CHARACTERIZATION OF ENZYME-TREATED ECO-FRIENDLY IRON TANNED LEATHER

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ABSTRACT. Tanning is the process of converting putrescible raw hides and skins into non-putrescible leather. The most common chrome tanning process is not eco-friendly at all. But the increasing demand for leather leads us to find an eco-friendly tanning process. Therefore, the elimination of pollution due to the use of chrome and dyeing material is a matter of concern here. The primary objectives of this study are the reduction of pollution from using chrome and dyeing materials in the tanning process and their impacts on human life as well as the environment. In this study, different types of iron salts, combinations of different iron salts, and iron with chromium salts are used for tanning and no dyeing material is used to give color to the leather. On the other hand, various types of enzymes were applied for the completion of the beamhouse operation. Finally, the physical and thermal properties of various tanned leather were summarized to propagate an eco-friendly new tanning method.
KEY WORDS: enzyme, iron tanning, chrome tanning, physical properties, eco-friendly

CARACTERIZAREA PIEILOR TABĂCITE CU SĂRURI DE FIER ȘI TRATATE CU ENZIME

REZUMAT. Tăbăcirea este procesul de transformare a pieilor brute putrescibile în piele care nu putrezește. Cel mai utilizat proces de tăbăcire, cel cu săruri de crom, nu este deloc ecologic. Însă cererea tot mai mare de piele ne determină să dezvoltăm un proces de tăbăcire ecologic. Prin urmare, eliminarea poluării din cauza utilizării cromului și a materialului de vopsire este o chestiune de interes. Obiectivele principale ale acestui studiu sunt reducerea poluării în urma utilizării cromului și a materialelor de vopsire în procesul de tăbăcire și a impactului acestora asupra vieții umane, precum și asupra mediului. În acest studiu s-au utilizat pentru tăbăcire diferite tipuri de săruri de fier, combinații de diferite săruri de fier, precum și săruri de fier și de crom și nu s-a folosit niciun material de vopsire pentru a da culoare pielii. Pe de altă parte, s-au aplicat diferite tipuri de enzime pentru finalizarea operațiunilor umede. În cele din urmă, s-a făcut un rezumat al proprietăților fizice și termice ale diferitelor piei tăbăcite în vederea dezvoltării unei noi metode de tăbăcire ecologică.
CUVINTE CHEIE: enzime, tăbăcire cu săruri de fier, tăbăcire cu săruri de crom, proprietăți fizice, ecologic

CARACTÉRISATION DES CUIRS TANNÉS AVEC DES SELS DE FER ET TRAITÉS AUX ENZYMES

RÉSUMÉ. Le tannage est le processus qui consiste à transformer les peaux brutes putrescibles en cuir non putrescible. Le procédé de tannage le plus utilisé, celui aux sels de chrome, n'est pas du tout respectueux de l'environnement. Mais la demande croissante de cuir nous amène à développer un procédé de tannage écologique. Il est donc d'un grand intérêt d'éliminer la pollution due à l'utilisation de chrome et de matériaux colorants. Les principaux objectifs de cette étude sont de réduire la pollution liée à l'utilisation de chrome et de colorants dans le processus de tannage et leur impact sur la vie humaine ainsi que sur l'environnement. Différents types de sels de fer, des combinaisons de différents sels de fer, ainsi que des sels de fer et de chrome ont été utilisés pour le tannage dans cette étude, et aucun matériau colorant n'a été utilisé pour colorer le cuir. D'autre part, différents types d'enzymes ont été appliqués pour réaliser la rivière. Enfin, une synthèse des propriétés physiques et thermiques des différents cuirs tannés a été réalisée en vue de développer une nouvelle méthode de tannage écologique.
MOTS CLÉS : enzymes, tannage au sel de fer, tannage au sel de chrome, propriétés physiques, écologique

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INTRODUCTION

The leather making industry is one of the primitive industries in Bangladesh and plays a vital role to develop the gross domestic product (GDP) of the country [1]. Bangladeshi leather has a reputation across the world for its fine grain pattern, uniform fibre structure, and smoothness [2]. Currently, most of the leathers are tanned by the conventional method using basic chromium (III) salts. It is one of the most polluting and time-consuming steps in leather making [3].

