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Suitability of Fish Skins for Making Leather: The Case of *Salmo salar* and *Lates niloticus*

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Abstract

Fibre structure, selected chemical and physical properties of *Salmo salar* (Linnaeus, 1758) and *Lates niloticus* (Linnaeus, 1758) skins and leathers were studied in order to establish the leathers' suitability in the manufacture of leather products. Microscopic examination revealed that fibres run as parallel sheets in both longitudinal and transverse sections of the fish body; this arrangement is considered to contribute to the increased strength of fish leather despite being thin. The skins' collagen content was found to be 61.2% and 72.0% for *S. salar* and *L. niloticus* respectively implying their suitability for leather making as this is in the same range as the conventional raw materials used in the leather industry. Due to the poor hydrothermal stability of raw fish skins, the degreasing was carried on wet blue leathers. The grease content was reduced from 23.7% and 13.0% to 5.9% and 5.5% for *S. salar* and *L. niloticus* respectively. The chromic oxide content was found to be 2.98% and 2.37% for *S. salar* and *L. niloticus* respectively. Shrinkage temperature was measured using DSC and Shrinkage temperature equipment and there was a strong positive correlation between the two approaches; r2 = 0.98. The shrinkage temperature of raw skins was 43.73oC and 60.71oC while that of wet blue leathers was 77.24oC and 88.75oC for *S. salar* and *L. niloticus* respectively. The average tensile strength was 14.13 N/mm2 and 21.63 N/mm2 whereas the single-edge tear strength was 21.68 N and 132.20 N for *S. salar* and *L. niloticus* respectively. The leathers were generally well stabilized and meet the requirements for various end uses.

Keywords: *Salmo salar, Lates niloticus, fish skins, collagen, leather, tanning*

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Introduction

Leather has historically been made from the hides and skins of mammals as well as other terrestrial animals. The fish leather has been made as a traditional craft in some regions where there are abundant fishery activities and such skills were localized (Puntener and Donkan, 2013); however, its industrial tanning is unpopular. This can be to the fact that its availability is not widespread and its tanning requires much attention as the fish skins cannot withstand some treatments of conventional leather tanning.

The skin is shown to be the largest organ of the animal body. Depending on the age and type/species of an animal, it can represent about 12% to 24% of body weight (Moriello, 2020). The study on fish by-products indicates that fish skins, bones and scales contribute about 30% of body weight (Bandara and Chalamaiah, 2019). It is therefore evident that fish skins have a

substantial contribution to wastes (by-products) from the fish processing industry.

Despite the abundance of fish in various water bodies, there has also been an increase and promotion of fish farming in recent years in different parts of the world (FAO, 2008; Puntener and Donkan, 2013; URT, 2019). Fish skins particularly those from fish farming can be considered more reliable compared to most of the traditional raw materials in the leather industry as it counters issues such as traceability which is currently among the major challenges of the industry (Bauer, 2021). It has been advocated that the worldwide production of fish leather is generally insignificant compared to the yield of available raw materials (John, 1996; BASF, 2007). Tanning of fish skins can therefore add appropriate, sustainable and traceable raw material to the leather industry.

In this study, the arrangement of fibre structure and selected chemical as well as physical properties of two fish species: *Salmo salar* (Linnaeus, 1758) and *Lates niloticus* (Linnaeus, 1758) were examined and determined. The recipes for tanning the skins were formulated based on the nature of the skins and the properties of the leathers were determined to establish its suitability for application in various end uses.

Application of fish leather

Palomino and Rahme, (2021) reported the traditional tanning of fish skins in the arctic region where the leather has been used as garments, shoes, mittens (gloves) as well as blankets. Due to the presence of pockets that remain after the removal of scales, fish leather is not slippery; it is therefore excellent for use in steering wheel covers and motor vehicle grips to prevent slippage (Karthikeyan *et al.,* 2009). Mares *et al.,* (2014) have shown the use of fish leather for cup holders, wallets and belts in Colombia, Peru and Costa Rica. Fish leather can therefore have numerous applications for the manufacture of conventional leather products as well as fashion goods due to its unique appearance. Tanning of fish skins can also be a good approach to control the rising populations of invasive species that put other aquatic organisms at risk of extinction (Inversa, 2022).

Materials and methods

Study Area

The study was conducted at the Institute for Creative Leather Technologies (ICLT), University of Northampton, UK from July to December 2022. Tannery equipment and machines at ICLT were used for tanning the skins. Skins and Leather examination and testing were carried out at Amanda Michel Microscopy Lab, Physical and Chemical Testing Laboratories all located at ICLT.

