THE *Journal* OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

December 2021 Vol. CXVI, No.12 *JALCA* 116(12), 417–456, 2021

Contents

116th Annual Convention

to be held at the
Eaglewood Resort & Spa
1401 Nordic Road
Itasca, IL 60143

DATE CHANGE:
June 21-24, 2022

For more information go to:
leatherchemists.org/annual_convention.asp

Distributed by
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An imprint of the University of Cincinnati Press

ISSN: 0002-9726

Communications for Journal Publication

Manuscripts, Technical Notes and Trade News Releases should contact:

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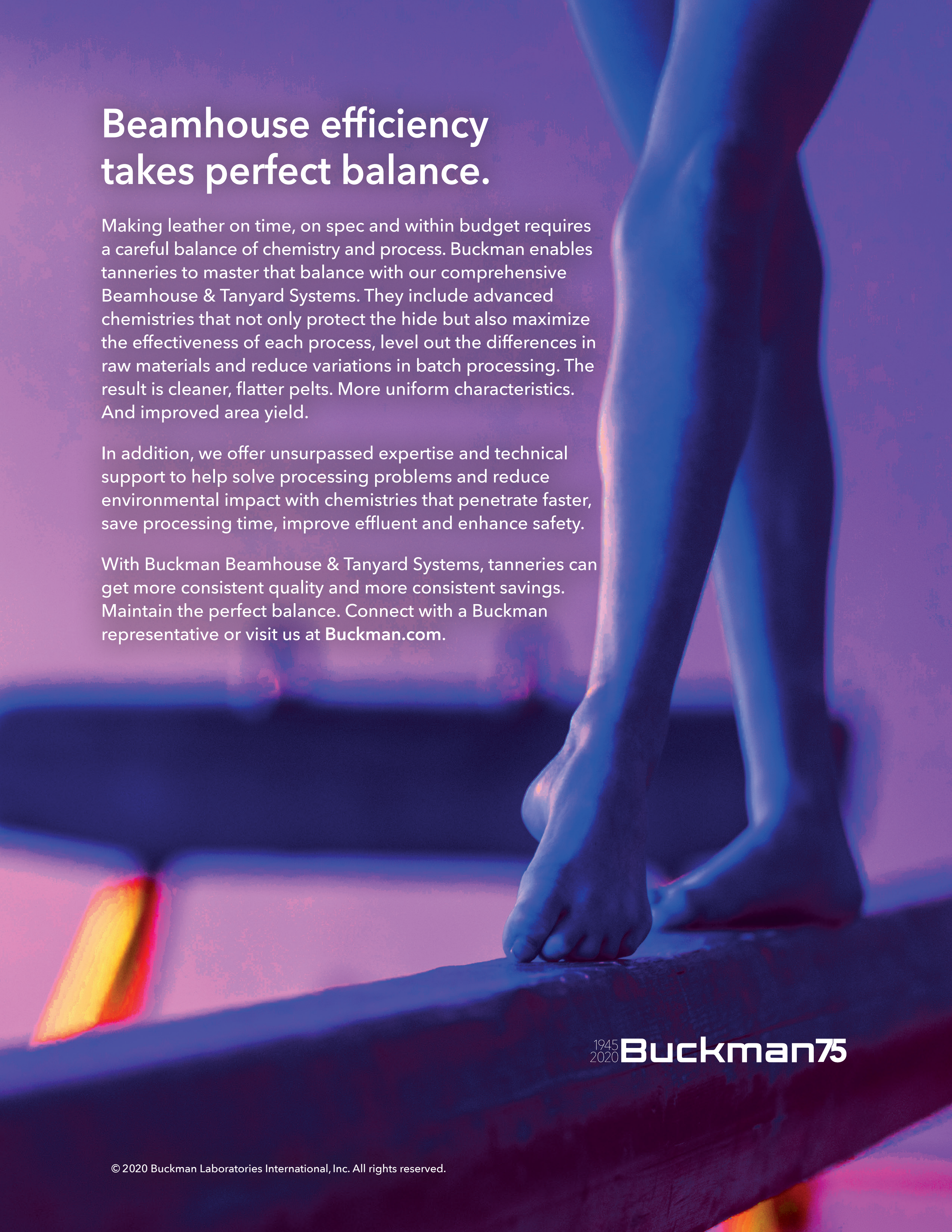

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THE JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION (USPS #019-334) is published monthly by The American Leather Chemists Association, 1314 50th Street, Suite 103, Lubbock, Texas 79412. Telephone (806)744-1798 Fax (806)744-1785. Single copy price: $8.50 members, $17.00 non-member. Subscriptions: $185 for hard copy plus postage and handling of $60 for domestic subscribers and $70 for foreign subscribers; $185 for ezine only; and $205 for hard copy and ezine plus postage and handling of $60 for domestic subscribers and $70 for foreign subscribers.

Periodical Postage paid at Lubbock, Texas and additional mailing offices. Postmaster send change of addresses to The American Leather Chemists Association, 1314 50th Street, Suite 103, Lubbock, Texas 79412.

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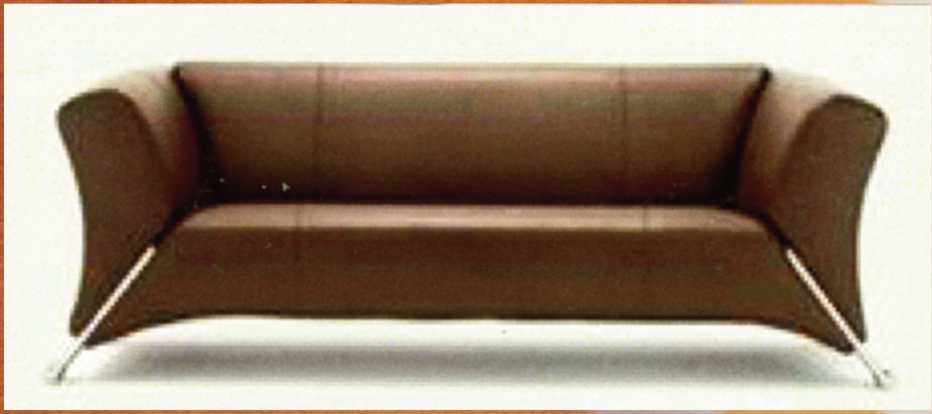

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Improving Tearing Resistance of Leather - Part 1
Prevention and Treatment of Low Tearing Strength in the Tannery

by
Ricardo Tournier* and Fernando Lado

Abstract

An appropriate tear strength is one of the main properties that concern customers and it is also a significant source of claims. The authors make a review of the production process, focusing on each step that can either damage the natural strength of collagen fibers or improve them and therefore, the leather. Although the authors' experience is in bovine hides, the general concepts presented in this paper may be applied to other types of hides and skins.

The aim of this work is to transfer field tannery experiences collected over 40 years of activity in different tanneries, to colleagues that are looking for world class leather production.

Introduction

The physical properties of leather and particularly the tearing strength are recurring problems in tanneries and demand urgent solutions.

Leather is a unique material, having several advantages over other materials and its strength is one of its remarkable attributes.

The massive demand for its supply, force tanneries to process as many hides as possible to conform with customers' orders.

Different strategies had been developed such as chemical products to disguise or cover natural imperfections in order to increase the number of pieces in saleable condition, sometimes lowering its natural beauty through sophisticated finishing procedures.

Furthermore, with the same target, tanneries process heavy weight hides to obtain low substance articles, that could compromise physical properties among them, tear strength.

But there are many other details that need to be taken into account throughout the prolonged and complex leather production process.

Once the problem of low tearing is installed in the tannery, leather technicians must find a quick solution or mitigation, to be able to keep production running while at the same time try to find out the main and subsidiary causes of the problem to make the necessary corrections.

At this point, technicians should want to look for help from experienced colleagues in this field and from leather books and journals. All these activities are time consuming and will delay reaching the answer to solve the problem.

In this work the authors give some basic ideas about which of the critical points to consider once the problem arises, and present some practicalities, theoretical and bibliography derived information from the authors' expertise which should help solve the problem.

This article is divided in 14 Sections:

Part 1

1.0 Collagen as raw material
2.0 Collagen destruction
3.0 Hides preservation
4.0 Soaking
5.0 Dehairing and Liming

Part 2

6.0 Deliming
7.0 Bating
8.0 Pickling,
9.0 Chrome tanning
10.0 How to select stronger hides
11.0 Vessels and mechanical action
12.0 Post tanning operations
13.0 Final Sampling
14.0 Artificial Improvement of Tearing

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Manuscript received August 8, 2021, accepted for publication August 26, 2021.

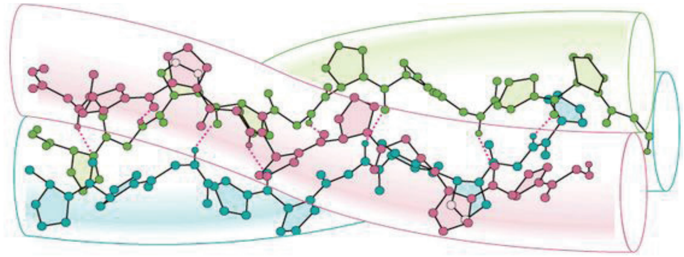

Figure 1. Triple Helix[3]

1.0 Collagen as raw material

1.1 Collagen and fibers[1]

Hides and skins are natural materials of fibrous structure mainly made out of collagen fibers interwoven in a three-dimensional structure, coexisting with other fiber forming molecules like elastin and soluble proteins like polysaccharides and proteoglycans. Collagen is the most abundant body protein, it is present in the skin, tendons, bones, conjunctive tissues, etc. There are several types of collagen. Collagen type I is the major component of hides and skins.

Collagens are characterized by a repeating triplet of amino acids that determine the helical shape of the molecule. The high content of β-amino acids causes the chain to twist into a left-handed helix. Three of these helix twist around each other in a right-handed triple helix that conforms the protocollagen molecule, structure Ramachandran, 1968[2] (Figure 1).

Triple helices bound together in bundles called fibrils that are the smallest units of collagen that are visible under the Scanning Electron Microscope (Figure 2).

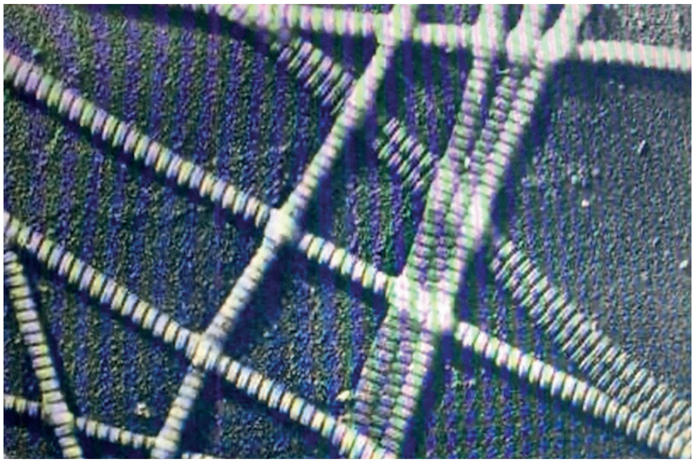

Figure 2. Collagen Fibrils, SEM
Calf Skin Collagen Fibrils 30.000 ×, Dr. J.Gross Collection,
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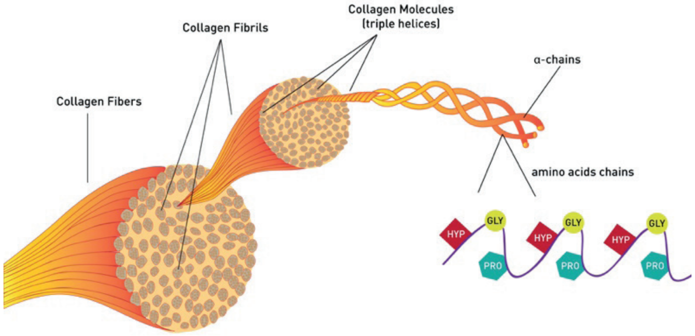

Figure 3. Collagen Structure[4]

Following the hierarchy of collagen structure comes the union of fibrils in the form of fibril bundles and afterwards the bundles come together to create collagen fibers (Figure 3) which are visible to the naked eye.

1.2 Fibers mechanical properties

It is well known that the strength of native collagen, present on fresh hides, is due to its fibrous nature and the ability of fibers and fibrils to slide over one another.[5]

Collagen and hence, hides, skins and leather are anisotropic materials, having different physical properties in different directions. They are strongest in the direction of the component fibers and weakest in the perpendicular direction.

Yang, W. et al., 2015[6] studied the salient micro-mechanisms of deformation and fracture in the skin that appears to have superior tear resistance to other natural materials. They attribute skin's tear resistance to the nano/micro-scale behavior of the collagen fibrils.

Using sophisticated equipment on samples of rabbit skin, the researchers identify and quantify four principal deformation mechanisms acting synergistically, namely:

- Curved fibrils orientate towards the force direction.
- The straightening and the stretching of collagen fibrils.
- The reorientation of fibrils towards the force application direction.
- The sliding of fibrils by the deformation and reformation of bonds between them.

This process is illustrated in the following sequence (Figure 4),[6] under authors permission.

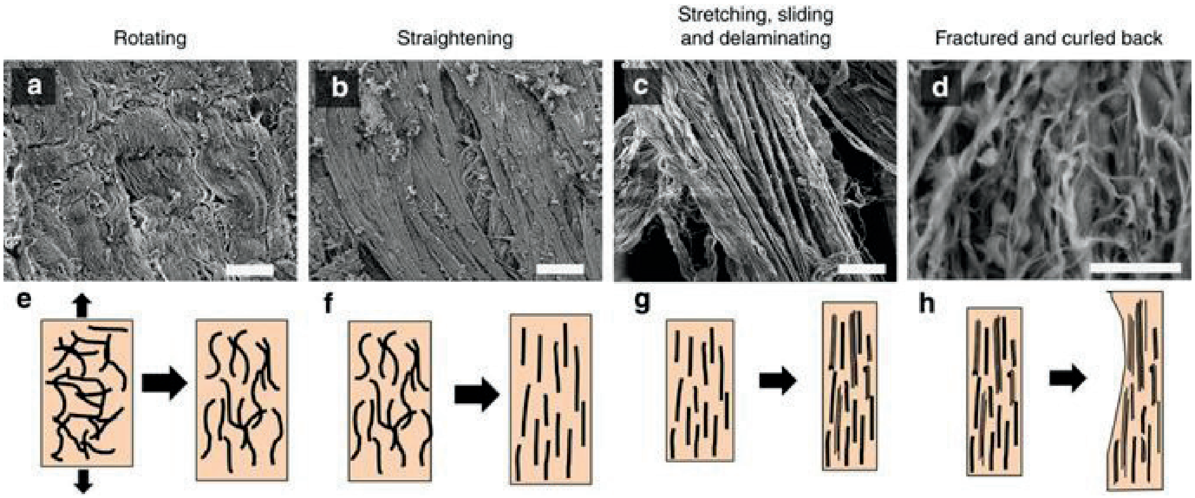

Figure 4. "SEM images **(a–d)** and schematic drawings **(e–h)** of the mechanisms during the four stages of tensile loading of rabbit skin, black arrows in a and e represent the direction of tension testing. **(a,e)** Curved collagen fibrils are oriented along the tensile axis; **(b,f)** collagen fibrils are straightening, larger and larger amount of the fibrils re-orient close to the tensile axis; **(c,g)** collagen fibrils are stretching, sliding, delaminating and orientated completely along the tensile axis; **(d,h)** collagen fibrils are fractured and curled back. Scale bars in a–d are 20, 20, 20, 50 μm, respectively."