Vegetable tanning materials used by the tanners are obtained from various plants. The tannins which appear to be by-products of the plants are water-soluble complex organic compounds [4-10]. Aluminum salts, in a dilute solution, hydrolyze in water with the formation of a colloidal precipitate of basic aluminum salts. As an example, aluminum chloride or sulfate in the solution has an acid reaction due to hydrolysis [11]. Iron tanning is done with the help of different types of iron salts. The properties of the leather are almost the same as chrome tanning and the cost of producing not putrescible leather is also budget-friendly [12]. Oil tannage has been used for the production of a specific type of high-quality leather. Zirconium is a metal belonging to the same group of elements as silicon and titanium. It accords with chromium in that it is sulfate and basic sulfate combines readily with the pelt.

A mixed ligand complex of iron with oxalic acid was synthesized and used for tanning experiments [13]. To continue this practice iron tanning as an eco-friendly process may play an influential role. Its outstanding ability to cross-link collagen with positive effects on leather filling and softness was emphasized in recent work [14]. As it contains no chrome in the tanning process so the disposal of iron waste is easier than chrome waste. To the aim of reducing chrome in this research, one goatskin is tanned with chrome and iron salt and the result is compared with iron tanning [15, 16]. It is an eco-friendly way as there is no dyeing material used in this iron tanning process. Dyeing materials also have negative impacts on human health as well as the environment [17, 18].

On the other hand, enzymes are an alternative to the conventional chemical process. Alkaline proteases from bacteria are used in the beamhouse operation due to their specificity, pH activity, and thermal stability. Various types of enzymes like alkaline protease, lipase, and keratinase, etc. are used in the leather industry to improve the final quality of the leather [19]. Enzymatic soaking, unhairing, and bating using alkaline protease, lipase, keratinase, and related kinetics were also studied.

EXPERIMENTAL

Materials and Method

Total seven (07) goatskin were taken and tanned with various techniques to compare the quality of the final product. $FeSO_4$ and Fe_2O_3 salts of iron and chrome salt are needed for tanning. Besides these, some of the chemicals are used in the conventional chrome tanning method but there are no dyeing chemicals used in this process for color. All processes are the same as conventional tanning instead of using chrome and dyeing materials. Five goat skins are taken and tanned with iron and a combination of iron and chromium salt. And another goatskin (S6) is taken and tanned with chrome tanning with dyeing materials.

- Goatskin (S1): Tanned with $FeSO_4$
- Goatskin (S2): Tanned with Fe_2O_3
- Goatskin (S3): Tanned with $FeSO_4$ + Fe_2O_3
- Goatskin (S4): Tanned with $FeSO_4$ + $Cr(OH)SO_4$
- Goatskin (S5): Tanned with $Cr(OH)SO_4$
- Goatskin (S6): Tanned with $Cr(OH)SO_4$ + acid dye

On the other hand, one goatskin (S7) is taken and tanned with various types of commercial enzymes that are used in the beamhouse operation, viz. Pelvit SPH for soaking, Erahvit MB for dehairing, and Ebranil PFE for bating. Enzymes are the catalysts of biological processes.

RESULTS AND DISCUSSION

Tanning has been done by using iron salts and without dyeing material to reduce environmental pollution and introduce a new cleaner technology for tanneries. All results of finished leather have been produced to be quite normal. It concluded that the leather produced using iron salt and a combination of iron and chromium salt were quite successful. It possesses good physical and chemical properties, whereas, the natural color of the finished leather is quite black or dark ash. It can be used easily in shoe uppers of natural color. It is very adaptable and easily competes in the domestic and global markets. On the other hand, goat skins were tanned by enzymatic treatment process to develop an eco-friendly processing technique. This result revealed that the physical and thermal properties of enzymatic-treated leather are highly appreciable (Figure 1).

