CHROMIUM REPLACEMENT WITH ZIRCONIUM MATERIALS IN THE LEATHER TANNING INDUSTRY TO REDUCE POLLUTANTS ON THE PHYSICAL FEATURES OF LEATHER

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ABSTRACT. Sheepskin has been used since ancient times for footwear, clothing, and accessories. Tanning transforms raw hide into a durable and stable product, protecting it from microbial degradation, heat, sweat, and moisture. However, traditional tanning processes use dangerous chemicals such as chrome, formaldehyde, and other volatile organic compounds that can pollute the environment and pose health risks. This research aimed to explore the use of zirconium as an alternative, more environmentally friendly tanning material in the sheepskin tanning process. The research method used a Completely Randomized Design (CRD) with four zirconium concentration treatments (7.5%, 10%, 12.5%, and 15%) and three replications. Observed variables include tensile strength, elongation, laxity, thickness, and tear strength of the skin, which are measured using ISO and SNI standards. The data obtained were analyzed using analysis of variance (ANOVA) and Duncan's Multiple Range Test (DMRT). The research showed that zirconium significantly increases the tensile strength, elongation, thickness, and tear strength of sheepskin. The highest tensile strength was at a concentration of 15% (2440.56 N/mm^2), and the lowest was at 7.5% (1339.05 N/mm^2). Skin elongation and thickness also increased with zirconium concentration, with the highest being at a concentration of 15% (115.59 mm). The highest tear strength was at 15% (393.97 N/mm), while skin laxity showed no significant difference between concentrations. The conclusion of this research is that zirconium can be used as an effective and environmentally friendly alternative tanning material in the sheepskin tanning process.
KEYWORDS: zirconium, sheepskin, mordant, tanning

ÎNLOCUIREA CROMULUI CU ZIRCONIUL ÎN INDUSTRIA DE PIELĂRIE PENTRU A REDUCE ACȚIUNEA POLUANȚILOR ASUPRA CARACTERISTICILOR FIZICE ALE PIEILOR

REZUMAT. Pielea de oaie a fost utilizată încă din antichitate pentru încălțăminte, îmbrăcăminte și accesorii. Procesul de tăbăcire transformă pielea brută într-un produs durabil și stabil, protejând-o împotriva degradării microbiene, căldurii, transpirației și umidității. Însă procesele tradiționale de tăbăcire folosesc substanțe chimice periculoase precum cromul, formaldehida și alte compuși organici volatili care pot polua mediul și care reprezintă riscuri pentru sănătate. Această cercetare și-a propus să exploreze utilizarea zirconiului ca material de tăbăcire alternativ, mai prietenos cu mediul, în procesul de tăbăcire a pielii de oaie. S-a utilizat un Design Complet Randomizat (CRD) ce a cuprins tratamente cu patru concentrații diferite de zirconiu (7,5%, 10%, 12,5% și 15%) și trei repetări. Variabilele observate includ rezistența la tracțiune, alungirea, flexibilitatea, grosimea și rezistența la sfâșiere a pielii, măsurate utilizând standardele ISO și SNI. Datele obținute au fost analizate folosind analiza de varianță (ANOVA) și testul Duncan pentru intervale multiple (DMRT). Cercetarea a arătat că prezența zirconiului conduce la o creștere semnificativă a rezistenței la tracțiune, alungirii, grosimii și rezistenței la sfâșiere a pielii de oaie. Cea mai mare rezistență la tracțiune a fost la o concentrație de 15% (2440,56 N/mm^2), iar cea mai mică la 7,5% (1339,05 N/mm^2). Alungirea și grosimea pielii au crescut, de asemenea, odată cu concentrația de zirconiu, cea mai mare fiind la o concentrație de 15% (115,59 mm). Cea mai mare rezistență la sfâșiere a fost de 15% (393,97 N/mm), în timp ce pentru flexibilitatea pielii nu au existat diferențe semnificative între concentrații. Concluzia acestei cercetări este că zirconiul poate fi utilizat ca un material de tăbăcire eficient și prietenos cu mediul în procesul de tăbăcire a pielii de oaie.
CUVINTE CHEIE: zirconiu, piele de oaie, mordant, tăbăcire

