Metal-Free Combination Tanning with Replenishable Polyphenols and Marine Oil

by

John Sundar V.* and Muralidharan C.

Leather Process Technology Department, CSIR-Central Leather Research Institute,

Chennai, India.

Abstract

In line with the resurgence of natural products in the global manufacturing industry, the leather industry is also relooking the increased use of organic materials. To exploit the benefits of the vegetable tanning materials and to couple with suitable organic material for overcoming the inherent shortcomings of vegetable tanning materials, studies were undertaken. Tanning materials like raw fish oil have advantageous properties to impart on leather such as softness, lightweight, and washability characteristics. Hence studies were undertaken on polyphenol-fish oil combination tannages.

The quantities of wattle and fish oil and process conditions were standardized. The study indicated that the oxidation of fish oil could take place in the presence of vegetable tannins. The leathers tanned by this combination tanning system could be converted into garment leathers of rich shades and possessed good strength and physical properties. Propelled by encouraging results, investigations were also made on the nature of interaction between vegetable tannins and fish oil with collagen. It was also observed that the vegetable tannins probably do not hinder the oxidation of oil. To sum up, the study leads to the development of a viable, versatile organic tanning system to gain eco-acceptability for the leather manufacturing process.

Introduction

There has been an increasing demand among consumers for metal free garment leathers with improved functional properties such as washability in recent years. Demand for these washable and dry-cleanable leathers continues to increase dramatically and this trend may continue. The latest technological developments in leather research made this increasing market trend possible at affordable production and consumer costs with minimal impact on environment.

Vegetable tannins are extracted from plant leaves, barks, fruits, roots of plants or trees and tannins are water-soluble polyphenolic compounds having molecular weight in the range of 500-3000 Daltons. Besides the usual reaction of phenols, vegetable tannins can convert animal/hides and skins into leather producing relatively dense, firm or solid leather. The primary purpose of tanning is to make collagen resistant to heat, hydrolysis, and resistant to microorganisms' action. Vegetable tannins are colloidal, amorphous, astringent in taste and acidic in nature. They consist of large polyphenol molecules with some acidic groups and numerous secondary functions. The acidic groups may combine with the basic groups of the protein displacing the water by hydration. Generally, acidic conditions (low pH) favor vegetable tannin fixation by increasing the protein basic groups' ionization.

The leathers processed through vegetable tanning have advantages such as compatibility with human skin, comfort and high dimensional stability. The tanning methodology adopted also affords viable treatment and disposal of spent liquors. However, the drawbacks associated with vegetable tanned leathers are lack of softness, poor fastness properties and high susceptibility for fungal growth.[1]

The conversion of skin into leather by fats and oils is undoubtedly one of the most primitive methods used by the early races in different parts of the globe. The oil-tanned leathers are lightweight, soft, air-permeable and resistant to washing.[2-4] Hence in the present work, to take advantage of both tanning agents, fish oil and organic tannins of myrobalan (hydrolysable) and wattle (condensed) are studied in detail.

Materials and methods

Wet salted goat skins of Indian origin in the weight range of one kilogram per skin, industrial grade wattle and myrobalan tannins and fish oil (Cod oil) were chosen for the tanning studies.

Tanning experiments

The skins were processed conventionally up to deliming and tanning experiments were carried out as per the procedure given below. In order to monitor the changes effectively, the skins were cut into two halves, one half was tanned by conventional vegetable tanning and the other using vegetable–oil tanning system, to avoid skin to skin variations. Based on shrinkage temperature, physical properties and

*Corresponding author email: johnsundar70@yahoo.co.uk

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visual assessment of leathers the quantity and other parameters were standardized.

Tanning process for control

The depickled pelts (pH 4.8-5.0) were processed as below.

Water	50%	
Pretanning syntan	1%	drum for 60 min
Myrobalan or Wattle powder	20%	drum for 6 hrs
Formic acid	1%	3×10+drum for 60 min

The tanned leathers were set, hooked to dry, staked and buffed as being done for vegetable tanned leathers conventionally.

Tanning process for experiments

The delimed pelts (pH 7.5-7.8) were conditioned and processed as below.

Water	50%	
Fish oil	10%	drum for 3 hrs
Myrobalan or Wattle powder	10%	drum for 6 hrs
Formic acid	1%	3×10+drum for 60 min

The tanned leathers were set, hooked to dry, lightly staked and buffed as being done for vegetable tanned leathers.

Determination of iodine value

Industrial grade fish oil was analyzed for iodine value by Hanus method and standard official methods were followed for acid value and saponification value determinations.[5]

Shrinkage temperature

Shrinkage temperature of control and experimental leathers was analysed with Theis shrinkage tester to evaluate tanning efficiency.