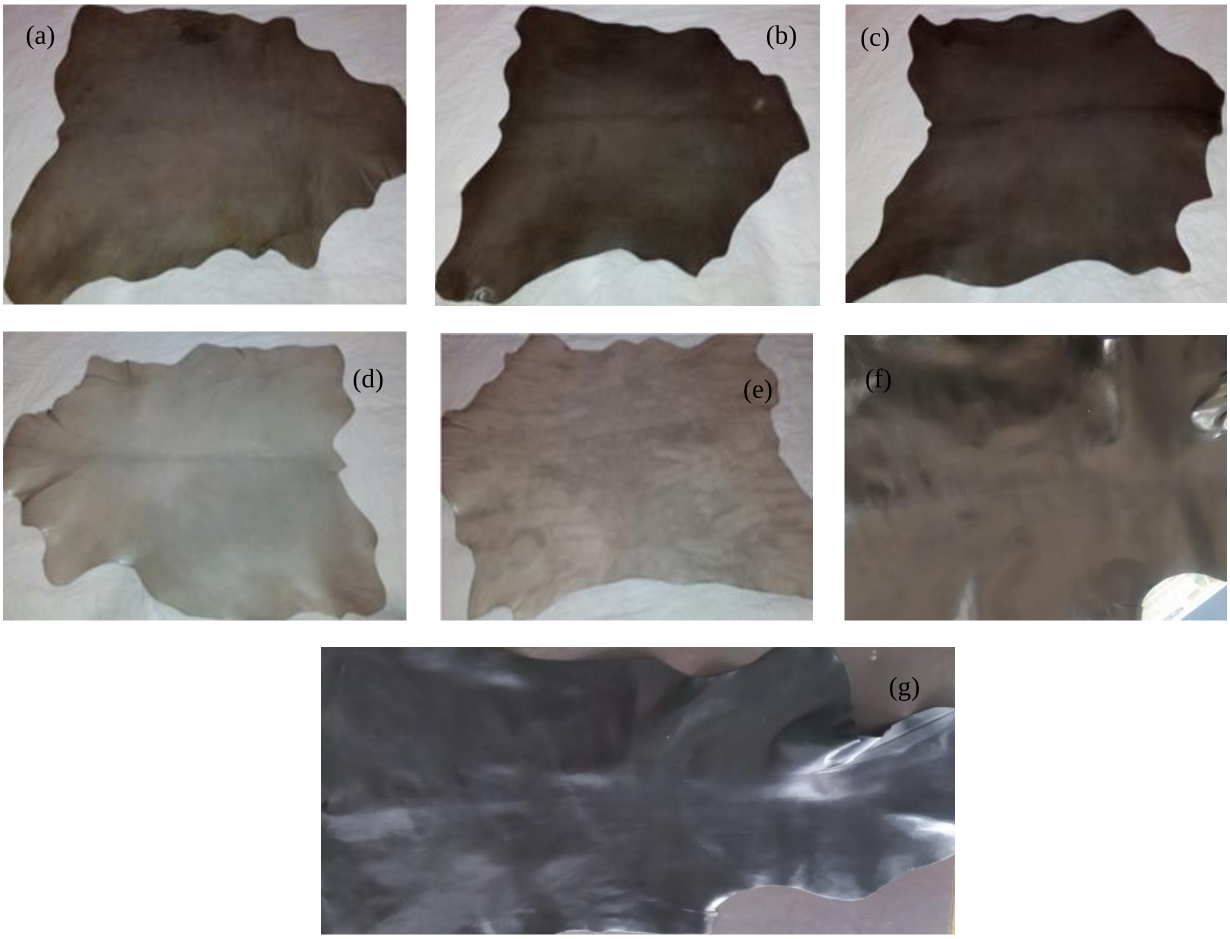


Figure 1. Final product images (a) tanned with basic chromium sulfate and ferrous sulfate, (b) tanned with Fe_2O_3, (c) tanned with $FeSO_4$ and Fe_2O_3, (d) tanned with $FeSO_4$, (e) tanned with basic chromium sulfate and with all this tanning this color is obtained without using any dyeing material, (f) tanned with $Cr(OH)SO_4$ + acid dye, (g) tanned with enzymes

Physical Properties

Physical tests of the iron-tanned, chrome-tanned, and enzymatic-treated leather namely tensile strength and percentage of elongation, stitch tearing strength, tongue tearing strength, split tearing strength, elastomer test, flexing endurance test, waterproofness test, bond strength test between leather and finish film, light fastness test, wet and dry rub fastness test, test for resistance to solvent of the finished film, moisture fastness test, water fastness test of finish film were determined according to ISO standard procedures and the results are summarized in Tables 1-11. It is observed that all physical properties of enzymatic-treated leather were found to be significantly higher than those of iron and chrome-tanned leather.

