Influence of Benzenecarboperoxoic Acid on Chamois Leather Process

by

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Abstract

Stabilization of collagen against heat and enzyme is a key objective in the tanning process. In oil tanning, fatty acid present in the oil is oxidised mainly into aldehydes which interects with Ɛ amino groups of collagen to form stable covalent cross links. Conventionally, oil tanning consumes time from two to three weeks which primarily depends on the type of oil and oxidation method for completion of tanning. In the present research, the duration of oil oxidation is reduced using benzenecarboperoxoic acid (PBA). It has been observed that PBA significantly reduces oil tanning duration from two weeks to 4 days. Moreover, the water absorption capacity of experimental leather has also increased by approximately 48% (1% PBA) compared to control leather. Physical strength properties such as tensile and percentage elongation values have also found to meet the standard norms. In addition to this organoleptic properties are also on par with control leather. The present study focus on the accelaration of chamois process for making leather, using PBA as an oxidising agent.

Introduction

Hides/skins are converted to leather finds valuable application in numerous fields.[1] The conversion of skin/hide into leather proceeds with several chemical changes in the collagen structure. The core of the leather making relies on the permanent preservation process called tanning, by treating skin/hides with suitable chemicals depending on the type of leather to be produced.[2] Some important properties of leathers such as strength, elasticity, fluffiness, waterproofing can be imparted by the use of oil and waxes during post tanning and finishing process respectively.[3] Commercially chrome and vegetable tanning are widely used because of their multifunctionality. Tanning system such as aldehyde base system is used for selective leather products. Oil tanning is a traditional method for manufacture of leathers with high water absorption capacity which are commercially known as chamois leather. The properties of chamois leather make its exclusive for applications such as cleaning, drying, filtration and apparel making.[4] Chamois leather finds applications in various other fields such as filtration of high-grade gasoline, cleaning of optical instruments, manufacturing of gloves and garments, for lining trusses and prosthetic devices, sweat and water/oil absorbent applications.[5]

Commercially, chamois leather manufacture is a time-consuming process which primarily depends on the atmospheric oxygen to oxidise the oil during tanning to convert fatty acid into aldehydes which intern reacts with leather making protein collagen. During oil tanning, oil is applied on the skin and hooked to atmospheric condition to complete the tanning process. Several attempts have been tried to reduce the oxidation duration, thereby increasing the production rate.[6,7] The process of making chamois is time consuming, the long duration of chamois process can lead to the adverse effect on production of chamois leather.[8-10] Hydrogen peroxide (H_2O_2), sodium per carbonate ($2Na_2CO3._3H_2O_2$) and ozone (O_3) are commonly used for oxidising oil. However, handling of these materials needs care due to their strong oxidizing ability and corrosive nature.[11-14] Hence there is a need for alternative oxidizing agents which needs minimal care in handling and yields effective oxidation. Therefore, the current investigation focused on developing new chamois process using PBA as an oxidising agent.

Materials and Methods

Materials

Indian sheep skins were procured from the local slaughterhouse, Chennai, India. Glutaraldehyde, sodium carbonate, fish oil and all other leather chemicals were of commercial grade.

The preparation of Benzenecarboperoxoic acid or peroxybenzoic acid (PBA)

A solution of 8.0 g. (0.102 mole) of sodium peroxide in 135 mL cold solution of water not exceeding 20°C. The solution is filtered using filter paper to remove the yellow suspended solids. The filtrate is placed in a 1000 mL beaker under stirring, then 175 mL of ethanol and a solution of 0.5 g of hydrated magnesium (in 15 mL of water) were added. The solution was brought to room temperature (37°C) and 11.6 mL (0.100 mole) of benzoyl chloride was added drop wise under constant stirring. The mixture was filtered to remove benzenecarboperoxoic acid. The filtrate was acidified with 20% of sulfuric acid and extracted with carbon tetrachloride. Six

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Table I

Detail description of process for making chamois leather

Process	Chemical	Percentage (%)	Time (min)	Remarks
Washing	Water	100	10	Wash and drain
Deliming	Water	100		
	Ammonium chloride	2	40	
				Check deliming using phenolphthalein
	Alkaline bate	0.5	30	Drain
Washing	Water	200	10	Wash and drain
Partial pickling	Water	80		
	Salt	8	30	
	Formic Acid	0.5	30	In 1:10 dilution with water
	Sulphuric Acid	0.2		In three feeds with 1:10 dilution with water, adjust pH to 4
	Glutaraldehyde	1	60	Drain, pile for overnight
Next day				
	Fish oil	25		
	Benzenecarboperoxoic acid (experiment)	X		
	Sodium carbonate	0.5		Mix using stirrer, make paste. add to drum along with skin
X= 0.25, 0.5, 0.75, 1				

extractions using about 75 mL portions resulted into 0.075 mole of benzenecarboperoxoic acid.[15]

