Successful use of Remnant: Attractive Reversible Grain Pattern Leather from Bovine Ear

by

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Abstract

At the present time, complete utilization of bovine parts will lead to the development of exotic leathers with attractive grain patterns. In this work an attempt has been made to prepare exotic leathers from the bovine ear, which is a solid waste from the slaughterhouse. Ears are the peculiar part of bovine, where a flexible cartilage (Type II collagen) is covered by the skin matrix (Type I collagen). The process for the preparation of the leathers from bovine ears has been optimized. The physical and morphological characteristics of the leathers have been carried out. The air permeability analysis revealed that the air permeability decreased with increase in the cartilage thickness. The processed ear possessed high resistance towards stitch tear and abrasion. The attractive reversible grain pattern along with genuine leather property provides an opportunity to utilize this material as a new source of raw material for leather making.

Introduction

Every year several million tons of both solid and liquid wastes are generated from the slaughter houses.[1] In recent years, there has been growing concern with regard to the disposal and proper utilization of wastes generated from the slaughtering of animals in abattoirs.[2] Generally, the generated solid wastes have been collected and dumped or disposed in an unhygienic manner. Continuation of such practices leads to serious environmental problems. It has been reported that slaughterhouse wastes constitute the inedible parts of animals. Inedible animal tissues (Ear, tail, ligaments, tendons, blood vessels, feathers, bone) can comprise up to 45% or more of the slaughtered animal.[3] The ear is predominantly made up of skin/cartilage.

The bovine ear is generally divided into the external, middle and inner ear. The external ear consists of the pinna and external ear canal. Both are composed of elastic cartilage, which is covered by skin. The major portion, the articular cartilage is a continuous thin sheet that forms the flat pinnal surface and rolls into a thicker tube or funnel proximally to form the outer portion of the external ear canal, leading into the middle ear. The type of collagen distributed over the surface and inner section is a combination of type I and type II. The cross sectional view of the bovine ear is shown in Figure 1. Normally, the distribution of type II collagen is considered to be the characteristics of cartilaginous tissues.[4] The presence of both the types of collagen will lead to its acceptance as a new raw material for leather making.

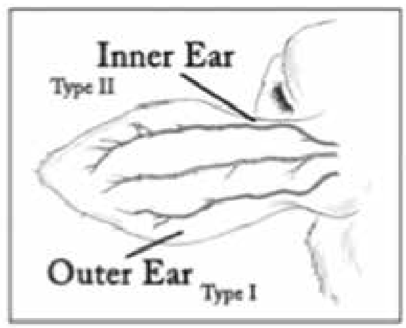

Figure 1. The cross-sectional view of bovine ear.

Globally, several attempts are being made to identify alternative sources for skin for leather processing, in an effort to reduce the dependence on less available commercial source for leather making. There are reports available on the utilization of skins/hides from different sources such as camel, pig, crocodile, alligator, stingray, ostrich, sea snake, moose, toad / frog fish, chicken / hen for obtaining exotic or high quality leathers.[5-7]

Utilization of bovine ear for leather making is of great importance. In the present work, for the first time, a novel attempt has been made to produce usable attractive leather from the bovine ear, waste from the slaughterhouse. The morphology, surface topography like the orientation of grain, surface smoothness of the processed crust leather has been studied thoroughly by using scanning electron microscopy technique (SEM). Air permeability and stitch resistance property of the leather also exhibits good results. From the results it is clearly divulged that bovine ear can act as an alternative source of raw material for producing flexible leathers with attractive reversible or dual grain pattern.

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Materials and Methods

Thirty fresh bovine ears having an average weight of 100 g were procured from slaughterhouse located at Perambur, Chennai, and Tamilnadu, India. The ears were washed with plain water and subjected to drum liming for hair removal. After the unhairing process, the ears were subjected to conventional chrome tanning and post-tanning process. The pre-tanning/tanning and post-tanning process recipe adopted for the conversion of ears into crust leather is given in Table I(a) and Table I(b) respectively.

