

# CHAPTER ONE

## INTRODUCTION

### 1.1 Introduction

Over the last 30 years, the footwear sector has placed significant effort in improving material efficiency, as well as eliminating the use of hazardous materials during the production phase. However, the environmental gains made in production are being overtaken by the negative impact of the considerable increase in the demand for footwear products (SMART, 2007).

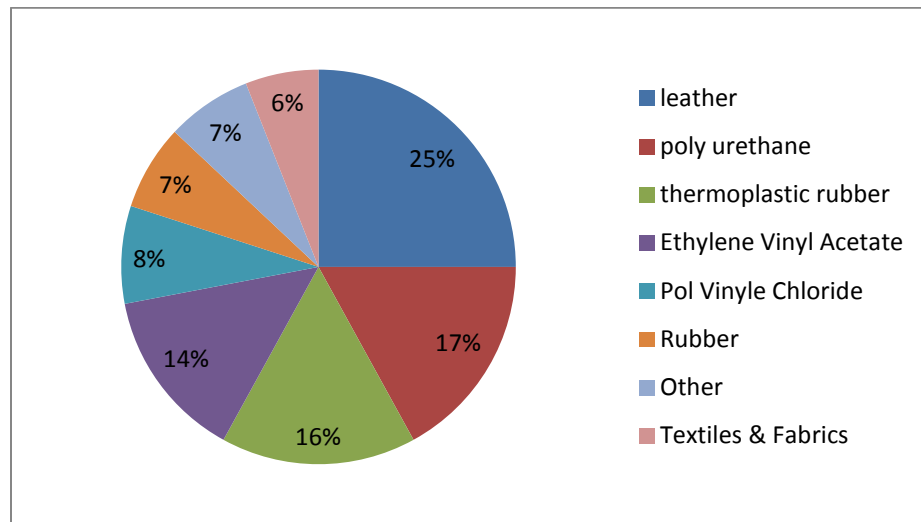
### 1.2 Historical footwear

The history of the use of Footwear by human kind can be traced back to the ice age about 5 million years ago. Due to unkind weather conditions the need for footwear started growing. Other evidences show that footwear came to use at the end of the Paleolithic Period, at about the same time the early humans learned the art of leather tanning. Earlier footwear was made of wrappings of dried grasses and only later on the art making footwear from pieces of leather was developed. Until the mid-nineteenth century shoes were made as straights i.e., there was no distinction made between the right and left shoes (Mohan Kumar *et al*, 1999)

### 1.3 Footwear materials

The footwear industry is a manufacturing sector which utilizes a wide variety of materials and processes to produce a range of distinctly different products, from sandals to specialized safety footwear. Shoes are designed to fulfill an array of consumer requirements relating to function and fashion, and incorporate varied range of designs and styles. In addition, a range of distinctly different materials such as leather, synthetic materials, rubber and

textile are commonly used in shoe manufacturing. These materials differ not only in their appearance but also in their physical qualities, their service life, the different treatment needs as well as their recycling and recovery options at the end of their useful life. There are approximately 40 different materials used in the manufacturing of a shoe. For example, Figure 1 represents the average composition of materials used in footwear (Abu Sayid Mia Md. *et al*, 2017)



**Figure 1-1: Material Composition in Average Shoe (%) (Abu Sayid, 2017)**

## 1.4 Footwear sole:

The polymer used to make the sole is chosen depending on the type of footwear, design, long life, features of resistance and cost. The most common materials are: SBR, SBS, PVC, EVA, PU and TPR (Harvey 1992).

Over the last 60 years there has been a major change in soling materials used in the footwear trade. Leather has been the traditional soling materials for footwear, but in 1980, only 5% of shoes have leather soles. Nowadays, most soles are made of rubber or plastic, which are classed as synthetic soling materials (Miller, 2013).

Leather was always the main soling materials. In recent years this has been largely superseded by other materials, for Example, rubber (both vulcanized and microcellular), crepe, synthetic resins, PVC and PU. Leather, the traditional soling material, has been modified and improved by tanners so that a high quality leather sole is now light and flexible, waterproof, and still retains breathability. Leather has all essential qualities of a good soling material except durability. Nevertheless for men's and women's dress shoes, true moccasins and some children's shoes.

Leather is accepted in trade as the most suitable soling material for high quality footwear, because it has essential qualities of a good soling material except durability. The reason that it has now been superseded is due to the fact that it is too expensive for most types of shoes (Harvey 1992).

Rubber is mainly used in the trade for vulcanised footwear. The main attribute of solid rubber is that it can be compounded to any quality required. It tends to be rather heavy due to its density (specific gravity 1.2). Microcellular Rubber is the same compound as solid rubber with a blowing agent added, which turns to gas at a certain temperature in the vulcanizing temperature range. The specific gravity of 0.85 makes it light in weight and cushions the foot better than soling rubber. Plantation Rubber- this is material made from pure rubber. It is produced by coagulating the rubber latex taken from the trees directly into sheet form. It is not extensively used because it is expensive and cannot be bonded directly to leather uppers, although it is hard wearing. Other disadvantages are that it is adversely affected by oils and petrols and that it softens and spreads in wear. Resin Rubber: the introduction around 1950 of synthetic material manufacture from a combination of butadienes (synthetic rubber) and styrene (plastic) revolutionized finishing operations. This brought about a complete change

in shoe manufacture processes, in so much as old finishing operations have been eliminated by prefinishing the complete sole and heel unit before it is attached to the bottom of the shoe. The majority of resin rubbers are used for women's footwear but a proportion has been used for men's and children's styles. Resin rubber is a uniform material and so lends itself to prefinishing. It may be used in sheet form or as a moulded unit. The advent of PVC as an injection moulded material for soles in the early 1960's was rapidly adopted by the footwear trade as an alternative to vulcanized rubber. It is suitable for direct moulding on to shoe bottoms or can be used to produce a wide variety of moulded unit soles. Fairly soft grades of P.V.C are used so that a good bond and good wearing properties (similar to that of medium grade rubber) can be obtained. PVC needs to have a patterned surface to overcome a tendency to slip (Harvey 1992).

Polyvinyl chloride, also known as PVC or vinyl, was first developed for commercial use in the 1920s and is now one of the most commonly used plastics. Global production is measured in tens of millions of tons, and it finds use in a wide range of diverse industries such as automotive, building materials, electronics, food packaging, and of course footwear. There is a considerable "anti-PVC" movement (not without good reason, as discussed below) but this is counteracted by the fact that it is so inexpensive to produce.

Within the footwear industry PVC is used in a number of different ways, including whole footwear (for example beach sandals and rain boots can be entirely made of PVC), coatings for upper materials, logos/appliques, and outsole units. For the latter application, PVC can be in cellular form but is more often seen as a solid material with a specific gravity typically around  $1.2 \text{ kg/m}^3$  (Harvey 1992).

Thermoplastic Rubber, the name thermoplastic rubber classifies a range of rubbers possessing the moulding and processing characteristic of a thermoplastic and physical properties are obtained by synthesizing a rubber that contains chemical groups or chemical arrangements that can act like cross-links under end-use conditions but can be dispersed under moulding and processing conditions by the action of heat simply, thermoplastic rubbers are polymers containing movable cross-links (Harvey 1992).

Polyurethane (PU) soling are formed by a process called reaction moulding. It is a sort of polymerization process, compounding process, and moulding process rolled into one. A polyurethane sole is made by metering the necessary chemical ingredients in liquid form (or ingredients rendered liquid by heating) into a mixing chamber, mixing them, and transferring the mixture into a mould. While they are still in the mould, the liquids react to form polyurethane. Gas is produced during the reaction, and this cause the polyurethane to assume a cellular structure (Harvey 1992).

Ethylene Vinyl Acetate (EVA), this material, produced by the copolymerization of ethylene and vinyl acetate, is used for soling in both thermoplastic and cross-linked forms. The properties of polyethylene are well known, and the vinyl acetate part of copolymer produce material that is softer and more rubbery than polyethylene (Harvey 1992).

## **1.5 Footwear sole properties**

Most soling properties can be quickly and accurately measured in the laboratory. However, such properties as slip resistance, durability, and chemical resistance are so dependent on actual conditions of wear that the conditions of the laboratory may not provide realistic answer. In this section, we'll examine all the methods of assessing soling performance, with

particular emphasis on the most realistic methods. The ideal qualities for soling materials are:

- a\ Durability
- b\ Flexibility
- c\ waterproof
- d\ Lightness in weight
- e\ Non slip
- f\ Uniformity

## **1.6 Problem statement:**

There are many claims about the physical and mechanical properties of all types of sole used in footwear these claims include:

- a\ less durability
- b\ not comfort during wearing
- c\ it is a adversely affected the mechanical properties
- d\ high cost

Furthermore, these are huge quantities of waste leather and plastic produced every year. This density affects the environment. To get rid of this waste the manufacturer has to pay large amount of money. Therefore, to pay back for this money the manufacturer has to increase the product cost.