REMPLACEMENT DU CHROME PAR DES MATÉRIAUX À BASE DE ZIRCONIUM DANS L'INDUSTRIE DU TANNAGE DU CUIR POUR RÉDUIRE L'IMPACT DES POLLUANTS SUR LES CARACTÉRISTIQUES PHYSIQUES DU CUIR

RÉSUMÉ : La peau de mouton est utilisée depuis l'Antiquité pour les chaussures, les vêtements et les accessoires. Le tannage transforme la peau brute en un produit durable et stable, la protégeant de la dégradation microbienne, de la chaleur, de la transpiration et de l'humidité. Cependant, les procédés de tannage traditionnels utilisent des produits chimiques dangereux tels que le chrome, le formaldéhyde et d'autres composés organiques volatils qui peuvent polluer l'environnement et poser des risques pour la santé. Cette recherche visait à explorer l'utilisation du zirconium comme matériau de tannage alternatif et plus respectueux de l'environnement pour le tannage de la peau de mouton. La méthode de recherche a utilisé un plan complètement randomisé (CRD) avec quatre traitements de concentration de zirconium (7,5 %, 10 %, 12,5 % et 15 %) et trois répétitions. Les variables observées incluent la résistance à la traction, l'élongation, la flexibilité, l'épaisseur et la résistance à la déchirure de la peau, mesurées selon les normes ISO et SNI. Les données obtenues ont été analysées par analyse de variance (ANOVA) et test de Duncan pour comparaison multiple des moyennes (DMRT). La recherche a montré que la présence du zirconium augmente significativement la résistance à la traction, l'élongation, l''épaisseur et la résistance à la déchirure de la peau de mouton. La plus haute résistance à la traction a été obtenue à une concentration de 15 % (2440,56 N/mm^2), et la plus faible à 7,5 % (1339,05 N/mm^2). L'élongation et l'épaisseur de la peau ont également augmenté avec la concentration de zirconium, avec un maximum observé à 15 % (115,59 mm). La résistance à la déchirure la plus élevée était de 15 % (393,97 N/mm), tandis que la flexibilité de la peau n'a montré aucune différence significative entre les concentrations. La conclusion de cette recherche est que le zirconium peut être utilisé comme un matériau de tannage efficace et respectueux de l'environnement dans le processus de tannage de la peau de mouton.
MOTS CLÉS : zirconium, peau de mouton, mordant, tannage

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INTRODUCTION

Sheepskin is a natural material that has been used since ancient times for various products, for instance footwear, clothing, and fashion accessories. Tanning is a crucial stage in leather production that transforms raw hides into durable and stable leather products. Deep tanning protects the skin from environmental factors such as microbial degradation, heat, sweat, and humidity [1]. Chromium sulfate has become the primary choice in tanning due to its ability to stabilize collagen fibers and prevent decay [2]. The conventional leather tanning process frequently utilizes harmful chemicals, including chromium, formaldehyde, and other volatile organic compounds. The use of chrome in tanning can lead to the contamination of water and soil with hazardous waste, which contains hexavalent chromium. Hexavalent chromium (Cr^{6+}) is a carcinogenic substance that poses significant risks to both human health and the environment. Apart from that, formaldehyde used in the tanning process is also known to be a compound that is dangerous to human health, especially if exposed in the long term [3].

The use of chromium in leather tanning may present health hazards, particularly concerning allergic contact dermatitis [4]. Organic tanning agents, such as wattle extract and active chlorine, show potential in effectively tanning skin while reducing environmental impact [5]. The development of a cleaner tanning process by replacing chemicals with natural alternatives, such as vegetable tanning, synthetic phenolic products, and aluminum salts, is urgently needed [6]. Incorporating natural plant extracts throughout the leather processing stages, including tanning, re-tanning, dyeing, and degreasing, provides a more sustainable and environmentally friendly approach to leather production [7]. Leather tanned with recycled chromium has similar physical and chemical properties to leather tanned with fresh chromium, indicating a potentially cost-effective and environmentally friendly method [8].