Experimental Techniques

Scanning electron microscopy technique (SEM) was employed to analyze the surface pattern and cross-sectional view of ear crust at different area. In this study the Phenom pro desktop SEM was used with an acceleration voltage of 5 kV. Air permeability of the ear crust leathers at different regions was measured by using PMI capillary flow porometer. The double hole stitch tear strength of leather was analyzed by the test method of ASTM D4705:2005. The Martindale (abrasion) resistance of the leather was measured by SATRA TM 31:2003.

Result and Discussion

The preparation of leather from different sources like goat, sheep, cow, and buffalo are commercially practiced by the leather industry. Reduction in the supply of resources and increasing demand for the leather-based products makes the technologists to think towards the use of different sources from the slaughter house. In the present work, bovine ear has been used as a newer raw material for leather making. The bovine ear leather displayed

Table I (a)

Pre-tanning/tanning recipe adopted for bovine ear processing. Raw Materials: Fresh bovine ear.

Process	Chemical Name	% Offered	Duration	Remarks
Pre-tanning Washing	Water	200	15 min	
Liming	Water Lime Sodium sulfide	300 8 2	Run 10 min for every 1 hr time interval up to 8 hr	Leave overnight. Next day run for 1 hr
Washing	Water	200	15 min	
Deliming	Water Ammonium chloride	100 0.5	-Run 30 min	Drain
	Ammonium chloride	1	-Run 60 min	
	Organic acid based deliming agent Water	0.75 10	- 2 x 10 min + 60 min	Check deliming completion by using phenolphthalein indicator
Washing	Water	200	15 min	Drain
Pickling	Water Salt Formic acid + Water	100 10 0.5 + 10	(2 x 5 min)+ 30 min	
	Hydrochloric acid + Sulfuric acid + water	0.3 + 0.5 + 10	(4 x 15 min) + 90 min	Cross-section pH: 2.8-3.0
	Acid/salt stable fatliquor + Water	3 + 20	30 min	Leave Over night
Tanning	BCS + Sodium formate Chrome stable fatliquor	8 + 1 2	(2 x 30 min) + 90 min 60 min	
Basification	Soidum formate Magnesium oxide	0.5 + 0.5 + 10	60 min	
	Sodium bicarbonate + Water	0.7 + 10	(4 x 15 min) + 90 min	Cross-section pH: 3.8-4.0 / Drain

excellent reversible grain pattern, which may act as best replacement for available trendy exotic leathers. This way of an attempt to utilize the slaughterhouse waste as the source is really interesting in order to augment the available sources.

Sedulous Processing of Bovine Ear Skins

The grain pattern and hair distribution of the bovine ear skins are similar to that of the bovine skin. Hence, the processing of bovine ear does not differ much. The presence of type II collagen (cartilage) in between the ear skins lead to slower penetration of chemicals. However, this can be overcome by sedulous process controls. Though the surface of the ear is covered with skin matrix, the internal part is made up of flexible cartilage. The fiber packing arrangement of cartilage is more cemented and less porous than skin matrix. Therefore, the selection of leather making auxiliaries plays an important role in ear processing. The fresh raw ears have been subjected to conventional unhairing process. But, the unhaired ears have not been subjected to reliming process because the development of osmotic pressure in the skin matrix would decrease the natural adherence between skin and cartilage. Due to the high cementing nature of internal cartilage, the selected leather making auxiliaries should have high penetrating power. Therefore, the conventional ammonium based deliming process has been replaced with the combination of organic acid and ammonium chloride based deliming system. In case of pickling the combination of both HCl and H_2SO_4 have been used. In addition to that, the acid/salt stable fatliquor and chrome stable fatliquor have been employed in pickling and tanning processes, respectively. During post-tanning the dye penetration and fatliquor exhaustion have been checked and it showed that the dye is distributed all over the surface as well as in the inner portions. But, the presence of flexible cartilage needed more fatliquors, so as to soften the final leather. In addition to all the steps of ear processing, time requirement is higher than conventional skin processing. It may be due to the presence of cemented cartilage. Photographic image of the bovine ear at different stages of leather processing was shown in the Figure 2.