Experimental design of chamois making using fish oil

Limed pelts were delimed and pickled to a pH of 4. The fibers were pre-stabilised using glutaraldehyde, as the chamois process was carried out by exposing skins to air for two to three weeks based on colour change (oxidation). These pre-stabilised skins resist petrifaction and helps maintain the structural integrity of the skin matrix. The detail description of oil tanning has been mentioned in Table I. Chamois leathers were made by adding fish oil mixed with small quantities of sodium carbonate (control) and various percentages of oxidizing agent (experimental) along with skin in a rotatory drum for 90 min to achieve thorough distribution of oil to the skin, the leathers were hooked for drying.

After a period of 96 h, skins turn to golden yellow colour indicating the completion of oil tanning (experimental). For control, the air oxidation process continued with regular monitoring for 14-15 days until leathers turn to golden yellow. Then, the leathers were washed with water (100%), soda ash (1%) and wetting agent (1%) for the complete removal of unfixed oil. After drying, leathers were subjected to staking and milling.

Analysis of chamois leathers

Hydrothermal stability is an important parameter to know the leathers resistance towards heat. Shrinkage temperature of chamois was analysed according to standard procedure.[16] Phenom Pro desktop scanning electron microscope (SEM) was used to analyse the morphology of chamois leathers, the instrument was equipped with light and electron optical modes operating at 5 kV acceleration voltage. PMI capillary flow porometer was used to measure the air permeability. The pressure was varying from 0-20 psi. Physical strength parameters of leather were studied after sampling; tensile strength was analysed according to the standard procedure.[17,18] Values reported were average of four samples. Measurement of water absorption was carried out as per the standard procedure.[19] Organoleptic Properties were assessed for softness, colour and odour by subjective evaluation and the rating was awarded on a scale of 0-10 points and higher points indicate better properties. The evaluation was carried out by two experienced leather technologists.

Results and Discussion

Plausible mechanism of interaction of PBA with oil and followed by collagen during the chamois process

Fish oil mainly consist of unsaturated double bonds which are susceptible for auto oxidation during the chamois process. When exposed to air, molecular oxygen reacts with double bonds of fatty acid present in the oil leads to the formation of aldehydes, ketones and other derivatives.[20] An oxidising agent may enhance the oxidation process of fatty acid present in the oil. When benzenecarboperoxoic acid is used to oxidize oil, the oxygen from benzenecarboperoxoic acid interact with the double bond present in

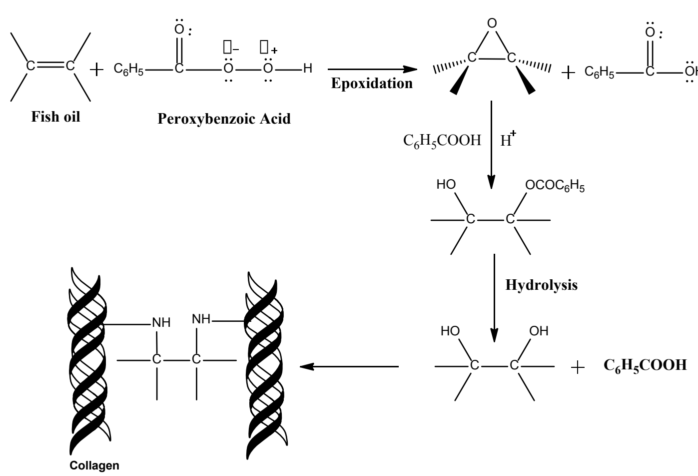

Figure 1. Plausible mechanism of oil tanning

Table II

Shrinkage temperature measurement of chamois leather

S No	Sample	Shrinkage Temperature (°C)
1	Control	78±1
2	PBA (0.25%)	78±1
3	PBA (0.50%)	79±1
4	PBA (0.75%)	79±1
5	PBA (1.00%)	80±1