An intriguing alternative in the leather tanning process is the use of zirconium. As a transition metal, zirconium possesses unique chemical properties, such as a high degree of stability and a propensity to form strong shell bonds. These characteristics make zirconium a compelling option as an environmentally friendly and efficient tanning agent. Typically, chromium sulfate and aluminum sulfate are employed in leather tanning to cross-link collagen molecules and stabilize the skin structure. However, zirconium offers similar tanning capabilities while potentially mitigating the environmental harms linked to chromium use [9]. The mixtures of zirconium with other tanning agents, such as multi-branched polymers, have been shown to increase the thickness, softness, and physico-mechanical properties of leather [10]. Zirconium salts mixed with aluminum salts have been identified for their good tanning ability, making them a viable alternative to traditional chrome tanning agents [11].

With increasing awareness of the environmental impact of the tanning industry, the use of zirconium as a tanning agent is becoming a more environmentally friendly alternative to chrome. Zirconium tanning offers advantages in improving the physical and mechanical qualities of leather, such as tensile strength, elasticity, and crack resistance, while reducing the toxic waste generated in the tanning process [12]. Compared to conventional tanning methods, zirconium produces leather with more stable characteristics, is more resistant to environmental degradation, and has a higher level of safety for industrial workers. Therefore, research into tanning using zirconium has the potential to be an innovative solution to create a more sustainable leather industry without compromising the quality of the final product.

Several studies have investigated the application of zirconium salts in leather tanning. [31] developed a green tanning method using POSS-COONa combined with zirconium for cleaner leather production. [21] assessed low pickle processing quality utilizing zirconium tanning systems. Moreover, [10] explored hyperbranched polymer systems incorporating zirconium salts to enhance leather quality. Despite these efforts, most research focuses on blending zirconium with synthetic polymers or other metal salts and utilizes industrial waste as raw material. There remains a paucity of comprehensive studies on the direct use of zirconium salts at varying concentrations, specifically for tanning fresh sheepskin while evaluating multiple critical physical attributes. This study uniquely investigates the direct impact of pure basic zirconium sulfate application at different concentrations on sheepskin quality, aiming to optimize a straightforward and eco-friendly tanning technique without the aid of complex chemical additives.

EXPERIMENTAL

Materials and Instrumentations

The materials used in this study were: sheepskin, plants, flowers, non-iodized salt (NaCl), sodium sulfide (Na_2S), quicklime ($Ca(OH)_2$), ammonium sulfate (ZA), Feliderm, formic acid, sodium formate, sulfuric acid (H_2SO_4). The equipment used in tanning included analytical scales, a fleshing machine, a fleshing knife, gloves, a plastic bucket, pH paper, and a thermometer.

The zirconium tanning agent used was basic zirconium sulfate ($Zr(SO_4)_2$), purchased from Sigma-Aldrich (purity: 99%). No additional chemical modifications were performed prior to application.

The treatments consisted of four levels:

- T1: 7.5% zirconium relative to the wet weight of pickled sheepskin;
- T2: 10% zirconium relative to the wet weight of pickled sheepskin;
- T3: 12.5% zirconium relative to the wet weight of pickled sheepskin;
- T4: 15% zirconium relative to the wet weight of pickled sheepskin.

The concentration percentage refers to the ratio of the zirconium tanning solution added, relative to the pickled pelt's weight.

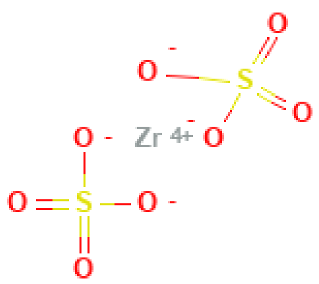

Figure 1. Chemical structure of basic zirconium sulfate: ($Zr(SO_4)_2$)

This complex enables effective cross-linking with collagen fibers during the tanning process, stabilizing the leather structure.