The finished bovine ear leather displayed a reversible grain pattern, which makes the leather more unique than others. Reversible grain pattern is really meant for presence of similar grain pattern on both side of the skin. In general, the grain and flesh side of the body skin is not uniform in pattern, but in the case of remnant it showed the similar grain pattern on both side. The texture and patterns are similar with presence of scaly grain pattern. After finishing, more than 20 samples have been selected and the average area of the same has been calculated. The average area of finished ear leather lies between 70-200 cm^2. The group of finished ear leather is shown in Figure 3, which may be greatly

Table I (b)

Post-tanning recipe adopted for bovine ear processing. Raw Materials: Chrome tanned bovine ear.

Process	Chemical Name	% Offered	Duration	Remarks
Neutralization	Water Neutralizing syntan + Sodium bicarbonate + water	100 1 + 0.5 + 10	(3x10 min) + 60 min	Cross-section pH: 5.2-5.5 Drain/Wash/Drain
Pre-fatliquoring	Water Synthetic fatliquor + Vegetable fatliquor	100 3 +1	30 min	
Retanning	Acrylic syntan	3	- Run 20 min	
	Low M.W phenolic syntan + Melamine based syntan	3 + 3	-Run 60 min	
Dyeing	Dye + water	2 + 10	-Run 90 min	Check penetration
	Fatliquors Synthetic + Sulphochlorinated fish oil + Semi synthetic + Water	6+4+2+50	- 3 x 15 min + 120	
Washing	Water	200	15 min	Drain
Fixing	Water Formic acid	10 3	(3 x 5 min) + 60 min	Check exhaustion /Drain/ Next day, slickering/ Drying/vibrator staking

suitable for preparation of different kinds of leather articles such as handbag edges, leather pouches, Baby shoes, Watch strap, Phone Back cases, Pen, Cash cover, Coin wallet, etc.

Scanning Electron Microscopic Analysis

Scanning electron microscopic technique has been employed to characterize the surface and also to study the internal morphology of the ear. The sampling position for SEM analysis of ear is shown in Figure 4.

The surface topography and cross sectional image of the ear at different magnifications are shown in the Figure 5 and 6, respectively. The surface topography of the crust ear leather showed an uneven distribution of hair pores as well as scaly grain pattern over the surface. The size of the grain pattern is considerably diverse with the grain pattern of body skin. The variation in the occurrence of short scaly fibers on the surface greatly tunes the grain pattern as well as the aesthetic look of leather made from the bovine ear. To further analysis the inner structural features, the cross section of the ear leather is analyzed. The general morphology of the leather made from the bovine ear is similar to the leather from body skin. The whole view of the leather looks varied in the fiber orientation among the three different regions like upper, middle and lower. The surface grain patterns of all the three regions are extremely uneven. In detail, the orientations of the hair and grain pattern of the upper portion are similar to conventional body skin. Qualitatively, the smaller grain pattern is observed to be more abundant in the middle portion than in the other two regions. The presence of tiny scale pattern in the lower region of the bovine ear gives a unique appearance. In addition to that cartilage to fiber ratio is varying at each portion of upper, middle and lower, which can easily be visualized through the cross-sectional image.

