

POTENTIAL OF VEGETABLE TANNING MATERIALS AND BASIC ALUMINUM SULPHATE IN SUDANESE LEATHER INDUSTRY

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Abstract

Ecological pressures on chromium have now forced the leather industry to look for possible alternatives. A vegetable- aluminum combination tannage has been studied, with special attention being given to intended final product. Aluminum is mineral tanning agents that are widely used to stabilize collagens in the leather industry. In this study, the crosslinking of vegetable and aluminum, with collagens, have been explored. This kind of chrome free tannage give us leathers with shrinkage temperature around 125°C, elongation at break 65.6%, tensile strength 38 N/mm², and tear strength 98 N/mm. The chemical properties of the combination tanned leathers are found to be quite normal. Among the combination system evaluated, a vegetable pretannage followed by retannage with basic aluminum sulphate was found to produce stronger leather with the durable characteristics. In contrast, pre-tanning with aluminum possibly tightens the collagen fiber network, preventing high molecular weight vegetable tannins from interacting with collagen fibres. Optimal results were obtained when 10% (w/w) vegetable tannins (garad) and 2% Aluminum sulphate was used.

Keyword: Combination tannage; Vegetable; Aluminum sulphate; Shrinkage Temperature; Collagen.

1. Introduction

Leather making is a very long process and consists of many different chemical and mechanical process steps. The most important tanning method is chrome tanning (Approximately 85% of world heavy leather making). There are many factors governing

Nomenclatures	
<i>A</i>	Hide substance weight, g
ALCA	American Leather Chemists Association
Al	Aluminum salts
Al ₂ O ₃	Aluminum oxide
Al (SO ₄) ₃ .18H ₂ O	Aluminum sulphate
<i>a</i>	Combined fat weight, g
<i>B, b</i>	Leather sample weight, g
<i>M</i> ₀	Mass of oven dry sample of Aluminum sulphate leather
Pre	Pretanning
Re	Retanning
rpm	Revolutions per minute
<i>T</i> ₁	Volume of sodium thiosulphate that used in the titration.
<i>t</i> ₁	Sample weight, g
	Weight of oven dry leather sample, g
<i>t</i> ₂	Ash weight, g
	Residue after drying of 50 ml water extract, g
SLTC	Society of Leather Technologists and Chemists
Veg	Vegetable Tanning material

the tanning effect: the type of the compound; its basicity, concentration, pH value and neutral salt content; the temperature of the tanning bath; and the time of interaction, which is long. The previous history of the skin material is also important. Many of these factors are interdependent and difficult to consider separately. The basic chrome tanning chemistry is well explained by [1, 2].

Most attempts to find suitable alternatives for chrome tanning have been undertaken primarily in order to reduce the pollution due to tannery effluents. In certain cases, such efforts were aimed at cost-reduction [3].

As regards Sudan, any attempt to reduce the use of chrome has multiple advantages. In the first instance, the Sudanese chrome ores have not yet been confirmed as being commercially exploitable so that the chrome requirements of tanneries are met through imports. The effluents from some of the Sudanese tanneries contain high amounts of chrome exceeding the standards set for discharges into streams/sewers system [4, 5].

The availability of imported chrome tanning agents is also irregular and costly. Mainly for purposes of import-substitution, but also for reasons of environmental pollution, studies were conducted towards finding suitable alternative tanning systems to replace or reduce the use of chrome in Sudanese tanneries.

Aluminum has been used in preservation of skins for centuries. In the form of alum, it was used in the tawing of skins and furs, in admixture with flour, egg yolk and salt. Although this helped in the preservation, the skin still lacked resistance to water. The ingredients used i.e. flour, egg yolk, salt and alum can be washed out, as they did not chemically combine with the pelt (collagen of the skin).

Current studies on the use of aluminum in the leather industry were motivated by demands for a white leather as a substrate for dyeing, to reduce environmental impact by replacing chrome and also strategic concern over chrome supplies [6].

The research and development work since the latter half of his century was oriented towards developing a tanning agent based on aluminum that is stable in solution and will form cross-links with collagen in such a way that real leather, resistant to water and with adequate hydrothermal stability is produced. Once such stable aluminum tanning agent is the basic aluminum sulphate wherein the aluminum is complexed with citrate anions [3].

Using this basic aluminum sulphate, in combination with vegetable tannins, other mineral tanning agents, and syntans, almost all types of leathers, which were previously tanned with chrome combination systems, could be produced [3].

