The effect of alum addition on shrinkage temperature, chemical properties, and morphology in the manufacture of vegetable-tanned leather

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Abstract. Vegetable-tanned leather has several disadvantages, which one of them is low thermal stability due to insufficient cross-linking with the collagen. The addition of aluminum sulfate in the vegetable tanning process will strengthen the cross-linking between the polyphenol and collagen, as well as forms the matrix in collagen. Thus, it will improve the thermal stability. The research aimed to figure out the addition of mimosa and aluminum sulfate on the shrinkage temperature, chemical properties, and morphology of leather. The research was conducted by using a variation of mimosa concentration (15%, 20%, 25% w/w) and aluminum sulfate concentration (3%, 6%, 9% w/w). The results showed that the treatment influenced the chemical properties and shrinkage temperature. The optimum treatment was the addition of 9% (w/w) aluminum sulfate to 25% mimosa which resulted to shrinkage temperature of 99.33° (rise 18.34%); nitrogen content (8.00 ± 0.0141)%; raw skins substance content (44.46 ± 0.0778)%; tannin bound content (28.29 ± 0.0424)% and the degree of tannage (62.93 ± 0.0141)%. Based on the SEM image, the addition of aluminum sulfate after mimosa has made the collagen fiber structure to be dense, which indicates the improvement of the cross-linking between the polyphenol and collagen.

1. Introduction

In general, tannin has a weak hydrogen bond, ineffective in stabilizing the leather structure. Thus it affects low thermal stability [1]. In contrary with chromium salts, the cross-linking, among the carboxyl group in protein, is more effective to stabilize the collagen structure to increase leather’s thermal stability.

Chromium, used in the leather tanning, is chromium (III) salts in the form of chromium sulfate. Chromium (III) can be oxidized into chromium (VI) which is happened during the tanning process. Chromium (VI) creates an allergic reaction and easy to go through the membranes, such as human skins [2]. Therefore, most of the researchers research chrome-free leather tanning to avoid the risk of chromium (VI) initiation and to manufacture a leather as good as chrome-tanned leather, in term of feels, fullness, softness, thermal stability [3,4].

Covington [5] explained that the environmental damage because of the chrome could be overcome by replacing it with others metal, such as Al(III), Ti(III)/(IV), Fe(II)/(III), Zr (IV), dan Lanthanide (III). The addition of aluminum sulfate in the vegetable tanning process will improve the forming polyphenol bond and the bond in collagen will create matrices and rise the hydrothermal stability [6]. Furthermore, Li et al. [4] reported that the vegetable-alum tanning could increase the shrinkage.
temperature. It is caused by the reaction between aluminum and hydroxyl phenolic of vegetable tannin in the form of ligand bond, then form a bond among vegetable tannin which produces a synergizing effect resulting in high shrinkage temperature.

According to Musa et al. [7], the interaction between tannin and non-tannin in vegetable tanning agent with complex aluminum will rise the fixation of vegetable tannin, especially vegetable-alum. The shrinkage temperature is defined as the temperature which the leather starts to shrink, which is a parameter in the form of leather [8]. Vegetable-tanned leather has a shrinkage temperature from 70° to 85 °C, while chrome-tanned leather could reach the temperature above 100 °C._raw skins/hides could only resist to heat up to 60 °C [5].

There are a lot of alternatives could be used to produce leather with good hydrothermal stability. Along with the rise of natural product domination in the global market, the leather industry is looking forward to any possibility to utilize organic-based materials. In this scenario, vegetable tanning could dominate its usage in the leather tanning industry for upcoming years. The application of vegetable tanning agent, in the leather industry, is an alternative to shifting the leather industry to green industry. The leather, tanned with a vegetable tanning agent, has several advantages, such as it results in comfort and compatible with human’s skins as well as high dimensional stability [9]. Meanwhile, it has low thermal stability which only has a shrinkage temperature at 70-85 °C, unlike chrome-tanned leather which has high thermal stability [5].

