STUDIES ON CHAMOIS TANNING - AN INVESTIGATION USING MODIFIED FISH OIL

by

S. HARI KRISHNAN, V. JOHN SUNDAR, N. VEDARAMAN, V. HARI BABU, C. MURALIDHARAN*, AND S. SADULLA

Central Leather Research Institute

ADYAR, CHENNAI - 600 020, INDIA

ABSTRACT

There is growing demand for chamois leather in the global market. The conventional material and methods often lead to inconsistent results. The odour of fish oil in chamois leather poses aesthetic problems. In order to minimise the odour and improve the water absorption characteristics, the fish oil has been esterified with various grades of poly ethylene glycol (PEG). The chamois leathers processed using the modified fish oil samples had better functional properties and the paper highlights the results obtained.

INTRODUCTION

The bulk of chamois leather is used as wash leather for cleaning windows, car bodies and similar surfaces where its particular merit is its softness and high water absorption. As a wash-leather for cleaning, the chamois skin must be very soft so that it does not scratch the surface to be cleaned. Any grit encountered in the cleaning process becomes enmeshed in the fibrous structure, thus minimising its scratching potential. The leather must wet back immediately on immersion in water and absorb a large bulk of water. The dirt cleaned should be easily removed from the leather by simple rinsing and wringing in water. It is important that wet leather can be easily wrung out by hand. The wrung out leather is used for polishing the surface, which involves rapid absorption of any dampness or drops of water on the surface. On subsequent drying it should retain these properties for further use.[1] Chamois leathers, conventionally made are associated with drawbacks such as non-uniformity due to variations in distribution and smell associated with fish oil.

In order to overcome the odour related problems and enhance the water absorption characteristics of the chamois leathers, the fish oil has been esterified using polyethylene glycol (PEG) of varying molecular weight. The results obtained using the modified fish oil are presented in this paper in comparison with conventional chamois leathers.

EXPERIMENTAL

Materials used for this study

Industrial grade cod fish oil and analytical grade PEG of molecular weight 200, 400 and 600 were used for this study.

Iodine Value

Iodine value of the raw fish oil and esterified fish oil were determined using Hanus method.[2]

Procedure for esterification

150 grams of fish oil was refluxed for 5 hrs at a temperature of 220 - 230 °C with 50 grams of PEG. The product obtained was used for tanning studies.

Thin layer chromatography

The oil sample treated with PEG were qualitatively analysed using TLC (Polygram SIL G/UV precoated plastic sheets of 0.25mm silica gel thickness) with chloroform as solvent and n-hexane/petroleum ether/acetone/methanol mixture in the ratio of 6:2:1:1 as eluent. The plates were exposed to UV for identification. The raw fish oil, PEG and PEG treated oil were simultaneously run to identify the chemical changes occurred.

Process Details

The typical process adopted for chamois leather making in the present study is given in the Appendix.

Microscopic studies of chamois leathers

Cross sections of experimental and control leathers were examined for changes in fibre structure and packing using FEI, Quanta 200 Scanning Electron Microscope. Leather samples were gold coated (Edwards E306 Sputter coater device) before SEM analysis.

SEM analysis was carried out at two different magnifications (X 150, X 500).

*corresponding author - phone: +91-44-24915730; fax: +91-44-2491 1589; email: cmurali62@yahoo.com

Physical testing methods

The following physical tests were carried out as per official methods.[3] Water absorption (SLP 19,IUP 7, Method 18), Sink test (IS 1017:1983 BIS), Stitch tear strength (IS 5914:1970LP-8), Tongue Tear Strength (SLP 7,IUP 8, Method 6) and Shrinkage Temperature. (SLP 18,IUP 16)

Results and Discussion

Characterisation of fish oil:

The iodine value of the raw fish oil and the modified fish oil samples are given in Table I. The values indicate that there is no major change in iodine value of the PEG treated samples thereby providing opportunity for using them for chamois making. However the odour of the oil had significantly reduced. The PEG treated samples were soluble in water confirming the formation of esters, which has been ascertained by TLC (see Figure 1). The UV irradiated chromatogram indicates that the fish oil has been esterified with PEG, though traces of raw fish oil were still present in some samples The RF values for fish oil-PEG 200, 400 and 600 esters were 0.307 (E1), 0.25 (E2) and 0.4 (E3) respectively. The RF value for fish oil was between 0.82-0.9 (0.89, 0.82,0.86). PEG 200, 400 and 600 could not be identified by UV radiation of the chromatogram. Typically the reaction between fish oil and PEG is expected to follow the scheme shown below.

