PHYSICAL PROPERTIES OF CHINESE HERRING (*Hilsentoli* sp.) LEATHER TANNED WITH CHROME AND RETAINED WITH SYNTHETIC AGENT

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Abstract

When the scales of Chinese herring (*Hilsentoli* sp.), like those of snakes or monitor lizards, are tanned, they exhibit a unique scaly texture with an attractive natural pattern. This study aimed to evaluate the physical properties of Chinese herring skin tanned with chrome and retained with a synthetic agent. The treatments consisted of a combination of chrome and tanning agents at various concentrations, ie. Chrome (C) 6% and tanning agent (S) 0% (C6S0), Chrome 8% and tanning agent 0% (C8S0), Chrome 10% and tanning agent 0% (C10S0), Chrome 6% and tanning agent 4% (C6S4), Chrome 8% and tanning agent 4% (C8S4), Chrome 10% and tanning agent 4% (C10S4), Chrome 6% and S 6% (C6S6), Chrome 8% and S 6% (C8S6), and Chrome 10% and tanning agent 6% (C10S6). Observations were conducted based on descriptive sensory, physical, and chemical tests, identification of functional groups of the leather, and morphology analysis of the skin leather. The results showed that a combination of chrome and synthetic tanning produced leather with a denser and fuller texture than leather tanned with the chrome tanning agent. C10S6 treatment produced the best physical properties of tanned skin of Chinese herring in terms of its high tensile strength, tear strength, stitch strength, and shrinkage temperature, along with the lowest elongation. The values are well within the Indonesian standard of SNI 0253:2009 for leather with fancy motifs on finished leather goods. The analysis of the cross-section of skin at various treatments using Scanning Electron Microscope (SEM) analysis indicates that retanning with synthetic tanning agents strengthened the collagen matrix, producing denser, more compact structures. This density is caused by the presence of collagen compound bonds and synthetic tanning materials, such as phenol and formaldehyde, which were detected as 2,4-dimethyl phenol in the Raman spectra shift at 208, 35 – 2445.87 cm^{-1}.

Keywords: Chinese herring, chrome tanning, physicochemical, tanned fish skin

Introduction

Chinese herring (*Hilsentoli* sp.) is predominantly caught in Merauke, Indonesia, from the productive waters of the Arafura Sea. Most fish weigh more than 500 g, producing skins wider than 10 cm. This fish has scales with small motifs like the scales of snakes or monitor lizards, and if it is tanned, it will have a unique scaly and attractive natural pattern (Kasmudjiastuti & Murti, 2019). If the herring skin can be tanned well, the skin provides a unique pattern with high commercial potential for luxury goods such as handbags, belts, shoes, wallets, and jewelry (Abid *et al.*, 2020). Tanned fish skin has actually been widely used by the well-known shoes industry, such as Puma, Adidas, and New Balance, by using fish skin such as tilapia, shark, skate, trout, and salmon, among others (Mares *et al.*, 2014). Although the size of fish skin is smaller than bovine or goat skin, it possesses collagen fibers whose fibers cross each other by forming alternating right and left helix layers. This structure produces leather with strength comparable to that of bovine or goat leather, whose collagen fibers are unidirectional (Abid, 2020; Duraisamy *et al*., 2016).

Tanning is a technique for transforming perishable raw skin into stable, durable tanned leather resistant to biological, chemical, and physical influences (Roig *et al*., 2011). It involves chemical between type 1 collagen proteins from fish skin and the active ingredients of the tanning agent. Tanning agents impacted to the intermolecular structure of collagen, which is responsible for the structure and strength of the skin (Ali *et al*., 2020; Jian *et al*., 2012). The tanned leather quality depends on the type, the concentration, and the combination of tanning materials used (Cavali *et al*., 2022; Wairimu *et al*., 2020). Commons tanning materials includes chrome tanning agent (minerals), vegetable tanning materials, aldehyde tanning materials, and synthetic tanning materials (Duraisamy *et al*., 2016).

In this study, chrome tanning was combined with retanning using synthetic agents. This approach was selected due to the thin structure of Chinese herring skin, which requires reinforcement. Retanning is known to enhance mechanical and physical properties of the resulting tanned leather (Maina *et al*., 2019; Pradeep *et al*., 2021). Retaining was done to produce more stable collagen fibers, and skin that is softer, more elastic, and fuller, so the quality is better (Wu *et al*., 2014; Covington, 2015). Chrome tanning materials are widely used in the leather industry (around 85 - 90%) (Bhavya *et al*., 2019; Cavali *et al*., 2022), because is relatively cheap, fast, and produces high quality, heat-resistant leather with stable colors (Ahmed *et al*., 2021; China *et al*., 2020; Gao *et al*., 2020). Fish skin tanning using chrome has been widely studied, including tanning of tilapia (Pahlawan & Kasmudjiastuti, 2012) and snapper, with chrome concentrations ranging from 6–10% (Kusmaryanti *et al*., 2016; Mustakim *et al*., 2007).

Re-tanning with syntan was done to produce a fish skin material that is stronger, thicker, softer, and fuller (Rajendran *et al*., 2008; Civington 2015). Tanning with synthetic materials is not done alone but in combination with other tanning materials such as chrome or vegetable tanning (Zhang *et al*., 2021). Synthetic tanning materials are high-molecular organic compounds used to make leather into a stable material called leather. Synthetic tanning is produced by condensing aromatic compounds such as phenol, phenol sulfonic acid, or naphthalene sulfonic acid with formaldehyde (Gao *et al*., 2020). Synthetic tanning exists in the form of sodium or ammonium salts and is made with certain properties (Rajendran *et al*., 2008). Tanning with synthetic tanning has a character that does not affect the colour of the leather, produces leather that is dense, soft, and resistant to the effects of acids and bases, and can increase the water resistance of the tanned leather (Pratama *et al*., 2018; Widari *et al*., 2013). Types of leather that are commonly processed by synthetic tanning methods include reptile skins such as snake skin, crocodile skin, monitor lizard, and chicken leg skin. Through the synthetic tanning technique, the relief that each skin has can be maintained as an art form that has its own artistic value (Anon, 2016). Re-tanning with a combination of chrome and synthetic tanning agents It is expected result in high-quality Chinese herring leather.

According Rachmawati *et al*. (2020) the use of chromium-formaldehyde combination tanning agents provides good effects on tensile strength, tear strength, and thickness. The purpose of this study was to evaluate the quality of Chinese herring leather re-tanned with a combination of chrome and syntan tanning agents and assess its potential as an alternative raw material for leather crafts in Merauke.