Raw Materials and Equipment

Twenty (20) *S. salar* skin sides were obtained from Aquascot Limited, Scotland and transported to ICLT. The total weight of the green fleshed skins was about 2.8 kg.

Twelve (12) dry-salted *L. niloticus* skin sides weighing a total of approximately 3.0 kg were sourced from Victoria Pearch Limited, Mwanza Tanzania and transported to the UK via courier service.

Industrial grade chemicals were used during tanning while laboratory grade reagents were used for examination of skin structure and chemical analyses. Tanning was conducted in Steel Drums, Type 14-400370/1/6 Dose Machinery GmbH, Germany.

Tanning Procedures and Trials

The skins of each fish species were treated separately in all the processes undertaken. Despite the variations in the properties of fish skins and hence the need for specific tanning recipes, inputs from some of the existing literature (Mares *et al.,* 2014); Fuchs and Fuchs (2000) and Wairimu *et al.,* (2019) were helpful in accomplishing this study. Trials involved the use of conventional tanning chemicals and procedures; however, some chemicals and steps were skipped based on the effects observed. The preparation for a working recipe took about one month and at least four trials were conducted to obtain a suitable recipe.

Due to the skins sensitivity to temperature during beamhouse operations, and the fact that

the degreasing requires relatively elevated temperatures (35°C – 40°C), the degreasing was carried out on the wet blue leather as the skins are already stabilized at this stage. A similar approach has also been reported by Palmer and Marsden, (1981) when working with sheep skins for making gloves.

Examination of skins and leathers' Cross-sections

Raw skin samples were fixed in formaline solution for at least 24 hours according to UoN, (2017). The samples were frozen using tissue freezing medium at -21°C and 60 microns sections were cut using Leica freezing microtome (Cryostat), hydrated and mounted on a glass slide using Farrant's medium. On the other hand, the crust leathers were conditioned at moisture of 14%, small sections were cut using a sharp razor blade and mounted onto a glass slide using double-sided seal tape.

The fibre orientation of the soaked raw fish skins and crust leathers were examined under light microscope using Leica M205 C, Leica Microsystems (Switzerland) Ltd. Unstained raw skin sections were less clear and for this reason, the samples were stained using Methylene blue to improve the clarity.

Chemical tests

Due to the small size of the skins, establishing Official Sampling Positions (OSP) and obtaining sufficient weight for some tests was a challenge. The samples were therefore taken from the middle part of the skins/leathers which had relatively average properties of other parts toward the head and toward the tail (Wairimu *et al.,* 2019).

Determination of Collagen

Collagen content in the soaked and pickled fish skins was determined as hydroxyproline according to SLC 21 (IUC 17). Samples were analysed in duplicate using Genesys 10S UV-Vis Spectrophotometer, Thermo Scientific at 555nm. Calculations were carried out according to the Journal of Society of Leather Technologists and Chemists (JSLTC) Vol. 64 pp 75 – 59, using the following formula:

$$\%Collagen = \frac{weight\ of\ hydroxyproline}{Dry\ weight\ of\ skins}\ x\ 8\ x100$$

Where: 8 is the conversion factor from hydroxyproline to collagen.

Determination of Substance Soluble in Dichloromethane (Grease Content)

The grease/fat content was determined in duplicate for soaked skins, pickled pelts and wet blue leathers according to BS EN ISO 4048:2018.

Determination of Chrome as Chrome oxide

Chromic oxide content was determined in duplicate for each species from the wet blue leathers according to BS EN ISO 5398-4:2019 by ICP-OES method using ICP Spectrometer iCAP 6000 Series, Thermo Scientific. Sample digestion was carried out using Mars 6 Microwave, One Touch Technology.

Calculations were done using the following formula:

$$wCr = \frac{\rho x 1.462 x V x F}{mo}$$

Where:

wCr - Chromic oxide content (%)

ρ – Concentration of chromium in a sample in milligram per litter (ppm)

V – Total volume of the sample (mL)

m_0 – Original mass of the leather in grams (g)

1.462 – The correction factor to convert Cr to Cr_2O_3

F – Correction factor for in percentage for volatile matter; F = 1 for dry leather sample.

Physical tests

Samples for physical tests were cut into relevant dimensions and conditioned according to BS EN ISO 2419:2012. The laboratory conditions were maintained at a temperature of 23.0 ± 2.0 °C and relative humidity of 50.0 ± 5.0 %.

