STUDY ABOUT POLYMER APPLICATIONS IN FOOTWEAR

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This thesis was written to study polymer uses in footwear and to define engineered polymers in footwear. How and why polymers are used nowadays in footwear. Though leather is a prime material for footwear but polymers are used for their some properties which are suitable for footwear. It is also significant in this thesis the comparison of leather and polymers as a footwear material. To describe the classification and mechanism of adhesive those are used in this sector is also a very important part. When comparing leather with polymer, bioactive is a very important property nowadays. So that bioactive polymer insole and leather insole or lining materials properties are also studied here.

Water vapor permeability and color rub fastness experiment for lining leather and insole was done and results were compared. Recycling of footwear is also very significant nowadays that is why suggestions were described. This study can help to know polymer uses in footwear and to go further more in this sector polymer uses.
INTRODUCTION

The general business and economic trend is that people want to get better and something different and usefull. For footwear sector polymer is a great change as a main material. Study about footwear materials and polymeric materials used in footwear are an important thing. Actually footwear market is a very considerable nowadays. There was a research done that Global Unit Volume Consumption of footwear 12.1 Billion Pairs in 2013 and it reaches the limit predicted and by amount it is $238 Billion by in 2013. This is a huge market. The global growth at annual rate of 4%.

Leather has been the prime material for shoes for a long time. But in a world with a rapidly growing population and dwindling resources it is time to rethink what our footwear should be made of. Modern technology can help to use our resources wisely. New material developments and production techniques push the boundaries of what can be made. Nowadays polymers are replaced in most of the cases as a cost effective materials. Also in some cases textiles are used. Polymers are used as a adhesive in shoes or footwear. Also for sole polymers are used. Polymers have grown to become a premier specialty plastic compounnder for the Footwear Industry. Polymers’ reputation in the Footwear Industry is the result of a commitment to use only the highest quality raw materials. This is very important because it connected with health issues. This material almost directly connected to the skin. So it is very important to consider health issues. Polymer manufacturers as well as rubber chemical suppliers are now working with shoe companies to develop new materials to specially meet the demands of today’s footwear.

Bioactive is a term that connected with health issues. In footwear this term is very important. To ensure comfort to the users of footwear worn in a work environment and in everyday settings, designers and manufacturers offer specially materials made of polymers. Protective footwear is intended to protect workers against hazards occurring at the workplace, such as mechanical injuries to the feet, burns, or the absorption of chemicals through the skin. Furthermore protective footwear should not affect foot physiology. In this way bioactive polymaterials are very significant for footwear sectors.
OBJECTIVES- Objectives of the study are

- To study and describe polymer materials in footwear.
- Define engineered polymers in footwear applications.
- To study of Comparison between polymers and leather in footwear.
- To describe the mechanism of polymer adhesive in footwear applications.
- To study bioactive insole as a polymeric material in footwear industry.
- To study about water vapor permeability and rub fastness experiment for lining leather.
- To compare the experiment results about lining leather.
Chapter 1  
History and classification of Footwear

1. What is footwear?
A shoe is an item of footwear intended to protect and comfort the human foot while doing various activities. Shoes are also used as an item of decoration. Footwear refers to garments worn on the feet, for fashion, protection against the environment, and adornment.

HISTORY- The easiest way to protect feet was to grab what was handy - bark, large leaves and grass - and tie them under the foot with vines. Few early shoes have survived. Fragments of Bronze Age footwear have been found in excavations but not enough to determine styles. But from the Roman times onwards many shoes have survived suggesting that there were many more shoe styles than one would expect. Spanish cave drawings from more than 15,000 years ago show humans with animal skins or furs wrapped around their feet. The body of a well-preserved “ice-man” nearly 5,000 years old wears leather foot coverings stuffed with straw. Shoes, in some form or another, have been around for a very long time. The evolution of foot coverings, from the sandal to present-day athletic shoes that are marvels of engineering, continues even today as we find new materials with which to cover our feet. In the following there are some very old footwear pictures those are used when people feel that they have covered their feet with something convenient. In figure 1, there are some old pictures of footwear.

![Figure 1: history of footwear](image)

There are evidences which show that the history of the shoe starts in 10,000 BC, that is, at the end of the Paleolithic period (paintings of this time in caves in Spain and in the south of France make reference to the footwear). Among the utensils of rock of the men of the caverns there are several that were used to scrape the skin, which indicates that the art of tanning is very old. In the Egyptian, whose age is between 6 and 7 thousand years, paintings were discovered representing the various stages of the preparation of the leather
and the footwear. In cold countries the moccasin is the protector of the feet and in hotter countries the sandal is still the most used. The Egyptian’s sandals were made of straw, papyrus or of palm fiber.

1.2 CLASSIFICATION OF FOOTWEAR-
Basically there are various types of footwear among men and women. Also there are some kinds of footwear as unisex and also for child. Athletes’ shoes are one kind of shoe and ked shoes also. Nowadays there are some special types of footwear for special people, like diabetes footwear. There are shortly descriptions about various kinds of shoes.

1.2.1 Men's Shoes
Oxford and Derby shoes are the basic classification of men’s footwear. There are shortly description about different types of men`s footwear.

Oxford– The main feature of this kind of shoe is vamp attached with laces part but vamp is on the top. As can be seen in figure -2, oxford shoes.

Derby - Similar looking as Oxford’s, but laces are attached to two pieces of leather that are glued or stitched to vamp. In figure -3 it is a picture of derby shoe.
Monk-Straps – This type of footwear don’t have laces, but instead uses buckle and strap to secure the shoe around the foot. Figure -4 shows monk shoes.

Figure 4 : monk shoe

Brogues – Nowadays brogue perforations can be found in many types of casual shoes. In this types of footwear decorative perforations and separations along the visible edges of material. Figure – 5 shows brogues shoe.

Figure 5 : Brogues shoe
**Slip-ons** - Shoes that don’t have any securing mechanism such as lacings or fastenings. As can be seen in figure 6. Loafers and elastic-side shoes are the most popular slip-on shoes.

![Figure 6: slip on shoes](image)

**Plain-toes** - Figure 7 shows plain toes men shoes. Basically design that doesn’t features additional layer of material on the vamp area of toes.

![Figure 7: plain toes](image)

**Cap-toes** - This type of shoe features extra layer of leather that caps the toes. Figure 8 shows cap toes shoes for men.

![Figure 8: cap toes](image)
Moccasin – This soft leather shoe has no heel and is usually intended for outdoor use. In figure 9, it shows moccasin shoes.

Figure 9: moccasin shoes

1.2.2 Women’s Shoes
High-heeled footwear – It features hill that is typically 2 inches high. Most commonly used in formal occasions and social outings. Figure -10 shows high heeled shoes for women.

Figure 10: high heeled shoes
**Stilettos** - This is invented as a high fashion accessory. It features long and very narrow heel post.

Figure -11, shows stilettos shoes for women.

![Stilettos](image)

**Sling backs** – This kind of shoes basically high heeled, and those are secured not by over the top straps, but ones that go behind the heel. In figure -12, it can be seen women sling back shoes

![Sling backs](image)
**Mules** - It can be small or high heel. Shoes or slippers that have no fastenings around the ankle and only fastenings are located around the toes and lower part of feet. Figure 13 shows mule shoes for women.

![Figure 13: Mules shoe](image)

**Ballet flats** – This type of footwear are very low and flat heel. It is popular in warm environment. Figure -14 shows ballet flats shoe.

![Figure 14: Ballet flats shoe](image)
Court shoes - Popular high-heeled shoes that can be easily slipped-on. As can be seen in figure -15 court shoes.

Figure 15 : Court shoes

1.2.3 UNISEX SHOES - Sandals and slippers are unisex shoes. Sandals feature minimal amount of straps that leave much of the foot exposed to the air. Slipper is used mostly in indoors, similar to sandals, only with the vamp that overs one half of the foot.

