

Effect of Syntan to Fatliquor Ratio on Porosity and Mechanical Properties of Wet-blue Leather

by

Murali Sathish, T S Bhuvanewari, Jonnalagadda Raghava Rao and Nishtar Nishad Fathima*
*Chemical Laboratory, Central Leather Research Institute, Council of Scientific & Industrial Research,
 Adyar, Chennai- 600 020, India*

Abstract

Different types of leathers with varied end applications can be made from same raw material. Post-tanning is the operation, which imparts the functional properties required for the final leather. The amount of post-tanning auxiliaries such as syntan (S) and fatliquor (F) used in the leather making, make it possible to convert the same animal skin into various leather types. In this work, the sheep wet-blue has been converted into garment (S:F 1:2) and upper (S:F 2:1) leather by varying the S to F ratio. Here, an attempt has been made to study the influence of S to F ratio on the porosity and mechanical properties of garment/upper leather with respect to sheep wet-blue as a control. Thermoporometry results show that the reduction in pore distribution of garment leather with respect to wet-blue leather is about 62.3% and that of upper leather is 83%. Capillary flow porometry results show that the maximum distribution of through pore throat diameter of upper leather is found to be shifted towards 0.1-0.2 μm from 0.3-0.5 μm (wet-blue leather), whereas in the case of garment leather pores are uniformly distributed in the range of 0.1-0.5 μm . The influence of post-tanning auxiliaries on air permeability reduction is higher for upper leather (83%) than garment leather (41%). Morphological analysis using SEM shows that loosely packed arrangement of wet-blue leather becomes cemented fiber structure in case of upper leather and uniform fine fiber splitting has been observed for garment leather. Tensile strength of wet-blue leather is decreased by about 23% when it is converted into upper leather and that of garment leather is increased to about 16%.

Introduction

Leather manufacturing involves converting putrescible raw hides/skins into non-putrescible leather and it can be used for different end-applications such as shoe, garment, bag etc. In many cases, the pre-tanning and tanning process is almost similar for different kinds of leathers. The tanned leather is used as the starting material for making of different articles like upper and garment leather. For example sheep wet-blue leather can be converted into sheep upper leather (final application for shoe) and the same can be converted

into sheep garment leather (final application for the jacket). However, the properties required for both upper and garment leather are not same. For instance garment leather requires a high degree of softness, drape (cloth like feel) and lightweight, whereas, upper leather requires roundness and less degree of softness.^{1,2}

Post-tanning process imparts the desirable organoleptic properties and color to the wet-blue leather. Syntans and fatliquors are the two important post-tanning auxiliaries tuning the organoleptic properties of wet-blue leather. The ratio of syntan (S) to fatliquors (F) determines the organoleptic properties of final leather. Generally, for garment leather manufacturing the S to F ratio is 1:2 and that for upper leather making is 2:1. The addition of higher quantity of fatliquors increases the degree of softness whereas increasing the quantity of synthetic tanning agents imparts tightness, roundness and also reduces the degree of softness. We know that breathability / air permeability is one of the unique features of leather over synthetic. The degree of breathability is mainly dependant on porosity (pore size and pore connectivity) of leather. Porosity of raw hides/skins is continuously altered throughout the leather processing. Pre-tanning process increases the porosity and the post-tanning process decreases the porosity.^{3,4}

Some attempts have been made to study the surface area and porosity of the un-tanned leather.^{5,6} Later on, the effect of hydrothermal shrinkage on the internal surface area and porous nature of un-tanned leather had been studied.^{7,8} The effect of various treatment processes such as dehydration, pickling, crosslinking with chromium(III) and vegetable tannins on the porosity of leather matrix had also been studied.^{9,10} Recently, Sathish and co-workers analyzed the pore size and its distribution in different areas of the sheep/goat wet-blue leathers¹¹ and also investigated the effect of finishing auxiliaries on the air permeability of final leather.¹² However, the porosity and mechanical properties of upper/garment leather produced from the same raw material have not been analyzed so far.