Physical properties of leather

Organoleptic properties were evaluated by practising leather technologists for the softness and fullness parameters. In this study, tensile strength, elongation at break and stitch tear resistance of leathers were determined by adopting official procedures.[6,7] The leathers were chosen of even thickness and same region for testing for reliable results.

Scanning electron microscopic analysis

The fiber structure of the tanned leathers was studied using SEM analysis. Leather samples were coated with gold using an Edwards E 306 Sputter coater and analyzed by a Cambridge stereoscan S 150 scanning electron microscope.

Pollution load

The control and experimental process liquors from tanning operation was quantitatively collected and analyzed for BOD, COD, Cl^-, TSS and TDS using standard analytical procedures.[8]

Results and discussion

The combination tannages of both fish oil with myrobalan and fish oil with wattle tanning agents were studied in detail. Preliminary experiments revealed that pre-tannage with fish oil considerably reduces the fixation of vegetable tannins and the degree of tannage is also reduced. Conventionally, vegetable tannins, are fixed to non-ionic groups of collagen. The affinity of keto-imide linkages for vegetable tannins had been indicated as a decisive factor in vegetable tanning. Several researchers had shown the precipitation of tannins by polyvinyl pyrrolidone due to —CO-NH-grouping. Thus, the decreased affinity shown by vegetable tannins (Catechol type) for an oil pretanned protein would indicate that oil tanning also involves the same reactive groups, namely the hydrogen bonding site CO-NH-groups of the polypeptide backbone and others.[9-11]

The possibility of the peroxides or hydroperoxides being bound by the secondary valency forces to the polypeptide backbone seems probable apart from the simultaneous fixation of some of the aldehydic products to the basic protein groups. Similarly, on pre tanning with vegetable tannins followed by oil tannage, less oil fixation is observed. As mentioned earlier, most hydrogen bond sites are blocked with vegetable tannins, the peroxides formed may not have the same number of sites for binding as regular oil tanning.[12-14]

Shrinkage temperature of tanned leathers

Various experiments have been carried out to optimize the quantity of oil and tannins and also to standardize the stage of offer. It has been known that during vegetable tanning, maximum amount of tannins are fixed unipoint and only a small portion fixed bi-functionally as —CO -.OH — V — O.. HO — (Or) — CO.. OH — V — OH...OC — between the — CO of one chain and — OH of hydroxypridine of another chain or between the —CO of one chain and the — CO of another chain as shown above. The results show the oil with wattle combination tanning resulted in higher shrinkage temperature compared with conventional wattle tanned leather (Table I). This could be due to formation of additional cross links by oil during combination tanning. Skins tanned with myrobalan and oil combination exhibited lower shrinkage temperature, less fullness characteristics probably because of inherent nature of hydrolysable polyphenols.[15,16]

Table I

Shrinkage temperature of tanned leathers

S.No	Quantity of Tannins (%)	Quantity of fish oil (%)	Shrinkage Temperature (°C)
1	Myrobalan - 20%	-	65±1
2	Myrobalan - 10 %	5%	70±1
3	Myrobalan - 10 %	10 %	74±1
4	Wattle - 20 %	-	83±1
5	Wattle - 5 %	10%	78±1
6	Wattle - 10 %	10 %	88±1
7	Wattle -15 %	5 %	84±1

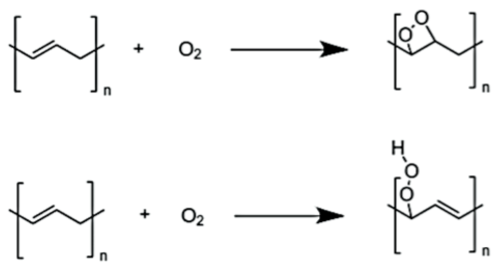

Figure 1. Fish oil degradation process

Wattle 10% and fish oil 10% combination tanned leathers possessed better thermal strength and functional properties when compared with other experimental leathers.

Iodine value

The rate of oxidation of oil is related to the iodine value of the oil. Obviously, the higher the iodine value, the greater would be the number of reactive centres available for oxygen absorption, leading first to the formation of peroxides or hydroperoxides as shown in

Table II

Iodine value

S.No	Type of tanning	Iodine value
1	Raw fish oil	140
2	Oil tanned leather (Fish oil – 20%)	80*
3	Myrobalan - 10% : Fish oil – 10% tanned leather	70*
4	Wattle - 10% : Fish oil – 10% tanned leather	60*

(*oil extracted from tanned leathers)

Figure 1, as a result of chain reactions then to further degradation into other products.

