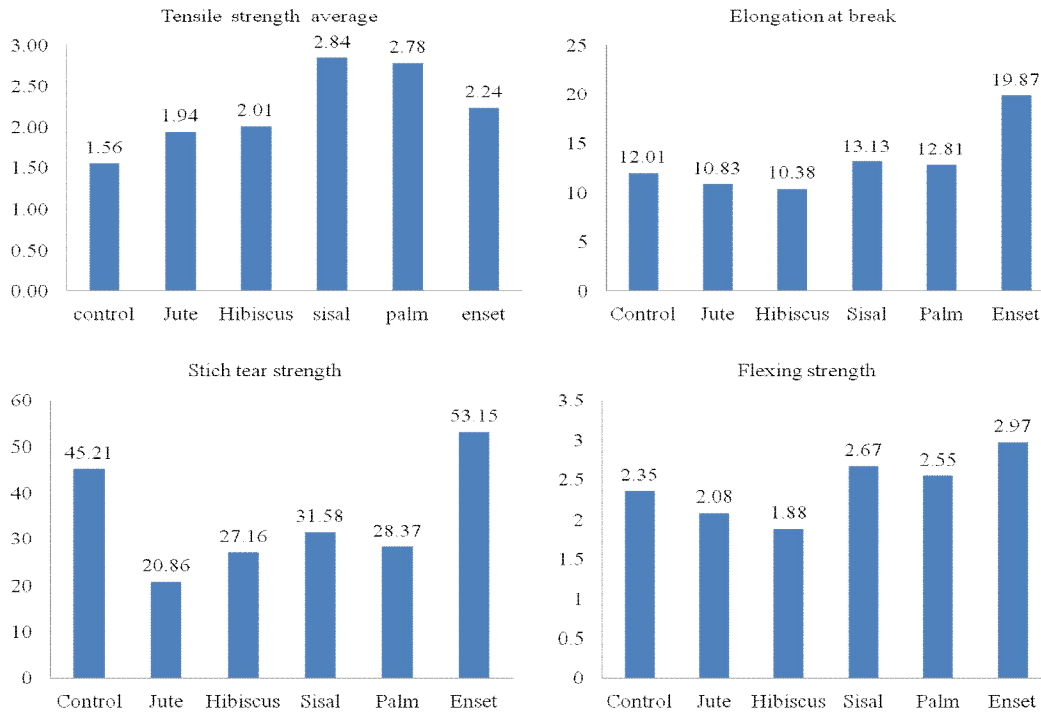


Figure 29: Comparison of the physical properties of composites prepared

As shown in Figure 29, four characteristics i.e., tensile strength, elongation at break, stitch tear strength and flexing strength of the composite boards prepared are compared based on their average values. RCL-S has greater average tensile strength value followed by RCL-P, RCL-E, RCL-H, RCL-J and control; In the case of elongation at break, the values are in decreasing order- RCL-E > RCL-P > RCL-S > control > RCL-J > RCL-H; In case of stitch tear strength, the values observed are in decreasing order i.e., RCL-E > RCL-S > RCL-P > RCL-H > RCL-J; flexing strength values have shown a decreasing order, RCL-E > RCL-S > RCL-P > control > RCL-J > RCL-H. Of all plant fibers RCL-E had better average stitch tear strength value (53.15 N/mm) even than the control (45.21 N/mm).

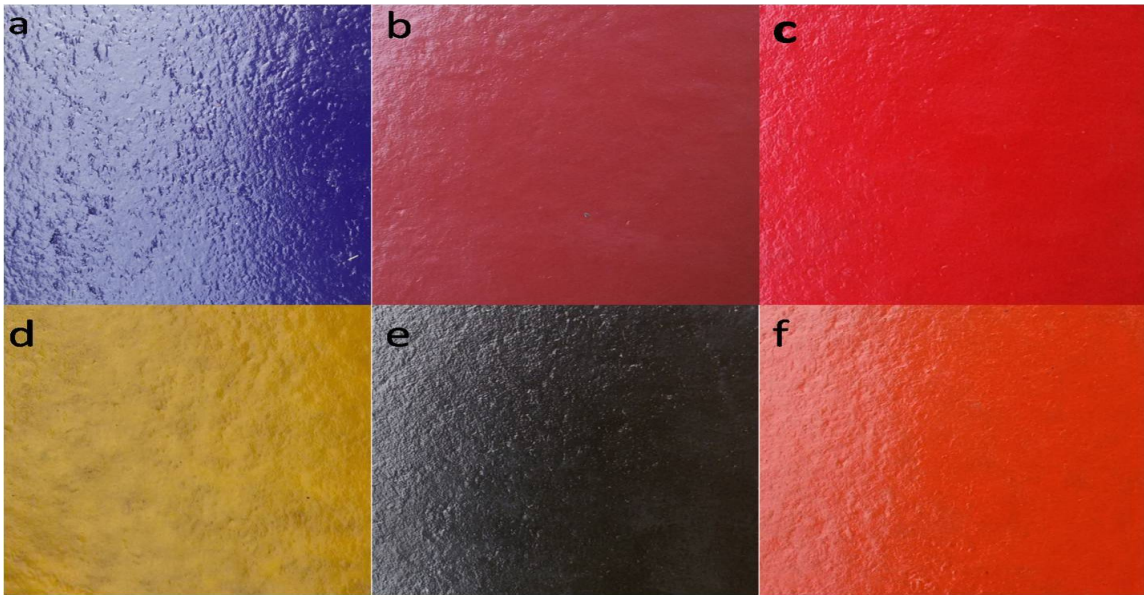


Figure 30: Pictures of finished leather boards made using the different PFs.
 a) Control board; b) RCL-J composite board; c) RCL-H composite board; d) RCL-S composite board; e) RCL-P composite board; and f) RCL-E composite.

As presented in (Figure 30), the pictures show the finished leather boards made using leather fiber with plant fibers of jute, hibiscus, sisal, palm, enset and natural rubber latex as binder. In Figure (30) (a-f), showed the pictures of smooth surfaced finished leather boards comparable to the control. The obtained final product can be used as a value added consumer product.

4.3.2. Surface morphology of composite boards

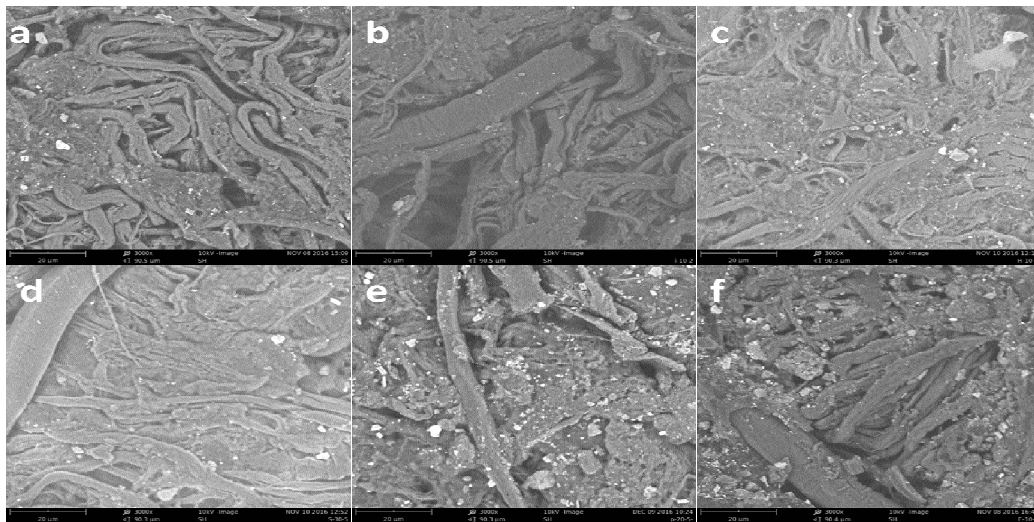


Figure 31: Scanned Electron Microscope Images of Composite Boards
 a) Control; b) RCL-J; c) RCL-H; d) RCL-S; e) RCL-P; f) RCL-E:

Scanning electron microscope

The scanning electron microscope (SEM) images of the samples are shown in [Figure 31](#). [Figure 31\(a\)](#) shows the SEM image of control. In this picture the leather fibers along with the adhesive/binder is seen. The network of fibers adhering with the NRL is clearly seen. The diameter of the individual fibers is more or less the same. This confirms that the composite nature of the leather fiber. The SEM picture of RCL-J reveals the binding of NRL with jute fibers and leather fibers. The width of jute fibers (742 μm) seems to be more than that of RCL fiber (166 μm). In the SEM picture of RCL-H, the micro fibers (766 μm) are clearly seen. The combination of leather and Hibiscus fibers bonded with NRL is apparent. The composite nature of RCL-S (370 μm) is clearly seen. It was looking that the fibers of leather and Sisal are embedded in the NRL. The porosity also seems to be less in this composite. The SEM picture of RCL-P reveals the blend of leather and palm fibers along with NRL. Porosity of composite is visible. In the RCL-E composite the micro fibers (324 μm) are seen as a bundle. In the fibers of enset, a beautiful blend of leather, enset and NRL is seen and porous nature of the composite is also clear.

4.3.3. Fourier transform infrared studies of composite of boards

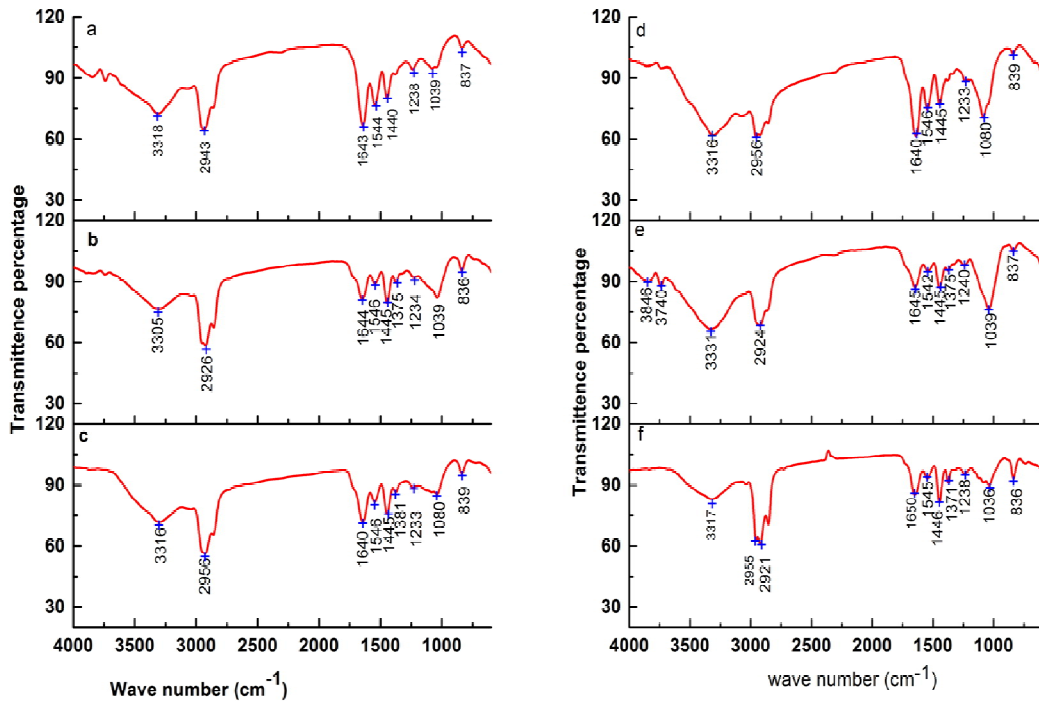


Figure 32: FTIR results of RCL-plant fibers composite boards:
a) Control; b) RCL-J; c) RCL-H; d) RCL-S; e) RCL-P; and f) RCL-E:

Fourier transforms infrared studies

The Fourier transform infrared (FTIR) spectra for the samples are shown in (Figure 32). The FTIR spectrum of control board shows the amide bonds of collagen fibers at 1643, 1544 and 1238 cm^{-1} representing amide I, II and III respectively. Strong absorption between 3600-3200 cm^{-1} region results from superimposed -OH and NH_3^+ stretching bands. A strong and sharp peak is observed at 2933 cm^{-1} representing C-H of rubber latex. A broad peak around 1080-1000 cm^{-1} represent bonded -OH groups in the sample. FTIR spectra of RCL-J composite sample shows a broad peak from 1038-1670 cm^{-1} representing C-O-C and C-O stretch (primary and secondary hydroxide groups) and bonds belonging to the glucoside linkage. The peak at 1445 cm^{-1} in this spectrum represents H-CH and O-CH in plane bending vibration. The peak at 1228 cm^{-1} represents -C-H bending at C-6 in the cellulose molecular structure. The FTIR spectrum of RCL-H shows similar trend to the RCL-J composite in (Figure 32) (b, c). However, it can be seen

in the plane -CH bending at 1374 cm^{-1} . In the spectra of RCL-S, RCL-P and RCL-E in (Figure 32) (d, e, and f) show more or less similar pattern.

4.3.4. Thermo gravimetric analysis studies of composite of boards

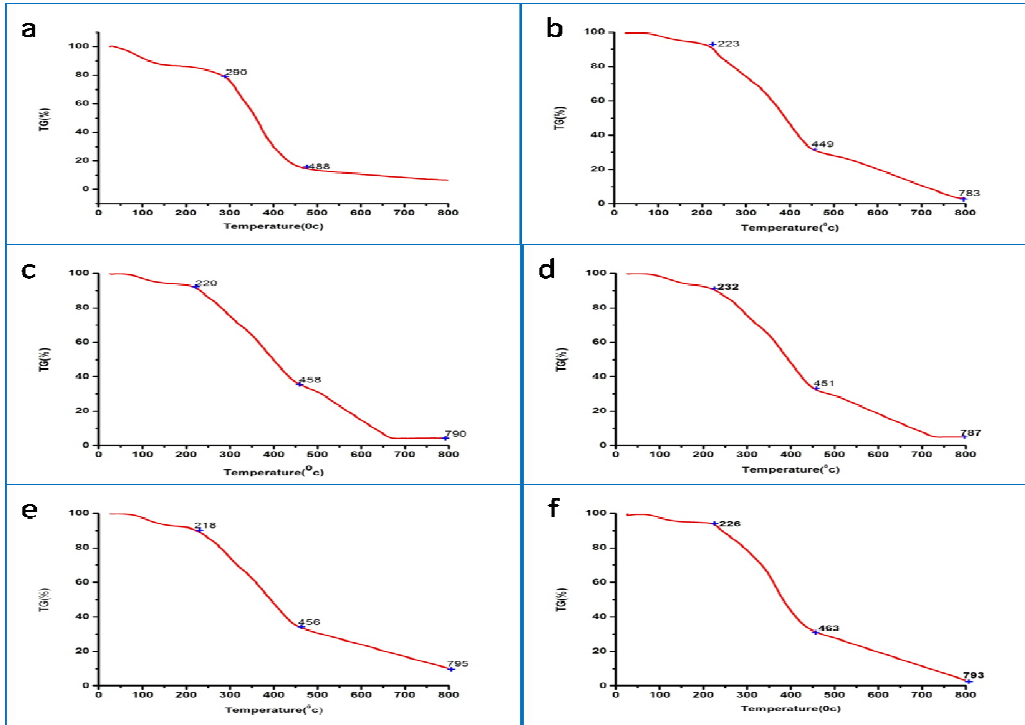


Figure 33: Thermo gravimetric analysis of RCL plant fiber composite samples a. Control; b. RCL-J; c. RCL-H; d. RCL-S; e. RCL-P and f. RCL-E

Thermo gravimetric analysis studies

The thermo gravimetric analysis (TGA) reveals loss of the weight of materials with the increase in temperature. In the present study, samples of the control and composite boards were subjected to TGA from $32\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$. In the control, a two step weight loss measured Figure (33a). The first weight loss (20 percent) was occurred up to $290\text{ }^{\circ}\text{C}$, this is due to loss of free water and bound water in the sample. The second major weight loss (63 percent) occurred between $290\text{ }^{\circ}\text{C}$ and $488\text{ }^{\circ}\text{C}$, this weight loss is due to the protein/collagen degradation in the sample. Around 6.4 percent of the residue was observed at $800\text{ }^{\circ}\text{C}$.