Materials and Methods

Materials

Chinese herring fish used in this study was obtained from local traders at the Merauke afternoon market. Each fish weighed a minimum of 500 g. The fish was then filleted to remove the flesh and skin. Other materials included technical-grade chemicals: calcium oxide (CaO), ammonium sulfate, sodium sulphide, oropon enzymes, formic acid, sodium bicarbonate, chrome, synthetic tanning (Sondotan), and Sulfonated Sandolic WWL leather dyes, all purchased from the chemical shop Harum Sari, Jakarta.

Equipments

The equipment used were knives, cutting boards, buckets, plastic baskets, rotary drums for the tanning process, boards for staging and drying the tanned skins, and a set of tools for analysing the physical and chemical properties of Chinese herring skin.

Methods

Tanning was carried out using chrome, followed by re-tanning with synthetic tanning agents. The synthetic tanning process was performed after the leather had been tanned with chrome, by applying the tanning agent concentrations as shown in Table 1.

Table 1. Combination of chrome and synthetic tanning agents (w/w)

Treatment	Chrome tanning agent (%)	Synthetic tanning agent (%)
C6 S0	6	0
C8 S0	8	0
C10 S0	10	*0*
C6 S4	6	4
C8 S4	8	4
C10 S4	10	4
C6 S6	6	6
C8 S6	8	6
C10 S6	10	6

Tanning procedure

a. Pre-tanning. Chinese herring fish skin was washed with clean water to remove blood, mucus, and other impurities. The fish skin were weighed to determine the required amount of material for the tanning process.

b. Liming. The skins were soaked in a solution containing 3% lime and 3% sodium sulfide (Na_2S) in a plastic bucket for 48 hours, with stirring for 5 minutes every 2 hours. The volume of lime solution used was 10 times the weight of the fish skin. The skins were then washed three times with water until free of lime and the pH was neutral (pH 6–7).

c. Lime removal (deliming). The cleaned skins were then placed in a rotary drum containing a 0.5% ammonium sulfate solution at a volume five times the weight of the skins. The drum was rotated for 30 minutes, after which 0.5% formic acid was added, and the rotation continued for another 30 minutes.

d. Bating. Protein removal was carried out using 2% oropon enzyme, and the drum was rotated for 2 hours. The fish skin was washed clean, then rotated again in a rotating drum using a 10% salt solution for 10 minutes. The skin was then acidified with a 2% formic acid solution until the pH of the solution reaches 2-3, and the drum is rotated for 1 hour.

e. Chrome tanning. Chinese herring skin was tanned with chrome at 6%, 8%, and 10% (Mustakim *et al*., 2007) and 2% Na_2CO_3. Chrome tanning was carried out by rotating the drum for one hour. After the chrome tanning process was completed, the skins were neutralized using a warm 2% Na_2CO_3 solution (40 °C). The drum was rotated for another hour, and the skins were then drained for 24 hours.

f. Retanning. Retanning was carried out using synthetic tanning agent (Sondotan) with tanning concentrations of 0%, 4% and 6% (Kusmaryanti *et al*., 2016). The synthetic tanning agent was dissolved in warm water (40°C), then added into a rotating drum containing Chinese herring skin, and the drum was rotated for 2 hours.

g. Dyeing and fatliquoring. The Chinese herring skin was dyed with 2% black color and rotated for 1 hour. The skin was then treated with oil using 4% Sandolix WWL and 4% Lipoderm in warm water (40°C) and rotated for 1.5 hours. The remaining dye was subsequently added, and the drum was rotated again for 30 minutes. Finally, 1% formic acid was added, and the drum was rotated for 30 minutes.

h. Finishing. The dyed fish skin was removed from the drum, washed twice with clean water, and drained overnight. The aerated skin was then stretched on a plywood board by nailing it along the edges so that it was evenly spread. The skin was left to dry overnight. The dried skin was removed from the board and trimmed by cutting the edges, particularly at the nail holes. The skin was then smoothed by sanding the flesh side, while the scale side was polished using a machine to produce a soft texture.

Observation of the Leather

Observation of the leather was carried out on organoleptic properties, physical properties, chemical properties, identification of the functional group, and morphology of the tanned leather.

Organoleptic properties.

The organoleptic properties were carried out descriptively at the Leather and Shoes Testing Laboratory of the Center for Standardization and Service of Leather, Rubber and Plastic Industry, Yogyakarta by skin specialists. Observations were made on the appearance and colour, softness and suppleness, shape, and presence of remaining meat on the fish skin inside the tanned skin, which was produced based on descriptive test.

The Physical properties

Tests for the physical properties of tanned Chinese herring skin were carried out on tensile strength and elongation, tear strength, sewing strength, shrinkage temperature and Chrome oxide.

Tensile strength (ISO 3376: 2020)

Tensile strength was measured with an Instron 1026, 3400 series made in USA. The dumbbell-shaped test specimen was gradually stretched by a tensile testing machine until it broke. Each sample was measured in triplicate, and the highest attainable load was taken as the breaking load. The tensile strength is expressed in Newtons (N).

Skin elongation (ISO 3376: 2020)

Measurement using tensile strength (KT-0710D2 series 74134) made in China. The tool was withdrawn using a probe at a speed of 2 mm/sec. The highest peak on the monitor screen indicates the value of the tensile strength of the sample, which is then measured for the elongation (elongation at break) of the sample expressed in %.

Tear strength (ISO 3377-2:2016)

An an Instron 1026, 3400 series made in USA was used to measure tear strength to the official method (IUP/8.2001). A hole with a diameter of 0.2 cm was made in a fish skin measuring 10 x 2 cm, 2 cm from the left side of the skin. Then, cut the skin so that a tongue-shaped hole is created at a distance of ± 3 cm from the previous hole. The tongue-shaped holes and cuts are then attached to the scorching machine clamps, which have been measured for thickness previously. The Instron machine is activated until the skin is completely torn. The amount of tear strength is affected by the force used to pull the leather as well as its thickness. Tera strength measured in Newtons per square centimeter.

Sewing Strength (SNI 06-1177:1989)

The determination of sewing strength was carried out by pulling the stitches using an Instron 1026, 3400 series made in USA vertically until the stitches break. Each sample was measuring 270 mm in length on both sides of the stitch and 100 mm in width parallel to the stitch line, will be tested for their stitch strength. The leather is then stitched vertically and horizontally. Each sample was measured in 5 repetitions The stitched leather is then pulled by the Instron machine until the stitch or the stitched leather breaks.

$$\text{Stitch Strength} = \frac{F}{n}$$

With : **F** = the maximum force (N or g) that can be sustained before the seam tears

n = the number of stitch holes per cm

The shrinkage temperature test (ISO 3380:2018)

It was carried out using leather shrinkage temperature teste GT-KC23 series made in China which has been set to a shrinkage temperature scale of 1°C with an accuracy of 0.5°C. The skin sample was cut at a length of 50 mm and a width of 5 mm. The top and bottom were given a hole approximately 5 mm from the end with a hole punch. The skin sample was put into a 1000 ml glass beaker containing distilled water and heated at 100°C. The skin will expand maximally as the heating temperature rises; after it expands completely, the skin will shrink at a certain temperature. The temperature at which shrinkage occurs is called the shrinkage temperature.