Leather thickness

The thickness of crust leather was determined according to BS EN ISO 2589:2016/SLP4(IUP4)

using SATRA Technology Center thickness gauge with a reading up to 0.01 mm. Measurements were taken as an average from the head, middle and tail parts.

Measurement of Area of Fish Leathers

The area of fish leathers was measured in square feet (Sq.ft) using Turner Pin-wheel Measuring Machine, J. Hewit & Sons Ltd.

Determination of Tensile Strength, elongation and Tear Strength

The tensile strength, elongation at break and single edge tear strength of the leathers were tested using Instron 5567 Testing Machine according to BS EN ISO 3376:2020 and BS EN ISO 3377-1:2011 respectively. Due to the small size of the fish skins, parallel and perpendicular samples were taken from the middle part of different fish leather sides.

Determination of Hydrothermal Stability

The shrinkage temperature of raw, limed and tanned skins were determined using Shrinkage Temperature testing equipment and Differential Scanning Calorimetry (DSC). Determination using Shrinkage temperature equipment was conducted according to EN ISO 3380:2015 and samples were tested in duplicate. The DSC analysis was carried out using Mettler Toledo, DSC2 STARe System under a Nitrogen atmosphere. The endothermic peak of the DSC thermogram was used to obtain the shrinkage temperature of the fish skins and wet blue leathers.

Results

Descaling and Liming

The use of sodium sulphide during descaling and liming was observed to be destructive on *S. salar* skins; skins treated with 3% lime and 2.5% sodium sulphide (added gradually) were observed to break into a thick mass. Therefore, more trials were carried out using the reduced quantity of sodium sulphide where skins treated without sodium sulphide were more intact and maintained some natural properties (Image 1). Furthermore, the fish scales were not broken down during descaling and liming.

Image 1. Limed S. salar skins treated with Sodium Sulphide 1.5% (Left) and 0% (Right)

Bating

While up to 0.5% by weight of bating agent was successfully used for *L. niloticus* skins, less amount between 0.1% to 0.2% was sufficient for *S. salar* as beyond this the skins became weak and developed some holes.

Pickling

Salmo salar skins treated with 0.5% formic acid and gradual addition of 0.7% Sulphuric acid were observed to roll and gelatinize. Upon more trials, it was considered necessary to skip the use of

sulphuric acid and formic acid alone was used to control the pickling pH.

Fibre structure examination

Examination of skins' cross-section using a light microscope revealed that collagen fibres appear as cross-linked sheets and run parallel in both transverse and longitudinal directions of the fish body (Figure 2 and 3).

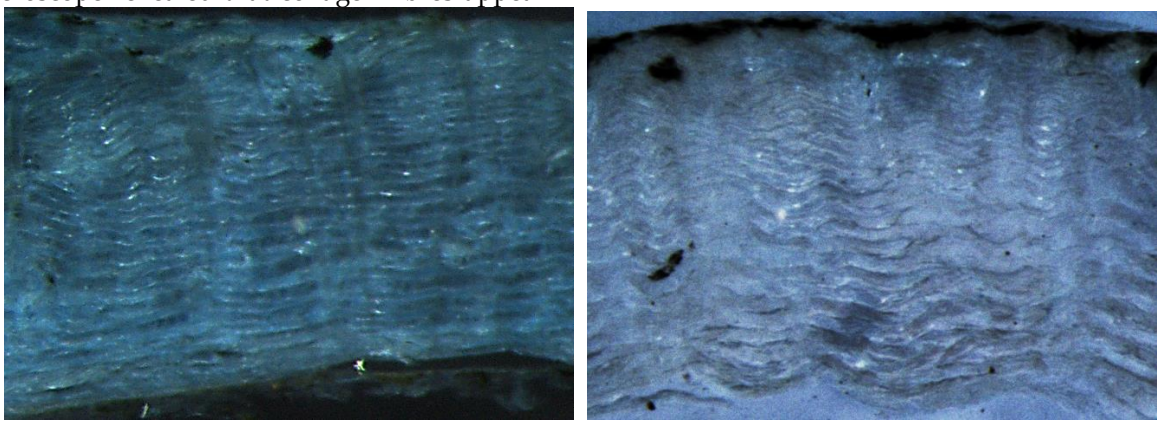

Image 2. Cross section of raw S. salar skins - Parallel to backbone (Left); perpendicular to backbone (Right) (80x Magnification)

