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SOFT LEATHERS FROM *HIMANTURA* STINGRAY SKINS

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Summary

The preparation of soft leathers from chondrichthyes fish such as stingray is unfamiliar to tanners processing conventional animal skins. The dorsal portion of stingray skins with calcified denticles has a very attractive and beautiful appearance. Due to calcification of the skeleton, stingray skin is very hard and tough and retains its hardness even after tanning. The calcium content of raw stingray skin has been determined by atomic absorption spectroscopy. SEM-EDAX investigations have been made on stingray denticles to reveal the mineral and structural characteristics. To prepare soft leathers from stingray skins a modified chrome tanning process has been adopted for better fibre opening and separation. Comparison skins were also processed by conventional chrome and vegetable tanning methods. SEM microscopy supported by histological examination of stingray skins and leathers supported the effectiveness of the new process.

Introduction

Conversion of fish skins into leather has gained interest among tanners due to their attractive and unique grain structure possessing high market value. Fish skins are generally considered weak and it is difficult to get raw material of uniform sizes. Unlike other fish, the stingray belongs to the cartilaginous family, they are found both in salt and fresh coastal waters including some rivers. The thickness of the raw skin after green fleshing ranges from 2-5mm with a beautiful grain structure, and it is traditionally used for the production of decorative leather for ornamental goods. Stingray skins have denticles[1] instead of scales, which give an attractive appearance to the finished leather. The stingray reaches a maximum size of just over 6 feet wide, 4 feet long, and about 100 pounds in weight with the females being larger than the males.[2]

The stingray skin is composed of various types of cartilage surrounded by a fibrous perichondrium. Calcified cartilage made by the calcification of Type II collagen, is the stiff material present in the skin of many chondrichthyean fishes.[3] The dorsal denticles of the *Himantura* family increase gradually in size with age. Denticles occur in two distinct sizes with smaller denticles intermingled between larger ones.[4]

Apart from producing ornamental goods from stingray leathers an attempt has been made at CLRI to utilize the stingray leathers for massage footwear, using the stingray leather as insole/insock material.[5] The leather with its unique grain structure has been used for the outer covers of steering wheels, motor cycle grips, tennis racket and cricket bat handles where the stingray leather imparts improved grip and could be used to stimulate the reflex points[6] on our palms. There are only a few stingray tanners in India and most of the raw skins are exported as dried fish.

A modified chrome tanning system to convert stingray skin into soft leather has been developed, the delimed pelts were treated with hydrochloric acid and the pickling process was repeated twice with intermediate ageing. The pickled pelts were then treated with fatliquor along with basic chromium sulfate.

Experimental procedure

Materials and methods

Stingray skins were collected from local fish markets in Chennai, Hydrochloric acid was purchased from SD Fine Chemicals, Chennai, Microbate was purchased from Tex Biosciences (P) Ltd., (previously Textan Chemicals (P) Ltd.), Chennai and other chemicals were purchased locally.

Determination of calcium content

The stingray skins were green fleshed, washed and samples were collected from middle and side portion of the skin. The calcium content in the raw stingray skin was determined by atomic absorption spectrophotometer (AAS). The sample was prepared as per the AOAC method.[7] Initially a known quantity of sample was ashed at 550°C and the ash was treated with 15ml of 1:1 HCl, filtered through a Whatmann No. 1 filter paper. The filtrate was washed with hot water, cooled and made up to 100ml with distilled water for AAS analysis.

Scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analysis of stingray denticle

A piece of denticle was cut from the stingray for SEM and EDX analysis using an Hitachi S-3400 N instrument. The sample was sputter coated with gold (Hitachi E-1010).

Tannage

Raw Material: Fresh stingray skins.
Green Flesh and rinsed with water for 15'.
Depigmentation: Dark brown coloration is invariably found on the entire dorsal portion of the skin which may not be removed in liming. It is a form of contamination and is not the natural skin colour.
A sulphide rich paste is applied to remove the pigments. Sodium sulphide flakes 4% (percentage based on green fleshed weight). Water 5%. Left for 12 hours or overnight. Next day, the skins are rubbed with a gunny sack or brush to remove the pigment (see Figs. 1 and 2).

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Fibre Opening: Lime 10%, Water 250%. Left for 3 days in a pit. Handled twice a day.