Aluminum sulphate is indigenously produced on a commercial scale from certain clay deposits in Sudan. So this study provides systematic research on potential of the combination tannages involving the locally available *Acacia nilotica* ssp *tomentosa* pods (garad) and aluminum sulphate with objective of producing real leather, resistant to water and with adequate hydrothermal stability.

2. Materials and Methods

2.1. Preparation of basic aluminum sulphate

Aluminum sulphate ($\text{Al}(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) was dissolved in an equal volume of water and masked with sodium citrate (8% on the weight of aluminum sulphate) and then basified carefully with soda ash (17.5% on the weight of aluminum sulphate) as a 10% solution. The resultant liquor was approximately 33% basic with 2% Al_2O_3 . It was used after ageing for 48 hours.

2.2. Preparation of vegetable tannin extracts

The weighed quantity of crushed *Acacia nilotica* (garad) pods (5 kg) containing the required amount of tannins was soaked overnight in 300 % of water; the whole infusion was used in the next day.

2.3. Tanning processes

The process was carried out using laboratory drums 150 mm wide and 300 mm diameter. The industrial chemicals typical of those used in tanneries were used. Four batches of combination tannage process were arranged for these tanning processes:

The first batch (B1) consists of *Acacia nilotica* (garad) pretannage and aluminum sulphate retannage. In this batch 20 pieces of pickled sheep skins of fairly similar size and backbone length and free from physical defects were used (Pickled process is process by which skins were first treated with 8% salt and 100% water at 25°C (on pelt weight) for 10 min, and then with 1.2% H_2SO_4 for 2 h in a drum, rotating at 12 rpm) [3]. The skins were thoroughly washed and the pH was adjusted to 4.2 prior to treatment with 20% (on pickled weight) of *Acacia nilotica* (garad) extract. After drumming for three hours with *Acacia nilotica* (garad) extract the bath was drained and the skins were left overnight on a horse. The skins were then given a retannage with basic aluminum sulphate offers (2% Al_2O_3) this percentage based on pickled weight. Thereafter the skins were

drummed for 4 hours with successive adjustments of pH to 3.9. These adjustments should be made very slowly and carefully to avoid aluminum precipitation. Finally neutralization to pH 4.5 was carried out in a fresh float in order to attain resistant of the tanned skins to boiling water. Then the leathers were piled and dried. The dried leathers were subjected to physical and chemical tests [3].

The control (20 pieces) was tanned only with 10% of *Acacia nilotica* (garad) extract (percentage based on pickled weight) and processed further as for the B1.

The second batch (B2) consists of aluminum sulphate pretannage and *Acacia nilotica* (garad) retannage compared to straight *Acacia nilotica* (garad) (control). In this batch 20 pieces of pickled sheep skins were then processed; the skins were pretanned with basic aluminum sulphate (2% Al_2O_3), basified to pH 3.8, piled, neutralized, fatliquored and then retanned with 10% *Acacia nilotica* pods extract using the garad infusion already prepared in section 2.1. This percentage based on pickled weight, and then the leathers were piled, neutralized, and dried. The dried leather subjected to physical and mechanical operations as in the first batch.

The third and fourth batches were done on the same ways as first and second with exception that we used 5% aluminum salts instead of 2%, and then the leathers were piled, neutralized, and dried. The dried leather subjected to physical and mechanical operations as in B1 and B2.

2.4. Chemical analysis

2.4.1. Preparation of sample

Leather was cut into small pieces, to pass through a screen with circular perforations of 4 mm. The pieces were thoroughly mixed and brought to a state of homogeneity by keeping them in a closed container for at least overnight. After determining their moisture content, they were stored in a jar for further analysis [7].

2.4.2. Determination of aluminum sulphate content

1 g of full aluminum sulphate was weight into a 500 ml conical flask. 5 ml of concentrated nitric acid followed by 20 ml of oxidizing mixture (perchloric acid/sulphuric acid, 2:1) were added. The mixture was heated in fume cupboard with the fan on until it turned orange and the heating was continued for 1 minute more. After cooling, approximately 15 ml of cold distilled water and a few anti bumping granules were added, and then the solution was heated to boiling for 10 minutes, to remove any free chlorine. The solution was allowed to cool and diluted to 250 ml with distilled water in a volumetric flask. 100 ml of the solution were pipettes into two conical flasks and 10 ml of 10% potassium iodide solution were added to each flask, using a measuring cylinder, then the flasks were stoppered and placed in the dark for 10 minutes. Starch indicator, 1 ml was added to each flask and they were titrated with 0.1 mol dm^{-3} sodium thiosulphate solution to a pale violet colour [8].