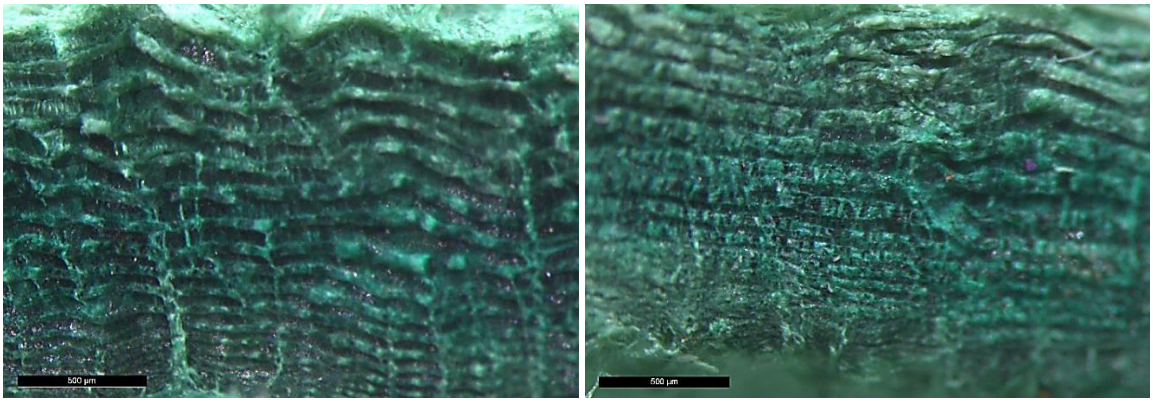

Image 3. Cross section of tanned L. niloticus leather: Parallel to backbone (Left); Perpendicular to backbone (Right) (80x Magnification)

Chemical Tests Results; Substances Soluble in Dichloromethane/Grease Content

The grease content of raw skins was found to be 23% and 13.0% while that of pickled pelt was 17.5% and 8% for *S. salar* and *L. niloticus* respectively. Upon degreasing the wet blue leathers, the grease content was reduced to 5.9% and 5.5% for *S. salar* and *L. niloticus* respectively.

Collagen Content

The collagen content of raw skins determined from the mass of hydroxyproline per dry weight of skins was found to be 61.2% and 72.0% for *S. salar* and *L. niloticus* respectively. On the other hand, the collagen content of pickled samples was 88.2% and 85.7% for *S. salar* and *L. niloticus* respectively.

Chromic Oxide Content of tanned fish skins

The chromic oxide content of wet blue fish leather was found to be 2.98% and 2.37% for *S. salar* and *L. niloticus* respectively.

Physical Test Results of Crust fish Leathers; The thickness of Fish Leather

The average (n = 6) thickness of crusted fish leathers was found to be 0.62 mm and 1.38 mm for *S. salar* and *L. niloticus* respectively.

Area of Fish Leather

The *S. salar* leathers were generally of the same size, the average area (n = 5) of crust leathers was 0.51 square feet (sq. ft). On the other hand, the area of *L. niloticus* leathers was highly variable and ranged from 1.1 sq. ft to 2.5 sq. ft.

The tensile strength and elongation at break

The average tensile strengths were found to be 14.13 N/mm^2 and 21.63 N/mm^2 for *S. salar* and *L. niloticus* respectively. The elongation at break was found to be 34.73 N and 54.93 N for *S. salar* and *L. niloticus* respectively.

Single edge tear strength

The average (n = 6) single edge tear strength of studied fish leather was found to be 22. 68 N and 132.20 N for *S. salar* and *L. niloticus* respectively.

Shrinkage temperature

The shrinkage temperature was measured at various stages of fish skins tanning (Figure 1). The shrinkage temperature of raw *S. salar* skins measured using DSC was found to be 43.73 ^oC while that of *L. niloticus* was 60.71 ^oC. On the other hand, the shrinkage temperature of wet blue leathers was found to be 77.24 ^oC and 88.75 ^oC for *S. Salar* and *L. niloticus* respectively.

The shrinkage temperature was also measured using the Shrinkage Temperature equipment and compared with DCS results. While in most occasions the Shrinkage temperature equipment results were higher than the DSC data, there were also instances where it was slightly lower than DSC. Generally, there was a close positive correlation between the values measured using the two approaches, $r^2 = 0.98$ (n = 10).