The skins were fleshed and the weight was noted. After weighing, the skins were piled grain to grain and secured with staples or stitched along the outside edge to protect the denticles of stingray from the mechanical action of the drum. This method of processing also avoids the folding of the skin and protects the unique grain structure from damage.

Deliming and Bating:
Water 100%
Ammonium chloride 1.0% drummed for 30'
Microbate 2% 45'
Fleshed and washed thoroughly.
After deliming the various tanning trials carried out were listed below.

Experiment 1. Partial pickling + Vegetable tanning
Experiment 2. H_2SO_4 pickling + Chrome tanning
Experiment 3. HCl Pickling + Chrome tanning + Fatliquor-modified process.

The process details are given in Table I.

Post-tanning

All the tanned leathers were shaved and then neutralized to pH5.5 before dyeing with 2% acid dye followed by fatliquor, retan, dry and buff.

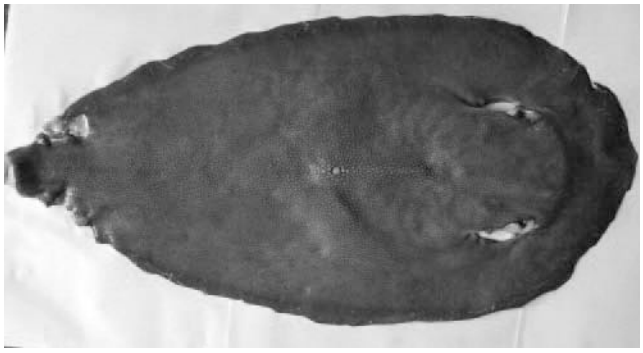

Figure 1. Showing pigment contamination. Before treatment.

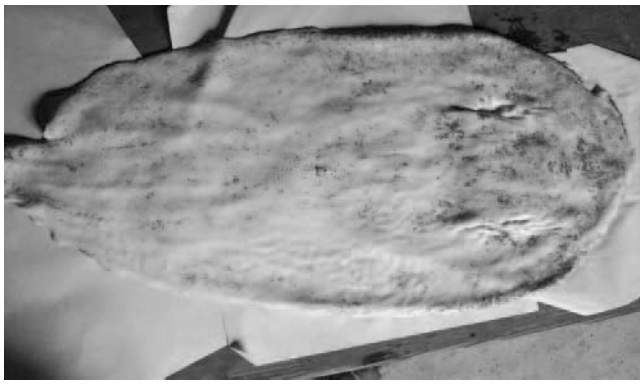

Figure 2. After treatment to remove pigmentation.

TABLE I
Stingray tanning trials

Experiment 1	Experiment 3	Experiment 3
Vegetable tanning (% based on pelt weight) Partial pickling Water 50% Salt 3% Formic acid 0.5% 2 x 10'+30' pH4-4.2. Drain. Pretanning syntan 3% 30' Wattle 10% 1hr. Wattle 10% 1hr. Myrobalan 5% 45' pH adjusted to 3.0-3.2. Drain, rinsed, piled overnight.	Chrome tanning (% based on pelt weight) Water 80% Salt 8% 10' Sulphuric acid 1% (in 10% water) 3 x 10' + 60' Leave over night. Next day add Sulphuric acid 0.5% (in 5% water) 2 x 10' + 30' pH2.8-3.0. Drain 50% pickle water. Add BCS powder 8% 90' Water 50% Sodium formate 1%(in 10% water) 30' Sodium bicarbonate 1% 3 x 10' + 60' (in 10% water) pH3.8. Drain, rinsed and piled overnight.	Modified Chrome tanning (% based on pelt weight) Water 100% Salt 10% 10' Hydrochloric acid 1% (in 10% water) 4 x 10'+ 60' Leave over night. Next day Hydrochloric acid 1% (in 10% water) 4 x 10' + 60' pH2.0. Leave over night in the bath. Next day the pelts were taken and piled for 10 days. Repickling Water 80% Salt 8% 10' Hydrochloric acid 1% (in 10% water) 3 x 10'+ 60' Pickle water 50% BCS powder 4% Cationic fatliquor 1% Nonionic fatliquor 1% Run the drum for 60' BCS powder 4% Cationic fatliquor 1% Nonionic fatliquor 1% Run the drum for 60' Water 50% 30' Sodium formate 1%(in 10% water) Sodium bicarbonate 1% 3 x 10' + 60' (in 10% water) pH 3.8 drain, rinsed and piled overnight.