Shrinkage Temperature:

The shrinkage temperature of leathers obtained by conventional and esterified fish oil tanned leather is given in Table II. The leather tanned with modified fish oil had relatively higher shrinkage temperature than the control.

TABLE I
Iodine Value of Oils

Experiment	Iodine Value
Fish oil (control)	130±2
Fish Oil esterified with PEG200	120±2
Fish Oil esterified with PEG400	122±2
Fish Oil esterified with PEG600	126±2

[Average from two determinations]

TABLE II
Shrinkage Temperature of Leathers

Experiment	Shrinkage temp (°C)
Fish oil (control)	83 ± 2
Fish Oil esterified with PEG200	89 ± 2
Fish Oil esterified with PEG400	90 ± 2
Fish Oil esterified with PEG600	92 ± 2

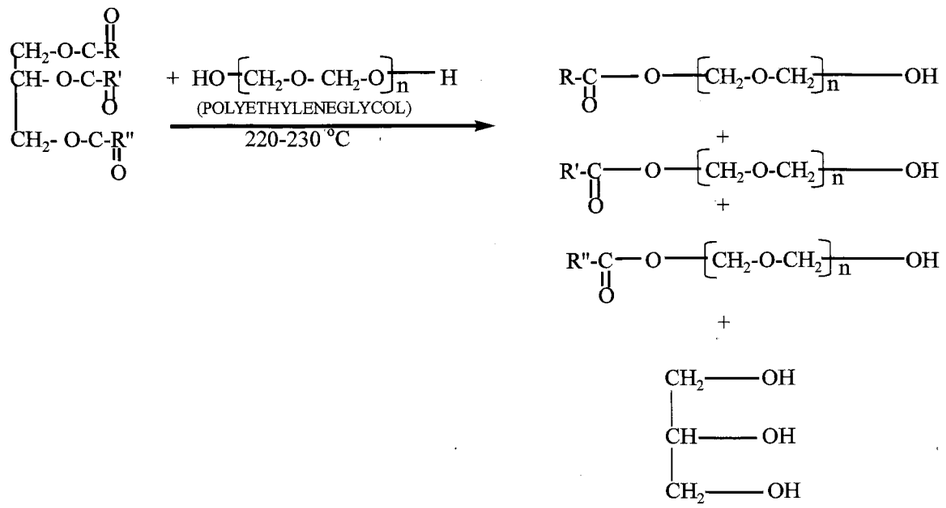
[Average from two determinations]

Sink Test:

The experimental leathers were able to absorb the water quicker than the control leathers as evidenced by the sink test results given in Table III. The leathers processed with fish oil modified with PEG 600 have sink test time of 50 sec compared to 2 min for conventional leathers. As PEG has the tendency to associate with water, esterification helps in higher uptake of water. Though the water absorption rate was higher, it was found that the leathers gave up water like the conventional chamois leathers.

Water absorption:

The leathers made using PEG modified fish oil had 5 - 15% higher water absorption than the fish oil as shown in Table



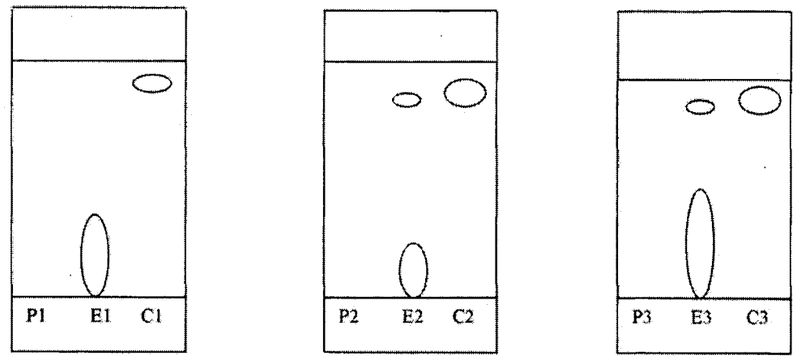


Figure 1: Thin layer chromatography of fish oil, fish oil-PEG esters and PEG 200, 400 and 600 (P1=PEG 200, E1=Fish oil esterified with PEG 200, P2=PEG 400, E2=Fish oil esterified with PEG 400, P3=PEG 600, E3=Fish oil esterified with PEG 600. C1, C2, C3 are raw fish oil)