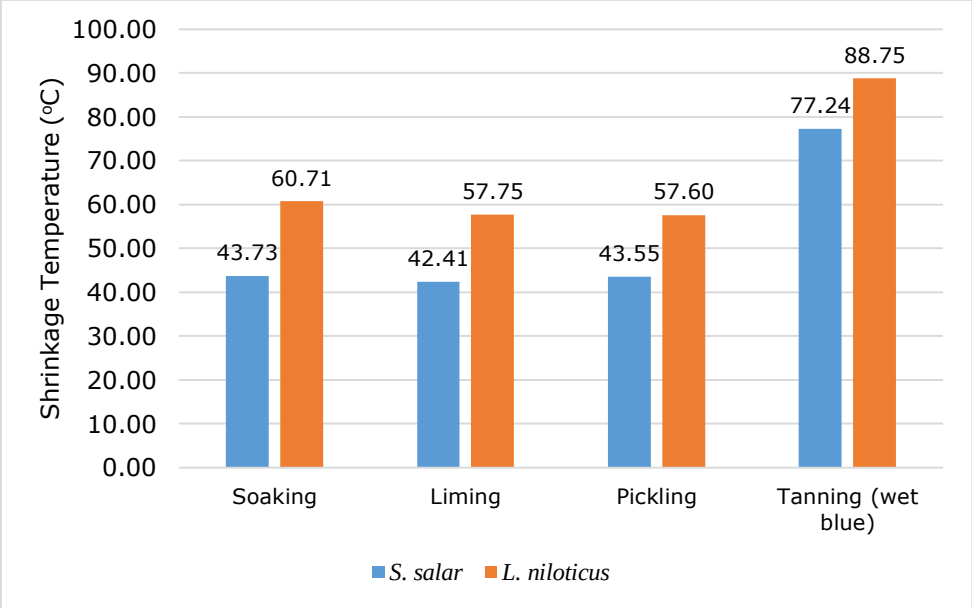

Figure 1. DSC Shrinkage temperature results of fish skins at various tanning stages

Discussions

Beamhouse Operations

As indicated in the results, sodium sulphide was observed to be detrimental to fish skins particularly the *S. salar*. Previous study by Fuchs and Fuchs (2000) has also shown the negative effects of sodium sulphide on the tanning of fish skins; its use was therefore skipped in the tanning of *S. salar* skins.

It was also noted that temperature changes in the surroundings can significantly affect the tanning process, especially during beamhouse operations. Special cases were recorded in July 2022 when the climate temperature in the UK rose to around 40 ^{o}C (Abdul, 2022) hence resulting to the breakdown of the skins. During such conditions, the temperature within the tanning drum was as high as 31^{o}C which is not advisable for fish skins tanning (John, 1996).

Apart from the hot climate, the use of steel/metallic drums which are good conductors of heat was also considered one of the contributing factors to temperature rise in the tanning bath hence the breakdown of the skins. Therefore, alternative drums that are poor conductors of heat such as wooden or polypropylene are more relevant in the tanning of fish skins.

Furthermore, the reduction of liming duration for delicate or immature skins/hides has also been suggested (Covington and Wise, 2020). From the experience gained in this study, reducing the duration for liming for fish skin tanning is also proposed.

The resistance of scales to chemical attack was due to the fact that they are much keratinized (Covington and Wise, 2020). It was therefore possible to collect them by filtration (screening) at the end of the soaking and liming processes. This suggests the reduced pollution load in the effluent since scales are not dissolved, unlike the hairs of hides/skins. The scales can therefore be utilized for other applications such as making glue (Braley, 2019).

Though bating is a useful process in the removal of remaining fleshy material and fats (TFL, 2009), the process was skipped for *S. salar* skins. Similar challenges during bating have also been reported by Fuchs and Fuchs (2000).
Due to the gelatinization of skins observed during pickling, sulphuric acid was believed to be a cause as the damage developed in the later stages of pickling. Blanco *et al.,* (2017) advocate that acids and heat have the tendency to gelatinize the fish skins and collagen. Therefore, sulphuric acid was skipped in the tanning of *S. salar* skins whereas *L. niloticus* where able to withstand the acid's treatment. Since formic acid is a weak acid, a higher ratio of up to 1.5% was required to decrease the pH up to around 3.0 for chrome tanning of *S. salar* skins.

Tanning
It has been shown that approximately 85% of global leather is chrome tanned due to its versatility (Daniels and Landmann, 2013). It has also been shown that a combination of different tanning agents can improve the quality of the leather (Sharphouse, 1995). Chrome retan (chrome followed by vegetable retanning) was therefore applied in this study as it has the ability to impart good properties compared to pure chrome or vegetable tanning alone.

Fibre Structure arrangement
Similar arrangement: parallel fibre structures of fish collagen have been reported by Mares *et al.,* (2014 and Puntener and Donkan, 2013). The collagen fibre arrangement in fish skins is therefore different from those of most raw materials used in the leather industry which are randomly oriented (Haines and Barlow, 1975; Clare, 2021). This fibre arrangement is considered to provide more strength to fish leather despite the skins being relatively thinner compared to most traditional raw materials.