1.3 Collagen types

In the diagram by Sharphouse[7] of a cross-section of bovine hide (Figure 5) the CORIUM fibers are composed of collagen Type I, the major component of hides and skins and the GRAIN, by mainly collagen Type III.

Collagen type I has the property to form fibers that interweave creating a strong woven structure resistant to stress in any direction, as mentioned before.

Collagen type III forms finer fibers, less resistant to stress than type I, that compactly bound and form the Grain Enamel, the most valuable part of full grain leather. Under low magnification, this layer appears as a homogeneous film, quite resistant to abrasion, covering the mixture of type I and III fibers underneath, that form the Junction of Grain and Corium. Because of this composition, grain and junction are weaker, less resistant to stress, than corium.

1.4 Species

Kelly et al., 2018[8] studying tear strength and collagen fibril orientation in bovine, ovine and cervine hides and skins, found that cervine leathers had the greatest overall strength followed by bovine and then ovine leathers. Ovine had the greatest variability in strength across the skin.

1. 5 Bovine Hides

In Sharphouse diagram (Figure 5), the weave pattern of fibers in leather shown is quite realistic on average. At the heart of the corium, the fibers are somewhat coarse and vertical, and they become finer and more horizontal as they approach the flesh. The flesh layer is stronger than the corium.

The horizontal fibers (low angle of weave) oppose maximum resistance to tearing force. The vertical ones (high angle of weave), oppose the minimum.

Tournier, 2015[9] in his paper about the evolution of tear resistance during the chrome tanning processes, showed that in normal hides, when split, the grain splits have lower resistance than those of flesh splits. The presence of the horizontal fibers in the flesh splits makes the flesh splits stronger.

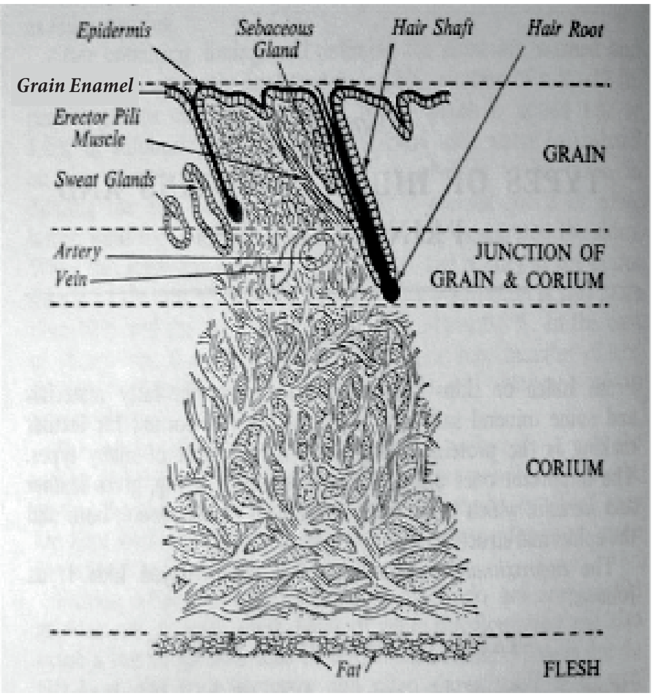

Figure 5. Diagram of cross-section of bovine hide.

Generally normal hides have an average orientation angle of 45° in the corium fibers. This orientation angle varies across each hide and so do the physical properties in different areas. The fibers reach 0° over the flesh side. When fibers in the corium reach 90° hides are known as affected with the so-called vertical fiber defect (VFD).

1.6 Vertical fiber defect, VFD

Amos[10] in 1958, was the first to identify a fiber architecture in hides that produce weak leather, when the fibers of most of the corium are vertical wise. Later, several researchers identified another type of fiber with this condition called high weave fiber defect. Peters and Bavinton, 1982[11] showed that the two forms have a different incidence depending on the breed of the animal. They suggested that whereas vertical fiber is a specific condition (mainly present in Hereford breed because of genetic transmission), high weave is probably one form of the normal weave and concluded that both produce weak leather.

Working with European, North American and South American hides, we found different percentages of weak leather throughout the years and in different tanneries, ranging between 2 to 10%.

Sometimes it is simple to identify areas with VFD by looking at crust leather flesh side, when in the butt region open fibers with cauliflower look, veiny and tearing like paper with edges showing short fibers are seen.

The question is, how to identify or segregate these types of hides early in the tanning process. (See Section 10)

1.7 Cattle breeds, weight, age, sex

Several authors have studied the physical properties of different cattle breeds and their crossings. They found small differences among them. There can be several causes for these differences, namely: age, sex, feeding, genetic, vertical and high weave fiber, climatic conditions, etc.

Regardless of all these, there is a fact that tannery technicians cannot ignore, and this is basically, that it is necessary to process the skins the tannery is able to buy and with the minimum of possible pre-selections.

When it comes to processing salted or brined hides, it is quite normal to classify them in function of weight and sex, but in the case of fresh hides the interval between the slaughter and the starting of the processes must be as short as possible to prevent the hides degradation. Hence, there is not too much time to sort them. In this case, we can apply a general segregation process, for instance bulls and calves or heifers.

In any case, the objective is to start processing those skins as soon as possible, preserving the original natural collagen fibers of the fresh hides without damage.

Betty Haines (1981[12]), studying breed differences in cattle hides, concluded that in undamaged fibers and in a first approximation, physical properties are more a function of original hide thickness than breed or age of slaughter. Thin hides are characterized by a small fiber pattern in the corium and a medium angle of weave (stronger). Thick hides tend to have larger fiber pattern and a higher angle of weave (weaker) as mentioned before in Section 1.6. Therefore, hides from beef cattle are normally thicker than dairy cattle, hence it is expected the latter to be stronger.

We will address this topic further in Section 10.

2.0 Collagen destruction

In this section the main processes that alter the integrity of the collagen fibers and their surroundings are treated and why these alterations result in lowering tearing strength.

2.1 Proteolytic action

This is one of the most dangerous and common sources of tearing problems. It destroys collagen to a higher or lesser degree, in all or part of hides and skins. It is responsible for the appearance of irregularities in the physical properties of supposedly uniform lots of hides.

When e.g., in a lot of fresh or salted hides, hair slippiness is detected, this is a sign that the lot has had excessive time and or temperature exposure after slaughter and this lot has the risk of having low and irregular tearing strength once in crust state. Generally, this comes associated with grain damages, grain looseness and veiny leathers, among other defects.

The delay in starting the soaking, the short time preservation or the medium time salt curing of fresh hides, together with high temperatures, are the root cause of the destruction of collagen fibers by means of autolysis (self-digestion) and bacterial activity.

As soon as the animal dies, the immune system ceases to function and the cells, that all over the body gave life, stop their coordinated work and, out of control, start to destroy the body. The blood vessels with remaining blood are the main sources of enzymes radiation and destruction.

As the hides are flayed, the abattoir handling contaminates the flesh side with bacteria from the hair side. These bacteria find in the flesh side an excellent nutritious media to proliferate and start to travel through the hide thickness, generating additional proteolytic enzymes destroying collagenous fibers, among other things. This process also takes place through grain side injuries or damaged epidermis.

The extensiveness of collagen fiber damage will depend on time, temperature, how dirty the animals were when arriving the abattoir, etc.

2.2 Proteolytic activity

Proteolysis, the breakdown or hydrolysis of proteins into smaller amino acids, takes place under the action of proteolytic enzymes. Among proteolytic enzymes, collagenases are the most important in our matter. They are present in the body and are produced by some bacteria. They break the peptide bonds of collagen that form fibrils, thus weakening the original fibers of the hides and skins and therefore weakening the leathers.

This activity in fresh hides can be measured directly and indirectly by several methods. It can be measured by the increment of soluble Nitrogen (Kjeldahl) of samples of fresh hides, see Figure 7. Or by measuring the hydroxy-proline* content of a water extract of samples of hides before soaking. Also, by microscopic examination.

But the most practical and extended method of controlling the deterioration of fresh hides in tannery is the bacterial count by means of the Standard Plate Count (SPC) technique, with serial dilutions, that reports the counts as colony forming units (CFUs) in 24 to 72 hr. By convenience the results are given as colony forming units per milliliter, CFU/mL. Nowadays, there are rapid tests that give the same result[13] within hours.

Counts of 10^4 and 10^5 are considered normal or with low risk of deterioration, and higher than 10^8 are considered with very high risk. This goes hand in hand with what was mentioned before, that hides with high and very high deterioration not only result in leather with low tearing strength but also with grain looseness, grain damages, veiny leather, etc.

Table I relates levels of risk in relation with the bacterial counts of hides arriving to the tannery. This relation may be used as a guideline to assess the level of risk.

Table I

Bacterial counts vs. Risks of fiber damage.

CFU/mL	Risk
10^4 y 10^5	Low
10^6	Marginal
10^7	High
$> 10^8$	Very high

Lots of fresh hides arriving in these conditions should be labeled in the "tannery traceability system" as RISKY.

It is mandatory that each lot of fresh or short term preserved hides arriving at the tannery must have this type of control or equivalent and keep records for future reference. Similar traceability controls and records hold for long term preservation as we will see later in Section 3.3.

2.3 Traceability

"Traceability in the leather industry, is the capability to keep track of the history of a piece of leather, all the way from the source of the raw hide up to the manufactured leather products, by means of documented, recorded identification", Tournier et al. 2019.[14]

It is the most important requirement for a supplier for making business, and for leather technicians to keep control of production and to investigate what went wrong facing a problem or a claim.

Regarding RISKY lots, it is very important that after evaluation in crust, the results are continuously compared with normal lots in order to confirm the pertinence of the RISKY parameters.

3.0 Hides preservation

This is a crucial step in the leather making process. It is so, because of the vulnerability of the recently flayed hides, the variability of ambient temperatures, the generally long distances between the abattoirs and the tanneries, the complex logistics to bring fresh hides as fast as possible to start the tanning processes and because failures in this step compromise not only physical properties of final leather but also produces other grain disqualifying defects such as loose grain, blemishes, veiny and empty leather, as said before.

Generally, this vulnerable stage for the hides lies outside the control of the tanner.

It is in this critical point where leather technicians must develop a system, that will adapt to each tannery infrastructure in order to protect the labile, valuable and noble natural material that is the collagen network that shapes fresh hides.

The designed system, that will not be cheap at a first glance, must be properly understood and strongly backed by the CEO of the company. It must target the protection of original characteristics of fresh hide collagen fibers, to avoid future problems in different leather properties.

3.1 Fresh hides

In the case of no preservation, hides can stand for the start the tannery process within 4 to 6 hr after slaughter, in hot weather. In the cold, this timing can be extended.

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*Almost uniquely present in collagen.[1]

Following graphs in Figure 6 are the results of several years of field experimentation on production lots of fresh hides.

Graph A and B are indicative for batch-lots of hides risking producing leather with low tearing strength, taking into account variations in ambient temperatures and elapsed time in hours, between start flaying in abattoir and start soaking or curing in tannery.

Full line graph A shows the limits between safe and risky lots without any type of treatment, and dotted line B shows the limits for hides cooled at 8-10°C as soon as they are flayed.

For instance, if an abattoir starts the flaying at 6 AM, with 30°C of ambient temperature (horizontal arrows in the graphs), a lot of hides generated during the slaughtering without any preservation, must start soaking in the tannery before 10 hrs. later, vertical arrow, that is 4 PM. If the same hides flayed at the same ambient temperature of 30 °C, are cooled to 8-10 °C as soon as they are flayed, they must start soaking before 26 hrs. later, vertical arrow Graph B, that is 8 AM next day. Lots exceeding these limits must be labeled RISKY of having collagen fibers damages and hence low physical properties, looseness, veininess, etc., because of delay in soaking or curing.

It is advisable that risky lots be directed to low demanded articles, otherwise be examined 100%, once in crust. In the case of tearing strength check piece by piece, by means of a hand dynamometer as it will be discussed later in Section 13.1.

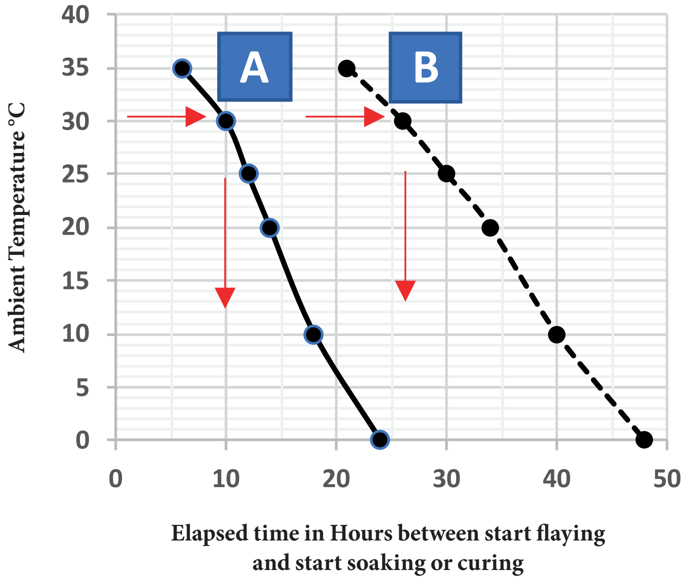

Figure 6. Risk of low tearing leather

3.2 Short term preservation

3.2.1 Cooling

First thing to do after flaying is to lower the body temperature of the hide as fast and as low as possible. If we do this with cold running water, we will wash at the same time bacterial load trapped in the hair and retard the action of autolytic enzymes and remaining bacteria.

As an example, in Appendix I there is the description of a very interesting system that was designed by a tannery and a slaughterhouse, that worked with very good results on leather, during several years.

It was an ecological system, no chemicals added. The thermal inertia of cold hides mass (4-6°C) allowed transport trucks to safely travel several hours, unload at tannery, flesh hair on hides and load soaking drums.

This type of processing slowly increased hides temperature arriving at soaking in between 20 and 25°C.

The temperature control of the lot as well as of individual hides is easily done by hand infrared thermometers.

Up to this moment, we have presented the use of cold as a short-term preservation method, because of the advantages that were mentioned before. But there are other methods to be considered.

3.2.2 Sodium Chlorite

Acidified Sodium Chlorite (ASC) in water produces chlorine dioxide (ClO_2) a strong bactericide, 2.5 times more powerful than hypochlorous acid (HOCl).[15] It is a rather safe microbicide normally used in the food industry; therefore, by-products can be used for food and medicinal purposes. It does not harm hides in normal concentrations or cause problems in effluent treatments. But it does not stop autolysis.

Regarding this product, in 1992 Flores[16] conducted a field investigation with lots of 15 to 30 fresh hides, applying ASC (300 g/l) in different concentrations in immersion tanks, spray gun and tanning drums. Treated hides were left in preservation periods of 24 and 48 hrs. with room temperatures from 24 to 32 °C. One lot without preservation as control.

Based on the information provided in Flores' paper and with the author permission, we have produced the following interesting graphs.

Figure 7 shows the generation of soluble Nitrogen with time in fresh hides without preservation and with different % of ASC. Hides were treated in a tanning drum with 20% water and 0.1%, 0.5% and 1.0% of ASC (300 g/l) with 15 min. of running time.

