Studies on the Development of Benzoyl Peroxide Catalysed Rapid Oil Tanning using Linseed Oil

by

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Abstract

Leather tanning is a stabilisation process of skin fibers. This is achieved by the interaction of collagen amino acids with tanning agents to stabilise skin from putrefaction. Tanning of collagen with oil is a special class of tanning known as chamois tanning. Chemically, the oil tanning involves oxidation of unsaturation present in the oil, which is generally achieved by exposing oil treated skins to air. In this study, Benzoyl peroxide has been used as an accelerating agent for oxidation of unsaturated bonds present in the linseed oil for oil tanning process. Results shows remarkable reduction in tanning duration from fifteen days to two days. The chamois leathers prepared using oxidation accelerant (Benzoyl peroxide) have been evaluated for physical properties such as water absorption (611%), tensile strength (18 N/mm^2) and percentage of elongation (66 %) which are found to be better than control leathers.

Introduction

Chamois leather finds application in various fields such as filtration of high-grade gasoline, cleaning and drying of optical instruments, manufacturing of gloves and garments, for lining trusses and prosthetics, and as sweat and water absorbent.[1] It is a mass market natural product having high demands for its utility and versatility in the application for satisfying the customer's needs. Yet, there are very few manufacturers of chamois leather that perpetuates to the ever-increasing demand for this product globally.[2,3]

In general, fish oil is known as the oil tanning agent for the manufacture of chamois leathers. Owing to unique fish oil smell in the final leather, research is being carried out to mitigate the effect.[4] Hence, alternate oils such as linseed oil,[5] jatropha oil,[6] rubber seed oil,[7] epoxidised oil,[8] have been utilised as an alternative source for fish oil for chamois tanning.

Linseed oil is known for its high unsaturation which makes it susceptible for oxidation. The presence of high unsaturation in linseed oil also has significant industrial applications in coatings such as floor covering and film formation[9] in order to protect it from oxidation a suitable antioxidant is required to enhance its shelf life.[10] The high linolenic acid content (>50%) makes it vulnerable to chemical reactions associated with double bonds, especially addition reaction.[11] Oxidation of oil is one of the most studied reactions where double bonds play important role. The two methods associated with oxidation of oils, are autoxidation and photo-oxidation of fatty acids present in the linseed oil. This can be catalysed by metals, oxidising agents and enzymes.[12]

The chamois process is a time-consuming operation which takes 10-15 days to complete the tanning process. To accelerate the chamois process, various oxidising agents have been used like for example, hydrogen peroxide,[13] sodium percarbonate,[14] ozone,[15] benzoyl peroxide,[16] benzenecarboperoxoic acid.[17] The use of these oxidation agents reduces the process time drastically compared to air oxidation process. Apart from the longer time duration required for making chamois leather, odor from the fish oil treated chamois is of concern.

In order to eliminate odor and reduce process time for preparation of chamois leathers, there is need for process modifications in chamois making. Use of natural oils may be a step forward towards an eco-friendly approach in chamois making. Also, the present study extensively deals with the effect of different percentage of benzoyl peroxide (BPO) on the rate of oxidation of linseed oil and the benefits imparted by the current process. The prepared chamois leathers were analysed for water absorption, tensile strength and organoleptic properties.

Materials and Methods

Materials

Linseed oil was purchased from local supplier, Chennai. Benzoyl peroxide was procured from Sigma-Aldrich, Chennai. All the other chemicals obtained were of commercial grade. Sheep skins were used as raw material for the chamois process.

Processing of chamois leather

Wet salted sheep skins were processed conventionally up to pickling process and then de-pickled and tanned using glutaraldehyde tanning agent (2%). The detail process is provided in Table I. The glutaraldehyde treated skins were piled overnight. The leathers were then sammyed and the grain was completely shaved off followed by oil tanning.