In the case of sample RCL-J [Figure 33\(b\)](#) a three step weight losses have occurred. The initial weight loss (9 percent) up to 223 °C is due to the loss of water molecules in the sample. The second major weight loss (63 percent) that has occurred up to 449 °C is due to protein and cellulose degradation. The third weight loss (26 percent) up to 800 °C may be due to decomposition of degraded products. Compared to the leather control board no sudden degradation was observed in the RCL-J. RCL-H, RCL-S, RCL-P and RCL-E [Figure 33\(c, d, e & f\)](#) samples exhibited more or less the similar thermo gravimetric pattern. However, a residue of 10.3 percent was observed in the case of RCL-P. This may be due to the more lignin content in the palm plant fiber.

4.3.5. Differential scanning calorimeter studies of composite boards

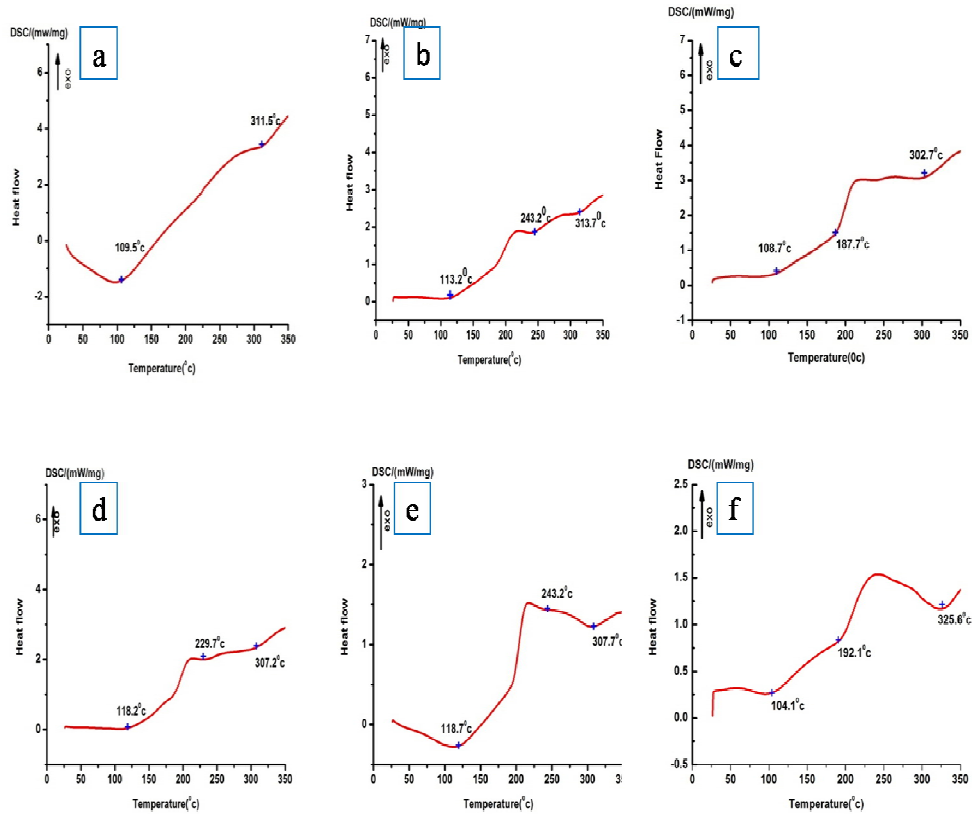


Figure 34: DSC thermograms of RCL composites: a) Control; b). RCL-J; c) RCL-H; d) RCL-S; e) RCL-P and f) RCL-E

Differential Scanning Calorimeter Studies

The DSC thermo gram control sample [Figure 34\(a\)](#) exhibited two endothermic peaks, initial endothermic peak (T_{m1}) appears at 109.5°C and another peak (T_{m2}) appears at 311.5°C . The initial endothermic peak may be due to bound water molecules present in the control sample and the other melting peak (T_{m2}) is related to denature of leather structure in the control sample.

We have incorporated different percentage of fiber contents in the composite board making process like jute, hibiscus, sisal, palm and enset, and studied their DSC thermogram. The thermograms of Hibiscus and Enset showed three endothermic transition temperatures. For RCL-H the initial endothermic peak (T_{m1}) appears at 108°C . This endothermic value is less than the control (109.5°C) and in the other two (T_{m2} and T_{m3}) endothermic transitions have lower values (187.7°C and 302.7°C) respectively than the control been observed [Figure 34\(c & f\)](#). However, better values at T_{m3} (325.7°C) was observed for RCL-enset sample. As shown in [Figure 34\(b, d, and e\)](#) the endothermic values of other fibers (RCL-J, RCL-S, and RCL-P) have higher (T_{m1}). The second and third endothermic peak values of those RCL composites are also shifted to higher temperatures because of the structural heterogeneity of leather and residual tanning materials that can induce the interactions between fibers and the leather.

4.4. Preparation of Composite Sheet Using Resin and Poly Urethane Binders

The evaluation approaches of composite sheets are presented in the next sections;

4.4.1. Mechanical properties of composite sheet using resin and polyurethane binders

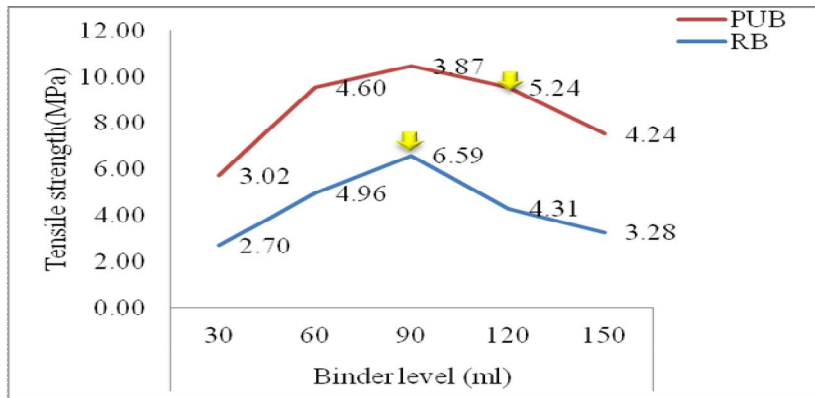


Figure 35: Standardizing of Poly urethane binder and resin binder

As presented in Figure 35, optimum values in tensile strength (TS) of both binders i.e., resin binder (RB) and poly urethane binder (PUB) were obtained at the levels of 90 and 120 ml (in weight/volume ratio) respectively, and these values were taken as reference to prepare controls as well as other composite sheets.

Table 22: Mechanical properties of leather fiber-hibiscus (LF-H) composite sheets

Sample No	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
Hibiscus							
1. RB	100:00	6.05±0.57	5.73±0.23	52.63±0.89	103.37±1.56	73.65±2.34	0.15±0.00
2. RB	90:10	8.25±1.48	8.33±0.33	49.82±0.02	65.16±1.06	74.62±0.57	3.02±2.08
3. RB	80:20	7.00±0.04	9.12±1.10	53.59±0.67	78.27±0.22	82.28±0.99	0.15±0.00
4. RB	70:30	6.14±0.71	7.40±0.08	46.99±0.14	92.17±0.98	72.03±3.09	0.83±0.68
5. RB	60:40	8.08±0.21	8.06±1.65	90.43±0.36	76.50±1.52	70.05±3.31	0.68±0.32
1. PUB	100:00	6.25±0.24	12.34±0.16	43.82±0.35	71.44±4.74	86.10±1.65	1.61±0.17
2. PUB	90:10	3.77±0.42	2.84±0.23	51.37±0.69	86.43±3.81	76.62±3.35	0.61±0.06
3. PUB	80:20	4.91±1.39	4.45±0.63	37.46±0.35	105.82±3.23	76.25±2.69	0.9±0.08
4. PUB	70:30	4.66±0.03	4.02±0.46	58.62±0.37	96.79±2.80	70.11±2.15	0.15±0.06
5. PUB	60:40	5.41±0.30	3.95±0.08	47.59±0.29	95.61±2.53	77.13±0.89	0.25±0.11

N=4; RB=Resin binder; PUB=Polyurethane binder

As presented in Table 22, composite sheets of LF-H were prepared using two different synthetic binders (RB and PUB) with their optimum respective tensile strength values of (8.25±1.48 and 5.41±0.30 MPa). All composite sheets prepared using RB showed better tensile strength values than their respective controls, however, sample 2 (8.25±1.48 MPa) has shown optimum values. But, composite sheets prepared using PUB showed lower

tensile values than their respective control, sample 5 (20 percent PF) (5.41 ± 0.30 MPa) has shown better values in this group. This observation implies that PUB might not be contributing much to the tensile strength of composite sheets, however in RB treated composite sheets the polymer seems to be more compatible and adhesive in nature to both PF and LF. The tensile strength values in most of these composite sheets prepared in this study did meet the required standard set by Central Leather Research Institute shoe design and development center (CLRI-SDDC) (4.0–7.0 MPa) for the insole/shank sheet of footwear as per the SATRA TM2: 1995 test method because their value is in the range of (4.66 ± 0.03 – 8.25 ± 1.48 MPa) except in the 10 percent plant fiber of PUB which has a tensile strength value of (3.77 ± 0.42 MPa).

Elongation at break of composite sheets prepared using RB showed better values than their respective control but in those prepared using PUB showed lower values their respective controls. The stitch tear strength of composite sheets prepared using RB have higher values than their controls in sample 3 (20 percent PF) (53.59 ± 0.67 N/mm) and sample 5 (40 percent PF) (90.43 ± 0.36 N/mm) with the optimum result being at sample 5 (40 percent PF), whereas in composite sheets prepared using PUB all except sample 3 (20 percent PF) (37.46 ± 0.35 N/mm) do have higher values than their respective controls with the optimum result being at sample 4 (30 percent PF) (58.62 ± 0.37 N/mm).

All water absorption values of composite sheets prepared using RB are lower than their respective controls, however in composite sheets prepared using PUB all results are above their respective controls with the optimum value being at sample 3 (20 percent PF). Water desorption properties of composite sheets prepared using RB have higher values in sample 2 (10 percent PF) and sample 3 (20 percent PF) than their respective controls but in those composite sheets prepared using PUB all have lower values than their respective controls. The results of flexing index in all except sample 2 (10 percent PF) (3.02 ± 2.08) of those prepared using RB are lower than their respective controls and did not meet the required standard for foot wear insole manufacturing, this low value might be due to the nature of the binders.

Table 23: Mechanical properties of leather fiber-sisal (LF-S) composite sheets

Sample No	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
Sisal							
1. RB	100:0	6.05±0.57	5.73±0.23	52.63±0.89	103.37±1.56	73.65±2.34	0.15±0.00
2. RB	90:10	4.61±0.68	7.78±0.95	39.87±0.49	92.07±3.19	94.51±2.53	0.44±0.13
3. RB	80:20	5.33±0.95	6.34±0.94	56.35±0.04	92.31±3.86	82.14±2.19	0.52±0.20
4. RB	70:30	8.57±0.85	7.84±0.08	61.92±0.19	97.04±0.71	81.34±0.65	1.08±0.09
5. RB	60:40	9.08±0.91	7.73±1.34	57.69±0.25	99.44±2.45	90.97±0.12	1.94±0.44
PUB							
1. PUB	100:0	6.25±0.24	12.34±0.16	43.82±0.35	71.44±4.74	86.10±1.65	1.61±0.17
2. PUB	90:10	3.71±0.91	4.50±0.71	62.51±0.10	77.32±1.28	117.19±2.76	0.23±0.07
3. PUB	80:20	4.59±0.70	4.06±0.40	37.11±0.04	129.30±0.88	87.96±2.96	0.34±0.16
4. PUB	70:30	6.45±0.78	3.95±0.71	43.02±0.28	106.24±3.54	85.05±1.49	1.03±0.06
5. PUB	60:40	8.02±1.62	4.19±0.58	46.36±0.21	138.67±4.93	88.43±2.45	1.65±0.40

N=4

As presented in Table 23, LF-S composite sheets were prepared using the two synthetic binders (RB and PUB). In the composite sheets prepared using RB sample 4 (30 percent PF) and sample 5 (40 percent PF) with their respective values of (8.57±0.85 and 9.08±0.91 MPa) do have better tensile strength values than their respective controls with their optimum value (9.08±0.91 MPa) seen in sample 5 (40 percent PF). In the composite sheets prepared using PUB sample 4 (30 percent PF) and sample 5 (40 percent PF) with their respective values of (6.45±0.78 and 8.02±1.62 MPa) do show better tensile strength than their controls. This indicates that the plant fibers are contributing to the strength of sheets.

Elongation at break of composite sheets prepared using RB showed better values than their respective controls with their optimum value being in sample 2 (10 percent PF), however in those composite sheets prepared using PUB, all samples exhibited lower values of elongation at break. This difference might be seen due to the difference in the nature of the binders. Stitch tear strength of composite sheets prepared using RB all except sample 2 (10 percent PF) do possess higher values than their respective controls. In the composite sheets prepared using PUB only sample 2 (10 percent PF) and sample 5 (40

percent PF) do have higher value whereas sample 2 has shown optimum value at (10 percent PF).

Water absorption properties of all composite sheets prepared using RB do have lower values whereas in those composite sheets prepared using PUB all do have better water absorption properties with the optimum result being in sample 5 (40 percent PF). Water desorption properties of all composite sheets prepared using RB do have better value than their respective controls with the optimum being in sample 2 (10 percent PF). In those composite sheets prepared using PUB all except sample 4 (30 percent PF) do have better water desorption properties, however, optimum value was observed in sample 2 (10 percent PF). Flexing index value of all composite sheets prepared using RB do have better values than their controls but in those composite sheets prepared using PUB all except sample 5 (40 percent PF) do have lower values of flexing index than their respective controls.

Table 24: Mechanical properties of leather fiber (LF-E) composite sheets

Sample No	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
Enset							
1. RB	100:0	6.05±0.57	5.73±0.23	52.63±0.89	103.37±1.56	73.65±2.34	0.15±0.00
2. RB	90:10	3.68±0.38	6.67±1.57	32.73±0.72	80.02±2.49	82.34±2.10	0.69±0.04
3. RB	80:20	4.24±2.14	5.39±2.43	41.66±0.70	88.61±3.32	89.24±2.40	1.22±0.24
4. RB	70:30	5.92±0.23	7.45±0.64	39.92±0.69	93.51±0.25	79.64±1.87	1.46±0.14
5. RB	60:40	5.43±0.36	5.84±0.54	48.28±0.36	106.25±0.80	90.44±3.62	1.35±0.15
1. PUB	100:0	6.25±0.24	12.34±0.16	43.82±0.35	71.44±4.74	86.10±1.65	1.61±0.17
2. PUB	90:10	2.98±0.01	4.45±0.35	24.16±0.42	134.77±0.20	84.21±2.56	0.93±0.05
3. PUB	80:20	4.24±2.14	5.39±2.43	26.80±1.08	85.89±0.03	83.79±3.06	2.58±1.43
4. PUB	70:30	1.84±0.58	2.06±0.23	33.91±0.20	103.36±2.52	81.93±1.50	1.27±0.25
5. PUB	60:40	3.71±0.57	2.67±0.78	44.11±0.71	105.72±2.18	82.28±2.74	1.38±0.17

N=4

Composite sheets of LF-E are prepared using RB and PUB. In all of the sheets prepared the tensile strength values of the composites are lower than their respective controls (Table 24), with the optimum value for RB being in sample 4 (30 percent PF) and for PUB in

sample 3 (20 percent PF). The elongation at break values of composite sheets prepared using RB are better than their respective controls except in sample 3 (20 percent PF) with sample 4 (30 percent PF) exhibiting the optimum value. In composite sheets prepared using PUB all do have lower values of elongation at break than their respective controls, sample 3 (20 percent PF) has shown optimum value. Stitch tear strength values of all composite sheets prepared using RB do have lower values than their respective controls and all except sample 5 (40 percent PF) of those prepared using PUB also do have lower values than their respective controls.

Concerning the water absorption properties of the composites all except sample 5 (40 percent PF) of those prepared using RB do have lower values than their respective controls but in composites prepared using PUB all do have better water absorption values than their controls. The water desorption properties of composites prepared using RB do have better values than their respective controls but in those composites prepared using PUB all do have lower values than their respective controls.

Flexing is another characteristic taken in to consideration. So, in all composite samples prepared using RB they do have better flexing values than their respective controls, however in those composite samples prepared using PUB all except sample 3 (20 percent PF) exhibited lower values than their controls. In all the composites whether control or other composites, the flexing properties don't meet the required standard for insole making this might be due to the nature of the plant fibers is compatible with the that of PF used in this experiment.