The results shown in Table II confirm that the oxidation of fish oil could take place in the presence of vegetable tannins. From the study, it is observed that vegetable tannins do not hinder the oxidation of fish oil, which is probably due to the lower percentage of vegetable tannins offered and thereby providing certain reactive sites of collagen, free to react with the peroxides or hydroperoxides and aldehyde products which formed during the oxidation of fish oil.[17]

Organoleptic properties

The leathers were evaluated for their organoleptic properties and found wattle 10% with fish oil 10% had better properties than other experimental leathers as described in Figure 2. Because of better oil lubrication the fiber matrix have better splitting and resulted in softness and fullness and less tightness compared with wattle tanned leather. The SEM images too confirmed the results.

Physical strength characteristics

The quality of leather is determined by its physical structure, chemical composition, and mechanical stability. The leathers tanned with wattle alone and wattle with fish oil were converted

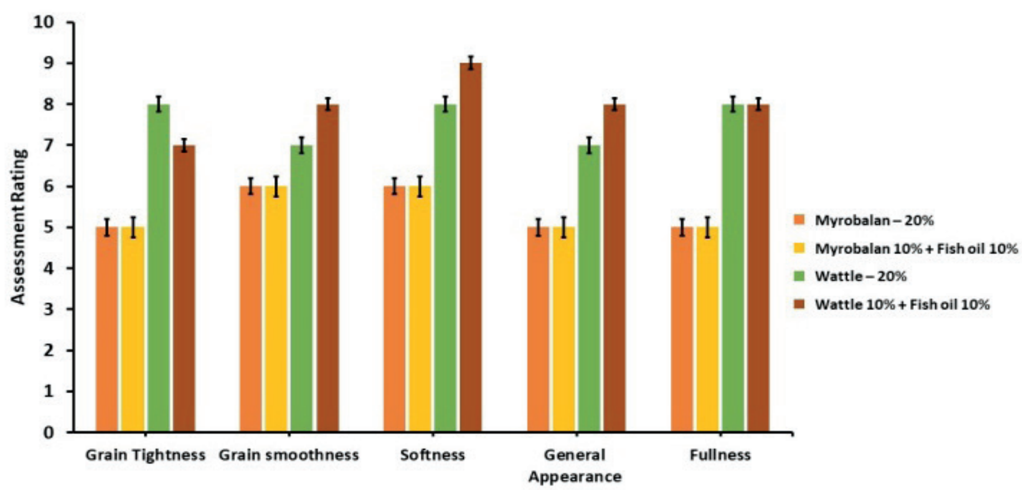

Figure 2. Organoleptic Properties of leathers

Table III
Physical strength characteristics

Tannage	Tensile strength (Kg/cm²)	Elongation at break (%)	Tear Strength (Kg/cm)
Wattle - 20%	200 ± 3	40 ± 2	25 ± 2
Wattle - 10% Fish oil – 10%	285 ± 2	52 ± 3	60 ± 5

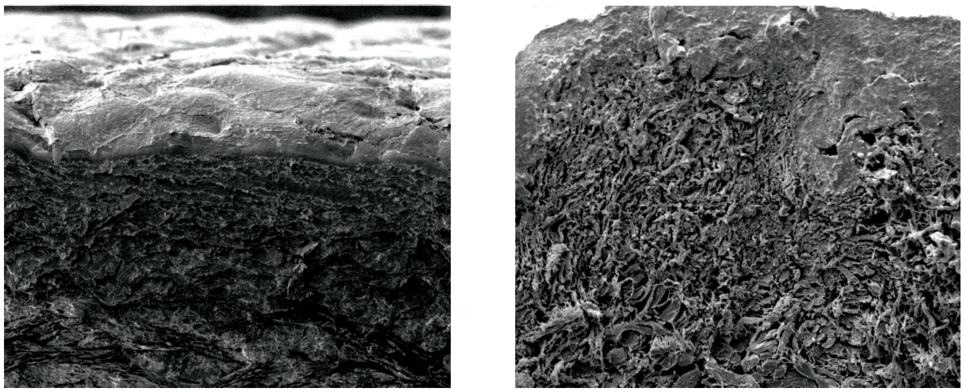

Figure 3. SEM of cross section of tanned leathers. **(3a)** Wattle tanned leather (500X) and **(3b)** Fish oil with wattle tanned leather (500X)

into crust leathers and subjected to mechanical strength testing. From the results of Table III, it is observed that the vegetable-oil combination tanning system had improved mechanical properties and could produce softer types of garment leathers with sufficient drape and softness. The leathers also possessed good appearance and feel with physical properties like tensile strength, tear resistance, etc.

Scanning electron microscopic analysis

A morphological study was carried out for the experimental leathers in comparison with wattle tanned leathers to show the effect of condensed tannin and fish oil combination tanning in the fiber bundles (Figures 3a & 3b).

