Neoteric Oxidizing Agent for Chamois Process

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Abstract

Auto oxidation of oil is a moderate free radical chain reaction, started by homolytic fission of allylic hydrogen, which is a very receptive site in unsaturated hydrocarbon. This procedure converts unsaturated oil to oxygenated compounds, for example, aldehydes, ketones, carboxylic acids, esters, anhydrides etc. When these secondary oxidized products, specially aldehydes, reacts with amino acids of collagen, they stabilize the skin. Stabilization of collagen with oil is well known as chamois leather processing. In this investigation, an attempt has been made to decrease the span of chamois leather process and comprehend the procedure of oil tanning utilizing benzoyl per oxide as an oxidizing agent. It is plausible that the generation of unsaturated aldehydes has been upgraded by the utilization of oxidizing agent, which thus decreased the tanning time from 15 to 4 days. The experimental chamois leather had high water absorption (higher by 26%) than the control oil tanned leather. Further, physical strength properties, for example, tensile, tear and percentage elongation of chamois leather were seen to be comparable to control leathers. Organoleptic properties, for example, color, softness and odor of chamois leathers were enhanced compared with control leather. This study opens another path in the search of new oxidizing agents as a catalyst to decrease the duration of chamois leather making.

Introduction

Tanning is a process where skin or hide protein interacts with tanning materials such as metal or vegetable tannoids or oil to convert it into leather. In metal tanning, basic chromium sulfate is used which at higher pH convert into poly chromium complexes which cross-linked with amino acids of collagen to tanned them.[1] In vegetable tanning, polyphenol astringent chemicals, obtained from natural sources like bark and leaves of plants, reacts with amino acids of collagen to form leather. Unlike metal and vegetable tanning, chamois leathers are made using oils.[2]

Chamois leathers are generally used for cleaning, due to their ability to absorb large amount of water, oils and excellent dirt removal capabilities. This leather also finds some high end applications such as filtration of fuel, cleaning optical instruments, glass windows, in making gloves, garments, and footwear.[3]

Most favored oil for making chamois is fish oil, due to the presence of high degree of unsaturation and low cost. Different authors have tried to replace the fish oil with natural oils to avoid the noxious odor from the chamois. Some natural oils extracted from rubber seed, linseed and jatropha were studied as a possible replacement of fish oil.[4] Oil is mainly applied on the surface of skin and are exposed it to the atmosphere for oxidation; the process is time consuming and usually takes about nine to fourteen days.[5] It is generally accepted that the linoleic acid is responsible for in situ polymerization of these oils. Though the exact mechanism of tanning is not well established, it is presumed that the oil coats the fibers of the skin and prevents it from putrefaction. Once the color of the leather changes to yellow after oxidation, the leathers are washed using alkali and dried.[6]

The process of making chamois is time consuming; There are few literatures reporting to reduce the time required for oil tanning using some oxidation accelerating agents such as hydrogen peroxide, sodium percarbonate and ozone.[7-10] However, handling of these materials needs care due to their strong oxidizing ability and corrosive nature. Hence there is a need for alternative oxidizing agents which needs minimal care in handling and effective oxidation.

In the present study, Benzoyl peroxide was used as an oxidizing agent and used for the optimization for chamois leather processing with fish oil.

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Materials and Methods

Materials

Indian sheep skins were procured from the local slaughter house, Chennai, India. Glutaraldehyde (BASF, Chennai), Benzoyl peroxide (BPO) (Himedia, Chennai), Fish oil (Chennai) and all other leather chemicals were of commercial grade.

Oil Tanning Using Fish Oil

Partially pickled skins were pre tanned using glutaraldehyde. Mixture of fish oil (25%), soda ash (0.5%) and benzoyl peroxide (X %) for experimental process were pre-mixed in a beaker and the mixture was applied on the leather in a rotating drum so that the oil is distributed throughout the surface. The process was carried out for 90 min continuously. The skins were hung up for oxidation in open drying stands. The completion of oil tanning was visually judged by the color of the skins turning 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. Final leathers were dried and subjected to staking, buffing and milling. Control chamois leather was made in the similar manner as explained above without the use of benzoyl peroxide. Detail description of leather processing is seen in Table I.