The chemical properties Chrome Oxide Levels (ISO 5398-1-2018)

The chromium present in the leather is solubilized in the hexavalent state followed by analysis of the solution and iodometric titration according ISO 5398-1:2018(E) IULTCS/IUC 8:2018(E). The result was expression in percent.

Identification of Functional Group (Araujo *et al*., 2028)

Identification of functional group was analyzed with the Horiba Series Raman Spectroscopy (HR 320 Japan). Samples of leather fish skin was cut with a size of 2 x 2 cm, then placed under the objective lens to form an image of a real object.

Scanning Electron Microscope (SEM)

The analysis of the cross-section of skin at various treatments was observed using a Thermo Fisher Scientific. Prima E Scanning Electron Microscope (SEM). Made in USA. The leather was cut into appropriately sized pieces for the Scanning Electron Microscope (SEM) sample chamber, ensuring the pieces were small and flat. The samples were cleaned to remove any debris, such as dust or oil, that could affect the test results, and then placed on a stub or holder, securing them firmly in place. The SEM was operated under vacuum conditions with distance of ±10mm and at an electron accelerating voltage of 10 kV. To di*sp*lay the micrograph details of the egg roll, contrast and brightness were adjusted, and readings were taken at a magnification of 1000 x.

Statistical analysis

All data were analysed using a Completely Randomized Design (CRD) with SPSS version 17. Significant differences among treatments were further tested using Honest Significant Differences (HSD) analysis.

Results and Discussion

Organoleptic properties of tanned Chinese herring fish skin

Descriptive observations of the tanned Chinese herring skins showed that all treatments produced a consistent small square-scale pattern. The tanned skins exhibited distinct characteristics, including a dark black color, uniform and homogeneous texture, and smooth, neat, and symmetrical surfaces. The flesh side was clean with no residual meat attached.

The panellists provided different descriptions of the skin condition, where tanning with synthetic tannins at 4% and 6% concentrations resulted in denser-tanned skin. Increasing the concentration of chrome tanning agent also produced tougher and denser tanned leather. This was attributed to the formation of additional cross-links between collagen carboxyl groups (COOH) and chromium compounds, which crated a more compact and stronger skin structure (Maina *et al.*, 2019; Roig *et al.*, 2011). The findings were supported by SEM micrographs, which showed that with higher chrome concentrations reduced empty spaces, producing denser and more compact tissue (Figure 2). This study is similar to a study by (Wairimu *et al.*, 2020) on tilapia skin tanned with chrome tanning agent, where higher the chromium salt used, promoted cross-linking between collagen chains and chrome. The collagen chain bundles can fill the empty spaces that occur during calcification so that the skin becomes compact, stiff, and very stable.

Organoleptically, leather retanned with 4% and 6% synthetic agents appeared denser and fuller than leather tanned only with chrome. According to (Duraisamy *et al.*, 2016), the re-tanning process using synthetic tanning can fill in the spaces between the collagen fibre bundles of Chinese herring fish skin so that the resulting tanned skin is denser and fuller (fullness), but gives a softer skin texture. Thus, retaining with synthetic tanning can produce tanned leather that is strong, dense, and full, compared to leather tanned only with chrome tanning. Re-tanning, according to (Murti & Sugihartono, 2020), will produce leather with better physical properties because the superior properties of each tanning agent will complement each other to produce higher-quality leather.

Surface observation of Chinese herring leather retanned with synthetic tanning revealed a clear scale pattern, with a pattern of finely arranged small scales with the specific characteristics of species. Re-tanning with synthetic tanning produces leather with a solid black color. This effect occurs because synthetic tanning products lighten the skin, which allows dyes like Sandolix WWF to penetrate the skin more deeply and produce results that are brighter and more uniform in color (Widari *et al.*, 2013). The shape of the skin is flat and symmetrical, and there is no residual meat attached to the skin of the tanned fish.

Physical properties

The tensile strength of the leather

Tensile strength is an important parameter for assessing the suitability of leather in the manufacture of leather goods and the leather goods industry. It reflects the strength of the bond between the collagen chains and the tanning agent. A proper tanning process will produce leather with high tensile strength (Pahlawan & Kasmudjiastuti, 2012). According to Hak (2013), a correct, careful tanning process and a matching tanning combination will produce tanned leather that has the highest tensile strength. In this study, the tensile strength of Chinese herring skin ranged from 190.45 N/cm^2 to 309.29 N/cm^2. All tanned Chinese herring skins produced from these various treatments showed tensile strength values in accordance with ISO 24092:2019 for bovine leather (>150 N/cm^2) (Murti & Sugihartono, 2020).

The statistical analysis revealed that the treatments caused substantially different tensile strengths in each treatment ($P<0.05$). Exception was observed in C10S0 (chrome 10%, syntan 0%), C10S4 (chrome 10%, syntan 4%), and C6S6 (chrome 6%, syntan 6%). The use of synthetic tanning resulted in significantly lower tensile strength ($P< 0.05$) as the concentration of chrome tanning used increased (Table 2). The tensile strength of Chinese herring skin that was tanned with chromium at a concentration of 6% was 220.2 ± 0.18 N/cm^2, which decreased to 190.45 ± 0.39 N/cm^2 when it was tanned with chrome tanning agent at a concentration of 10%. The lower the value of the tensile strength, the lower the quality of the leather produced. According to Mustakim *et al.* (2007), excessive levels of chromium in collagen will actually reduce the physical strength of tanned leather as the amount of chromium bound increases. This is due to the fact that the polypeptide chain receives too much tanning agent, which exceeds the load capacity of the skin fibres so that the collagen fibres are easily broken, leading to reduce the tensile strength. This result is in line with the results of a study by Untari *et al.* (2014), who reported that rabbit skin tanned with a 12% chrome tanning agent, had lower tensile strength compared with those tanned with 9% chrome.