TABLE III
Sink Test of Leathers

Experiment	Time (Sec)
Fish oil (control)	120±5
Fish Oil esterified with PEG200	90±5
Fish Oil esterified with PEG400	75±5
Fish Oil esterified with PEG600	50±5

[Average value of 3 tests]

TABLE IV
Water Absorption of Leathers

Experiment	%(w/w)
Fish oil (control)	300 ± 5
Fish Oil esterified with PEG200	315 ± 5
Fish Oil esterified with PEG400	325 ± 5
Fish Oil esterified with PEG600	350 ± 5

[Average value of 2 tests]

IV. This is likely to enhance the performance characteristics of the chamois leathers.

Visual assessment of leather tanned with fish oil & esterified fish oil:

The visual assessment of leathers shown in Table V indicates that leathers treated with fish oil modified with PEG 600 possessed properties as that of conventional leathers but had very less odour. The modified oil is likely to overcome the odour related issues when employed in large scale.

The physical properties of leathers for conventional fish oil tanned and esterified fish oil tanned leather are shown in Table VI. The experimental leathers had comparable strength characteristics.

The SEM analysis carried out for raw fish oil tanned and esterified fish oil tanned leathers given in Figure 2 and 3.

TABLE V
Visual Assessment of Leathers

Experiment	Softness	Fluffiness	Surface characteristics	Appearance	Odor
Control	7	6	8	7	4 - 5
Fish oil esterified with PEG 200	6	7	8	8	6 - 7
Fish oil esterified with PEG 400	5	5	4	8	6 - 7
Fish oil esterified with PEG 600	7	7	8	7	8 - 9

(On Ten Point Scale 0-poor 10-excellent) The data is the mean of the values given by three experts

TABLE VI
Physical Property of Leathers

Properties	Control (Fish oil)	Fish oil Esterified with PEG 200	Fish oil Esterified with PEG 400	Fish oil Esterified with PEG 600
Tongue tear strength (Kg/cm thickness)	51.2 ± 0.5	52.0 ± 0.5	66.7 ± 0.5	54.0 ± 0.5
Stitch tear strength (Kg/cm thickness)	125.3 ± 0.5	189.3 ± 0.5	199.8 ± 0.5	142.4 ± 0.5

[Average from two determinations]

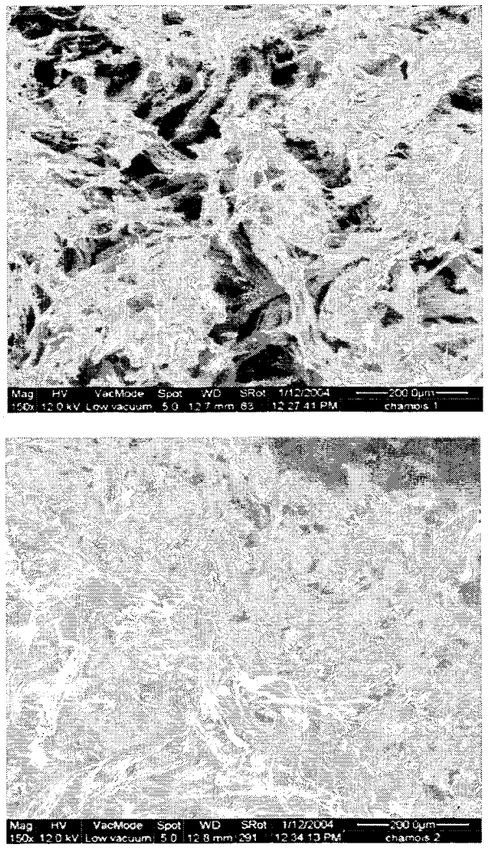


Figure 2. - Scanning Electron Micrographs (x150) of cross section of chamois leather *Top: Control; Bottom: Experiment*

The micrograph indicates that leathers tanned with modified fish oil had opened up structure and were porous in nature, probably indicating reason for increased rate of water absorption characteristics.