Calculations:

$$\text{Aluminum oxide (Al}_2\text{O}_3\text{), \%} = \frac{T_1}{M_o} = \frac{0.00253}{100} \quad (1)$$

1 ml 0.1 N titrant = 0.00173 g Al or 0.00253 g Al_2O_3

2.4.3. Determination of hide substances by total Kjeldahl method

After determination of total matter soluble in water, the leather sample was completely dried, and 0.6 g were taken and placed into a dry 250 ml Kjeldahl flask with 15 to 20 ml of concentrated sulphuric acid, as well as some glass beads. The flask was heated gently in the inclined position. The flask was equipped with a small funnel to prevent loss of acid during hide destruction. 5g of potassium sulphate and 5 g of copper sulphate was added to the flask, and heated up to boiling until the solution became clear and the colour stopped changing. This procedure took about 30 minutes. After cooling, the solution was quantitatively transferred into ammonia distillatory. Through a dropping funnel, sodium hydroxide solution (0.05 M) was added until the solution colour became black. During the distillation, the quantity of ammonia was reduced to one third. The ammonia was distilled into 100 ml of sulphuric acid (0.05 M) in the presence of methyl orange as indicator. Usually, after obtaining about 150 ml distillate it can be considered that all ammonia has been distilled and this procedure takes about 40 minutes. The excess acid was back titrated with 0.05M NaOH [8].

Calculations:

$$\text{Hide substances, \%} = \frac{A}{B} \times 100 \quad (2)$$

2.4.4. Determination of fat content

A portion of the sample (20 g) was placed into a Soxhlet apparatus to be extracted by petroleum ether (boiling point 40-60°C) for 5 hours, at least 30 siphons. After extraction, the solvent was concentrated under vacuum to thick syrup in a tared round bottom flask and then dried in an oven at 103±3°C [8].

Calculations:

$$\text{Fat content, \%} = \frac{100 - a}{b} \quad (3)$$

2.4.5. Determination of total matter soluble in water

The leather samples were used after determination of the fat content, dried from the solvent and placed into conical flask of a shaking apparatus, then water was added to cover the sample and it was shaken for 4 hours, then it was left at room temperature (30-36°C) overnight. The extract was then collected in a liter volumetric flask and made up to volume with water. 50 ml of the extract was pipette into a tarred porcelain dish, evaporated on a water bath, then dried in an oven at 100 ± 2°C to constant weight [8].

Calculations:

$$\text{Total matter soluble in water, \%} = 100 \times 20 \frac{t_2}{t_1} \quad (4)$$

2.4.6. Determination of ash content

Portion of prepared sample (5 g) were placed in porcelain crucible of determined constant weight. First, the sample was carbonized on a hot plate under a fume cupboard and then placed in a furnace at about 800°C until constant weight was achieved. If it was difficult to burn off all carbon, concentrated ammonium nitrate solution was added to the residue and it was heated again. If, even after this step, complete burning off was not achieved, hot water was added to the residue, the solution was filtered and the residue, on ashless filter paper was washed. Then it was placed in the same crucible, and then dried to constant weight [8].

Calculations:

$$\text{Ash, \%} = \frac{100 - t_2}{t_1} \quad (5)$$

2.5. Physical analysis

2.5.1. Conditioning

The specimens for physical testing were kept in a standard atmosphere of temperature 20±2°C and relative humidity 65%±2% during the 48 hours immediately preceding its use in a test [3].

2.5.2. Measurement of tensile strength and percent elongation

2.5.2.1. Tensile strength

The samples were cut parallel and perpendicular to the backbone using a dumbbell shape. The thickness and width of the specimen were measured in the same position using standard thickness gauge and vernier calipers respectively i.e. measured one at the mid point and the other two midway. The width must be measured on the flesh and grain side, and then the mean thickness (mm) and width (cm) are calculated. The area of cross section of each specimen was calculated by multiplying its width by its thickness [8]. The jaws of the tensile machine (Instron 1026) were set 50 mm apart, and then the sample was clamped in the jaws, so that the edges of the jaws lie along the mid line. The machine was run until the specimen was broken and the highest load reached was taken as the breaking load. Tensile strength load is in newtons or kilograms [8].