Table 2. The results of the analysis of tensile strength, elongation, and tear strength of Chinese herring leather in various treatments

Treatment	Tensile strength (N/cm^2)	Elongation (%)	Tear Strength (N/cm
C6S0	237.48±1.024[d]	95.55±0.23 [g]	200.74±0.49[b]
C8S0	220.20±0.18 [e]	79.75±0.19[e]	240.56 ±0.35[d]
C10S0	190.45±0.39 [a]	76.13±0.33[d]	250.66 ±0.1[f]
C6S4	270.67±0.28 [f]	81.98±0.19[f]	210.08 ±0.12[c]
C8S4	260.3±0.17 [c]	81.70±0.16 [f]	190.67±0.24 [a]
C10S4	190.73±0.17 [a]	75.45±0.11[c]	200.69±0.12[b]
C6S6	191.88±2.73 [a]	79.57±0.13 [e]	250.26±0.19[f]
C8S6	240.88±0.07[b]	74.99±0.33 [b]	280.48±0.21[g]
C10S6	309.29±2.12 [g]	68.74±0.14 [g]	360.34±0.21[h]
Standard 06-4263-1996	152.95	70	150

Note: The same letters indicate no significant difference.

While the combination of chrome tanning and synthetic tanning improved the tensile strength of the resulting tanned Chinese herring skin, different patterns were observed depending on the concentration of each agent. At 4% chromium tanning combined with synthetic tanning agent, increasing chromium concentration significantly decreased tensile strength ($P<0.05$). While a different pattern is shown if the concentration of the synthetic tanning agent is increased to 6%, the higher the concentration of chrome used, the higher the tensile strength of the leather produced significantly ($P<0.05$). Duncan's test confirmed that treatment with 10% chrome and 6% synthetic tanning produced the highest tensile strength and was significantly different from the other treatments ($P<0.05$). This suggests that the excessive chrome concentration, when compared to synthetic tanning, results in a decrease in the tensile strength of the resulting tanned leather. Synthetic tanning has a large ionization capacity in the tanning process, so when the tanning combination between chrome and synthetic tanning is well matched, the tanning agent penetrates well and binds perfectly to the collagen protein from the skin so that it can increase the tensile strength of the resulting tanned leather (Murti & Sugihartono, 2020; Pratama *et al.*, 2018).

High-quality tanned leather is produced by the complicated active ingredient in synthetic tanning, polyhydroxy benzoles, which contain big (positive and negative) hydroxyl groups and react precisely with leather collagen to form a hydrogen bond (Covington, 2015). According to this study, increasing the cross-linking between collagen chains and tanning materials by first tanning with chromium and then tanning again with 6% synthetic tanning may result in interlocking cross-linkages that are stronger and more stable (Wairimu *et al.*, 2020).

Meanwhile, according to Covington (2015), leather that has been tanned using chrome and then re-tanned with synthetic tanning will be more compact, dense, and stiff than leather tanned using only chrome. This demonstrates that re-tanning with synthetic tanning resulted in a more fully tanned Chinese herring fish skin than simply tanning with chrome tanning agent. A similar study was also demonstrated by (Murti & Sugihartono (2020), where the combination of 4% chrome tanning with 2% mimosa on red snapper (*Lutjanus* sp.) produced leather with superior tensile strength, sewing strength, and burst resistance.

In this study, the highest tensile strength (309.29 N/cm^2) was with 10% chrome and 6% synthetic tanning. This value is comparable to tensile reported for the bovine (320.39 N/cm^2) and goat skins (290.08 N/cm^2) (Ali *et al.*, 2020). The relatively high tensile strength may also be attributed to the size of the fish used, with a minimum weight of 500 g. Larger fish generally have more stable fibril and collagen fibre diameters, which contribute to higher tensile strengths compared to smaller fish (Mares *et al.*, 2014).

The Elongation of the leather

Elongation refers to the percentage increase in length of leather when stretched until it breaks, compared with its original length (Pahlawan and Kasmujiastuti (2012). It is directly related to the elasticity of leather. A lower percentage of elongation indicates better quality leather (Farid *et al*., 2015). The results of the statistical analysis of the elongation of tanned Chinese herring skin showed that the higher concentration of chrome tanning and re-tanning with synthetic tanning significantly reduced elongation in Chinese herring leather ($P<0.05$). This demonstrates that the higher the concentration of chrome used, the higher the quality of the tanned leather or the difficulty in stretching the tanned leather.

Re-tanning using synthetic tanning compensated for the weakness of chrome-tanned leather; the resulting leather is more flexible, denser, and filled with leather, which contributed to reduced elongation. As shown in Table 2, the treatment with 6% chromium and 0% synthetic tanning (AC6S0) produced the maximum elongation (95.55%), significantly different from other treatments ($P<0.05$). This indicates that the skin of Chinese herring tanned only with 6% chromium exhibit nearly double its initial length before breaking. Meanwhile, the combination of chrome and synthetic tanning produces a lower level of elongation, which indicates a better quality of tanned leather. Retaining 6% synthetic tanning produced a better quality of elongation and was significantly different ($P<0.05$) compared to retaining 4% synthetic tanning. Synthetic tanning serves as a filler. The formaldehyde and phenol in the synthetic tanning agent create cross-links with the collagen chains, strengthening the structure and reducing suppleness (Wells *et al*., 2013; Widari *et al*., 2013).

In this study, only treatments for 10% chrome and 6% synthetic tanning produced elongation values (68.74%) that complied with ISO 3376:2011 standards, which require elongation≤70%. According to Setiawan *et al*. (2015), high elongation percentages are often associated with reduced elastin during the liming and bating. Elastin is a protein that forms highly elastic fibers, so the more elastin, the more elastic the resulting tanned leather. When the tension is applied, it will stretch and return to normal when the tension is released. Leather elasticity is particularly important for finished goods such as shoes and gloves. Tanned leather that has low elongation will become stiff and uncomfortable when used as shoes. In the shoe industry, if the percentage of leather elongation is too high, it causes the shoes to increase in size and change shape during use because the skin increases in length and the shoes become loose. Conversely, if the percentage of elongation of the resulting tanned leather is low, it causes the leather to break or crack during the shoe-making process during heating (Pahlawan & Kasmudjiastuti, 2012); Hergiyanti *et al*. (2018) found that the skin of snapper, tilapia, and milkfish tanned with 7.5% zirconium tanning agent had low elongation values of 27.49±0.06%, 25.22±0.02%, and 28.74±0.03%, respectively.