Table III

Physical testing data of chamois leathers

S No	Sample	Tensile strength (N/mm2)	Percentage elongation (%)	Water Absorption (%)
1	Control	14±0.70	62±3.10	463±23.5
2	PBA (0.25%)	16±0.80	58±2.80	396±19.8
3	PBA (0.50%)	17±0.85	60±3.00	448±22.4
4	PBA (0.75%)	25±1.25	61±3.05	560±28.0
5	PBA (1.00%)	27±1.35	64±3.20	688±34.4

fatty acid though the formation of three-membered ring.[21] Further three membered oxirane ring by subsequent side reactions generate diols which can interact with Ɛ amino group of collagen matrix. The plausible mechanism of interaction of reactive species is shown in the Figure 1

Analysis of chamois leather

Hydrothermal Stability or Shrinkage temperature of chamois leathers were analysed to understand the irreversible deformation of leather under hydrothermal heat. From Table II, shrinkage temperatures of experimental leathers were in the range of 78-80 ±1°C, which is comparable to conventional oil tanning of 78 ±1°C. The reported values are measured for average of 4 samples.

Physical strength properties were analysed to understand the chamois matrix strength to withstand load. Leathers were analysed for tensile strength property measurement. From Table III, it can be seen that the tensile strength increased with increase in percentage of oxidizing agent. Another important functional property of chamois leathers is water absorption; from the table it can be observed that the percentage water absorption of chamois leathers increased by 48% (1% PBA) compared with control leathers made without use of oxidizing agent

Cross sectional morphological changes were analysed using SEM. Fiber alignment of control leathers have been found to be compact compared to experimental leathers. From Figure 2, it can be seen that the fiber alignment is more opened compared to control leathers.

The wider the aligned fibers the higher degree of porosity, which is a desirable quality of good chamois leathers.

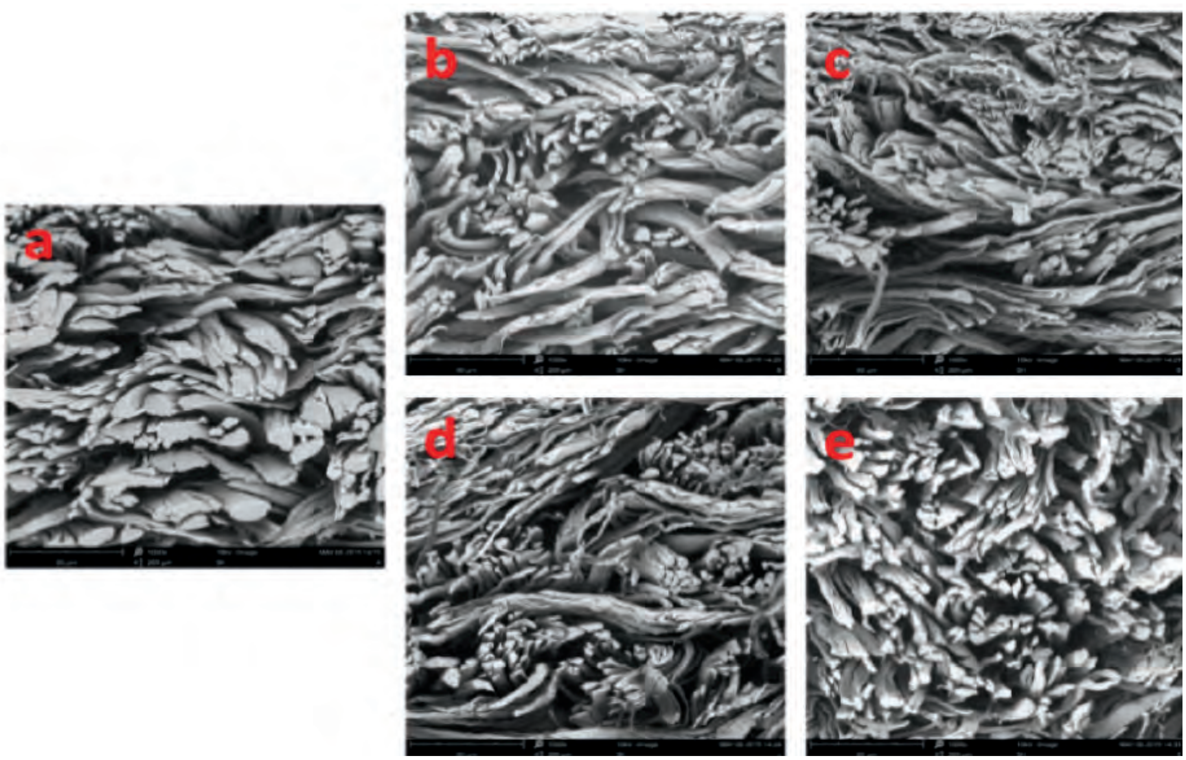

Figure 2. SEM images of chamois leathers control (a), PBA (0.25-b, 0.5-c, 0.75-d, 1%-e)