Histological studies

Histological examination was carried out on the soaked, limed, bated and tanned stingray skins. Samples were taken and preserved in 10% formalin for 48 hours. The fixed samples were dehydrated in an aqueous alcohol series series (50 to 100%) and then cleared in xylene. Samples were finally embedded in paraffin wax and 10μm sections were cut on a microtome, mounted and stained with Van Giesen stain.

SEM examination of stingray leather

Samples measuring 5mm x 2mm were cut from the crust leather and mounted both vertically and horizontally on aluminium stubs before sputter coating with gold (Edwards E-306). The micrographs of the cross-section were obtained with the FEI-Quanta 200 microscope at an accelerating voltage of 15kV.

Physical testing and assessment of the leathers

The samples for physical testing were conditioned at 20 ± 2°C and 65 ± 4% RH for 48 hours. The tensile strength, and tear strength were determined as per IUP 6 and 8 methods respectively.[8,9] Lastometer testing was carried out as per method IUP 12.[10] The crust leathers were assessed for softness by an experienced leather technologist.

Results and discussion

Elemental and structural characterization of stingray skin.

Commercial tanners producing stingray leathers in India find that the leather is hard, especially in the middle part. This is due to the calcification of the stingray skin at the mature stage. The calcium content of the raw stingray skin determined by AAS method is given in Table II.

TABLE II
Calcium content of stingray skin

Sample	Calcium content as Ca (% w/w)
Middle of skin	6.6
Side of skin	5.2

The calcification in the middle layer of the skin is greater than in other parts of the skin - in the middle portion of the skin 6.61% Ca w/w and in the side portion it is 5.16% Ca w/w. To minimize the calcium content and to improve fibre opening and splitting the pickling process was modified. The pickle is repeated twice using hydrochloric acid followed by ageing, this completes the dissolution of Ca salts from the skin. During the first pickling, when it is left for overnight in the bath, the pH increases to around 5.0. due to the dissolution of calcium salts.

The EDX spectrum of a stingray denticle is shown in Figure 3. The EDX spectrum confirms that Calcium, Phosphorus and Nitrogen are concentrated in the denticle surface.

The scanning electron micrographs of a stingray denticle at a magnification of 100 000x and 300 000x are shown in Figures 4 and 5 respectively. The calcification of stingray denticle is very clear in the micrograph taken at higher magnification.

Histological studies

The optical microphotographs taken for the soaked, limed, bated and tanned stingray skins are set out in Figures 6-9. The microphotographs confirm that the stingray skins have compact parallel fibre bundles arranged in a lamellar manner. The compactness of the fibre bundles decreases in size during the bating stage but increases after tanning. Good fibre separation for softness depends on the interplay of tanning, and fatliquoring, for this main reason we added the fatliquor during tanning in the modified chrome tanning process (Expt. no. 3).

Effect of tanning system on the fibre structure

SEM cross-sections of vegetable tanned, chrome tanned and modified chrome tanned stingray leathers at magnifications of 80x and 500x are given in Figures 10-15. An SEM of the surface of vegetable tanned stingray leather at a magnification of 100x is given in Figure 16.

The micrographs confirm that the leathers produced with the modified chrome tannage have loose packing of fibre bundles. The modification of the pickling process and the fatliquor added in tanning have created a soft leather through improved fibre separation. The fibre bundles of

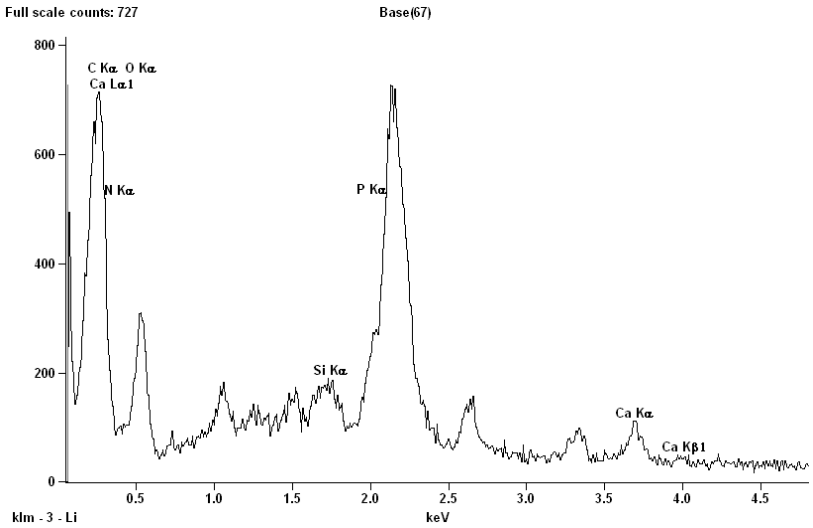

Figure 3. EDX spectrum of stingray denticle.