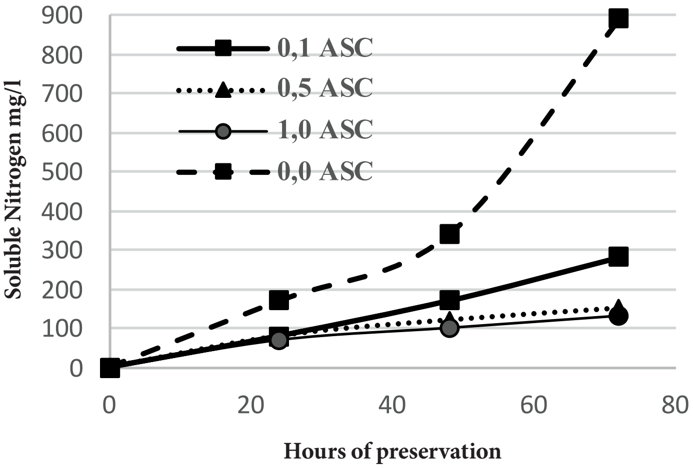

Figure 7. Soluble Nitrogen generation vs. Hours of preservation

After treatment all the hides were processed as usual in the tannery and the final evaluations were done in the crust.

The evaluation of the resistance to tearing was done by IUP 8. Figure 8 shows the evolution of tearing with increasing quantities of bactericide.

Tensile strength has a similar evolution. Therefore, by using an efficient bactericide it is possible to avoid losing important amounts of physical strength.

The paper includes in the crust evaluations, other leather properties as looseness, grain abrasion, etc., that are in line with physical improvements.

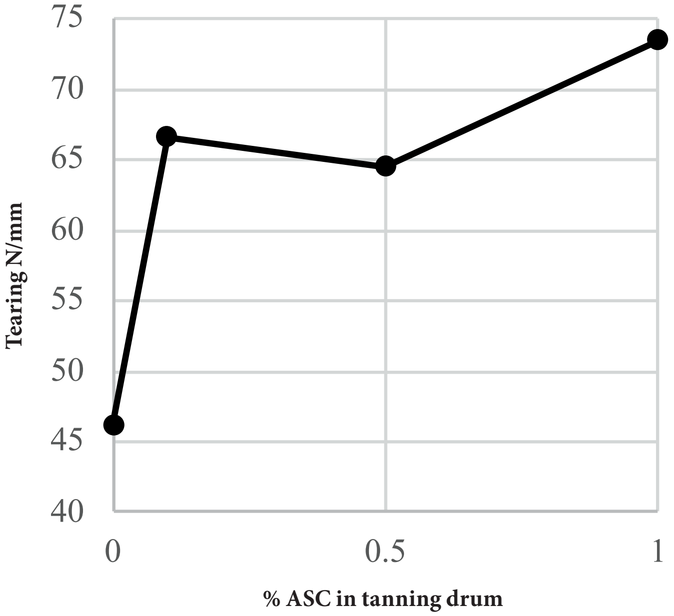

Figure 8. Tearing 24 hr preservation vs. different %ASC

Flores proved that there is a relationship between soluble Nitrogen and proteolytic activity, that reflects in the physical properties and in other grain characteristics.

3.2.3 Other bactericides

There are other commercial bactericides available in the market, some of them include autolytic collagenase enzyme inhibitors. This gives a broader protection to fresh hides.

Each supplier gives precise instructions for their use, but the tannery must be sure that these products are safe for human handling, do not interfere with wastewater treatment plants, and there will not remain residues of them in the by-products that can be destined for animal or human consumption.

3.3 Long term preservation

In this section, only the curing that is attained by the utilization of curing salt or saturated brine solutions is mentioned. These are well known procedures, that will not be treated in detail, but there are some important points to take into account.

- Fresh hides to be salted, must be treated with the same care mentioned before to protect them from autolysis and bacteria, to preserve the integrity of collagen fibers.
- Lots exceeding the limits of Figure 6 regarding elapsed time between start of flaying and salting, must be labelled as RISKY and should be salted apart with proper traceability.
- Even if no delay happened between flaying and salting, there can be irregularities in the salting operation itself, and damages in collagen fibers may occur, so it is mandatory to control salted hides before starting tannage processes.
- Properly cured hides must have moisture content between 40 and 48%, and this moisture must be at least 85% saturated with salt, giving an ash to moisture ratio above 30:100.
- In the authors experience, properly salted hides give slightly higher tearing strength values on average, than fresh hides. This phenomenon can be explained because salted hides, when soaked, never reach the original hydration, so they remain somehow more compact than fresh hides and, if shaved both at same thickness, salted hides have more fibers per millimeter.

Lately in 2019, Sarker et. al,[19] studied at laboratory scale the action of mixtures of different bactericides in sodium chloride solutions with 35% saturation to be applied for short- and long-term preservation. In such paper, there are interesting proposals targeting not only microbial contention but also environmental protection.

In summary, from the authors' point of view regarding protection of the environment and the hides, proper cooling and rapid processing is the best option.

4.0 Soaking

As several authors pointed out, soaking is one of the crucial steps in leather making. And this is true also regarding tearing strength.

In the first place, and according to what was seen before, it is critical to use enough bactericide to keep control of microbial action and to be sure that the enzymes used to speed up the depletion of non-structured proteins do not contain proteolytic enzymes.

Second, Tournier[17] in his paper about soaking control, points out that some of the consequences that a defective soaking can produce are limed or tanned hides showing drawn grain, pronounced growth wrinkles, poor grain, poor handle, scud, poor or uneven softness, difficulties in reaching shrinkage temperature in chrome tanned leather and poor physical properties. Tearing strength is among the poorest physical properties. This is related to problems associated with under soaking due to remnants of Hyaluronic Acid that stick to the fibers when leather is dried and do not let them align along physical stress.

The conclusion is that in this step it is very important to warrant a proper soaking and keep record and control of each lot outcome, labeling as RISKY in the traceability system of the tannery, any lot of leathers that do not comply with the required tannery standard for future reference.

5.0 Dehairing and Liming

At this step, due to working with high pH values bacterial activity ceases to be a problem but again, if enzymes are included in formulations, they must not include proteolytic enzymes.

In such high pH conditions, the hydrolytic reactions are favored and then, hides are subjected to a "controlled damage", as some authors name it. The hydrolysis is directed mainly to eliminate non-structured proteins to produce, together with controlled plumping and swelling, the "opening up of fibers" phenomenon. But some of the collagen is also hydrolysed, mainly the one that was already damaged by autolysis and bacteria in the fresh hide's state. It is possible that the lime hydrolysis tends to complete midway actions started previously by the enzymes.

Liming time is also important regarding the degree of hydrolysis as shown by Gratacos' Graphs,[18] Figure 9. Below 20°C collagen degradation is very low, but generally the process occurs around 26-30 °C or at even higher temperatures. In the liming baths, where there are potassium or sodium hydroxides, the alkaline hydrolysis is more intense. It must be pointed out that in this way the original collagen structure continues to be modified and degraded.

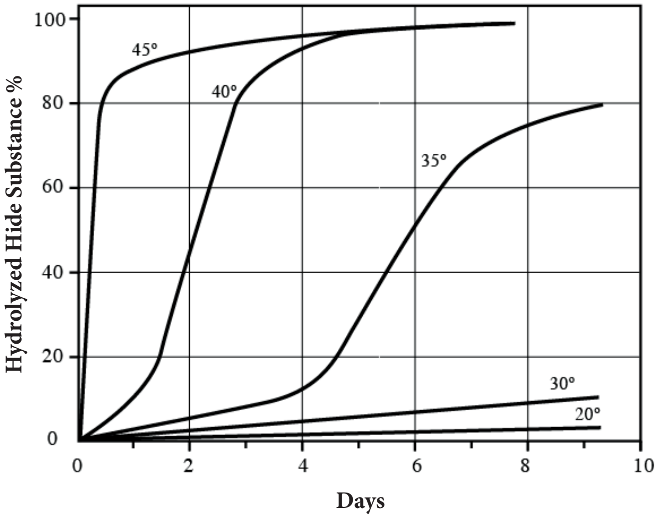

Figure 9. Hydrolysis of hide substance as a function of the time of permanence in saturated calcium hydroxide solution at different temperatures. Bath ratio: 100% on collagen dry weight.

There are three variables that need to be under control at this stage, plumpness, degree of swelling, and time of liming that means prolonged hydrolysis. Plumpness and swelling bind and imbibe water in hides' collagen, these disrupt fiber structure, can exacerbate VFD (Section 1.6) and add to debilitate strength.

Nevertheless, thin leathers for clothing and upholstery can stand longer liming times than tight and thicker shoe upper. For the latter, weekend liming is discouraged, not only for danger of low tearing but also for loose grain.

Despite these previous warnings, Tournier[9] in his paper about evolution of tear resistance in tanning processes, showed that for fresh hides that were cooled down as soon as they were flayed in the way described in Appendix I and processed as soon as they arrive to the tannery, with a well-balanced soaking and liming formulation, the results can be encouraging. Namely, the absolute tearing strength of fresh hides increases when tested after soaking, dehairing and liming. This behavior was explained because the correct opening up of the fibers associated to a proper increase of water content, can lead to a better mobility of collagen fibers, facilitating them to oppose the tearing force.

This speaks about the integrity of original fibers being maintained with proper care of fresh hides and an equilibrated swelling and plumping.

Lots that do not comply with formulations or have long liming times, should be labelled RISKY.

Appendix I

Example of hides cooling at slaughterhouse.

After flaying, hides were water slid to a pressure resistant metal receiver. After 3 to 6 hides, the receiver was closed and immediately subjected to a high-pressure blow of compressed air. The hides travelled approx. 60 m through a 12" diameter metal duct, arriving to a cyclone separator that dropped the hides into the insulated metal cooling pool on the ground. The pool, designed to hold about 1,000 fresh bovine hides, received also ice cubes as hides were dropped.

At the end of slaughtering there was a mixture of hides, ice cubes and water at 4-8°C. A 5-finger crane grabber, helped to mix the contents in order to uniform the temperature and to take hides out of the pool and load the transport truck to the tannery.

The original design of the system used recirculated cold water from cooling equipment because it was the cheapest way to cool down hides. But the buildup of blood and small debris of grease and flesh, clogged separators, filters and cooling coils, making it impossible to go on with it and obliged to change to an ice cube maker machine. The results were fewer problems and maintenance.

Continue in Part 2: JALCA, Volume 117 (1)

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Analysis of Process Safety and Occupational Health in Leather Process Industry: A Holistic Approach

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Abstract

Process Safety and Occupational health (PSOH) aspects in process industries are essential and need more consideration along with development in manufacturing and processing. In this regard, PSOH aspects are essential for the leather industry in order to prevent health hazards associated with it and improve upon adequate measures. Better safeguards and practices are necessary in PSOH for the benefit of not only for people working in the industry but for the environment at large. The situation is significant wherever hazardous chemicals or chemicals which could lead to compromise on safety in the workplace are involved. The degree of toxicity or hazard and exposure limit associated for some of them, inside factory premises are of major concern. In addition to the chemicals, other aspects such as dusts, noise levels, lighting, ergonomics, ventilation, personal safety and hygiene are worth considering. As mentioned above, the present paper analyzes various aspects of PSOH in leather process industries as a holistic approach.

Introduction

Figure 1. Model Pilot tannery Drum yard in CSIR-CLRI: Source: www.clri.org

In recent years, better techniques leading to improved process efficiency and cleaner production have been the focus of most of the research activities in leather processing.[1-3] Leather industry today is one of the leading process industries in terms of indigenous employment generation (both skilled and unskilled) as well as export earnings in most of the countries. Even though some measures are taken, there is a wide scope for the leather industry to improve upon environmental management as well as process safety as a Model Pilot Tannery (Figure 1). In this regard, Process Safety and Occupational health (PSOH) in process industries is of paramount importance and need attention while development with respect to manufacturing and processing are given priority. Leather industry utilizes several chemicals, some of which are harmful in nature. Such chemicals (both liquid and solid form) pose health concerns when they come in to contact with skin or through inhalation of gases. Some of the unit operations also lead to release of toxic gases *in-situ* during the process as explained in this paper. Better safeguards and practices are necessary in PSOH for the benefit of not only the people working in the industry but for the environment at large as holistic approach. The situation is significant wherever toxic chemicals or hazards are associated in the industry. The degree of toxicity or hazard and exposure limit associated with these chemicals in factory premises are of major concern. In addition to the chemicals, other aspects such as dusts, noise levels, lighting, ergonomics, ventilation, personal safety and hygiene are worth considering. While these safety and occupational health concern systems are more advanced in other industrial sectors, there is a need for leather industry in general to further augment their capacity in this regard. Even though, some earlier reports in this area for tanneries are available,[4–7] they have not covered all the aspects of PSOH in the leather industry. Approaches towards tannery modernization and up-gradation as Leather Industry 4.0 through multi-disciplinary approach has been reported recently,[8] including safety and health environment in tannery; however, detailed analysis on this topic has not been provided. Therefore, the present paper analyzes and reviews the various aspects of PSOH in leather process industries. These aspects require more and imperative attention in case of sectors like leather where process industries are concentrated at large. This analysis shall also be applicable to effluent treatment plants and storage facilities.

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Manuscript received June 10,2021, accepted for publication as a technical note July 29, 2021.

Figure 2. Flow chart for chrome tanning process

The sequence of leather processing with several unit operations is presented[9] as Figure 2. Uptake of chemicals/ auxiliaries employed in these processes were analyzed through mass balance in leather processing[10,11] as given in Table I. This indicates significant amount of chemicals are released and left underutilized as waste which require proper attention. Major chemicals used in various operations in leather processing and associated material safety and toxicity information are presented in Table II.

Ammonia generation in deliming processing

Deliming is one of the unit operations in leather processing which is carried out to remove the bound lime present in the limed pelt. Conventionally, ammonium salts are used in deliming for neutralizing lime, leading to release of toxic ammonia gas. The reaction can be represented as,

i) with ammonium chloride:

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_4OH + CaCl_2$$

ii) with ammonium sulfate:

$$(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow 2NH_4OH + CaSO_4$$

Environmental and health hazards associated with ammonia

Based on the reports of Occupational Safety and Health Administration (OSHA),[12] USA and National Institute for Occupational Safety and Health (NIOSH), USA, with regard to ammonia in workplaces; OSHA's former exposure limit (Table III) for ammonia was 50 ppm for a 8-hour Time Weighted Average (TWA). OSHA proposed to revise this limit to 25 ppm TWA and to add a 35-ppm 15-minute Short-term exposure limit (STEL), based on the limits established by the American Conference of Governmental Industrial Hygienists (ACGIH). Exposure limit

Table I

General Chemical Utilization Levels in Leather Processing Based on Mass Balance (% Based on Skin/Pelt/Sammed Wet-Blue Weight)

S. No	Unit operation	Chemicals used	% Utilization
1	Soaking	Wetting agent, Preservative	60-80%
2	Liming	Lime, Na_2S	20-30% 20-35%
3	Deliming	NH_4Cl or NH_4SO_4	60-80%
4	Pickling	Acids, NaCl	65% 50%
5	Chrome tanning	Basic Chromium Sulfate, Formate, Bicarbonate,	60-70%
6	Vegetable tanning	Vegetable Tan Extracts from Tannin bearing plant material	75-80%
7	Retanning, Dyeing, Fatliquoring	Synthetic tanning agents (Phenolic, Resins, Acrylics etc.); Synthetic Dyes; Oil-Water Emulsions.	70-80%

Table II

Material Safety and Toxicity Date for Major Chemicals Employed in Various Unit Operations in Leather Processing