Calculation:

$$\text{Tensile strength} = \frac{\text{Maximum breaking load (Nm}^{-2} \text{ or kgcm}^{-2})}{\text{Cross - sectional area}} \quad (6)$$

2.5.2.2. Percent elongation at break

The initial free length between the clamps before and after final free length at the instant of break was measured. The initial free length was set at 5 cm and the elongation calculated from graphical read out [8].

Calculations:

$$\text{Elongation, \%} = \frac{\text{Final free length} - \text{Initial free length}}{\text{Initial free length}} \quad (7)$$

2.5.3. Shrinkage temperature determination

The shrinkage temperatures of the tanned skins were measured using a micro-shrinkage meter as described below using the standard method [9]. A small strip of fibre was cut and placed on a water-grooved microscope slide. The slide in turn was placed on a heating stage along with a microscope mounted above the heating stage. The rate of heating was maintained at 2°C/min. The temperature at which the fibre shrinks to one-third of its length was taken as the shrinkage temperature [9].

2.5.4. Measurement of tear strength

This method is intended for use with any types of leather. The specimens were cut as a rectangle 50 mm long and 25 mm wide by use of a press knife which cuts out the specimen and slot in one operation (Template machine) parallel and perpendicular at each position. Instron 1026 having a uniform speed of separation of the jaws of 100±20 mm per minute was used, and the readings of load fall in that part of the scale which has been shown by calibration to be correct within 1%. The machine was run until the specimen was torn a part and the highest load reached during tearing was recorded as the tearing load. Tearing load is in newtons or kilograms [8].

2.5.5. Assessment of softness

The leather sample was placed in the tester (ST-300 softness tester) so that it covered the bottom clamp completely. The top arm was lowered by pressing down; the leather was now clamped in the tester. The load plunger deflects the leather and this deflection is measured and displayed on the dial. After the reading was obtained, the top arm released button is pressed and top arm lifts, allowing the leather to be removed; the actual measurement was obtained by taking the mean value in mm [8].

3. Results and Discussion

Tanning is a chemical process by which additional crosslinks are introduced into collagen, binding active groups of tanning agents to functional groups of protein [10]. So, the tanning effect mainly depends on the extent of cross-linking between collagen molecules and the thermodynamic stability of the cross-linking bonds. Animal skins or hides generally have a substantial thickness, thus penetration of tanning agents is also very important for characterizing the tanning process. Only complete penetration and uniform distribution of tanning materials along the hide cross-section will lead to a satisfactory tanning effect.

All the parameters of the physical and chemical properties were determined and used to describe the tanning effects in this work. As we know, animal hides

are not uniform, which means there are big differences in thickness and type of fibril weaving existing in the different areas of a hide or skin. So, skin pieces from adjacent positions were chosen in each sampling group, one of which served as the control, for every experiment. Results within experiments are comparable (due to samples being adjacent), but results between experiments are not easily comparable, due to inhomogeneities between samplings [10].

The introduction of basic aluminum sulphate into the tanning system as a retannage produces a definitive improvement in the strength properties of the leather. The high values for shrinkage temperature, tensile strength, elongation at break, tear strength, and softness in respect of *Acacia nilotica*- aluminum combination tanned leathers, were obtained when using 10% vegetable tannins offer as pretannage with 2% offer of Aluminum sulphate as retannage compared to 10% and 5% offer respectively (Table 1).

Shrinkage temperature, defined as the temperature at which a hide or leather sample begins shrinking, is one of the main parameters signaling leather formation. The high shrinkage temperature indicates greater hydrothermal stability due to the increased formation of cross-links (Fig. 1). Aluminum, as one element of the vegetable –aluminum combinations tanning systems, plays a vital role in the bond formation and stability of the complexes and thus increasing the hydrothermal stability of the resultant leathers (Fig. 1) [11-15].

The combination tanned leathers were found to be soft, full and possessed tight grain; these leathers, having better hydrothermal stability, strength properties and porosity lend themselves to being dyed and fatliquored at higher temperatures to produce different types of leathers intended for varied uses (Table 1) [15].

Table 1. Physical Properties of Leather Using Combination of *Acacia nilotica* ssp tomentosa pods (veg) (10%) and 2%, 5% Aluminum Salts.

Characteristics	10%Veg pre +2%Al re	2%Al pre +10% Veg re	10%Veg pre+5%Al re	5%Al pre +10% Veg re	Veg Tanning (control)
Elongation at break, %	60.5	65.5	17.0	32.0	50.5
Softness, mm	2.6	3.8	1.6	3.4	1.2
Water vapour permeability mg/cm ² /hr	6.8	7.9	6.8	7.9	6.2
Water uptake during water vapour permeability mg/cm ² /hr	150.8	130.6	140.8	125.6	120.9

pre= pre tanning, re= retanning, Veg= Vegetable tannin

On the other hand 10% offer *Acacia nilotica* pretannage and 2% offer aluminum retannage also yielded leathers with greater porosity (as evidence by the increased values for water vapor permeability and water intake) (Table 1) .