Data Collection and Statistical Analysis

Raw hides, freshly separated from the animal through the skinning process, usually still contain a lot of dirt, hair, and fat. The first stage in the Beam House is soaking where the hides are immersed in water to remove blood, salt, and other impurities. After soaking, the skin will go through a liming process to loosen unwanted hair and tissue. This is done using alkaline solutions such as calcium hydroxide and sodium sulfide. Loose hair is then removed through unhairing, and excess tissue such as the epidermis, is removed through fleshing. After that, the leather undergoes a deliming process to neutralize the chemicals used in shaving and ends with a bating process involving enzymes to soften the leather and remove protein residues, followed by acidification and the final stage of chrome or vegetable tanning. The observation variables in this study are tensile strength, elongation, softness, thickness, and tear strength. The data obtained were tabulated in an Excel program. Analysis of variance (ANOVA) was used to test the effect of various zirconium concentrations in the SPPS program. Mean values between treatments were compared using Duncan's multiple range test (DMRT) when the model detected a significant effect of treatment ($p < 0.05$).

Before entering the discussion of the leather production process as a whole, Table 1 is first presented, which shows the comparison of measurement results between semi-finished products and finished leather products. This table aims to provide an initial understanding of the changes in the physical characteristics and quality of leather during the tanning and finishing process, so that it can be a reference in assessing the effectiveness of each stage in the production process.

Table 1: Differences in measurement results between semi-finished products and finished leather products

Parameters	Semi-finished Products	Finished Leather Products
Thickness (ISO 2589:2002)	Evaluate the tanning process	Ensure consistency of the final product
Softness (ISO 17235:2011)	Checking initial flexibility	Assessing comfort of use
Tensile Strength (ISO 3376:2011)	Assessing raw material quality	Assuring product durability
Elongation (ISO 3376:2011)	Checking basic elasticity	Determining final flexibility
Tear Strength (ISO 3377-1:2011)	Ensures that it does not tear easily before finishing	Tests durability in use

Before describing the process that occurs in the beam house stage in detail, Table 2 summarizes the main stages and the operational parameters used. This table provides a comprehensive overview of the process sequence, the types of chemicals used, and the conditions such as time, temperature, and concentration, required in each stage, thus facilitating an understanding of the entire leather pre-treatment flow.

Table 2: The beam house process

1. Soaking Process			
Percentage %	Recipe	Round	Description
200	Water	60 minutes	Rinsed 2x
Washing for 60 minutes to 200% water			
0.3	Wetting Agent	30 minutes	
Rotated 60 Minutes and Rinsed with Flowing Water 40 Minutes			
2. Liming Process (Calcification)			
Percentage %	Recipe	Round	Description
Water conditioned to 100%			
3	Quicklime	20 minutes	
1.5	Na_2S		
Rested 20 minutes			
Run for 40 minutes			
3	Quicklime	20 minutes	
1.5	Na_2S		
Added water up to 300%			
Run for 20 Minutes			
Overnight			
Rotated 150 minutes pH 12-13			
Wash until skin is clean 30 minutes			
3. Reliming Process (Re-fortification)			
Percentage	Recipe	Round	Description
2	ZA	60 Minutes	pH 11
200	Air		
Discharged Water			
4. Deliming Process (Lime Disposal)			
Percentage %	Recipe	Round	Description
200	Air	60 minutes	pH 7-8
2	ZA		
0.3	H_2SO_4		
Reduce water by 50%			
5. Degreasing Process (Fat Elimination)			
Percentage %	Recipe	Round	Description
100	Water	20 minutes	
0.5	Peltech PH-C		
2	ZA		
0.5	H_2SO_4		Diluted with water 1:20 side entry
6. Bating Process (Protein Erosion)			
Percentage %	Recipe	Round	Description
2	Feliderm	60 minutes	Each treatment is rotated together and checked by permeability test/thumb test.
Wastewater			

Percentage %	Recipe	Round	Description
	7. Pickle Process (Acidification)		
10	Salt	10 minutes	
100	Water		
1.5	FA	5x15 minutes	Dissolved with water 1:10
0.5	H_2SO_4	2x20 minutes	Dissolved with water 1:20
	BCG test pH 2.5		
	Rotated 60 minutes		