Unit operation	Chemicals employed	Material safety and Toxicity date
Liming	Quick Lime	Hazardous substance with delayed health effects on Exposure in Air through Respiration OSHA PEL (8-hour TWA) = (5 mg respirable dust/m^3); NIOSH REL* (8-hour TWA) = 0.05 mg respirable dust/m^3
Liming	Sodium sufide	Hazardous substance with NFPA rating of 3 for Health. LD50 = 208 mg/kg (Rat); < 340 mg/kg (Rabbit)
Delming	Ammonium salts Ammonium chloride	10 mg/m^3 TWA (fume); 20 mg/m^3 STEL (fume)
Pickling	Formic acid Sulfuric acid	OSHA: 5 ppm TWA; 9 mg/m3 TWA OSHA: 1 mg/m^3 TWA & Oral, rat: LD50 = 2140 mg/kg
Tanning	Basic chromium sulfate	0.5 mg/m^3 USA. ACGIH Threshold Limit Values (TLV)
Retanning	Phenol- formaldehyde resin Acrylics	OSHA PEL: 5 ppm TWA OSHA PEL: 0.75 ppm TWA Oral LD50 = 2500 mg/kg (Rat)
Fatliquoring	Sulfated or Sulfonated oils: Sulfated Castor oil	NIOSH PEL: TWA 10 mg/m^3 (Total)
Dyeing	Azo dyes	–
Finishing	Solvents Polyurethane Acrylic Nitro cellulose Lacquer	Please Refer Table V

*REL – Recommended Exposure Limit

Table III

Exposure Limits and Health Factors Associated with Ammonia Gas; [Source: OSHA, US Dept. of Labor[12]]

Exposure Limit	Limit Values	Health Factors and Target Organs
OSHA Permissible Exposure Limit (PEL) - General Industry See 29 CFR 1910.1000 Table Z-1	50 ppm (35 mg/m^3) TWA	Temporary blindness
		Pulmonary edema
		Marked eye, skin, and respiratory irritation
OSHA PEL – Construction Industry See 29 CFR 1926.55 Appendix A	50 ppm (35 mg/m^3) TWA	Temporary blindness
		Pulmonary edema
		Marked eye, skin, and respiratory irritation
OSHA PEL – Shipyard Employment See 29 CFR 1915.1000 Table Z-Shipyards	50 ppm (35 mg/m^3) TWA	Temporary blindness
		Pulmonary edema
		Marked eye, skin, and respiratory irritation
National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL)	25 ppm (18 mg/m^3) TWA 35 ppm (27 mg/m^3) STEL	Marked eye, skin, and respiratory irritation
American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) (2001)	25 ppm (17 mg/m^3) TWA 35 ppm (24 mg/m^3) STEL	Marked eye, skin, and respiratory irritation
CAL/OSHA PELs	25 ppm (18 mg/m^3) TWA 35 ppm (27 mg/m^3) STEL	Marked eye, skin, and respiratory irritation

Note:

EPA Inhalation Reference Concentration (RfC): 1x10^{-1} mg/m^3

Agency for Toxic Substances and Disease Registry (ATSDR) Inhalation Minimal Risk Level (MRL): 1.7 ppm (acute); 0.1 ppm (chronic)

NIOSH Immediately Dangerous to Life or Health (IDLH) concentration: 300 ppm

Table IV

Major Odorous Gases Emanating from Various Unit Operations in Leather Processing

S. No.	Unit operation	Odorous gas generated
1	Soaking	Ammonia
2	Liming	Ammonia, H_2S
3.	Deliming	Ammonia
4.	Pickling	Sulfurous gases
5.	Retanning, Dyeing and Fatliquoring	Phenolics, Formaldehyde etc.
6.	Finishing	VOC's (Solvents, Polymers and Resins)

Table V

Major VOC Causing Gases Caused in Various Unit Operations Causing and their PEL's (Permissible Exposure Limit) for 8-Hour TWA (Time Weighted Average) [Source: OSHA, US Dept. of Labor[13]]

S. No.	VOC causing gases	Exposure limit (ppm) OSHA	
		(ppm)	mg/m^3
1.	Ammonia	50	
2.	Acetic acid	10	
3.	Cr(III) compounds		0.5
4.	Carbon di oxide	5000	
5.	CaO		5
6.	HCl	5	
7.	H_2SO_4		1
8.	Formic acid	5	9
9.	H_2O_2	1	
10.	Chlorine	1	
11.	SO_2	5	
12.	Phenol	5	
13.	Methyl ethyl ketone	200	
14.	n-Hexane	500	
15.	Aniline and Homologs	5	
16.	Formaldehyde	0.75	
17.	Acetone	1000	
18.	Tri chloro ethylene		
19.	Napthalene		
20.	Xylene	100	
21.	IPA	10	
22.	Oxalic acid		1
23.	Particulates a) Total b) Respirable fraction		 15 5
24.	PCP		0.5
25.	Ozone	0.1	
26.	Quinone	0.1	
27.	Dichloro methane	12.5	
28.	Benzidine (based dyes)		<0.1% (by weight)*

values and Health factor associated with Ammonia gas are given by OSHA, US Department of Labor[12] in Table III.

Odor causing gases in the tannery

Major odorous gases emanating from various unit operations in leather processing are given in Table IV. Permissible exposure limit (PEL) is a regulatory limit on the amount or concentration of a substance in the air. This is usually based on an eight-hour TWA, although some are based on STELs. Major chemical components of VOC and other gases from leather processing PELs for 8-hour TWA exposures as per OSHA[13] are given in Table V.

Toxic gas generation in drains

Formation of toxic gases also takes place in drains while mixing of two reactive substances from the spent liquors. When pickle liquor and lime liquor come into contact in drains it can lead to the formation of toxic hydrogen sulphide gas.

$$H_2SO_4 + Na_2S \longrightarrow H_2S + Na_2SO_4$$

$$2HCl + Na_2S \longrightarrow H_2S + 2NaCl$$

Therefore, this should be avoided by segregation of spent liquors in drains as sectional streams in order to avoid the formation of toxic gases through reactions.

Occupational Hazards in Leather Industry and Possible Solutions

Solutions to air pollution in tannery environment

As per Tables II to V with regards to air pollution involving odorous gases as well as toxic gases, the best solution is to eliminate the use of those hazard causing substances in the process through alternative measures. There are earlier reports available for odor abatement in tanneries.[14,15] The toxic gases generated could be treated through suitable system such as shown in Figure 3. The workers should be advised to wear suitable safety personal protective equipment such as respirators for preventing the hazardous gas entering the body.

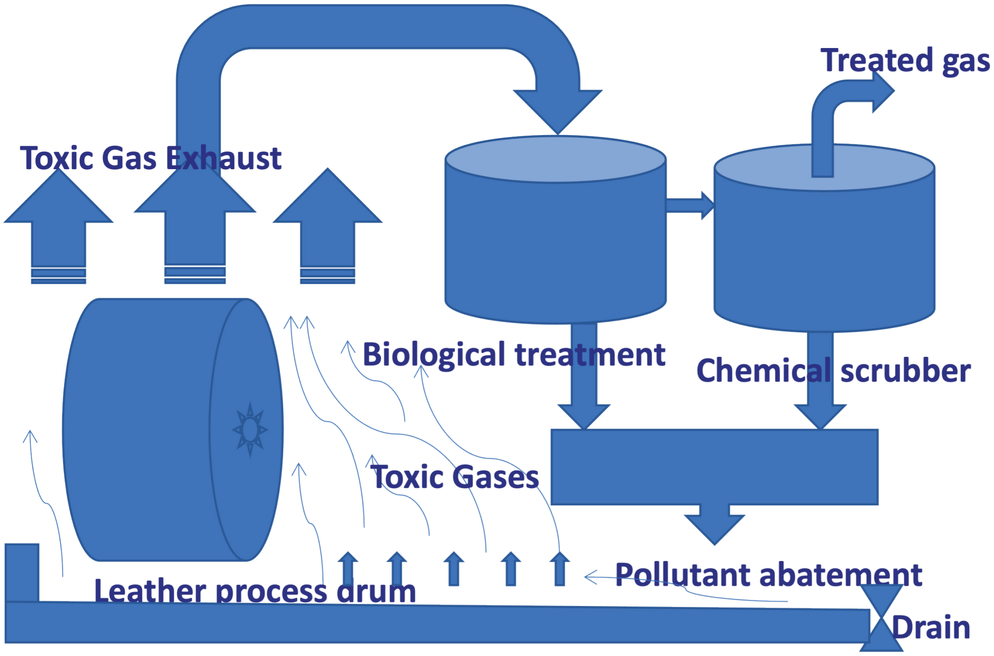

Figure 3. Odor control system for gases from tannery yard

Particulate matters hazard

Leather processing utilises several chemicals in powder form; improper handling of these chemicals could lead to particulate pollution. Details of particulate matters emanating from tannery causing dust pollution in various stages of leather processing are given in Table VI. Particle pollution contains microscopic solids or liquid droplets that are so small that they can get deep into the lungs and cause serious health problems. The size of particles is directly linked to their potential for causing health problems. Small particles less than 10 micrometers in diameter pose the greatest problems, because they can get deep into lungs, and some may even get into the bloodstream.[16]

Some of the unit operations such as Beamhouse, Retanning, Dyeing and finishing operations subscribe to particulate matters <10 μ in size, which require proper attention. Mechanical operations like shaving and buffing operations generate leather particulate matters of fine nature,[17,18] which require adequate measures. Systems like electrostatic precipitators for dust particle removal could be useful. The workers should be advised to wear suitable safety personal protective equipments such as respirators for preventing the particulate matters entering through the nose.

Noise pollution in leather and leather products industries

Leather processing utilises several heavy-duty machineries, which lead to noise pollution while in operation. The National noise pollution (regulation and control) rules 2000, India[19] on ambient air quality standards in respect to noise is given in Table VII. The regulation gives maximum value of 75 dB in industrial zone during

Table VI

Details of Particulate Matters Emanating from Tannery Causing Dust Pollution

S. No.	Unit operation/ stage	Particulate matter	Particle Size (microns)
1.	Raw skins/hides	Dust	1-40
2.	Raw skins/hides	Salt	0.5-1
3.	Beam house	Anthrax Other Bacteria	1-10 0.3-60
4.	Liming	Lime dust	10-1000
5.	Shaving	Chrome shavings	25-1000
6.	Retanning	Syntan powder	10-100
7.	Dyeing	Dye powder	1-10 microns
8.	Tanned leathers	Moulds	3-12
9.	Buffing	Buffing dust	10-1000
10.	Finishing	Finish spray with Binders, Pigments	5-10

Table VII

The National Noise Pollution (Regulation and Control) Rules, 2000, India on Ambient Air Quality Standards in Respect of Noise

Area Code Category of Area/Zone		Limits in dB(A) Leq*	
		Day Time	Nighttime
(A)	Industrial area	75	70
(B)	Commercial area	65	55
(C)	Residential area	55	45
(D)	Silence Zone	50	40

Note:

*dB(A) Leq denotes the time weighted average of the level of sound in decibels on scale A which is relatable to human hearing.

A “decibel” is a unit in which noise is measured.

“A”, in dB(A) Leq, denotes the frequency weighting in the measurement of noise and corresponds to frequency response characteristics of the human ear.

Leq : It is an energy mean of the noise level, over a specified period.

the daytime. As reported by OSHA, median noise measurement level for Leather and Allied manufacturing industry is at 86.56 dB. Most of the machineries employed in leather and related processes exceed the standard limit, which necessitates suitable measures.[20] Average noise level for footwear and leather products have been reported in the range of 78.55 to 102.77 db, which exceeds the standard limit.[21] There are some significant health hazards associated with noise pollution such as generated from equipment/machinery as reported.[22] The workers should be advised to wear suitable safety personal protective equipments such as ear muffs, ear plugs for preventing the health hazards associated with noise pollution in leather industry.

Safety personal protective equipment

Protecting and safeguarding tannery workers/ staff from various hazards in leather industry is desirable and could be assisted by personal protective equipment. List of safety/personal protective equipments recommended and hazard associated with various unit operations in leather or leather products making are given in Table VIII. The workers should be advised to wear suitable safety personal protective equipments in order to minimise the health hazards associated with different unit operations in leather industry. These aspects were studied and reported earlier[23].

Mechanical and electrical hazards

Determination of chemical and physical risk factors in the leather industry in terms of occupational health and safety has been reported.[24] Mechanical hazards are mostly arising out of machinery having revolving/moving cylinders with blades or knives such as Fleshing, Shaving, Splitting, Setting and Buffing machines; without blades such as Drum/paddle. Hazards associated with them are accidental putting of body parts such as hands; hence suitable shields as personal protective equipment are necessary. Therefore,

Table VIII

List Safety Personal Protective Equipments for Various Unit Operations in Leather or Leather Products

S. No.	Unit operation/ stage	Hazard	Safety/ Personal protective equipments
1.	Raw skins/hide handling	Microbial, Dust	Gloves, Respirator, Safety shoes
2.	Beam house	Chemical, Toxic gases, Dust	Gloves, Waist wear, Respirator, Safety shoes
3.	Mechanical operations	Noise, Mechanical	Earmuff, Ear plug, Interlock, Alarm, Safety shoes
4.	Pickling	Acid	Gloves, Respirator, Safety shoes
5.	Tanning	Chemical, Dust	Gloves, Respirator, Safety shoes
6.	Retanning, Dyeing	Chemical, Dust	Gloves, Respirator, Safety shoes
7.	Finishing	VOC, Dust	Gloves, Respirator, Safety shoes
8.	Leather products	Noise, Mechanical	Ear muff, Ear plug, Interlock, Alarm, Safety shoes

interlock or sensor systems, which would automatically shut down the machines whenever hands are put in the wrong place, are necessary. Guards surrounding the moving/rotating parts such as Drums are essential. Fuses, trip or alarm systems are also necessary whenever there is a danger such as electrical short circuits.

Conclusions

PSOH in the leather process industry is very much important, not only for health concerns with regard to staff in work place but also for the environmental safeguard as a holistic approach. These aspects require more and imperative attention in the case of developing countries, where process industries are concentrated in large clusters in different places. Various hazards in a tannery environment such as toxic gases, noise levels, particulate matters, mechanical hazards have been analyzed and reviewed in this paper and possible solutions or remedial measures are arrived. The present analysis would provide a process safety, clean and hygienic environment in and around leather process industries such as tannery, effluent treatment plants, storage facilities for providing safety features.

Acknowledgements

The author thanks CSIR–CLRI for the support.

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Long-Term Releasing Kinetics of Chromium from Leather

by

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Abstract

The release of chromium from leather inevitably results in potential risks and this study is conducted to investigate the long-term releasing behavior. The leaching tests proceed using water at solid to liquid ratio of 1:20 and rotational speed 60 r/min for 240 hours to simulate the release of chrome leather under natural conditions. The experimental data successfully fit with the Pseudo-second-order equation, Elovich equation, and Weber-Morris model, indicating the long-term leaching behavior of chromium in heterogeneous leather is controlled by liquid-solid film, while the interparticle and intraparticle diffusion also play important roles. The leachable chromium accounts for 2.8-4.5% total chromium in leather and increases with temperature. The Three-compartment model depicts the releasing process as rapid, slow, and very slow stages, and temperature mainly affected the very slow stage. The amount of released chromium in rapid and slow stages slightly increases with temperature, which could be used to assess the hazard of chrome leather.