Table 25: Mechanical properties of leather fiber-jute (LF-J) composite sheets

Sample No	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
Jute							
1. RB	100:0	6.05±0.57	5.73±0.23	52.63±0.89	103.37±1.56	73.65±2.34	0.15±0.00
2. RB	90:10	5.82±0.69	6.34±1.25	73.86±0.25	60.29±1.06	88.87±3.30	1.32±0.60
3. RB	80:20	5.98±1.26	8.28±0.71	55.73±0.36	78.80±34	75.62±0.40	1.60±0.19
4. RB	70:30	5.37±0.10	7.06±0.40	45.08±0.16	90.78±1.04	73.92±0.90	1.79±0.24
5. RB	60:40	5.21±0.76	5.28±0.40	54.97±0.76	82.12±2.15	67.98±1.24	1.65±0.22
PUB							
1. PUB	100:0	6.25±0.24	12.34±0.16	43.82±0.35	71.44±4.74	86.10±1.65	1.61±0.17
2. PUB	90:10	5.17±0.28	4.23±0.16	51.38±0.70	104.81±1.82	68.76±1.17	1.15±0.13
3. PUB	80:20	4.15±0.37	3.84±0.08	50.94±1.56	102.99±0.33	70.09±2.67	1.08±0.11
4. PUB	70:30	4.98±0.87	5.06±0.08	38.17±1.08	100.65±2.75	74.26±0.62	1.56±0.30
5. PUB	60:40	4.45±0.25	4.17±0.08	56.35±0.86	85.51±1.04	96.00±2.28	1.15±0.13

N=4

As shown in Table 25, LF-J composite sheets are prepared using RB and PUB like the others. In these composites all the experimental samples have shown lower values of tensile strength than their respective controls with the optimum value of being (5.98±1.26 MPa) in sample 3 (20 percent PF) for RB and (5.17±0.28 MPa) in sample 2 (10 percent PF) for PUB. Concerning the elongation at break composite sheets prepared using RB all except sample 5 (40 percent PF) exhibited better values than their respective controls. The stitch tear strength of composite sheets prepared using RB all except sample 4 (30 percent PF) do have better value. Composite sheets prepared using PUB have also shown better values except in sample 4 (30 percent PF).

All composite sheets made using RB do have lower values of water absorption than their respective controls whereas those composite sheets prepared using PUB do have better values than their respective controls this difference might arise due to binder difference. The water desorption properties of the composite sheets prepared using RB all except sample 5 (40 percent PF) do possess better values than their respective controls however in those composite sheets prepared using PUB all except sample 5 (40 percent PF) do possess lower values than their controls. Flexing index of composite sheets prepared using

RB have higher values than their respective controls, but in those composite sheets prepared using PUB all do have lower values than their respective controls.

Table 26: Mechanical properties of leather fiber- palm (LF-P) composite sheets

Sample No	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
Palm							
1. RB	100:0	6.05±0.57	5.73±0.23	52.63±0.89	103.37±1.56	73.65±2.34	0.15±0.00
2. RB	90:10	8.08±1.43	10.45±1.73	71.06±0.17	68.80±0.35	82.75±3.41	2.13±0.33
3. RB	80:20	7.46±0.76	10.01±0.78	62.01±0.36	83.96±1.81	83.24±0.91	3.00±0.31
4. RB	70:30	3.24±0.52	4.12±0.47	30.72±1.03	103±1.28	56.85±0.26	1.21±0.11
5. RB	60:40	4.95±1.02	7.67±1.57	52.93±0.62	102.55±2.65	52.64±2.17	1.92±0.11
PUB							
1. PUB	100:0	6.25±0.24	12.34±0.16	43.82±0.35	71.44±4.74	86.10±1.65	1.61±0.17
2. PUB	90:10	3.91±0.24	3.89±0.47	30.95±0.86	100.56±3.43	85.89±1.44	1.36±0.17
3. PUB	80:20	4.31±0.23	3.73±0.54	32.78±0.35	130.72±1.08	69.42±2.60	1.17±0.15
4. PUB	70:30	5.87±1.34	7.56±1.34	49.92±0.86	107.45±1.09	62.20±2.22	1.69±0.01
5. PUB	60:40	4.24±0.01	3.78±0.62	35.22±0.70	157.18±2.35	59.36±1.15	1.30±0.14

N=4

Composite sheets of LF-P were prepared using RB and PUB (Table 26). Among the composite sheets prepared using RB only sample 2 (10 percent PF) and sample 3 (20 percent PF) have shown better tensile strength than their respective control whereas those sheets prepared using PUB have exhibited lower values of tensile strength than their respective controls. Elongation at break of composite sheets prepared using RB all except sample 4 (30 percent PF) do have better values however, in those composite sheets prepared using PUB all samples possess lower values than their controls with the optimum value of (7.56±1.34 MPa) being at sample 4 (30 percent PF). The stitch tear strength properties of composite sheets prepared using RB all except sample 4 (30 percent PF) do have better values than their respective controls but in those composite sheets prepared using PUB all except sample 4 (30 percent PF) do possess lower value than their respective controls.

Concerning water absorption properties all of the composite sheets prepared using RB do possess lower values than their respective control however in those composite prepared

using PUB all do have better values than their respective controls in both cases all meet the requirement set by CLRI-SDDC to prepare industrial and high quality foot wear (minimum of 35 percent) as per the test method of SASTRA TM9:1993. The water desorption properties of composite sheets prepared using RB sample 2 (10 percent PF) and sample 3 (20 percent PF) do have better values than their respective controls but in those composite sheet prepared using PUB all do have lower values than their respective controls. The flexing strength of composite sheets prepared using RB all do have better values than their respective control and only sample 3 (20 percent PF) meet the requirement needed to prepare light use footwear set by CLRI-SDDC as per the test method of (SASTRA TM3: 1999).

Table 27: Mechanical properties of the pooled data of composite sheets

Sample No	LF/PF (percent)	Tensile strength (MPa)	Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
controls							
RB	100:0	6.05±0.57	5.73±0.23	52.63±0.89	103.37±1.56	73.65±2.34	0.15±0.00
PUB	100:0	6.25±0.24	12.34±0.16	43.82±0.35	71.44±4.74	86.10±1.65	1.61±0.17
Hibiscus							
RB	90:10	8.25±1.48	8.33±0.33	49.82±0.02	65.16±1.06	74.62±0.57	3.02±2.08
PUB	60:40	5.41±0.30	3.95±0.08	47.59±0.29	95.61±2.53	77.13±0.89	0.25±0.11
Sisal							
RB	60:40	9.08±0.91	7.73±1.34	57.69±0.25	99.44±2.45	90.97±0.12	1.94±0.44
PUB	60:40	8.02±1.62	4.19±0.58	46.36±0.21	138.67±4.93	88.43±2.45	1.65±0.40
Enset							
RB	70:30	5.92±0.23	7.45±0.64	39.92±0.69	93.51±0.25	79.64±1.87	1.46±0.14
PUB	80:20	4.24±2.14	5.39±2.43	26.80±1.08	85.89±0.03	83.79±3.06	2.58±1.43
Jute							
RB	80:20	5.98±1.26	8.28±0.71	55.73±0.36	78.80±34	75.62±0.40	1.60±0.19
PUB	90:10	5.17±0.28	4.23±0.16	51.38±0.70	104.81±1.82	68.76±1.17	1.15±0.13
Palm							
RB	90:10	8.08±1.43	10.45±1.73	7.106±0.17	68.80±0.35	82.75±3.41	2.13±0.33
PUB	70:30	5.87±1.34	7.56±1.34	49.92±0.86	107.45±1.09	62.20±2.22	1.69±0.01

As can be seen from the pooled data (Table 27) the tensile strength values of the composite sheets are above their respective controls in Hibiscus using RB, in sisal using both

binders and in palm using RB whereas the rest do have lower results than their respective controls which implies that the plant fibers are not contributing to the strength of the products. Among all of the plant fibers sisal performed better than the others in tensile strength. This indicates that it is contributing better to the tensile strength as compared to the other plants.

Figure 38 shows the images of the raw materials used and products prepared at different level.

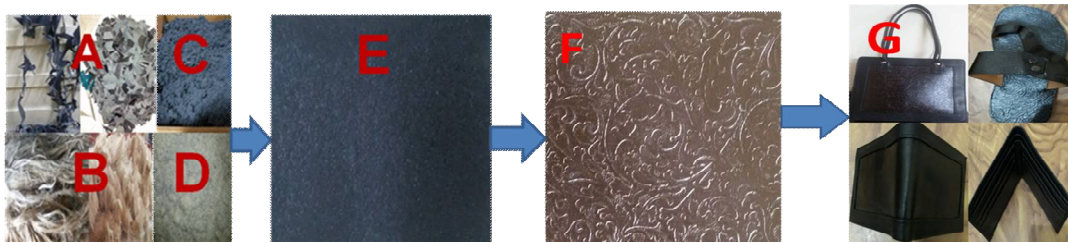


Figure 36: Prepared products.

A. Leather scrap; B. Plant fiber; C. Leather fiber; D. Small sized plant fiber; E. Raw sheet; F. Finished sheet; G. Final products prepared

As presented in Figure 36, the pictures exhibited the raw materials used for the manufacturing process and products prepared i.e. the different fibers used Figure 36 (A-D), raw composite sheet Figure 36 (E) the finished composite sheet Figure 36 (F) and the final products prepared from these composite sheets as major raw material Figure 36 (G). As can be seen from these pictures, the different products (composite sheets) were prepared from leather and plant fiber in combination with the synthetic binders have attractive look and are suitable for consumer use.

4.4.2. Surface morphology of composite sheets

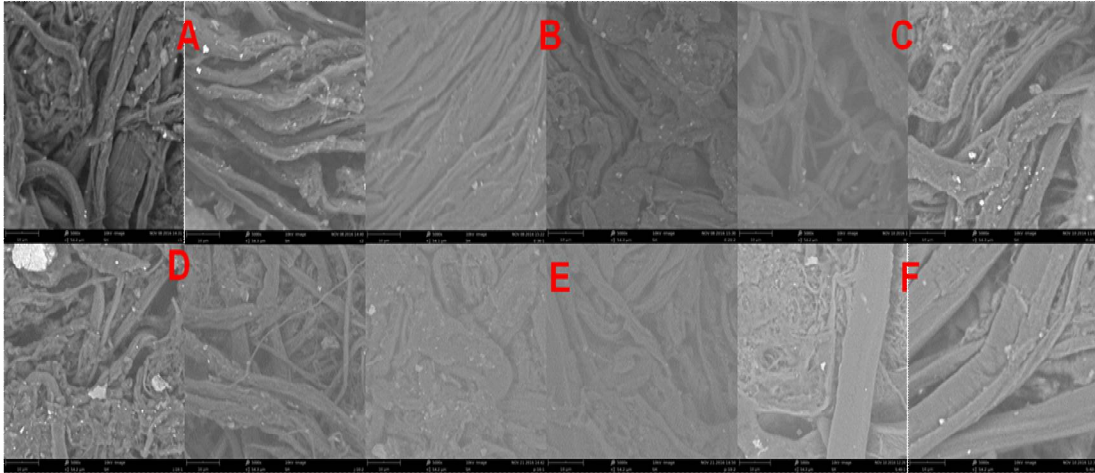


Figure 37: Scanned electron microscope images of composite sheets
A. LF-Cb; B. LF-Eb; C. LF-Hb; D. LF -Jb; E. LF -Pb; and F. LFS-Sb

Scanning Electron Microscope

The SEM images of sampled composite sheets are shown in Figure 37 and this 37 (A) indicates the SEM image of the sheet made from leather fiber as control (LF-Cb) (112 μm). In this image the network of leather fiber adhering with binder is clearly seen. This confirms that the composite nature of the leather fiber. The diameter of individual fibers is more or less same.

The SEM image of LF-Eb shown in Figure 37 (B) reveals the binding nature of the binder with leather and inset fibers. The width of inset fiber (129 μm) seems to be more than that of the control (112 μm). The composite nature of this sample is evident. In SEM image of LF-Hb as shown in Figure 37 (C), with its fiber width of (120 μm) is clearly seen. This shows that the combination of leather and hibiscus fiber with binder is obvious. As seen in Figure 37 (D), width of the LF-Jb is (139 μm). In the LF-Pb of Figure 37 (E) SEM image, it looks that the fiber is well-established in the binder with its width of (129 μm). In LF-Sb image of Figure 37 (F), it is observed that the fiber is well embedded with the binder and it seems less porosity of the composite.

4.4.3. Fourier transform infrared studies of composite sheets

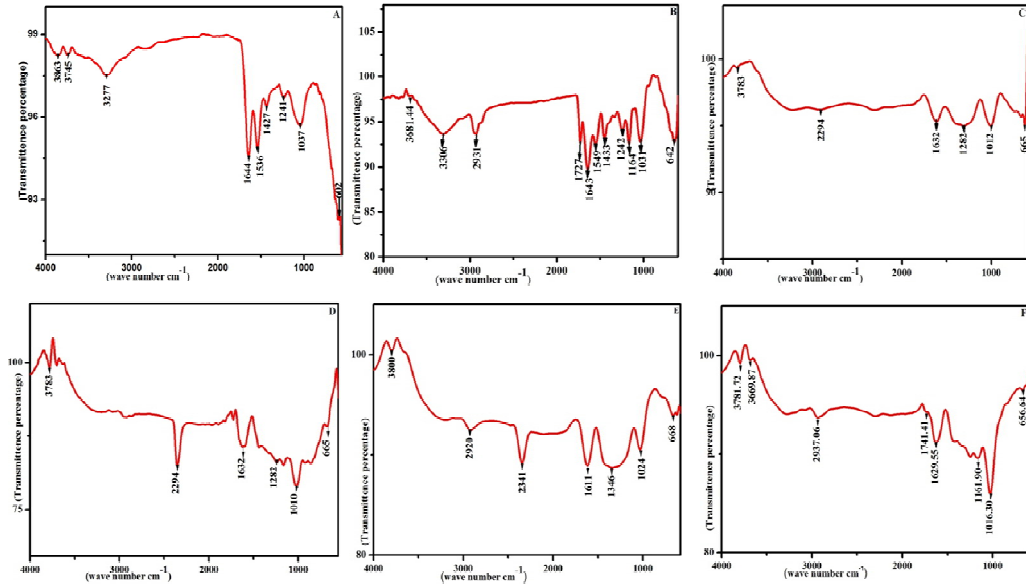


Figure 38: FTIR results of Leather-plant fibers composite sheets using two synthetic binders. A. control; B. Enset; C. Hibiscus; D. Jute; E. Palm and F. Sisal

Fourier Transform Infrared Studies

The Fourier transform infrared (FTIR) spectra of the samples prepared in this study are shown in Figure 36. The FTIR spectrum of the control sheet as shown in [Figure 38 \(A\)](#) indicates the amide bands of collagen fibers at 1644 cm^{-1} (amide I), 1536 cm^{-1} (amide II) and 1427 cm^{-1} (amide III). FTIR spectra of LF-Eb composite sample [Figure 38 \(B\)](#) showed a broad peak from $1031\text{--}1727\text{ cm}^{-1}$ representing C-O-C and C-O stretch (primary and secondary hydroxide group). The peak at 1443 cm^{-1} in this spectrum represents H-CH and O-CH in plane bending vibration. The peak at 1242 cm^{-1} represents -C-H bending at C-6 in the cellulose molecular structure.

The FTIR spectrum of LF-Hb composite sample [Figure 38 \(C\)](#) shows a similar trend to LF-Eb composite. However, we can see in the plane C=O stretch bending at 1632 cm^{-1} , in the spectra of LF-Jb; LF-Pb; and LF-Sb [Figure 38 \(D, E & F\)](#), showed more or less similar patterns. The reason for this similarity might be due to the similar nature of cellulose in all the samples representing collagen and cellulose.

