The Structural and Chemical Properties of the Nile Perch Fish Leather

by
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Abstract

The conversion of skin to leather involves structural, chemical and physical changes to the material. The changes to the material is often after every subsequent process that the skin goes through before getting to the final leather. The leather processing involves three sub stages; pretanning, tanning and post tanning. The aim of the study was to determine the structural and chemical properties of chrome tanned Nile perch fish leather. The structural properties were determined using scanning electron microscope (SEM). The materials were analyzed for both the surface and cross section. The structural properties were carried out on the raw material then the material was subjected to tanning and there after the structural properties were determined in order to note the change that the tanning has on the structural properties of this particular material. Chrome content was analyzed using atomic absorption spectrometer (AAS) and amount was reported in percentage content. The moisture content was quantified and reported in percentage value.

From the structural analysis it was noted that the raw material is less compacted as compared to the chrome tanned leather. The fibers of the materials runs in one direction. The speed of the drum needs to be regulated to reduce the destruction of the collagen fibers which largely affects the physical properties of the leather. The average values of chemical properties were reported as follows: Chrome content of 2.45 % and Moisture content of 13.33 ± 1.88 % .The chrome content that was offered in the leather was satisfactory to give it a good hydrothermal stability.

Introduction

Collagen is a general extracellular structure protein involved in the formation of connective tissue.[1] The fish skin has type I collagen. The most abundant type I collagen comprises two identical α1 (I) chains and a different α2 (I) chain. Each of them has the repeating triplet amino acid sequence of Gly-X-Y, in which X and Y are frequently proline (Pro) and hydroxyproline (Hyp), respectively.[2] Nile perch collagen is said to contain more imino (Pro and Hyp) acids than most fish species.[3] The existence of reactive capable imino groups, helps in the ability to change the characteristic of the collagen giving it increased rigidity and thus hydrothermal stability.[4] Composition of the skin in relation to amino acids has a great influence during the processing of the fish skin and this gives the ability to change the properties of the collagen.[5] The crosslinking of the collagen is different in various ages since as the animal ages the crosslinking of their collagen increases and the type of cross link changes.[6] The leather stability is attributed to the strong interlocking of the collagen fibers with the tanning agent.[7]

Different fish species have different surface morphology. Stingray skins have denticles instead of scales giving a beautiful grain structure which give an attractive appearance to the finished leather. The skin is used for the manufacture of decorative leather for ornamental goods.[8] Sturgeon fish is a cartilage hard scale fish, sturgeon skin belongs to the class of fine miscellaneous skin which is an important raw material for manufacturing high-grade leather. Collagen fibers of sturgeon skin are very fine, with a basically parallel weave in the skin, the fibers which are vertical to the surface are fewer and also have zero weave angle.[9] In optical microscopy it was observed that the leather fibers are oriented and perpendicular to each other. For Dourada leather the fiber interlacing is more widely spaced compared to Piraíba leather which presents more compact fibers.[10] A. Stellatus Fish Skin black or brown star shaped pattern is visible only on the dorsal side, while ventral side is non-pigmented. Spines were aligned on dorsal and ventral sides of fish, coverage of spines were dominant in these areas. Leathers made from this fish skin were used for making gloves owing to existence of spines on the surface of leather.[11]

The chemical properties of the leather are dependent on the types of chemicals used in the process, the quantity used, variation in the processing recipe and the type of raw material. The chemical properties assessed in leather include the moisture content and chrome content among others depending on the intended purpose

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Manuscript received February 18, 2020, accepted for publication March 28, 2020.

of the leather.[12] The amount of moisture in the final leather is also dependent on the drying method that the leather was subjected.[13] Legal restrictions have recently been set for chrome feed and discharge having appropriate rules put in place throughout the world. Thus there is need to determine the chrome content in leather. From the literature Zengin, et al. [14] who tanned Carp, Sturgeon and Conger obtained chrome content of 1.41 %, 2.89 % and 2.26 % of Cr_2O_3 (%) respectively and Pessoa da Silva, et al. [10] who processed two species cat fish skins obtained 2.43 % and 2.70 % of Cr_2O_3 (%) for Dourada and Piraíba respectively.

The utilization of the raw fish skins has increasingly become one of great interest to researchers due to the potential end use of the leather in exotic, fancy and luxury type of leather production. This study was aimed at evaluation of the structural and chemical properties of chrome tanned Nile perch fish leather.

Material and Methods

Raw material

The raw materials were obtained from Obunga market in Kisumu. Nile perch fish skins were wastes from the fish filleting factories located in Obunga, Kisumu. The raw skins were cured with salt before transportation to the tannery for processing to avoid deterioration. The chemicals used in all stages of the leather processing were of commercial grade and were purchased locally.