Utilization of leather and plastic wastes for manufacturing footwear sole and Effect will be studied using different percentage materials on the physical properties of blends.

## **1.7 Objectives:**

The objectives of this research can be as follows:

1. Manufacturing of new sole using a binder and/ or equivalent binder from local materials.
2. Study and determination of the physical properties of the new sole.
3. Comparison between new product and conventional sole.
4. Economical aspects and observation.

# **CHAPTER TWO**

## **LITERATURE REVIEW**

### **2.1 Leather Industry**

Leather industry is the one of the most wide spread important industries in Sudan. Over the past 100 years, leather tanning industry has been into consideration concerning their environmental impact. The low level of cleaning technology standard has given rise to environmental issues awakening the people to think in a new way for the creation of green sustainable process.

Tanning is the most polluting operation during the leather making process. The agents such as chromium can be highly toxic and polluting depending on its existing form. In European countries, EU directives for leather industry have limited the use of chrome tanning which made it important to establish new techniques and strategies to ensure environmental protection (Ali 2014).

### **2.2 Leather wastes**

Leather is a natural polymer consisting of collagen fibers cross linked in a three dimensional structure. Chrome leather tanning results in improved appearance, physical properties and chemical and biological resistance to leather but the process leads to emission of solid, liquid and gaseous wastes into the environment.

The environmental pollution is the main problem for leather industry. The leather making process generates substantial quantities of liquid and solid wastes (hides and skins, fats, shaving and trimmings, buffing dust,



process effluents, sludge). The most common way to manage solid wastes is by disposing of them on land sites (Kanagaraj *et al* 2006).

The leather processing industry produces large amounts of solid organic wastes in the form of un-tanned (trimmings, fleshings, splits) and tanned (trimmings, splits and shavings) waste from raw hides and skins, semi processed leather as well as sludge as a result of wastewater treatment. If this solid waste are not properly treated and disposed of, they can cause environmental damage to soil and groundwater as well as emissions of odour and poisonous greenhouse gases into the atmosphere (Kanagaraj *et al* 2006).

Leather industry has been categorized as one of highly polluting industries and there are concerns that leather-making activity can have adverse impact on the environment. The global production of about 24 billion m<sup>2</sup> of leather by 2005 present a considerable challenge to the industry considering the harmful nature of some of the chemicals used in leather process. The tannery effluents are characterized by high contents of dissolved, suspended organic solids giving rise to high oxygen demand and potentially toxic metal salts and chromium metal ion. The disagreeable odor emanating from the decomposition of proteinous waste material and the presence of sulphide, ammonia and other volatile organic compounds are also associated with tanning activities. Solid waste generated in leather industries contributes mainly skin trimming, Keratin wastes, fleshing wastes, chrome shaving wastes and buffing wastes. It constitutes protein as the main component. If this protein and other chemical, which are present in the chemical treated protein, are not utilized properly it will pose hazardous pollution problem to the environment (Kanagaraj *et al* 2006).

## 2.3 Waste from leather manufacturing

### 2.3.1 Leather industry wastewater

Leather industry wastewater samples were collected from leather processing laboratory, Central Leather Research Institute, The leather industry wastewater was filtered through filter paper to separate the solid particles present in the wastewater. After filtration, the physicochemical parameters such as pH, color, COD, total dissolved solids (TDS), and electrical conductivity were measured and the filtrate was also analyzed by ionic chromatography. The results were given in the Table (2-1) The filtrate was analyzed by Cary 500 UV–vis spectrophotometer (Varian, Palo Alto, CA) and subjected to solvent extraction to separate organic compounds present in the filtrate (FAO, 2014).

**Table 2-1: Physicochemical parameters of leather industry wastewater**

No.	Parameters	Values
1	Color	Brown
2	pH	8.20
3	COD (mg/L)	8.20
4	Total dissolved solid (ppm)	1770
5	Electrical conductivity (mS/cm)	3.55
6	Chloride (mg/L) <sup>a</sup>	696.8
7	Sulfate (mg/L) <sup>a</sup>	157.7
8	Fluoride (mg/L) <sup>a</sup>	1.6
9	Fluoride (mg/L) <sup>a</sup>	7.0

In other words, besides the 30-35 m<sup>3</sup> waste water disposed to environment during the processing of every 1 ton of rawhide in world leather industry, the

data from FAO reveals that approximately 8.5 million tons of solid waste is generated during the production of 11 million tons of rawhide processed in the world (FAO, 2014).

### **2.3.2 Solid wastes in leather**

Leather industry is responsible for generation of large amount of solid tanned waste throughout tanning process, which converts raw skins/hides into leather. These solid wastes can be generally classified as untanned hides/skins, tanned leather and wastes from finished leather (Ozgunay *et al*, 2007).

The transformation of 1000 kg of rawhide into leather provides only 200 kg of leather final product, along with 250 kg of non-tanned and 200 kg of tanned waste (Lakraflı *et al*, 2012).

The solid waste in leather manufacturing process generates a variety of solid wastes (UNIDO, 2000). The selected wastes having a chemical composition comparable to finished leather include:

- › wet blue (WB) splits, trimmings and shavings,
- › leather trimmings,
- › leather dust.

The main waste production ratios used by UNIDO (2000) is summarised in the Table (2-2).

**Table 2-2: waste ratios regarding the leather manufacturing process**

	ratio for heavy bovine leather	ratio for light bovine leather	ratio for sheep and goat leather
	(t / t finished leather)	(t / million m <sup>2</sup> finished leather)	(t / million m <sup>2</sup> finished leather)
Unusable WB splits, WB shavings and WB trimmings	171.0	513.0	180.0
Dry leather wastes (trimmings, dust ..)	27.7	83.2	151.3

WB= wet blue

In the calculations for this table, we consider that the heavy bovine finished leather weights about 3 kg/m<sup>2</sup> and a sheep/goat finished leather measures about 0.75m<sup>2</sup> (UNIDO, 2000).

Nowadays chrome tanning is the predominant method in leather manufacture, which results in a large amount of chrome-containing solid waste. It is an important environmental problem of tanning production for its relatively high content of environmentally damaging Cr(III) salts. Stather and Pauligk has addressed the question regarding the minimum tanning material quantities required for conversion of hide to leather (Reich, 2007) in Table 2. Usually chrome content of fully tanned leather is 4 % Cr<sub>2</sub>O<sub>3</sub> (Covington, 2009).

Thousands of tones of chrome tanned leather wastes are generated every month by the leather and apparel industries. Currently, in several countries, these kinds of waste are burned, or, even worse, are buried in suburban fields. About 30% of leather substance processed in tanneries is rejected, mainly after the shaving process, in the form of protein wastes containing 3–5% of chromium (III). These wastes are partly utilized, but

mainly they are deposited in storage yards, posing a hazard to the environment. The most often proposed technological solution to the problem of waste shavings utilization is the production of secondary or artificial leathers designed for footwear elements, fancy goods or non-woven fabrics as substrates for leather - like materials. (Natarajan *et al* 2018)

Reduced cost Quantum of solid wastes produced from processing 1-metric ton of raw material is shows in table 2-3.

**Table 2-3: Quantum of solid wastes produced from processing**

S.No	Solid Waste	Quantity
1	Salt from Desalting	80 Kgs
2	Salt from solar evaporation Pans	210 Kgs
3	Hair	110 Kgs
4	Lime sludge	65 Kgs
5	Raw trimmings	55 Kgs
6	Fleshing	110 Kgs
7	Wet blue Trimmings	30 Kgs
8	Chrome tanned unusable splits	65 Kgs
9	Chrome Shaving	90 Kgs
10	Buffing dust	60 Kgs
11	Crust trimmings	45 Kgs
12	Dry Sludge from ETP	125 Kgs

## 2.4 Solid Wastes Generation

Solid wastes generated by the leather industry in these stages of processes may be classified as follows:

- i. Wastes from untanned hides/skins (trimmings, fleshing wastes).

- ii. Wastes from tanned leather (shaving wastes, buffing dust).
- iii. Wastes from dyed and finished leather (trimmings from leather).

Data obtained from research reveals that 80% of solid wastes are generated during pre-tanning processes, while 20% of the wastes are caused by post-tanning processes.

## 2.5 Properties of solid leather wastes:

Onur Yılmaz (2006) said that the tannery wastes – chromium- and vegetable-tanned shavings and buffing dust – The chromium- and vegetable-tanned shavings (CTS and VTS) were shredded into the rectangular pieces (1 cm×0.5 cm). Buffing dusts (BD) was used as received. Some properties of wastes are given in Table 2-4.