The vegetable tanning agent is not suitable to replace chromium tanning agent. However, the combination of it with metal salts or aldehyde compound could be as a potential alternative to replace chromium tanning agent and also could produce leather that stable on the heat. The combination tanning processes, i.e., vegetable-oxazolidine, vegetable-zinc, vegetable-acrylic, and vegetable-aluminum, have been conducted and has a good result. The interaction between tannin and non-tannin in vegetable tanning agent and complex aluminum will rise the fixation of the tanning process [7] and this synergy would level-up the shrinkage temperature [10]. Several investigations on the usage of vegetable tanning agent, combined with aluminum, have been applied and increased to shrinkage temperature. Musa et al. [7] reported that a combination tanning process of Henna (Lawsonia inermis) and aluminum resulted in an eco-friendly upper leather with the shrinkage temperature at 97±1 °C. Moreover, a combination of Garad (Acacia nilotica sub sp.nilotica) and aluminum resulted in the shrinkage temperature at 101±1 °C [11], while Haraz (Faidherbia albida) – aluminum reached 101±1 °C [10] and Myrobalan – aluminum reached 110-114 °C [7]. Those researches used aluminum sulfate \(\text{Al}_2(\text{SO}_4)_3\cdot18\ H_2\text{O}\) with sodium citrate and sodium tartrate ligands also. This research uses alum of \(\text{KAl}(\text{SO}_4)_2\cdot12\ H_2\text{O}\) which is easy to use and more affordable. Alum is a chemical compound made from the hydro molecule and two types of salt, which one of them is \(\text{Al}_2(\text{SO}_4)_3\). Alum is tervalent in its compounds. Aluminum ions (\(\text{Al}^{3+}\)) form uncolored salts with uncolored anions. This study aims to investigate the effect of a combination between mimosa and alum in the tanning process on the shrinkage temperature, chemical properties and morphology of the leather.

1.1. Materials
As the raw material, this study used cow pickled-hides from Magetan. Materials, used in the tanning process, consist of mimosa tanning agent (tannin content 30.63%), glutaraldehyde, oxalic acid, Novaltan PF, sodium formate, alum, syntan, dyestuff, synthetic fatliquor, vegetable fatliquor, liquid dyes, binder, filler, lacquer, and other chemical auxiliaries. All of the materials are obtained from leather chemical suppliers in Yogyakarta.

1.2. Instrumentation
The study used several instruments, such as rotating drum (Otto Specht serial number 80304), toggling unit, staking vibration machine, spray gun, shrinkage temperature test kit, and Scanning Electron Microscopic (SEC type SNE 3200 M).
1.3. Procedure
1.3.1. Leather tanning process
The research used a different concentration of mimosa and alum. The tanning process applied mimosa with the concentration of 15, 20 and 25% (w/w), while the alum concentrations are 3, 6 and 9% (w/w) as shown in table 1. Table 2 and Table 3 reflect the formula used in the tanning process and the finishing process.

| Table 1. Research design matrix |
|-------------------------------|
| Mimosa concentration (w/w) | Alum concentration (w/w) |
| 15% (M1) | M1 (I) 6% (II) 9% (III) |
| 20% (M2) | M2 (I) M2 (II) M2 (III) |
| 25% (M3) | M3 (I) M3 (II) M3 (III) |