In this study the pre-pore determined sheep wet-blue leather has been converted into garment/upper leather and its porous nature also been analyzed. The main focus of this study is to analyze

*Corresponding author e-mails: nishad.naveed@gmail.com; nishad@clri.res.in, Fax: +91 44 24911589; Tel: +91 44 24437188

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how the Syntan to Fatliquor ratio affects the porous nature and mechanical properties of garment and upper leather with respect to wet-blue leather (before post-tanning).

Materials and Methods

Sampling for Analysis of Porosity

Wet-salted red hair sheepskin was conventionally processed into sheep wet-blue leather.^{13, 14} Then, the small portions of wet-blue leather were subjected to thermoporometry, capillary flow porometry and scanning electron microscopic analysis. The pre-pore analyzed wet-blue leather (before post-tanning) had been taken as raw material for further studies. The pre-pore analyzed wet-blue leather was cut into half along the backbone and marked as left and right. The left/right half were converted into the garment and upper leather, respectively. Figure 1 represents the detailed experimental design and the post-tanning recipes for garment/upper leather making are given in Table I. After, the post-tanning process garment/upper leather was subjected to thermoporometry, capillary flow porometry and scanning electron microscopic analysis. Prior to capillary flow porometry and scanning electron microscopic analysis wet-blue leather was freeze dried and conditioned at 25 °C / 65% (RH) for 24 hrs.

Sampling for Analysis of Mechanical Properties

Unlike, the porometry technique the requirement of sample size is higher for mechanical properties analysis and the single sheepskin would not be sufficient to conduct the mechanical properties analysis before/after post-tanning process. Therefore, two sheep wet-blue leathers were cut into halves along the backbone and marked as 1L, 1R, 2L and 2R. 1L and 2L were freeze dried and subjected to conventional mechanical operations. Whereas 1R, 2R converted into garment and upper leather respectively as per the

post-tanning process given in Table I. The sampling was done at the official sampling position of matched pair garment leather before (1L) and (1R) after post-tanning as well as matched pair upper before (2L) and after (2R) post-tanning process.

Thermoporometry Analysis

Differential scanning calorimeter was employed for thermoporometry analysis. The sample (3-5 mg), having moisture content about 65% were placed inside the encapsulated aluminium pans. Then, the temperature of the system was dropped to -40 °C from room temperature and slowly increased to 5 °C at the heating rate of 1 °C min⁻¹. The pore characteristics were calculated from the thermogram details as reported earlier.¹⁵⁻²⁰

Capillary Flow Porometry Analysis

The pore size distribution and air permeability of the samples were analyzed through PMI capillary flow porometry technique (Porous Material Inc., USA). In this analysis, the dried samples were conditioned for 24 hrs at 25°C/65% RH and the thickness was noted. Then, the specimen was held between two "O" rings and compressed air (pressure 0-60 psi) applied on the grain side and allowed to pass out through flesh side. After that, the same sample was wetted with calwick wetting liquid (Surface tension: 15.9 dynes cm⁻¹) through which the above-mentioned gas was applied. Capillary flow porometer monitored the airflow rate as a function of pressure for both dry and wet-sample. From these airflow rates, the pore characteristics and air permeability were calculated by using the software from Porous Materials Inc., USA.²¹⁻²³

Scanning Electron Microscopic Analysis

The freeze-dried wet-blue leather and the matched pair upper/garment crust leather were cut into specimen and subjected to scanning electron microscopic analysis. In this study the Phenom pro desktop scanning electron microscope was used to analyze the cross-sectional view of wet-blue, upper and garment leather.

Mechanical Properties

The mechanical properties such as tensile strength, % elongation at break, tear strength, load at grain crack and distension at grain crack were examined for both matched pair of the garment/upper leather before and after the post-tanning process. The specimens for above-mentioned testing were obtained as per the IULTCS standard method.²⁴⁻²⁶ Prior to analysis, the specimens were conditioned for 25± 1 °C and 65% RH.