**Table 2-4: The properties of tanned shavings and buffing dust**

Type of waste Properties	Chromium-tanned	Vegetable-tanned	buffing dust
Proximate analysis (wt. %)			
Moisture	7.1	5.9	5.2
Volatile matter	67.0	59.0	67.7
Ash	9.6	3.9	6.7
Ultimate analysis (dry, wt. %)			
C	44.3	52.4	42
H	3.1	0.9	6.1
N	14.2	6.6	11.0
S	1.8	1.1	2.1
O <sup>a</sup>	36.6	39.0	38.0

## 2.6 Characterization of leather waste

Buffing dust is a fine powder of collagen fibril, which is generated when the finished leather is subjected to abrasion process in order to get a smooth and fine feel. The Characteristics properties of waste leather are shown in table (2-5) (Tushar *et al*, 2016).

**Table2-5: Characteristics properties of waste leather**

Tests	Values
Humidity (wt %)	7.92 ± 0.22
Greases and Oils (wt %)	1.97 ± 0.36
Ash (wt %)	12.86 ± 0.20
Chrome Oxide (wt %)	3.41 ± 0.10
pH in water Extract (wt %)	4.15 ± 0.20
Nitrogen (wt %)	9.71 ± 1.41
Protein (wt %)	54.58 ± 3.80
Decomposition Temperature (°C)	323.0 ± 10.0
Diameter Average (µm)	4.52 ± 0.03
Length Average (µm)	258.5 ± 2.50

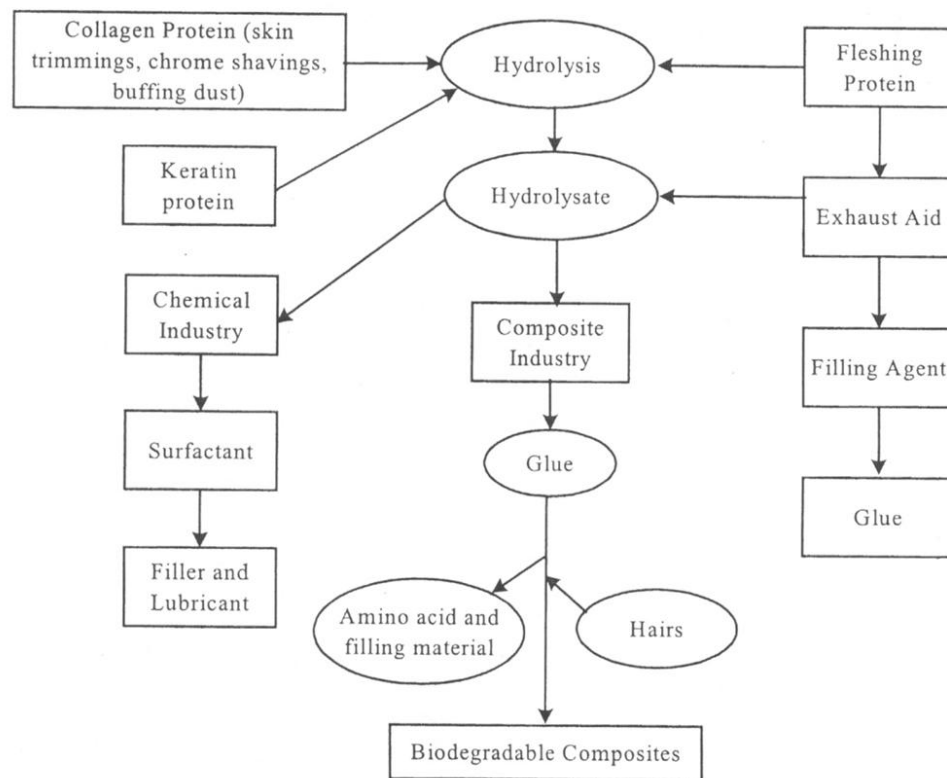
(Ponsubbiah. S *et al* 2016)

## 2.7 Solid Wastes Utilization

Kanagaraj (2006) said that the Out of 1000 kg of raw hide; nearly 850 kg is generated as solid wastes in leather processing. Only 150 kg of the raw material is converted into leather. Tannery generates huge amount of solid waste as follows: fleshing, 50-60%; chrome shaving, chrome splits and buffing dust, 35-40%; skin trimmings, 5-7%; and hair, 2-5%. Solid wastes in the leather processing constitute: beam house, 80%; tanning, 19%; finishing,

1%. The solid wastes can be hydrolyzed and used as a useful byproduct, shown in Figure 2-1.

Solid wastes generated in the leather industry pose pollution problem in terms of sludge, BOD and TDS. Raw trimmings and wet blue trimmings are useful in developing glue and gelatin. Keratin hydrolysate can be used as an exhaustive aid for chrome tanning. Similarly fleshing hydrolysate 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. Chrome and buffing dust are useful in developing retanning agent, poultry feed, fertilizer and landfill sites (Kanagaraj *et al*, 2006)



**Figure 2-1: Flow diagram of solid wastes utilization**



## 2.8 Current utilization of solid waste:

There are so many low value products are developed from leather solid waste. The list of Composite from Leather Waste was shown in table (2-6). (Natarajan *et al*, 2018).

**Table 2-6: Utilization of solid wastes**

S.No	Solid Waste	Utilization
1	Salt from Desalting	Recovered for curing
2	Salt from solar evaporation Pans	Recovered for curing
3	Hair and wools	Non woven fabrics
4	Lime sludge	Land filling
5	Raw trimmings	Pet treats in food industry
6	Fleshing	Protein meal and Glue & Gelatin
7	Wet blue Trimmings	1.Leather meal making 2.Leather board making 3.parchment like leather making 4.Acoustic building materials
8	Chrome tanned unusable splits	Leather washers, Industrial Gloves etc,
9	Chrome Shaving	1. Leather board making 2.Leather threads making 3.Clothing making 4.preparation of parchment like materials 5.leather like materials 6. Glue and Gelatin 7.Leather fertilizer 8.Fuel for boilers
10	Buffing dust	Leather board making
11	Crust trimmings	Glue and gelatin making
12	Dry Sludge from ETP	Land filling

## 2.9 Rubber sole manufacturing

The broadest categories of latex polymers are natural rubber latexes and synthetic latexes. Natural rubber latexes include high ammonia latex, low ammonia latex and graft polymer latex. In the *Hevea Brasiliensis* (rubber) tree, the latex is stabilized by protein. Once it is tapped from the tree, the natural protein is susceptible to attack by bacteria upon exposure to oxygen in the atmosphere. This degradation of the protein and subsequent coagulation of the latex renders the “field latex” putrid and rancid.<sup>1-15</sup> Field latex contains approximately 30% rubber, 5% of natural protein, fatty acids and impurities, and 65% water. In this state, it would not be economically efficient for industrial use or for transportation. Centrifuging is the major means by which the solids concentration is increased from 30% to 60% and higher. Creaming, another method of layer separation, is also used, but to a lesser extent (Omprakash *and* Nautiyal, 2012).

High ammonia latex is the result of increased stabilization by the addition of further ammonia following concentration of the latex. The additional ammonia raises the pH of the latex to approximately 11 to 12. Low ammonia latex was developed because manufacturers objected to the noxious ammonia odor in their factories. A popular method to minimize the amount of ammonia in latex is to replace part of it with a combination of zinc oxide and the accelerator tetramethylthiuramdisulfide (METHYL TUADS® (TMTD)). The pH of this latex is approximately 10 to 11. Graft polymer latex<sup>1</sup> is a copolymer of natural rubber latex (polyisoprene) and polymethylmethacrylate. It is used primarily in the adhesives industry. The poly methyl-methacrylate contributes specific adhesion as well as high modulus (immediate strength) to the natural latex. Due to its superior

physical properties, which are un-matched by any synthetic latex, the applications of natural latex are numerous. They include medical devices like condoms, surgeon and examination gloves, lineman gloves, thread used in clothing and undergarments, balloons, molded goods and novelties. However, the recent awareness that the natural protein stabilizer can cause allergic reactions has limited its use. Because of this consideration, natural rubber latex products have been replaced to some degree by synthetic rubber products, especially in unsupported examination gloves. Synthetic rubber latexes include styrene butadiene rubber (SBR), acrylonitrile butadiene rubber (NBR), polychloro-prene rubber (CR), butyl rubber (BR), and synthetic poly-isoprene rubber (IR). There are other specialized synthetic rubber latexes, such as HYPALON® latex and EPDM latex, but they will not be discussed because of their limited application (Omprakash *and* Nautiyal, 2012).

## **2.10 Rubber waste:**

The use of rubber in so many applications results in a growing volume of rubber waste. With the increase in demands, the manufacturing and use of rubber and the rubber products has increased tremendously both in the developed and less developed countries. About 242 million tyres are discarded every year in the United States alone. Less than 7 percent are recycled. 11 percent are incinerated for their fuel value and another 5 percent are exported. The remaining 78 percent are either landfilled, or are illegally dumped. According to a recent report of the US Environmental Protection Agency (U.S EPA), this has resulted in a national stockpile of over 2 billion waste tyres. But with the decreasing scope of available sites and due to the corresponding cost explosion this process of waste rubber disposal is no

longer feasible. Land filling with waste tire is, also the most unwanted due to environmental problems and has no future possibility (Eldho Abraham *et al*, 2011).