Percentage %	Recipe	Round	Description
	8. The Tanning Process		
7.5	Chrome Sulfate	60 minutes	Penetration check
7.5	Zirconium	60 minutes	Penetration check
10	Zirconium	60 minutes	Penetration check
12.5	Zirconium	60 minutes	Penetration check
15	Zirconium	60 minutes	Penetration check
	Overnight		
	Run for 60 minutes		
2	Natrium Phosphate	2x20 minutes	
	In BCG check pH <4		
0.5	Baking soda	2x20 minutes	Dissolved with water 1:10
	BCG check (yellow color)		
0.5	Baking soda	2x20 minutes	Dissolved with water 1:10
	100°C wrinkle temperature test		
0.5	Baking soda	2x20 minutes	
	Overnight		
	Run for 120 minutes		
	Wrinkle temperature tested with glycerin solution		

RESULTS AND DISCUSSIONS

The laboratory analysis results indicated that varying levels of zirconium had a highly significant impact on tensile strength, elongation, thickness, and tear strength (P>0.01), while the effect on laxity was not significant (P>0.05). The average skin quality data from the study are summarized in Table 3. The results of tanning with zirconium during the study period were highest at 15% concentration and lowest at 7.5%. The results of tensile strength, elongation, softness, thickness, and tear strength ranged from 2440.56 N/mm^2, 115.59%, 7.36%, 1.24 mm, and 393.97 N, respectively.

Table 3: Results of quality testing of tanned leather with zirconium

Percentage	Materials	Tensile strength (MPa)	Elongation (%)	Softness (%)	Thickness (mm)	Tear Strength (N)
7.5%	Chrome	1205.00±85.53a	49.43±3.37a	5.45±0.81	0.86±0.27a	181.91±11.83a
7.5%	Zirconium	1339.05±94.94a	59.17±5.56a	6.66 ± 0.94	0.96 ± 0.11a	189.91±14.99a
10%	Zirconium	2125.25±72.63b	72.89±2.14b	7.18 ± 0.60	0.98±0.70a	260.62±19.79b
12.5%	Zirconium	2242.31±87.18c	89.06±2.48c	7.26 ± 0.95	1.10±0.15b	284.16±18.64c
15%	Zirconium	2440.56±90.19d	115.59±9.50d	7.36 ± 0.30	1.24 ± 0.08b	393.97±17.54d

Note: Different superscripts indicate that the treatments have significantly different effects (P>0.01).

Tensile Strength

The highest tensile strength was recorded at a 15% zirconium concentration (2440.56±90.19d), while the lowest was observed at a 7.5% concentration (1339.05±94.94a). Generally, tensile strength increases with higher tanning agent concentrations due to enhanced dispersion of collagen fibers within the skin, which is driven by the tanning agent [13]. Tensile strength measures the ability of leather to withstand tension without being damaged. In the study, results showed that the pre-mordant method produced the highest tensile strength compared to other methods. The use of chromium at 4% also increased the tensile strength of the leather [14-16]. The increased interaction between the tanning agent and collagen fibers contributes to higher tensile strength by regulating the charge properties of the tanned skin [17]. According to [18] higher tannin concentration leads to better tensile strength properties. Tannin concentration can increase tensile strength and provide additional benefits such as resistance to microbes and improved color retention in tanned leather [19]. One of the main penetration mechanisms is the electrostatic interaction between tanning agents and collagen fibers. [20] showed that negatively charged tanning agents diffuse into collagen fibers due to electrostatic attraction with positively charged amino groups present in collagen.

Similarly, the study highlights that chrome-free tanning agents, which often include synthetic tannins, result in superior tensile and grain strength due to their effective filling of the leather matrix. One of the main reasons for the increase in tensile strength is the effective interaction between the tanning agent and the collagen fibers. This improvement is due to the ability of the tanning agent to fill the leather matrix more effectively, resulting in better fiber bonding [21]. The duration of exposure to tanning agents also affects penetration depth. [22] noted that the interaction between chrome tanning agents and collagen fibers is influenced by the soaking time, which can enhance the penetration of these agents into the collagen matrix. [23] found that adjusting the pH during the tanning process promotes the deprotonation of carboxyl groups on collagen, enhancing their interaction with chromium ions and facilitating deeper penetration into the collagen matrix.