1.2.4 ATHLETES FOOTWEAR AND KEDS-- Athletes footwear is especially for sports and physical exercise. In athletes footwear polymers are used more compare to other footwear. This is a matter of comfort and strength also for this kind of footwear. Athletic shoes are typically designed with specific materials that offer flexibility, support, and stability .In exercise and sport it’s affect a lot in footwear. That is why it is very important to choose correct athletes footwear. There are also various types of keds for men, women and kids also. In these types of footwear rubber sole are used a lot. Nowadays this is used a lot for fashion and for comfort also. Figure- 16 and 17 shows athletes footwear and two types of keds respectively.

Figure 16 : Athletes footwear
1.2.5 SPECIAL FOOTWEAR, LIKE DIABETES FOOTWEAR - Proper footwear is an important part of an overall treatment program for people with diabetes, even for those in the earliest stages of the disease. There are also more foot problem those needs special footwear. Figure -18 and 19 shows diabetes and other special case footwear respectively.

Figure 18 : Diabetes footwear

Figure 19 : Other special case footwear
Chapter 2
Description of various parts of footwear

2.1 VARIOUS PARTS OF FOOTWEAR-

Figure 20: Various parts of men and women shoes

Figure 21: Various parts of sinkers or keds
In figure -20, 21 and 22 various types of parts of footwear for men and women are mentioned here.
2.2 Description about main various parts of footwear:

**Upper**: The whole part of the shoe that covers the foot after attaching different small parts of the shoe. It is called as upper.

**Vamp**: The section of upper that covers the front of the foot and it is joined to the quarter.

**Quarter**: The quarter is part of a shoe's upper that covers the sides and the back of the foot. In some shoe styles, the quarter is a separate piece that is sewn to the vamp of a shoe.

**Sole**: The sole is the bottom part of the shoe. This is the part that comes in direct contact with the ground.

**Tongue**: The tongue is a strip that runs up the top-centre of the shoe and sits on the top part of the foot. The purpose of a shoe tongue is to protect the top of the foot.

**Laces**: Laces are inserted through the eyelets of a shoe, and used to bring the sides of the shoe together.

**Lining**: Most shoes attach a lining on the inside of the shoe, around the vamp and quarter. These linings improve comfort, and can help increase the lifespan of the shoe.

**Insole**: A layer of material that sits inside the shoe that creates a layer between the sole and the foot. The insole adds comfort for the foot, while hiding the join between the upper.

**Welt**: A welt is a strip of leather, rubber, or plastic that is stitched to the upper sole of a shoe, as an attach-point for the sole.

**Heel**: The heel is the outer part of the shoe that is placed under the rear of the shoe. Shoe heels come in a wide variety of styles, shapes and heights.

**Shank**: A piece of metal or wood inserted between the sole and the insole lying against the arch of the foot.
2.3 ATHLETIC SHOES:
Considering various types of footwear Athletic shoes are those where polymers are mostly used compared to others. When anybody jump, run, or play, legs and feet can take on the pressure of up to seven times of normal weight. Modern shoes usually contain various types of polymers that absorb shock at the same time as they provide support, flexibility, and traction. Polymers are used because it is easy to make material with polymers achieving the right properties.

In the following figure -23 it can be seen that there are some main parts where polymers are used in athletic footwear

Figure 23 : Athletics shoes with different parts
**Mid sole:** Most of a shoe’s shock absorption takes place in the midsole. The most common material used today is a springy foam polymer called ethylene vinyl acetate. Some sports shoes use a denser foam polymer that chemists developed from polyurethane – the same material as skateboard wheels, just with air bubbles in it. High-tech plastic materials are also used.

**Upper:** The upper portion contains the laces, color, and design. It is usually made from leather or a synthetic material—depending on the sport or activity the shoe will be used. For instance, most running shoes are made from a synthetic polymer called polyester, also known as “mesh”. It is lightweight and helps with support and breathability.

**Insole:** The insoles also absorb shock to keep your muscles from working too hard during normal activities. Insoles come in a variety of different types, including plastic foam and silicone gel.

**Laces:** Most shoelaces are made of leather, cotton, or a mix of natural and synthetic polymer materials.

**Toe box:** By controlling how rubber is made, it can change how it feels. For example, a harder type of rubber may be used to protect toes in soccer or baseball cleats, and a softer type may be used in jazz shoes for dancing on tiptoes.

**Outer sole:** The soles need to be long-lasting and provide good grip to a playground or gym floor. Various forms of rubber are most often used here.
CHAPTER 3
The aspect of expenditure and production process of footwear.

3.1 What makes a shoe costly and where the cost goes?

Here is a sneaker shoe and cost goes by the various divisions:

![Pie chart showing cost percentages](image)

Figure 24: graph about cost percentage of various divisions.

In all upper parts 34%. Hardware and foam, laces, logo printings, tongue etc. In this section polymers are used a lot. For hardware and foam, most of the time they uses polymers like nylon fibers for laces, logo printing is also polymers. Leather is used 16%. Lop mean; Labor, Overhead and Profit. For this part cost goes almost 27%. Outsole this is totally depend on polymers. Cost goes 14% on this unit. The shoe bottom unit is called outsole. Various types of polymers are used in sole part. Like- EVA, PVC, thermoplastic rubber etc. In packing part polymers are also needed. Mold amortization 3%. If there is new tooling it can be paid per pair instead of buying the new molds all at once. To follow all this it is very significant that in a shoe; cost goes almost 30%-45% to polymers. As can be seen in figure 24, where cost goes in a sneaker shoe mostly.
3.2 How to make a shoe

In a footwear company mainly there are five departments in which a progressive route is followed for producing finished shoes. These are

- Designing and pattern making.
- Clicking or Cutting Department.
- Closing or Machining Department.
- Lasting & Making Department.
- Finishing Department.

**Designing and pattern making** - This department is the key department in a company this department is called product development also. Here designing should be done and then various part of the design pattern or design part cut out according to the design. A designer have to know all the things to design a shoe then pattern is coming out for the next step.

**Clicking or Cutting Department** - In this department shoe’s all parts should be cut out to making ready. The worker cuts out pieces of various shapes that will take the form of "uppers". This operation needs a high level of skill as the expensive leather or other polymer material or different materials which need to cut for shoe has to be wasted at the minimum level possible. Materials may also have various defects on the surface such as barbed wire scratches which needs to be avoided, so that they are not used for the uppers.

**Closing or Machining Department** - This department is very sensitive. In this step all parts need to be stitch or attached as a sequencly. The component pieces are sewn together by highly skilled machinists to produce the complete upper. This work is divided in some stages. In early stages, the pieces are sewn together on the flat machine. After that the upper is no longer flat and has become three dimensional. In the later stages, when the upper is become three-dimensional, the machine called post machine is used. The sewing surface of the machine is elevated on a post to enable the operative to sew the three dimensional upper. Various edge treatments are also done onto the leather or polymeric material for giving an attractive look to the finished upper. The eyelets are also inserted at this stage in order to accommodate the laces in the finished shoes.
**Lasting & Making Department:** The completed uppers are molded into a shape of foot with the help of a "Last". Last is a plastic shape that simulates the foot shape. It is later removed from the finished shoe to be used further in making other shoes. Firstly, an insole to the bottom of the last is attached. It is only a temporary attachment. Sometimes, mostly when welted shoes are manufactured, the insole has a rib attached to its under edge. The upper is stretched and molded over the last and attached to the insole rib. After the procedure completes, a "lasted shoe" is obtained. Now, the welt - a strip of leather or plastic - is sewn onto the shoe through the rib. The upper and all the surplus material is trimmed off the seam. The sole is then attached to the welt and both are stitched together. The heel is then attached which completes the "making" of the shoe.