Chemical Test Results
Substances Soluble in Dichloromethane (Grease Content)
The grease content of raw skins was observed to be higher than the pickled pelt; this is due to the fact that grease is normally eliminated during some beamhouse operations such as deliming and bating (Thorstensen, 1993). The grease content of raw *S. salar* skins was higher (23.7%) compared to *L. niloticus* skins (13%). The variation in grease content of the raw fish skins can be attributed to the physiological adaptation of the species to their climatic conditions; feeding has also been reported to cause variation in grease content (Palmer and Marsden, 1981). High fat deposition can be considered as an adaptation to cold climates as fat provides an insulation mechanism. The fact that *S. salar* is native to cold climate and were bred in cages contribute to the likelihood of having higher fat deposition than *L. niloticus* which is native to the hotter tropical climate and obtained through wild catch.

The results of this study correlate well with some previous observations by Kacukakin *et al.,* (2016) who reported a grease content of 24.47±1.76% for Skipjack Tuna (*K. pelamis),* especially for *S. salar*. The results, however, differ from observations by Zengin *et al.,* (2015) who reported grease content of 40%, 43% and 44% in raw skins of sturgeon, conger and carp fish respectively.

Owing to the presence of relatively higher grease content in the pickled fish skins, the degreasing process was therefore considered inevitable in this project as grease would cause a fishy smell in the leather (Espada *et al.,* 2020). Excessive grease can also impair the penetration of dyeing chemicals (Palmer and Marsden, 1981).

A natural grease content of less than 4.5% has been recommended in order to prevent various grease defects in leather (Palmer and Marsden, 1981). The degreasing was carried on wet blue leathers which can withstand increased processing temperature (up to 35^{o}C). Consequently, the grease content was reduced to 5.9% and 5.5% for *S. salar* and *L. niloticus* respectively. Though the recommended level in literature was not attained, organoleptic testing showed that there was no fish smell in the leather. The degreasing process was therefore considered to sufficiently eliminate the polyunsaturated fatty acids and hence odour/smell in fish skins as well as avoiding any other defects that might be associated with high grease content.

Collagen Content

The collagen content of raw *S. salar* skins was observed to be less than that of *L. niloticus* and this can be due to species variations. The collagen content of raw skins was in line with the previous study on fish skins by Blanco *et al.,* (2017) who reported collagen content up to 61% for blue sharks (*Prionace glauca*).

Generally, the observed collagen content of raw skins is in the same range as most of the raw materials used in the leather industry. According to Sharphouse (1995), the dry skin/hide of animals used in the leather industry is composed of about 60% - 70% collagen by weight. The results of this study are however in disharmony with Kacukakin *et al.,* (2016) who studied Skipjack tuna fish skins and reported that the skins had less collagen content compared to other raw materials used in the leather industry. This disagreement can be due to species differences as it has been evident that collagen content varies among animal species.

Moreover, the study on the molecular composition of skins of various raw materials used for leather making by Naffa *et al.,* (2019) reported 36%, 59%, 62% and 71% of collagen content for raw skins/hides of sheep, goat, deer and cow respectively. As a major structural component of leather, the results of this study confirm that fish skins are capable of producing leather that can be utilized by the industry as its collagen content is in the same range as skins of most raw materials used in the leather industry.

Chromic Oxide Content

The chromic oxide content of leather describes the amount of tanning material(s) fixed into the collagen fibres (John, 1996); it therefore has implication on the level of stabilization of hides or skins.

These findings are in line with the observed shrinkage temperature results where the *S. salar* shrinkage temperature of raw skins increased by 33.51 ^{o}C while that of *L. niloticus* skins increased by 28.58 ^{o}C indicating more stabilization of *S. salar* skins. The higher capacity for uptake of chrome by *S. salar* skins as compared to *L. niloticus* can be due to the fact that the skins were stored for a relatively shorter time suggesting that collagen fibres were more intact and not affected by storage defects. A related study on fish skins reported a chromic oxide content of 2.43% and 2.70% for Dourada and Piraiba catfish respectively (Da Silva *et al.,* 2017).

The chromic oxide between 2.5% – 3.5% has been recommended for various specifications for quality assurance purposes (John, 1996; Nothing to Hide, 2014; Covington and Wise, 2020). While using a similar technique (ICP-OES) for bovine leather used in car upholstery, Zeiner *et al.,* (2011) reported chromic oxide content from 1.9% to 3.2%. The studied fish leathers are therefore considered to be well stabilized and can meet requirements for various applications in the

leather industry as end use has varying requirements with respect to chromic oxide content.