Elongation

Based on the mean values in Table 1, which are 59.17±5.56a (7.5%), 72.89±2.14b (10%), 89.06±2.48c (12.5%), and 115.59±9.50d (15%), the elongation of sheepskin increased with the addition of zirconium concentration. Skin elasticity is the ability of the skin to stretch or elongate without damage to its structure. Leather can withstand elastic deformation and return to its original shape after the stretching force is released. Leather elongation is important in various applications, including in the tanning industry [24]. Zirconium, as a tanning agent, interacts with the collagen structure, promoting cross-linking between collagen molecules. These cross-links are essential for improving the elasticity and flexibility of leather. Studies have shown that zirconium can produce improvements in the mechanical properties of leather, including elongation at break [21]. The addition of certain concentrations of tanning agents can improve the physical characteristics of sheepskin, including elongation. The tanning process alters collagen fibers, increasing their stability and elasticity [9].

Elongation of tanned leather can vary based on the source and age of the leather. Skins cut from elderly subjects tend to exhibit decreased elongation ability, which may affect the overall elongation properties of tanned leather [25]. The use of mimosa tannins can increase tensile strength and elongation, which indicates its effectiveness as a tanning agent not only preserves leather but also improves its physical properties [19]. The greater amount of collagen fibers in sheepskin leads to increased tensile strength and elasticity, which are essential to achieve the desired elongation at fracture [26]. Fatliquoring is the process of incorporating oil into the leather. Fatliquoring methods to increase the softness and elasticity of tanned leather, thereby improving its elongation properties [27]. Elongation or stretchability of leather refers to how far the leather can stretch before breaking. The best elongation results are generally found in leathers tanned with methods that take into account natural ingredients, such as enzymes or plant extracts. Elongation values ranged from 40-60% in some of these studies, indicating sufficient stretchability for the needs of the textile industry and leather-based products [16, 28, 29].

Softness

Table 1 shows that the best skin laxity can be seen from the highest average, which was 7.36±0.30 found in the 15% zirconium concentration treatment. The density and compactness of the skin can affect its ability to retain moisture and lubrication. When the skin is tight and dense, there is less space for oil to lubricate the skin fibers, which can lead to decreased skin laxity [30]. Tanning agents can get between the skin's collagen fibers, creating gaps between them that increase their range of motion. This allows the skin's collagen fibers to become more elastic and increases its relative laxity [31]. Zirconium sulfate has optimal filling properties that facilitate the dispersion of collagen fibers. This significantly increases skin density and laxity, providing better results [32].

The mechanical properties of leather, including its elasticity and tensile strength, play an important role in determining softness. The arrangement of collagen fibers within the skin can affect its softness. A looser fiber structure usually results in softer leather. The drying process during leather production can increase softness, as the drying process causes fine spaces between the fibrils, making the leather softer and more flexible [33]. The structural integrity of collagen fibers within the skin also affects its softness. The arrangement and density of these fibers can affect how well moisturizing agents can penetrate and lubricate the skin. A well-distributed collagen network allows for better oil absorption, leading to increased softness [19]. The incorporation of zirconium in the tanning process results in an improvement in the softness of the leather, which is due to the effective interaction between zirconium ions and the collagen matrix [34]. The concentration of zirconium plays a crucial role in determining the final softness of the leather. As noted by [10] the use of zirconium in tanning processes can lead to enhanced softness, which is essential for producing high-quality leather. The level of leather softness is influenced by the technique used in the tanning process. In the tanning study, pre-mordant resulted in the highest softness value. The use of gelatin in finishing was also shown to retain the softness of the leather after the coating process, which is suitable for products such as jackets and bags [35, 36].