That was the process for heeled shoes. When a flat shoe is in the making, there are considerably fewer operations. The insole in this case is flat and when the uppers are 'lasted', they are glued down to the surface of the inner side of the insole. The part of the upper that is glued down is then roughed with a wire brush to take off the smooth finish of the leather. This is done because rough surface absorbs glue to give a stronger bond. The soles are usually cut, finished and prepared as a separate component so that when they are glued to the lasted upper, the result is a complete and finished shoe. Soles can also be pre-molded as a separate component out of various synthetic materials and again glued to the lasted upper to complete the shoe.

**Finishing Department:** The finishing of a shoe depends on the material used for making it. If made of leather, the sole edge and heel are trimmed and buffed to give a smooth finish. To give them an attractive finish and to ensure that the edge is waterproof, they are stained, polished and waxed. The bottom of the sole is often lightly buffed, stained and polished and different types of patterns are marked on the surface to give it a craft finished look. A "finished shoe" has now been made.

For shoe room operation, an internal sock is fitted into shoe which can be of any length - full, half or quarter. They usually have the manufacturers’ details or a brand name wherever applicable. Depending on the materials used for the uppers, they are then cleaned, polished and sprayed. Laces and any tags that might have to be attached to the shoes, such as shoe care instructions, are also attached. The shoes, at last, get packaged in boxes.
CHAPTER 4
Material of footwear

4.1 FOOTWEAR MATERIALS-
There are various types of materials used in footwear. Different types of materials used in different types of footwear parts. Polymers are widely used in sole. Following materials are used in footwear.

- Leather
- Synthetic polymers
- Rubber
- Plastics
- Textiles
- Plaiting materials
- wood
- cork
- Some cases steel.

These are the main materials used in footwear. For upper materials leather is the prime one. Leather is the best upper material for footwear because of its breathability, perspiration and durability properties. There are various types of leather those are used in footwear depends on fashion, design and needs. It has all ideal properties those are important for footwear. There are various types of leather. Smooth leather, Nubuck leather, side leather, exotic leather, patent leather, drape able leather, suede leather, pig skin, calf skin, coated leather, sole leather. In leather there are lots of pores and it allows fresh air to insert the shoes and also from inside to outside. The circulation of air is very important inside shoes. Moisture absorbance is one of the most important properties of leather. Leather absorbs moisture away from the foot and out of the shoe. Durability is also much needed property. Leather can be stretched and shaped to fit. In the following there is some description about various types of leather-

In the following these are the preferable types of leather those are used in footwear

**Smooth leather**- This type of leather can be matt or shiny. It has small pores with texture surface.

**Nubuck leather**- Buff nubuck is special category leather. In this type of leather there is a special type of buffing operation operated on the outer surface to create a very fine nap. Which even fine contact with fingers or other objects leaves traces, which can be brushed out.
**Sole leather** - This is a special type of cow or buffalo leather to make sole. It is uneven surface and very thick and hard only for use in sole. In various types of fashionable shoes, sole leather is used as a sole.

**Coated leather** - Coated leather is especially used in athletic shoes. This is actually a leather where coated with a thin layer of other material, such as polyurethane. This ensures durability and easier maintenance for the leather as an upper material.

**Other leathers** – instead of this there are some other type of material which are already mentioned. This various types of leather needed for various types of fashion and design and to fulfill criteria as a footwear material. It depends on the production operation when leather is coming out as a finished leather.

### 4.2 SYNTHETIC POLYMERS AS A FOOTWEAR MATERIAL

- Nylon
- Polypropylene
- Polystyrene
- Polyethylene
- Polyvinylchloride
- Bakelite
- Epoxy resins
- Organic glass
- Polyurethane
- Synthetic rubber
- Biopolymers
- EVA
- (…)
In shoemaking industry is used soft PVC (with 20 - 50% softener), mainly for producing soles, heels and all injected shoe.

- Single PVAC is unsuitable for forming, so it is mostly used as a copolymer with PVC.

In shoemaking industry it is used for producing fillings, heels and insoles.
Polypropylene

is obtained by polymerization of the propylene

In shoemaking industry it is used for producing all height of heels, shoe molds and filling.

Polystyrene

is obtained by polymerization of styrene

In shoemaking industry it is used for producing shoe soles and low heels.
Polyamide

is usually obtained by condensation and polymerization of diamine and dicarboxylic acid

\[
\begin{align*}
\text{HO-}R'\text{-COOH} + n \text{H}_2\text{N-}R'\text{-NH}_2 & \rightarrow \text{HO-}C\text{-R-C-N-R'}\text{-N} & \text{H} & \text{C-}R'\text{-COOH} \\
\text{O} & \text{O} & \text{-} & \text{C} & \text{-} & \text{C} & \text{-} & \text{N} & \text{H} & \text{H} & \text{-} & \text{N} & \text{H} & \text{C} & \text{-} & \text{R}\n\end{align*}
\]

In shoemaking industry it is used for producing shoe soles, sports shoes, high heels and thin heel piece.

Polycarbonate

is saturated polyesters of carbonic acid of the general formula

\[(-\text{ORCO-})_n\]

In shoemaking industry it is used for producing soles and heels.

Ethylenevinylacetat

is obtained by polymerization of ethylene and vinyl acetate

\[
\begin{align*}
\text{H}_2\text{C} \leftrightarrow \text{CH}_2 + n \text{H}_2\text{C} = \text{CH} & \rightarrow \left[\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}\right]_n \\
& \text{OCOCH}_3 & \text{OCOCH}_3
\end{align*}
\]

Can be used alone or in combination with other polymers. (Commonly) is produced as expanded material in plates ÷ sole cropping (soles for lightweight summer shoes, middle soles)
4.3 Last-The shoe last is the heart and single most important element of the shoe. It is the most scientific and complex part of the whole shoe making process and it is the foundation upon which much of the shoe related foot health depends. It is responsible for the size, fit, shape, feel, wear, style, tread and even the making of the shoe. A shoe last is the reproduction of the approximate shape of the human foot. The shoe last is hard and firm, while the foot is softer and more flexible. The foot has separate toes, while the toe end of a shoe last is solid. His back curve is greater on shoe last to help the shoe grip the foot. In the shoe last the heel height is present but in foot is not as it is very simple. To prevent the pressure on foot shoe last length is greater than the foot. To help the shoe to grip the foot around the quarters the front part of shoe last is thinner compare to foot. There is a significant part it is called toe spring in last. There are various types of last girths and sizes. Figure -25 shows last for footwear.

![Shoe Last Image](image)

**Figure 25 : Shoe last**

Since the shoe shape is depended on the shoe last, the last can take of the shape of the foot with some modifications. Very important matter in here is the interfacing of the foot and the last should be made with the knowledge of the foot anatomy and shapes.
4.3.1 Types of shoe last- There are few types of shoe last those are uses to making shoes.

- Solid last
- Scoop block last
- Hinge last
- Telescopic last
- three piece last.

Figure 26 : Solid last

Solid last- This is simple last and it is basically used to make low heel shoes and sandals. Figure- 26 shows solid last.

Figure 27 : Scoop block last

Scoop block last- To make manual shoe production this type of last is used in shoe making factory. Figure- 27 shows scoop block last. The shoe last have a wedge on the top and it be detached from the main body. By removing the wedges last can be easily taken out.
**Hinge last**- This kind of lasts are used for all kind of shoe production. This last have fore and back part those are connected by a spring. The last can be bent to shorten at the v cut hinge. In this way the last can be removed from the shoe without deforming and damaging the shoe. Figure -28 shows hinge last.

**Telescopic last**- This kind of last are the similar as hinge last but without the V- cut. The last will reduce the length while slipping. Figure -29 shows telescopic last.