The tear strength of the leather

High-quality leather must sufficient flexibility and resistance to tearing to prevent cracks in leather products such as shoes, which require strong tear resistance. Tear strength is influenced by the arrangement of collagen chain in the fish skin. During tanning, collagen chains form cross-links with tanning agents, thereby increasing tear resistance (Roig *et al*., 2011). The tear strength for tanned Chinese herring skin that was only tanned with a chrome tanning agent from 200.69 N/cm^2 to 250.66 N/cm^2. When combined with a synthetic tanning agent, values increased to 250.26 N/cm^2 t - 360.34 N/cm^2 (Table 2). All treatments met the SNI 06-4586-1998 (SNI, 1998) standard for chrome-tanned freshwater snake leather, which requires a minimum tear strength of 150 N/cm^2. This is due to the tanning of 10% chrome and 6% synthetic tanning, which produce a combination of mutually reinforcing crosslinks for the best tear strength resistance. This improvement was attributed to cross-links between the tanning agent and the strong COO^- of collagen chains to form a strong structure of the leather (Dewi *et al*., 2021; Nunung Kholifah *et al*., 2014). In contrast, the active ingredient in synthetic tanning is polyhydroxy benzoles, which have a high ionisation capacity and a lot of hydroxyl groups (both positively and negatively charged). This causes the collagen protein to be strongly attracted to the tanning agent throughout the tanning process (Covington, 2015)

The more functional groups of collagen protein that are bound to chrome and synthetic tanning, the better the quality of the resulting tanned leather. Statistical analysis revealed significant differences among treatments ($p < 0.05$), except for C6S0 and C10S4. At 6% synthetic tanning, higher chrome concentrations significantly increased tear strength ($p < 0.05$), as confirmed by Duncan's test. Chinese herring skin that was tanned with 6% chrome had a tear strength of 200.74 N/cm^2, increasing to 250.66 N/cm^2 when tanned with 10% chrome. Tanning with a combination of chrome and 4% synthetic tanning produced a different pattern than tanning with 6% synthetic tanning. However, when combined with 4% synthetic tanning, increasing chrome concentration (C6S4 to C8S4) significantly reduced tear strength ($p < 0.05$).

In contract, retaining with 6% synthetic tanning, produced tanned leather with increased tear strength that differed significantly ($P<0.05$) with increasing chrome concentration, with the highest tear strength was recorded in 10% chrome and 6% synthetic tanning (C10 S6). These results suggest that a minimum of 6% synthetic tanning is required to substantially improve tear resistance.

According to Hayati *et al.* (2013) and Kusmaryanti *et al.* (2016), Several factors influence tear strength, including skin thickness, collagen density, collagen fiber orientation, and corium thickness. A Chinese herring skin is relatively thin, its collagen structure is less compact, which explains its generally lower tear strength compared with thicker skins (Duraisamy *et al.*, 2016). The tear strength is equivalent to the tensile strength of leather and is inversely related to elongation, when the tensile strength is high, the tear strength tends to be high, while elongation decreases. The tear strength of the tanned Chinese herring skin produced in this study tanned with 10% chrome and retained with 6% synthetic tanning is better when compared to the results of Pratama *et al.* (2018) research on red snapper tanned with 5% mimosa and 12% synthetic tanning, which is 266.84 N/cm^2. As well, when compared with the results of a study by Nunung Kholifah *et al.* (2014), tilapia skin tanned with mimosa at a concentration of 30% had a tear strength of only 235.69 ± 4.77 N/cm^2.

The sewing strength of the leather

Sewing strength, which is closely related to tensile strength and tear strength, determines a leather product's resistance to the mechanical force exerted along sewing threads (Mustakim *et al.*, 2007). In general, leather with high tensile and tear strength also exhibits high sewing strength. Factors influencing sewing strength include skin thickness, collagen quality and density, the orientation of collagen fibers, and corium thickness (Kusmaryanti *et al.*, 2016). In this study, increasing chrome tanning agent concentration improved sewing strength. Tanning with chrome at a concentration of 6% achieved a sewing strength of 564.7 N/cm^2, which would increase to 615.8 N/cm^2 with 10% chrome. When combined with 10% chrome tanning, the sewing strength of leather showed a pattern of decreased sewing strength at 4% and increased sewing strength at 6% of synthetic tanning. The combination of 10% chromium tanning and 4% synthetic tanning concentration produces a sewing strength of 599 N/cm, increasing to 797.2 N/cm^2 if the synthetic tanning concentration is increased to 6%. This indicates that the combination of chrome tanning and synthetic tanning was not sufficient to produce Chinese herring leather with sewing strength comparable to bovine leather. For comparison, Wiyodiningrat *et al.* (2012) reported that bovine leather treated with 4% chrome and 6% synthetic tanning achieved a sewing strength of 1633.33 N/cm, substantially higher than the values obtained in this study. This discrepancy is likely due to the thinner structure and lower collagen density of fish leather compared to bovine hides.

Morphologically, the skin of Chinese herring fish has a thin thickness, so the collagen content is lower than in thicker skin. As a result, achieving high sewing strength requires higher concentrations of syntans during retanning. Zengin *et al.* (2016) reported that improving the mechanical properties of thin fish leather necessitates adjustments in the tanning process, particularly during liming and bating. Such modifications include altering the proportion of lime and protease enzymes used. Similarly, Farid *et al.*

Table 3. The results of the analysis of sewing strength, Shrinkage Temperature and Chromium oxide of Chinese herring leather in various treatments

Treatment	Sewing Strength (N/cm^2)	Shrinkage Temperature (^{o}C)	Chromium Oxide (%)
C6S0	564.7±0.34 ^{d}	73.33±0.13 ^{c}	1.58±0.08^c
C8S0	583.9±2.59^e	66.67±0.33 ^{a}	0.96±0.07^a
C10S0	615.8±1.15^g	73.33 ±0.42 ^{c}	1.56±0.09^c
C6S4	666.4±1.04^h	78.60 ±0.22 ^{e}	1.42±0.05^{bc}
C8S4	524.7±1.59^b	72.67±0.09 ^{b}	0.74±0.15^a
C10S4	599±2.31^f	79.33 ±0.35 ^{f}	1.41±0.16^{bc}
C6S6	516.6±1.31^a	79.33 ±0.08 ^{f}	1.38±0.15^{bc}
C8S6	542.33±0.25^c	75.00 ±0.19 ^{d}	1.21±0.09^b
C10S6	797.2±1.8 ^{I}	80.67±0.19 ^{g}	1.48±0.15^c
Standard 06-4263-1996	min 900	Min 70	Max 3

Note: The same letters indicate no significant difference.

(2016) observed that soaking tilapia skin in 1% bovine pancreas for 60 minutes improved the tear strength of the resulting tanned tilapia skin.