Tanning process

The skins were first weighed. The tanning process was performed as follows: Soaking with 300 % water, 1 % anionic surfactant and 1 % bactericide for overnight in a static drum. Liming was done with 150 % water, 4 % lime, 2 % sodium sulfide and the drum run overnight at 4 rpm. Re-Liming was done with 150 % water, 1 % lime, 1 % sodium sulfide and drum run for one hour. The swelling of the pelts was checked and the tanning drum was drained then limed pelts washed with clean water. The pelts were then fleshed before deliming. The pelts were weighed. During the deliming process, 100 % water and 2 % ammonium sulfate were used and the drum run for one hour at 8 rpm. The pH was checked. The delimed pelts were then bated with 1% bate powder in a 100% water for one hour. Degreasing was done with 100 % water and 1 % degreasing agent for one hour. Pickling was done with 100 % water, 10% salt was added and drum run for 10 minutes, 0.2 % formic acid was added and drum run for 20 minutes, 0.8 % sulfuric acid was added in three batches after every 10 minutes and then the drum run for additional one hour. The pH was checked.

Tanning was done using pickle bath 4 % basic chromium (III) sulfate was added and drum run for one hour at 15 rpm, additional 4 % basic chromium (III) sulfate was added and drum run for one and a half hours. The pH and chrome penetration was checked. In the basification process 1 % of Sodium formate was added to the tanning bath and drum run for 30 minutes at 8 rpm, 1 % of sodium bicarbonate was added and drum run for one hour. The pH was checked, drum drained, washed and then drained. The materials were left overnight for ageing. The materials were weighed. Neutralization was done with 100 % water, 0.5 % sodium formate and 0.5 % sodium bicarbonate and the drum run for one hour. The pH was checked, drum drained, washed and then drained. Retanning was done with 100 % water, 2 % mimosa powder and drum run for one and half hours at 8 rpm, 2 % universal syntan was added and drum run for one hour. Fatliquoring was done with 100 % water at 60°C and 5 % synthetic fatliqour and drum run for two hour. The materials were dyed using 3 % brown dye for one hour. Dye penetration was checked. Fixation was done with 1 % formic acid and the drum run for one hour. The pH was checked, drum drained, washed and drained. The materials were horsed up overnight and then they were toggle dried.

Structural analysis of the leather.

To demonstrate the degree of structural change using scanning electron microscopy analysis was carried out on the raw material and tanned Nile perch leather samples.

Specimen samples of approximately 15 mm diameter were taken from raw material and processed fish leathers for morphology examination using a scanning electron microscope. The sampling for both samples was done within the same area, which is at the center of the material, so as to have consistent results. Wet specimen samples taken from the raw material were dried at low temperatures in the oven and finally put in desiccator for overnight to ensure complete dehydration of samples. For dried dyed crust leather samples, the specimens of approximately 15 mm diameter were cut using surgical blade and kept overnight in the desiccator to ensure the removal of trace amount of moisture. The samples were carbon coated with carbon stripes (Fig 1, 2, 4 &5). Other samples were sputtered with gold (Fig 3 & 6). The specimens were mounted on aluminum specimen stubs with dual face adhesive tape. The micrographs of surface and cross-section of the specimens were obtained using Zeiss Field Emission Gun scanning microscope working with smart SEM version 5.04 software while a 3345-JENWAY (USA) under high vacuum mode with different magnifications.

Chrome content determination

Chrome content determination was conducted using official method SLC 8, 2000. A 1 gram of milled sample was weighed on a platinum dish and ashed in muffle furnace at 550˚C. The ashed sample was digested with 25 mL of a 1:1 solution of HCl for about 20 minutes to a quarter the initial volume. The sample was filtered using Whatman No. 1 filter paper into a 100 mL volumetric flask and distilled water was added to the mark. The sample concentration was determined using an AAS Shimadzu AA-6300. This process was repeated for other two samples to get a triplicate.

Determination of shrinkage temperature

The shrinkage temperature of the pelt and chrome tanned leather was measured using SATRA STD 114 test apparatus according to the official method IUP 16, 2001. A 50 × 2 mm sample was cut out from the pelt and tanned leather and hung vertically in water. The temperature at the first definite sign of shrinking of the samples was taken as the shrinkage temperature.