Introduction

Now leather has been an indispensable item in the form of shoes, clothing, belting and other upholstery articles.[1,2] It is estimated the leather output every year is about 1.67×10^9 m^2 in the worldwide and perhaps 90% of leather is manufactured by using chromium(III).[3,4,5] During leather production, a large amount of leather waste containing chromium is also generated.[6,7] Typical full-chrome tanned leather generally contains 2.0 wt% to 3.0 wt% of chromium, and of this amount 2% chromium is simply adsorbed by the collagen matrix according to Brown et al findings,[8] in spite of washing following chrome tanning during the manufacturing process. Theoretically such chromium loosely bound would release easily from leather during the process of utilization as product or waste. Under certain conditions, low toxicity Cr(III) could be oxidized to highly toxic Cr(VI)[9] which is hazardous and toxic to both environment and health.[10-14] Indeed, leather attracts more and more attention for this alleged environmental impact and potential health risk of chromium. The kinetic behavior of chromium releasing from leather plays a key role in the assessment of the safety of chrome leather. Although there are many efforts to minimize the release and conversion of chromium in leather,[15] little attention has been paid to the releasing process. Zhou et al. focused on the release of chromium in chrome tanning and post tanning processes in order to reduce chromium discharge in leather processing,[16] and Erdem et al.[17] investigated the effects of liquid/solid ratio, contact time, pH and sequential extraction on the leaching behavior of chromium in chrome shavings to indicate the pollution potential. In the production process of chrome leather, Cr(III) is attached to collagen fibers by dominant strong covalent complexation and weak adsorption, which is similar to chemisorption accompanying physical adsorption.[18] Then the release process of chromium is opposite to the adsorption.[17] The leaching kinetics of metal such as cobalt, vanadium from waste are studied by Pseudo-first-order kinetic equation, Pseudo-second-order kinetic equation, Webber-Morris and Elovich equation,[19-21] and the main control factor of leaching process was obtained.

In this study, the kinetics of chromium release from chrome leather and the main factors of chromium releasing are investigated. This research would contribute to waste management and assessing the risk of chrome leather.

Materials and Methods

Materials and reagents

The chrome leather sample was supplied from a tannery in Hebei (China). The leather sample was homogenized by oven at 40±5°C in standard laboratory atmosphere (20±2°C and 65±5% relative humidity) for 48 hours, ground by Retsch SM100 (Retsch GmbH, Germany) with 4×4mm sieve and thoroughly homogenized for this experiment. All chemicals were of analytical grade or better, provided by Chengdu Jinshan Chemical Reagent Co Ltd.

Experimental method

Leaching experiment

Four grams of leather powder and 80 mL ultrapure water (18.2 MΩ/cm, Milli-Q system, Millipore, USA) were added to 250 mL-conical flask, then shaken at 60 r/min by using the thermostatic oscillator (ZWY-2102C, shanghai, China) with contact time from 1 h to 240

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Manuscript received May 31, 2021, accepted for publication July 29, 2021.

h at 20, 25, 30,35°C with the precision of ±0.1°C, respectively. The filtrate passed through 0.45μm membrane to analyze at once. All the tests were done in duplicate.

Chromium analysis

The leather powder and leachate were digested to measure total chromium content. For leather powder, 1.0 g sample was digested by mixed solution of 65% HNO_3 and 30% H_2O_2 with HNO_3-to-H_2O_2 volume ratio 3:1 in a 250 mL-conical flask using electric stove[22]. The filtered digestion liquor was diluted with ultrapure water to analyze the total chromium content by inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 8000, USA). The chromium standard stock solutions (1000 $mg{\cdot}L^{-1}$) was obtained from National Nonferrous Metals and Electronic Materials Analysis and Testing Center (Beijing, China) and diluted to the calibration standards (1.0-50.0 $mg{\cdot}L^{-1}$). For the leachate, 40 mL liquor was digested by 8.0 mL of the above mixed solution of HNO_3 and H_2O_2 in a 250 mL conical flask using an electric stove, and the operation was repeated till the solution was clear and transparent. The conical flask was washed three to four times by ultrapure water and mixed with digestion liquor, then set to 25 mL and measure the total chromium as the above. The chromium in leachate could be calculated based on C_t=0.625C, where C_t and C represent the chromium concentration of leachate (mmol/L) and that from ICP-OES (mmol/L) respectively, and 0.625 represents the dilute ratio.

Cr(VI) in leather is detected by ISO 17075-1:2017, and that in leachate by GB/T15555.4-1995 using colorimetric reagent 1, 5-diphenylcarbazide at 540 nm[23] (UV-1800 BPC, Mapada Instruments Co., Ltd.).

The organics released

The total organic carbon (TOC) analyzer (DKSH vario TOC, Germany) was used to analyze the dissolved organic carbon in leachates. For the leachate, 5.0 mL was transferred to 25-mL volumetric flask and set to volume by deionized water, and analyzed directly.

Scanning electron microscope and differential scanning calorimetry

The leather powder before and after leaching experiments were characterized by scanning electron microscope (SEM, FEI Nova Nano SEM 450, FEI Co.) and differential scanning calorimetry (DSC, NETZSCH 204 F1, Germany). Before the characterizations, the samples were homogenized in oven at 40±5°C about 48 h. The temperatures of DSC experiments range from 20°C to 200 °C under a nitrogen atmosphere with a heating rate of 10 K/min.

Nitrogen adsorption analysis

For nitrogen adsorption analysis, 0.3 g leather powder was used with a TriStar 3000 analyzer (Micromeritics, USA). The surface area, total pore volume and average pore size were obtained to characterize the leather fiber before and after leaching.

Result and Discussion

The characterization of chrome leather leached and unleached

The total chromium in chrome leather sample was measured to be 20.6721 g/kg leather, which is consistent with previous reports of about 2.0 wt% of chromium in full-chrome tanned leather[24]. No Cr(VI) was detected in leather. SEM characterization of leather powder is presented in Figure 1. It can be observed the improving dispersion degree of collagen fibers after 240-h leaching, and the voids between collagen fibers are enlarged, which could be further confirmed by the results of nitrogen adsorption (Figure 2). The surface area, total pore volume and average pore size increased from 3.34 to 3.57 m^2/g, 3.25 to 5.12 uL/g and 3.9 to 5.74 nm respectively after leaching. It is clear that the leaching of chrome leather in water had a good effect on separating fibers, which is also one of the tanning effects.[25] These results suggest leaching makes the chromium bound in lower level fibrils accessible for water, and indicate that the leaching of chrome leather involve complex physico-chemical interaction resulting in the further dispersion of fibers.

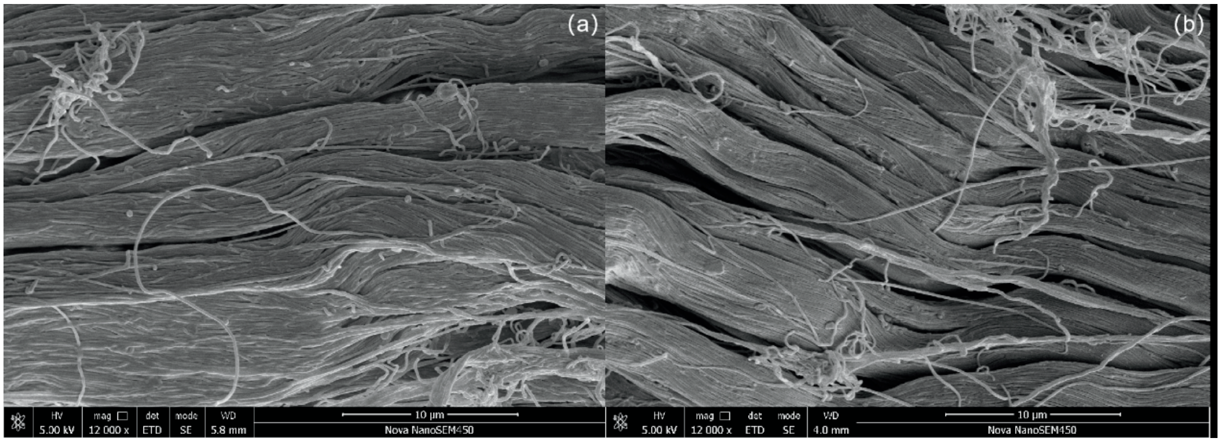

Figure 1. SEM images of chrome leather [(**a**)12000×] and after10-day leach[(**b**)12000×]

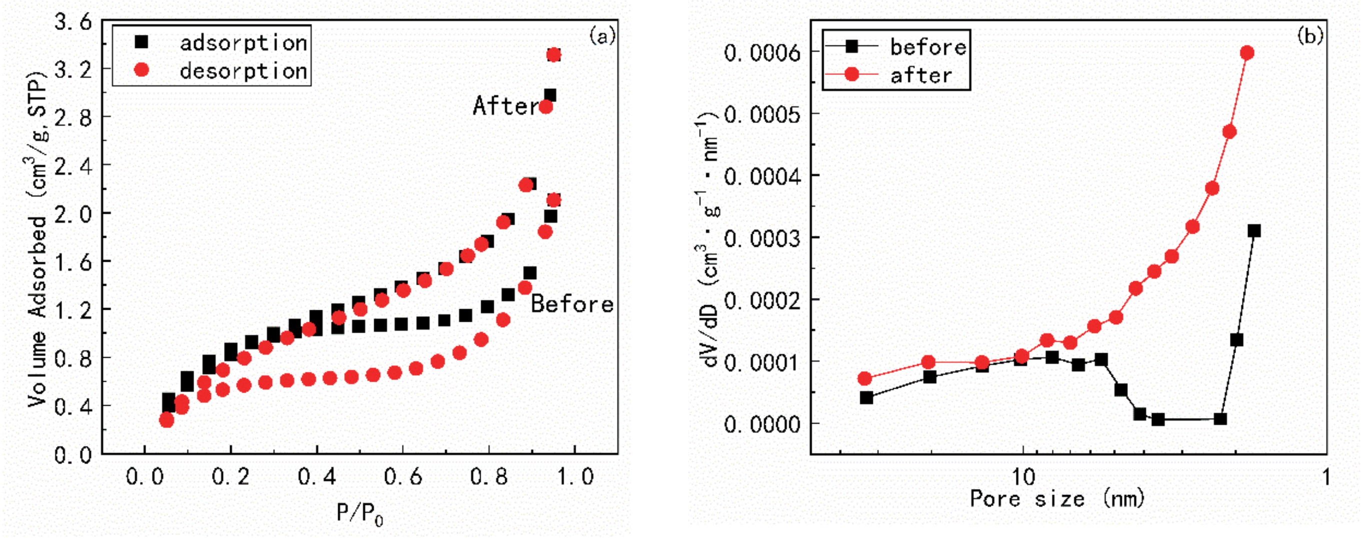

Figure 2. N_2 adsorption-desorption isotherms **(a)** and pore size distribution **(b)**

The denaturation temperature of leather powder before and after leaching is found to be similar around 72°C as shown in Figure 3, much lower than that of chrome leather(> 90°C),[26] which may be ascribed to the grinding in the sample preparation. The DSC results suggest no essential structure changes in the collagen fiber matrix during leaching.

Chromium released from leather at various temperatures

Figure 4 shows the tendency of the leached chromium(a) and organics(b) from chrome leather powders varying with time at different temperatures. As seen from Figure 4(a), the released chromium increases parabolically with time at each temperature, indicating the leaching of chromium is controlled by the dissolution and diffusion.[17] No Cr(VI) was detected in leachate at each temperature. The release of chromium is substantially influenced by temperature especially after 24 hours. However, the release of organics is very different. In the initial 24 hours, the increasing temperature obviously intensifies the release of organics, which does not differ significantly with prolonged contact time after 48 hours. The results support the speculation that the solid-phase extraction techniques in the ISO 17075 protocol may result in underestimation of Cr(VI) in leather for the parallel release of organics as reducing agent.[27, 28]

In the initial 24 hours at each temperature, the released chromium increases rapidly, which might come from the diffusion of soluble chromium in void water. During the leaching time from 24 h to 168 h, the change of chromium content is comparatively small. This could be attributed to the release of chromium adsorbed onto the leather. 168 h later, the increase of chromium in leachate is very low, which might be derived from the shift of coordination equilibrium involving Cr(III) and collagen carboxyl groups, and

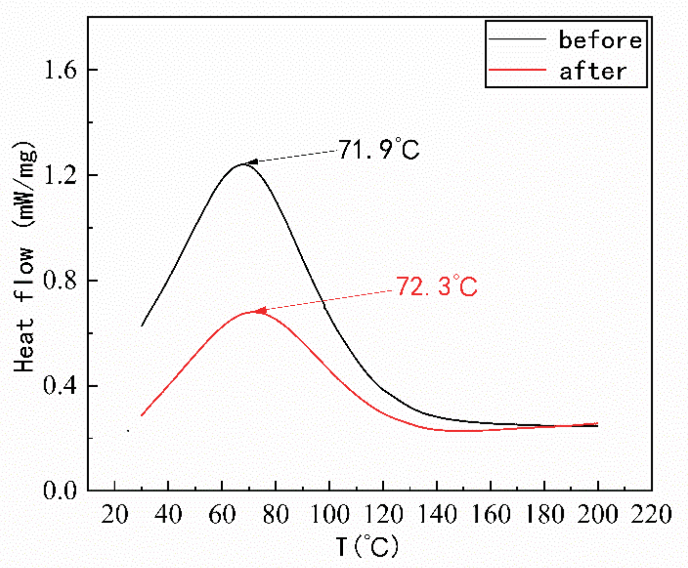

Figure 3. DSC of chromed leather shavings (before leaching and after leaching)

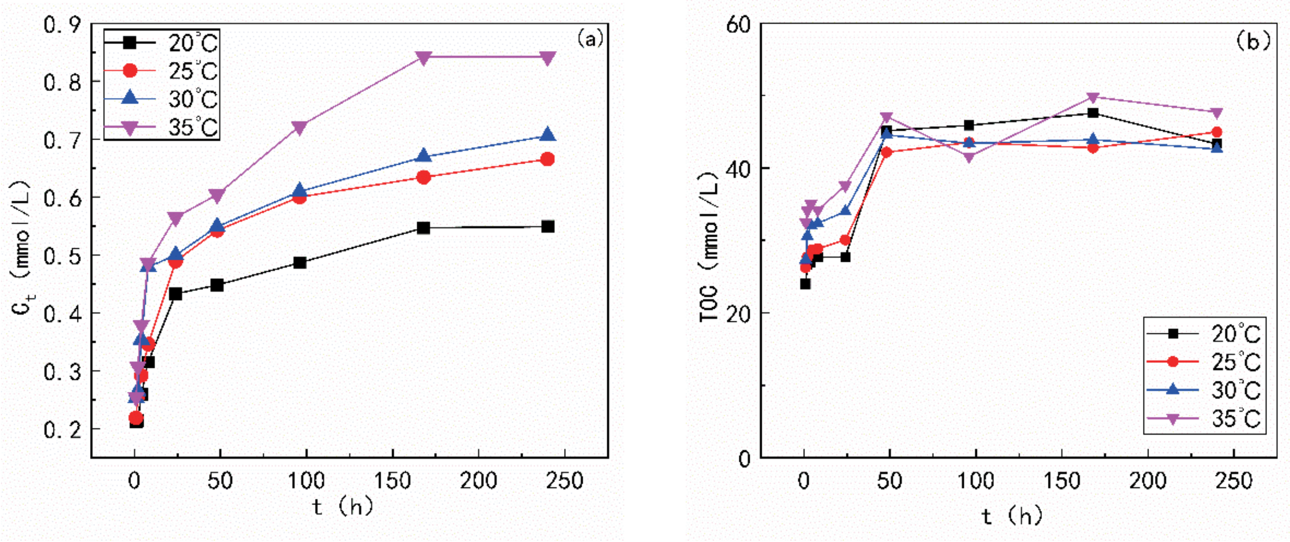

Figure 4. Releasing behavior of Cr**(a)** and organics**(b)**at different temperature

chromium concentration in leachate fluctuates slightly with time at each temperature. The released chromium concentration exceeds 10 mg/L after 1.0 h at each temperature, far beyond the maximum allowable limit 5 mg/L given by USEPA, indicating that the waste leather in this test is a pollutant. The released chromium content increases steadily as the leaching time, and is remarkably affected by temperature. For example, the released chromium concentration is beyond 15 mg/L after 4 h at 20°C and 2 h at 35°C. An increase of 15°C from 20°C to 35°C facilitates the chromium releasing, suggesting that the release of chromium from the leather scraps is an endothermic reaction. Obviously, it is very important to explore the mechanism of chromium releasing from chrome leather for the management of chrome leather wastes.