4.4.4. Thermo gravimetric analysis studies of composite sheets

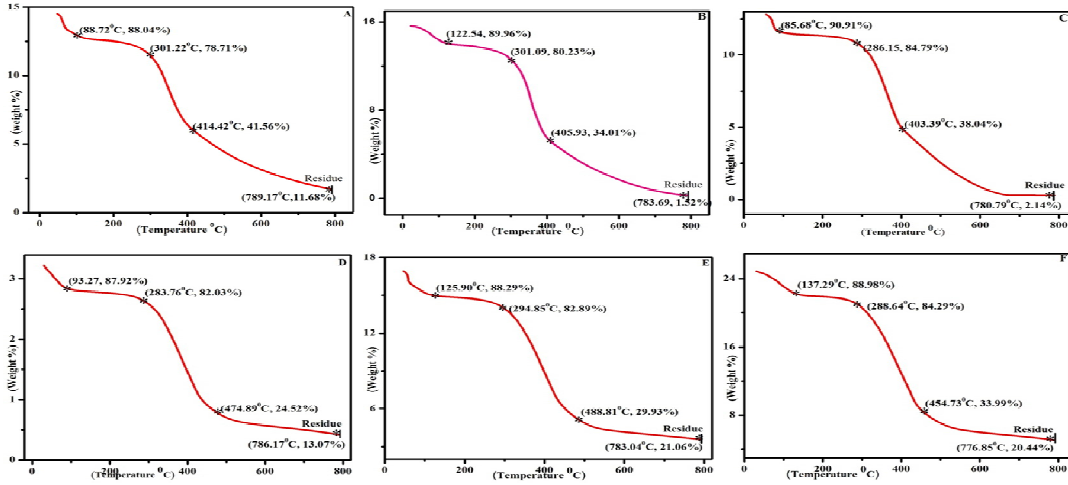


Figure 39: Thermo gravimetric analysis of composite samples A. Control; B. LF-E; C. LF-H; D. LF-J; E. LF-P; and F. LF-S

Thermo Gravimetric Analysis Studies

As shown in Figure 39, the thermo gravimetric analysis (TGA) study revealed weight loss of materials with increase in temperature is inevitable. In this study, samples of control and composite sheets were subjected to TGA from 32 °C to 800 °C. In the control sheet Figure 39 (A), a three step weight loss was observed. The first weight loss (21.29 percent) was due to the loss of free and bound water up to 301.22 °C. The second major weight loss (37.15 percent) up to 414.42 °C was due to collagen degradation in the samples. The final major weight loss (11.68 percent) up to 789.17 °C was due to decomposition of degraded products.

In the case of LF–Eb Figure 39 (B), three step weight losses have been occurred. The initial weight loss (12.02 percent) up to 179.50 °C is due to the loss of water molecules in the sample. The second major weight loss (60.75 percent) that has occurred up to 464.17 °C is due to protein and cellulose degradation. The third weight loss (16.38 percent) which occurred up to 786.85 °C may be due to the decomposition of the degraded products. In composite samples of LF-Hb, LF-Jb and LF-Sb as seen in Figure 39 (C, D, E & F), exhibited more or less the same thermogravimetric pattern.

4.4.5. Differential scanning calorimeter studies of composite sheets

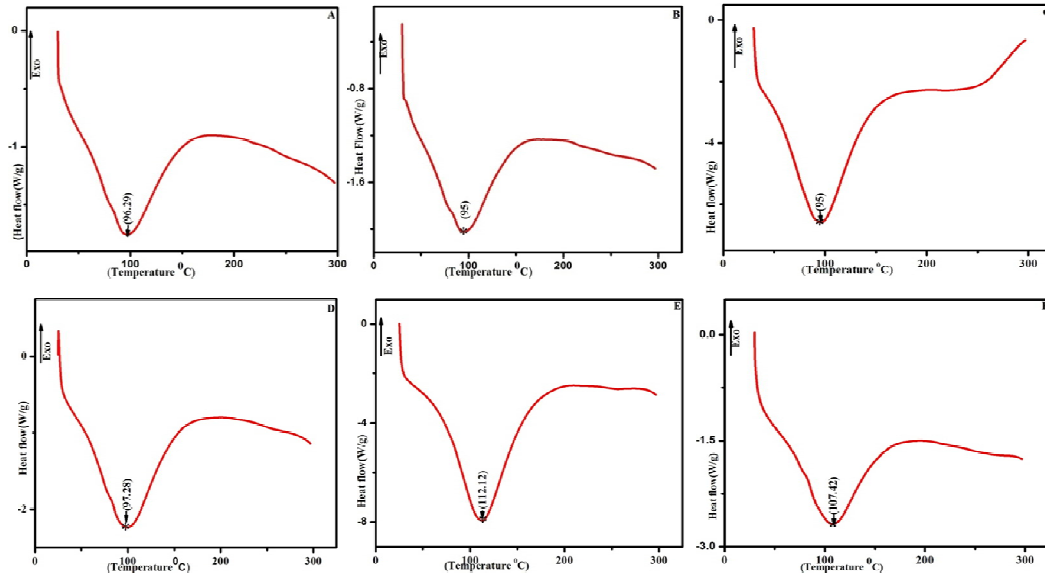


Figure 40: DSC thermograms of RGL composite sheets
A. Control; B. LF-Eb; C. LF-Hb; D. LF-Jb; E. LF-Pb; and F. LF-Sb

Differential scanning calorimeter studies

Differential scanning calorimetry (DSC) is a technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. Only a few mg of material are required to run the analysis.

The DSC thermogram of the control sample in this study as seen in Figure 40 (A) exhibited its peak or melting temperature (T_m) at 96.29°C . This T_m peak is higher than the peaks of composite sheets of B (enset) and C (Hibiscus) peak which do have 95°C each Figure 40 (B and C). But lower than D (Jute), E (Palm) and F (Sisal) each having 97.29 , 112.12 and 107.42°C respectively Figure 40 (D, E and F). The better melting temperature (T_m) for these samples than their respective control could be due to the fact that all the fibers were well dispersed in the leather matrix, so that their melting phase has shifted to higher temperature.

4.5. Preparation of Composite Sheet Using Natural Rubber Latex and Resin Binder

The evaluation methods of composites prepared using natural rubber latex and resin binder are outline as follow;

4.5.1. Mechanical properties of composite sheets using natural rubber latex and resin binder

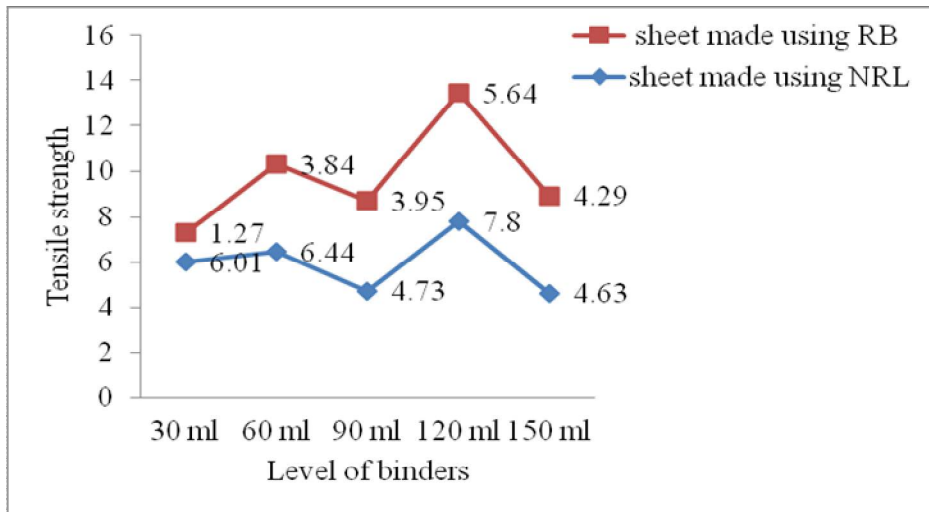


Figure 41: standardization the binders using NRL and RB

As presented in Figure 41, optimum values in tensile strength (TS) of both binders (resin binder and natural rubber latex) were obtained at the level of 120 ml and is taken as reference level to prepare controls as well as other composite sheets prepared.

Table 28: Mechanical property of finished leather scrap-enset (FLS-E) composite sheets

Sample No	LF/PF (percent)	Tensile strength (MPa)		Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
		Dry	Wet					
ENSET								
1- RB*	100:0	7.94±1.15	3.94±0.15	14.78±2.98	89.40±0.55	47.23±4.88	79.56±5.62	3.80±0.00
2- RB	90:10	3.43±1.01	2.37±0.11	7.67±1.57	51.93±0.70	60.02±2.79	78.50±2.57	1.51±0.56
3- RB	80:20	6.01±0.63	2.56±0.45	6.95±0.86	43.82±0.37	76.1±2.71	78.17±3.05	1.58±0.14
4- RB	70:30	4.65±0.99	2.09±0.02	8.06±2.43	45.39±0.37	71.97±2.26	88.69±0.74	1.25±0.12
5- RB	60:40	3.92±1.15	2.60±0.36	5.59±0.55	31.95±0.71	97.08±2.54	81.99±2.23	1.39±0.18
NRL								
1.NRL*	100:0	9.43±2.74	8.65±0.64	15.17±8.56	62.88±0.21	21.27±0.76	77.39±0.40	3.71±0.01
2.NRL	90:10	7.44±0.24	5.89±1.06	27.62±2.75	58.58±0.75	16.49±0.22	78.17±2.57	4.03±0.01
3.NRL	80:20	5.26±0.30	4.49±0.45	22.56±1.26	64.43±0.36	36.94±3.49	74.04±2.20	3.29±0.38
4.NRL	70:30	6.50±0.70	5.59±0.04	21.56±4.40	73.82±0.38	17.96±1.57	77.70±2.18	3.76±0.07
5.NRL	60:40	6.33±1.52	5.84±0.01	15.39±4.64	50.89±0.82	20.39±1.74	73.26±2.40	3.44±0.09

N=4; *RB (Resin binder); *NRL (Natural rubber latex)

Results in (Table 28) showed mechanical properties of controls and composite sheets made from FLS-E fiber mix with RB and NRL binders. The tensile strength values of composite sheets prepared using RB in the dry as well as the in wet condition showed lower values than their respective controls. The tensile strength values of these composite sheets did not meet the required standard set by Central Leather Research Institute shoe design and development center (CLRI-SDDC) (7.0-4.0 MPa) in the wet condition for the insole/shank board of footwear as per the SATRA TM2:1995 test method because their value is in the range of (2.09±0.02-2.60±0.36 MPa). However, this product can serve for other purposes. In the case of composite sheets prepared using NRL, even though, the results are lower than their control, they are fit for insole board making, since all results meet the required standard value (4.49±0.45-5.89±1.06 MPa), with its optimum in sample 2 (10 percent PF) (7.44±0.24 MPa).

Elongation at break values of composite sheets made using RB showed lower values than their respective control, but in case of NRL all do have better values than their respective control. Results of stitch tear strength revealed that sample 2 (10 percent PF) of composite sheets made using RB and all sheets made using NRL do meet the required standard (50-70 N/mm) set by CLRI-SDDC as per the SATRA TM5:2000 test method. In sample 3 (20 percent PF) and sample 4 (30 percent PF) the results are above the value of their

control, this indicates that the plant fiber contributed to the stitch tear strength of the composite sheets and optimum result is seen in sample 4 (30 percent PF).

In their water absorption results, all composite sheets made using RB have better values than their control and all meet the standard values required for insole board making but in composite sheets made using NRL except sample 3 (20 percent PF) all including the control did not meet the required standard value which means it is not comfortable if used for insole board as it can't absorb water to the required level and enable to create more moisture inside the shoe. The water desorption values of all composite sheets in both binders are fit for needed product preparation with their optimum values of $(88.69 \pm 0.74$ percent) in sample 4 (30 percent PF) for RB and $(78.17 \pm 2.57$ percent) in sample 2 (10 percent PF) for NRL.

In the case of flexing strength, composite sheet prepared using RB fail to meet the required standard set for insole board by CLRI-SDDC as per (SATRA TM3:1999) test method. All composite sheets prepared using NRL, meet the standard optimum value.

Table 29: Mechanical properties of finished leather scrap-hibiscus (FLS-H) composite sheets

Sample No	LF/PF (percent)	Tensile strength (MPa)		Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
		Dry	Wet					
HIBISCUS								
1- RB	100:0	7.94±1.15	3.94±0.15	14.78±2.98	89.40±0.55	47.23±4.88	79.56±5.62	3.80±0.00
2- RB	90:10	9.21±0.04	2.92±0.14	12.34±0.63	77.21±0.34	58.74±0.64	99.62±0.32	3.01±0.14
3- RB	80:20	5.77±0.66	2.60±0.27	8.90±2.04	76.77±0.29	63.65±3.32	74.74±2.47	1.37±0.37
4- RB	70:30	7.84±1.58	2.54±0.01	11.17±0.86	55.07±0.38	73.72±0.37	74.33±3.54	1.38±0.57
5- RB	60:40	7.26±0.33	2.40±0.03	8.67±0.63	53.68±0.37	66.69±1.07	84.17±1.81	2.05±0.19
NRL								
1-NRL	100:0	9.43±2.74	8.65±0.64	15.17±3.56	62.88±0.21	21.27±0.76	77.39±0.40	3.71±0.01
2-NRL	90:10	7.69±1.70	6.49±0.18	18.51±7.15	84.61±0.37	26.23±1.30	100.17±0.19	3.33±0.03
3-NRL	80:20	7.11±0.78	4.85±0.57	18.06±1.18	50.95±0.43	27.85±0.85	89.96±0.46	3.38±0.08
4- RL	70:30	6.87±0.23	5.87±0.74	13.06±0.40	77.59±0.23	23.80±1.38	82.84±2.93	3.23±0.16
5-NRL	60:40	5.83±1.67	5.75±0.23	9.34±3.15	57.93±1.07	39.89±0.80	79.53±0.28	2.22±0.57

N=4

As presented in (Table 29), FLS-H fiber composite sheets were prepared using synthetic polymer (RB) and natural rubber latex (NRL). In this experiment, the tensile strength of the control is better in NRL (9.43 ± 2.74 MPa) than in the RB (7.94 ± 1.15 MPa). This difference in tensile strength among the controls might be due to the compatibility of the binder to the leather fiber or the nature/quality of the binder. The optimum tensile strengths of the composite sheets (FLS-H) in NRL and RB were (7.69 ± 1.70 MPa) and (9.21 ± 0.04 MPa) respectively. The optimum results in both composite sheets were obtained in sample 2 (10 percent PF) in the dry state. According to the CLRI-SDDC, in wet condition the required tensile strength for industrial and high quality footwear; fashion and comfort footwear; and light use footwear are 7.0;6.0;and 4.0 MPa respectively (as per the SATRA TM2:1995 test method). As per this standard requirement, among the prepared composite sheets, only those made using NRL meet the required tensile strength value for all levels of footwear preparation even though values are lower than the control (8.65 ± 0.64 MPa) but the composite sheets prepared using RB did not meet the required value for any footwear. The tensile strength values of these composite sheets prepared using NRL is lower than their respective control, whereas those prepared using RB exhibited higher values.

The optimum result in elongation at break of composite sheets made using RB (12.34 ± 0.63 percent) is seen in sample 2 (10 percent PF), however, the value is lower than the control sheet (14.78 ± 2.98 MPa). Composite sheets prepared using NRL showed better value (18.51 ± 7.15 percent) in sample 2 (10 percent PF). The stitch tear strength values of all composite the sheets prepared using RB have lower values than those of control (89.40 ± 0.55 N/mm) this means the plant fibers are not contributing to stitch tear strength, however all composite sheets satisfy the required standard for industrial use with the minimum values of (53.68 ± 0.37 N/mm). Except sample 3 (20 percent PF) having its value of (50.95 ± 0.43 N/mm), all composite sheets made using NRL exhibited higher values than those of control. According to the recommendation of CLRI-SDDC, the minimum requirements are (70 N/mm) for industrial and high quality footwear; (60 N/mm) for fashion and comfort footwear; and (50 N/mm) for light use footwear as per the SASTRA TM5: 2000 test method.

The water absorption and desorption requirements for insole board are minimum of 35 and 40 percent respectively. In this respect, all sheets prepared using RB meet the required standard value but in case of NRL except sample 5 (40 percent PF) with its water absorption value of (39.89±0.80 percent), all including the control sheets didn't meet the required standard value for water absorption. The flexing indexes for insole boards according to CLRI-SDDC are 3.70 percent for industrial and high quality footwear; 3.20 percent for fashion and comfort footwear; and 2.70 percent for light use footwear as per the SATRA TM3:1999 test method. The flexing index values for composite sheets made using RB and NRL are 3.80±0.00 percent and 3.71±0.01percent respectively. In the composite sheets all compositions have lower values than those of their respective controls. Only sample 2 (10 percent PF) made using RB exhibited the required standard value for light use footwear. In NRL except sample 5 (40 percent PF), all the composite sheets meet the required standard for fashion and comfort footwear.