Moisture content determination

Amount of moisture content was done according to official method SLC 401, 2000. The test sample was reduced into small pieces by use of scissors then ground to fine material using a grinding machine. Empty crucible was weighed using a weighing balance and weight recorded. The sample was put in the crucible and the weight recorded. The sample was placed in the oven for 3 hours at 105°C and after the 3 hours the sample were taken from the oven and placed in a desiccator for cooling for about 20 minutes, then weight of the samples was recorded and moisture content calculated using Equation below.

$$\text{Moisture percent by weight} = \left(\frac{W_2 - W_1}{W_1}\right) \times 100$$

Where: W_1 = Weight in g of the material taken for test.
W_2 = Weight in g of the residue left after drying.

Results and Discussion

Raw material was first examined for the surface morphology and the cross section using SEM as shown in Figures below.

Results in Figure 1 show the microphotograph of the cross section of the raw material. It shows that the skin has two distinct layers where there is an outer layer and an inner layer. The outer layer is loosely packed while the inner layer is densely packed in comparison to the outer layer. These are the two distinct layers, viz. an outermost layer, the epidermis and an inner layer dermis or corium. The outer layer is composed of several layers of flattened and moist epithelial cells thus the looseness in the packing. The inner layer mostly comprises a large system of collagen fibers that form irregular layers of right and left helices twisted about the long axis thus the compactness.[15]

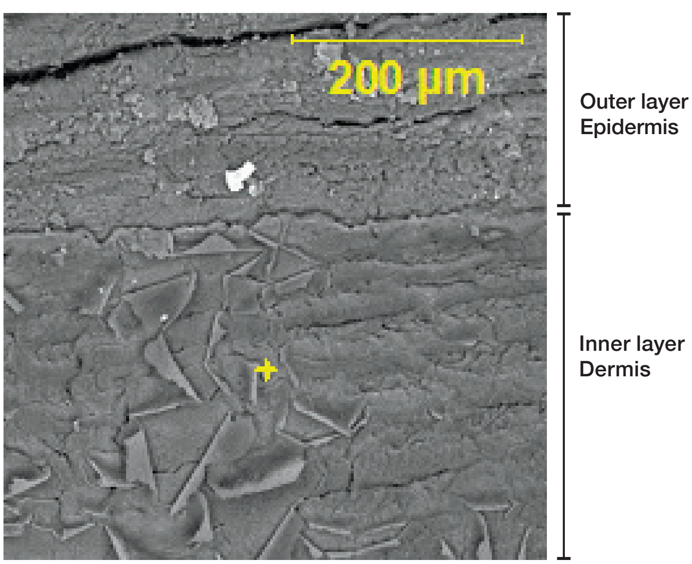

Figure 1. Scanning electron microphotograph of raw Nile perch Skin Cross section at 250 × magnification

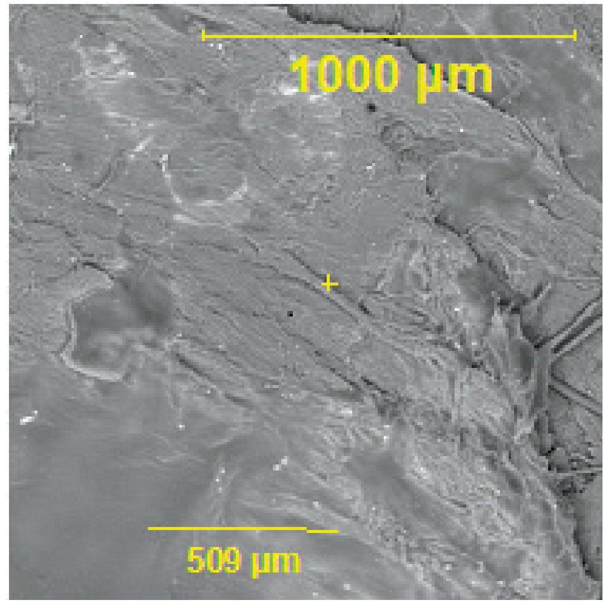

Figure 2. Scanning electron microphotograph of raw Nile perch skin surface morphology at 250 × magnification

From Figure 2 for the surface morphology examination the fiber bundles are seen compact. The direction of the fibers was not that visible from this figure thus a more enhanced view was created and it is reported in Figure 3 below.