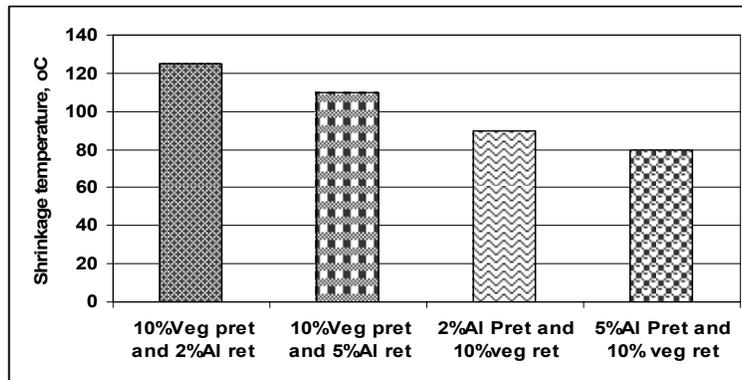


Fig. 1. Shrinkage Temperature of Combination Tanning Using *Acacia nilotica* ssp *tomentosa* pods (Vegetable Tannins) (10%) and Aluminum Salts (2%, 5%).

Hydrothermal stability or shrinkage temperature of combination tanning using *Acacia nilotica* ssp *tomentosa* pods and aluminum sulphate was shown in Fig. 1. The shrinkage temperature for 10% *Acacia nilotica* pretanning with different aluminum retanning was found to be 125 and 110°C respectively. This is due to the increased formation of cross-links and the effects of aluminum, as one components of the vegetable –aluminum combination tanning systems, on the stability of the complexes and bond formation thus increasing the hydrothermal stability of the resultant leathers [11, 14, 15]. On the other hand the hydrothermal stability of the leather was not improved by using aluminum as pretanning agent this because the synergistic interaction between the polyphenol and the aluminum may arise from one of the following options [6]:

Collagen-Al-Veg-Al-Collagen
Collagen-Veg-Al-Veg-Collagen
Collagen-Veg-Al-Collagen

It is known that applying the aluminum salts before the vegetable tannins produces only moderate shrinkage temperature, with characteristics of aluminum salts alone (Fig. 1). Therefore, the first and third options are unlikely. The most probable mechanism is for the aluminum salts (III) to crosslink the vegetable tannins. In fact, the cross linking polyphenol on collagen is itself crosslinked, to form a matrix within the collagen matrix, to stabilize the collagen by multiplicity of connected hydrogen bonds in the new macromolecule [6,16].

Tensile strength and tear strength of vegetable pretanning followed by aluminum retanning showed higher values compared to aluminum pretanning and vegetable retanning (Figs. 2 and 3). And this due to the fact that the fibre bundles are well separated in the case of Al-Veg tanned leather; while Veg-Al tanned leather shows cemented fibres bundles. This would lead to the conclusion; Veg-Al tanned leather would exhibit high tensile strength and tear with low softness where as Al-Veg tanned leather would exhibit low strength with high softness (Figs. 1 and 2). Whilst Al-Vegetable tanned leather would show high elongation (Table 1)

The chemical characteristics of the combination tanned leathers are found to be quite normal. The total metal oxide content satisfies the leather requirement (Table 2).

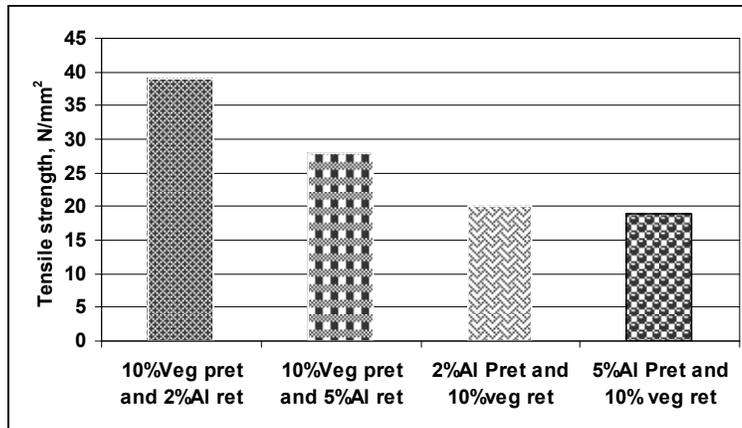


Fig. 2. Tensile Strength of Combination Tanning Using *Acacia nilotica ssp tomentosa* pods (Vegetable Tannins) (10%) and Aluminum Salts (2%, 5%).