Physical Tests Results

The thickness of fish leather; Previous studies show that, the average thickness of crusted sturgeon, carp and conger fishes as 0.62 mm, 0.65 mm and 1.29 mm respectively (Zengin *et al.,* 2015). Da Silva *et al.,* (2017) have reported thickness of 1.03 mm and 1.17 mm for Dourada and Piraiba (catfishes) respectively. The thickness for some end uses are 0.6 mm to 1.0 mm for garment nappa leathers; 1.2 mm to 1.8 mm for shoe upper; and 1.1 mm to 1.4 mm for car upholstery (John, 1996).

The thickness of *S. salar* and *L. niloticus* leather can therefore meet various applications in leather products making; it can also be used with lining materials in it so as to fit the application in products that require relatively higher thickness.

Area of fish leather

As indicated in the results section, the area of fish leather is generally dependent on the fish species and harvesting age. While larger species may produce leather with a relatively larger area sufficient for making a product, leather from smaller species can be used as decoration on other products or joined together to create a larger area for making any desired product. The designers and manufacturers can arrange and fit them in an appropriate pattern so as to fully utilize the skins and also obtain a larger area for intended end use.

Tensile Strength and elongation at break

The tensile strength ranging 25.3 N/mm^2– 27.6 N/mm^2 have been reported for *L. niloticus* (Wairimu *et al.,* 2019). In another study, Karthikeyan *et al.,* (2009) has reported tensile strength ranging from 20.4 to 28.0 N/mm^2 for chrome tanned Himantura stingray fish leather. Similarly, the tensile strength of conger, sturgeon and carp fish were reported as 9.78, 14.23 and 18.33 N/mm^2 respectively (Zengin *et al.,* 2015).

The tensile strength of studied fish leathers are therefore in the same range as the previous studies though *L. niloticus* has shown substantial decrease compared to records in literature. This can be linked to prolonged storage of the skins; according to John 1996, too long storage of hides/skins can result to reduced strength of leather.

In general, it has been shown that the tensile strength for most of the raw materials used in the leather industry range between 8 - 25 N/mm^2 (Leather Dictionary). The results of this study therefore suggest the suitability fish leather for application in the leather industry in terms of their tensile strength.

Karthikeyan *et al.,* (2009) reported elongation at break for chrome tanned stingray fish leather as 34%. Fuchs and Fuchs (2000) reported elongation of 40% for carp fish leather. The results of this study are therefore correlate with other fish leathers previously studied; they are also in similar range with other animals: cow 42% and goat 47% as reported by Ali, Kamal and Islam (2020). The minimum recommended elongation for some end uses such as shoe upper has been shown to be 40% (BASF, 2007).

The *L. niloticus* fish leather therefore meets the strenghth requirements of most end uses. The *S. salar* leather was however observed to have poor extensibility, this can be associated to ineffective post-tanning in this study as the leather handle was observed to be bony/papery. Smit and Zoon (2022) has clearly shown that inefficient post-tanning and fatliquoring can reduce the strength and extensibility of leather. Nevertheless, it was not possible to correct the shortcoming due to sample and time limitations.

Single edge tear strength

Single edge tear is another important parameter that determines the strength of the leather, it provides the information on fibre quality and resulting changes due to tanning (John, 1996). The tear strength of 43.97 N, 46.8 N and 83.83 N have been reported for conger, carp and sturgeon fishes respectively (Zengin *et al.,* 2015). Similarly, Wairimu *et al.,* (2019) has reported the tear strength of 49.53N for *L. niloticus*. In a study on cow and goat leather, Ali, Kamal and Islam, (2020) have reported tear strength of 68N and 135N for goat and cow leather respectively. The

leather from the studied fish have sufficient tear strength particularly for *L. niloticus* whose tear strength was higher than that of goat leather and in the close range to that of cow leather. The poor tear strength of *S. salar* leather can be explained in terms limitations in the post-tanning operations as highlighted above.

The minimum tear strength of 30 N, 40 N and 50 N has been recommended for fashion footwear, shoe uppers and upholstery leathers respectively (BSI, 2007; BASF, 2007). Therefore, the *L. niloticus* fish leathers have sufficient tear strength for use in different leather products; however, *S. salar* is unsuitable for use in such products. Nevertheless, the *S. salar* fish leather also possess potential for higher strength upon improved post-tanning processes.