Table 30: Mechanical properties of finished leather scrap-jute (FLS-J) composite sheets

Sample No	LF/PF (percent)	Tensile strength (MPa)		Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
		Dry	Wet					
JUTE								
1- RB	100:0	7.94±1.15	3.94±0.15	14.78±2.98	89.40±0.55	47.23±4.88	79.56±5.62	3.80±0.00
2- RB	90:10	7.43±1.41	2.66±0.39	11.23±2.99	70.22±0.71	42.50±1.60	75.24±3.53	2.45±0.34
3- RB	80:20	6.07±0.20	1.78±0.94	8.95±0.86	65.92±0.23	64.88±1.54	70.80±1.46	1.26±0.15
4- RB	70:30	5.06±0.85	2.13±0.16	8.50±0.71	48.92±0.62	71.79±0.08	77.43±2.43	2.82±0.28
5- RB	60:40	6.23±0.90	2.50±0.18	8.95±2.12	58.21±0.68	68.43±2.16	98.76±0.21	2.15±0.29
NRL								
1- NRL	100:0	9.43±2.74	8.65±0.64	15.17±8.56	62.88±0.21	21.27±0.76	77.39±0.40	3.71±0.01
2- NRL	90:10	5.29±1.17	4.06±0.28	11.06±4.79	63.90±0.68	36.24±2.19	85.85±1.32	2.05±0.60
3- NRL	80:20	4.40±0.33	4.69±0.63	4.95±0.08	47.37±0.78	51.34±0.28	72.02±1.70	1.72±0.26
4- NRL	70:30	9.82±0.17	8.12±0.31	16.40±1.49	77.06±0.25	20.79±0.23	77.83±0.78	3.55±0.15
5- NRL	60:40	9.44±1.48	7.53±1.92	11.01±0.63	74.82±0.64	25.59±0.14	95.38±0.21	2.36±0.28

N=4

Table 30 represents data of FLS-J composite sheets. As presented in the Table, all tensile strength values of composite sheets prepared using NRL except sample 4 (30 percent PF) and 5 (40 percent PF) in the dry state, are below their respective control values. All of the

composite sheets made using RB, have no suitable values in the wet condition ranging (1.78 ± 0.94 - 2.66 ± 0.39 MPa) but those sheets made using NRL binder, meet the required standard values ranging from (4.06 ± 0.28 - 8.12 ± 0.31 MPa) in the wet condition. Except, in sample 4 (30 percent PF), with its elongation at break value of (16.40 ± 1.49 percent), all composite sheets made using NRL do have lower values than their controls.

In the case of stitch tear strength values, all composite sheets made using NRL, except sample 2 (10 percent of PF) do possess lower values than their respective controls. However, from quality measurement point of view, all composite sheets meet the required standard set for footwear. From water absorption perspective, all composite sheets prepared using RB meet the required standard (minimum 35 percent as per SATRA TM9:1993) with the optimum values of (71.79 ± 0.08 percent) but in composite sheets made using NRL, sample 2 (10 percent PF) and 3 (20 percent PF) sheets meet the requirement with 20 percent PF being optimum (51.34 ± 0.28 percent). The water desorption property of all the composite sheets in both binders meet the standard value (minimum 40 percent as per SATRA TM9:1993). Flexing strength values of all the composite sheets are below their respective controls. All samples of composite sheets made using RB and all except sample 4 (30 percent PF) of the sheets made using NRL didn't meet the required standard set (2.7- 3.7 percent) as per SASTRA TM3: 1999 test method.

Table 31: Mechanical properties of finished leather scrap-palm (FLS –P) composite sheets

Sample No	LF/PF (percent)	Tensile strength (MPa)		Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
		Dry	Wet					
PALM								
1- RB	100:0	7.94±1.15	3.94±0.15	14.78±2.98	89.40±0.55	47.23±4.88	79.56±5.62	3.80±0.00
2- RB	90:10	8.21±0.59	3.60±0.03	14.56±0.47	66.60±0.38	51.15±0.60	55.60±3.73	3.69±0.26
3- RB	80:20	8.30±0.06	3.66±0.88	16.56±0.78	58.57±0.49	65.10±2.45	80.06±3.38	3.75±0.03
4- RB	70:30	5.82±0.47	1.97±0.55	10.89±2.83	52.51±0.71	87.43±2.60	74.40±2.77	1.90±0.25
5- RB	60:40	6.11±0.00	2.37±0.56	8.00±0.00	51.12±1.22	79.94±1.44	79.78±3.81	2.03±0.25
NRL								
1- NRL	100:0	9.43±2.74	8.65±0.64	15.17±8.56	62.88±0.21	21.27±0.76	77.39±0.40	3.71±0.01
2- NRL	90:10	6.44±0.51	4.63±0.84	24.34±3.77	75.46±0.53	16.11±0.06	83.71±3.04	3.71±0.12
3- NRL	80:20	8.62±0.29	6.21±0.72	26.56±1.41	66.94±0.22	18.98±1.06	66.08±2.82	3.65±0.02
4- NRL	70:30	4.87±0.57	2.96±0.09	13.98±4.55	65.09±0.36	46.73±1.43	64.49±1.68	2.55±0.28
5- NRL	60:40	6.80±0.35	3.46±0.33	22.67±0.78	51.67±1.56	42.87±1.32	75.50±1.88	3.08±0.08

N=4

Table 31 represents the mechanical property values of FLS-P composite sheets. As shown in the table, sample 2 (10 percent PF) in the sheets made using RB has optimum tensile strength value of (8.30±0.06 MPa in dry and 3.66±0.88 MPa in wet) conditions. All composites except sample 2 (10 percent PF) (8.21±0.59 MPa) and 3 (20 percent PF) (8.30±0.06 MPa) in this test showed lower values than those of their control (7.94±1.15 MPa). In the NRL composite sheets, all compositions do possess lower value than the control (9.43±2.74 MPa) in dry condition. In wet condition, composite sheets made using RB didn't meet the standard requirement set by CLRI-SDDC for footwear (insole) but in case of composite sheets prepared using NRL all of them meet the standard requirement even though they are all lower than their control (8.65±0.64 MPa). Therefore, in these sheets, even though both binders do show reasonable values in the dry condition, only NRL is suitable for preparing the footwear accessory products (insole).

Concerning the elongation at break property of composite sheets, sample 3 (20 percent PF) prepared using RB do possess (16.56±0.78 percent). In the sheets made using NRL all except sample 4 (30 percent PF) (13.98±4.55 percent) do have better values than those of their respective controls. The stitch tear strengths values of all composite sheets meet the

required standard for footwear. In the composite sheets made using RB, the results are lower than their respective control (89.40 ± 0.55 N/mm) but in those sheets prepared using NRL, all except sample 5 (40 percent PF) (51.67 ± 1.56 N/mm) do have better values than their respective control (62.88 ± 0.21 N/mm).

Water absorption of all composite sheets prepared using RB showed better values than their control and satisfies the requirement set by CLRI-SDDC (35 percent minimum) for insole board preparation. However, sheets prepared using NRL except sample 4 (30 percent PF) (46.73 ± 1.43 percent) and 5 (40 percent PF) (42.87 ± 1.32 percent), including the control did not meet the set standard requirement. Water desorption properties of all composite sheets made using both binders meet the standard requirement set by CLRI-SDDC (minimum 40 percent). Composite sheets prepared using RB showed optimum

Water desorption value of (80.06 ± 3.38 percent) and is above the control at sample 3 (20 percent PF), whereas in NRL optimum value (83.71 ± 3.04 percent), which is above the control is registered in sample 2 (10 percent PF). All flexing strength values of composite sheets in both binders are lower than their controls. Only Samples 2 (10 percent PF) and 3 (20 percent PF) made using RB meet the flexing strength requirement. All the composite sheets prepared using NRL, except sample 4 (30 percent PF) (2.55 ± 0.28 MPa) meet the required flexing strength value for footwear insole board manufacturing.

Table 32: Mechanical properties of finished leather scrap-sisal (FLS –S) composite sheets

Sample No	LF/PF (percent)	Tensile strength (MPa)		Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
		Dry	Wet					
SISAL								
1- RB	100:0	7.94±1.15	3.94±0.15	14.78±2.98	89.40±0.55	47.23±4.88	79.56±5.62	3.80±0.00
2- RB	90:10	4.62±0.00	7.81±1.17	8.67±0.47	45.58±0.06	72.06±1.58	78.26±0.32	0.80±0.24
3- RB	80:20	3.28±0.35	1.34±0.14	5.67±1.10	33.97±0.07	76.32±2.33	91.17±1.52	0.77±0.37
4- RB	70:30	6.32±1.02	1.46±0.86	8.00±0.31	44.02±0.73	85.87±0.40	83.34±0.34	2.83±0.20
5- RB	60:40	10.23±1.42	3.04±0.40	10.17±0.86	50.77±0.40	74.32±3.37	94.97±3.66	2.20±0.68
NRL								
1- NRL	100:0	9.43±2.74	8.65±0.64	15.17±3.56	62.88±0.21	21.27±0.76	77.39±0.40	3.71±0.01
2- NRL	90:10	5.39±0.66	10.23±1.42	33.23±6.13	70.14±0.04	17.76±3.61	156.01±7.11	3.46±0.09
3- NRL	80:20	6.02±0.23	5.05±0.10	24.23±1.73	77.95±0.05	29.69±2.48	78.41±3.11	3.42±0.12
4- NRL	70:30	9.02±0.16	5.64±0.09	26.01±0.78	74.87±0.66	37.23±0.38	86.78±2.97	3.72±0.03
5- NRL	60:40	7.81±1.17	5.05±0.59	13.28±2.43	74.83±0.21	31.04±0.45	91.19±3.77	3.41±0.06

N=4

As shown in (Table 32), optimum tensile strength value of FLS-S composite sheets prepared using RB is obtained in sample 5 (40 percent PF) in the dry state and this result (10.23±1.42 MPa) is better than that of control (7.94±1.15 MPa). All composite sheets prepared using NRL showed lower tensile strength values than the control (9.43±2.74 MPa), the optimum value (9.02±0.16 MPa) is seen in sample 4 (30 percent PF). In the wet condition, composite sheets prepared using RB showed optimum tensile strength value (7.81±1.17 MPa), in sample 2 (10 percent PF) and this meets the desired requirement. All tensile strength values of composite sheets prepared using NRL meet the required standard for all levels of footwear. The optimum value (10.23±1.42 MPa) is recorded in sample 2 (10 percent PF) and is better than its control (8.65±0.64 MPa).

Elongation at break of the sheets prepared using RB showed lower values than their respective control (14.78±2.98 percent) with the optimum value of (10.17±0.86 percent) being in sample 5 (40 percent of PF). In case of the composite sheets prepared using NRL, all but sample 5 (40 percent of PF) have better values than their respective control (15.17±3.56 percent). The stitch tear strength values of control are better than those of all the composite boards using RB. However, all the composite sheets prepared using NRL exhibit better results compared to those of control, with sample 3 (20 percent PF) show-

ing optimum stitch tear strength value of $(77.95 \pm 0.05 \text{ N/mm})$. Water absorption values of composite sheets prepared using RB do have better values than their respective control and all meet the required standard for shank/insole board making. Among the composite sheets prepared using NRL, only sample 4 (30 percent PF) satisfy the standard requirement needed for manufacturing of insole board (35 percent minimum), however sample 1 (control), sample 2 (10 percent PF), sample 3 (20 percent PF) and sample 5 (40 percent PF) didn't meet the standard requirement.

In case of water desorption property all prepared samples meet the standard requirement (40 percent minimum). Concerning the flexing strength aspect, all composite sheets prepared using RB do possess lower flexing and didn't meet the required (2.7 -3.7 percent) standard value except sample 4 (30 percent PF) that showed flexing strength of $(2.83 \pm 0.20 \text{ MPa})$ which is suitable for light use footwear insole manufacturing.

Table 33: Comparison of plant fiber having optimum values pooled from all tables

Sample No	LF/PF (percent)	Tensile strength (MPa)		Elongation at break (percent)	Stitch tear strength (N/mm)	Water absorption (percent)	Water Desorption (percent)	Flexing index (percent)
		Dry	Wet					
1.CONTROL								
1.RB	100:0	7.94±1.15	3.94±0.15	14.78±2.98	89.40±0.55	47.23±4.88	79.56±5.62	3.80±0.00
2.NRL	100:0	9.43±2.74	8.65±0.64	15.17±8.56	62.88±0.21	21.27±0.76	77.39±0.40	3.71±0.01
2. ENSET								
1.RB	80:20	6.01±0.63	2.56±0.45	6.95±0.86	43.82±0.37	76.1±2.71	78.17±3.05	1.58±0.14
2.NRL	90:10	7.44±0.24	5.89±1.06	27.62±2.75	58.58±0.75	16.49±0.22	78.17±2.57	4.03±0.01
3.HIBISCUS								
1.RB	90:10	9.21±0.04	2.92±0.14	12.34±0.63	77.21±0.34	58.74±0.64	99.62±0.32	3.01±0.14
2.NRL	90:10	7.69±1.70	6.49±0.18	18.51±7.15	84.61±0.37	26.23±1.30	100.17±0.19	3.33±0.03
4.JUTE								
1.RB	90:10	7.43±1.41	2.66±0.39	11.23±2.99	70.22±0.71	42.50±1.60	75.24±3.53	2.45±0.34
2.NRL	70:30	9.82±0.17	8.12±0.31	16.40±1.49	77.06±0.25	20.79±0.23	77.83±0.78	3.55±0.15
5.PALM								
1.RB	80:20	8.30±0.06	3.66±0.88	16.56±0.78	58.57±0.49	65.10±2.45	80.06±3.38	3.75±0.03
2.NR L	80:20	8.62±0.29	6.21±0.72	26.56±1.41	66.94±0.22	18.98±1.06	66.08±2.82	3.65±0.02
6.SISAL								
1.RB	60:40	10.23±1.42	3.04±0.40	10.17±0.86	50.77±0.40	74.32±3.37	94.97±3.66	2.20±0.68
2.NRL	70:30	9.02±0.16	5.64±0.09	26.01±0.78	74.87±0.66	37.23±0.38	86.78±2.97	3.72±0.03

(Table 33) shows the pooled data of optimum plant fiber composite sheets. As indicated in the above table, by observing the optimum values of the composite sheets from each plant and binder, the tensile strength value in dry condition of FLS-S composite sheet made using RB ranked first with its value of $(10.23 \pm 1.42 \text{ MPa})$ at its (40 percent PF) and this value is better than the value of its control $(7.94 \pm 1.15 \text{ MPa})$ followed by jute $(9.82 \pm 0.17 \text{ MPa})$ prepared using NRL at its (30 percent PF). However, in wet condition Composites prepared using NRL and jute ranked first with its tensile strength value of $(8.12 \pm 0.31 \text{ MPa})$ at (30 percent PF) followed by hibiscus $(6.49 \pm 0.18 \text{ MPa})$ at its 10 percent PF. All composite sheets prepared using NRL have shown very good tensile strength values in the wet condition and all meet the requirement needed for insole board making.

In its elongation at break values, enset ranked first $(27.62 \pm 2.75 \text{ percent})$ at its (10 percent PF) followed by palm $(26.56 \pm 1.41 \text{ MPa})$ at its (20 percent PF) and sisal $(26.01 \pm 0.78 \text{ MPa})$ at its (30 percent PF). All of these results are above their respective controls indicating that the plant fibers are contributing to elongation property of the composite sheets. As seen from the pooled data the optimum values of plant fiber may vary depending on the type of binder used and ratio of the plant. The stitch tear strength of all the composite sheets except 20 percent enset $(43.82 \pm 0.37 \text{ N/mm})$ prepared using RB fulfills the required standard $(70\text{-}50 \text{ N/mm})$ set by CLRI-SDDC; however, all have stitch strength values below their respective control.

The stitch tear strength values of composite sheets made using NRL all except 20 percent of enset $(58.58 \pm 0.75 \text{ N/mm})$ have values above their control and all including the 20 percent of enset meet the required standard set by CLRI-SDDC for insole board making as per the SATRA TM5: 2000 test method . The water absorption values of composite sheets prepared using RB are better than their control and meet the required standard for insole board making. However, the results of composite sheets prepared using NRL all except the 20 percent of sisal don't meet the required standard set by CLRI-SDDC as per the SATRA TM 9: 1993 test method. In water desorption study, all composite sheets prepared using two binders meet the required standard. The flexing strength values of 10

percent enset (4.03 ± 0.01 percent) and 20 percent palm (3.75 ± 0.03 percent) prepared using NRL showed better values than their respective control.