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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 de-liming 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				
	Linseed oil	25		
	Benzoyl peroxide (experiment)	X1/X2/X3/X4		
	Sodium carbonate	0.5		Mix using stirrer, make paste. add to drum along with skin

X1 to X4= 0.25, 0.5, 0.75 and 1% of BPO

For the control process (X), glutaraldehyde tanned sheep skins were treated with 25% of linseed oil along with 0.25% of Soda ash. The oil tanning process was carried out in the drum for 2 h. The skins were hung up in the oxidation chamber having good air circulation for 15 days. The completion of oil tanning was ascertained by the golden yellow color on the surface of leather. Finally, the leather was washed with water (100%), soda ash (1%) and wetting agent (1%) for the removal of unfixed oil.

The resultant leathers were squeezed and hung up for drying. After drying the leathers were staked and buffed on both sides to get a uniform nap on both the sides. Finally, the leathers were dry milled for a period of 2 h to open up the fibers and the rigid fibers and increase softness.

Effect of Benzoyl peroxide

The linseed oil (L) was mixed with 0.25, 0.50, 0.75 and 1% (based on oil weight) of the benzoyl peroxide to obtain oil catalyst mixtures; X1, X2, X3 and X4 respectively. The oil and catalyst ratio was mixed thoroughly until a turbid mixture formed. This mixture was employed for oil tanning. The glutaraldehyde tanned sheep skins were treated with 25% of the linseed oil mixture and 0.25% of soda ash and drummed for 2 h followed by above said process.

Scanning electron microscope analysis

Scanning electron microscopy technique was employed to understand the morphology of leather fibers. The cross sections of chamois leathers were examined under Phenom Pro desktop scanning electron microscope (SEM). The instrument is equipped with light and electron optical modes operating at 5 kV acceleration voltage.

Porometry analysis of chamois leathers

PMI capillary flow porometer was used to measure the air permeability. The pressure varied from 0-20 psi.

Water absorption

Water absorption is the ability of leather to absorb water per unit weight of leather and expressed in percentage. Water absorption is an important parameter in determining the quality of chamois leather, as the main use of the leather is for filtering, cleaning and drying this requires high water absorption capability. The higher the water absorption capacity of the chamois leather, the better is its quality. Measurement of water absorption was carried out as per the standard procedure.[18]

Shrinkage temperature measurement

Shrinkage temperatures of the experimental and control leathers were measured according to standard procedure.[19] Hydrothermal shrinkage of chamois leathers was measured to understand the leathers behavior towards hydrothermal heat.

Physical, chemical and organoleptic characterization of the chamois leather

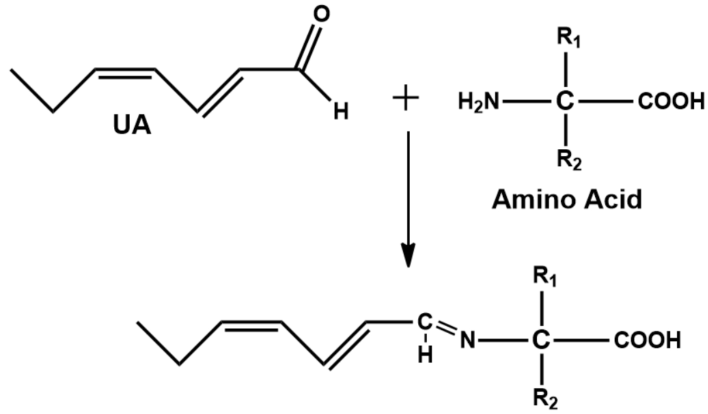
The leathers were subjected to physical characterization in order to ascertain whether they can withstand the standard requirements of chamois leather. The leathers were sampled from the official sampling location.[20] The leathers were characterized for tensile strength and percentage of elongation.[21] Organoleptic properties were assessed by four experienced leather technologists, four samples of chamois leathers were assessed for softness, fullness, odor and visual appearance.