Figure 3 shows that the collagen fibers run in one direction of the skin. The fibers are of different sizes which constitutes the fiber bundles. The fibers have a strong ordering but we observe large regions of loosely tethered fibrils which are in contrast to the straight arrangement of the fibrils in the tightly packed bundles. This has

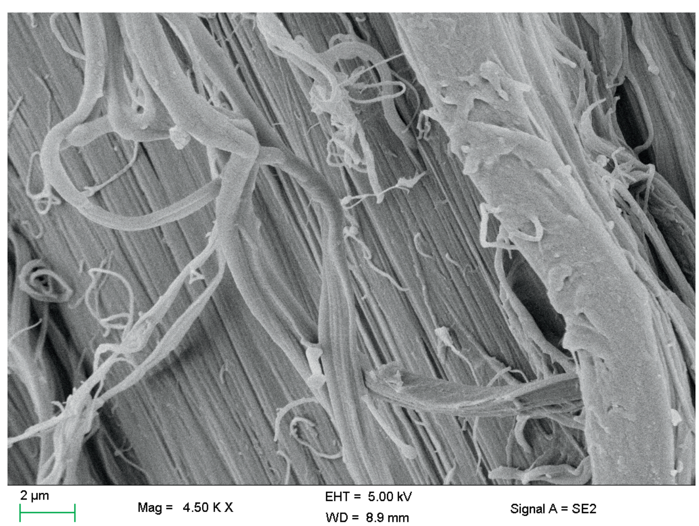

Figure 3. Scanning electron microphotograph of raw Nile perch Skin Surface.

an implication on the physical characteristics of the leather. Due to this arrangement of the fibers in a straight manner the elongation is expected to differ between parallel and perpendicular directions of the test pieces.

Examination of chrome tanned material was also done for both the surface and cross section as shown in Figure 4 & 5 below.

From the micrographs in Figure 4 & 5 it was observed that the chrome tanned material is more compact as compared to the raw material. This can be due to the event that chromium salts have filled in the void spaces which were opened up in the liming step. The liming step opens up the fiber structure and splits the fiber bundles into fibrils. The chromium salt reacts with the collagen forming crosslinks and making the structure compact which helps the leather to be rigid and very stable. For the cross section only one layer was observed as compared to the raw material where two layers of the skin were observed. This is because the layer is removed during the liming process thus opening up the fibers.[16]

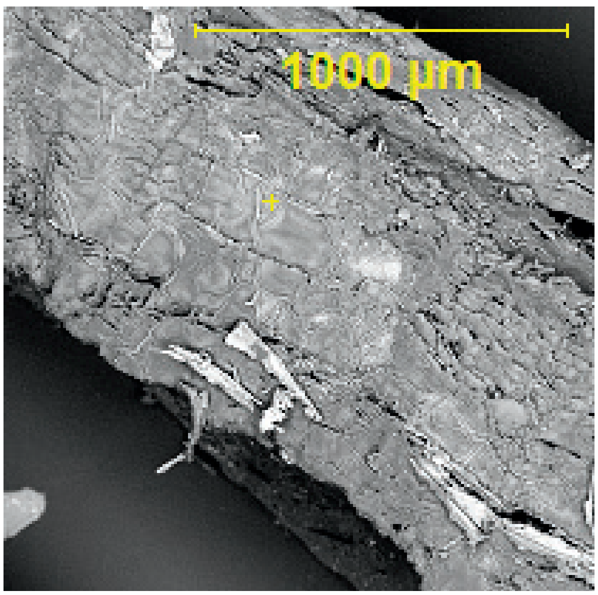

Figure 4. Scanning electron microphotograph of chrome tanned Nile perch leather cross section at 100 × magnification.

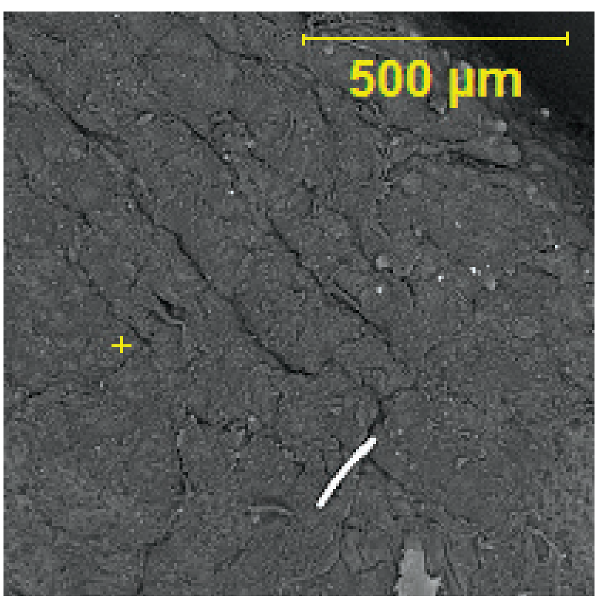

Figure 5. Scanning electron microphotograph of chrome tanned Nile perch leather surface at 100 × magnification.

A more enhanced view of the chrome tanned surface was created and the result is shown in Figure 6 below.