Kinetics analysis for Cr release

In order to investigate the kinetic mechanism involved in the long-term releasing process, four kinetic models namely Weber-Morris diffusion, Elovich, Pseudo-second-order and Three-compartment rate model have been adopted to fit the kinetic data. Results show that chromium releasing from the leather is successfully depicted by the kinetic models according to the significant R^2 values demonstrated in Table I.

As can be observed, R^2 values of Weber-Morris are lower than the other three models, indicating intra-particle diffusion should not always be rate-determining step in the long leaching process, which is very different from our previous short-term leaching behavior of chromium from leather.[24] The details of fitting are shown in Figure 5. Therefore, chromium release data are further analyzed by the Elovich, Pseudo-second-order, and Three-compartment rate equations, respectively.

Elovich equation

Elovich equation is suitable for highly heterogeneous media such as soil, and the adsorption systems of natural lignocellulose with Cr^{3+} has been well described by it.[29] The high heterogeneity implies the material fixes metal in multilayer manner, and each layer exhibits a different activation energy.[30] The dimensionless Elovich equation could be expressed as:[31]

$$\left(\frac{C_t}{C_{ref}}\right)=R_E\ln\left(\frac{t}{t_{ref}}\right)+1 \tag{1}$$

Where C_t and C_{ref} are the concentration of chromium in leachate at time t and the longest operating time t_{ref} in leaching process respectively, R_E is an approaching equilibrium factor of the Elovich

Table I

Coefficients of determination (R^2) for the kinetic models of chromium leaching from leather

T(°C)	Weber-Morris diffusion	Elovich	Pseudo-second-order	Three-compartment
20	0.8616	0.9785	0.9973	0.9916
25	0.9043	0.9889	0.9977	0.9982
30	0.9229	0.9962	0.9958	0.9983
35	0.9289	0.9821	0.9933	0.9900

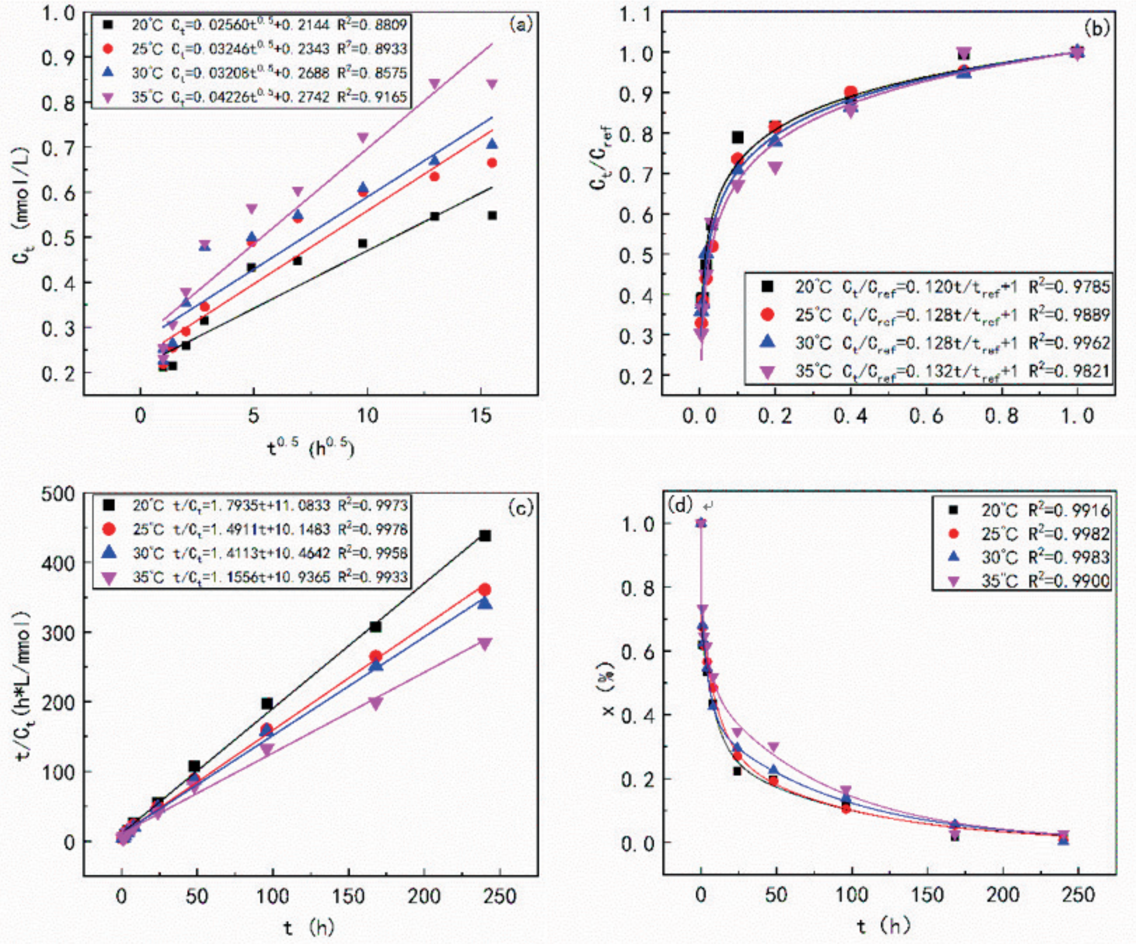

Figure 5. The fitting of Weber-Morris diffusion equation(**a**), Elovich equation(**b**), Pseudo-second-order equation(**c**) and Three-compartment rate model(**d**)

equation. Then the fitting of Elovich equation with experimental data is shown in Figure 5(b).

The correlation coefficients between Elovich equation and experimental data at four temperatures are all above 0.97, indicating the leaching process of chromium is not a single reaction mechanism process but a complex heterogeneous dispersion process with large changes in activation energy during the reaction process.[32] The hierarchical structure of collagen fiber makes chromium fixed into the leather matrix with different stability. For example, the dominate coordination interactions include mononuclear mono-coordination, mononuclear chelating coordination, polynuclear mono-coordination, polynuclear multi-coordination,[33] which leads to various activation energies during leaching process including the chemical equilibrium shift of coordination, as well as inter-, and intra-particle diffusion. The R_E values shown in Figure 5(b) of four temperatures are around 0.12, indicating the release of chromium proceeds mildly.[31]

The Pseudo-second-order rate equation

The finished leather contains sufficient voidage and shows excellent hydrophilicity,[34, 35] which is conducive to the free diffusion of water into the interior of the fiber, therefore the leaching of chromium could be viewed as occurring in liquid films throughout the fibers. The Pseudo-second-order model is extensively used in the leaching process of metal ions from inorganic material such as cement.[36, 37] The equation for the Pseudo-second-order kinetics can be expressed as follows:[38, 39]

$$\frac{t}{C_t} = \frac{t}{C_s} + \frac{1}{k_2 C_s^2} \qquad (2)$$

Where C_t is the concentration of chromium in leachate at time t, and C_s is the concentration of chromium in leachate at the equilibrium state. While k_2 (L×mmol^{-1} ×h^{-1}) is the rate constant of leaching reaction in Pseudo-second-order equation. The fitting of experimental data with Pseudo-second-order kinetic equations is shown in Figure 5 (c).

The linear coefficients R^2 of Pseudo-second-order rate equation are all above 0.99 for the four temperatures, indicating that the rate-determining step of the leaching process is liquid–solid film. Thus, the releasing process of chromium could be described as the following. At first, the driving force of the fresh water is enough to make chromium adsorbed on the surface of leather fiber release, which leads to the rapid increase of chromium in the leachate just as shown in Figure 4(a). Meanwhile a reacted layer with fewer chromium is formed, and the chromium inside the leather fiber could subsequently diffuse out through it and enter the leachate. In this stage, the driving force of the leachate is much weaker than the previous fresh water due to the higher concentration of chromium in the leachate, and the releasing rate of chromium becomes slower just as the case from 48 h to 168 h shown in Figure 4(a). Then the chromium on leather matrix might further release because of the equilibrium shifts to a new equilibrium. In this stage, the releasing rate of chromium should be much slower.

According to the Pseudo-second-order rate equation, we could obtain the equilibrium concentration of chromium in leachate at leaching equilibrium, which was 0.56, 0.67, 0.71 and 0.87 mmol/L respectively at 20, 25, 30, 35°C. The equilibrium concentration could be used to estimate the leachable chromium in leather under natural conditions. About 2.8-4.5% of total chromium in leather could be leached and increases with temperature. However, after leaching 168 h the released chromium exceeds 94% of the leachable chromium which could be calculated from the Pseudo-second- order rate equation at the four test temperatures. Obviously, the risk assessment of chrome leather and its waste should pay more attention to this period.

The better fitting of Pseudo-second-order kinetic equation and Elovich equation show the multi-step releasing process of chromium involving multi-phasic mass transfer with various activation energies. The collagen fiber network of the leather consists of modules of different dimensions in terms of diameter, length and surface area, which results in the leather matrix porosity and capillarity. Then the leather would contain two types of water, including those bound by hydrogen bond such as intramolecular water and multilayer water enveloped on the surface of the fibrils, elementary fibers and fibers, as well as the mobile capillary water. During the leaching process, the chromium desorbed firstly into the adsorbed water, then transferred to the capillary water by diffusion and liquid phase transport, ultimately leached out by the convective diffusion of eluent. The dissociation of chromium from coordination compound Cr-collagen is very difficult under mild conditions, so chromium desorption should play the key role during the long-term intermittent leaching process in nature.

Three-compartment model

Chromium in leather exists at equilibrium state before leaching, and the release curve shown in Figure 4(a) could be divided into three additional contributions dominated by the bulk eluent water, capillary water and adsorbed multilayer water based on the structural hierarchy of leather. Chromium adsorbed on fibers releases into eluent water firstly in the initial stage of leaching, then those adsorbed on fibrils, elementary fibers desorbed. Finally, very slow increase of Cr concentration in leachate could be ascribed to those adsorbed inside the microfibrils and then possibly dissociated from coordination compound Cr-collagen. Thus, the rapid, slow, and very slow leaching process could be described by the sum of three exponential functions as the following:[40]

$$C_t/C_0=F_{rap}\exp(-k_{rap}t)+F_{slow}\exp(-k_{slow}t)+F_{vs}\exp(-k_{vs}t) \qquad (3)$$

where C_t is the concentration of Cr in leachate at time t, and C_0 is the leachable concentration of chromium in leachate at leaching equilibrium state, while F_{rap}, F_{slow} and F_{vs} are the chromium ratios of the rapid, slow, and very slow leaching stages respectively, and k_{rap}, k_{slow} and k_{vs} are the rate constant of the corresponding stage, h^{-1}. Using the equilibrium concentration fitted by Pseudo-second-order equation as the total leachable chromium in leather, the chromium ratios of three leaching stages should satisfy:

$$F_{rap}+F_{slow}+F_{vs}=1 \qquad (4)$$

The correlation coefficients are all above 0.99, indicating the Three-compartment model gives a statistically significant improvement over Elovich. The fitting parameters are shown in Table II, and the fitting figure is listed as Figure 5(d).

With the increase of temperature, the leachable chromium increases, and the releasing fraction shifts from almost even distribution at 20°C to the very slow fraction. The total amount of chromium

Table II
The parameters of Three-compartment model

T(°C)	rapid stage		slow stage		very slow stage		R²
	F_{rap}	$k_{rap}(h^{-1})$	F_{slow}	$k_{slow}(h^{-1})$	F_{vs}	$k_{vs}(h^{-1})$	
20	0.316	89.9	0.389	0.112	0.295	0.0108	0.9916
25	0.297	90.1	0.393	0.0912	0.310	0.0112	0.9982
30	0.248	90.6	0.364	0.193	0.387	0.0115	0.9983
35	0.230	91.0	0.271	0.185	0.498	0.0124	0.9900

released in rapid stage and slow stage at four temperatures is similar and increases slightly with temperature. Obviously, the increased leachable chromium with temperature is mainly derived from the very slow stage, which may be caused by the presence of more micropore and thermodynamically favorable regions of the leather from which trapped chromium cannot be easily released. The fitted rate constants for rapid, slow, very slow process are about 90, 10^{-1} and 10^{-2} h^{-1}, respectively, and generally increased with temperature. The magnitude of observed release rate constants demonstrates the rationality of the division of chromium release process into three releasing fractions.

Conclusion

The leachable chromium in leather is mainly in the form of weak binding or free state with water as extractant under natural conditions, accounting for 2.8-4.5% of the total chromium in leather. The long-term leaching behavior of chromium in heterogeneous leather is controlled by liquid-solid film fitted well by Pseudo-second-order kinetic equation, meanwhile the interparticle and intraparticle diffusion also play important roles. The releasing curve of chromium from leather is deduced to be three compartments: fast, slowly, and very slowly releasing fractions, and the rate constants of the three compartments are distinguished. The very slowly releasing compartment increases significantly with temperature, which may consist mainly of thermodynamically more favorable chromium in leather. The rapid and slow releasing compartment at four temperatures fluctuates slightly around 2% of total chromium in leather. This value could be used to assess the risk of chrome leather, such as the transport to ground water and uptake by organisms that feed from water, or the transport to the leather surface and contact with skin.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (No. 2018YFC1802201). We also appreciate Dr. Hou Xu from the Analytical and Testing Center of Sichuan University for her helping in the measurement of the total Cr.

Availability of data and materials

The data used to support the findings of this study are available from the corresponding author upon request.

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Development of Leather Cutting Board from Plastic Waste

by

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Abstract

Cutting is the process in which goods or garment material are cut and converted into pattern shapes of the goods or garment components. There are two methods of Leather cutting, which are hand cutting and machine cutting. Hand cutting is done with the use of hand knife, cutting board and cutting patterns. Machine cutting can be done using semi-automatic cutting machines or fully-automatic cutting machines. Currently, in Ethiopia, different local and foreign investors are participating in leather products manufacturing. Most of the leather product manufacturing industry and some Small and Medium enterprise's (SME's) in the country are using leather cutting machines in order to cut leather goods or garment parts. Most of the industry and SMEs are using imported cutting board made of plastics and rubbers. However, these cutting boards are expensive.

This research aimed at developing a cutting board made from HDPE (High-Density Polyethylene) plastic waste as main material, calcium carbonate as a filler and glass fiber as a reinforcing material. Primary and secondary data gathering techniques were applied simultaneously. Primary data were collected through interview and field observation. Secondary data was gathered by reviewing different literature. The cutting board developed through collecting HDPE plastic waste, washing, shredding and melting the shredded plastic with filler and reinforcing material. The melted plastic poured in to cutting board mold and cooled. The developed cutting board was compared with HDPE cutting board available in the local market. The developed board showed relative compression and hardness properties with the HDPE cutting board available in the market. In the cost analysis, the developed cutting board is cheaper than the cutting board which available in the market. However, the cutting board in the market has better surface texture and quality than the developed cutting board. Melting HDPE plastic waste using metal or clay cooking pots and charcoal fire is a tedious task and smoke from the fire will cause human health problem and will affect environment. Consequently, manual plastic melting method is not feasible for mass production, because it is difficult to control the amount of heat (charcoal fire) during melting process. Based on this the authors recommend using machine based plastic melting and molding during HDPE and related plastic recycling.