## **2.11 Reclamation of rubber products**

One of the various problems which mankind faces as it enters into the 21st century is the problem of waste disposal management. Since polymeric materials do not decompose easily, disposal of waste polymers is a serious environmental problem. Large amounts of rubbers are used as tires for aeroplanes, trucks, cars, two wheelers etc (Adhikari B. et al; 2000). Reclaimed rubber is the product resulting when waste vulcanized scrap rubber is treated to produce a plastic material which can be easily processed, compounded and vulcanized with or without the addition of either natural or synthetic rubbers. Regeneration can occur either by breaking the existing cross links in the vulcanized polymer or by promoting scission of the main chain of the polymer or a combination of both processes. Reclaiming of the waste rubber can be a difficult process.

There are many reasons, however why waste rubber should be reclaimed or recovered;

- Recovered rubber can cost half that of natural or synthetic rubber.
- Recovered rubber has some properties that are better than those of virgin rubber.
- Producing rubber from reclaim requires less energy in the total production process than does virgin material.
- It is an excellent way to dispose of unwanted rubber products, which is often difficult.

- It conserves non-renewable petroleum products, which are used to produce synthetic rubbers.
- Recycling activities can generate work in developing countries.

At the end of 1950s, only about one fifth of the rubber hydrocarbon used by the United States and Europe was reclaimed. By the middle of 1980s less than 1% of the worldwide polymer consumption was in the form of reclaim. At the beginning of 20th century half of the rubber consumed was in the form of reclaim.

## **2.12 Reuse of waste rubber products**

Polymers may be divided into two main groups: thermoplastics and thermosetting materials. Thermoplastics soften when heated, and so may be molded and then cooled to obtain the desired shape. In principle, this process may be repeated either by direct reheating or preferably after grinding into granules, of scrap products. Thermosetting materials like rubbers on processing and molding are crosslinked, and therefore cannot be softened or remolding by heating again. Chemical additives (mostly in minor quantities) are generally incorporated into both thermoplastics and thermosets as stabilizers, flame-retardants, colorants, plasticizers etc. to optimize product properties and performance. Thus thermoplastics are more readily recyclable than thermoset polymers and rubbers. Thus recycling of thermoplastics simply involves a reversible physical change by heating the resin above its processing temperature for shaping it and then cooling it to room temperature to obtain the desired recycled product (Adhikari B. *et al*; 2000).

But in case of thermosetting materials like rubbers recycling is not easy. The three dimensional network of the thermoset polymer system must be broken down either through the cleavage of crosslinks, or through the

carbon–carbon linkage of the chain backbone. This is a much more severe process and the fragmented products obtained by such cleavage are entirely different from the starting thermoset or even its precursor thermoplastic material. Thus recycling of thermoplastics is less troublesome and so the technology for its refabrication is both well established and economical. Thus a recycled thermoplastic material competes directly with the virgin polymer. Its commercial viability depends upon the performance/cost benefit of the finished product. In contrast, the technology for recycle of thermoset polymers including rubbers is complex, costly and less viable commercially (Adhikari B. *et al*; 2000).

In case of recycling of thermoplastics, reclaim thermoplastics are used along with virgin resins and fresh additives in the formulation to obtain desired properties in the product. As with the properties of recycled plastics which undergo significant reduction of physical property in its recycle, still it retains an acceptable fraction of virgin resin properties. Similar picture is also found in reclaim rubber (Adhikari B. *et al*; 2000).

Although reprocessing of thermoset is difficult still the use of reclaimed/ reground thermoset resins in new polymer formulations is found with some influence on flow and deformation characteristics during processing. Perhaps these are used as fillers. Whereas crosslinked elastomers (thermosets) are easily reclaimed to a thermoplastic mass suitable for subsequent crosslinked product although remaining present in a virgin matrix polymer. Although chemical conversion of waste thermoplastic materials can regenerate their respective monomer providing value added products but till date there is no such endeavor to regain monomeric constituent from corresponding elastomeric waste (Adhikari B. *et al*; 2000).

## **2.13 PVC sole in footwear**

Over the last 60 years there has been a major change in soling materials used in the footwear trade. Leather has been the traditional soling materials for footwear, but in 1980, only 5% of shoes have leather soles. Nowadays, most soles are made of rubber or plastic, which are classed as synthetic soling materials (Harvey 1992).

The advent of PVC as an injection moulded material for soles in the early 1960's was rapidly adopted by the footwear trade as an alternative to vulcanized rubber. It is suitable for direct moulding on to shoe bottoms or can be used to produce a wide variety of moulded unit soles (Miller, (2013). State fairly soft grades of P.V.C are used so that a good bond and good wearing properties (similar to that of medium grade rubber) can be obtained. PVC needs to have a patterned surface to overcome a tendency to slip (Miller, (2013).

## **2.14 PVC waste**

PVC is the second most important polymer worldwide and a large-scale chemical product. Thanks to its excellent cost/performance ratio and outstanding chemical and environmental resistance, it is today mainly used for long-life applications. In some countries like France, PVC is used too in large volume for bottles. Pure PVC scrap can be recycled without any problems. Although many applications for such products of recycled PVC have been developed and pilot plants for recycling exist, only small volumes have been recycled up to now. Only bottles made from PVC for drinking water in France, which is a large market, are already separately collected, recycled in large quantities, and transformed into such articles as water pipes. Specialist organisations deal with this business. In such cases like

kitchen waste, where PVC is part of mixed plastics waste for example, sorting and separation of the PVC is necessary (Menges, 1996).

## **2.15 PVC recycling**

The issue of plastic waste management is a complex process and there is no simple solution for reducing this waste. Incineration, recycling, and land filling are some of the traditional methods for handling plastic waste. However, these methods are costly and often create new environmental difficulties. The best solution according to many scientists in the world like Rajashree Patil et al (2012) is a combination of solutions that includes use of biodegradable plastic, plastic recycling, and bioremediation of plastic waste (Rajashree *and* Bagde, 2012).

## **2.16 Natural rubber/leather waste composite**

Nelissa et al (2014) are manufactured A new eco-friendly material and recycling approach from Natural rubber/leather waste for making composite foam The leather fibers were shredded to diameters of 16 mm using a mill with rotating knives and a 30 mesh sliver from MARCONI model MA880, in order to obtain short fibers and leather fiber Granules.

The effect caused by incorporating leather waste on natural rubber to produce an expanded composite is related to the amount of leather in the mixture, which influences directly on cells structure and on mechanical properties. The cell structure was analyzed by microscopy and the results showed that the leather shavings tend to hamper the expanded process, resulting in smaller and fairly uniform cells, which define different densities for the composites. The mechanical properties were investigated and the composites exhibited a great strength and energy absorption capacity. The increase of leather shavings on the mixture improves the hardness of the



composite, elevating the necessary force to strengthen the composite. Therefore, it is possible to produce composites with leather waste with different characteristics that can be directed to many applications according to foam density and the hardness required (Nelissa *et al*, 2014)

Semih *et al* (2018) are incorporated chrome-tanned leather wastes into natural rubber and styrene-butadiene rubber and their blends in various ratios by using a Banbury mixer and two-roll mill, subsequently. Effects of the wastes on rheological, thermal, mechanical, aging, and morphological properties of the blends were investigated. Different penetration ability and distinct cure rates of the two rubbers caused interesting rheological characteristics. Original mechanical properties of styrene-butadiene rubber and its blends were retained after waste incorporation. Furthermore, thermal aging resistance of natural rubber matrix could be improved. The most significant effect of leather particles is the enhancement of the tear strength of all the vulcanizates by shifting the tear mechanism towards the tortuous fracture pathway ( Semih *et al*, 2018).

## **2. 17 Polylactic Acid (PLA) Biocomposites Filled with Waste Leather Buff (WLB)**

Tushar, *et al* (2016) are developed eco-biocomposites using waste leather buff (WLB) as filler in Polylactic acid (PLA) matrix to reduce the environmental issues and provide sustainable solution. WLB/PLA composites were prepared by twins screw micro extruder varying the WLB content from 2% to 30 wt%. These composite were extensively characterise by several techniques. Tensile properties of the composites showed addition of WLB resulted in improvement of tensile property of composite and reduction in percentage crystallinity of PLA matrix observed with increase

in WLB content. The effect of WLB on properties of interfacial adhesion and dispersion in WLB/PLA composites were studied by SEM. Wettability of composites was tested by contact angle and water absorption studies. WLB/PLA composite showed increase in water absorption with WLB loading. This WLB/PLA composite could be used to develop low cost eco-friendly product material (Tushar *et al*, 2016).