Results and Discussion

Plausible chemistry

The autoxidation of monounsaturated acid (oleic acid) can be achieved at high temperatures while polyunsaturated acids such as linolenic and linoleic acids undergo rapid oxidation even at room temperature.[22] The reactivity of bis allylic methylene group is mainly because of its resonating stabilised structure after the removal of active hydrogen atom along with less bond dissociation energy between carbon and methylene hydrogen.[12] This activity is taken into consideration for initiation of the oxidation of Polyunsaturated Fatty Acids (PUFAs) of the linseed oil. Linseed oil contains active methylene groups, therefore experience more exposure towards oxidation. These PUFA radicals quickly get attached with oxygen to form peroxyl radicals which again can undergo resonance stabilisation. The peroxyl radical can attract a hydrogen atom from another fatty acid chain of linseed oil to form the primary oxidation product, a Lipid Hydroperoxide (LOOH) leaving behind another reactive PUFA radical which can again start the process and the propagation will continue. The lipid hydroperoxides (ROOH) are unstable and rapidly decompose into alkoxyl radical which further decompose to form several secondary oxidised products such as saturated aldehydes, unsaturated aldehydes, short-chain ketones, alcohols, acids, esters, ethers and hydrocarbons.[23-26] The rate of oxidation of oil found to be increased by the use of oxidising agents which play accelerator for the chemical process.[27,28]

The aldehydes being highly diffusible compound interact with amino acids of skin and form stabilised cross-linked protein (Scheme 1). The chemistry behind the stabilisation of protein during oil tanning is of great interest if the oxidation can be accelerated by the presence of oxidising agents such as BPO which can enhance the rate of abstraction of bis allylic methylene hydrogen atom in the initiation step.[16]



Scheme 1. Interaction of Unsaturated Aldehydes (UA) generated from series of oxidation of linseed oil with amino acids of protein collagen

Leather Processing

Conventionally, the oxidation of oil tanned leathers requires 10-15 days. In order to minimize the duration of oxidation process, benzoyl peroxide has been used as a catalyst to enhance the oxidation of oil. Adoption of the new process technique has reduced the oxidation duration to two days.

Characterization of chamois leather

The chamois leathers made using linseed oil have comparable properties to that of the fish oil treated chamois.[16] The chamois leather was characterized for various physical and organoleptic properties and the results are discussed below.

Water absorption

Chamois leather is known for high water absorption.[29] The water absorption results for chamois leathers obtained from different benzoyl peroxide ratios with linseed oil are shown in Table II. It has been observed that the percentage of water absorption gradually increasing from 0.25 to 0.75% (from 463.35 to 611.11) and again slightly decreasing to 555.35%.

By this observation it can be concluded that the addition of 0.75% of BPO (X3) can produce chamois leather with greater water absorption capacity (611.11%) than the control leathers tanned

Table II

Water absorption capability of chamois leathers

S No.	Sample	Water Absorption (%)
1	X	441±20
2	X1	463±20
3	X2	511±25
4	X3	611±30
5	X4	555±27

Table III

Shrinkage temperature analysis of chamois leathers

S No.	Sample	Shrinkage temperature
1	X	78 ± 2 °C
2	X1	77 ± 2 °C
3	X2	78 ± 2 °C
4	X3	78 ± 2 °C
5	X4	77 ± 2 °C

Table IV

Physical strength properties of chamois leathers

S No.	Sample	Tensile Strength (N/mm^2)	Percentage elongation (%)
1	X	12±2	52±5
2	X1	12±2	58±6
3	X2	14±2	57±6
4	X3	18±2	66±7
5	X4	17±2	54±5

using linseed oil alone (441.17%). The slight decrease in water absorption with the addition of 1% BPO indicates that the better performance can be achieved by the use of appropriate percentage BPO (0.75%) which may have high impact on the rate of oxidation of linseed oil. It is also observed that the experimental leathers are showing better water absorption than that of leathers prepared using linseed oil (using goat skin) and fish oil with benzoyl peroxide. [5,16]

Shrinkage temperature analysis of chamois leather

Shrinkage temperature of chamois leathers was analysed to understand the stability of the leathers towards heat. In general oil tanned leathers exhibit hydrothermal stability of up to 78±2⁰C. The experimental leathers in this study resisted temperature of up to 77-78°C compared to control of 78°C, the results are mentioned in Table III. The data also gives information about the hydrothermal stability of leathers, which is not impacted by the addition of oxidising agent in the leather processing.