Result and Discussion

Thermoporometry Analysis

The principle of the above-mentioned technique is based on the pore size and melting temperature of frozen water present in the sample. Gibbs-Thomson effect (A small crystal of liquid melts at a lower temperature than bulk liquid crystal) is the basic principle of thermoporometry technique. The full

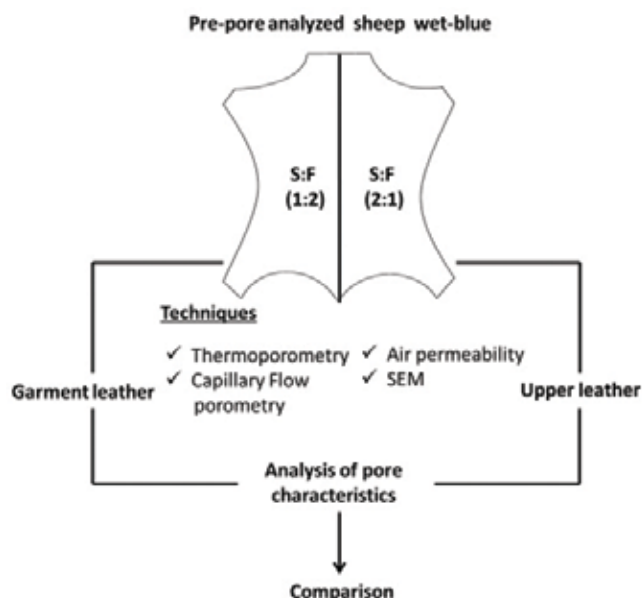


Figure 1. Experimental design for the porosity measurement.

thermodynamic relationship involved in the thermoporometry technique was explored by Burn. The melting temperature of the ice crystals present in different pore size was monitored through differential scanning calorimetry.

The following equation describes the relationship between the pore size (Radius-Rp) and melting temperature of the ice crystals.

$$R_p = \frac{-32.33}{T - T_0} + 0.68 \quad (1)$$

Where, R_p - Pore radius, T_0 - Melting temperature of the pure solvent (Water: 0 °C), T - Melting temperature of the frozen solvent in different pore size. The pore volume distribution is estimated by using equation-2.

$$\frac{dV}{dR_p} = \frac{\Delta V}{T_i - T_{i+1}} \quad (2)$$

where, ΔV - Pore volume.

The pore size and pore volume distribution are calculated by substituting the calorimetric information given in the equation 1 and 2. The graphs of pore size versus pore volume of wet-blue leather (before post-tanning), garment leather and upper leather have been shown in Figure 2.

It has been observed from Figure 2 that the wet-blue leather having pore radius in the range of 5-40 nm whereas in the case of garment leather it is in the range of 5-35 nm. In addition to that, the pore volume distribution of garment leather is lower than wet-blue leather. It is also evident from Figure 2 that the pore size and pore volume distribution of upper leather is reduced when compare to the garment and wet-blue leather. The percentage (%) reduction in porosity of garment/upper leather with respect to wet-blue leather has been calculated by measuring the area under the curve. The following equation (3) has been used to measure the porosity reduction (%).

Table I
Process recipe for the manufacture of garment and upper leather.

Garment Leather Process (S:F 1:2)			Upper Leather Process (S:F 2:1)		
Nature of Chemicals	%Offer	Remarks	Nature of Chemicals	% Offer	Remarks
Neutralization Sodium formate	1%		Neutralization Sodium formate	1%	
Sodium bicarbonate	1%	pH:5.5-5.8 Drain and Wash	Sodium bicarbonate	0.5%	pH:5.0-5.2 Drain and Wash
Retanning Water Poly acrylic filler	100% 2%	30 min	Retanning Water Poly acrylic filler	100% 3%	30 min
Melamine polymer	3%	60 min	Melamine polymer	6%	90 min
Phenolic polymer	3%		Phenolic polymer	6%	
Vegetable Tannins	2%		Vegetable Tannins	5%	
Fatliquoring Synthetic oil Semi-synthetic oil Vegetable oil Water	10% 6% 4% 50%	2 Feed, Run for 90 min	Fatliquoring Synthetic oil Semi-synthetic oil Vegetable oil Water	4% 4% 2% 50%	2 Feed, Run for 90 min
Protein Filler	2%	20 min	Protein Filler	2%	20 min
Fixing Formic acid Water	3% 10%	3 feed+ 60 min	Fixing Formic acid Water	3% 10%	3 feed+ 60 min

$$\% \text{ Reduction in Porosity} = \frac{A_{WB} - A_{G/U}}{A_{WB}} \times 100 \quad (3)$$

where, A_{WB} : Area under the curve of wet-blue leather, $A_{G/U}$: Area under the curve of garment/upper leather.