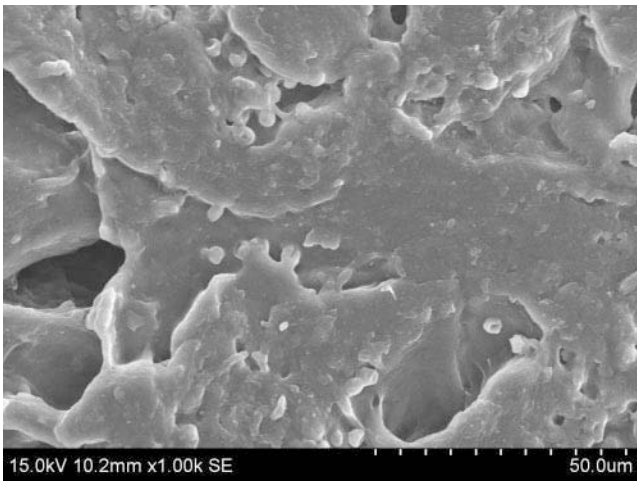

Figure 4. Scanning electron microphotograph of stingray denticle at 100 000x magnification.

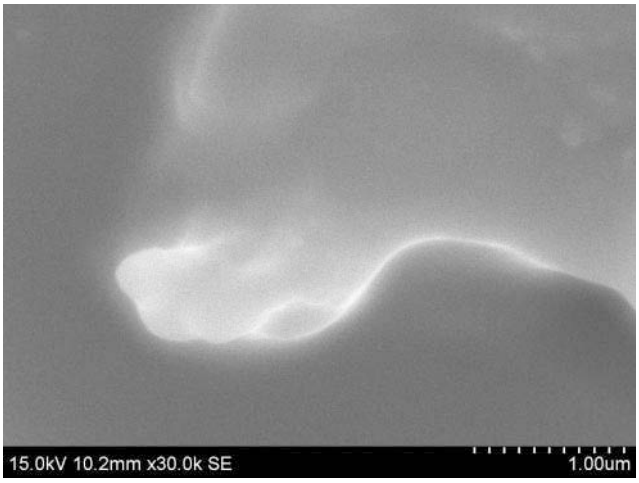

Figure 5. Scanning electron microphotograph of stingray denticle at 300 000x magnification.

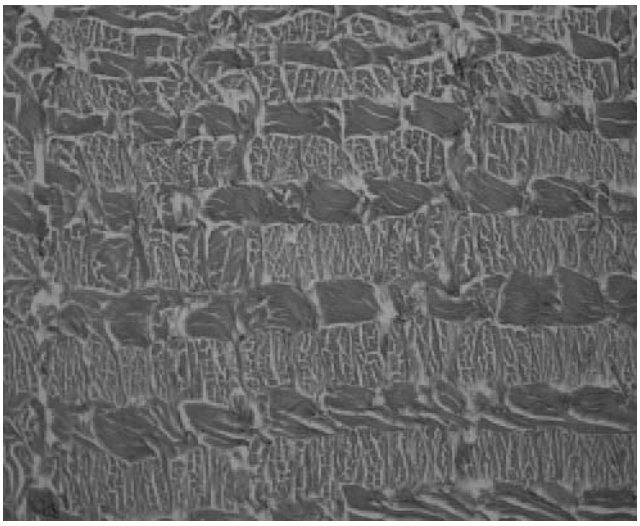

Figure 6. Optical microphotograph of soaked stingray skin at 100x magnification.