The Shrinkage Temperature

The shrinkage temperature of Chinese herring leather in this study ranged from 66.67°C to 80.67°C. All treatments met the shrinkage temperature standards issued by SNI 00253 2009 of e” 70°C (SNI, 2009), except for the 8% chrome treatment. The shrinkage temperature of the Chinese herring fish skin that was tanned with chrome tanning agent ranged from 66.60 °C- 73.33°C, while the addition of 6% synthetic tanning significantly increased shrinkage temperature 75.00°C - 80.67°C. The increase in shrinkage temperature was attributed to the greater number of cross-links formed between collagen amino groups and tanning agents. As more collagen fibres bind to the tanning agent, the leather structure becomes more stable, resulting in higher shrinkage temperatures (Jian *et al.*, 2012; Nuraini, 2019). Statistical analysis showed no significant difference ($p > 0.05$) between C6S0 (6% chrome only) and C10S0 (10% chrome only). However, leather tanned with 8% chrome had the lowest shrinkage temperature (66.67 °C), which was significantly different ($p < 0.05$) from the other treatments. Retanning with synthetic tanning generally caused significant increases in shrinkage temperature ($p < 0.05$), except in C10S4 and C6S6.

The shrinkage temperatures observed in this study were relatively low compared with tilapia leather tanned with 15% gambier (*Uncaria gambier*), which reached 104 ± 2.00°C according to research by Setiawan *et al.* (2015).

This suggests that tilapia tanned with gambier has greater thermal stability and can withstand temperatures close to 100 °C. High shrinkage temperatures provide safety margins for washing and ironing processes, as these are usually conducted below the shrinkage threshold. The tanning agent strongly influences shrinkage temperature. Chrome-tanned leather may reach values above 100 °C, up to 115 °C (China *et al.*, 2020). In contrast, vegetable-tanned leather typically shows shrinkage temperatures of 80–85 °C, while aldehyde-tanned leather ranges from 70–80 °C (Maina *et al.*, 2019). According to China *et al.* (2020), Leather with higher shrinkage temperatures tends to last longer, as it demonstrates superior heat resistance. The shrinkage temperature is also associated with the content of amino acids, especially hydroxyproline, which contributes to collagen's thermal stability. The amount of hydroxyproline depends on the environmental temperature where the fish live (Wairimu *et al.*, 2020). The shrinkage temperature of Chinese herring skin in this study had a higher shrinkage temperature than those reported by Dewi et al. (2021) for grouper skin tanned with 6% chrome tanning agent and 2% mangrove extract at 71.23 ±1.2°C. For comparison, Wairimu et al. (2020), found that raw tilapia skin had a shrinkage temperature of 53.33 ± 0.94°C, which increased to 98.67± 0.47°C after chrome tanning.

The chemical properties

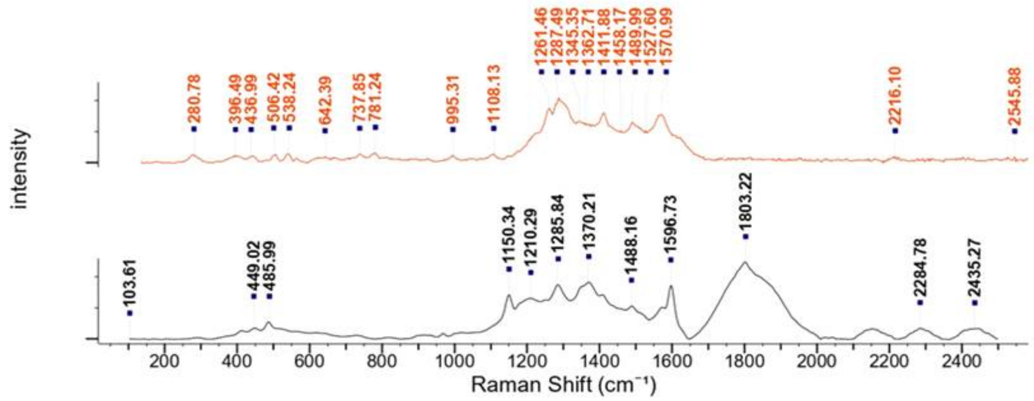
The content of chrome oxide

Chrome tanning is widely considered the most effective and efficient method because it enhances the hydrothermal stability of leather, reduces tanning time, improves overall leather quality, and provides flexibility in its applications (Zhu et al., 2020). However, chrome tanning also has drawbacks, particularly the potential formation of hexavalent chromium (Cr VI), which is toxic and associated with cancer, skin allergies, and liver and kidney necrosis (Sharma et al., 2022). According to ISO 24092:2019, the permissible limit for Cr VI in chrome-tanned bovine leather used for finished goods is d”3 mg/kg (Murti & Sugihartono, 2020). In this study, the chrome oxide content of Chinese herring leather ranged from 0.96% to 1.58%, which was below the maximum permissible level specified by ISO 24092:2019 (Table 3).

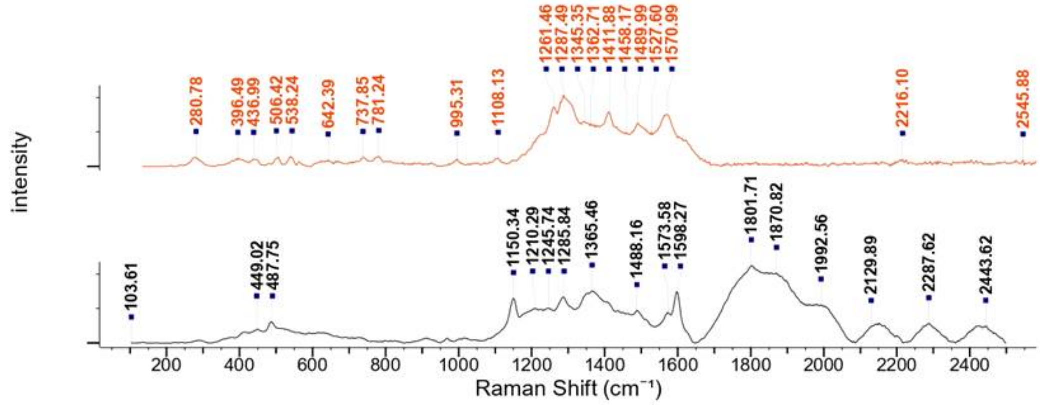
Statistical analysis showed significant differences among treatments ($p < 0.05$), except for C8S0 and C8S4, which had the lowest levels (0.74–0.98%). The relatively low chrome oxide content in these treatments suggests that the chrome did not bind effectively with collagen and was instead lost during the washing process (Jian *et al.*, 2012). Overall, leather tanned with 6% and 10% chrome exhibited higher chrome oxide levels than that tanned with 8% chrome. To minimize residual chromium, Murti & Sugihartono (2020), recommended thorough washing to remove excess tanning agents and chemicals. Additionally, drying leather should be carried out in shaded conditions, as direct sunlight can oxidize Cr (III) into the more harmful Cr (VI).