| Table 2. Leather tanning process formula |
|-------------------------------|
| Process | % | Materials | Run (min.) | Remarks |
| Wetting back | 200 | Water | 30 |
| | 20 | NaCl | Be 8 – 10 |
| | 0,5 | Wetting agent | |
| | 2 | Bating agent | Drain |
| Depickling | 100 | Water | |
| | 10 | NaCl | Be 8 – 10 |
| | 1 | Sodium formate |
| | 0,5 | Sodium bicarbonate | 30 |
| | | | pH 5,2 – 5,5 |
| Pre-tanning | 2 | Relugan GT 50 | 30 |
| | 1 | Basyntan DLX-N | |
| | | Vegetable fatliquor | |
| Tanning | 15; 20; 25 | Mimosa | 180 |
| | | | 3X run @ 60’ stop 30’ menit (3X), O/N |
| | | | 60 |
| Basification | 3; 6; 9 | Alum | 60 |
| | 0,75 | Sodium bicarbonate | 3X15+30 |
| | 1 | White syntan | 30 |
| | | | pH = 5 |
| | | | Drain, aging O/N, shaving, weighting |
| Washing | 400 | Water | 2X @ 10 | Drain |
| Bleaching | 200 | Water | 30 |
| | 1 | Oxalic acid | Drain, wash |
| | 0,5 | Wetting agent | |
| Neutralising | 100 | Water | 45 |
| | 2 | Novaltan PF | 30 |
| | 2 | Neutralising syntan | |
| | 1 | Sodium formate | 30 |
| | 0,5 | Sodium bicarbonate | 3 x 20 + 30 |
| | | | pH = 5.5-5.8 |
| | | | Drain, wash |
| Process     | % | Materials                 | Run (min.) | Remarks                             |
|-------------|---|---------------------------|------------|-------------------------------------|
| Retanning   | 100 | Water (40 °C) | 45         |                                     |
|             | 2   | Basyntan DLX-N           | 30         |                                     |
|             | 3   | Ipertan 502             | 60         |                                     |
| Dyeing      | 100 | Water (50 °C) | 10         |                                     |
|             | 2   | Havana dyestuff         | 60         | Discharge the float 50%             |
| Fatliquoring| 50  | Water (50 °C) | 30         |                                     |
|             | 3   | Vegetable fatliquor      | 60         |                                     |
|             | 2   | Taural ICN               | 30         |                                     |
|             | 1   | Tannit LSW               |            |                                     |
|             | 0,05| Anti mold               |            |                                     |
|             | 1,5 | Formic acid             | 3x @ 10+ 30| Drain, wash, aging, toggling, staking|

### Tabel 3 Leather finishing formula

| Materials | Coating | Remarks          |
|-----------|---------|------------------|
|           | A       | B                |
| Water     | 475 gram|                  |
| Acrylic medium soft | 150 gram | A. Spray 3 -4 X   |
| Urethane resin        | 75 gram  |                 |
| Protein binder         | 50 gram  |                 |
| Soft acrylic resin     | 100 gram |                 |
| Wax filler            | 30 gram  |                 |
| Penetrator            | 20 gram  |                 |
| Pigment              | 75 gram  |                 |
| Liquid dyes           | 25 gram  |                 |
| Lacque solvent        | 200 gram | B. Spray 1 – 2 X |
| Thinner super         | 800 gram | Plate 80 °C, 125 Bar, 3 sec. |
| Slip agent           | 15 gram  |                 |

1.3.2. Shrinkage temperature measurement

The shrinkage temperature measurement is applied to the hides sample before and after the addition of alum in accordance to SNI 06-7127-2005 - “Cara Uji suhu pengkerutan kulit tersamak.”

1.3.3. Chemical properties testing

Chemical properties testing include nitrogen content, hide substance content, tannin bound content and degree of tannage.

Degree of tannage determination:

\[
\text{Hide substance content} = \text{nitrogen content} \times 5.62
\]

\[
\text{Tannin bound content} = 100\% - (\text{water content} + \text{fat content} + \text{water soluble matter} + \text{insoluble ash content} + \text{hide substance})\%
\]

\[
\text{The degree of tannage} = \frac{\text{tannin bound content}}{\text{hide substance}} \times 100\%
\]
1.3.4. Scanning Electron Microscopic (SEM) analysis
Scanning Electron Microscopic (SEM) is used to observe and analyze the collagen structure, before and after the addition of alum.

2. Results and discussion

2.1. Shrinkage temperature
The shrinkage temperature of samples, obtained before and after the addition of alum, is shown in Figure 1.

![Figure 1. The shrinkage temperature before and after the addition of alum.](image)

Figure 1 indicates that the initial shrinkage temperature (before the addition of alum) in the tanning process with 15%, 20%, and 25% (w/w) mimosa was 87.40; 86.0 and 83.93 °C respectively. The graph shows that the addition of alum, at all concentrations, affects the shrinkage temperature when it is combined with a mimosa at all of the concentrations used. The shrinkage temperature tends to increase along with the concentration of alum added in the process. The lowest shrinkage temperature (91.33 °C) was reached by the use of 25% (w/w) mimosa and 3% (w/w) alum. The highest shrinkage temperature (100.33 °C) was achieved by the use of 20% (w/w) mimosa and 9% (w/w) alum. Table 4 represents the rising percentage of shrinkage temperature after the addition of alum in all treatments.