Shrinkage Temperature

BASF, (2007) indicated that the shrinkage temperature of raw fish collagen range between 40 ^{o}C – 45 ^{o}C. When working with *L. niloticus* skins, Wairimu *et al.,* (2019) reported shrinkage temperature of 54 ^{o}C. The results of this study therefore correlate well with literature particularly for the case of *S. salar*. The deviation of the shrinkage temperature of *L. niloticus* skins from literature may be linked to other factors such as age of fish (Palmer and Marsden, 1981) as well as living climate (Covington and Wise, 2020). On the other hand, hydrothermal stability has been shown to increase with decreasing moisture of the leather (Covington and Wise, 2020); for this reason, since some parts of the dry salted *L. niloticus* skins were observed to resist wetting even after soaking for 24 hours, it can be concluded that skins were not well moistened hence the slightly higher shrinkage temperature than in previous studies.

The shrinkage temperatures of raw skins of both fish species were observed to slightly drop by up to 3 ^{o}C during beamhouse stage before increasing abruptly after tanning. This drop can be attributed to decreased stability of collagen at this stage; Covington and Wise (2020) urge that there is increased solubilization of collagen under alkaline conditions due to rapid hydrolysis of the skins/pelt. Furthermore, the rise of shrinkage temperature after tanning is an indication of impact of stabilization of the skin collagen by tanning materials. This stabilization is due to covalent complexation of collagen hydroxyl groups and chromium ions used as tanning agent (Covington and Wise, 2020; Clare, 2021).

Generally, the shrinkage temperature of *L. niloticus* skins and hence leather was observed to be higher than that of *S. salar*; this variation can be linked to skins composition of hydroxyproline or collagen content (Blanco *et al.,* 2017). As shown above, the hydroxyproline and hence collagen content of *S. salar* skin was lower than that of *L. niloticus* skins. It has been shown that there is direct correlation between hydrothermal stability (shrinkage temperature) and hydroxyproline/collagen content of hides and skins (Gustavson, 1956). Covington and Wise, (2020) argue that hydroxyproline deficiency of collagen results to thermally unstable collagen; this therefore explains for the observed lower shrinkage temperature of the *S. salar* skins and leathers as compared to those of *L. niloticus*.

While working with other fish species, Zengin *et al.,* (2015) reported shrinkage temperatures of 63 ^{o}C, 78 ^{o}C, and 90 ^{o}C for crusted leathers of sturgeon, conger and carp fish respectively. The tanned fish leathers in this study have therefore a similar trend of shrinkage temperature, especially with respect to conger and carp. On the other hand, Wairimu *et al.,* (2019) reported a comparatively higher shrinkage temperature of 98 ^{o}C for *L. niloticus* wet blue leather. This variation may be due to the long storage duration of the *L. niloticus* skins used in the present study. The chromic oxide test results are also in agreement with this observation: it can therefore be concluded that the collagen has been degraded due to long storage duration hence less fixation of chrome and consequently lower hydrothermal stability than expected. The *L. niloticus* skins therefore have a potential for attaining higher shrinkage temperature if tanned without prolonged storage.

The shrinkage temperature equipment has also shown its reliability in the control of the tanning process as its results correlated well with DSC. This observation is also in line with a previous study by Siddique *et al.,* 2014 where Shrinkage Temperature Equipment values were slightly higher than DSC. These results indicate that the

Shrinkage Temperature equipment is still useful equipment for control purposes in the tanneries to monitor the progress of the tanning process.

Conclusion

It should also be appreciated that tanning of fish leather requires some degree of manual work and craftsmanship as machines cannot be utilized in some stages such as fleshing. This is however much dependent on the type of fish skins being processed as different fish skins will need relatively different kinds of treatment.

Due to the sensitivity of the skins to temperature, wooden or polypropylene drums are highly recommended in hotter regions or during hot summers for this kind of raw material as these drums are poor conductors of heat. Nevertheless, metallic drums can also work perfectly during cold seasons.

Generally, with a properly designed recipe for tanning fish skins, it is possible to attain requirements for various end uses in the leather manufacturing industry, especially for small articles, luxury goods and other products that do not need leather with a large area. Generally, it is upon the designers' discretion to find proper application as the fish leathers can also be joined together to suit the use in products that need a relatively larger area. The increasing availability of skins through aquaculture systems, the reduced water footprint and easy traceability all favour the sustainability of fish leather. The fish skins are therefore valuable raw material that is worth consideration by the leather and fashion industry.

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