Identification Functional Group

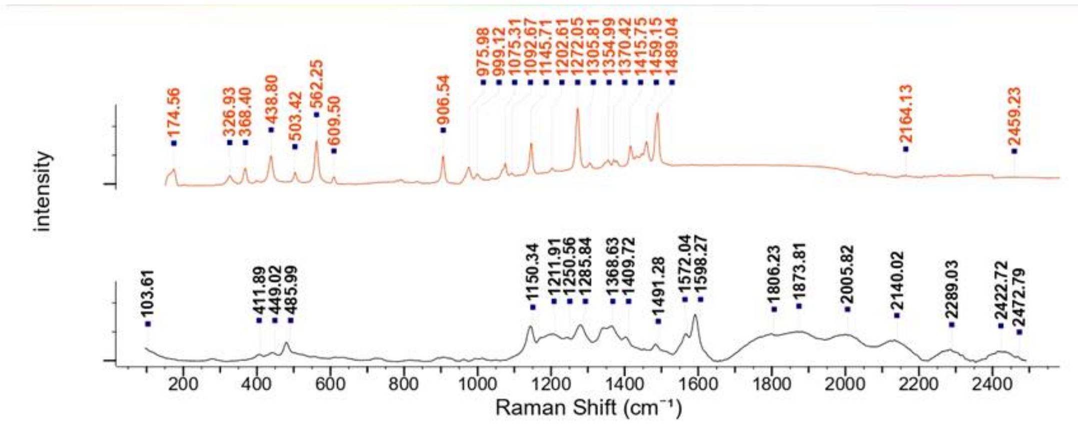
The identification of the Chinese herring-tanned functional groups can be seen in Figure 1. Figure 1 shows the absorption peaks in the Raman shift region, ranging from 200 to 2500 cm^{-1}. The absorption pattern that appears has an absorption pattern that is almost the same as collagen; this is because more than 50 - 70% of fish skin is composed of collagen protein (Jafari *et al.*, 2020). Therefore, tanned fish skin has the same absorption pattern as collagen and a specific absorption pattern that occurs due to the tanning process. In this



C10 S0



C10 S4



C10 S6

Figure 1. Raman spectra of functional groups fish-skin tanned using 10% chrome and 0%, 4% 6 % synthetic agent.

tanning process, cross-links occur between chrome tanning materials and carboxyl groups ($COOH^-$) from collagen amino acids and between collagen amino acids and formaldehyde and phenol from synthetic tanning agent (Murti & Sugihartono, 2020; Roig *et al*., 2011).

The identification of functional groups on tanned Chinese herring skin showed absorption at the Raman shift of 485 cm^{-1}, signifying the existence of an á-helix bond formed by the amino acid structure between the NH2 and COOH- groups and the C atom of the amino acid. The á-helix component of the amino acid collagen in the Raman shift has an absorption area of 432–488 cm^{-1} (Luo *et al.*, 2022), and this study indicated that there is absorption in the Raman shift of 445.49–485.99 cm^{-1}. Another absorption that appears at the Raman shift of 1148–1150 cm^{-1} indicates the presence of vibrational absorption of the C=N nitrile group from amide 3. The presence of amide 3 with N=H bonds is indicated by the absorption at the Raman shift of 1284-1287 $cm^{-1.}$ Amida 3 has a surface area absorption at the Raman shift 1230 to 1300 cm^{-1} (Prokopi *et al.*, 2021). Absorption at Raman shift 1488.16 cm^{-1} is the amide 2 group with a C-H bond. According to France *et al*. (2014), the amide 2 group has an absorption area on the Raman shift ranging from 1480 to 1580 cm^{-1}. While the absorption at a wavelength of 1596.73-1598.23 cm^{-1} is amide I with C=O. Amida I has an absorption with a Raman shift and a range of 1600–1690 cm^{-1}. In this study, amide 1 was identified with a slightly smaller shift in the Raman shift absorption region. Two spectra that stood out were identified as amide 1 and amide III, which are collagen peptides in fish skin (Zhang *et al.*, 2019). The collagen spectrum has an absorption on the Raman shift, which is identified as amide 1 with an absorption area of 1600–1800 cm^{-1}, with a light source from stretching C = 0. Amida II has a light source from the N-H bend coupled with C-N stretching and an absorption area of 1590–1650 –1650 $cm^{-1.}$ (Jafari *et al.*, 2020). Whereas Luo et al. (2022) showed that the C-H stretching vibration of the amide II structure occurred at the Raman shift of 1452–1456 cm^{-1}, Amida III had an absorption region at the Raman shift of 1210–1350 cm^{-1}. There are two types of vibrations, namely stretching between carbon and nitrogen and methyl group bonds and stretching between carbon and hydrogen atoms (C-H) (France *et al.*, 2014). The peptide vibration that occurs at the peak of the Raman shift is around 1367.95–1385.16 cm1 and is quite sharp; in the Raman spectroscopy library, it is shown as Lumi chrome (-Cr-OOC-). This absorption always appears on the fingerprint of each treatment sample observed. It is suspected that this absorption is due to a compound that occurs due to a bond between the amino acids of the collagen protein and the chromium compound used as a tanning agent. resulting in interlocking cross-linkages that make the skin dancer (Wairimu *et al.*, 2020). While the absorption at the Raman shift of 1803–1804 cm^{-1} is the absorption of the vibration of the ketonic group (C=O) (Martinez *et al.*, 2019).

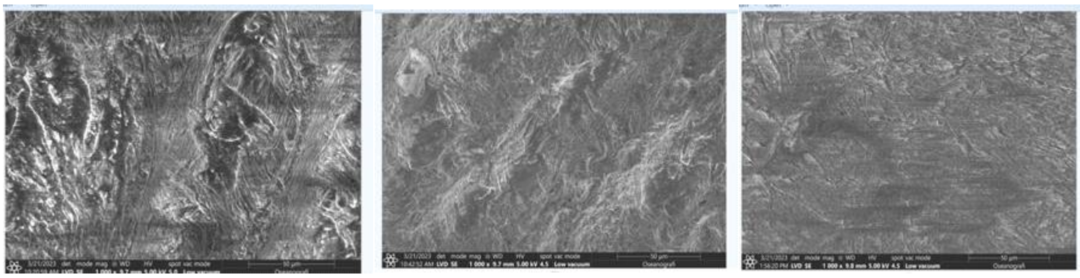
The analysis of Raman shift spectra showed that increasing chrome concentrations resulted in a greater number of Raman fingerprints. Re-tanning with synthetic tanning agents also enhanced the visibility and intensity of Raman peaks. As shown in Figure 1, Chinese herring leather tanned with 10% chrome and re-tanned with 0%, 4%, and 6% synthetic tanning exhibited distinct spectral patterns. The fewest Raman fingerprints were observed in leather tanned without synthetic tanning (0%), whereas the highest number of peaks appeared in samples treated with 10% chrome and 6% synthetic tanning. This indicates that higher chrome concentrations promote stronger cross-linking between collagen molecules and chrome compounds. The addition of synthetic tanning further strengthens these interactions by providing additional bonding sites, resulting in more stable and complex collagen–tannin structures.