| Code | Shrinkage temperature (°C) | Improvement (%) |
|------|-----------------------------|-----------------|
| M1 (I) | 94,00 | 7,55 |
| M1 (II) | 97,33 | 11,36 |
| M1 (III) | 98,67 | 12,78 |
| M2 (I) | 95,67 | 11,20 |
| M2 (II) | 97,33 | 13,13 |
| M2 (III) | 100,33 | 16,62 |
| M3 (I) | 91,33 | 8,81 |
| M3 (II) | 98,33 | 17,15 |
| M3 (III) | 99,33 | 18,34 |
Vegetable-tanned leather has shrinkage temperature at 70-85 °C, and chrome-tanned leather has at least 100 °C [5]. It is a fact that the addition of alum in the vegetable tanning process, with mimosa, could improve the leather’s shrinkage temperature, although it could not be as good as chrome tanning process which reached a shrinkage temperature at 102 °C. The rise of shrinkage temperature depends on the size of polyphenol molecules and the amount of OH group. Moreover, it is also determined by the effectiveness of the tanning agent’s molecules to create a tough molecules group cross-linking. The shrinkage temperature depends on the kinetic stability of interactions between tanning agent molecule and protein’s side-chain [5]. Even though alum, used in this research, is not aluminum sulfate which is not the ligand of sodium tartrate and sodium citrate, it can increase the shrinkage temperature.

Alum addition in vegetable tanning process will enhance the cross-linking between polyphenol and collagen with a stable complexity. The bond will form a matrix. Thus it will improve its hydrothermal stability [6]. Aluminum will react with vegetable tannin’s phenolic hydroxyl in a ligand form; then it creates a crosslinking among vegetable tannin which results in a synergistic effect to gain high shrinkage temperature [4]. The interaction of which is shown in Figure 2.

2.2. Chemical analysis

This research investigated the chemical properties, i.e., nitrogen content, rawhide content, tannin bound content and the degree of tannage. The mean of chemical analysis results is shown in Table 5.

| Code  | Nitrogen content (%) | Hide substance content (%) | Tannin bound content (%) | Degree of tannage (%) |
|-------|----------------------|---------------------------|--------------------------|-----------------------|
| M1 (I) | 9.56 ± 0.0707        | 53.70 ± 0.0353            | 20.99 ± 0.4311           | 39.10 ± 0.8343        |
| M1 (II) | 8.90 ± 0.0141        | 50.01 ± 0.0707            | 24.41 ± 0.2192           | 48.70 ± 0.6081        |
| M1 (III) | 8.75 ± 0.0141        | 49.17 ± 0.0848            | 26.43 ± 0.3677           | 53.75 ± 0.8343        |
| M2 (I)  | 8.64 ± 0.0217        | 48.66 ± 0.1131            | 27.15 ± 0.2334           | 55.89 ± 0.3464        |
| M2 (II) | 8.76 ± 0.0141        | 49.23 ± 0.0778            | 26.77 ± 0.2043           | 54.39 ± 4.2355        |
| M2 (III) | 8.38 ± 0.0141        | 47.09 ± 0.0848            | 27.83 ± 0.2192           | 59.11 ± 0.3535        |
| M3 (I)  | 8.39 ± 0.0141        | 47.15 ± 0.0778            | 27.87 ± 0.0565           | 59.11 ± 0.0212        |
| M3 (II) | 9.19 ± 0.0141        | 51.64 ± 0.0778            | 21.33 ± 0.3535           | 41.30 ± 0.6222        |
| M3 (III) | 8.00 ± 0.0141        | 44.46 ± 0.0778            | 28.29 ± 0.0424           | 62.93 ± 0.0141        |