From the cross-section micrographs, it is clear that the experimental leather fibers were separated from one another, but in the case of conventional wattle tanned leather fiber aggregation can be noticed.

Effluent characteristics

The spent liquors of tanning were analyzed for their impact on environment as expressed by parameters such as BOD, COD, TDS, etc. Conventional vegetable tanning requires pickling and repickling processes which generates huge amounts of chlorides and TDS as shown in Table IV. But in the experimental process, the skins were treated with fish oil after deliming which is at neutral pH. Hence the results indicate huge reduction in effluent parameters of chlorides and TDS. It's proven that fish oil-wattle combination tanning system is eco-friendly and skin friendly.

Table IV
Spent liquor Characteristics

Tannage	Biochemical Oxygen Demand	Chemical Oxygen Demand	Chlorides	Total Suspended Solids	Total Dissolved Solids
Wattle - 20%	6000 ± 30	20000 ± 30	55000± 30	7550± 20	47500 ± 50
Wattle - 10% Fish oil - 10%	3550 ± 25	9750 ± 30	7500± 30	5600± 20	18050 ± 25

Conclusion

Extensive studies have been carried out using vegetable tanning agents - wattle and myrobalan along with fish oil. Based on the analytical results and obtained leathers, it is found that the leathers possessed combined advantage of both the tanning agents. The results showed oil with wattle tanned leathers had higher shrinkage temperature than conventional vegetable tannage. The fringe vegetable tannage probably provided an opportunity for the oil to oxidize even in the presence of vegetable tannins, as inferred from the iodine value of oil extracted from the tanned leathers. Further the amount of vegetable tannins used in the new system is only 50% of the conventional system. Hence the combination tanned leather color has not darkened like conventional leathers. Also, the leathers produced through this tannage were able to be converted into variety of finished leathers, indicating potential versatility of the system with excellent organoleptic and strength properties. The combination tanning system studied could emerge as a viable alternative for conventional tanning systems, as both the tanning materials used organic in nature and are replenishable sources.

References

1. Sharphouse J.H. (1983) Leather Technicians Handbook. Northampton, UK: Leather Producers Association.
2. Benson, G.O.; Research Advances in Oil Tanning Technology, *JALCA* **116**, 3-10, 2021.
3. Gubitz, G.M., Mittelbach, M and Trabi, M; Exploitation of the tropical oil seed plant Jatropha curcas. *Bioresour Technol* **67**, 73–82, 1999.
4. Wainaina, P.N., Tanui, P and Ongarora, B.; Extraction of Oil from Tannery Fleshings for Chamois Leather Tanning, *JSLTC* **103**, 159-162, 2019.
5. Cocks L, Rede CV (1976) Laboratory Handbook for Oils and Fat Analysis. Academic Press, London.
6. International Commission of Physical Testing, IUP: 6, (2000), Measurement of tensile strength and percentage elongation. *JSLTC* 317-321.
7. International Commission of Physical Testing, IUP: 8, (2000) Measurement of tear load-double edge tear. *JSLTC* 327-329.
8. Eaton, AD, Clesceri, LS, Greenberg, AE (1995) Standard methods of the examination of water and wastewater, 19th Edition APHA., Washington D.C.
9. Mathur, B.N. Theory of oil tannage, *JALCA* **22**, 2-44, 1927.
10. Sharphouse J.H Theory and practice of modern chamois leather production. *JSLTC* **69**, 29-43, 1985.
11. Covington A, (2009) Tanning Chemistry: The Science of Leather. Cambridge, UK: Royal Society of Chemistry.
12. Covington, A.D. Theory and mechanism of tanning: Present thinking and future implications for industry. *JSLTC* **85**(1):24-34, 2001.
13. Mattei, V and Roddy, W.T.; The use of fish oils for fat liquoring leather. Menhaden oil and cod oil fat liquors. *JALCA* **54**, 12-30, 1959.
14. Sundar, VJ and Muralidharan, M.; An Environmentally Friendly Mineral-Free Tanning of Animal Skins – Sustainable Approach with Plant Resources, *Environ Proces* **7**, 255–270, 2020.
15. Vedaraman, N., Sandhya, K.V., Sundar, V.J., Velappan, K.V and Muralidharan, C.; Studies on Use of Fish Oil Methyl Ester for Chamois Leather Manufacture, *JALCA* **107**, 422-428, 2012.
16. Suparno, O.N.O and Kartika, I.K.A.A.; Chamois leather tanning using rubber seed oil. *JSLTC* **93**, 6, 2000.
17. Sundar, V.J., Vedaraman, N., Balakrishnan P.A and Muralidharan, C.; Chamois Leather – An approach for accelerated oxidation, *JALCA* **88**, 256-259, 2004.