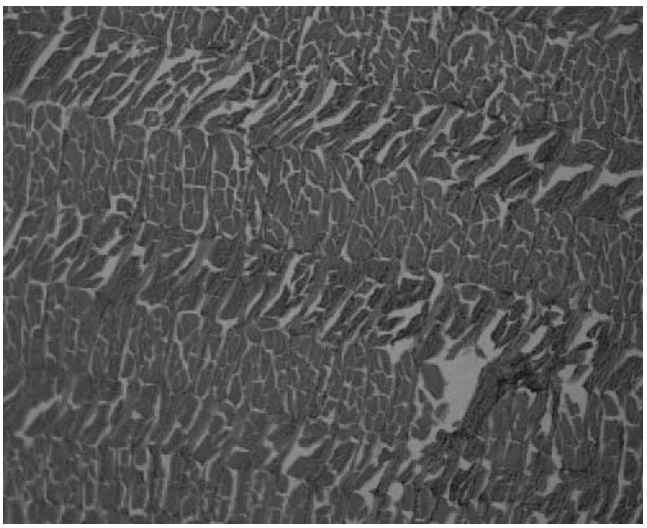

Figure 7. Optical microphotograph of limed stingray skin at 100x magnification.

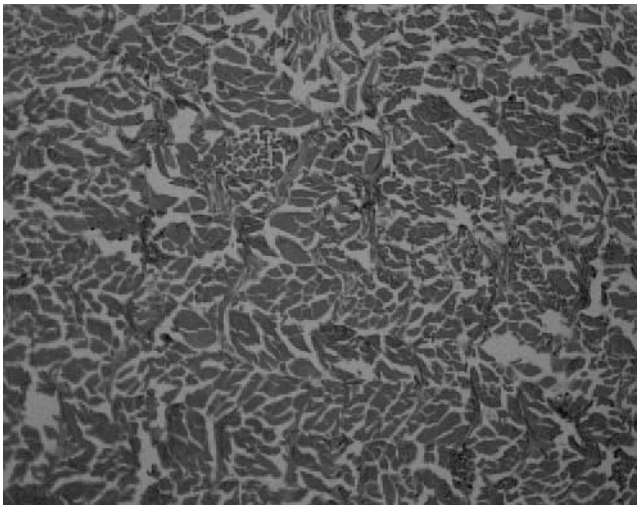

Figure 8. Optical microphotograph of bated stingray skin at 100x magnification.

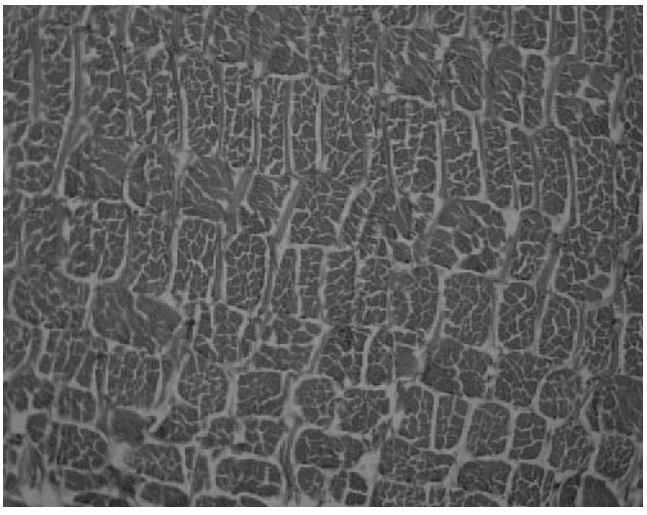

Figure 9. Optical microphotograph of tanned stingray skin at 100x magnification.

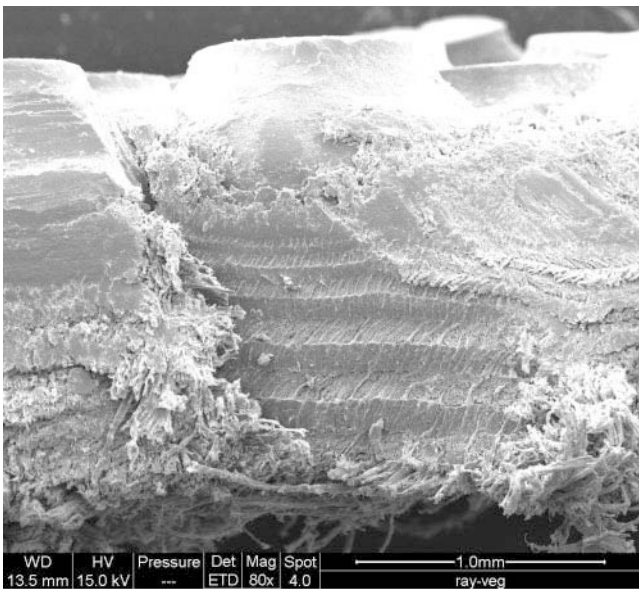

Figure 10. Scanning electron microphotograph of vegetable tanned stingray leather at 80x magnification.