**Three piece last**- This type of last are mainly used for the force lasting boot or reverse slippers. There are three parts in this last. When slipping the middle and the back pieces will be removed. After removing the back and middle part, it is then very easy to remove the front part. Figure- 30 shows three piece last.
4.4 Materials those are used in last making - there are few numbers of materials those are used in last. Shape retaining characteristics is the most important for the materials. The shoe last shape must not change in heat, humidity and other environmental factors. Nowadays to make shoes factories are used very modern machineries. So that the last must be strong enough to withstand the forces of mass production machinery. For example, the mass applied by the pull over machines when bottoming the shoe and must also be able to hold tacks. This is one type of nail which are used while lasting operation is going on. This tacks or nails are used to hold shoe parts together temporarily before the sole is attached. The most common used materials to make last are wood, HDPE (high density polyethylene) and aluminium. Wooden shoe last has low durability. While lasting operation is going on there are few damages are happened in wooden last. This shoe last may swell or shrink with temperature and humidity. HDPE is used extensively for all kinds of shoe lasts. Those shoe lasts are made by high density polyethylene are less expensive. These can be recycled for new shoe last. Low production cost and dimensional stability and ease of workmanship mean that HDPE shoe last are widely used. The shoe last made from aluminum is used for solid or scoop shoe last but are very expensive. Aluminum shoe lasts are used for making rubber boots. Figure -31, 32 and 33 shows wooden last, High density polyethylene and aluminum last respectively.

Figure 31 : Wooden last

Figure 32 : HDPE Last

Figure 33 : Aluminum last
CHAPTER 5
Adhesives uses in footwear and their mechanism.

5.1 What is an adhesive?
An adhesive is a material used for holding two surfaces together. An adhesive must wet the surfaces, adhere to the surfaces, develop strength after it has been applied, and remain stable. Adhesion is a specific interfacial phenomenon. There are three main theories of adhesion: adsorption, electrical and diffusion. All probably apply to most adhesives. Surface preparation before applying the adhesive is of prime importance. The raw materials for adhesives are mainly polymeric materials, both naturally occurring and synthetic. A useful way to classify adhesives is by the way they react chemically after they have been applied to the surfaces to be joined. Adhesive plays an important role in the footwear industries nowadays. Only those adhesives are used in footwear industries are chosen to describe here. Some advantages of adhesive bonding are the thin film and the small particles. Adhesive bonding is faster than stitching or mechanical fastening of nails. The bond strength must also not be affected by rain, snow, wind, ultraviolet light, temperature changes, and whatever other elements to which the shoe will be exposed. In addition to providing high performance properties and durability, the adhesives and bonding processes that are used in the footwear industry must also offer good early strength and workability for fast and efficient production. The adhesive bond must be invisible or at least aesthetically pleasing to the shoe's design.

Adhesives are widely used in the manufacture of most types of footwear, and most importantly for the attachment of the upper to the sole. There are a number of different methods for sole attachment but the use of adhesive is the most common. Generally adhesives are used for footwear making are either solvent based or water based. Although there are other types of adhesives which are used less frequently such as hot melt adhesives.

So basically there are three types of adhesive those are used in footwear industries.

- Solvent base adhesive
- Water based adhesive
- Hotmelt adhesive.
In footwear industries solvent based adhesives have been the predominant type adhesive for decades. Nowadays they are gradually replaced with water based adhesives. The main reason for this because the volatile solvents evaporate into the atmosphere this is why there are environmental issues concerns about factory emissions of such vapors, and also the vapors can be hazardous to the health of workers. In the industries if the proper ventilation is not implemented then these volatile organic compound which are called VOC are easily regulated to many cities as well as countries also. So there is a pressure to change this types of adhesives from the buyer nowadays.

On the other way there are some more reasons for the footwear industries including price, ease of use and perceived problems with achieving good bond strengths with water based system.

5.1.1 What is solvent based adhesive?
Solvent based adhesives are composed of a polymer dissolved in a solvent such as toluene, typically in a ratio of one part polymer to three or four parts solvent. Two types of polymer are extensively used as adhesives in industries. Polychloroprene rubber generally known as neoprene, and polyurethane.

5.1.2 What is Water based adhesive?
Polymers do not properly dissolve in water, water-based adhesives are in the form of an emulsion - small particles (as opposed to individual molecules) of the polymer are suspended in the water. In this most case PU is the most commonly used polymer.

5.1.3 What is hot melt adhesives?
Hot melt adhesive is a form of thermoplastic adhesive. hot melt adhesives provide several advantages over solvent-based adhesives in case of industrial use. Hot melt adhesives have long shelf life and usually can be disposed of without special precautions.

Polychloroprene- Polychloroprene cementing has the property of auto adhesion. It enables the footwear manufactures to freshly cement the two components apart. Then after considerable open time the adhesive film can be re activated by heating with infra-red lamps until tack is fully restored. Then the surfaces are joined together. With polychloroprene adhesive all types of sole can be attached except PVC, TPR and PU sole. Different types of materials require the correct type of adhesives and the right method. It is very important to preparing the substrate surfaces before adhesive is applied. Adhesives bonding is depend of there is no roughness if the surfaces and all dust particles are removed.
Polyurethane- Polyurethane adhesives are the more popular adhesives in footwear industries. Because it is compatible with a greater number of different materials. However some materials need pretreatment to enable the PU to bond to the surface. As an example: rubbers must be pretreated with a chemical solution in a process called halogenation. As it is happened polychloroprene systems no longer hold the PVC with uppers. The introduction of new polymer materials for sole and uppers has introduced new problems for the adhesives manufactures. Bond failure happens on occasion due to migration of the plasticizers into the adhesive films. Solvent based polyurethane adhesive is unaffected by these chemical compound. So that PU adhesive is the solution of this problem. When using PU adhesive few points need to be taken follow.

- 7-10% hardeners must be mixed with PU adhesive before use.
- Leather uppers & soling materials must be properly roughed to remove loose fibers from the surface.
- PVC & resin rubber soles must be wiped with dilute iso-cynate solution in MEK before application of cement.
- Cemented surfaces must be heat reactivated under infrared lamp before joining two surfaces together & press while hot.

5.2 Some very important process to make the adhesive bond very effective.

Halogenation- Thermo plastic rubber (TPR) soles usually require halogenation for getting proper bondage with upper. The surface edge of a sole are treated with a chlorine based solution in a volatile solvent. Halogenation is a hazardous process, due to the high risk of dermatitis. Consequently the only protection is that offered by nitrile rubber gloves. However, providing that adequate safety standards are observed halogenation, when properly used, has great benefits in making the bond.

Heat Reactivation: The dried films of cement on both uppers and sole must be heat activated before the sole is pressed on the lasted upper. This is often done by infrared heat or on the more recent models by a quartz halogen lamp. For attaching Micro rubber soles to the upper, heat is not required; beside this, all other soles like: TPR/PU requires heat activation. A machine has been developed where we can put a pair of lasted upper and unit sole for heat activation. Temperature & required time is set by the operator as per the type of sole. Commonly it is 80°c -90°c & time is 30-45 seconds. Both surfaces must get the same temperature which ultimately joins them. The surfaces thus stuck and pressed are chemically reacted to ensure a good permanent bondage.
5.3 Mechanism of adhesive – To understand the mechanism of adhesive it is very important to know the basic requirements for good adhesive bond.

The basic requirements for a good adhesive bond are:

- Proper choice of adhesive.
- Good joint design.
- Cleanliness of surfaces.
- Wetting of surfaces that are to be bonded together.
- Proper adhesive bonding process (solidification and cure).

Proper Choice of Adhesive -

There are a lot of adhesives available for bonding materials. Selection of the adhesive type and form depends on the nature of adherends, performance requirements of the end use, and the adhesive bonding process.

Good Joint Design

It is possible to impart strength to a joint by design. A carefully designed joint can yield a stronger bond by combining the advantages of the mechanical design with adhesive bond strength to meet the end use requirements of the bonded part.