## **2. 18 Polyethylene and Hydrolyzed Collagen Blend:**

Puccini et al (2015) are developing of novel materials by blends of synthetic and natural polymers which can help to reduce the environmental impact of plastics. Hydrolyzed collagen (HC) from leather industry is an inexpensive natural biopolymer and it is a promising material for blending with synthetic polymers (e.g., polyethylene) to produce different types of item (it is no food competition, low cost, and biodegradable-compostable). Due to the wide difference in polarity, the natural polymer does not disperse easily in nonpolar thermoplastics, therefore the structural differences between polyethylene and collagen hydrolyzate make them incompatible. Thus, in that work compatibilizing agents as maleic anhydride functionalized ethylene elastomers have been used. The content of HC in polyethylene matrix varied between 10 and 50 wt%. Transparent, cohesive and flexible films, having an average thickness of 60  $\mu\text{m}$ , were obtained by using the film blowing technique. Film blowing is a shaping technique used extensively to produce most plastics films and bags for packaging applications. The extruded films were characterized through mechanical testing, scanning electron microscopy, and thermal analysis. The films containing up to 20 % of collagen hydrolyzate, in the presence of compatibilizing agents, are characterized by satisfactory thermal-mechanical

properties. Thus HC/PE blends appear as promising candidate for the production of innovative material suitable for production of thermoplastic items for applications in packaging and agricultural segments Puccini *et al*, 2015).

## **2.19 Waste Leather Buff and Cellulose Biocomposites**

Guangmei et al (2015) are utilized waste leather buff (WLB) as filler in cellulose and make biocomposites for packaging applications such as wrappers. Cellulose was dissolved in the environmentally friendly ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl). To this solution, WLB was added in amounts of 5 to 25 wt.% of cellulose. The cellulose and cellulose/WLB composite films were prepared by regenerating the corresponding cast solutions in a water coagulation bath followed by washing and drying. These films were tested for their tensile properties, thermal stability, and morphology. The tensile modulus and strength of the composite films were lower than those of the matrix. The lowering of the tensile modulus and strength with increasing WLB loading was attributed to the random orientation of the leather fibers of WLB in the composites. However, the % elongation at break of the composite films was found to be higher than that of the matrix and increased with increasing WLB content. The possible interaction between the matrix and WLB filler was probed using FT-IR analysis. The thermal stability of the composite films was higher than that of the matrix. The increase in thermal stability of the composite films was attributed to cross-linked collagen protein leather fibers in WLB. The fractographs of the composite films indicated good interfacial bonding between cellulose and leather fibers of WLB. These composite

films may be considered for packaging and wrapping applications (Guangmei *et al*, 2015).

## **2.20 Leather waste with polymer composite**

Jacob *et al* (2017) there are utilized industrial wastes of leather industry and automotive glass industry as useful materials. For studied composite plates have been prepared with recycled Poly Vinyl Butyral (PVB) as matrix and wet blue leather trimming waste and buffing dust as reinforcement materials. PVB is the industrial waste from automotive glass industry. Buffing dust and wet blue leather trimming waste are the industrial wastes from leather industry. Weight fraction of matrix as well as reinforcement in the composite has been maintained as 50%. Both wastes were compounded using two roll mill at a temperature of 90°C. After milling, the composite plates were compression moulded at a temperature of 95°C to improve surface finishing and a final thickness of 3 mm has been obtained. Specimens for mechanical testing were punched out from the composite plates as per ASTM standard. Characterization result indicates that these composites could be used as a replacement of conventional O-ring and insulation materials. Proper utilization of these waste materials not only reduces the production costs but also drive down environmental pollution (Jacob *et al* 2017).

## **2.21 PVC blend**

Samira *et al* (2013) they are study the improved physicochemical properties of mixtures of polymers and PVC-PVC \* HDPE \* by the addition of stabilizers deferential percentages (2%-5% -10%). According to the study of mechanics and in general it was found that the mixture containing recycled PVC once has mechanical properties - before and after higher than

the other blends (HDPE / recycled PVC).the addition of PE in the blend PVC (50% HDPE 50% PVC) makes a big change in the structure of the polymer PVC (fall gradually properties tensile). The thermal stability of the blend HDPE / recycled PVC increase with the growth percentages of stabilizers. In addition in the same mixture this latter decreases with increasing rate of recycled PVC. The stabilizing 81KA Baeropan the stabilizer is the most recommended rate 2% and improved mechanical properties of PVC resin on the other hand Baeropan MC87-03 altered these properties has rate 10 % and 5% (Samira, 2013).

According to the Environmental Protection Agency (EPA) “recycling” is considered to be processing of waste to make new article. There are divided three distinct approaches to the recycling of post-consumer plastic materials 1) it could be reused directly; 2) undergo physical reprocessing, for example, grinding, melting and reforming; 3) be subjected to chemical treatment, when components are isolated and reprocessed for use in manufacture. A new widespread nomenclature of recycling was adopted by EPA. Primary recycling involves the use of pre-consumer industrial scrap and salvage, while physical reprocessing refers as secondary recycling and chemical processing as tertiary recycling (Samira, 2013).

Pre-consumer industrial scrap and salvage is the recycling of clean, uncontaminated single-type waste. The recycled scrap or waste is either mixed with virgin material to assure product quality or used as secondary grade material . Reuse could be considered as “zero order”. In simply reuse, the plastic article remains intact and is reused in its original form. However, plans for reuse of plastic bottles could include a limit on the number of use cycles a bottle will undergo, an expiration date for the use of such articles, a visual inspection system for gross contamination and damaged bottles. A

fourth operation of plastic waste management is the recovery of its energy content by incineration (combustion). Incineration, aimed at the recovery of energy, is currently the most effective way to reduce the volume of organic material, that, owing to a lack of other recycling possibilities, may then end up disposed of in landfills. Plastics, either thermoplastic or thermosetting, are actually high-yielding energy sources. There are six main plastics which arise in municipal solid waste – high density polyethylene, low density polyethylene, polyethylene terephthalate, polystyrene, polypropylene and polyvinyl chloride (Virginija *et al*, 2008).

## **2.22 Leather waste and LDPE/LLDPE blend Composites**

Jacob *et al* (2015) they mentioned that fabrication of composites material as a useful product by the utilization of industrial leather wastes and postconsumer milk pouches. Due to industrialization, quantity of solid waste generated from the industrial operations is increasing day by day and this causes enormous pollution to the environment. Therefore an attempt has been made in our present research that explores a possible utilization of leather industry trimming wastes and household garbage wastes for the fabrication of LDPE/LLDPE composites followed by their characterization. Post-consumer milk film consists of LDPE/LLDPE (50:50) blend. Both wastes are compounded using two roll mill at a temperature of 403 K. At this temperature both wastes are mixed and stacked together. After milling the composite sheets were compression molded at a temperature of 368 K and about 20 ton of pressure to shape in the form of sheets. A final thickness of 3 mm was obtained for the samples to be used in mechanical tests. To find out the properties of fabricated composites sheets, sheets were punched

out as per ASTM standard for tensile testing properties, hardness, abrasion resistance and tear strength. Thus different kinds of waste materials have been successfully utilized as filler in polymer composites with an objective of reducing the production and material costs thereby reducing environmental pollution (Jacob *et al*, 2015).

## **2.23 Poly (Vinyl Butyral)- Leather Fiber Composites**

Ambro' *et al* (2011) are studied the preparation and characterization of composites with recycled poly vinyl butyral (PVB) and wet blue leather fiber with leather contents of 30, 50, and 70 wt%, using an extruder equipped with a Maillefer single screw operated with a flat extrusion die. The components of the composites were characterized using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and Fourier transform infrared spectroscopy (FTIR). After extrusion, the PVB/leather composite plates were compression-molded to obtain specimens for testing the tensile properties, hardness, abrasion resistance, and tear strength. The morphologies of the composites were analyzed by scanning electron microscopy (SEM). The DMA and FTIR analyses showed that the recycled PVB contained plasticizer remained in the polymer matrix after extrusion. The SEM analysis revealed good interfacial adhesion between the PVB matrix and the leather fibers. Increasing the leather content in the composites led to a significant increase in the tensile modulus and a reduction in the tensile strain at breaks. The Shore hardness of the composites increased with the wt% of leather, whereas the abrasion resistance decreased (Ambro' *et al*, 2011).