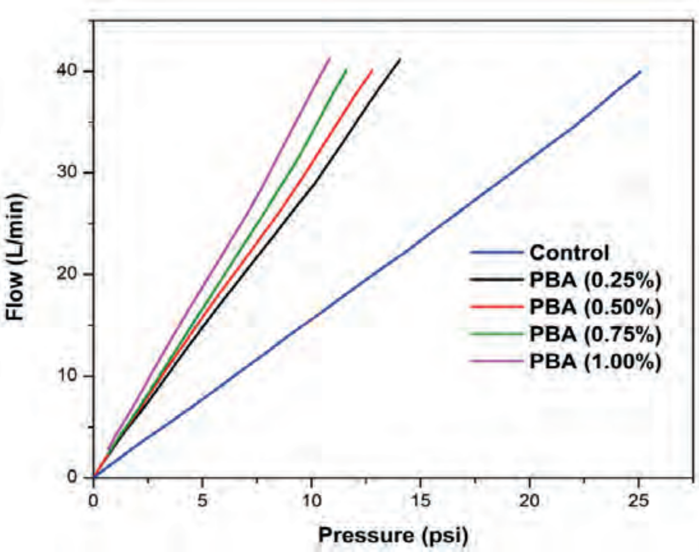

Figure 3. Porometry analysis of chamois leathers

Porosity of chamois leathers were analyzed to understand the pore structure of the matrix. From Figure 3, it can be observed that the porosity of the chamois leathers increased with the use of PBA with varying percentages.

With minimal pressure (1-12 psi) the air flow rate (liter per minute) of the experimental leathers increased drastically. It can also be safely concluded that the leathers made using the PBA exhibit good porosity comparable to control leathers, this can further have verified using SEM images for visual conformation, the alignment of fibers can be observed to be more open for experimental leathers.

From Figure 4, the organoleptic properties of chamois leathers were assessed for softness, color and odor. It can be seen that the softness of chamois leathers improved when higher concentrations of oxidizing agent were used for chamois making. The color of the experimental chamois leathers did not show any effect with variation of the PBA percentage. As the chamois leathers are made using fish oil, odor is one of the main concerns on the final leathers, though the unreacted fish oil from the process is removed by alkali washing, small quantities remain and contribute to odor.

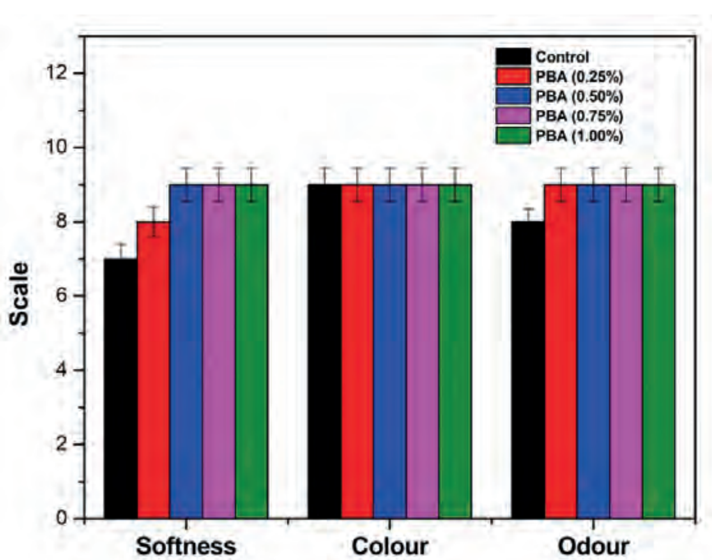

Figure 4. Bulk properties of control and experimental chamois leathers

Conclusions

The present study provides an insight on the application of benzenecarboperoxoic acid to reduce the duration of oxidation of oil for chamois manufacture. The use of benzenecarboperoxoic acid as an accelerant to oxidize fish oil in chamois making process reduces the process duration from 15 to 4 days. Water absorption capacity has also been increased by approximately 48 % (1% PBA) as compared to conventional chamois leathers. Further, shrinkage temperature of the chamois leathers was comparable with control leathers along with other organoleptic properties such as softness, color and odor. Hence, it can be concluded that the use of benzenecarboperoxoic acid in chamois making not only reduces the time but also have positive benefits on the physical properties of chamois leathers.