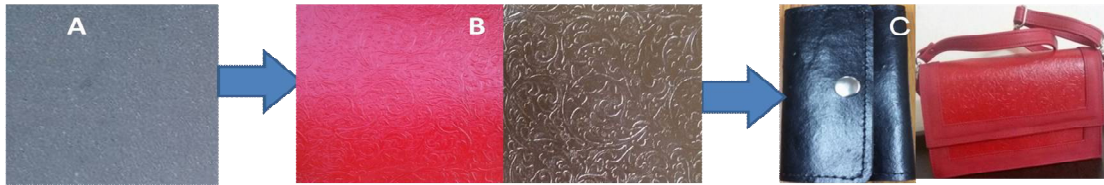


Figure 42: final products of composite sheets

(A) Raw composite sheet, (B) finished composite sheets & (C) final products

Figure 42 exhibits products prepared using the composite boards made in the study. The pictures show raw composite sheet Figure 42 (A), the finished composite sheet Figure 42 (B) and the final products prepared from these composite sheets Figure 42 (C) final products. As can be seen from these pictures, the different products prepared from these composite sheets made of the leather fiber and plant fibers in combination with binders have smooth feel, attractive look and are suitable for consumer service.

4.5.2. Surface morphology of composite sheets

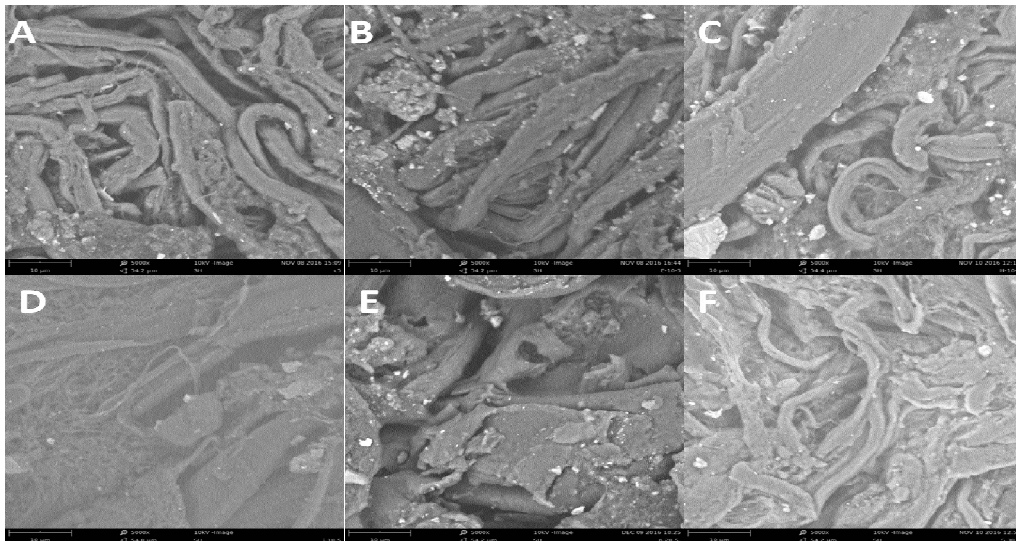


Figure 43: Scanned Electron Microscope Images

A. Control; B. FLS -E; C. FLS -H; D. FLS -J; E. FLS -P; and F. FLS -S

Surface morphology of composites

Scanning electron microscope (SEM) images of the sampled composite sheets are shown in [Figure 43](#). [Figure 43 \(A\)](#) shows the SEM image of the finished leather scrap (FLS) sheet as control. In this image the network of leather fiber adhering with binder is clearly seen. This confirms that the composite nature of the leather fiber. The diameter of individual fibers is more or less same. The SEM image of FLS-E has shown in [Figure 43 \(B\)](#) reveals the binding nature of the binder with leather and enset fibers. The width of enset fiber (82 μm) seems to be more than that of the control sheet (48 μm). The composite nature of this sample is evident. SEM image of FLS-H, as shown in [Figure 43 \(C\)](#), the fiber width of (52 μm) is clearly seen. This shows that the combination of leather and hibiscus fiber with NRL binder is obvious. As seen in [Figure 43 \(D\)](#), width of the FLS-J is (56 μm). In the FLS-P of [Figure 43 \(E\)](#) SEM image, it looks that the fiber is coated with binder. In FLS-S image of [Figure 43 \(F\)](#), it is observed that the fiber is well embedded with the binder and it appears less porosity in the composite. All composite sheets prepared in this experiment exhibited an intermingling of fibers along with the binder with no significant difference among the samples in their SEM images revealing that they have composite nature.

4.5.3. Fourier transform infrared studies of composite sheets

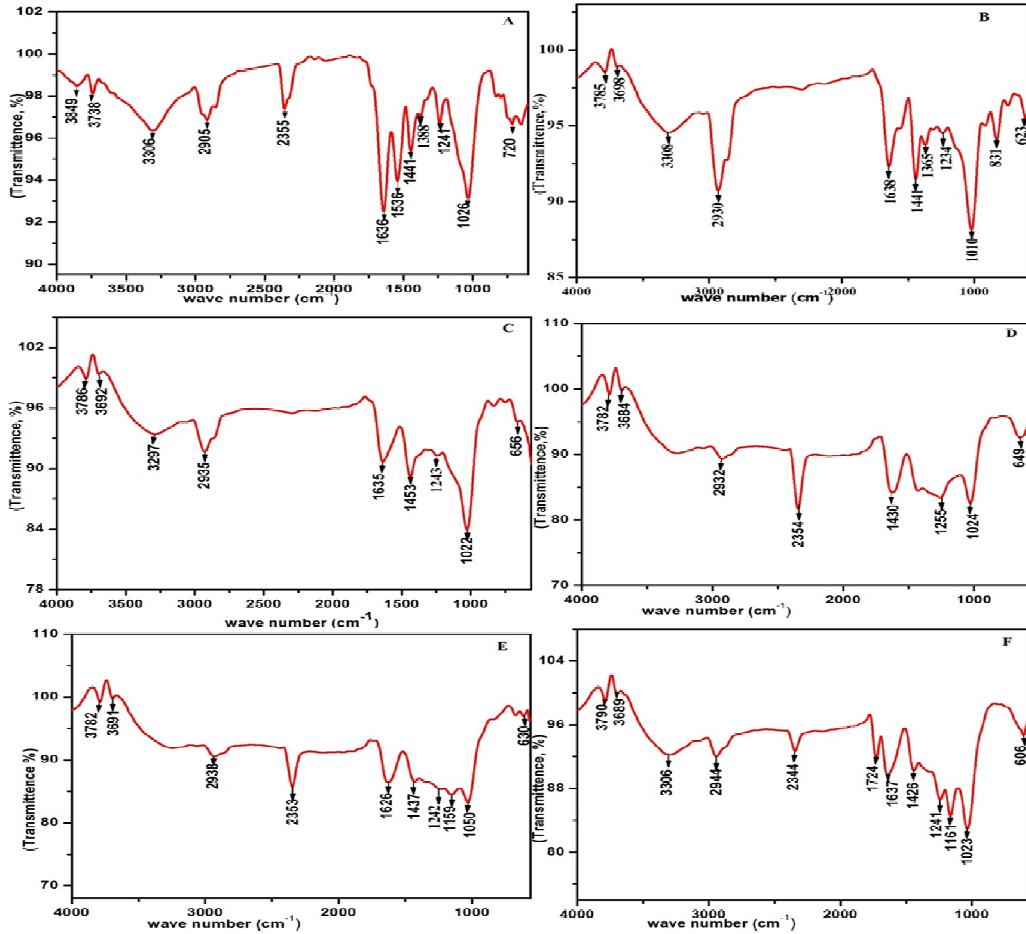


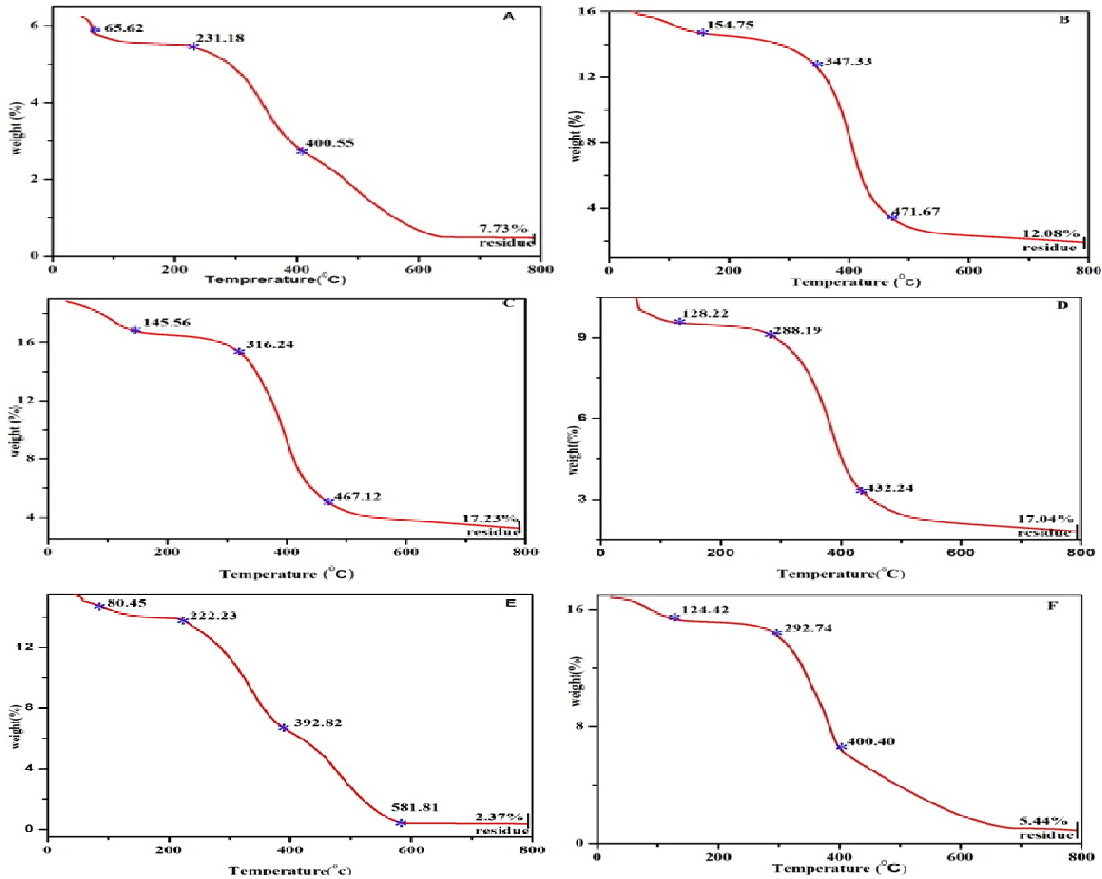
Figure 44: FTIR results of Leather-plant fibers composite sheets
 A. Control; B. FLS -E; C. FLS -H; D. FLS -J; E. FLS -P; and F. FLS -S

Fourier Transform Infrared Studies

The Fourier transform infrared (FTIR) spectra of the samples prepared in this study are shown in Figure 44. The FTIR spectrum of the control sheet as shown in Figure 44 (A) indicates the amide bands of collagen fibers at 1636 cm^{-1} (amide I), 1536 cm^{-1} (amide II) and 1241 cm^{-1} (amide III). Strong absorption bands are seen between $3600\text{--}3200\text{ cm}^{-1}$ region resulting from superimposed -OH and NH_3^+ stretching bands. Sharp peak is observed at 2905 cm^{-1} representing C-H of the rubber latex and a broad peak around $1080\text{--}1000\text{ cm}^{-1}$ showing bonded -OH groups in the sample.

FTIR spectra of FLS-E composite sample [Figure 44 \(B\)](#) shows a broad peak from 1010-1638 cm^{-1} representing C-O-C and C-O stretch (primary and secondary hydroxide group). The peak at 1445 cm^{-1} in this spectrum represents H-CH and O-CH in plane bending vibration. The peak at 1234 cm^{-1} represents -C-H bending at C-6 in the cellulose molecular structure. The FTIR spectrum of FLS -H composite sample [Figure 44 \(C\)](#) is similar to FLS-E composite. However, we can see in-plane CH bending at 1453 cm^{-1} ; in the spectra of FLS-J; FLS-P; and FLS-S [Figure 44 \(D, E & F\)](#), more or less similar pattern is observed.

4.5.4. Thermo gravimetric analysis studies of composite sheets



[Figure 45](#): Thermo gravimetric analysis of composite samples
 A. Control; B. FLS-E; C. FLS-H; D. FLS-J; E. FLS-P; and F. FLS-S

Thermo Gravimetric Analysis Studies of composites

As shown in [Figure 45](#), the thermo gravimetric analysis (TGA) study revealed weight loss of materials with increase in temperature. In this study, samples of control and composite sheets were subjected to TGA from 32 °C to 800 °C. In the control sheet [Figure 45 \(A\)](#), a three step weight loss was observed. The first weight loss (13 percent) was due to the loss of free and bound water up to 231 °C. The second major weight loss (42 percent) up to 400 °C was due to collagen degradation in the samples. The final weight loss (38 percent) was due to decomposition of degraded products. Around 7.7 percent residue was observed at about 800 °C. In the case of FLS-E [Figure 45 \(B\)](#), three step weight losses have been occurred. The initial weight loss (21 percent) up to 347 °C is due to the loss of water molecules in the sample. The second major weight loss (57 percent) that has occurred up to 471 °C is due to protein and cellulose degradation. The third weight loss (9 percent) which occurred up to 800 °C may be due to the decomposition of the degraded products. Residue of 12 percent was also registered in this sample.

In composite samples of FLS-H, FLS-J and FLS-S as seen in [Figure 45 \(C, D, & F\)](#), exhibited more or less the same thermogravimetric pattern. However, residues of 17.23 percent and 17.04 percent were observed in FLS-H and FLS-J respectively. This higher value might be due lignin content present in these plant fibers or mineral fraction. In FLS-P [Figure \(E\)](#), four step weight losses was observed. First weight loss (11 percent) that has occurred up to 222 °C was due to loss of water molecules in the sample. Second weight loss (47 percent) which has occurred up to 392 °C may be due to protein and cellulose degradation. Third weight loss (40 percent) up to 589 °C and fourth weight loss (0.47 percent) up to 800 °C might be due to decomposition of degraded products. Residue of 2.37 percent, the least residue of all samples was also seen in this sample.

4.5.5. Differential scanning calorimeter studies of composite sheets

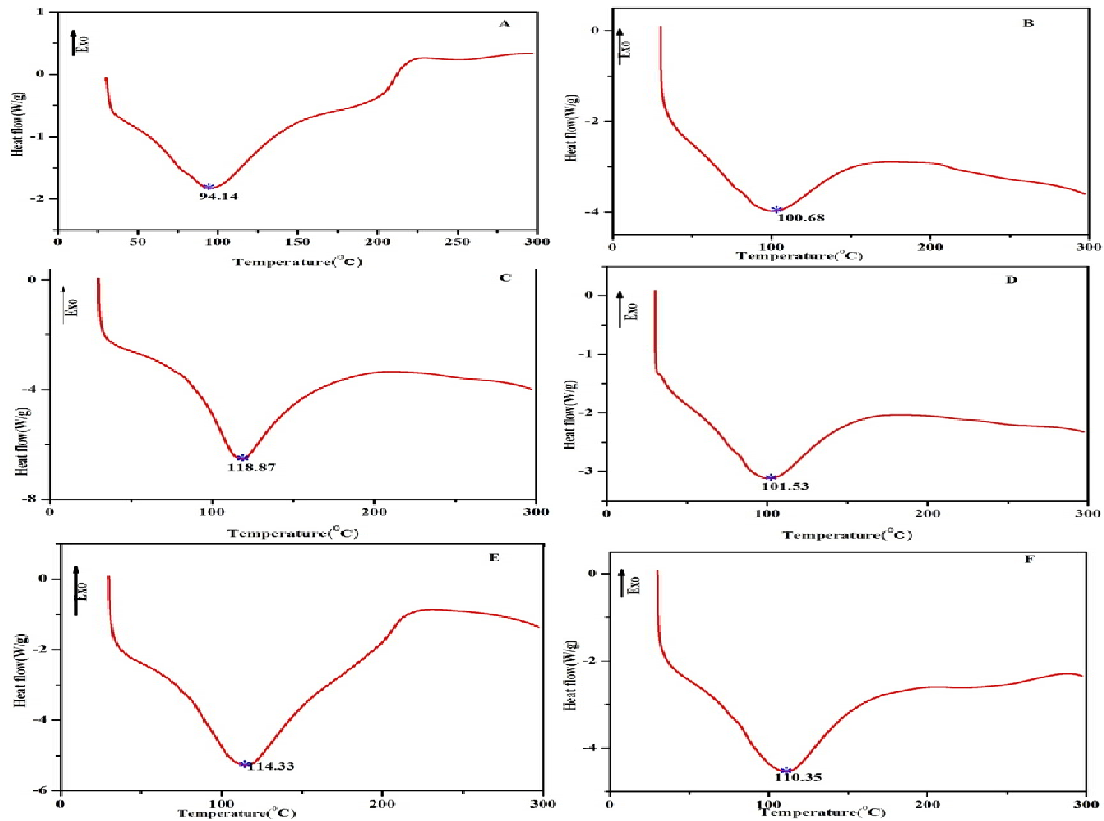


Figure 46: DSC Thermograms of leather-plant composite sheets
A. Control; B. FLS -E; C. FLS -H; D. FLS -J; E. FLS -P; and F. FLS -S

Differential scanning calorimeter studies of composites

The DSC thermogram of the control sample Figure 46 (A) exhibited melting temperature(T_m) at 94.14 °C. This T_m peak is lower than the other leather-plant composite sheets peak temperatures 100.68 °C for Figure 46 (B), 118.87 °C for Figure 46 (C), 101.53 °C for Figure 46 (D), 114.33 °C for Figure 46 (E) and 110.35 for Figure 46 (F). All of the leather-plant composite samples showed higher endothermic temperature (T_m).