Physico-chemical Characterizations

Shrinkage Temperature Measurement

Hydrothermal stability of chamois leathers was assessed in order to understand the leathers resistance towards heat. Shrinkage temperature of leathers in accordance to standard test procedure.[11]

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 3.5-4
	Glutaraldehyde	1	60	Drain, pile for overnight
Next day				
	Fish oil	25		
	Benzoyl per oxide (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				

SEM Analysis

SEM analysis was carried out using Phenom Pro desktop scanning electron microscope, which has light and electron optical modes operating at 5 kV acceleration voltage at room temperature of 25°C and 50% relative humidity. Samples were cut into 2 X 2 cm^2 sections and mounted on the adhesive stub for examination.

Porometry Analysis

PMI capillary flow porometer was used to measure the air permeability, the conditioned samples were mounted between two "O" rings and the compressed air was applied on the grain surface and allowed to pass out through flesh side. The pressure was varied from 0-20 psi. The pressure (psi) and its corresponding flow rate (L/min) were plotted to understand the permeability of the samples.

Measurement of Physical Strength Properties

Physical strength parameters of leather were studied after sampling. Tensile strength and percentage elongation properties were analyzed according to the standard procedure.[12,13] Values reported were average of four samples. Tensile strength of control and experimental leathers were determined through standard procedure.

Water Absorption Analysis

Water absorption is the ability of the leather to absorb water per unit weight of leather and expressed in percentage. Measurement of water absorption was carried out as per the standard procedure.[14] Test samples are subjected to expose the grain surface to silica gel beads which were placed in a container. This container is subject to cyclic rotations for 12 h duration and differential weight of the container is noted and water.

Evaluation of Organoleptic Properties

Organoleptic Properties were assessed for softness, fullness and grain smoothness by standard hand evaluation technique. Experts rated the leathers on a scale of 0-10 points for each functional property, where higher points indicate better properties exhibited.

Results and Discussion

Chamois Leather Processing

For making chamois leathers, fish oil was taken based on the leather weight and mixed with various percentages of the oxidizing agent (Benzoyl peroxide: 0.25, 0.50, 0.75, and 1%) and sodium carbonate (0.5%) shown in the Figure 1. This combination was mixed thoroughly until a turbid mixture was formed. The mixture was applied to skin using rotatory drum for 90 min at 8 rpm, ensuring better penetration and distribution of oil to the skin. The leather was hooked for drying in room temperature for oxidation. Regular examination of skins was carried out in order to observe the changes. After a period of 72 h, skins turn to golden yellow color indicating the completion of oil tanning. Then, the leathers were washed with water (100%), soda ash (1%) and wetting agent (1%) for the complete removal of unfixed oil. After drying, hooking was done followed by staking and buffing. Finally, the leather was dry-milled for the opening up of the rigid fibers and for obtaining softness.

Plausible Mechanism of Oil Tanning and the Effect of Oxidizing Agent in Chamois Making

Poly unsaturated fatty acid are exceedingly reactive to oxidation. Unsaturated oils are inclined to autoxidation, which is the immediate response of molecular oxygen with hydrocarbons of fatty acids of oil.[15] Reactivity towards oxidation is directly related to unsaturation of oil more the unsaturation more will be the affection towards oxidation. The use of benzoyl peroxide enhanced the concentration of oxygen radical by breaking of internal oxygen- oxygen bond shown in Figure 2.

Oil oxidation is free radical chain reaction and to initiate the reaction the preferred step will be hydrogen abstraction from allylic carbon – hydrogen bond. The amount of energy required for elimination of hydrogen from allylic carbons is approx.