## **2.24 Plasticizing Polystyrene with Waste Leather**

Ganesh (2001) used chrome-tanned wastes from buffing leather dust for plasticizing atactic polystyrene (PS). This waste material, after preliminary characterization, has been dispersed in solvated polystyrene. Resultant composites prepared therefrom via solution cast method exhibit a drastic drop in surface hardness up to certain modifier concentration, beyond which it increases. Addition of surfactants during dispersion of the buffing dust at the optimum level further reduces surface hardness. Para-toluene sulphonic acid (PTSA) has been found to be a better compatibilizer than more conventional sodium lauryl sulphate (LS) in this system. The compatibilized composites show substantial “yield behaviour” when stretched and the breaking strain has been improved drastically from 0.2% in pure polystyrene to 25% in PTSA compatibilized system without any loss in strength. Accordingly, the breaking energy has been increased to much greater than that of the virgin polymer. Effective plasticization of the composites has lowered the glass transition temperature ( $T_g$ ); PTSA containing composite has shown the minimum value, possibly due to generation of more free volume around the rigid polystyrene molecules on account of its effective adsorption over finer dust particles. Accelerated thermal degradation study shows greater thermal stability of the composites as compared to virgin polymer and this possibly resulted due to the presence of chromium content in the waste, which acts as heat sinks (Ganesh, 2001).

## **2.25 High-Density Polyethylene with leather composite**

The potential of solid tannery waste as filler in high-density polyethylene (HDPE) was studied by examination of mechanical properties, morphology and thermal properties of the composites produced. The



Composites were prepared by two roll melt mixing and compression moulding technique for varying fiber contents from 0% to 60%. The parameters tested were tensile, impact and hardness in accordance with ASTM specification. The morphology and thermal properties of the matrix and composites were studied by scanning electron microscopy and thermogravimetric analysis. The results of stress-strain behaviour of the composite was similar to those of thermoplastic polymer, the tensile strength and yield stress of the control (HDPE) was higher than that of the prepared samples by 8% and 5%. Hardness was better than HDPE by 12.86%. When 3.5g of Mg (OH)<sub>2</sub>, 0.3g of Ti<sub>2</sub>O, 10g of NR, 0.5g of trimethyl quinolene (TMQ), 2g of ethylene vinyl-acetate (EVA) copolymer and 2ml of Acrylic acid were incorporated into the formulation, 52.2%, 39.2% and 29.1% enhancement in yield stress, tensile and impact strength. SEM scan shows ductile tensile fractured surface of composites with better thermal stability than the control. Composite of HDPE/fibers waste (90: 10) presents good mechanical performance with enhanced thermal stability (Musa *et al*, 2017).

# **CHAPTER THREE**

## **MATERIALS AND METHODS**

### **3.1 Materials**

In this research the wastes were used for manufacture footwear sole. The materials used for this research include: chrome shavings collected from tannery, Buffing leather wastes collected from buffing machine at tannery (**Fig I**), Buffing rubber wastes collected from buffing machine at footwear industry (**Fig 2**), PU adhesive, PVC from injection and extrusion grades.

### **3.2 Methods**

Three methods were used form manufacture of sole for footwear industry

#### **3.2.1 Method one: Manufacture of sole from leather shaving and rubber wastes**

In this method the chrome shavings were mixed with rubber buffing wastes and binder solution and formed dough for making sheet.

#### **3.2.2 Method two: Manufacture of sole from Leather buffing and Rubber Waste blends**

In this method leather buffing wastes were mixed with rubber buffing wastes in PU adhesive.



**Figure 3-1 Buffing leather waste**



**Figure 3-2 Buffing rubber waste**

Leather buffing wastes mixed with rubber buffing wastes in PU adhesive. The blend composite ratio (leather/rubber) include 90/10, 80/20,

70/30, 60/40, 50/50, 40/60, 30/70, 20/80 and 10/90 and make up the blend weight to 150g. Table 3-1 showed the different percentages of leather/rubber blends ratio. The Compression moulding machine used to produce sole from the experimental blend. (Fig 3-3)

**Table 3-1: Composition percentages of leather/rubber blends Ratio**

No	Materials	
	Leather waste (Wt %)	Rubber waste (Wt %)
A	90	10
B	80	20
C	70	30
D	60	40
E	50	50
F	40	60
G	30	70
H	20	80
I	10	90



**Figure 3-3 Compression moulding machine**

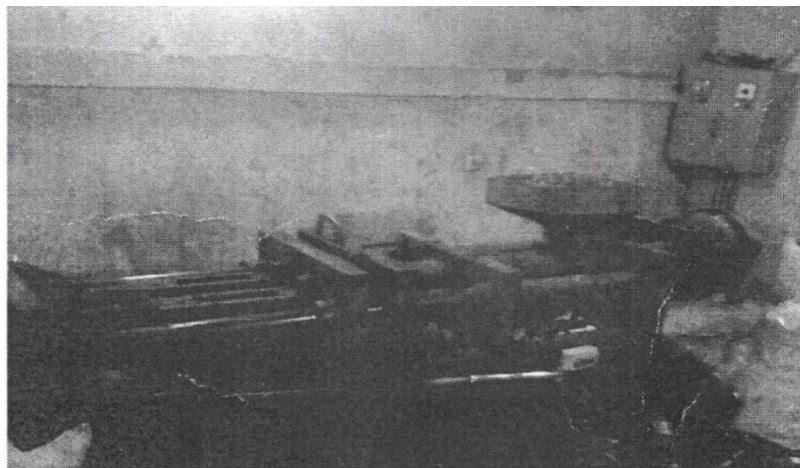
### **3.2.3 Method three: Manufacture of sole from PVC wastes grades blend**

Two different grades of PVC waste were used in this work to manufacture PVC footwear sole. The waste of PVC Injection grade from shoes products mixed with PVC extrusion waste from tube products. The blend prepared from extrusion and injection according to the following PVC extrusion/ PVC injection compositions ratio: 70/30, 60/40 and 50/50 to make up a total of 3Kg blend. The injection molding machine used to produce the PVC sole from the experimental blend. Table 3-2 shows the different percentage of materials used.

**Table 3-2: Composition percentage of PVC injection grade and PVC extrusion grade blends**

No	Materials	
	PVC injection grade (Wt %)	PVC extrusion grade (Wt %)
A	50	50
B	40	60
C	30	70

The vertical injection machine wear used to produce the samples of PVC sole (**Fig. 3-4**).



**Figure 3-4 shown the injection molding machine**

### **3.3 Testing Methods**

Required test specimens were punched out from the prepared soling material using die. Mechanical properties such as tensile strength, percentage of elongation at break and hardness, Density test have been determined as a physical test were measured in leather incubator laboratory.

### 3.3.1 Tensile Strength

The tensile strength does not directly influence the properties and expectation of the soling materials yet it is one of the parameter to be judged as a general characteristic. Tensile strength refer to break load per unit cross sectional area. Break load is the quantum of force that can break a material under specific condition. A rectangular or dumbbell shape test specimen after measuring its width and thickness is filled with both the jaws in a tensile tester. The force is applied to pull the specimen to determine. By dividing the force with the cross sectional area with the same apparatus the “percentage of elongation at break” is calculated by noting down the initial length and the final length when it break the % of elongation is then mathematically calculated i.e. :Elongation at break” is an important parameter for determining the flexibility which indirectly influence the durability too (**Fig. 3-5**) (Somenath Ganguly; 2005)

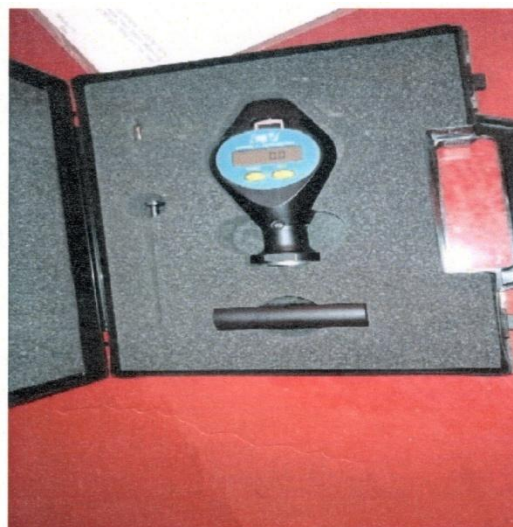


**Figure: 3-5 the Tensile strength machine**



### 3.3.2 Hardness

The hardness of soling materials is judged by measuring the penetration of a rigid ball into the test pieces under specific condition by an apparatus known as hardness tester. The measured penetration is converted into International Rubber Hardness Degree (IRHD). The harder materials will give higher reading. Then the hardness sample is checked with the standard only by acceptance or rejection. Then the hardness sample is checked with the standard only by acceptance or rejection. The hardness of the samples was measured using Shore A. the hardness devices used shown in **Fig. 6** (Somenath Ganguly; 2005).



**Figure: 3-6 the hardness devices**

### 3.3.3 Density

Density is related to the weight of the materials and is expressed as mass per unit volume. This indicates how a materials becomes heavier or lighter. The higher the density, the heavier the materials and vice- versa. To measure the



density of flat materials, the test specimen of uniform thickness are taken in either a circular or square shape container. Both the thickness and diameter\ length were measured and accordingly the volume is ascertained. Subsequently the test specimen is measured to its mass and density is determined by dividing mass with volume. It is somehow difficult to measure the volume of a molded unit sole dye to un-even surface of it. However, the volume in this sample sole is taken both in normal condition and in immersed condition in water. Loss of weight in water) determiner the volume of water replaced which is equivalent to the sole unit and then density can be calculated by using formula (Somenath Ganguly; 2005).