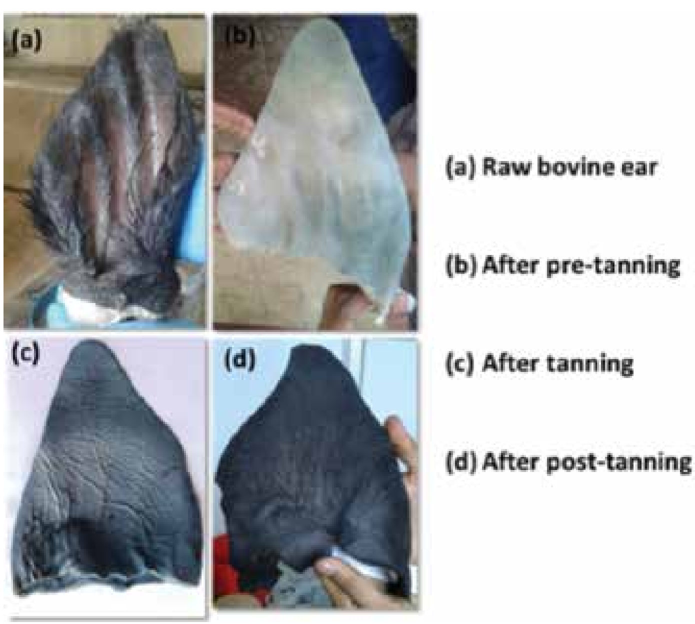

Figure 2. The photographic images of ear from different unit processes.

The serial magnification from cross section showed variation in cartilage to skin ratio. In detail the cross sectional view of ear at upper, middle and lower of magnification 165X showed the variation in length of the cartilage depends on the portion of the ear. Moving from upper to lower portion there is a threefold increase in the cartilage length and it was shown in the Figure 6 (b-b_2). The bridging cartilage between the fibers bundles appears to be denser and longer in lower portion than other portions. The extension of outer skin covers the cartilage completely as a protective layer. The collagen fibrils are oriented in a parallel direction along the cartilage in upper portion, continuing towards the surface to form the outer skin pattern. Collagen fibrils present in the middle and lower are look shorter and clustered towards the centered cartilage. Collectively the fibrils are appeared to be connected by cartilage, which formed the bridged fibrils, all of which orient towards the cartilage.

Figure 3. Group of finished ear leather.

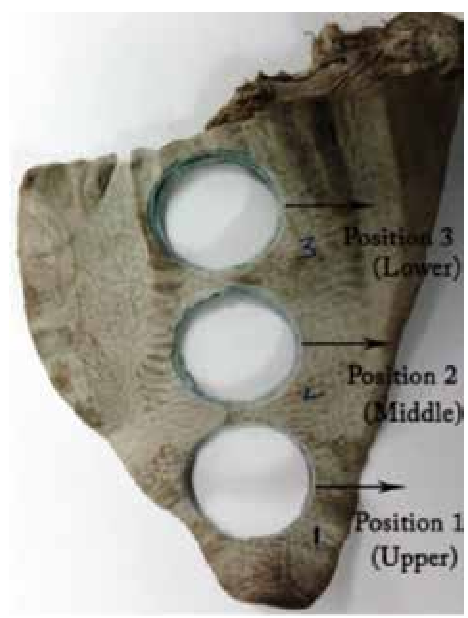

Figure 4. Sampling region.

To further analysis the exact structure of the ear, the extremely variant lower portion was magnified and visualized. The surface image of the ear skin has been viewed for the grain pattern. The presence of scaly patches of grain displayed a pattern, which enhanced the aesthetic look of the leather compared to body skin for various unique applications. A micrograph of the interior structure of the cartilage is shown at higher magnification in Figure 6 (b_2). The surface of the interior cartilage showed such a compact structure with voids. Although the cartilage is slightly stiffer, the presence of porous structure makes this more flexible. The interior microstructure of higher magnification clearly demonstrates the clumsy fiber orientation with a lot of voids. This is helpful for enhancement in the uptake of chemicals. This variation in structural orientation makes the processing more difficult than conventional due to poorly textured nature of the bovine ears. It is noteworthy that the presence of reversible pattern over the surface will increase the leather value.