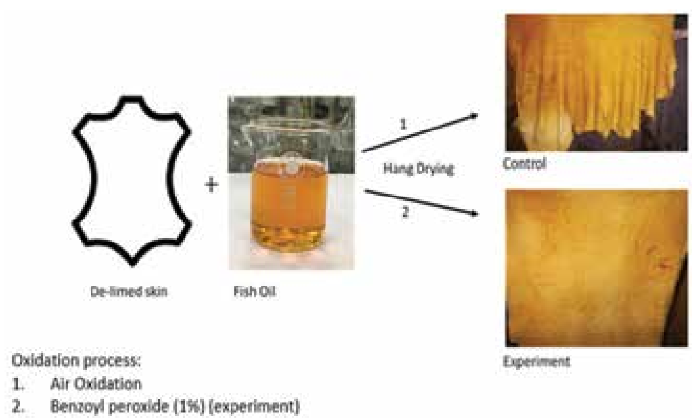

Figure 1. Over view of chamois leather processing.

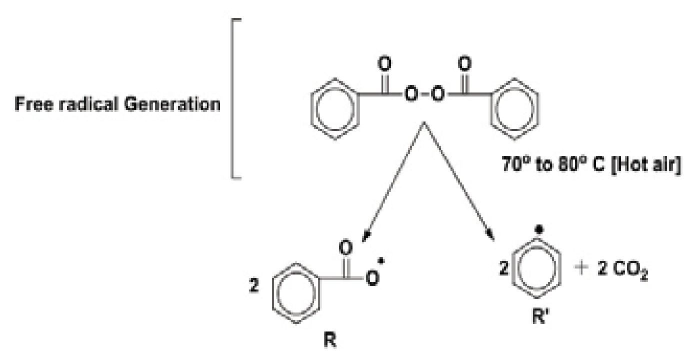

Figure 2. Benzoyl peroxide free radical generation.

75-90 kcal/mol which is lowered by 9 kcal mol^{-1}, compared to a saturated carbon-hydrogen covalent bond; this makes hydrogen abstraction more inclined.[16] The generated alkyl free radical is stabilized through resonance provides two reactive sites for chain reaction, oxygen in excited state will be in singlet and triplet state, high number of unsaturation favors the association with triplet oxygen than singlet. Obstruction of the triplet oxygen electron and alkyl radical formed in the first step, prompts the development of a high-vitality peroxyl radical ($ROO^{\cdot}$).[17] Because of the high reactivity of peroxyl radicals it effortlessly extracts a hydrogen from other allylic carbon of fatty acid of oil.[18] This response prompts the gathering of hydroperoxides, and poly unsaturated fatty acid radical which can propagate the chain reaction. Hydroperoxides are again highly unstable species which, after breakdown, provides alkoxyl radicals which again on decomposition give some high reactive molecules such as unsaturated aldehydes.[19] The rate of above reaction enriched by benzoyl per oxide.

Unsaturated aldehydes (UA) generated during propagation step with their free aldehyde group interacts with amino group of amino acid of collagen via Shiff base formation along with hydrogen bond formation with carboxylic acid group of collagen. This provide a network of cross linkages of oxidized oil with collagen as shown in Figure 3.

Hydrothermal Stability of Chamois Leathers

Shrinkage temperature measurement of chamois leather provides the information about the leather resistance towards load due to hydrothermal shrinkage, which in turn gives the idea of oil tanning occurred due to the treatment of fish oil. It has been observed from Table II that, shrinkage temperatures of experimental leathers were in the range of 78-79°C, which is comparable to conventional oil tanning.

Table II
Shrinkage temperature measurement of chamois leather.

SNo	Sample	Shrinkage temperature (°C)
1	Control	78±1
2	BPO (0.25%)	78±1
3	BPO (0.50%)	78±1
4	BPO (0.75%)	78±1
5	BPO (1.0 %)	79±1

Physical Strength Properties of Chamois Leathers

Chamois leathers were tested for strength and water absorption capabilities. Tensile strength of the chamois leather increased with increase in benzoyl peroxide percentage. This may be because of the complete oxidation of the fish oil and improving the tanning efficiency. From Table III, it can be seen that the tensile strength of the chamois leather increased with increase in concentration of the benzoyl peroxide. Percentage elongation of the leather samples were comparable with control leathers. Also, chamois leathers are known for their water absorbing capability, water absorption test was carried out to understand the effect of oxidizing agent in chamois making. Water absorption by the experimental leathers increased in the range 1 to 26 % as compared to control leather. Higher water absorption by chamois leather was exhibited at benzoyl peroxide concentration of 1%.