The sample was taken in any shape with a volume to find out mass and volume and then calculating density using the formula. Fig. 3-7 shown the equipment used for density.



**Figure: 3-7 density equipment tests**

# **CHAPTER FOUR**

## **RESULTS AND DISCUSSION**

The mechanical studies of blends are very important characteristics because the products made have to bear the mechanical stress exerted when used by the consumer. The mechanical properties of the composites prepared in this study were examined. The mechanical properties such as tensile strength, elongation at break, hardness and density as physical test were examined.

The two experimental methods were gave best results. The method one used leather buffing wastes and rubber buffing wastes for manufacture footwear sole. The method two used Poly Vinyl Chloride (PVC) injection waste grades and Poly Vinyl Chloride (PVC) extrusion grades for manufacture of footwear sole.

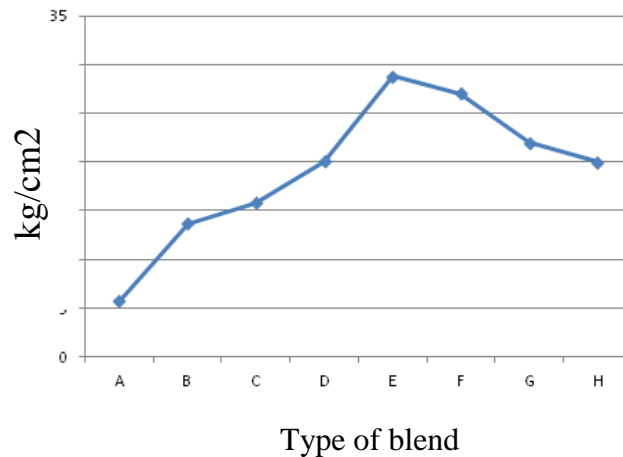
### **4.1 Method one: Manufacture of sole from Leather / Rubber Wastes blends**

The sample from each blend was tested and average is calculated. The mechanical and physical properties of experimental samples viz. tensile strength, ( $\text{kg/cm}^2$ ), percentage of elongation (%), density ( $\text{g/cm}^3$ ) and hardness (shore A) were evaluated (Table 4-1).

**Table 4-1: The mechanical and physical properties of different composites**

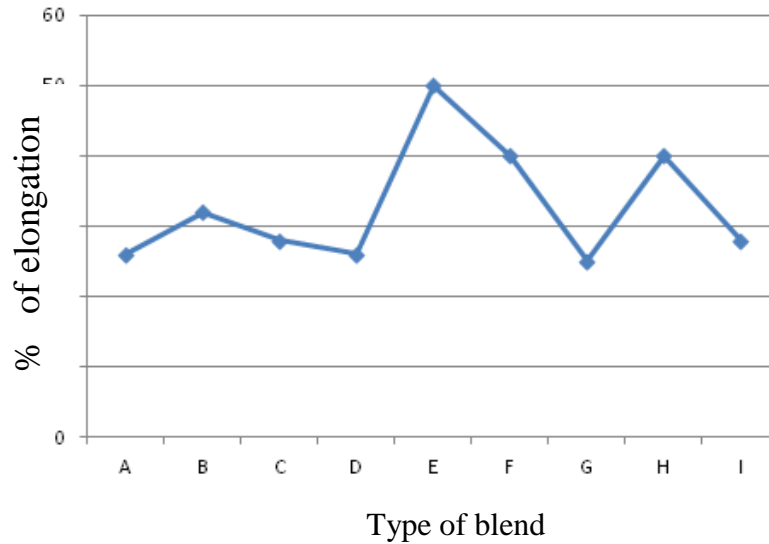
Composite	properties	Tensile strength (kg/cm <sup>2</sup> )	Percentage of Elongation %	Density (gm/cc)	Hardness (Shore A)
<b>A</b>		<b>5.7</b>	<b>26</b>	<b>0.94</b>	<b>65</b>
<b>B</b>		<b>13.7</b>	<b>32</b>	<b>0.98</b>	<b>80</b>
<b>C</b>		<b>15.8</b>	<b>28</b>	<b>0.90</b>	<b>83</b>
<b>D</b>		<b>20.1</b>	<b>26</b>	<b>0.89</b>	<b>85</b>
<b>E</b>		<b>28.8</b>	<b>50</b>	<b>0.91</b>	<b>81</b>
<b>F</b>		<b>27</b>	<b>40</b>	<b>0.98</b>	<b>80</b>
<b>G</b>		<b>22</b>	<b>25</b>	<b>1</b>	<b>75</b>
<b>H</b>		<b>20</b>	<b>40</b>	<b>0.97</b>	<b>74</b>
<b>I</b>		<b>9.7</b>	<b>28</b>	<b>0.87</b>	<b>67</b>

Figure 4-1 shows the tensile strength of different composites. All tests have been carried out at room temperature. The tensile strength of all blends was below the range of the rubber standard expect E blend (50/50) in the normal range.



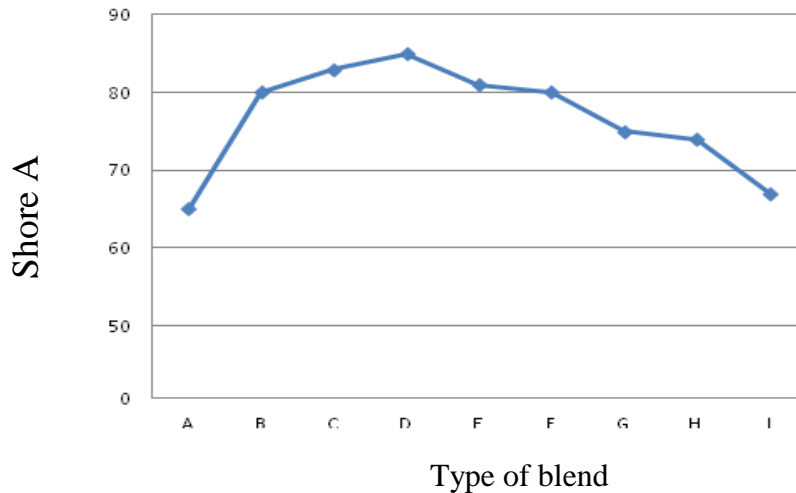
**Figure 4-1: The Comparison of Tensile Strength in different composites**

As shown in figure (4-2) The Percentage of elongation of rubber materials is 175 and elongation of percentage the different composites were below the range, and that indicated all the specimens have poor elasticity.



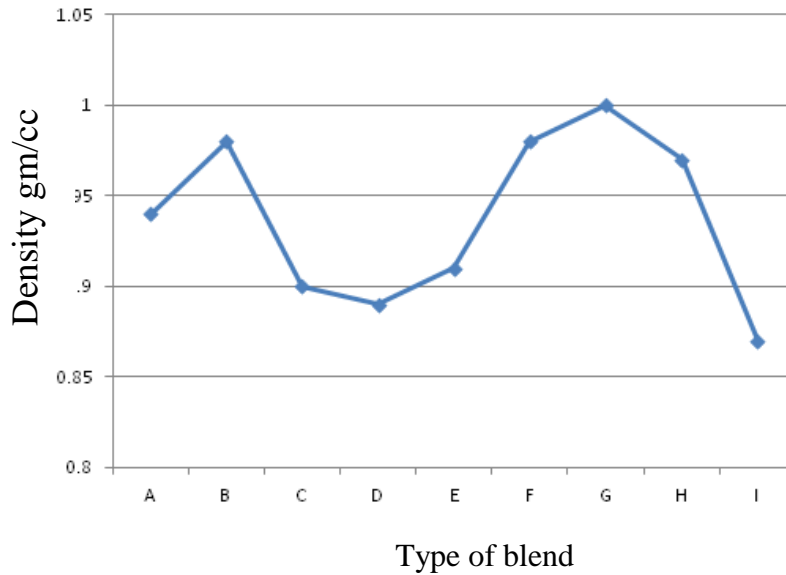
**Figure 4-2: The Comparison of Elongation in the different composites**

The hardness values of different composites were above the rubber hardness range of blend sole i.e. 40 shows in (Fig. 4-3).



**Figure 4-3: The Comparison of hardness in the different composites**

The density of different composites sole were evaluated the all specimens is above the range compared with the rubber density 0.8 g/cm<sup>3</sup>. It was shown in (Fig. 4-4).



**Figure 4-4: The Comparison of density in the different composites**

## **4.2 Method two: Manufacture of sole from PVC wastes grades blend**

Three samples from each blend were tested and average is calculated. The mechanical and physical properties were evaluated.