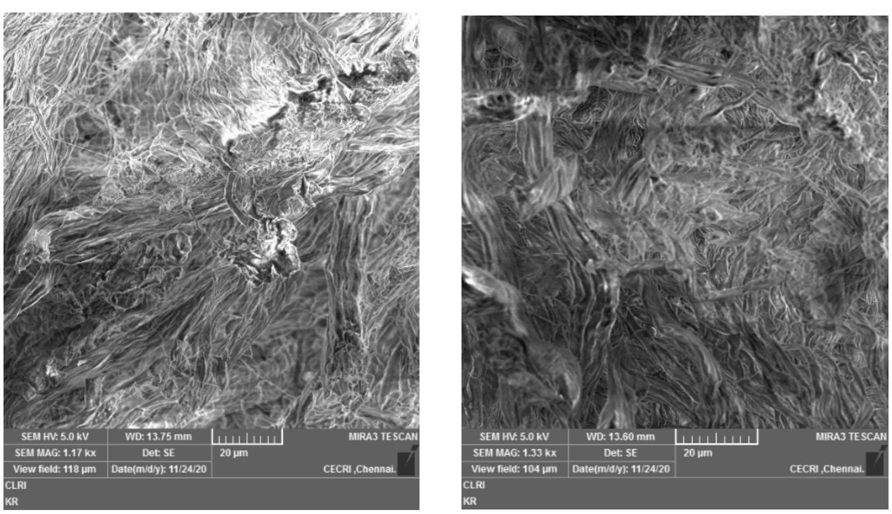
Scanning electron microscopy analysis of chamois leathers

Scanning electron microscopy imaging shows the fiber alignment of the chamois leathers. This gives information about compactness of the leathers. It can be seen from Figure 1 (a) and (b), that the fiber alignments of control leathers and experimental leathers (X3) show the compact fiber structure, which also influences the porosity of the oil tanned leathers. With the increase in percentage of the oxidizing agent in chamois processing there was an increase in pore size which is an expected quality of high performance chamois leathers.[16]

Physical strength and organoleptic properties of the chamois leather

The chamois leather made using linseed oil has been evaluated for physical strength parameters. Tensile strength and percentage elongation parameters of leathers have been analysed to understand the leathers' ability to withstand force. The results are tabulated in Table IV.

It is worth noting that the tensile strength of the chamois leather made out of linseed oil and oxidising agent shows better results as compared to control. The graphical representation of organoleptic properties of leathers are shown in Figure 2. It can be observed that control and experimental leathers are comparable for softness, fullness, odor and visual appearance values. The performance of X3 leather treated with 0.75% of oxidizing agent performed better compared to other experimental leathers, which can be confirmed



(a) (b)

Figure 1. (a) Scanning electron microscopy analysis of control chamois leathers; **(b)** Scanning electron microscopy analysis of experimental chamois leathers