Tensile Strength

Tensile strength is the load required to break the unit cross-sectional area of the leather sample. 110 mm long and 25 mm wide specimens for testing each experiment were taken. The average thickness of the specimen was determined.

Table 1: Comparison of tensile strength

Tensile strength and % of elongation	S1	S2	S3	S4	S5	S6	S7
Result = Breaking load ÷ cross-sectional area (kg/cm^2)	250	164.8	168.5	265	240	200	280
% of elongation = (Final length-initial length)÷initial length×100%	120%	125%	125%	66%	54%	75%	52%

Stitch Tear Strength

Stitch tear strength is used for the determination of fiber strength. For this test, the load (kg) required to tear the sample of the leather between two holes of 2 mm diameter each and whose centers are 6 mm apart express its unit thickness (cm).

Table 2: Comparison of stitch tear strength

Stitch tear strength	S1	S2	S3	S4	S5	S6	S7
Result = load÷ thickness (kg/cm)	83.3	54.94	72.10	79.20	92	66.6	93

Tongue Tear Strength

Tongue tear strength is used to determine the fiber strength of leather. In this case, the load is required to tear a leather sample if the thickness is 1cm.

Table 3: Comparison of tongue tear strength

Tongue tear strength	S1	S2	S3	S4	S5	S6	S7
Result = load÷ thickness (kg/cm)	47.60	54.30	40.80	40.40	45.40	40.50	57.50

Bauman Tear Strength

To determine the fiber strength as in this test few fibers are ruptured at a time. In this case, the load in kg is required to continue the split in the leather specimen if the thickness of the leather is 1cm.

Table 4: Comparison of Bauman tear strength

Bauman tear strength	S1	S2	S3	S4	S5	S6	S7
Result = load ÷ thickness (kg/cm)	47.60	47.05	43.60	49.90	54.50	55.07	56.03

Lastometer Test

The bursting strength is an index of the overall strength of the finished leather. To know whether the leather will stand the load of lasting during shoe malling.

Table 5: comparison of lastometer test

Grain crack strength	S1	S2	S3	S4	S5	S6	S7
Result = load ÷ thickness (kg)	18	19	17.50	20	22	21	22.50

Waterproofness Test

A square test sample is bent into two V-shaped flanges that end in a trough. The trough is then immersed in water and the clamps oscillate at a steady rate so that the sample is bent repeatedly. The test is stopped when the water enters the test specimen.

Table 6: Comparison of waterproofness test

Waterproofness test	S1	S2	S3	S4	S5	S6	S7
Result after 15 minutes	Water penetrates leather	Water penetrates leather	Water penetrates leather	Water penetrates leather	Water penetrates leather	Water penetrates leather	Water penetrates leather

Lightfastness Test

Half of the leather sample is covered with a starch-free cotton cloth. It is then kept in contact with sunlight or a Xenon lamp for 72 hours. Then a comparison is made by grayscale to the covered and uncovered portion.

Table 7: Comparison of lightfastness test

Lightfastness test	S1	S2	S3	S4	S5	S6
Grayscale rating	5	5	5	5	5	4

Color Rub Fastness Test

Starch-free cotton felt of dry-type felt rubbed with loaded into the leather. How much color is replaced in dry felt and wet felt is visually assessed.

Table 8: Comparison of color fastness test

Color rub fastness test	S1	S2	S3	S4	S5	S6
Grayscale rating	5	5	5	5	5	5

A Solvent of Finish Film Test

To carry out this test organic solvent such as Benzene, Ketone, Acetone, Alcohol, or chlorinated hydrocarbon is applied on the flesh side of the finished film of the leather. Then on the grain side, a dry rub fastness test is carried out and a comparison is made by grayscale to assess the color change. The color change rating should be 5-3. Excessive color change indicates a bad result.