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References

1. Nayudamma, Y. Leather in Our National Life. *Resonance*, 2014.
2. Suresh, V.; Kanthimathi, M.; Thanikaivelan, P.; Rao, J. R.; Nair, U.B. An improved product-process for cleaner chrome tanning in leather processing, *Journal of Cleaner Production*, 9 (6), 483-491, 2001.
3. Duraisamy, R.; Shamena, S.; A Review of Bio-tanning Materials for Processing of Fish Skin, *Chemistry and Materials Research*, 8 (9), 2224- 3224, 2016.
4. Prakash, A. J; Aravindhan, R.; Fathima, N. N.; Rao, J. R. Dyeing of Chamois Leather using Water Soluble Sulphur Dyes. *JALCA* **111**, 383-388, 2016.
5. Lollar, R.M. The Tanning Process and the Production of Finished Leather Goods, *ADMERE,* Part of the Advances in Meat Research Series book series, 8, 35-65,1992.
6. Sandhya, K. V.; Vedaraman, N.; Sundar, V. J.; Mohan, R.; Velappan, K. C.; Muralidharan, C. Suitability of different oils for chamois leather manufacture. *JALCA* 110, 221-225,2015.
7. Vedaraman, N.; Muralidharan, R.; Sundar, V. J.; Velappan, K. C.; Muralidharan, C. Modified jatropha oil for making chamois leather. *Biotechnol. Ind. J.* 9, 203-205, 2014.

8. Suparno, O.; Kartika, I. A.; Muslich. Chamois leather tanning using rubber seed oil. *J Soc Leath Tech Che,* 93, 158-161,2009.
9. Zhongyin, X.; Zhang, X.; Zhihua, S.; Xinshen, Z. Study on pretanning technology of chamois leather, *China Leather*, 21,2004.
10. Sharphouse, J.H., Theory and practice of modern chamois leather production, *AGRIS*, 69(2) 29-43,1985.
11. Hongru, W.; Yuanyue, M.; Yue, N. An oil tanning process accelerated by oxidation with sodium percarbonate. *J Soc Leath Tech Che,* 92, 205-209, 2008.
12. Sundar, V.J.; Vedaraman, N.; Balakrishnan, P. A.; Muralidharan, C. Chamois leathers - An approach for accelerated oxidation. *J Soc Leath Tech Ch,* 88(6), 256-259, 2004.
13. Suparno, O.; Gumbira-Sa'id, E.; Kartika, I. A.; Muslich, An Innovative New Application of Hydrogen Peroxide to Accelerate Chamois Leather Tanning. Part II: The Effect of Oxidation Times on the Quality of Chamois Leather. *JALCA* 108, 180-187, 2013.
14. Sundar, V. J.; Muralidharan, C.; Sadulla, S.; Ozonation—An Emerging Inevitable Option for Chamois Making, *The Journal of the International Ozone Association*, 29, 5405-5409, 2007.
15. Moyer, J. R.; Manley, N. C. NEW- An Improved Synthesis of Peroxybenzoic Acid, *J.Org. Chem.* **29**, 2099-2100, 1964.
16. IUP 16, Determination of shrinkage temperature up to 100°C. *J Soc Leath Tech Ch*, 84, 359,2000.
17. IUP 2, Sampling, *J Soc Leath Tech Ch*, 84, 303, 2000.
18. IUP 6, Measurement of tensile strength and percentage elongation. *J Soc Leath Tech Ch,* 84, 317-321, 2000.
19. IUP 7, Determination of the static absorption of water. *J Soc Leath Tech Ch,* 84, 323,2000.
20. Lembke, P.; Schubert, A. Chapter 37 - Introduction to Fish Oil Oxidation, Oxidation Prevention, and Oxidation Correction. *Omega-3 Fatty Acids in Brain and Neurological Health*, 455-460,2014.
21. David W.; Marks Richard C. Larock. The conjugation and epoxidation of fish oil. *J Am Oil Chem Soc*, 2002, 79(1), 65–68,2002.