Cleanliness

To obtain a good adhesive bond, it is important to start with a clean adherend surface. Foreign materials, such as dirt, oil, moisture, and weak oxide layers, must be removed; else the adhesive will bond to these weak boundary layers rather than to the substrate. There are various surface treatments that may remove or strengthen the weak boundary layers. These treatments generally involve physical or chemical processes, or a combination of both.
Wetting

Wetting is the displacement of air (or other gases) present on the surface of adherends by a liquid phase. The result of good wetting is greater contact area between the adherends and the adhesive over which the forces of adhesion may act.

5.4 Adhesive Bonding Process

Successful bonding of parts requires an appropriate process. The adhesive must not only be applied to the surfaces of the adherends but the bond should also be subjected to the proper temperature, pressure, and hold time. The liquid or film adhesive, once applied, must be capable of being converted into a solid in any one of three ways. The method by which solidification occurs depends on the choice of adhesive. The ways in which liquid adhesives are converted to solids are:

- Chemical reaction by any combination of heat, pressure, and curing agents,
- Cooling from a molten liquid,
- Drying as a result of solvent evaporation.

The requirements to form a good adhesive bond, processes for bonding, analytic techniques, and quality control procedures are very significant.

Mechanism of adhesives can be describe as mechanical interlocking, electrostatic, diffusion, and adsorption/surface reaction theories. More recently, other theories have been put forward for adhesive bonding mechanism. It is really difficult to fully describe adhesive bonding to an individual mechanism. A combination of different mechanisms is most probably responsible for bonding with adhesive system. The extent of the role of each mechanism could vary for different adhesive bonding systems. An understanding of these theories will be helpful to those who plan to work with adhesives.
5.5 Theories of adhesives-
In table 1 different types of traditional and recent theories are mentioned and their action types also.

Table 1: Theories of adhesives

<table>
<thead>
<tr>
<th>Traditional</th>
<th>Recent</th>
<th>Scale of Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical interlocking</td>
<td>Mechanical interlocking</td>
<td>Microscopic</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>Electrostatic</td>
<td>Macroscopic</td>
</tr>
<tr>
<td>Diffusion</td>
<td>Diffusion</td>
<td>Molecular</td>
</tr>
<tr>
<td>Adsorption/surface reaction</td>
<td>Wettability</td>
<td>Molecular</td>
</tr>
<tr>
<td></td>
<td>Chemical bonding</td>
<td>Atomic</td>
</tr>
<tr>
<td></td>
<td>Weak boundary layer</td>
<td>Molecular</td>
</tr>
</tbody>
</table>


5.5.1 Mechanical Theory
This theory proposes that adhesion forms by the penetration of adhesives into pores, cavities, and other surface irregularities on the surface of the substrate. The adhesive displaces the trapped air at the interface. So that it is concluded that an adhesive penetrating into the surface roughness of two adherends can bond them. A positive contribution to the adhesive bond strength results from the “mechanical interlocking” of the adhesive and the adherends. This theory is not universally applicable, since good adhesion also takes place between smooth surfaces.

Enhanced adhesion after abrading the surface of an adherend may be due to mechanical interlocking, formation of a clean surface, formation of a highly reactive surface, and an increase in contact surface area. It is believed that changes in physical and chemical properties of the adherend surface produce an increase in adhesive strength. It can be debated whether mechanical interlocking is responsible for strong bonds or an increase in the adhesive contact surface enhances other mechanisms.

5.5.2 Electrostatic (Electronic) Theory
According to this theory, adhesion takes place due to electrostatic effects between the adhesive and the adherend. An electron transfer is supposed to take place between the adhesive and the adherend as a result of unlike electronic band structures. Electrostatic forces in the form of an electrical double layer are thus formed at the adhesive–adherend interface. This theory get support from the fact that electrical discharges have been noticed when an adhesive is peeled from a substrate.
5.5.3 Diffusion Theory
In this theory adhesion is developed through the interdiffusion of molecules in between the adhesive and the adherend. The diffusion theory is primarily applicable when both the adhesive and the adherend are polymers with relatively long-chain molecules capable of movement. The nature of materials and bonding conditions will influence whether and to what extent diffusion takes place. The diffuse interfacial (interphase) layer typically has a thickness in the range of 10–1,000 Å (1–100 nm). Solvent cementing or heat welding of thermoplastics is considered to be due to diffusion of molecules.

5.5.4 Wetting Theory
This theory proposes that adhesion results from molecular contact between two materials and the surface forces that develop. The first step in bond formation is to develop interfacial forces between the adhesive and the substrates. The process of establishing continuous contact between the adhesive and the adherend is called wetting. For an adhesive to wet a solid surface, the adhesive should have a lower surface tension than the critical surface tension of the solid. This is precisely the reason for surface treatment of plastics, which increases their surface energy and polarity. As can be seen in figure-34 the difference between smooth and rough surface.

![Figure 34](image_url)

Figure 34: Example of (a) good and (b) poor wetting by an adhesive spreading across a surface
5.5.5 Chemical Bonding

This mechanism attributes the formation of an adhesion bond to surface chemical forces. Hydrogen, covalent, and ionic bonds formed between the adhesive and the adherends are stronger than the dispersion attractive forces. In general, there are four types of interactions that take place during chemical bonding: covalent bonds, hydrogen bonds, van der Waals forces, and acid – base interactions. The exact nature of the interactions for a given adhesive bond depends on the chemical composition of the interface. Table 2/, shows the type and example of chemical bond.

Table 2 : Type and example of chemical bond.

<table>
<thead>
<tr>
<th>Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent</td>
<td>C – C</td>
</tr>
<tr>
<td>Ion – Ion</td>
<td>Na + ... Cl –</td>
</tr>
<tr>
<td>Ion – dipole</td>
<td>Na + ... CF 3 H</td>
</tr>
<tr>
<td>Dipole – dipole</td>
<td>CF 3 H ... CF 3 H</td>
</tr>
<tr>
<td>London dispersion</td>
<td>CF4,... CF4</td>
</tr>
<tr>
<td>Hydrogen bonding</td>
<td>H 2 O ... H 2 O</td>
</tr>
</tbody>
</table>


5.5.6 Weak Boundary Layer Theory

This theory proposes that bond failure at the interface is caused by either a cohesive break or a weak boundary layer. Weak boundary layers can originate from the adhesive, the adherend, the environment, or a combination of any of these three factors.

Weak boundary layers can occur in the adhesive or adherend if an impurity concentrates near the bonding surface and forms a weak attachment to the substrate. When failure takes place, it is the weak boundary layer that fails, although failure appears to take place at the adhesive adherend interface. Polyethylene and metal oxides are examples of two materials that may inherently contain weak boundary layers.
5.6 Mechanisms of Bond Failure
Adhesive joints may fail adhesively or cohesively. Adhesive failure is an interfacial bond failure between the adhesive and the adherend. Cohesive failure occurs when a fracture allows a layer of adhesive to remain on both surfaces. When the adherend fails before the adhesive, it is known as a cohesive failure of the substrate. Cohesive failure within the adhesive or one of the adherends is the ideal type of failure because with this type of failure the maximum strength of the materials in the joint has been reached. In analyzing an adhesive joint that has been tested to destruction, the mode of failure is often expressed as a percentage cohesive or adhesive failure. The ideal failure is a 100% cohesive failure in the adhesion layer.

Some adhesive – adherend combinations may fail adhesively, but exhibit greater strength than a similar joint bonded with a weaker adhesive that fails cohesively. The ultimate strength of a joint is a more important criterion than the mode of joint failure. An analysis of failure mode can be an extremely useful tool in determining whether the failure was due to a weak boundary layer or due to improper surface preparation.