5. DISCUSSION

5.1. Defect Assessment in Hides and Skins

The defect assessment study results in the sampled Ethiopian tanneries are discussed in the next sections

5.1.1. Prevalence of hides and skins defects

In agreement with the reports of [Zemene and Addis \(2012\)](#); [Kahsay *et al.*, \(2015\)](#) and [Behailu *et al.*, \(2017\)](#), the findings of this study proved that no single hide or skin was found free of defects implying the high prevalence of the factors that undermine the quality of the raw material. Supports the findings of the present study [Zemene and Addis \(2012\)](#) and [Assefa *et al.* \(2012\)](#) reported that cockle, scratches, flaying defects, and putrefaction were the most prevalent problems in both hides and skins.

The same studies have documented high prevalence of pre-slaughter defects such as cockle caused by ectoparasites and mechanical damages such as wounds and scratches. [Behailu *et al.* \(2017\)](#) reported that peri-slaughter defects are more prevalent than pre-slaughter defects; while the present study clearly indicated that defects occurring on live animals caused by ectoparasites and animal handling problems are dominant over peri- and post slaughter defects. This difference might be due to the fact that most of the pre-slaughter defects caused by disease problems may not be adequately discernible on raw hide and skins.

In agreement with the findings of the present study, several studies have also ascertained that peri-slaughter defects such as flay cuts and post-slaughter defects like putrefaction also prevail in processed or unprocessed raw hides and skins examined from different parts of Ethiopia ([Kidanu, 2001](#); [Zemene and Addis, 2012](#); [Kahsay *et al.*, 2015](#); [Behailu *et al.*, 2017](#)). However, the proportion of hides and skins affected by post-slaughter defects was much lower than the other two categories.

As the case in the present study for which cockle, one of the major pre-slaughter defects was found much more prevalent in sheepskin than in goatskin and cattle hide in Addis Ababa and Modjo tanneries, other authors ([Bisrat, 2013](#); [Zemene and Addis, 2012](#); [Azene et al., 2015](#)) also reported that majority of the cockle-affected pickled skins at Bahir Dar tannery were sheepskins compared to goatskins. This might be attributed to the denser hair/wool of sheep than that of goats and cattle that provide conducive environment to the cockle causing ectoparasites such as sheep ked and lice, which predispose the animals to higher infestation.

The higher state of the occurrence of scratches found on goatskin and cattle hides than on sheepskin in the present study may be related to animal management and/or the wool/hair cover of the animals. While [Azene et al. \(2015\)](#) found no difference between sheepskin and goatskin. [Kahsay et al. \(2015\)](#) reported a much higher prevalence of scratch on wet blue hides, goatskins and pickled sheepskins. This suggests that mis-management of live animals could be the cause of scratch defect. This can be evidenced from the fact that majority of the livestock in Ethiopia roam freely in the wilderness that subject them to thorny and shrubby vegetation which could result scratch on their skin/hide.

In this study, flay defects were found to be much more common in cattle hides and goatskins than in sheepskins. Contrary to this observation, [Azene et al. \(2015\)](#) reported that flay defects were more prevalent in sheepskins than in goat skins. The perception and attitudes of slaughter workers may have caused variations in the attention given to the raw materials during flaying leading to less carefulness. This is supported by the report of [Juhar et al. \(2015\)](#) that indicated that sheepskin in most places is much more valued than goatskin and cattle hide, often leading to keeping the latter for home use, which does not necessarily deserve much care on flaying.

The result of the present study that identified putrefaction as the dominant post-slaughter defect was in agreement with the reports of [Kahsay et al. \(2015\)](#) that reported that the higher rejection and depreciation in value of hides and skins was caused as a result of post slaughter defects mainly putrefaction. On the other hand, a much lower prevalence

of this defect was noted by [Azene et al. \(2015\)](#). Since putrefaction is a result of bacterial action due to inappropriate preservation, such variations may arise from lack of awareness on the value of the raw hide/skin, improper storage, delayed and inadequate preservation technique as well as inadequate access to markets that discourage selling the materials soon after skinning.

5.1.2. Association between cattle hide and shoat skins plus their quality grades

Ethiopian hides and skins have for long been considered as one of the finest products in the world market ([Mohammad, 2000](#)). However, given the widespread prevalence of defects that could potentially undermine the values of hides and skins, it is unwise to expect higher grade quality hides and skins in large number in the tanneries included in this study. As in the case of the present study, a research done at Bahir Dar tannery ([Azene et al., 2015](#)) has ascertained absence of two best quality grades (grades 1 & 2) among pickled sheep and goatskins. Similarly, [Behailu \(2015\)](#), in his study at Colba tannery in Ethiopia, has concluded that only 0-2.1 percent of hide and skins were found falling under grades 1 and 2.

Grading of hide and skins is affected by the stage in the process of production. For instance, [Zembaba et al. \(2013\)](#) have shown that the proportion of grade 1 sheep and goatskins collected and stored by collectors in Bahir Dar town was between 21 and 30 percent in fresh or salted stage.

Most pre-slaughter defects are visualized only after the hairs are removed during tanning process. This is further supported by the fact that these authors failed to report any pre-slaughter defects. This indicates that in recent years, Ethiopian tanneries and the nation as a whole is experiencing an alarming situation that calls for the careful resolution of the problem.

A study conducted by [Muleken \(2001\)](#), showed that the proportion of best grades in raw sheepskin and goatskin have shifted towards the lower and reject grades in 2001 as

compared to 1989, indicating quality deterioration of raw skin over 10 years. According to tanners' report for the period from 1970-1980, the share of grade 1-3 pickled sheep and wet blue goatskins from Ethiopia was between 60-70 percent of total skins supplied to the world market. From 1989/88-1991/92, the share of grade 1-3 skins dropped to 40 to 50 percent of total skins supplied. In 1996/97 the share further dropped to 20-30 percent and in 1997/1998, only 10-20 percent of skins were grades 1 to 3 (Muleken, 2001). Behailu (2017) also reported that tanneries state that only 10 to 15 percent of harvested skins qualify for top grades (grades 1 to 3), the rest being downgraded and rejected mainly due to deteriorations resulting from skin diseases and various defects. The present study has shown that a reasonably lower rate of grades 1-3 almost none existent that confirms the declining trend from time to time.

Despite the tremendous efforts made to control ectoparasite in different pockets of Ethiopia, cockle alone, can still cause categorization of 66-73 percent and 17-18 percent of hides and skins under low grade (5-6) and reject (grade 7), respectively. A similar finding was documented by Azene *et al.* (2015). However, in the latter study, the hides and skins were not selected against cockle problem only. Hence, the downgrading could be a combined effect of cockle and other factors. The present study has clearly shown the impact of cockle caused mainly by ectoparasites on the quality grades of hides and skins in the absence of all other confounding factors. Nafstad *et al.* (2001) concluded that inflammations caused by lice lead to partly irreversible changes in the dermis resulting in grain loss when the epidermis was removed during the liming in the tanning process. This suggests that controlling ectoparasite alone can significantly improve the quality of the raw materials.

Although the widespread presence of other defects have undermined the magnitude of the real effect of scratches on populations of hides and skins, among those filtered out to have only this problem, it was responsible for 5 to 13 percent rejection rate with a further 45-82 percent of the products earning low grades (5 to 6). This defect caused more reduction in quality in hides and sheepskins when compared to goatskin. Scratches give leather unaesthetic appearance and if deep, cause considerable loss of tear strength espe-

cially on skins. The leather whose depressions looked like scratches could be a consequence of the animal's effort to get relief from irritations by frequent rubbing of the body against an object (Gbolagade *et al.*, 2009). Consequently, the raw materials might fetch lower prices (Mohammad *et al.*, 2002).

Careless use of knives coupled with inadequate flaying skill of slaughter men contributes to flaying defect (Mohammad *et al.*, 2002), which was one of the most prevalent perislaughter defects, that caused significant rate of rejection (22 to 24 percent) mainly in hides and sheepskins and lower grading of goatskins suggesting the its significant impact on quality of the processed product.

The higher occurrence of putrefaction that caused major rejection in cattle hide and goatskins compared to sheepskin could be attributed to discouragement of producers and collectors to give care as they do for sheepskin during storage and transportation due to low pricing (Juhar *et al.* 2015).

5.2. Performance of Tanneries and Quantities of Solid Leather Waste Generated

The performance of Ethiopian tanneries and the quantities of solid leather wastes generated in the production processes are outlined as follow

5.2.1. Solid waste physical composition and Performance of Ethiopian tanneries

The information generated in this study is in agreement with previous reports on assessment and estimation of physical composition of the solid waste generated by tanneries (Andualem, 2005; Zulfikar, 2012; Sethuraman *et al.*, 2013). The lower performance of the Ethiopian tanneries (67 percent) for hides and 50.25 percent) for skins implies that thought there are opportunities to use this sector, the utilization potential at present however, is in critical situation that need focus to solve the problems.

5.2.2. *Estimating Solid waste generated*

This solid waste generated from tanneries under this study is sent to land fill in open environment without any careful consideration to the community health as well as to the environment (Figure 28). The finding of this study is in line with the concept stated by Mulat (2016) which describes that environmental pollution becomes an alarming issue of the time in most parts of the world including Ethiopia. In agreement to this finding Buljan (2005) reported that the amount of solid waste generated varies greatly and largely depended on the quality of the raw materials characteristics, technology, the type of leathers produced, size of the product, and skill of the operators. Yet, the results of this study was lower (7.54-26.48 percent) than the report of Senthil *et al.* (2014), which indicates that in India, about 20-30 percent of leather is discarded as waste during footwear and leather goods production.

5.3. Preparation of Composite Boards Using natural rubber latex

The evaluations mechanical properties, surface morphology, FTIR and DSC of composites are outlined as follow;

5.3.1. *Mechanical properties of composites*

The higher tensile strength of the boards prepared using sisal and palm fiber found in this study might be attributed to the high concentration of lignin in the plants (Sun *et al.*, 2004). The tensile properties of the boards prepared in this study are more or less similar to those prepared by Sekar *et al.* (2009). However, stitch tear strength values are much higher compared to boards prepared by the same author. The reason for this difference might be due to variation in plant species and finished leather fiber or nature of the binders used.

5.3.2. Surface morphology of composite boards

The composite boards of the present study have shown more or less similar SEM characteristics and appearance as those prepared by [Sekar *et al.* \(2007\)](#) using chrome shaving and various binders. This composite nature observed in the boards enhances the physical and mechanical properties of the boards and thereby these materials are amenable for the preparation of products for consumer application.

5.3.3. Fourier Transform Infrared Studies

The FTIR (Fourier Transform Infrared) spectrum of control board showed the amide bands of collagen fibers at 1643, 1544 and 1238 cm^{-1} representing amide I, II and III respectively ([Ramnath *et al.*, 2012](#)). According to [Bandekar \(1992\)](#) as cited in ([Adriana and Gabi, 2011](#)) nine amide vibration modes identified and the most used IR bands to reveal the conformational changes of the proteins and peptides are Amide I (1600–1690 cm^{-1} , C=O stretching), amide II (1480–1575 cm^{-1} , CN stretching, NH bending), and amide III (1229–1301 cm^{-1} , CN stretching, NH bending). Strong absorption between 3600–3200 cm^{-1} region results from superimposed -OH and NH stretching bands representing amide A ([Bandekar, 1992](#)).

A strong and sharp peak is observed at 2933 cm^{-1} representing -C-H of rubber latex. A broad peak around 1080–1000 cm^{-1} represent bonded -OH groups in the sample. FTIR spectra of RCL-J composite sample shows a broad peak from 1038–1670 cm^{-1} representing C-O-C and C-O stretch (primary and secondary hydroxide groups) and bonds belonging to the glucoside linkage and possibly to due to lignin ([Sekar *et al.*, 2009](#)). The peak at 1445 cm^{-1} in this spectrum represents H-CH and O-CH in plane bending vibration. The peak at 1228 cm^{-1} represents -C-H bending at C-6 in the cellulose molecular structure. The FTIR spectrum of RCL-H resembles to that of RCL-J in [Figure \(32\)](#) (b, c). However, in plane blending vibration of H-CH and O-CH bonds is observed at 1374 cm^{-1} ([Sekar *et al.*, 2009](#)). In the spectra of RCL-S, RCL-P and RCL-E in [Figure \(32\)](#) (d, e, and

f) show more or less similar pattern. This is due to the similar nature of cellulose in all the samples representing collagen and cellulose.

5.3.4. Thermo Gravimetric Analysis Studies

The thermo gravimetric analysis (TGA) reveals loss of the weight of materials with the increase in temperature. In the control, a two-step weight loss was occurred (Figure 33 a) the first weight loss (20 percent) being due to loss of free and bound water and the second major weight loss (63 percent) occurred between 290 °C and 488 °C, this weight loss was due to the protein/collagen degradation. The three step weight losses seen in the case of sample RCL-J (Figure 33 b); initial weight loss (9 percent) occurred up to 223 °C was due to the loss of water molecules. The second major weight loss (63 percent) that has occurred up to 449 °C was due to protein and cellulose degradation while the third weight loss (26 percent) occurred up to 800 °C may be due to decomposition of degraded products into carbon dioxide and water. This might be due to the presence of cellulose; hemicelluloses and lignin present in Jute fiber (Flandez *et al.*, 2012). RCL-H, RCL-S, RCL-P and RCL-E (Figure 33 c, d, e & f) samples exhibited more or less similar thermo gravimetric pattern. However, a residue of 10.3 percent observed in the case of RCL-P could be due to the more lignin content in the palm plant fiber (Sekar *et al.*, 2009).

5.3.5. Differential Scanning Calorimeter Studies

The initial endothermic peak (T_{m1}) seen in the DSC (Differential Scanning Calorimeter Studies) thermogram control sample (Figure 34 a) might be due to bound water molecules present in the control sample and the other melting peak (T_{m2}) could be related to denature of collagen structure in the control sample ().

The less value in endothermic transitions of the thermograms of Hibiscus and Enset (Figure 34 c & f) seen might be due to the presence of water and volatile contents in the samples in the progressive heating than the control board. The higher T_{m1} endothermic values of fibers (RCL-J, RCL-S, and RCL-P; Figure 34 b, d, and e) might be due the fact

that all the fibers were well dispersed in the leather matrix which could have resulted in shifting of melting phase to higher temperature. The second and third endothermic peak values of those RCL composites were also shifted to higher temperatures because of the structural heterogeneity of leather and residual tanning materials that could have induced interactions between fibers and the leather. However due to lack of similar study reports we are unable to make a comparison.

5.4. Preparation of Composite Sheet Using Resin and Polyurethane Binder

The evaluation methods of composites are outlined as follows;

5.4.1. Mechanical properties of composite sheet using resin and polyurethane binder

The higher performance of sisal in tensile strength indicates that it was contributing to enhance tensile strength as compared to the other plant fibers used in this study. The tensile strength results in this study were much better than those of samples prepared by [Senthil et al. \(2014\)](#). The tensile strength values of the boards prepared from different plant fibers using NRL binder by [Senthil et al. \(2014\)](#) were in the range of 0.38 ± 0.01 - 0.91 ± 0.03 MPa, whereas those results obtained in this study were in the range of 1.56 - 2.78 MPa.