Table 9: Comparison of a solvent of finish film test

Resistance to solvent of finish film	S1	S2	S3	S4	S5	S6
Grayscale	4	4	4	4	4	3-5

Moisture Fastness Test

Two samples are collected from the same leather. One is preserved in atmospheric conditions and the other is preserved in desiccators containing water at the bottom to ensure 100% relative humidity. Color rub fastness is carried out for both specimens or samples and the samples are compared with the help of grayscale.

Table 10: Comparison of moisture fastness test

Moisture fastness test	S1	S2	S3	S4	S5	S6
Grayscale rating	5	5	5	5	5	4-5

Perspiration Fastness Test

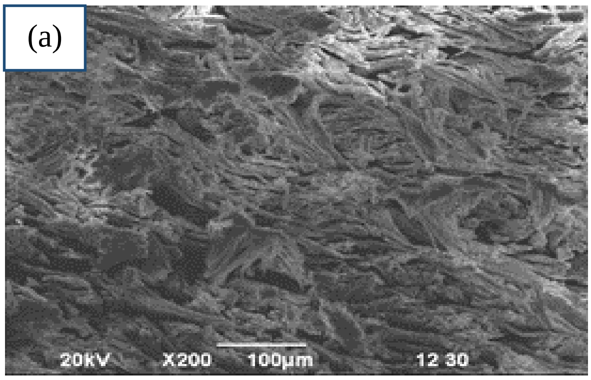
A piece of 100 ✕ 36 mm^2 specified undyed cloth is taken and wet with artificial perspiration. Then it is placed in the oven for three hours after drying the specimen and cloth assess the change with the grayscale.

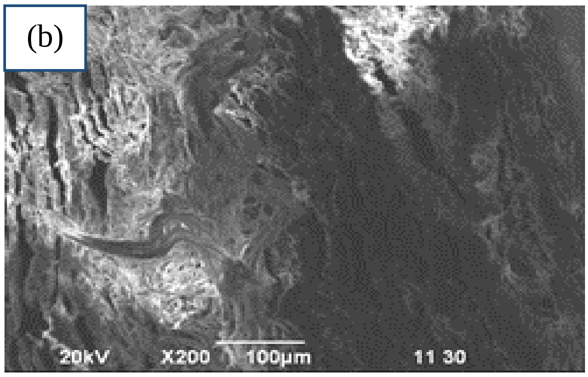
Table 11: Comparison of perspiration fastness test

Perspiration fastness test	S1	S2	S3	S4	S5	S6
Grayscale rating	5-4	5-4	5-4	5-4	5-4	3-4

Scanning Electron Microscopic Analysis of Tanned Leather

Scanning electron microscopy test for tanned leather of $FeSO_4$ shows more uniform penetration of tanning material than Fe_2O_3. This test shows that chrome tanning penetration is good and fiber structures are more uniform than iron tanning (Fig. 2). On the other hand, Fig. 2g shows the cross-sectional view of the sample that has been treated with various enzymes in beamhouse operation. There was uniform penetration and the fibres structure was intact, and had a far better fiber orientation compared to iron and chromium-tanned leather. Hence, the enzymatic treatment leather shows better strength properties and greater surface area.