It has been calculated from the equation (3) that the percentage reduction (%) in the porosity of garment leather is 62.3% whereas for upper leather it is 83%. This results clearly indicates that the addition of a higher quantity of synthetic tanning agents in the post-tanning process of upper leather manufacturing decreasing the porosity of wet-blue leather than garment leather. Whereas in the case of garment leather making, the addition of a higher quantity of self-emulsified oil (fatliquors) may lubricate the fiber and keep separate from each other which in turn increase the porosity when compare to upper leather.

Capillary Flow Porometry Analysis

The hierarchical level of the collagen structure makes the skin matrix highly heterogenic in nature. Due to the irregular pattern of the collagen fiber arrangement, the skin contains wide spectrum of pore size ranging from micro (<2 nm), meso (2-50 nm) to macro (>50 nm) and also having different types of pores such as blind pore, open pore, closed pore and through pore. Capillary flow porometry is the only technique which determines the most constricted part of the through pore which is also known as throat pore. The porosity profile of the wet-blue, garment and upper leather are shown in Figure 3.

It is evident from Figure 3 that the wet-blue leather has a pore size in the range of 0.1-1.3 μm in which the maximum distribution has observed in the range of 0.3-0.5 μm. When the same wet-blue leather converted into garment leather, the pores are uniformly distributed in the range of 0.1-0.5 μm, whereas in the case of upper leather, the maximum pore distribution is observed in the range of 0.1-0.2 μm. The air permeability profile of

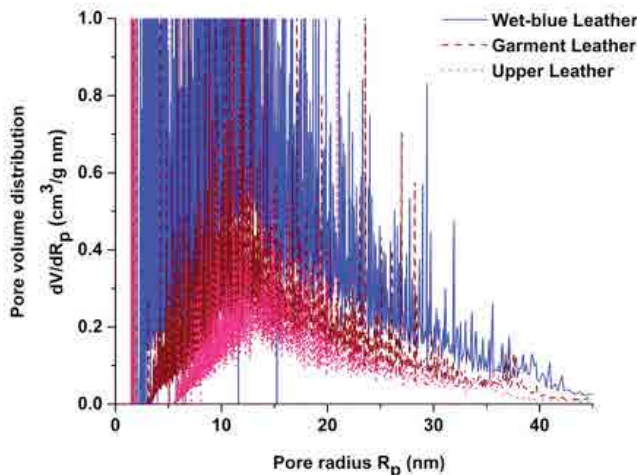


Figure 2. Thermoporometric investigation of wet-blue, garment and upper leather.