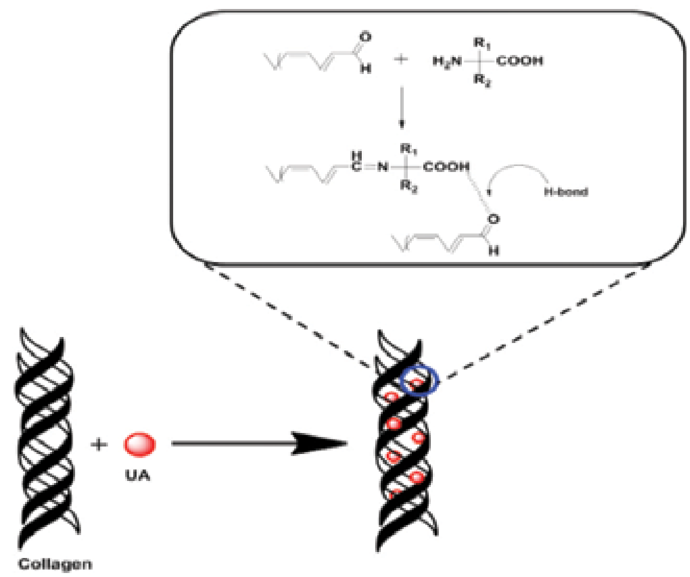

Figure 3. Plausible interaction of Unsaturated aldehydes, generated from oil oxidation with collagen as a tanning agent.

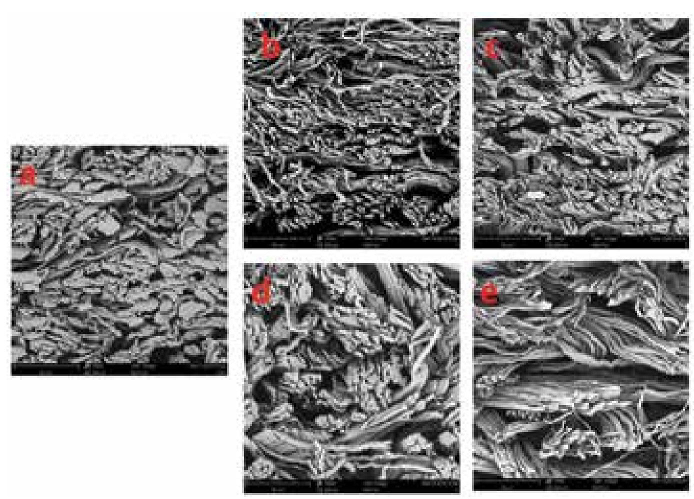

Figure 4. SEM analysis of chamois leathers control (a), BPO (0.25-b, 0.5-c, 0.75-d, 1%-e).

SEM Analysis of the Chamois Leathers

SEM analysis was carried out to understand the fiber alignment of the experimental and control chamois leathers. Fiber alignment of control leathers have been found to be compact whereas experimental leathers shows more opened structures, compared to control leathers. Fiber alignment in experimental leathers were widely aligned which indicate more porous structure, which is a desirable quality of a good chamois leathers shown in Figure 4. Also, the plausible reason for higher water absorption capability of the experimental leathers might be due to the ability of the polymerized oil to hold the collagen fibers from sticking together. Hence the extent of fiber separations increased with the increase in the percentage of oxidizing agent.