### **4.2.1 Tensile Strength (N/mm<sup>2</sup>)**

The tensile strength of the different blends composites PVC were evaluated and results for experimental footwear sole (**Table 4-2**)

**Table 4-2: Tensile strength of different composites (N/mm<sup>2</sup>)**

No Samples	Specimen 1	Specimen 2	Specimen 3	Mean
Standard	13.5	13.5	13.5	13.5
A	19.18	17.16	17.38	17.91
B	15.23	16.81	17.79	16.61
C	14.1	17.55	16.94	16.18

#### **4.2.2 Percentage of elongation (%)**

The elongation of the different blends composites PVC were evaluated and result for experimental footwear sole (**Table 4-3**)

**Table 4-3: Elongation of different composites (%)**

No Samples	Specimen 1	Specimen 2	Specimen 3	Mean
Standard min.	300	300	300	300
A	210	182	176	189
B	166	184	194	181
C	152	184	160	165

### 4.2.3 Hardness test (shore A)

The hardness test results were evaluated for experimental footwear sole (Table 4-4)

**Table 4-4: Hardness of different composites**

No Samples	Specimen 1	Specimen 2	Specimen 3	Mean
Standard Max.	74	74	74	74
A	85.7	82.7	87.5	85.3
B	83.8	86.4	84.2	84.8
C	84.6	82.6	82.5	83.3

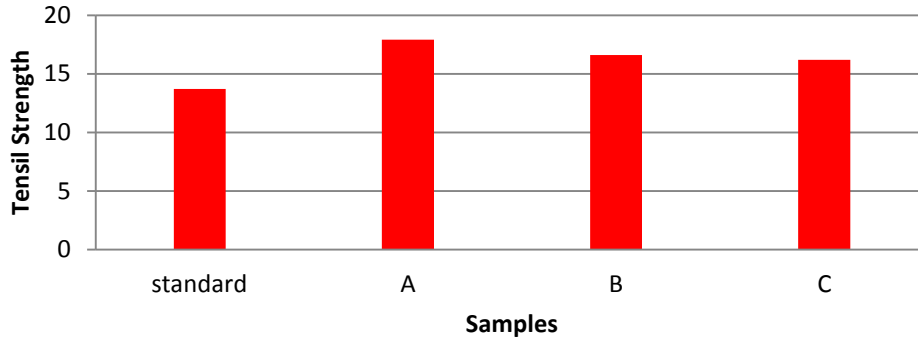
### 4.2.4 Density ( $\text{g/cm}^3$ )

The density of the experimental footwear sole from different composites was evaluated (Table 4-5)

**Table 4-5: Density of different composites ( $\text{g/cm}^3$ )**

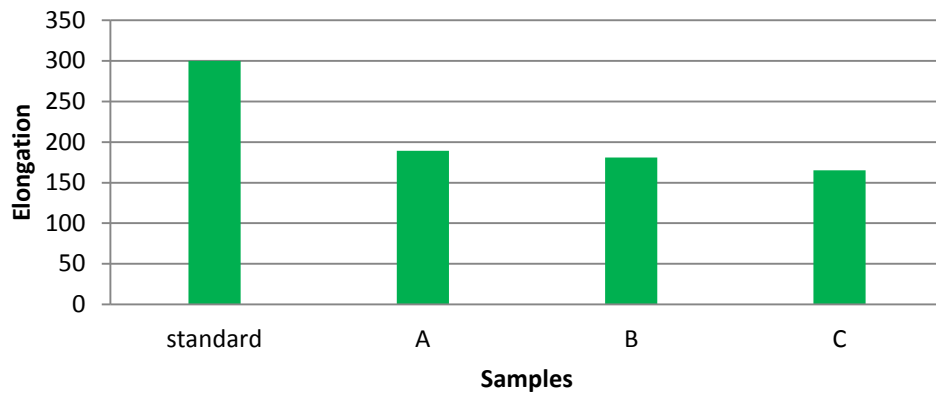
No Samples	Specimen 1	Specimen 2	Specimen 3	Mean
Standard	1.2	1.2	1.2	1.2
A	1.13	1.4	1.22	1.25
B	1.33	1.18	1.15	1.22
C	1.08	1.13	1.28	1.16

The importance of tensile strength and breaking load per unit cross-sectional area in soling specification depends on the soling. The specimens shows in (Fig.4-5) increased tensile strength so that indication of stiffness and overall poorer wear performances.



**Figure 4-5: The Comparison of Tensile Strength in different composites**

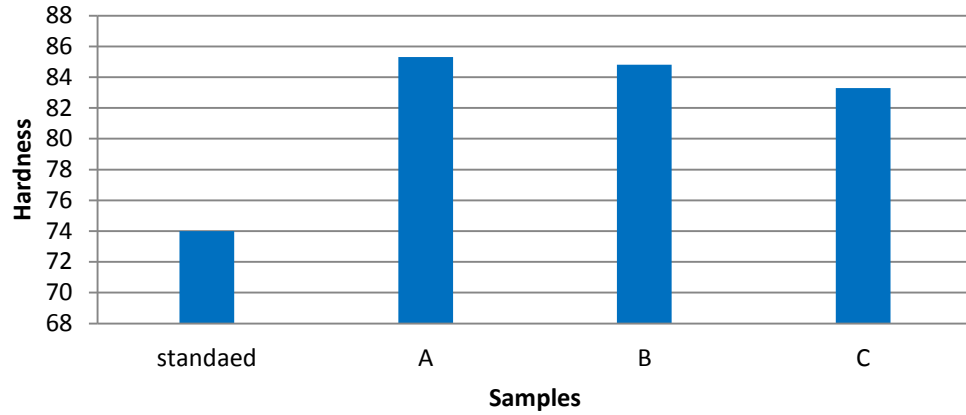
The tensile strength is above the range so the elongation will be less than the range, all the composites were less than the range of PVC sole i.e. 300(Fig. 4-6 )



**Figure 4-6: The Comparison of Elongation in the different composites**

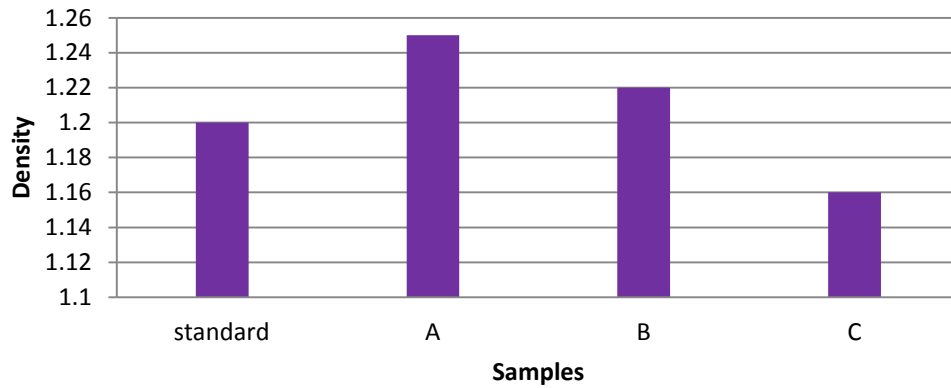
The hardness values of different composites were above the normal hardness range of PVC sole i.e. 58-74 (Fig. 4-7)





**Figure 4-7: The Comparison of hardness in the different composites**

The density of different composites PVC blend sole were evaluated A and B above range and the C less than range with the normal 1.2 g/cm<sup>3</sup>. (Fig. 4-8).



**Figure 4-8: The Comparison of density in the different composites**

## CHAPTER FIVE

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 CONCLUSIONS

Incineration and landfill of chrome tanned leather wastes pose significant environmental problems. In this study, we have shown that utilization of wastes for manufacture footwear sole.

Different composites of leather and rubber buffing wastes blend were investigated. The composites successfully blended and the mechanical properties were evaluated with the rubber range. The leather waste improves the hardness of the composite of the mixture. It is concluded as tensile strength was 28.8 (kg/cm<sup>2</sup>), elongation 50 (%), hardness 81 (shore A) and density 0.91 (gm/cm<sup>3</sup>). The optimum composition ratio of leather and rubber buffing wastes blends (leather\rubber 50:50) provided good mechanical and physical properties for sole.

The PVC injection grade and PVC extrusion grade blends were useful for manufacture footwear sole and improve with important in durability. Three different composites of PVC blend were investigated. The optimum composition of PVC grades blends were evaluated i.e. (extrusion/injection 70/30). This blend provided good mechanical and physical property.

## **5.2 Recommendations**

- ▶ Studying the use of solid leather waste in composites materials.
- ▶ To make more benefit of wastes from leather, rubber, plastic landfills.
- ▶ It will be necessary to carry out more studies and researches in composites materials.
- ▶ More research is needed to determine the relationship between leather waste and natural rubber or any plastic waste.

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