The exact cause of premature adhesive failure is very difficult to determine. If the adhesive does not wet the surface of the substrate completely, the bond strength is certain to be less than maximal. Internal stresses occur in adhesive joints because of a natural tendency of the adhesive to shrink during setting, and because of differences in physical properties of adhesive and substrate. Fillers are often used to modify the thermal expansion characteristics of adhesives and limit internal stresses. Another way to accommodate these stresses is to use relatively elastic adhesives.

The types of stress acting on completed bonds, their orientation to the adhesive, and the rates at which it is applied are important factors in determining the durability of the bond. Sustained loads can cause premature failure in service, even though similar unloaded joints may exhibit strength when tested after aging. Some adhesives break down rapidly under dead load, especially after exposure to heat or moisture. Most adhesives have poor resistance to peel or cleavage loads. A number of adhesives are sensitive to the rate at which the joint is stressed. Rigid, brittle adhesives sometimes have excellent tensile or shear strength but have very poor impact strength. Operating environmental factors are capable of degrading an adhesive joint in various ways. If more than one environmental factor (e.g., heat and moisture) is acting on the sample, their combined effect can be expected to produce a synergistic result of reducing adhesive strength. If it is possible adhesive joints should be evaluated under simulated operating loads in the actual environment.
5.7 Factors involved in producing satisfactory bond:

- The adhesive chosen is correct and compatible on the surfaces need to be joined.
- The material used in the process is according to the minimum quality specifications.
- The preparation of surfaces is very important and it is need to be correct.
- To ensure right amount of application of adhesive and correct drying before assembly.
- Ensure uniforms and sufficient pressure after assembly.
- Where brush is need to apply adhesives it is very important to determine the consistency.
- Determination of drying time & open tack time.
- To check containers of adhesive must be mix well before use.
- Hardener containers must be kept always air tight after use.
- Adhesive must be applied in well ventilated room with exhaust fan to drive out solvent vapour.
CHAPTER 6
Bioactive insole and lining material

6.1 What is bioactive insole?
Footwear is only garments that are taken care of for aesthetic and preservation reasons. To ensure comfort to the footwear users in a work place or daily life designers and manufacturers offers a various types of materials for insole and lining. Like textiles leather polymers etc. In this case the crucial functional features are appropriate mechanical and hygienic properties. On the other hand this is also very important to impart good bioactive properties to materials. To prevent development of microorganism those are grow inside footwear is very essential for health issue. People who are using footwear for long time in a day there is a chance 50% for pathological changes in their skin. So that it is a very important issue. So for using footwear to prevent the fungal diseases it is very important to select the material. Though there are few materials like leather and textile bioactive insole is a good choice for insole.

People who works in their work place for long time or who uses their footwear for long time in a day for those people it Is very important to protect their feet against hazards occurring their workplace such as mechanical injuries to the feet, burns, or the absorption of chemicals through the skin. Bioactive material is more likely to use in protective footwear.

The most used bioactive insole material is a three layer thin polymeric material. It consists three layers those are- top, midle and bottom layer. Top layer is conductive-diffusive and it remaining in contact with the user’s foot. Midle layer is the main layer for bioactive function. It improving hygenic properties by ensuring protection against bacteria and fungi. The bottom layer is external and it attached with sole parts. It should be stiffening. All those parts are basically from polymers. The main materials are from polymers. Figure -35 shows different types of layers for bioactive insole.

![Figure 35: Schematic of the layers of the composite for protective footwear insoles; A - hydrophobic layer of two-layer woven fabric, B - hydrophilic layer of two-layer woven fabric, C - two-layer woven fabric, D - biocidal nonwoven, E - stiffening nonwoven.](image)
6.2 Materials of bioactive insole - It is mentioned earlier that this product consists of three layers. The materials used in the top layers are polyester and polypropylene or loycell woven with an elementary warp satin weave. It is very important to be fabric designed. In this design, one side is polyester or polypropylene hydrophobic fibers and the other side is hydrophilic loycell cellulose fibre. In the middle layer, there are three kinds of commercially available polymers used: MOPLEN HP 456 J polypropylene (manufactured by Lyondell Basell, Germany); LEXAN Resin polycarbonate (manufactured by General Electric Plastics, USA), and AQUAMID 6 polyamide (manufactured by Aquafil Engineering Plastics, Italy). As this layer is very important for the main function of the product to prevent bacterial and fungal infection so that in this layer a biocidal substance is added. The bioactive agent applied is certified by the Ministry of Health for commercial. (Certificate No. 2623/05). This is used as a biocidal product. In the bottom layer, a nonwoven consisting of polypropylene fibers of an area weight of 500 g/m² is used. Bioactive agent in the form of commercially available magnesium monoperphthalate is added at the stage of polymer fibre formation.

\[
\begin{align*}
\text{O} & \text{C} - \text{O} - \text{O} - \text{Mg} \\
\text{C} & - \text{O} - \text{O} \\
\text{O} &
\end{align*}
\]

This chemical structure is magnesium monoperphthalate.

Source- Mariann Holmberg.
Table 3 and 4 shows characteristics of melt blown nonwovens and variants of bioactive composites produced for protective footwear insoles respectively.

Table 3: Characteristics of melt-blown nonwovens used in the composites.

<table>
<thead>
<tr>
<th>Type of biocidal nonwoven</th>
<th>Average area weight/m²</th>
<th>Average fibre fineness, nm</th>
<th>Average nonwoven fineness, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamide nonwoven</td>
<td>430</td>
<td>3.2</td>
<td>3.9</td>
</tr>
<tr>
<td>Polypropylene nonwoven</td>
<td>371</td>
<td>8.4</td>
<td>3.5</td>
</tr>
<tr>
<td>Polycarbonate nonwoven</td>
<td>314</td>
<td>3.0</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Table 4: Variants of bioactive composites produced for protective footwear insoles.

<table>
<thead>
<tr>
<th>Variant</th>
<th>Structure of bioactive composites for protective footwear insoles</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Bottom layer: Stiffening polypropylene nonwoven</td>
</tr>
<tr>
<td>II</td>
<td>Middle layer: Polypropylene nonwoven with a biocidal agent</td>
</tr>
<tr>
<td>III</td>
<td>Top layer: Lyocell fabric/polyester</td>
</tr>
<tr>
<td>IV</td>
<td>Bottom layer: Polycarbonate nonwoven with a biocidal agent</td>
</tr>
<tr>
<td>V</td>
<td>Middle layer: Lyocell fabric/polypropylene</td>
</tr>
<tr>
<td>VI</td>
<td>Top layer: Lyocell fabric/polyester</td>
</tr>
</tbody>
</table>

Table 5 and 6 shows mechanical and hygienic parameters for bioactive insole respectively.

**Mechanical parameter**

Table 5: Mechanical parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mechanical parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>PN-EN ISO 5084:1999</td>
</tr>
<tr>
<td>Longitudinal/ transverse tearing resistance</td>
<td>PN-EN ISO 20345:2007</td>
</tr>
<tr>
<td>Resistance to abrasion</td>
<td>PN-EN ISO 20345:2007</td>
</tr>
</tbody>
</table>
### Requirements

<table>
<thead>
<tr>
<th></th>
<th>Thickness of commercially manufactured insoles, 3 - 7 mm</th>
<th>Tear force minimum 15 N for an insole made of coated and textile material</th>
<th>Number of cycles before damage is done to the surface of the insole:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.54</td>
<td>192 / 202</td>
<td>dry rubbing: 25.600; wet rubbing: 12.800</td>
</tr>
<tr>
<td>2</td>
<td>5.54</td>
<td>172 / 202</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5.95</td>
<td>215 / 218</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6.08</td>
<td>163 / 205</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6.49</td>
<td>232 / 208</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6.71</td>
<td>199 / 193</td>
<td></td>
</tr>
</tbody>
</table>