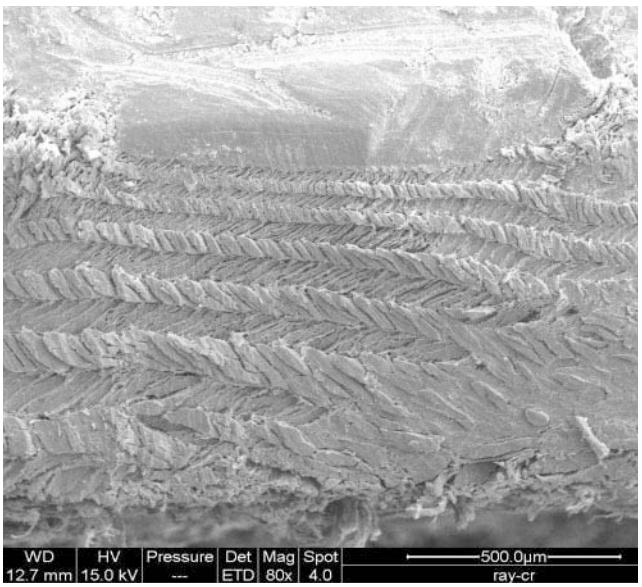

Figure 11. Scanning electron microphotograph of chrome tanned stingray leather at 80x magnification.

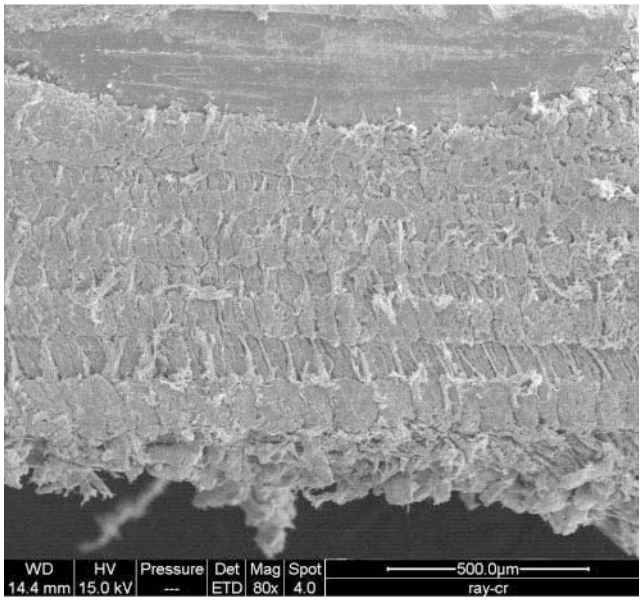

Figure 12. Scanning electron microphotograph of modified chrome tanned stingray leather at 80x magnification.

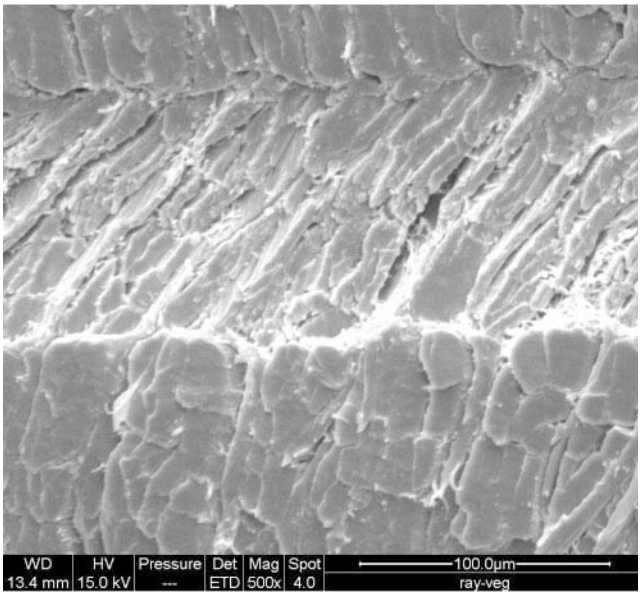

Figure 13. Scanning electron microphotograph of vegetable tanned stingray leather (middle layer) at 500x magnification.