The Raman shift spectra revealed additional compounds in samples re-tanned with synthetic tanning agents. These compounds are believed to promote cross-linking between collagen amino acids and synthetic tannins. Synthetic tanning agents are typically synthesized through the condensation of aromatic compounds—such as phenol, phenol sulfonic acid, or naphthalene sulfonic acid with formaldehyde (Maina *et al.*, 2019). Spectral analysis using the Raman spectrophotometer library identified a compound similar to 6-amino-2,4-dimethylphenol, which contains aromatic groups exhibiting C=C double-bond vibrations within a broad Raman shift range of 208.35–2445.87 cm^{-1}. The strong absorption observed between 2125 and 2450 cm^{-1} corresponds to stretching vibrations of the N=C=O double bond, typically appearing within 2250–2300 cm^{-1}. Additionally, vibrations of the N=C=S bond were detected between 2200 and 2000 cm^{-1} (Martinez *et al.*, 2019). These findings indicate that re-tanning with synthetic tanning introduces aromatic functional groups capable of forming additional bonds with collagen, thereby enhancing molecular interactions and improving the structural stability of the leather.

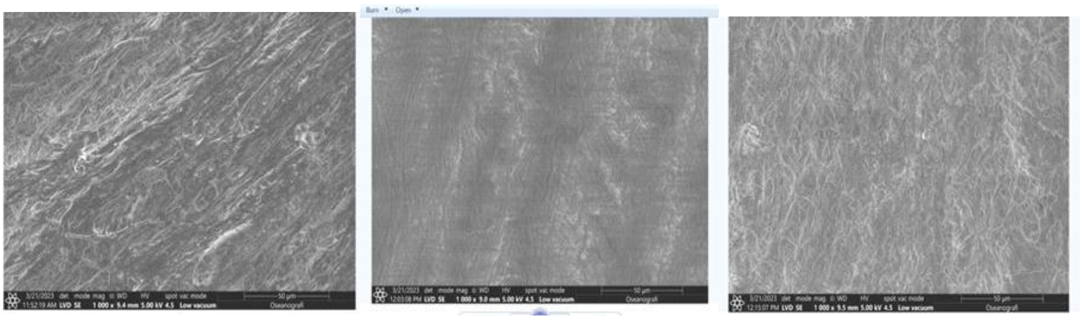
Scanning Electron Microscope

The results of the characterization of the skin of Chinese herring fish using SEM-Thermo Scientific Prima E with a magnification of 1000 x under various treatments are presented in Figure 2. The cross-section of leather that was only tanned with chrome at a concentration of 6% without retaining it with synthetic tanning agents showed a less compact skin. The higher the concentration of chrome used (C8S0 and C10S0), the denser and more compact the skin tissue produced. This is attributed to the increased availability of carboxyl groups (–COOH) from collagen that can bind with chromium compounds, resulting in a stronger and more cohesive skin matrix (Roig *et al.*, 2011). Although re-tanning with synthetic tanning agents at 4% and 6% concentrations improved structural uniformity, the micrographs still revealed less compact tissue compared with samples tanned using higher chrome concentrations (8% and 10%). These results confirm that higher chrome levels enhance fiber cross-linking, producing tighter collagen networks and denser leather morphology.

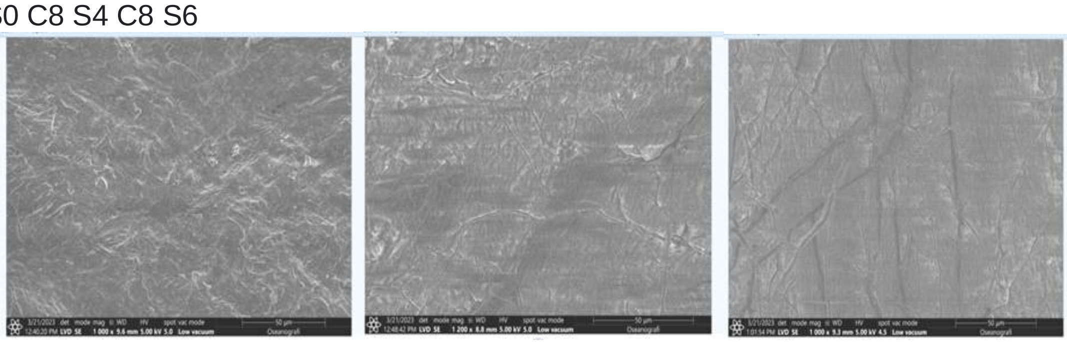
Retaining with synthetic tanning agents showed a denser cross-section of the skin. The process of re-tanning with synthetic tanning can fill the spaces between collagen fibre bundles in the skin of Chinese herring fish, resulting in denser and more compactly tanned skin (Duraisamy et al., 2016). Complex active ingredients used in synthetic tanning take the form of polyhydroxybenzole groups, which can attach to skin collagen to create hydrogen bonds and result in skin that is more compact and denser (Covington, 2015). Thus, re-tanning with synthetic tanning agents can produce denser and more compactly tanned skin compared to skin tanned only with chrome tanning agents. It is evident that retaining a 6% synthetic tanning agent shows denser skin tissue in the fish compared to the skin directly retained with a 4% synthetic tanning agent. The higher the concentration of chrome and synthetic tanning agents used, the denser and more compact the tanned skin produced. In this study, it was seen that treatment C10S6 had a denser and more compact cross-section compared to other treatments.



C6S0 C6S4 C6S6



C8 S0 C8 S4 C8 S6



C10 S0 C10 S4 C10 S6

Figure 2. Analysisis cross-section of skin at various treatments using Scanning Electron Microscope.

Conclusion

Chinese herring leather tanned with a combination of chrome and synthetic tanning agents was denser and fuller than leather tanned solely with chrome. Physical tests demonstrated that this combination improved tensile strength, tear strength, shrinkage temperature, and sewing strength, while reducing elongation. These findings indicate that the overall quality of the tanned leather was enhanced. The optimal results were obtained using 10% chrome and 6% synthetic tanning agents, producing leather with the highest tensile, tear, and stitch strength, the greatest shrinkage temperature, and the lowest elongation.

These properties complied with the specifications of SNI 0253:2009 for patterned leather. The tanning process that combines chrome and synthetic retanning agents shows strong potential for further development in regions producing Chinese herring. This approach represents a promising method to increase the economic value of fish by-products through sustainable leather production.

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