**Hygienic parameters for bioactive insole**

**Table 6:** Hygienic parameters

<table>
<thead>
<tr>
<th>pH of aqueous extracts</th>
<th>Permeability to water vapor</th>
<th>Water vapor coefficient</th>
<th>Water absorption</th>
<th>Water desorption, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN-EN ISO 20345:2007</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH &gt; 3.2 m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>11.8</td>
<td>95.2</td>
<td>230</td>
<td>108</td>
</tr>
<tr>
<td>4.3</td>
<td>11.7</td>
<td>94.4</td>
<td>215</td>
<td>106</td>
</tr>
<tr>
<td>4.2</td>
<td>12.8</td>
<td>103.2</td>
<td>207</td>
<td>105</td>
</tr>
<tr>
<td>4.3</td>
<td>12.5</td>
<td>100.9</td>
<td>223</td>
<td>107</td>
</tr>
<tr>
<td>4.3</td>
<td>11.3</td>
<td>92.1</td>
<td>220</td>
<td>106</td>
</tr>
<tr>
<td>4.4</td>
<td>10.9</td>
<td>89.6</td>
<td>241</td>
<td>106</td>
</tr>
</tbody>
</table>

Source: Table 3,4,5 and 6 - Irzmańska E, Brochocka A, Majchrzycka K. Textile Composite Materials with Bioactive Melt-Blown Nonwovens for Protective Footwear. FIBRES & TEXTILES in Eastern Europe 2012; 20, 6A(95): 119-125.(Online)

6.3 Lining materials-
There are different types of lining materials. Nowadays most useful is leather and textile. The leathers used for linings are light types of leather from ship and goat skins, skivers and split leathers as well as cow hide grain splits, calf skins and pig skins also. In general leathers of medium to low quality are used as lining leathers. The should meet the criteria for good softness, pleasing handle, high fastness to perspiration, water vapor permeability and absorbing capacity. It should also contain only small amounts of substances that are removable by washing. At the end of tanning operation and before drying, leather shall be treated with suitable fungicides in requisite proportions. Fungicides used to promote mildew resistance in leather shall be effective and non-toxic and shall be as agreed to between the purchaser and the supplier. Preservatives containing pentachlorophenol (PCP) shall not be used and the manufacturer shall give a declaration to this effect along with the consignment. Lining leather shall also pass the fungicidal efficacy test, when tested in accordance with LB: 2 of IS 6191.

6.3.1 Lining leather vegetable tanned-
Vegetably tanned light types of leather are very popular as a lining material. In this type of leather to ensure a good absorbing capacity of the leathers strong fat liquor of the surface should be avoided. The properties of this leather matches with the properties of lining leather. This is very soft and the perspiration properties are very fine. Also it is good for health reason compare to other leather though other leather is also contain good properties but for lining material vegetable tanned leather is preferable. There are also two types of lining leather which are called combined tanned and chrome tanned. In combination tanned excessive fat content and large amounts of soluble substances should be avoided. This is basically a combination of vegetable and chrome tanned. This is also popular lining material. In chrome tanned lining leather chrome salts that are easily removable by washing deposits of Sulphur and, above all, hexavalent chromium compounds should be avoided. All lining leathers can be processed on the natural grain side, smooth or roughened, and also on the velvet side. Depending on the requirements of the fashion they are also dyed od finished. When dyeing lining leathers it is absolutely necessary to use dyes which are fast to perspiration and bleeding as well as to dry and wet rubbing. Highly coating or sealing top coats should not be used for leathers to be finished in order not to impair absorbing capacity and water vapour permeability.
### 6.3.2 The most important quality requirements for shoe lining leathers-

In this page Table 7 shows requirements for sole linings.

Table 7: Requirements for sole lining.

<table>
<thead>
<tr>
<th>Test</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rub fastness</td>
<td>rub cycle</td>
</tr>
<tr>
<td>Leather, dry test fabric, dry</td>
<td>Aniline leather finished</td>
</tr>
<tr>
<td>Leather, dry test fabric, wet</td>
<td>&gt;rating 4</td>
</tr>
<tr>
<td>Leather, wet test fabric, dry</td>
<td>&gt;rating 4</td>
</tr>
<tr>
<td>Leather, dry test fabric with perspiration solution</td>
<td>&gt;rating 3</td>
</tr>
<tr>
<td>pH 9.0</td>
<td>&gt;rating 4</td>
</tr>
<tr>
<td>Leather, dry test fabric with benzene</td>
<td>&gt;rating 3</td>
</tr>
<tr>
<td>Fastness to water</td>
<td>no staining of the zone of diffusion above rating 3(gray scale)</td>
</tr>
<tr>
<td>Water vapour permeability</td>
<td>min 1.0 mg/cm².h</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>min 25%</td>
</tr>
<tr>
<td>sheep skivers unlaminated</td>
<td>min 30%</td>
</tr>
<tr>
<td>sheep skivers laminated</td>
<td>min 30%</td>
</tr>
<tr>
<td>other leathers</td>
<td>min 30%</td>
</tr>
<tr>
<td>Split tear strength</td>
<td>Only for lining leather as reinforcement. In 15 N</td>
</tr>
<tr>
<td>Mineral substances removable by washing</td>
<td>not above 1.5%</td>
</tr>
<tr>
<td>pH value</td>
<td>not below pH3.5</td>
</tr>
<tr>
<td>Substances extractable with dichloro methane</td>
<td>not more than 10%</td>
</tr>
</tbody>
</table>

In Table 8 it can be seen the requirements of lining material. After that Table 9 shows some restrictions of hazardous chemical those are used to produce lining leather.

**Some more tests of lining leather or materials**-

Table 8: Tests results for lining material

<table>
<thead>
<tr>
<th>Test</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, MN/m² (kgf/cm²), Min</td>
<td>15 (150)</td>
</tr>
<tr>
<td>Tongue tear strength, kN/m (kgf/cm) thickness, Min</td>
<td>20 (20)</td>
</tr>
<tr>
<td>Stitch tear strength (double hole), kN/m (kgf/cm) thickness, Min</td>
<td>44.0 (44.0)</td>
</tr>
<tr>
<td>Abrasion resistance, Not worse than:</td>
<td></td>
</tr>
<tr>
<td>a) 25 600 cycles of dry rubs</td>
<td>Moderate abrasion</td>
</tr>
<tr>
<td>b) 6 400 cycles of wet rubs</td>
<td>Moderate abrasion</td>
</tr>
</tbody>
</table>


**Restriction of hazardous chemicals:**

Table 9: Restrictions of hazardous chemical

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Requirement</th>
<th>Methods of Test, Ref to</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde, mg/kg, Max</td>
<td>150</td>
<td>LC : 3 of IS 14898</td>
</tr>
<tr>
<td>Pentachlorophenate, mg/kg, Max</td>
<td>5</td>
<td>IS 14575</td>
</tr>
<tr>
<td>Coupled amines released from azo-dyes (sum parameters), mg/kg, Max</td>
<td>30</td>
<td>LC : 4 of IS 14898</td>
</tr>
<tr>
<td>Hexavalent chromium, mg/kg, Max</td>
<td>3</td>
<td>LC : 2 of IS 14898</td>
</tr>
</tbody>
</table>

Source: BUREAU OF INDIAN STANDARDS, DOC: CHD 17 (1600) C. (Online)

http://www.bis.org.in/sf/chd/CHD17(1600)C.pdf (Accessed- 03.04.2015)
CHAPTER 7
Tests for lining and insole

7.1 Water vapour permeability test for leather lining and insole -

Introduction: For lining material water vapour permeability is very an important property. There is a machine for this test it is called water vapour permeability tester. There are different types of company those are made this machine but it was done by made of SATRA.

In this case the machine tests the quality of material to water vapour permeability. How strongly material allows water vapour to go through it. Figure -36 shows water vapour permeability tester machine for lining material.

Method: Standard: ISO 20344, ISO 20345 for SATRA.