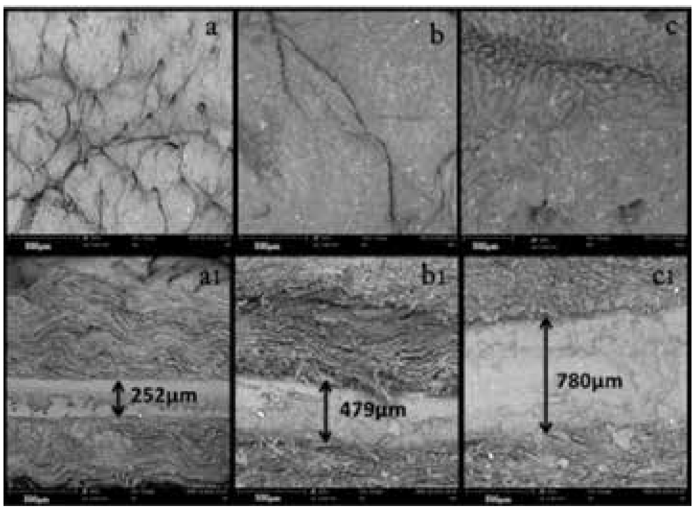

Figure 5. The Scanning Electron Microscopic image showing the details of grain surface of (a) Upper, (b) Middle, (c) Lower portion. Then (a1), (b1), and (c1) are their corresponding cross sectional image.

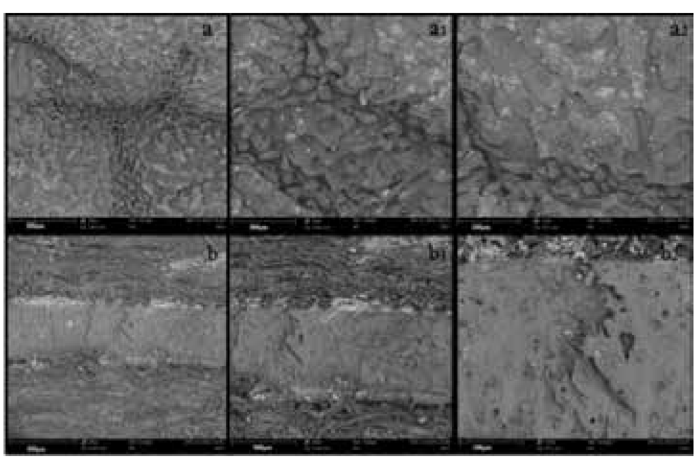

Figure 6. The Scanning Electron Microscopic image showing the details of grain surface of lower portion at magnification of (a) 500µm, (a1) 300µm , (a2) 100µm. Then (b), (b1), and (b2) are their corresponding cross sectional image.

Air Permeability Measurement

The permeability is the one of the most precious physical property of the leather, which may greatly affect the breathability and the comfortable properties provided by the leather. Concerning importance of breathability, the crust ear leathers have been evaluated for porosity and permeability at three different regions. The results are provided in Figure 7. The results reveal that the permeability is greatly influenced by the cartilage present in the center of the skins. Mainly, the presence of cartilage at the center influences the breathable property of the leather made from bovine ear. The presence of larger cartilage at the lower portion showed less permeability than the upper portion containing smaller cartilage. Overall the permeability is greatly influenced by the flexible cartilage present in the center, instead of orientation of the fibers. The percentage variation in air permeability with respect to upper portion has been calculated by using the following equation (1).

Where, A_U: Area under the curve (upper portion), $A_{M/L}$: Area under the curve (Middle/Lower portion)

The result shows that the air permeability of middle portion is 168 and 530% times higher than upper and lower portions, respectively. This may be due to the increase in thickness of the cartilage from upper to lower side. Therefore, the air permeability is directly proportional to the thickness of cartilage.

Stitch Tear Resistance and Abrasion Resistance

Stitch tear resistance and abrasion resistance is also vital when the leather is taken for product making. It is important to analyze the leather resistivity against stress applied during the sewing process. The stitch tear resistivity of the crust leather made from bovine ear has been tested at three regions, which includes lower, middle and upper. The stitch tear strength results shown in the Figure 8 revealed that the resistivity is greatly influenced by the presence of inner cartilage and variation in their thickness. The lower portion displayed the high stitch tear