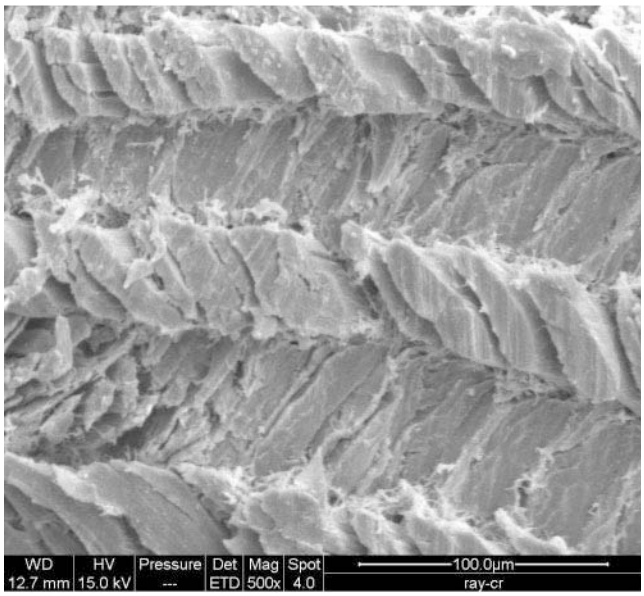

Figure 14. Scanning electron microphotograph of chrome tanned stingray leather (middle layer) at 500x magnification.

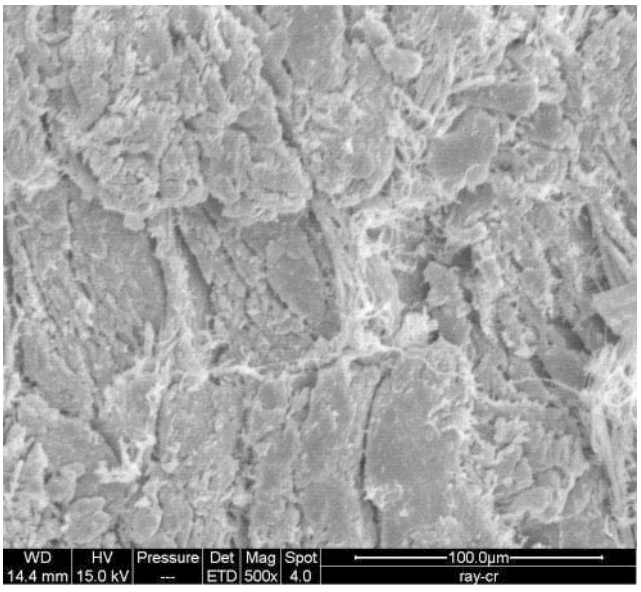

Figure 15. Scanning electron microphotograph of modified chrome tanned stingray leather (middle layer) at 500x magnification.

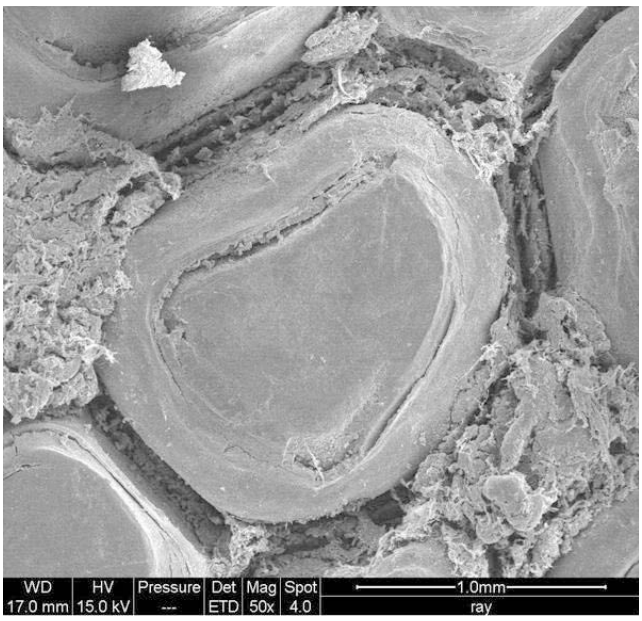

Figure 16. Scanning electron microphotograph of stingray leather surface at 100x magnification.

standard chrome and vegetable tanned stingray leathers remain compressed even after post-tanning resulting in a rigid leather, this is very clear from the micrographs at 80x magnification showing the cross-section of crust leather.