The collagen fibers are seen more tightly bound to each other meaning the degree of interlacing has become bigger as compared to the raw material in Figure 3. The interlacing contributes to the strength of the tanned material. Thus the more crosslinks formed the stronger the material, which implies that a product made from that material will be durable. There are some tiny uneven fibers among the collagen fibers which are scattered all over the surface of the material. These are the fibers which were destroyed during the processing since a drum at a speed of 15 rpm was used. Thus to prevent the damage of the collagen fibers which in turn affects the physical property lower drum speed is recommended. From research done by Karthikeyan,[8] the SEM micrographs indicated that chrome tanned leather fiber bundles remains compressed even after post tanning but when the leather is chrome modified the collagen fibers give a loose packing which contributes to soft and pliable leather due to improved fiber separation. His study also showed micrographs of vegetable tanned leather which were more filled than that of chrome tanned leather. This is because the vegetable tanning materials have the tans and non-tans which are responsible for the filling effect. The method used in this study, chrome tanning, gives less filling effect on the leather and thus when retanning the leather in post tanning operation mimosa was used to enhance the filling effect which results in rigid leather. From the above micrographs it is evident how the structural properties of the material changes during the processing.

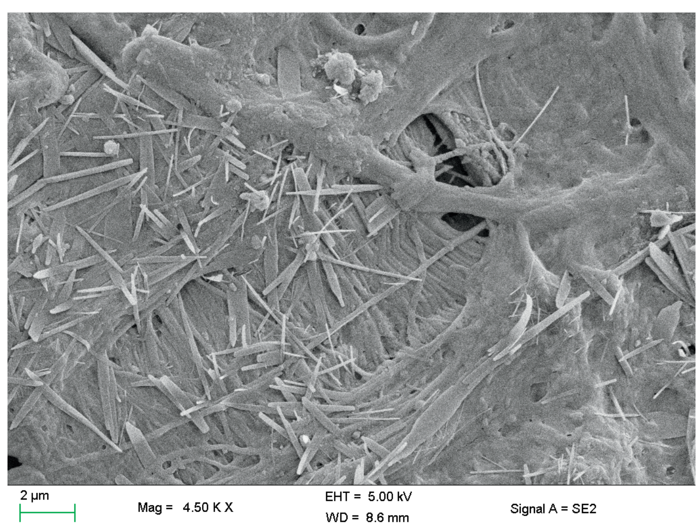

Figure 6. Scanning electron microphotograph of chrome tanned Nile perch leather surface.

Chrome content

In this study the percentage chrome content of the leather was determined and was found to be 2.45 %. The chrome content indicated that the chrome feed of 8 % basic chromium (III) sulfate to the pelt was sufficient in the leather. From the results the chrome content contributed to the stability of the leather with this 2.45 % of Cr_2O_3 giving a 98.67 ± 0.47°C shrinkage temperature. The pelt which was tested for its stability gave a shrinkage temperature of 53.33 ± 0.94°C. The low shrinkage temperature was due to lack of chromium salts in the pelt. The percentage of chrome content which was obtained was good enough to give performance characteristic. The recommended chrome content ought to include a minimum of 2.5 % chromic oxide.[17]

Moisture content

In this study toggle drying was used as a drying method after the wet processes, which aided in the gradual drying of the leather as opposed to sun dying or drying under high temperatures which a gives a rapid drying effect that can cause the leather to be stiff.

The average moisture content of the crust leather was found to be 13.33 ± 1.88 %. The values of the moisture content were within the required range of moisture content of leather after drying which is 8-14 % according to.[17] According to the study done by Liu, et al.[13] remaining water content in the leather is an important factor for softness thus the moisture content that was obtained in the leather crust in this research contributed to the degree of softness of the final leather.

Conclusion

The structural analysis provided the information on the transformation of the skin to leather. The SEM micrographs indicated that the Nile perch fish skin had two layers. Only one layer was observed in the tanned Nile perch fish leather. This means that the outer layer was removed during the liming process. The micrographs also indicated that the fibers of Nile perch fish skin run in one direction. The Nile perch fish leather indicated more compactness than the raw Nile perch fish skin, this is due to the effect of tanning process on the material. The leather indicated sufficient chemical properties having a moisture content which contributed to the softness and flexibility of the leather. The chrome penetrated well to the leather and there was no chrome patches on the surface of the leather. This chrome content was enough to provide the leather with the shrinkage stability. Future research may be focused on the effect of other tanning agents to the Nile perch fish leather.

Acknowledgment

The authors would like to thank African Development Bank (AfDB) and Dedan Kimathi University of Technology (DeKUT) for their financial support and also for their technical support.

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