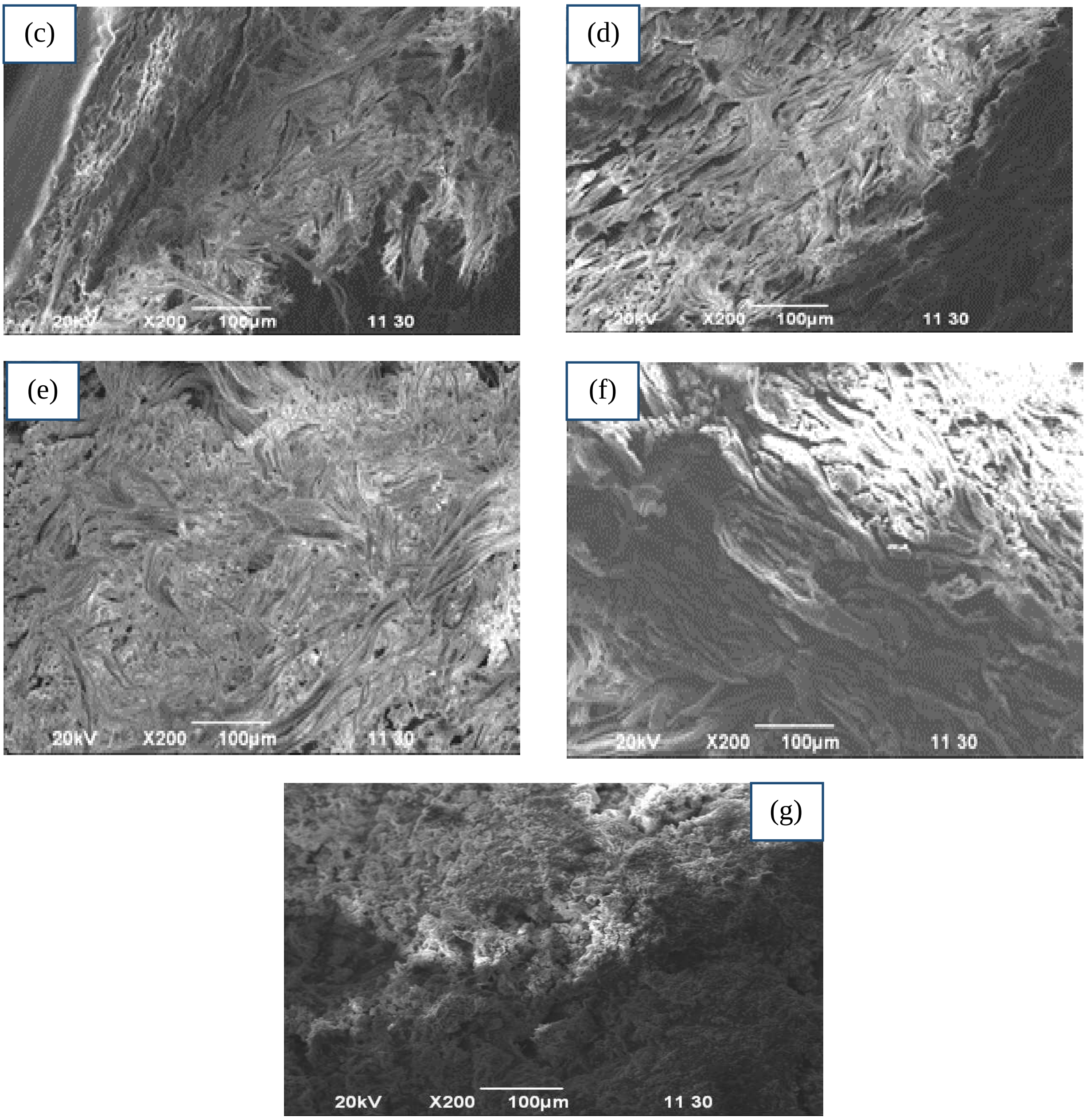
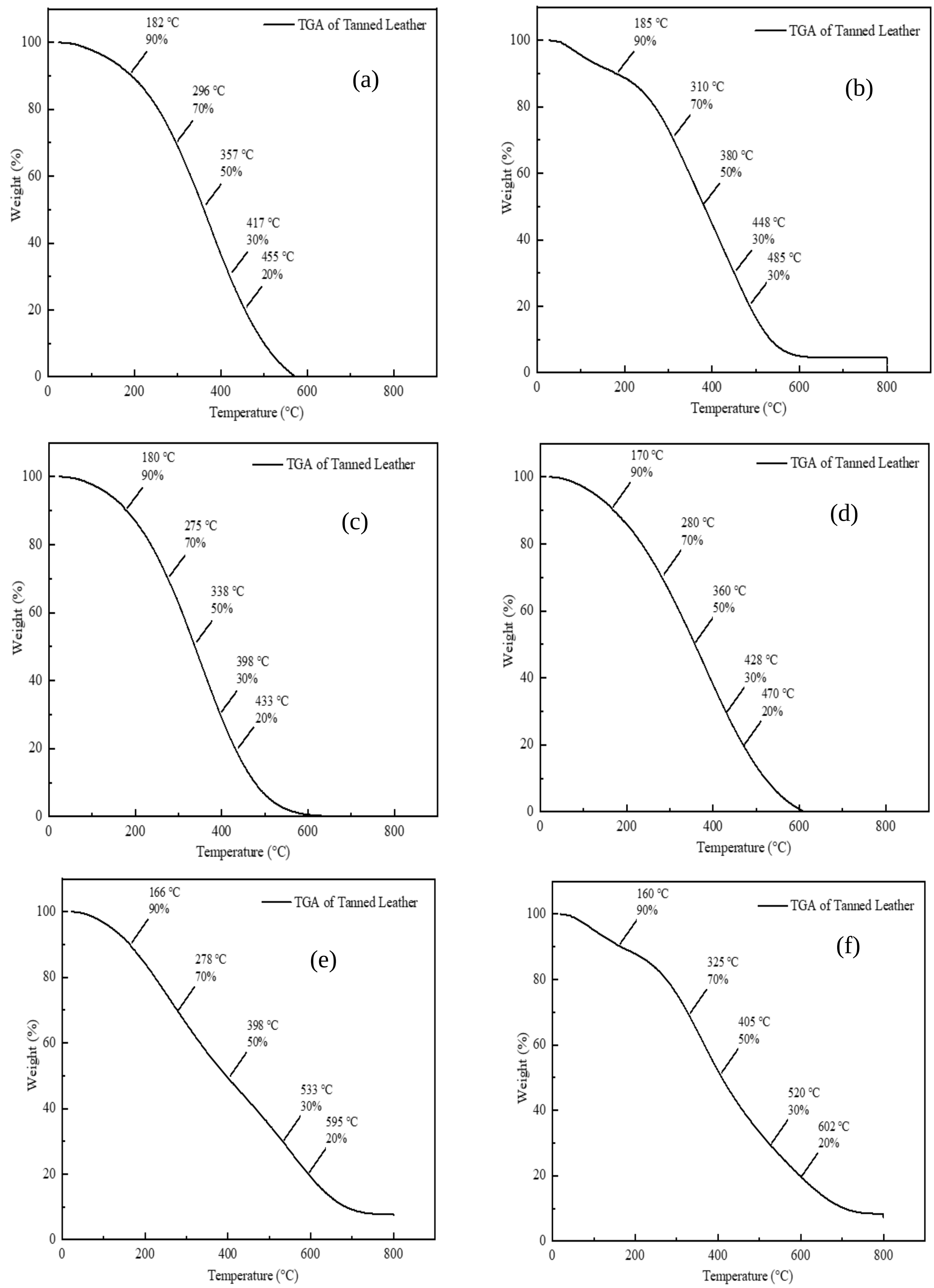