Introduction

Cutting is the process in which goods or garment material are cut and converted in to the shape of the patterns of the component of the goods or garment.[1] There are two methods of leather cutting, which are hand cutting and machine cutting. Hand cutting is method of cutting leather or any other leather product making material with use of scissors and special knifes. This allows producing individual unique items whose value is not determined by functionality but based more on visual effects and design features. Machine cutting is also the method of cutting leather or any other Leather product making material using cutting board and metal dies.[1, 2] Both cutting methods require a cutting board on which to place material for cutting and the board protects the cutting knife and the work surface underneath (such as a desk or table).

The cutting board is certainly a rigid type of board that can be used for a plethora of arts and crafts endeavours. Cutting boards are made of variety materials from wood, tempered or toughened glass and different plastics. Recently the accumulation and potential impacts of plastic pollution has been recognized as an emerging environmental issue.[3-5] Currently in Ethiopia, a huge amount of plastic is generated and some wastes are dumped in landfills. In the country, waste plastics are blocking drainage and sewage systems resulting in water logging, flooding and spread of water borne diseases.[6-8]

To overcome this problem, recycling is a viable alternative in getting back some of the plastic waste for different applications for different household product, packaging, construction materials etc. Plastic recycling is the process of recovering scrap or waste plastic and reprocessing the material into useful products, sometimes completely different in form from their original state.[9-11] Plastics that can be readily recycled are thermoplastics and can be repeatedly reformed into new products and are the focus of this technical note.

In the country, some Small and Medium Enterprise's (SME's) are engaged in plastic waste recycling for different applications including plastic water containers, plastic cloth washing basins, plastic bags, detergent bottles etc.[12-14.] However, this study focused on developing leather cutting board made from plastic waste and reinforcing materials in order to substitute for imported cutting boards.

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Manuscript received December 21, 2020, accepted for publication May 6, 2021.

Plastic and plastic board

Plastic boards are usually called PE (polyethylene) cutting boards, or HDPE (high-density polyethylene plastic), the material of which these boards are made.[15] Polyethylene (PE) is the most widely-consumed thermoplastic in the world by volume. Polyethylene is classified by its density and branching. There are two main types of PE; High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE).[16]

High Density Polyethylene (HDPE)

This plastic consists of essentially linear molecules of repeating ethylene units. Its density is 0.94-0.965 g/cc. It has a milky, translucent appearance and is usually used to make bottles for milk, drinking water, laundry products, cleaning and other household chemicals.[17] HDPE Thermoplastic materials become liquid between 120°-180°C. During plastic converting processes, some kinds of additives are mixed with plastics to impart properties. Fillers are relatively cheap, solid inert substances that are added in fairly high percentages to plastics, paints, and paper to adjust volume, weight, costs, or technical performance.[18] They are typically used to lower the cost of plastics. They also significantly increase rigidity and stiffness but decrease both impact and tensile strength. Filler concentration is commonly in the range of 10 to 50% by weight.[19] Calcium carbonate is the dominant filler, accounting for about 70% of the world filler consumption in plastics. Calcium carbonate is white, odorless and tasteless powder with a density of 2.71 g/cc and a Mohs scale of 3. It is used for polyvinyl chloride, polyethylene, polypropylene, silicone and polyacrylate.[18] HDPE is one of a type of plastics that can be molded again and again.

Plastic additives

Organic or inorganic compound additives can be blended into most plastics. The average content of additives is a few percent. Many of the controversies associated with plastics actually relate to the additives, some particularly toxic. Typical additives includes stabilizers, fillers, plasticizers, colorants etc.[20-22]

Materials and methods

Materials

HDPE plastic waste, Calcium Carbonate, glass fiber, metal cooking pots, clay cooking pots, metal mold etc. were used for cutting board development. The authors used three metal molds having a dimension of 43cm × 27cm × 2cm, 35cm × 22cm × 1cm, 34 × 24 × 1.5cm (Length × Width × Height).

Methods of data collection

Primary and secondary data gathering techniques were applied simultaneously. Primary data were collected through interviews and field observations. As well, secondary data was gathered by reviewing different literature. The authors selected Bahir Dar city purposively for amount of plastic waste estimated, due to the rapid population growth and increasing amount of plastic waste generation in the city.

Research design and method

As there is no international consensus on the method of solid waste characterization, there is a variety of methods used to assess household waste composition. Some methods are standardized, while others are used in one or a few studies. Many methods have been developed to keep track of the waste production within a specific country. While most methods physically sample the waste produced within a certain timeframe from a certain portion of the whole assessed population, some methods are based on product flow and Life Cycle Assessments to predict and estimate the waste that will be produced.[23]

Based on Dahlén, Lisa & Lagerkvist,[23] material flow analyses is made using physical methods, which mainly include sampling of collected HDPE plastic waste and sold plastic through trucks by plastic shredding SME's found in Bahir Dar city. Mbande[24] suggested that interviews are also an appropriate approach for collecting estimated waste quantities in developing countries where municipal solid waste is not collected to the same degree. Thus, plastic shredding and recycling SME's owners found in Bahir Dar city were interviewed to estimate the amount of waste HDPE plastic in the city.

Method of HDPE plastic waste amount estimation

Bahir Dar is the former capital of Gojjam province and the current capital of the Amhara National Regional State (ANRS) located in north-western Ethiopia. The city has more than 324,000 inhabitants including rural areas in 2015. Bahir Dar city is one of the big cities in Ethiopia that generate about 50.19 tons of municipal biomass solid waste per day. The city has prepared a report on solid waste characterization and quantification. As indicated in Table I, the report confirmed that the composition & generation rate of the waste in tonne per day.[25, 26]

The total wastes generated from all sectors were 98.8 tonnes per day and it shows that the residential areas are the primary generators of wastes.[26, 27] Thus, utilizing the municipal solid waste as potential raw materials for recycling and reuses are the most promising methods to overcome the current challenges. Utilization of plastic wastes for different product has environmental and ecological advantages.

Cutting board can be made from different materials including plastics (PVC, HDPE, etc.), wood, glass, etc. The authors mainly

Table I

Composition & generation rate of the waste at Bahir Dar city

S/n	Material	tonne/day
1	Commercial	24.2
2	Institutional	17
3	Street sweeping	3.56

Figure 1. Shredded HDPE plastic waste

focused to develop a cutting board from HDPE code-2 plastic waste, because recycling HDPE is considered eco-friendly, it is the easiest plastic to recycle and commonly used to produce commercial products such as food and water related containers. Consequently, shredded HDPE waste plastic is easily available in Bahir Dar city. Based on Abdalqader[28] and Saidan,[29] the authors used manual assessment method of plastic waste estimation, in order to predict and estimate the minimum amount of HDPE plastic waste generated in Bahir Dar city.

The assessment mainly based on investigating HDPE-code 2 type of plastic waste, when flowing out from HDPE waste plastic shredding SME's at Bahir Dar city. For HDPE-Code 2 plastic, interviews were conducted with shredding SME's owners living in Bahir Dar city. The selected SME's owners are engaged in shredding HDPE and PP waste plastics and sell it for plastic recyclers from Bahir Dar nearby cities and Addis Ababa. Most of waste plastic shredding SME owners in Bahir Dar city were interviewed. Also, when one plastic waste shredding SME owner was found, they could often name others and gave contact information. Accordingly, laborers working in plastic shredding small and medium enterprises were asked some questions related to plastic waste shredding.

Based on interviews and observations, currently in Bahir Dar city there are more than 13 plastic waste collectors and 10 plastic waste shredding SME's. During the field work, 10 plastic waste shredding SME's owners were interviewed about prices and amounts of the HDPE shredded plastic they produce and sell for their customers.

The plastic collectors gather plastic waste from different sources, such as household, private sales, government organizations and landfill. Most of the shredders are engaged in shredding of HDPE code-2 plastic waste including yellow edible oil bottles, green water containers (jerrycans), milk bottles, detergent bottles, etc. The shredders also produce (chopping) PP (polypropylene) plastic items including plastic cloth washing basins, plastic bags etc, but the source and amounts this type of plastic (PP) waste was not assessed.

The shredders are purchasing HDPE type (code -2) plastic waste of 1Kg with $0.51 from plastic collectors in the area. The waste plastic material will be sorted and washed. Then, the plastic will be shredded or chopped by plastic shredding machine into small pieces. The shredded plastic is then sold to waste plastic recycling SME's in Bahir Dar, nearby city and Addis Ababa. Currently, the plastic shredding SME's are selling shredded plastic between $0.77/Kg-$1.02/Kg. Based on observations and interviews made with waste plastic shredding SME owners in Bahir Dar city. The shredding SME produce around 60 Kg – 100 Kg of shredded HDPE plastics per day. Most of the shredders do not have recorded documents about the quantity of shredded plastic they produced and sell, the estimated amount was derived during interviews with shredding SME owners. By basing on a shredded HDPE waste estimate, it can be used as a benchmark (point of reference) to what is the probable minimum available HDPE shredded plastic in the area.

As shown in Figure 1, one shredding SME will produce an average of 480 Kg shredded plastic (i.e. 80Kg/day * 6days/week) and 10 shredding SME will produce an average of 4800Kg of plastic waste/week and 1,228,800 Kg/Year (i.e. 240 working days per day). These estimates will be used in this analysis and do not indicate the total amount of HDPE plastic waste generated in Bahir Dar city, because different nearby cities plastic collectors and shredders are purchasing waste plastic bottles. The estimation is used to indicate the minimum amount and availability (feasibility) of HDPE plastic waste in the city.

Currently, the shredders are selling shredded plastic between $0.77/Kg-$1.02/Kg (i.e. an average of $0.89/Kg) to recycling companies and SME's. Most of the shredders were loading (selling) the shredded plastic in ISUZU FSR truck minimum once per week for plastic recycling customers coming from Bahir Dar and nearby city. The authors bought yellow color and green color HDPE-Code-2 shredded plastic waste with a cost of $0.77/Kg from "Adane waste plastic shredding SME (company)" which is located around Kebele 12 in Bahir Dar city.

Figure 2. Visiting Amhara Pipe Factory (Bahir Dar city, 2020)

Cutting board development procedures

Physical properties of original plastic products, additives used in the plastic and the washing regime used in recycling are all important to the expected behavior and applicability of the products.[10] As shown in Figure 2, the authors visited Amhara pipe factory found in Bahir Dar city and they made overview of the company's plastic production unit. The authors understand how plastic melting takes place and the process of plastic molding. Currently, the factory is using different input materials including LPDE, HDPE, PVC, $CaCO_3$, Master batch (*plastics coloring material)* and different additives for production of PVC Pipes, HDPE Pipes, screen and casing pipes, flexible hose, geo-membrane sheet, green house film.

The authors initially bought shredded HDPE waste plastic and carried out washing the plastic pellets with water and soap in order to remove impurities such as oils. The plastic pellets mixed with $CaCO_3$ (filler) and glass fiber. The mixture melted and poured into cutting board mold and pressure applied before it is left to stand for cooling.

Cutting board development

As shown in the Table II, the authors used shredded HDPE waste, glass fiber in order to increase the strength of cutting board and $CaCO_3$ as a filler.[30]

Cutting Board development trial 1:

In order to develop a cutting board, melting of the shredded and pouring the melt in to a metal mold is necessary. The authors mixed 2Kg of Shredded HDPE plastic waste, 100g of glass fiber and 200g of $CaCO_3$ and melted the mixture using 5L metal cooking pot for 3.5 hours using a household electrical stove having120°C heating power as shown in Figure 3.

During melting, the cooking pot was closed in order to increase the temperature and protect the melt from contamination. Then, the melt was poured into a mold, but the molded board showed irregularity in surface texture and dimensions due high melt viscosity (thick melt).

Table II

Material used for cutting board development

S/n	Material	Weight	Remark
1	Shredded HDPE plastic waste	2Kg	
2	Glass fiber	100g	5% weight of Shredded HDPE
3	$CaCO_3$ (Filler)	200g	10% weight of Shredded HDPE
	Total weight	2.3 Kg	

Figure 3. Melting Shredded HDPE waste plastic using metal pot by electrical stove and molded cutting board

Figure 4. Melting Shredded HDPE waste plastic using metal pot by wood fire and plastic, and molded cutting board

Here the authors understand that the viscosity of the melt should be less (thinner) and the electrical stove used is not fast to melt the mixture, because the stove that used for melting has 120˚C heating power. HDPE has melting temperature between 120°C to 180˚C.[31] Based on this, the authors decided to use another melting method or heat source, which is wood fire.

Cutting board development trial 2:
The authors mixed 2Kg of Shredded HDPE, 100g of glass fiber and 200g of $CaCO_3$ and melted the mixture using 5L metal cooking pot using wood fire with manual blowing for 2 hours as shown in Figure 4. Again, the melt was poured into a mold and the mold cooled.

The authors observed that, the second molding trial was better than the first molding trial, but the mold texture requires improvement and the melting time needs to be reduced. The authors decided to use charcoal fire with blowing fan to increase the melting temperature and to reduce melting time.

Cutting board development trial 3:
The authors mixed 2Kg of shredded HDPE, 100g of glass fiber and 200g of $CaCO_3$ and melted the mixture using 5L metal cooking pot using charcoal stove with fire blowing fan for 30 minutes as shown in Figure 5. The viscosity of the melt decreased (thinner) from the first and second melting trials (visual identification). Then, the melt was poured into a mold and cooled.

The molded board showed better surface texture than the second molding trial, but as shown in Figure 5, the metal cooking pot failed (pierced) in the bottom due high amount of heat by charcoal stove with fire blowing fan. The authors understood that the charcoal stove with fire blowing fan has high heat and metal cooking pot has less

Figure 5. Melting Shredded HDPE waste plastic using metal pot by charcoal stove with fire blowing fan, molded cutting board and failed pot

Figure 6. Melting Shredded HDPE waste plastic using clay pot by charcoal stove with fire blowing fan, molded cutting board

resistance for the heat. Then the authors decided to use clay cooking pot for melting.

Cutting board development trial 4:

The authors mixed 2Kg of Shredded HDPE, 100g of glass fiber and 200g of $CaCO_3$ and melted the mixture using 5L clay cooking pot using charcoal stove with fire blowing fan for 30 minutes as shown in Figure 6. The viscosity of the melt decreased (thin) from the first melting trial (visual identification). Then, the melt was poured into a mold and cooled. The molded board showed better surface texture than the first, second and third molding trial. The clay pot shows good resistance for charcoal heat with blowing fan and better surface molded board was made.

Results and discussion

Amount of input mold material and output developed mold weight analysis

In order to get the difference between shredded plastic input material and molded board weight difference, the authors measured the molds weight and got 1.95 Kg, 1.84Kg, 1.8Kg and 1.75 Kg for mold trial 1, 2, 3, and 4 respectively. The average mold weight was1.83 Kg.

The above Table III indicate that, during molding an average of 0.47 Kg material input weight loss is observed and the average weight loss is 20.43%. This indicate that, from 1Kg of molding input material, around 200 gram will be lost during molding process.

Table III

Amount of input mold material and output mold weight

S/n	Input Material	Input material weight	Output mold weight	Percentage of weight loss
1	Shredded HDPE plastic	2Kg	1.83Kg	20.43%
2	Glass fiber	100g		
3	$CaCO_3$ (Filler)	200g		
	Total weight	2.3 Kg		

Table IV

Developed cutting board cost analysis

S/n	Material (Task)	Cost/Kg ($)	Input material cost ($)	Remark
1	Shredded HDPE plastic (2Kg)	$0.77/Kg	$1.53	-
2	Washing	-	$0.128	-
3	Melting cost	-	$0.77	-
4	Glass fiber	$5.12/Kg	$1.53	100g Glass fiber used
5	$CaCO_3$ (Filler)	$1.53/Kg	$0.256	200g $CaCO_3$ used (10% weight of HDPE)
6	Metal mold	-	$0.512	
	Total cost		$4.726	Developed cutting material weight was 2.3 Kg and output mold was 1.83Kg (20% weight loss)

Figure 7. Cutting board sample preparation

Cost analysis

Cost comparison of cutting board in the market with the developed cutting board was made. The authors bought a white plastic cutting board for $16.60, the board having a dimension of 60 × 40 × 1.5 cm (L × W × H). The board weight was 3Kg. In order to get the cost of the board per Kg (value to weight ratio), the cost of the board divided by the weight of board and yielded$5.53/Kg.