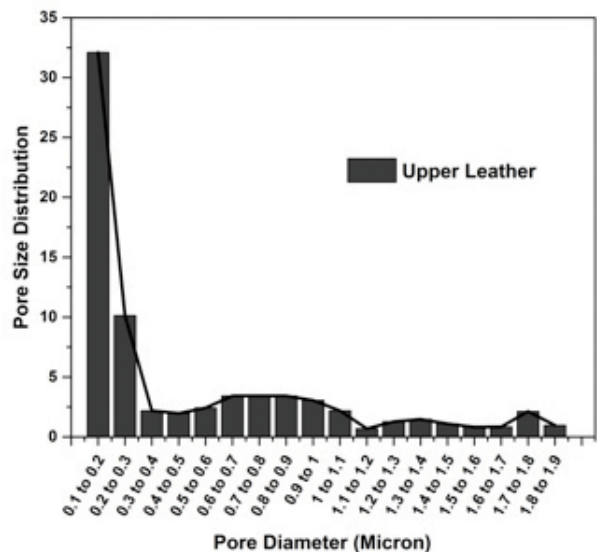
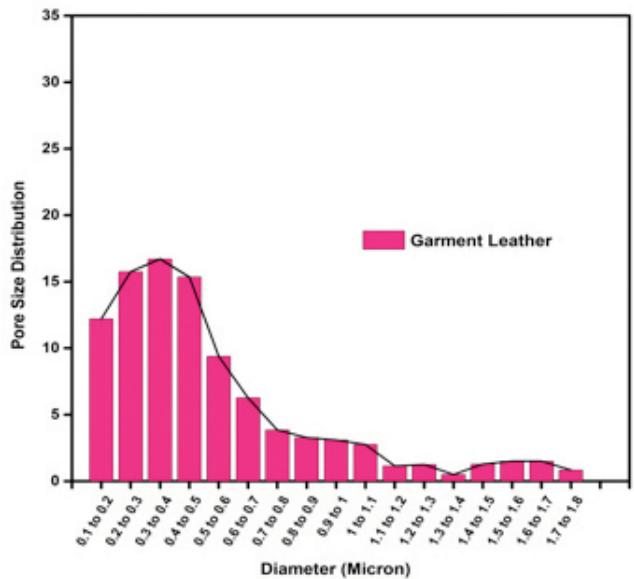
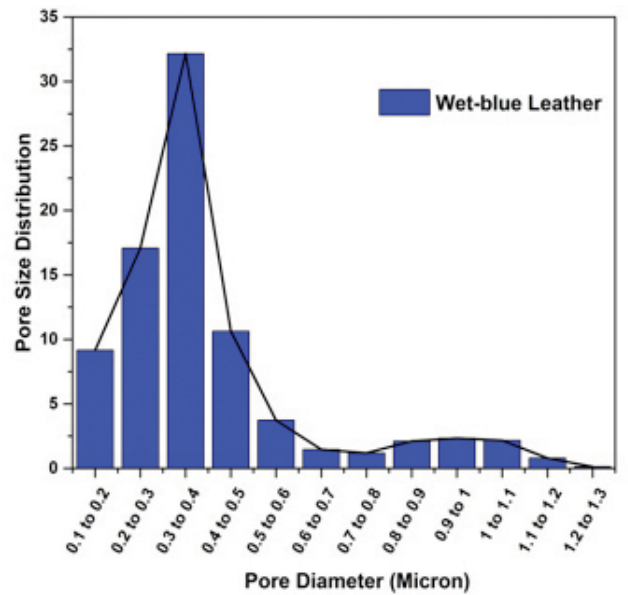


Figure 3. Pore size distribution of wet-blue, garment and upper leather.

wet-blue, garment and upper leather is shown in Figure 4. It is evident from Figure 4 that the air permeability profile of wet-blue leather is decreased when converted into garment leather and its further decreases for upper leather. The percentage reduction (%) in air permeability has been calculated by using the following equation (4).

$$\% \text{ Reduction in Air Permeability} = \frac{A_{WB} - A_{G/U}}{A_{WB}} \times 100 \quad (4)$$

where, A_{WB} : Area under the curve of wet-blue leather, $A_{G/U}$: Area under the curve of garment/upper leather.

The result clearly indicates that the air permeability of wet-blue leather is reduced up to 41% when it is converted into garment leather, whereas for upper leather the reduction is 83%. It is very clear from the above results that the post-tanning auxiliaries significantly reduce the pore distribution. However, the size of largest throat pore diameter increases when the wet-blue leather (1.3 μm) subjected to garment (1.8 μm) and upper leather manufacturing (1.9 μm). It may be due to the disruption of fiber packing arrangement as well as a reduction in contact between fibers.

Scanning Electron Microscopic Analysis

The cross-sectional view of wet-blue, garment and upper leather at two different magnifications are shown in Figure 5. It can be seen that the fiber bundles of wet-blue leather are smaller in size and not as tightly packed as in the garment/upper leathers. In the case of garment leather, fine fiber splitting has been observed, whereas for upper leather the fiber bundles are cemented in nature. It is also evident that the fiber bundles are uniformly dispersed throughout the thickness of garment/upper leather, whereas for wet-blue leather the top layer is cemented than the bottom layer. It may be due to the influence of syntans and

fatliquors added in the post-tanning process. It is very clear from the figure that the air pockets and fiber suppleness of garment leather are higher than wet-blue/upper leather. It may be the reason for the drape property of garment leather.