Figure 2. SEM images (magnification ×2000) of the cross-section of undyed leather tanned with (a) $FeSO_4$ (b) Fe_2O_3, (c) $FeSO_4$ and Fe_2O_3, (d) $FeSO_4$ and $Cr(OH)SO_4$, (e) $Cr(OH)SO_4$, (f) dyed with $Cr(OH)SO_4$, and (g) enzyme treated leather

Thermogravimetric Analysis for Tanned Leather

Thermogravimetric analysis is a thermal analysis technique in which changes in the chemical and physical characteristics of the samples provided are measured. Generally, a sample loses weight when heated as a result of decomposition, reduction or evaporation. The results of this work are highly promising indicating that iron salts and iron, chrome combination tanned leather using no dye also give good results (Fig. 3).

Fig. 3 (a) and (f) represent the thermograms of samples tanned with $FeSO_4$ and $Cr(OH)SO_4$ with acid dye, respectively. The temperatures needed for 10%, 30%, 50%, 70%, and 80% weight loss of sample tanned with $FeSO_4$ were 182, 296, 357, 417, and 455 °C, respectively while the same weight loss occurred at 160, 325, 405, 520, and 602 °C for the sample of $Cr(OH)SO_4$ tanned with acid dye. On the other hand, Fig. 3 (g) represents the thermograms of enzymatic-treated leather samples. The temperatures needed for 10%, 20%, and 30% weight loss of the sample were 268, 362, and 532 °C, respectively. Moreover, high temperatures are required for weight loss of enzymatic-treated leather samples due to the formation of strong tanning agent-collagen complexes.