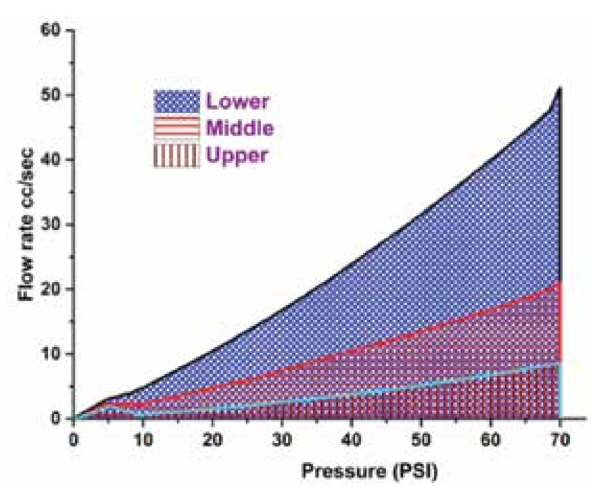

Figure 7. The change in the permeability of the ear crust leather at three different positions

value of 176.87 N/mm (Figure 8(a)), whereas the upper portion showed 132.43 N/mm (Figure 8(b)). SEM data also supports the observation that variation in the cartilage thickness, results in variation of tear resistance property. In another hand, the middle region showed the stitch tear resistance of 149.23 N/mm (Figure 8(c)). As on whole the stitch tear resistance of all the three regions showed comparable and high resistance value, which may be useful to develop various types of leather articles.

Abrasion resistance is an important property of any leather, which determines its durability and wear property. Finished leather with high abrasion resistance can protect itself from wear by friction, ensuring their aesthetic appearance and durability under constant use.[8] In general, the abrasion resistance of the leather is dependent on the hardness of the material to some extent and to the presence of bone like cartilage in between the skins. This cartilage has the ability to dissipate the load during the deforming process. It could be inferred from the results that the bovine ear shows better abrasion resistance both in wet (>12800 cycles) and in dry stage (>25600 cycles). The photograph of the measured abrasion resistance (upper surface) of the bovine ear leather is shown in Figure 9. Thus, it is very clear that the bovine ear leather exhibits balance of all the required properties and an enhanced durability.

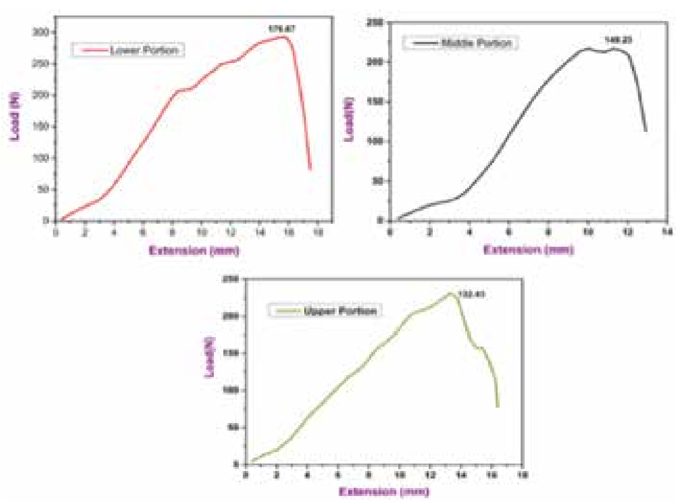

Figure 8. Stitch tear strength property of the crust leather made from bovine ear at a) Lower, b) Middle and c) Upper portion.

Figure 9. The photograph of the abrasion resistance measured upper leather surface.

Conclusion

An attempt has been made to prepare leather from bovine ear skin, which is a waste from the slaughterhouse. Leather with reversible grain pattern has been developed through adopting slightly modified conventional leather making process. Endeavour to utilize bovine ear solid waste in leather processing opens up new avenues for research towards newer alternatives to hides and skins for the manufacture of leather. One of the salient findings of this study is that, it is essential to have a controlled osmotic pressure development inside the skin, in order to avoid the skin/cartilage separation. It is noteworthy that the characterisation like SEM, abrasion resistance of the prepared leather showed reversible grain pattern with good durability. The high stitch tear value registered for crust leather ensures the possible applicability of leather for different end products.

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