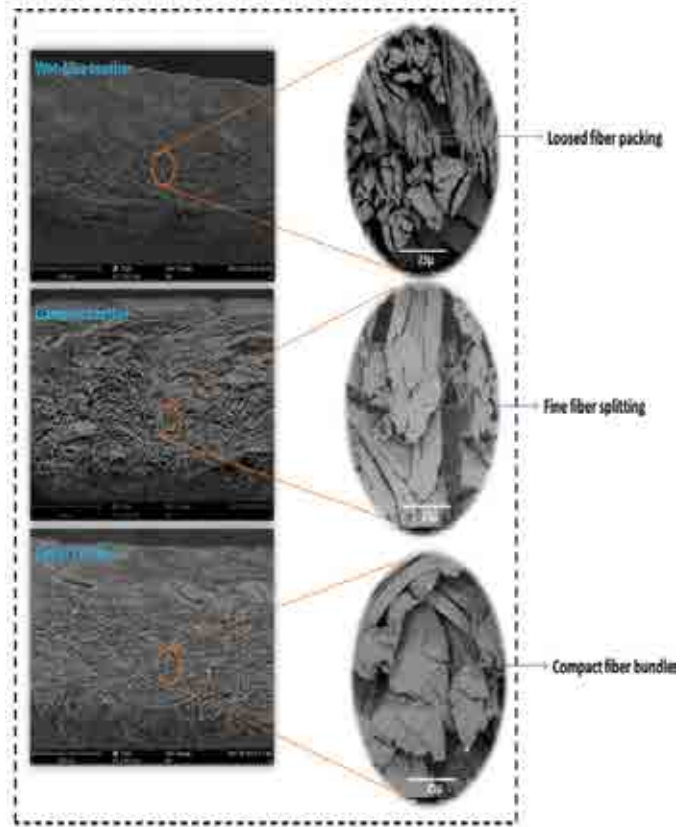


Figure 5. Scanning electron micrographs of wet-blue, garment and upper leather at two different magnifications.

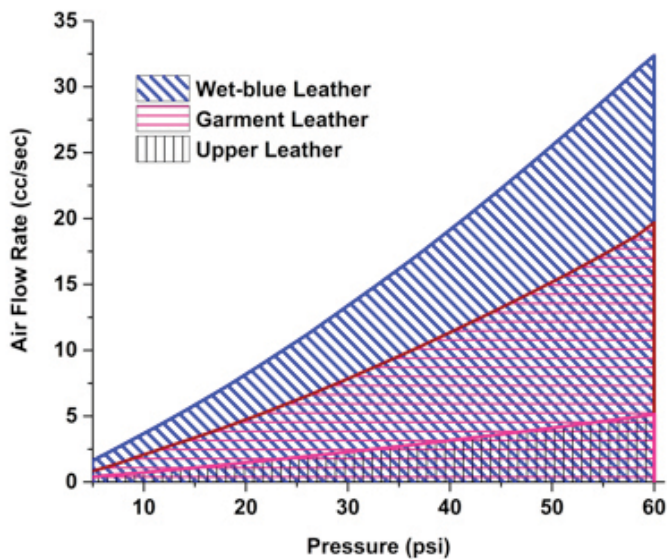


Figure 4. Air permeability of profile of wet-blue, garment and upper leather.

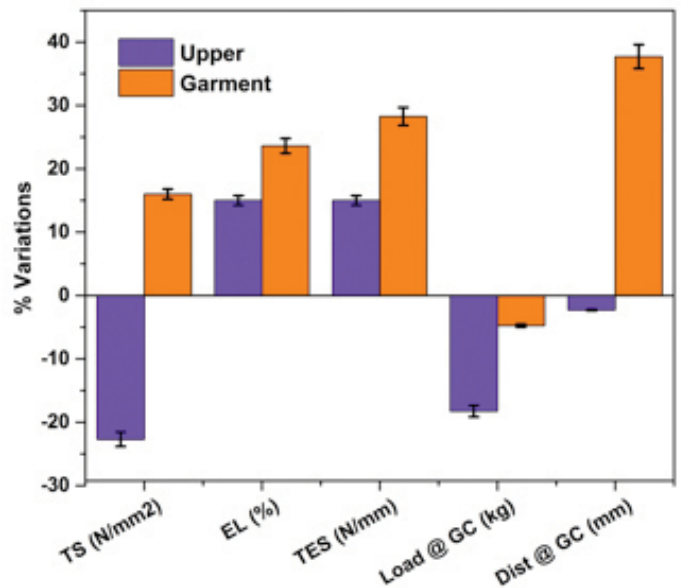


Figure 6. Variations in mechanical properties of upper and garment leather with respect to wet-blue leather.