As shown in the Table IV, the total cost for input cutting board material (2.3Kg) is $4.73, but the average output molded cutting board weight is 1.83Kg, the weight reduced due to evaporation during melting. In order to get the cost of the board per Kg (value to weight ratio), the cost of the board was divided by the weight of board yielding $2.58/Kg (i.e. $4.73/1.83Kg).

The cost for cutting boards in the market is $5.53/Kg and the cost to produce new cutting board is $2.58/Kg. This indicate that, the new cutting board cost is very cheap compared to cutting board in the market. However, the market cutting board has better quality than the new cutting board.

The financial analysis has only been used to consider the feasibility of recycling HDPE plastic waste for cutting board development. The research will initiate the plastic making industries to produce cutting board from plastic waste material rather than using virgin HDPE plastic.

Cutting board physical properties testing

The developed cutting board was tested for both compression test and hardness test. Cutting board which is available in the market used as a standard for testing and as shown in Figure 7, a testing sample was prepared.

Compression test for cutting board purchased from market (standard)

As shown in Figure 8, compression test for cutting board purchased from market was performed using Universal compression testing machine found at Mechanical and Industrial Engineering Faculty, Bahir Dar University.

Figure 8. Compression test for standard cutting board (market)

Compression test result for cutting board purchased from market:

Market cutting Board Material: Rigid HDPE - Initial measurement Length: 14 cm; Specimen diameter: 80 mm

Figure 9 shows the compression test result of standard cutting board (market). In the force elongation, when 43.12 kN applied the sample deform about 0.80 mm and when 43.69 kN (highest load) applied the sample deform about 0.83 mm. Based on in the range of 43.12-43.69 kN, the sample deforms in the range of 0.80-0.83 mm.

Compression test for developed cutting board

Compression test for the developed cutting board was performed in order to compare the result with purchased cutting board compression test result. As shown in Figure 10, compression test for developed board was performed using Universal compression testing machine found at Faculty of Mechanical and Industrial Engineering, Bahir Dar University.

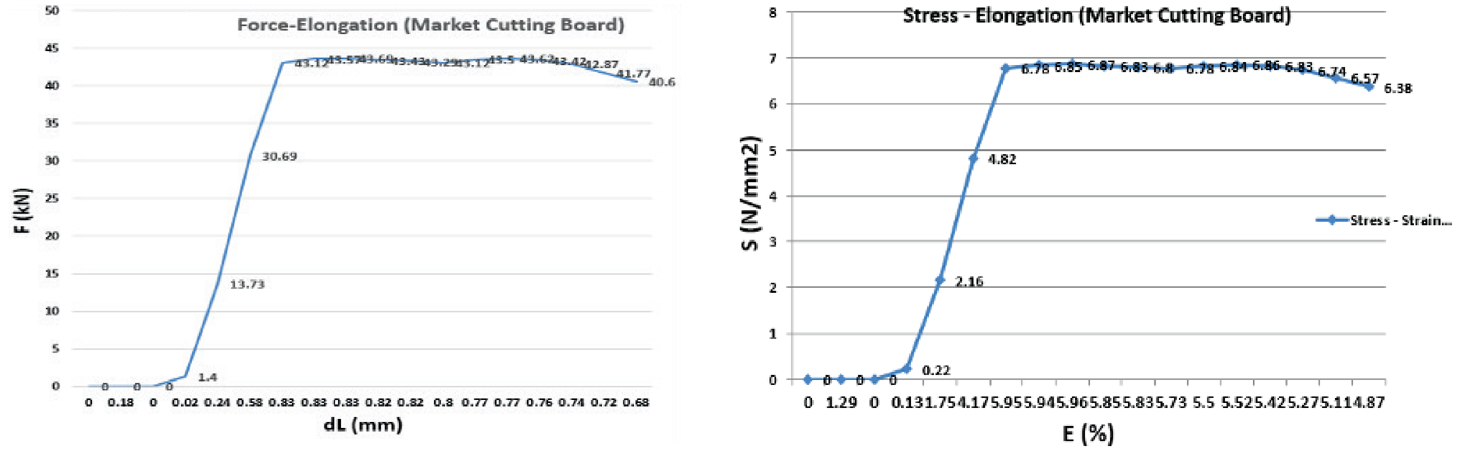

Figure 9. Compression test result for standard cutting board (market)

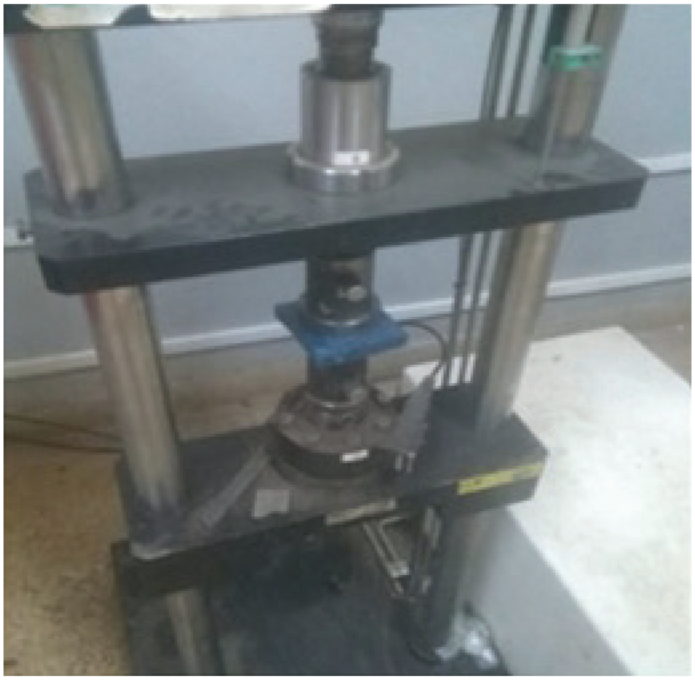

Figure 10. Developed cutting board compression test.

Compression test result for developed cutting board:
Developed cutting Board Material: HDPE; Initial measurement Length: 14 cm; Specimen diameter: 80 mm.

Figure 11 shows the compression test result of developed cutting board. In the force-elongation test result, when 43.04 F (kN) applied the sample deform about 0.85 dL (mm) and when 43.76 F (kN) (highest load) applied the sample deform about 0.87 dL (mm). Based on, in the range of 43.04-43.76 F (kN), the new cutting board sample deform in the range of 0.85-0.87 dL(mm). This indicate that, the developed cutting board has related compression strength with the standard cutting board (market) sample which is 0.80-0.83 dL (mm) in the range of 43.12-43.69 F (kN).

Hardness Test

Rockwell hardness testing machine was used for Hardness test[32] and based on Rockwell hardness scale, scale L No. 10, 60Kg load and ¼" ball indenter is used for both developed and market cutting board hardness testing. As shown in Figure 12, Hardness test was performed using Rockwell hardness tester found at Faculty of Mechanical and Industrial Engineering, Bahir Dar University. Each test trail done for 30 seconds.

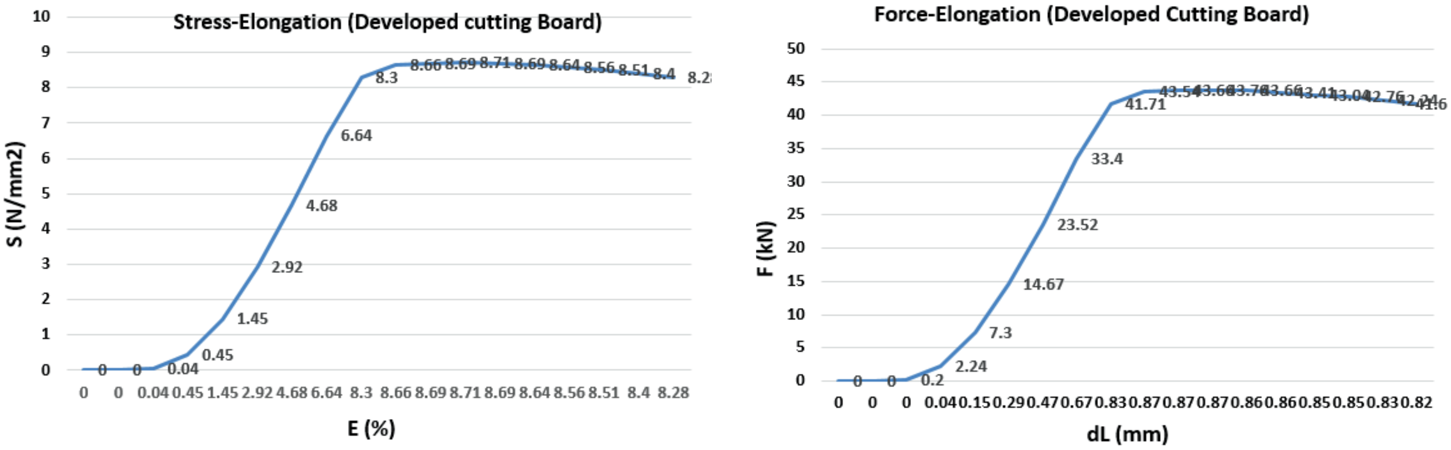

Figure 11. Developed cutting board compression Test

Table V

Hardness Test for standard cutting board (market) and developed cutting board

Test trial	Standard cutting board (market) hardness Test result (HRB)	Developed cutting board hardness Test result (HRB)
Test trial 1	47	80
Test trial 2	42	75
Test trial 3	53	68
Test trial 4	47	55
Test trial 5	55	60
Average Test result	48.8	55.6

Table V shows, the market cutting board average Hardness Test result is 48.8 and the developed cutting board average hardness test result is 55.6. This indicate that, the developed cutting board hardness test result approached to the market cutting board hardness test result. However, the market cutting board has better has better resistance to indentation. Based on these results, it is required to increase the compactness of the developed cutting board.

Conclusion

It is known that plastic waste is the main reason for pollution in the world, because plastic material takes long time to decompose. Plastic recycling is a good option to protect the environment. Thus, the authors developed a cutting board from HDPE plastic waste. The developed cutting board showed relatively lower hardness and compression test result when compared with HDPE cutting board in the market. Developing cutting board from HDPE plastic waste is cheaper and recycling has a good impact in the environment. However, the developed cutting board showed some pores in the surface which reduced the quality of the board. The authors assumed that the reason for the pores in the board will be due to moisture absorbance during manual melting and it is difficult to regulate the amount of charcoal heat (temperature) during manual melting.

The plastic flow analyses indicated the minimum amount of shredded HDPE plastic waste in Bahir Dar city. The minimum HDPE shredded plastic waste amount produced in the city was estimated to be around 1,228,800 Kg/year. Most of the shredded plastic sold to recycling SME's is found in Addis Ababa. This indicate that, Bahir Dar has a good source for HDPE shredded plastic waste and a good opportunity for plastic recyclers engaged in the area and also opportunities for new investors for plastic recycling in the area.

Recommendation

Manual melting at home is a tedious task and it not feasible for mass recycling/production. During Amhara plastic factory visit by authors, melting HDPE plastic by machine has no bad smell. However, during manual HDPE plastic waste melting by authors,

Figure 12. Market cutting board and developed cutting board hardness test

the melt had a bad smell and it is not good for human health. The authors recommend that, melting HDPE plastic waste using plastic melting machine is preferable.

Acknowledgements:

The authors wish to express their sincere thanks to Ethiopian Institute of Textile and Fashion Technology, Bahir Dar University for the support in successful completion of the work.

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Lifelines

Fernando Lado has a Bachelor's degree in Chemistry, Universidad de la República, Uruguay in 1992 and further studies in Biochemistry in 2000. Since 1992 is working in the leather industry, starting in Curtiembre Branaa in Montevideo which later became in Zenda Leather and finally as part of JBS group. Started as leather technician in Wet-End with several works and developments in this field, then he assumed as Project Manager the development of chrome-free leather in 1998 for automotive OEM. Since 2009 to 2016 was in charge for global operations in Zenda and up to present is responsible manager for finishing and cutting in Uruguay, Mexico and Europe.

Ricardo Tournier earned a degree in Chemical Engineering from Universidad de la República, Montevideo, Uruguay in 1968 and a MSc in Chemical Engineering from University of South Carolina, USA in 1971. In 1974 he attended a Dyestuff Course at the Chemistry Department of Turin University and a Practical Course on hide tanning at Instituto "Baldracco," Turin, Italy. Started in the leather industry in 1971 at Lanza Tannery, Uruguay, for 9 years. Later he worked for 20 years as Technical Manager at Paycueros Tannery, a member of SADESA Group. From 2000 to 2012 he was Technical Assistant to the General Manager at Zenda Leather, Uruguay. His works on leather problems and defects have been published in international and regional journals. He is currently working as a freelance consultant.

Venkatasubramanian Sivakumar, see *JALCA* **113**, 72, 2018.

Wenjun Long received his Bachelor's degree in Light Chemical Engineering at College of Biomass Science and Engineering, Sichuan University in 2020. Now he is undertaking his Doctor's degree research at Sichuan University. His research focuses on the relationship between moisture and properties of leather.

Liangqiong Peng, see JALCA 115, 87, 2020.

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Wenhua Zhang, see JALCA 100, 432, 2005.

Fitsum Etefa Ahmed has been a Senior Lecturer at the Ethiopian Institute of Textile and Fashion Technology (EiTEX) at Bahir Dar University since 2015. He graduated from Bahir Dar University-EiTEX in Ethiopia with a Bachelor's degree in Textile Engineering in 2015 and a Master's degree in Leather Product Design and Engineering in 2018. He served as the Head of Leather Engineering Program at Bahir Dar University, EiTEX, from September 8, 2017 to March 18, 2020 and serving as the Director of the Leather Processing & Product Engineering Research and Innovation Center since March 2020. He has mentored and supervised 16 undergraduate students in data collection and analysis for their BSc Thesis, as well as the preparation and presentation of research findings, since 2015. Leather product design, supply chains, waste management and composite materials are among his research interests.

Rotick K Gideon has been a Senior Lecturer and Researcher at Bahir Dar University's, Ethiopian Institute of Textile and Fashion Technology (EiTEX) since 2015. He received both his Master's Degree in Textile Science and Engineering in 2012, and PhD in Textile Engineering, Composite Materials in 2015, form Donghua University, Shanghai, China. He has over 17 articles published in reputable journals, and he has supervised more than 13 postgraduate students. Technical Textiles, natural fibers, composite materials, mechanical behaviour of materials are among his research interests.

Obituary

Bruce A. Rittel, 83, of New Bedford, MA passed away, Tuesday, September 21, 2021, at St. Luke's Hospital. He was born a son of the late William and Rose (Yaskinski) Rittel and had lived in New Bedford for the last two years. Prior to that he had spent most of his life in Taunton. Mr. Rittel was a Systems Analyst for AT&T. He also owned and operated his own Tanning/ Taxidermy business along with a tannery consulting and supply business. He was a member of The American Leather Chemists Association from 1991 to 2011. Bruce was a Navy veteran during the Vietnam War. He was a member of the American Legion and Elks. Survivors include a daughter Linda Cruz of New Bedford, a sister Joyce Carlin, a granddaughter Caroline Cruz, several nieces, and nephews. He was the father of the late Bruce A. Rittel, Jr. and brother of the late Jeffrey Rittel.

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