The measured nitrogen content shows the amount of nitrogen in the hides. Table 5 indicates that the lower content of nitrogen and hide substance in the leather, the higher tannin bound content and the degree of tannage. In contrast, the higher content of nitrogen and hide substance, the lower tannin bound content. The high content of protein/nitrogen, in the leather, indicates that the bating process is not completely done. Thus it avoids the penetration of tanning agent into the hide. Bating process is removal the non-collagen proteins, such as albumin, globular, elastin, and epidermis in the hide, to facilitate the bond of tanning agent with collagen, so that results in good quality and soft leather [13–15]. The lowest nitrogen content and hide substance content is achieved by the M3 (III) treatment, 8.00 ± 0.0141% and 44.46 ± 0.0778% respectively, which has tannin content 28.29 ± 0.0424% and
degree of tannage at 62.93 ± 0.0141%. High tannin content refers to the ability of tannin to defuse into the collagen fiber without any obstacles from unnecessary matters (non-collagen protein) so that the tannin could be linked with the collagen fiber [15]. High tannin bound content in the M3 (III) indicates a faster diffusion rate than other treatments. The rate of diffusion depends on some factors, i.e., mechanical movement, contraction/viscosity of tannin and temperature. After the tannin is diffused into the fiber, tannin’s molecules will be linked in the collagen. The link is affected by the pH of float and the type of tanning agent as well. The treatment M1 (I) has the highest nitrogen content and hide substance content, 9.56 ± 0.0707% and 53.70 ± 0.0353%, while tannin bound content at 20.99 ± 0.4311% and degree of tannage at 39.10 ± 0.8343%.

The research indicates that higher concentration of mimosa and alum, used in the process, tends to reach higher tannin bound content. Tannin bound content is caused by a sum of tanning agent which is diffused into the fiber [16] — diffusion of tanning agent into the hide fiber or the hide’s polypeptide chain due to a presence of reactive polyphenol groups (-OH) in the tannin. This phenolic group will be attached with an amino group (-NH$_2$) and a carboxyl group (-CO) on the hide’s polypeptide chain and forms a hydrogen bond [5]. The forming of this hydrogen bond will create a more compact leather’s fibers. Figure 3 exhibits the interaction model of the tanning agent, which contains the polyphenol group, and the peptide chain in the hide.

![Figure 3](image)

**Figure 3.** Interaction of tannin’s polyphenol and polypeptide chain in hides [5].

According to SNI 06-0994-1989, “derajat penyamakan adalah tingkat kemasakan kulit tersamak, dihitung berdasarkan kadar tanin terikat dibagi kadar zat kulit mentah,” while “kadar zat kulit mentah adalah protein yang terdapat dalam kulit tersamak.” Based on those definitions, it assumes that the degree of tannage is affected by tannin bound content and hide substance content. More tannin bound content will decrease the hide substance content. Thus the degree of tannage will be higher [17]. Table 5 exhibits the effect of alum addition, along with mimosa concentration, on the degree of tannage. The more alum added will raise the degree of tannage. Similarly, more mimosa concentration will improve the degree of tannage obtained. The use of 9% (w/w) alum and 25% (w/w) mimosa is the best formula in this research. The highest degree of tannage (62.93%) is obtained from the treatment of M3 (III), while the lowest (39.10%) is achieved in the treatment M1 (I).

2.3. Scanning Electron Microscope (SEM) observation

The change of vegetable-tanned leather’s morphology, before and after the addition of alum, is observed by using a Scanning Electron Microscope (SEM). The SEM observation limits to the optimum treatment. The optimum treatment was the use of 25% (w/w) mimosa and 9% (w/w) alum. The SEM image of the optimum treatment, with 350x magnification, is displayed in Figure 4.
Based on Figure 4, it seems that there is space among the leather fiber before the addition of alum. Meanwhile, the addition alum makes the fiber structure more compact, where space is filled, that indicates there is a crosslinking between tannin’s molecules and alum. Thus, it enhances the fixation and penetration of tannin into the collagen fiber. The addition of alum in the vegetable tanning process, with mimosa, promotes the crosslinking of polyphenol and collagen and establishes matrix in collagen [6].

3. Conclusion
The study concludes that the addition of alum, on the vegetable tanning process with mimosa, effects the shrinkage temperature, chemical properties and morphology of the leather. The optimum treatment was the use of 9% (w/w) alum and 25% (w/w) mimosa which reached the shrinkage temperature at 99.33 °C (rise 18.34%), had the nitrogen content of 8.00 ± 0.0141 %, hide substance content 44.46 ± 0.0778%; tannin bound content 28.29 ± 0.0424% and degree of tannage 62.93 ± 0.0141%. SEM images reflect that the tanning process with mimosa and alum creates a compact collagen structure which indicates the improvement of polyphenol and collagen cross-linking.

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