The inference from the SEM and optical microscopic studies is that the fibre structure of stingray skin becomes more compact after tanning and the leathers fatliquored after tanning *i.e*. during post-tanning remain compact resulting in a rigid leather.

Physical testing and visual assessment data

The strength properties of stingray crust leathers are given in Table III. The chrome tanned and modified chrome tanned leathers are stronger compared to vegetable tanned stingray leather. In stingray skins the parallel collagen fibre bundles are associated with the calcified denticles, and this imparts high strength properties to the crust leather. The softness values for stingray crust leathers are given in Figure 17. The leathers obtained from the modified chrome tanning experiment are the softest.

TABLE III
Properties of stingray leathers

Property	Vegetable tanned	Chrome tanned	Modified chrome tanned
Tensile strength (kg/cm$^{2)}$	208	286	275
Elongation at break (%)	23	34	38
Tear strength (kg/cm$^{2)}$	76	108	92
Grain crack load (kg)	27	34	32
Distension at grain crack (mm)	4.8	5.2	5.7

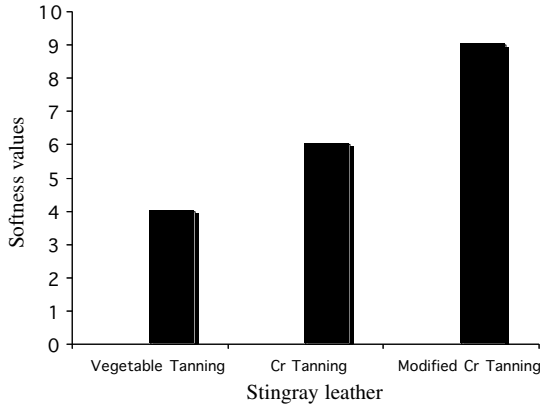

Figure 17. Visual assessment data of stingray leather.

Conclusion

This investigation offers a feasible way to tanners to manufacture soft and pliable leathers from stingray skins. Fibre splitting during pickling and fatliquoring during tanning result in a soft leather. Scanning electron microscopic analysis indicates that stingray leathers from modified chrome tanning experiment are soft and pliable compared to leathers from standard vegetable and chrome tanning method.

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References

1. Talwar, P. K. and Jhingran, A. G., Inland fishes of India and adjacent countries. (eds.) A. A. Balkema, Rotterdam, (1991), **1**, 43-44 Oxford & IBH Publishing Co. Pvt. Ltd., New Delhi.
2. Chaudhuri, B. L., Freshwater sting-rays of the Ganges,. *J. Proc. Asiatic Soc.,* 1912, **7**, 625-629.
3. Dean, M. N., Chiou, W. A. and Summeres, A. P., Morphology and ultrastructure of prismatic cartilage calcification.,*Microsc. Microanal*. 2005, **11**, 1196-1197.
4. Last, P. R., Manjaji-Matsumoto, B. M. and Kailola, P. J., *Himantura hortlei* sp.nov., a new species of whipray (*Myliobatiformes: Dasyatidae*) from Irian Jaya, Indonesia. *Zootaxa,* 2006, **1239**,19-34.
5. Karthikeyan, R., Rathinasamy, V., Ramalingam, S. *et al.*, *Ray Fish Leather as a Novel Reflexology Tool*, Proceedings of Innovations in Leather Science & Technology, Central Leather Research Institute, 2006, 59.
6. Sandifier, Q. D., Managing care. *Journal of Public Health Medicine*, 1997, **19,** (3), 301-306.
7. Official Methods of Analysis of the AOAC International (Association of Official Analytical Chemists) 18th Edition, 2005, United States.
8. IUP: 6 Measurement of tensile strength and percentage elongation. *J. Soc. Leather Technol. Chem*., 2000, **84**, 317.
9. IUP: 8 Measurement of tear load - Double edge tear. *J. Soc. Leather Technol. Chem*., 2000, **84**, 327.
10. Official methods of analysis, *Society of Leather Technol. Chem*; Herts., (1965).