Mechanical Properties

The effect of two different post-tanning processes on the physical strength characteristics of the matched pair upper/garment leather before and after post-tanning process have been analyzed. The percentage variations in the physical strength characteristics of upper/garment leather before and after post-tanning process have calculated using equation 5 and the results are shown in Figure 6.

$$\% \text{ Variations} = \frac{SBP - SAP}{SBP} * 100 \quad (5)$$

where, SBP- Strength before post-tanning, SAP- Strength after post-tanning

It is evident from Figure 6 that tensile strength of wet-blue leather is decreased about 23% when it is converted into upper leather whereas 16% increment for garment leather. It may be due to the addition of more amounts syntan in upper leather processing disrupting the texture of fiber arrangement and also increasing the friction between fibers. Elongation and tear strength of both upper and garment leather are increased after the post-tanning process. It has also been observed that the load at grain crack for both upper and garment leather decreases after post-tanning whereas upper leather has a higher effect. And also the post-tanning process has a negative effect on the distension at grain crack of upper leather, but garment leather has a positive effect. It could be due to the high stretchiness of garment leather than upper leather.

Table II

Comparison of the pore characteristics/mechanical properties of wet-blue leather before and after post-tanning.

Technique name	Pore Characteristics		
	Before Post-tanning	After Post-tanning	
	Wet-blue leather	Garment leather (S:F 1:2)	Upper Leather (S:F 2:1)
Thermoporometry	<ul style="list-style-type: none"> • Pore radius: 5-40 nm • Pore volume is higher 	<ul style="list-style-type: none"> • Pore radius: 5-35 nm • Pore volume is lower than wet-blue leather • 62.3% of the wet blue porosity has been arrested 	<ul style="list-style-type: none"> • Pore radius: 7-30 nm • Pore volume is lower than wet-blue and garment leather • 83% of the wet blue porosity has been arrested
Capillary flow porometry	<ul style="list-style-type: none"> • Throat pore diameter: 0.1-1.3 μm • Maximum pore distribution: 0.3-0.5 μm 	<ul style="list-style-type: none"> • Throat pore diameter: 0.1-1.8 μm • Maximum pore distribution: 0.1-0.5 μm • 41% of the wet blue leather air permeation has been arrested 	<ul style="list-style-type: none"> • Throat pore diameter: 0.1-1.9 μm • Maximum pore distribution: 0.1-0.2 μm • 83% of the wet blue leather air permeation has been arrested
Scanning Electron Microscope	<ul style="list-style-type: none"> • Fiber bundles are thin • Loosely packed arrangement 	<ul style="list-style-type: none"> • Fiber bundles are thick • Uniform fine fiber splitting 	<ul style="list-style-type: none"> • Fiber bundles are thick • Cemented fiber packing
Mechanical Properties		<ul style="list-style-type: none"> • 16% increase in tensile strength when compare to wet-blue leather • Increased elongation and tear strength • Grain crack resistance is decreased 	<ul style="list-style-type: none"> • 23% decrease in tensile strength when compare to wet-blue leather • Increased elongation and tear strength • Grain crack resistance is decreased

Note: Pore characteristics of the wet-blue leather were analyzed first. Pre-pore analyzed wet blue leather was converted into garment and upper leather and their pore characteristics were studied

Conclusion

The influence of syntan to fatliquor ratio on porosity and mechanical properties of garment and upper leather produced from wet blue sheepskin has been analyzed. The salient features of the present study have been clearly compared and outlined in Table II. To the best of our knowledge, this is the first attempt to study the porosity and mechanical properties of leather before and after post-tanning process. This knowledge may help to understand the organoleptic properties of garment and upper leather in a better way and design suitable post tanning recipe for the intended end use of leather.

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