The elongation at break results of this study were better than the values obtained in those prepared by [Senthil et al. \(2014\)](#) which ranged 0.41 ± 0.05 percent - 0.95 ± 0.02 percent using different plant fibers and NRL binder, but lower in most of them than that of [Teklay et al. \(2017\)](#) which ranges 10.38 percent -19.87 percent using different binder and methodology but similar plant fibers.

Stitch tear strength values in this study (57.69 ± 0.25 N/mm- 52.63 ± 0.89 N/mm) were better than the values recorded by ([sekar et al., 2009](#)) which is maximum of 34.36N/mm using different fibers and binders.

5.4.2. Surface morphology of composite sheets

The clear evident network of leather fiber adhering with binder as measured by SEM images of sampled composite sheets in this experiment confirmed the composite nature of the leather fiber. The SEM images in this study have more attractive appearance when compared to those of composite sheets made in the earlier study of [Sekar *et al.* \(2007\)](#) which might be attributed to the difference in the method of preparation.

5.4.3. Fourier transform infrared studies of composite sheets

The Fourier transform infrared (FTIR) spectra of the samples prepared in this experiment indicated the amide bands of collagen fibers at 1644 cm^{-1} , 1536 cm^{-1} and 1427 cm^{-1} representing amide I, II and III respectively ([Ramnath *et al.*, 2012](#)). FTIR spectra of LF-Eb composite sample ([Figure 38 B](#)) showed a broad peak from $1031\text{-}1727\text{ cm}^{-1}$ representing C-O-C and C-O stretch (primary and secondary hydroxide group) and bonds belonging to the glucoside linkage and possibly due to lignin ([Sekar *et al.*, 2009](#)).

The peak at 1443 cm^{-1} in this spectrum represents H-CH and O-CH in plane bending vibration. The peak at 1242 cm^{-1} represents -C-H bending at C-6 in the cellulose molecular structure. The FTIR spectrum of LF-Hb composite sample [Figure 38 \(C\)](#) was comparable to LF-Eb composite. However, one can see in plane C=O stretch bending at 1632 cm^{-1} ([Sekar *et al.*, 2009](#)) in the spectra of LF-Jb; LF-Pb; and LF-Sb ([Figure 38 D, E & F](#)). All showed more or less similar pattern. The reason for the similarity perceived between the three IR spectra might have been due to the similar nature of cellulose in all the samples representing collagen and cellulose.

5.4.4. Thermo gravimetric analysis studies of composite sheets

Three-step weight loss observed from thermo gravimetric analysis (TGA) study of control composite sheet ([Figure 39 A](#)), the first (21.29 percent) was due to the loss of free and bound water up to $301.22\text{ }^{\circ}\text{C}$. The second major weight loss (37.15 percent) up to $414.42\text{ }^{\circ}\text{C}$ was due to collagen degradation in the samples while the final major weight

loss (11.68 percent) up to 789.17 °C was due to decomposition of degraded products. From the three step weight losses seen in the case of LF–Eb (Figure 39 B), the initial weight loss (12.02 percent) up to 179.50 °C was due to the loss of water molecules in the sample. The second major weight loss (60.75 percent) that has occurred up to 464.17 °C was due to protein and cellulose degradation (Flandez *et al.*, 2012) while the third weight loss (16.38 percent) which occurred up to 786.85 °C might be due to the decomposition of the degraded products (Abdullah and Ahmad, 2013). In composite samples of LF-Hb, LF-Jb and LF-Sb as seen in Figure 39 (C, D, E & F), exhibited more or less the same thermogravimetric pattern. The similarity of the thermogravimetric patterns could be mainly because the ingredients in all the samples were cellulose and collagen.

5.4.5. Differential Scanning Calorimeter Studies

The DSC thermogram of the control sample in this study as seen in Figure 40 (A) exhibited its peak or melting temperature (T_m) at 96.29 °C. This T_m peak is higher than the peaks of composite sheets of B (enset) and C (Hibiscus) peak which do have 95 °C each (Figure 40 (B and C)). But lower than D (Jute), E (Palm) and F (Sisal) each having 97.29, 112.12 and 107.42 °C respectively (Figure 40 (D, E and F)). The better melting temperature (T_m) for of these samples than their respective control could be due to the fact that all the fibers were well dispersed in the leather matrix, so that their melting phase has shifted to higher temperature.

5.5. Evaluation of Composite Boards Prepared from Leather Fibre Using Natural Rubber Latex and Resin Binder

The evaluation methods of composites are outlined as followed;

5.5.1. Mechanical properties of composite sheets using natural rubber latex and resin binder

The tensile strength values obtained in these experiments were much better than the values of previous studies done by Sekar *et al.* (2009) using chrome shavings and NRL

(2.96 ± 0.06 MPa) and that of [Senthil et al. \(2014\)](#) from regenerated leather boards (5.88 ± 0.09 MPa) using leather fibers and NRL. The reason for such difference might arise from variation in plant fibers or preparation methods.

5.5.2. Surface morphology of composite sheets

Scanning electron microscope (SEM) images of the sampled composite sheets were also evaluated and all composite sheets prepared in this experiment exhibited an intermingling of fibers along with the binder with no significant difference among the samples in their SEM images revealing that they have composite nature. The SEM image results in this study were comparable to those of composite boards made in the earlier study ([Sekar et al., 2007](#); [Senthil et al., 2014](#); [Teklay et al., 2017](#)).

5.5.3. Fourier transform infrared studies of composite sheets

The Fourier transform infrared (FTIR) spectrum of the control sheet indicated the amide bands of collagen fibers at 1636 cm^{-1} , 1536 cm^{-1} and 1241 cm^{-1} representing amide I, II and III respectively ([Ramnath et al., 2012](#)).

The Fourier transform infrared spectra of FLS-E composite sample showed a broad peak from $1010\text{--}1638\text{ cm}^{-1}$ representing C-O-C and C-O stretch (primary and secondary hydroxide group) and bonds belonging to the glucoside linkage and possibly due to lignin ([Sekar et al., 2009](#)). The peak at 1445 cm^{-1} in this spectrum represents H-CH and O-CH in plane bending vibration. The peak at 1234 cm^{-1} represents -C-H bending at C-6 in the cellulose molecular structure. The FTIR spectrum of FLS -H composite sample ([Figure 44 C](#)) is similar to FLS-E composite. However, we can see in-plane CH bending at 1453 cm^{-1} ([Sekar et al., 2009](#)); in the spectra of FLS-J; FLS-P; and FLS-S [Figure 44 \(D, E & F\)](#); more or less similar pattern is observed. The reason for this similarity might be due to the similar nature of cellulose in all the samples representing collagen and cellulose.

5.5.4. Thermo gravimetric analysis studies of composite sheets

Three step weight loss observed in the control composite board on the thermo gravimetric analysis (TGA) study revealed that the first weight loss (13 percent) was due to the loss of free and bound water up to 231 °C. The second major weight loss (42 percent) up to 400 °C was due to collagen degradation in the samples whereas the final weight loss (38 percent) was due to decomposition of degraded products (Flandez *et al.*, 2012)

In the three step weight losses occurred in the case of FLS-E, the initial weight loss (21 percent) up to 347 °C was due to the loss of water molecules in the sample. The second major weight loss (57 percent) that has occurred up to 471 °C was due to protein and cellulose degradation and the third weight loss (9 percent) which occurred up to 800 °C might be due to the decomposition of the degraded products (Flandez *et al.*, 2012). In composite samples of FLS-H, FLS-J and FLS-S exhibited more or less the same thermogravimetric pattern. However, residues of 17.23 percent and 17.04 percent were observed in FLS-H and FLS-J respectively. This higher value might be due lignin content present in these plant fibers or mineral fraction.

The four step weight losses observed in FLS-P, the first weight loss (11 percent) that has occurred up to 222 °C was due to loss of water molecules in the sample. The Second weight loss (47 percent) which has occurred up to 392 °C might be due to protein and cellulose degradation (Flandez *et al.*, 2012) while the third weight loss (40 percent) up to 589 °C and fourth weight loss (0.47 percent) up to 800 °C might be due to decomposition of degraded products (Abdullah and Ahmad, 2013).

5.5.5. Differential Scanning Calorimeter Studies

The DSC thermogram of the control sample in this study as seen in Figure 46 (A) exhibited melting temperature (T_m) at 94.14 °C. This T_m peak is lower than the other leather-plant composite sheets peak temperatures 100.68 °C for Figure 46 (B), 118.87 °C for Figure 46 (C), 101.53 °C for Figure 46 (D), 114.33 °C for Figure 46 (E) and 110.35 for Fig-

ure 46 (F). All of the leather-plant composite samples showed higher endothermic temperature (T_m) than their respective control. This could be due to the fact that all the fibers were well dispersed in the leather matrix, so that their melting phase has shifted to higher temperature. However due to lack similar studies we are unable to make comparison.

6. CONCLUSION AND RECOMMENDATIONS

6.1. Conclusion

The study on defects and qualities of hides and skins has clearly ascertained that: none of the hides and skins examined at wet blue stage was free of defects, often harboring more than one type of problem. Majority of the raw materials reaching tanneries is of poor quality that immensely contributing to lots of waste generation in tanneries. It was observed that remarkable amount of solid waste is generated from the tanning industry that could be as the result of; quality deterioration of hides and skins as well as natural tannery process and played important role in posing critical environmental and society health issues. Therefore, something has to be done to curb this threat. In this regards, the study has clearly demonstrated that leather solid wastes can be converted into value added product especially when blended with plant fibers. Jute, hibiscus, palm, sisal, enset fibers were tried to be blended with finished leather fibers to make composite boards of various purposes. To bind the fibers together, natural rubber latex, resin, polyurethane binders were used and, results showed natural rubber latex is better binder when compared with the others. The mechanical and physicochemical tests for quality of the prepared boards were measured and such parameters were evaluated for products like insole/shank board and other leather products such as insole, stiff hand bags, key chain etc. In the composite boards prepared using natural rubber latex as a binder; 10% enset, 10% hibiscus, and 30% jute have shown quality values within the standard set for footwear insole/shank board application except for water absorption capacity. However, when they are compared with the control (leather fiber alone) they did not show better performance. Sisal fiber at 30% ratio in the presence of NRL as binder has shown extraordinary performance, when compared with both the standard values and the control; except for its lower value in tensile strength in wet state than its control. All boards prepared in the study have shown very attractive look and smooth surface so that can be used to prepare value added consumer products such as stiff hand bag, ladies hand bag, wallet, keychain, chappal upper, false roofing, interior decorations and wall cover other than for insole/shank boards making. Scanning electron microscope (SEM), Fourier transform infra red (FTIR), thermo gravimetric analysis (TGA) and deferential scanning calorimetry (DSC) studies have confirmed the composite nature of the sheets prepared.

6.2. Recommendations

- ❑ It was observed that almost all of raw materials entering tanneries were not free of major defects. If the quality of these raw materials has to be improved and waste to be minimized, a lot has to be done at the production levels(pre slaughter to post slaughter stages);
- ❑ Assessment of tanneries has shown a lot of solid leather waste was generated (could be due to poor quality raw materials and/or natural tanning process). Therefore to minimize the environmental impact of this waste and maximize its use, stakeholders in the sector have to invest in research and development works to mitigate the problem from its source and convert waste in to value added products.
- ❑ Over all estimates of the economic feasibility of the prepared products, providing estimates of annual mass production and price of waste leather, latex, plant fibers, dyeing agents for finishing, demand and price of composite boards, machine costs and energy requirement for (cutting, fiberizing, pressing, plating) to make it applicable at marketable level need to be done;
- ❑ Companies in this sector should take part in developing this research output in to commercial product(technology transfer);
- ❑ Future study is needed to improve the limitations observed on leather sisal composite using natural rubber latex especially the lower values of tensile strength in wet state.

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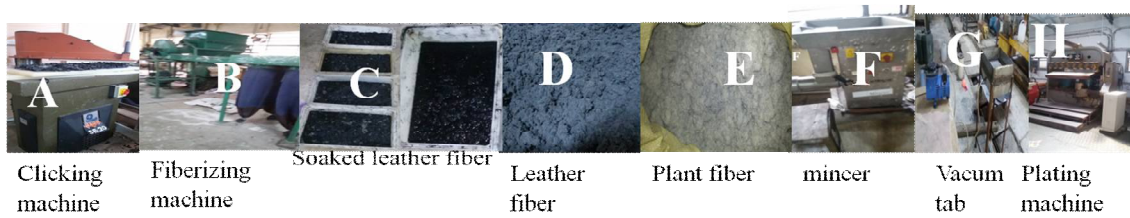
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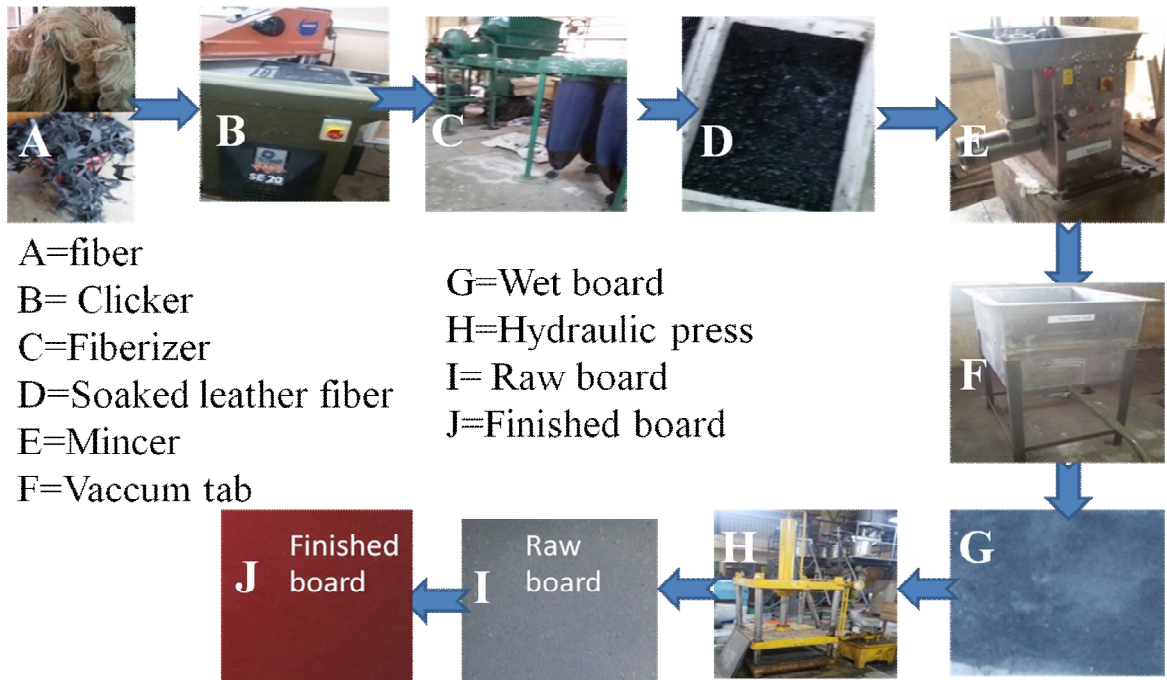
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8. Appendices

Appendix 1. Equipments and Fibers Used



Appendix 2. Flow Chart of Composite Making



Appendix 3. Definition of terms

- *Flaying*- the removal of hide and skin from carcass of an animal by hand or machine.
- *Flesh*- the tissue (usually meat, fat or connective tissue) adhering to the flesh side of the hide or skin, equivalent to the hypodermis.
- *Fleshing*- the removal of flesh from the hide or skin.
- *Bleeding* - the loss of blood from an animal during or soon after slaughter.
- *Brine*- a solution of salt in water.
- *Brining* - the method of preservation based on the immersion of hides or skins in saturated brine. Particular methods include pit (static) and raceway-brining.

- *Pattern* -the overall shape of a hide as determined by the type of ripping and or trimming.
- *Ripping*-the insertion of cuts in to a hide or skin prior to flaying.
- *Trimming*- the removal of superfluous material from around the edges of hide or skin.
- *Pre-slaughter*-the period before the time of slaughter.
- *Peri-slaughter*-the period around the time of slaughter.
- *Post-slaughter*-the period after the time of slaughter.