Conclusions

This experimental study shows that the use of esterified fish oil enhances the rate of water absorption significantly as evidenced by sink test, which improve the performance of the leathers. In addition the leathers had higher water absorption (upto 15%), which enhances the functional properties of the leathers. Another significant observation noticed was substantial reduction in odour in case of tanning with esterified fish oil. The microscopical analyses carried out corroborate the Physico-chemical test results. The best results have been obtained using fish oil esterified with PEG 600.

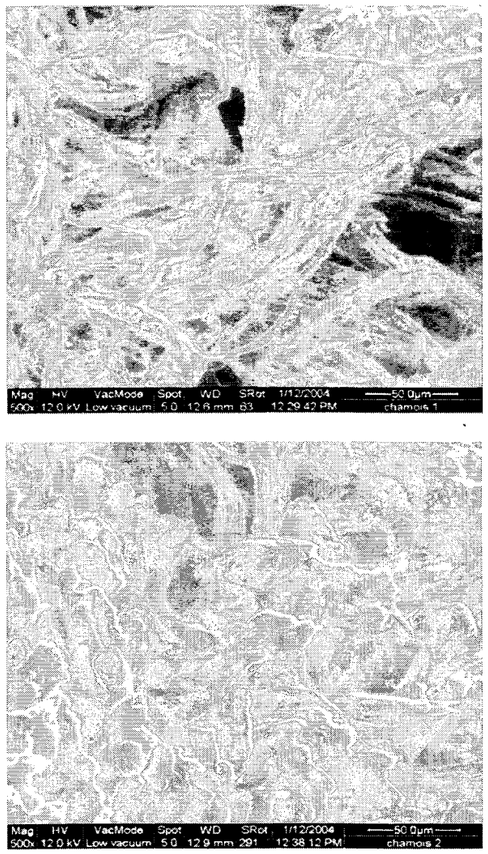


Figure: 3 - Scanning Electron Micrographs (x 500) of cross section of chamois leather *Top: Control; Bottom: Experiment*

References

1. J. H. Sharpouse, "Theory and practice of modern chamois leather production", JSLTC, Vol 69 , Pg. 29-43, 1985
2. L. V. Cocks and C. Van Rede, Laboratory handbook for oils and fat analysis, Academic Press, 1966
3. SLTC official methods of analysis.

Appendix

Process Details:

Raw material: Wet salted goat skins weighing one kilo per 5 sq ft piece have been used for the study.

Soaking: (% on raw weight)
The skins were washed three times with 300% water with an interval of 2 hrs.

Liming:

Lime	10%
Sodium Sulphide	2%

Made into a paste using 25% water and applied on flesh side and left over night. Next day the skins were unhaired.

Reliming:

Lime	10%
Water	100%

Kept in the reliming bath for 4 days. Next day taken for fleshing and pelt weight was noted.

Deliming: (% based on pelt weight)

Water	100%
Ammonium chloride	1%
Run for 30 min	
Bate	1%
Run for 60 min	

Completion of deliming was checked and drained out.

Washing:

Water 100%
Run for 10 min and drain

Formaldehyde Tanning:

Formaldehyde	2%
Water	100%
Run for 60 min	
+ Soda ash	0.5%
Water	5% - 3x10'+30 min

The pH was adjusted to 8.5 and the skins were piled for 12 hours. Then the grain layer was shaved and taken for oil Tanning.

Oil tanning: (% on shaved weight)

Experiment No: 1	
Raw Fish oil	20%
Calcium Carbonate	4%
Experiment No: 2	
Fish oil Esterified with PEG 200	20%
Calcium Carbonate	4%
Experiment No: 3	
Fish oil Esterified with PEG 400	20%
Calcium Carbonate	4%
Experiment No: 4	
Fish oil Esterified with PEG 600	20%
Calcium Carbonate	4%

The oil was applied on both sides of the skins uniformly. The skins along with the balance of the oil were drummed for 6 hours and then taken for oxidation. After completion of oxidation, the leathers were taken to alkali washing.

Alkali Washing:

Water	400%
Soda ash	0.25%
Wetting agent	0.5%

The leathers were washed three times with this float and dried on hooks. Then the leathers were buffed on the flesh side with different grit papers and then dedusted.