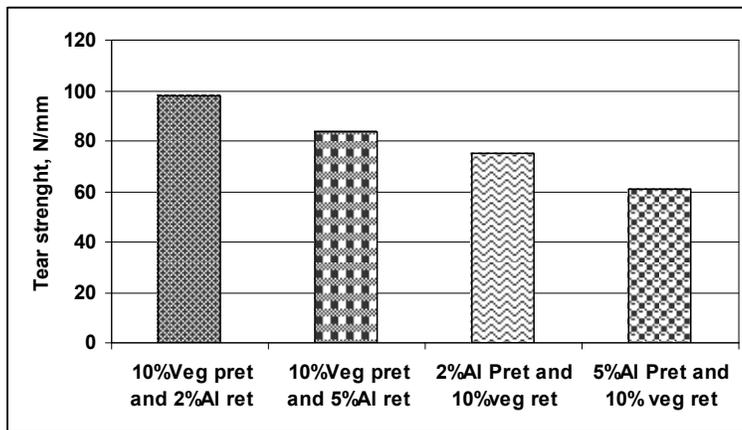


Fig. 3. Tear Strength of Combination Tanning Using *Acacia nilotica ssp tomentosa* pods (Vegetable Tannins) (10%) and Aluminum Salts (2%, 5%).

The free oils and fats present in Veg-Al tanned leather are comparable to those of normal tanned leather (Table 2). The reduced water soluble (Table 2) indicates that the aluminum tannages using basic aluminum sulphate ensure better water resistance[10]. The studies thus indicate that vegetable-mineral combination tannages using indigenous *Acacia nilotica ssp tomentosa* pods and aluminum sulphate can be easily adopted in the tanneries in Sudan and those in the sub-region. Their use will reduce imports of chrome and will lessen the attendant pollution. Cost-benefit studies may also show considerable benefits for non-Sudanese users of *Acacia nilotica ssp tomentosa* pods who may not have access to indigenous aluminum tanning agent. Depending on the particular quality needed in the final leathers, aluminum can either be used as a pretanning or retanning agent.

Table 2. Chemical Properties of Combination Tanning Using 10 % Offer *Acacia nilotica ssp tomentosa* pods and 2%, 5% Aluminum Salts.

Characteristics	10%Veg pre+2% Al re	2%Al pre +10% Veg re	10%Veg pre+5% Al re	5%Al pre+10% Veg re	Veg tanning (control)
Moisture, %	19.6	20.9	17.8	15.6	16
Fat content, %	60.5	55.5	40.5	32.8	50.5
Insoluble ash, %	0.9%	2.0	75.0	60.6	60.8
Hide substances, %	125.0	100.0	98.0	85.3	75
Al ₂ O ₃ -content, %	1.6	1.3	1.6	1.4	1.2
Water soluble,%	3.0	5.0	3.0	5.0	6.2

pre= pretanning, re= retanning, Veg= Vegetable tannins

4. Conclusions

In this study, we have shown that a combination tannage involving a vegetable tan (garad) and aluminum sulphate uniquely cross-links collagens, producing leather with high shrinkage temperature around 125°C. The sequence of addition of the tanning agents was shown to be important with best results from samples tanned first with vegetable tanning agents then re-tanned with aluminum. Previous studies indicated that vegetable tannins are able to penetrate the collagen inter-fibrillar space making the collagen peptide groups more accessible to aluminum tannins. In contrast, pre-tanning with aluminum possibly tightens the collagen fiber network, preventing high molecular weight vegetable tannins from interacting with collagen fibres. The other possibility is that the free amino acid side chains of collagens are exhausted on pre-tanning with aluminum, reducing the number of collagen–aluminum–vegetable tannin cross-links when vegetable tannins are introduced. Optimal results were obtained when 10% (w/w) vegetable tannins (garad) and 2% aluminum was used. In conclusion, we have presented evidence for the possible chemical modifications of collagen brought about by vegetable aluminum combination tanning. This will further add to our understanding of tanning of leather that might confirm the mechanism of Aluminum tanning as postulated by [17].

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