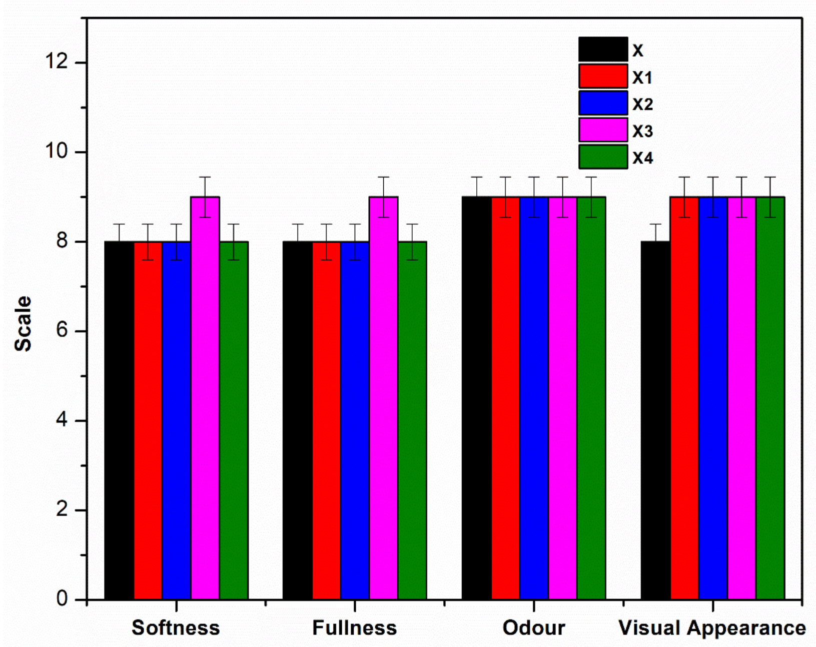


Figure 2. Organoleptic properties of chamois leathers

from the SEM analysis. Similarly, when the experimental leathers are compared to the earlier studies[5,16] where the preparation of chamois leathers was carried out using linseed oil (using goat skin) and fish oil with benzoyl peroxide respectively. The odor from the chamois leathers was avoided in this study by the use of vegetable oil instead of fish oil. Also, the color and visual appearance of the experimental leathers (X1 to X4) improved by the use of linseed oil with benzoyl peroxide. The intensity of yellowing on the experimental leathers was observed to be lighter compared to leathers prepared using linseed oil (using goat skin) and fish oil with benzoyl peroxide.[5,16]

Porometry analysis of chamois leathers

Porometry analysis of chamois leathers gives information about the pore structure of the leather matrix. Porosity of the experimental leathers increased with increase in BPO content, it can be inferred from the Figure 3, that leathers made up of 0.25% BPO (X1) show porosity similar to control leathers. With increase in concentration of BPO, leathers exhibited improved porosity values. The chamois containing 0.50 % of BPO (X2) along with linseed oil exhibited better flow rate values compared to X4 (1% BPO) with fish oil.[16] The leathers X3 and X4 (0.75 % and 1 % of BPO) prepared using linseed oil shows excellent flow rate compared to the leathers treated with BPO with fish oil.[16]

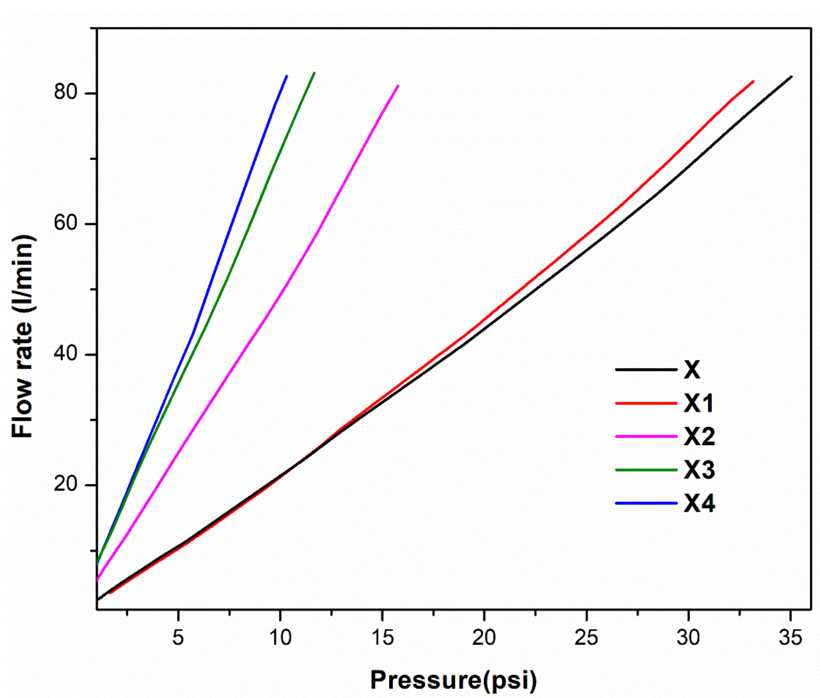


Figure 3. Porometry analysis of chamois leathers

Conclusion

The oil tanning, using linseed oil with 0.75% of benzoyl peroxide as a catalyst, shows better quality chamois leather through rapid oxidation of oil as compared to leather which is tanned with linseed oil alone (control). The study concentrated on the complete elimination of characteristic odor of fish oil associated with conventional fish oil tanned chamois leather and reduction in process time over conventional chamois making. The water absorption property of the experimental leather increased greatly compared to control. Physical strength and organoleptic properties of experimental leathers are comparable with the control.

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