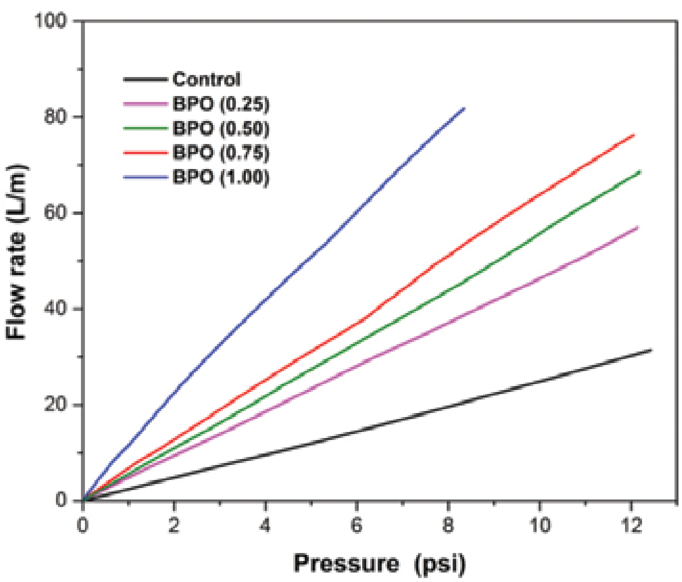

Figure 5. Porometry analysis of chamois leathers.

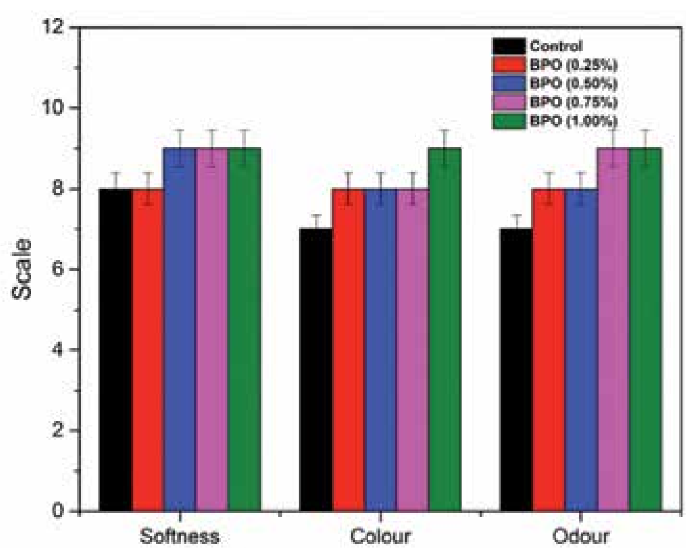

Figure 6. Organoleptic properties of chamois leathers.

Porometry Analysis of the Chamois Leathers

Porosity of chamois leathers were analyzed to understand the pore structure of the matrix. From Figure 5, it can be observed that the porosity of the chamois leathers increased with the use of benzoyl peroxide with varying percentages. Flow rate (liter per minute) of the experimental leathers increased drastically with application of small amount of pressure (1-12 psi) on the leather samples. It can also be concluded that the leathers made using benzoyl peroxide exhibited higher porosity compared to control leathers, this can further be strengthened from the SEM analysis, where the fiber alignment was more open in the case of experimental leathers.

Organoleptic Properties of Chamois Leathers

Organoleptic properties of chamois leathers were evaluated for softness, color and odor. From Figure 6, it can be noticed that the softness of chamois leathers improved with increase in percentage of oxidizing agent, better softness was achieved when higher percentage of oxidizing agent was used in making chamois leather. Similarly, color of the experimental chamois leathers were lighter yellow compared to golden yellow of the control leathers when the percentage of oxidizing agent was increased to 1%. Chamois leathers were made, using fish oil as tanning agent, hence odor is one of the important quality to be assessed. Although the unreacted excess fish oil from the process is removed by alkali washing, there is a chance for the residual oil to be left in the skin.

Table III

Physical testing data of chamois leathers.

S.No	Sample	Tensile Strength N/mm^2	Elongation (%)	Water Absorption (%)
1	Control	11±0.5	73±2	464±10
2	BPO (0.25%)	13±0.5	70±5	467±10
3	BPO (0.50%)	16±0.5	78±2	504±10
4	BPO (0.75%)	17±0.5	76±1	585±10
5	BPO (1.0 %)	18±0.5	72±5	587±10

Conclusions

In the present study, we have shown the use of benzoyl peroxide as an accelerant to oxidize fish oil in chamois making. It was also shown that the time required for making chamois leather was significantly reduced from 15 to 4 days with the use of benzoyl peroxide as oxidation aid. Water absorption capability increased by 1 to 26 % compared to convention 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. It can be concluded that the use of benzoyl peroxide in chamois making not only reduces time but also have positive benefits on final quality of leathers.

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