Thickness

As shown in Table 1, the mean thickness values were 0.96±0.11a (7.5%), 0.98±0.70a (10%), 1.10±0.15b (12.5%), and 1.24±0.08b (15%), indicating that sheepskin thickness increases with higher zirconium concentrations. Thickness is a critical factor that greatly influences leather quality and characteristics, affected by variables such as leather type, tanning process, and composition. Different animal skin regions—hips, upper shoulders, back, ribs, and girdle—exhibit variations in thickness, with some areas being thicker [37]. The tanning process plays a crucial role in determining hide thickness, as the amount of tanning agent affects collagen binding and fills empty spaces within the skin fibers, thus impacting overall thickness [38]. The higher the thickness increases, the higher the tanning agent solution diffuses into the collagen matrix [39].

The histological characteristics of the skin, including its thickness, can vary not only between species but also within the same species based on factors such as age, nutrition, and environmental exposure [26]. In addition to biological characteristics, the choice of tanning agents also plays a crucial role in determining the thickness of the final leather product. The amount of tanning agent bound to the collagen and the filling of empty spaces within the skin fibers can significantly affect the overall thickness of the tanned leather [18]. environmental conditions, such as seasonal changes, can also impact skin thickness. [40] noted that seasonal variations could lead to differences in the mechanical properties of tanned furs, which are closely related to the thickness of the skin. This suggests that the time of year and the conditions under which the animals are raised can have lasting effects on the quality of the leather produced. The thickness of the leather is regulated through the tanning method and the materials used. In research with tanning, thickness is optimized through processing with plants or other natural substances. The thickness of the leather is usually maintained to maintain strength while remaining flexible to the needs of the final product [15, 16, 29].

Tear Strength

The average values presented in Table 1 reveal that the highest tear strength occurred at the 15% concentration (393.97±17.54c), whereas the lowest was at 7.5% concentration (189.91±14.99a). This is consistent with the study by [41] that tear strength values for different breeds of sheep were reported to be around 401.5 N/mm for one group, 361.2 N/mm for another, and 421.0 N/mm for a third, highlighting the influence of genetic factors on skin quality. Increasing the concentration of the tanning agent enhances the tear strength of the skin due to the formation of bonds between the agent and the skin's protein structure, resulting in improved strength and resilience [42]. Several factors, including fiber toughness, flexibility, compactness, and the uniformity of collagen fibers, influence tear strength [43]. Additionally, the tear strength quality may be attributed to differences in the polyphenol profile, which can affect fiber interactions and material durability [44]. Increased collagen fiber alignment was associated with increased tear strength and peel strength, indicating that structural collagen is a key factor in the mechanical performance of leather [45]. In addition to the type of tanning agent, specific characteristics of the animal hide also contribute to tear strength. [26] reported that the arrangement of leather fibers, which is denser in the dorsal spine area, can result in higher tensile and tear strength. Structural differences between the fiber and corium layers of the skin also affect tear strength. The structure of the corneal fiber is better able to inhibit the spread of the tear through mechanisms such as blunting of the tear tip and fiber drag. Tear strength measures the resistance of leather to forces that can cause tearing. Methods such as the use of iron salts or pre-mordanting in tanning show improvement in tear strength. Tear strength ranged from 10-15 N/mm in some test samples, indicating good durability for applications that require high durability [35, 36, 46].

CONCLUSION

Zirconium presents itself as a highly promising, environmentally benign alternative to traditional chromium-based tanning agents. By forming strong bonds with collagen fibers, zirconium not only enhances the physical and mechanical properties of the leather but also minimizes hazardous waste production. This research provides a simpler, more sustainable leather tanning solution that maintains high leather quality without reliance on auxiliary chemical modifications.

Conflict of Interest

The Authors have declared no conflict of interest.

Novelty Statement

The novelty of this study lies in its direct application of pure zirconium salts at varying concentrations on sheepskin without combining additional complex additives. The approach simplifies the tanning process while significantly improving tensile strength, elongation, and tear resistance, offering a practical, sustainable alternative to chromium tanning.

Author Contribution

AP, YE, MZA, and RAA designed and coordinated the study. AP, YE, and MZA supervised the experiment. RAA experimented, analyzed the data, and drafted the manuscript. AP, YE, and MZA took part in critically checking this manuscript. All authors read and approved the final manuscript.

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