Sample: 4 test samples are taken. It should be in circle and in a diameter of 4.5 cm. If this test is to be performed on a material of already finished whole footwear, 1 piece of shoe from every size (smallest, mid, biggest) is needed.

Figure 36 : Water vapour permeability tester machine
Results-

<table>
<thead>
<tr>
<th>Water vapour permeability</th>
<th>min 1.0 mg/cm$^2$.h</th>
</tr>
</thead>
</table>

Discussion - Feet get warm and humid during long walk or run, which causes the vapour occurs. If material does not allow the vapour to go through it, the feet get sweat, humid and cold, which reduces the comfort and pleasure of wearing. Therefore material must allow certain degree of water vapour permeability. For this property the requirement is 1.0 mg/cm$^2$.h and the test result got exactly same.

7.2 Color rub fastness test for leather lining material.
Introduction - Color rub fastness test is also very important. Sometimes footwear lining is directly touched with skin. That is why it is very important. If color is coming out from leather it can be dangerous for health issues. For this there is a machine it test color resistance by rubbing the leather. Figure -37 shows the machine for color rub fastness (leather, textiles, lining).

Method- EN ISO 105 E04.

Sample- Material that allows cutting 2 separate test samples of dimensions 2. 5 X 13 cm.

Design Specification Lining:

Table 10 : Material specifications for lining leather

<table>
<thead>
<tr>
<th>Materials</th>
<th>Location</th>
<th>Origin</th>
<th>Tanning</th>
<th>Color</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leather</td>
<td>1st Strap</td>
<td>Cow</td>
<td>Chrome</td>
<td>Tan</td>
<td>0.8 mm</td>
</tr>
<tr>
<td>Leather</td>
<td>2nd Strap</td>
<td>Cow</td>
<td>Chrome</td>
<td>Tan</td>
<td>0.8 mm</td>
</tr>
<tr>
<td>Leather</td>
<td>3rd strap</td>
<td>Cow</td>
<td>Chrome</td>
<td>Tan</td>
<td>0.8 mm</td>
</tr>
<tr>
<td>Leather</td>
<td>Joining Strap</td>
<td>Cow</td>
<td>Chrome</td>
<td>tan</td>
<td>0.8 mm</td>
</tr>
</tbody>
</table>
**Design Specification for sample:**

Table 11: 2mm thickness leather for color rub fastness test material specification.

<table>
<thead>
<tr>
<th>Use as</th>
<th>Material</th>
<th>Material type</th>
<th>Thickness</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>lining material</td>
<td>leather</td>
<td>chrome tanned leather</td>
<td>2mm</td>
<td>Gray</td>
</tr>
<tr>
<td>lining material</td>
<td>leather</td>
<td>vegetable tanned leather</td>
<td>2mm</td>
<td>White</td>
</tr>
</tbody>
</table>

Figure 37: Color rub fastness

**Result:**

Table 12: Results of color rub fastness for lining leather

<table>
<thead>
<tr>
<th>test</th>
<th>method</th>
<th>result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color fastness for All linings</td>
<td>EN ISO 105 E04</td>
<td>Leather Color change: grade 4 min Color stain: 3min</td>
</tr>
</tbody>
</table>


Table 13: Result for 2mm leather test.

<table>
<thead>
<tr>
<th>test</th>
<th>method</th>
<th>result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color fastness</td>
<td>EN ISO 105 E04</td>
<td>Leather Color change: grade(4-5) min Color stain: 3min₂</td>
</tr>
</tbody>
</table>

Rating of gray scale-

Rating 5- no transfer of color
Rating 4- slight transfer of color
Rating 3- moderate transfer of color
Rating 2 marked transfer of color
Rating 1 very marked transfer of color

Discussion-

Walking initiates rubbing between shoe interior materials and socks. If the color of material is not sustainable enough, material starts to lose color, which can be than unpleasantly transformed on the sock and skin. It also reduces the visual attractiveness of product. This is why testing of material to color abrasion is needed. If the material is a bit thick result changes to higher grade. In this case when 2 mm thickness of leather was taken results got between 4 and 5 grade in gray scale.
CHAPTER 8
Environment issue of footwear

8.1 Recycling of footwear:
Nowadays in the world there are 20 billion pairs of footwear produced in a year. This is huge amount. In footwear there are almost forty types of materials needed. Many of these are stitched or glued to each another. Every year, across the globe, millions of pairs of shoes end up in landfills or disposed of in some other way, creating a lot of waste. Much of what we consider unwanted waste can actually be recycled or repurposed. It is estimated that 85% or more of these unwanted items end up in our landfills, No matter what age we are; most of us have at least a few pairs or more of unwanted shoes hanging out in our closets. Some may be shoes we just don’t wear, shoes we have outgrown, or those that have gotten a little worn around the edges. That is why it is very necessary to think about footwear recycling. Now in this modern era still we are not thinking in a broad way in this very important issue. 20 billion pairs of shoes or footwear is not a small amount. The only way of avoiding the landfilling of unwanted shoes has been to deposit them in 'shoe banks' for second-hand use, recycle them in a way or extend the research in a way that footwear can be made with the material which is possible somehow to be recycled. Now this is time to rethink like in this way.

There are some branded companies those are already started thinking about this recycling matter. In the following there are few:

8.2 NIKE about recycling footwear:

Reuse A Shoe and Nike Grind
- Collects used athletic shoes from any brand.
- Recycle used shoes & scrap material from manufacturing into Nike Grind.
- Nike Grind is then incorporated into material used in sports surfacing (i.e. basketball courts, tracks)
- Shoes could be donated in stores as well as special events & recycling programs.
- 25,056,779 pairs collected globally since 1990 to recycle or re use the parts.

8.3 Timberland about recycling:
- At least 50% of the Boot can be recycled or re-used.
- Leather is refurbished at the company’s factory in the DR.
- 42% recycled Green Rubber outsole can be recycled at a factory in Georgia.
- Metal Hardware is removed and reused
- 50% recycled Polyester lining, can be recycled into new polyester products.

There are few research are carried out about this issue. Loughborough University’s Innovative Manufacturing and Construction Research Centre is one of them where carried out a research and the suggestions about recycling footwear are following-

- Recovered leather fibres can be reformed to produce bonded leather sheets.
- Reclaimed rubber can be used as a running track or playground surfacing product.
- For some types of footwear rubbers, finely ground rubber can be put back into new shoe soles - achieving so-called ‘closed loop’ recycling.
- Recycled foams can be used in underlay material for laminate floors and carpets.
- A key use for mixed textiles and other lighter residues could be as insulation material for buildings
**Conclusion** - As nowadays polymers are used widely in all sectors. Footwear is one of them. This study helps to know how and why polymers are used in footwear and some further informations. Though it is very difficult to replace polymer with leather as a prime material in footwear sector but nowadays industries are trying to use more and more for cost, comfort and durability. For fashion and style it helps a lot for the designers.

As a material, polymers are used in footwear in different way. Though leather is a prime material for upper in footwear Different types of polymers are used as a mesh product. To consider all the properties those are need for good quality footwear still leather is ahead for their natural properties. For example water vapour permeability is a key property. Nowadays recycling is also a big factor for polymeric material used in footwear. Because a huge number of footwear used in a whole year. The number is almost more than 12 billion pair. Most of the companies and people are not concern about this. Those large numbers of pairs of footwear after use need to be recycled is a future challenge. However it is increasing gradually.

On the other hand footwear is directly touched with skin that is why hygienic and safety is very important. Now there is few company those are very concern about these issues. So for manufacturing various types of polymers it is important to use some hygienic additives to make bioactive material for footwear. Also various types of adhesives are used. These are mainly based on solvent base. It is also a matter of environment. So now the time comes to do more research on the mechanism of these adhesives to replace solvent based adhesives in this sector.
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