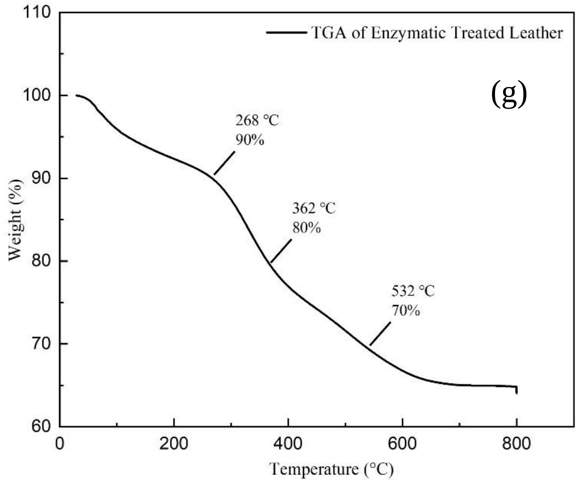


Figure 3. TGA of undyed leather tanned with (a) $FeSO_4$ (b) Fe_2O_3, (c) $FeSO_4$ and Fe_2O_3, (d) $FeSO_4$ and $Cr(OH)SO_4$, (e) $Cr(OH)SO_4$, (f) dyed with $Cr(OH)SO_4$, and (g) Enzyme treated leather

Differential Scanning Calorimetric Analysis for Tanned Leathers

A differential Scanning Calorimetry test here has been done to know about the shrinkage temperature of the tanned leathers. Fig. 4 revealed that the DSC thermograms of Iron, chromium, and enzymatic-treated tanned leather. The shrinkage temperature of enzymatically treated leather was far better than that of iron and chromium-tanned leather. Hence, enzymes act as catalysts to facilitate the chemical-free beamhouse operation without impairing the final quality of the leather. Therefore, the fixation of the tanning agents increased with the enzymatically treated pelt. All the leather passes the test result.

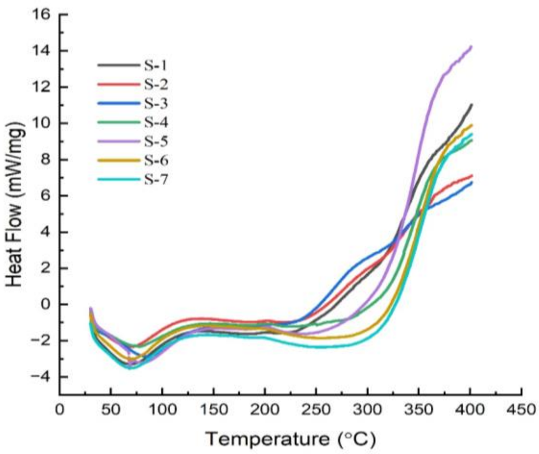


Figure 4. DSC thermograms of undyed leather tanned with (a) $FeSO_4$ (b) Fe_2O_3, (c) $FeSO_4$ and Fe_2O_3, (d) $FeSO_4$ and $Cr(OH)SO_4$, (e) $Cr(OH)SO_4$, (f) dyed with $Cr(OH)SO_4$, and (g) Enzyme treated leather

CONCLUSIONS

In this study, it is shown that different salts of iron and iron mixed with chrome-tanned leather give the best result, similar to conventional chrome-tanned leather, and here without using any dyeing material makes it more eco-friendly. Moreover, the enzymatic-treated leather showed the best result compared to other tanning methods. Various types of physical tests were carried out to compare the result of enzymatic-treated leather and other ones. Conventional methods for the tanning process discharge an enormous amount of pollutants due to the use of chemicals. Therefore, enzymatic treatment in beamhouse operation has been studied to facilitate the process without impairing the quality of finished products.

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Conflicts of Interest

The authors do not disclose any conflict of interest.

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