Cleaner sheep leather tanning process using *uncaria gambir*: the influence of rebating on leather properties

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Abstract. Black-cube-gambir (pale catechin) is a processed gambir (*Uncaria gambier*) extract. Containing condensed tannin, black-cube-gambir could be used as a vegetable tanning agent in the leather making process. Some industries in Indonesia use pickled hide/skin as raw material for the next process that the previous bating process is uncontrolled. Therefore, this study aims to determine the effect of rebating in the re-pickle stage on the leather tanned with *Uncaria gambir*. For alum-gambir tanned leather, rebating increased its softness, tear strength, and hydrothermal stability, while for glutaraldehyde-gambir tanned leather, rebating increased its tensile strength, degree of tannage, and tannin bound. The broad DSC peak revealed that the distribution of collagen molecules of all samples was unequal. Rebating could increase and decrease the quality of leather.

1. Introduction
These Gambir (*Uncaria gambier*) is one of the traditional export plants from West Sumatera, Indonesia [1] that traditionally used as a vegetable tanning agent because it contains condensed tannin [2]. Gambir plants could be extracted by boiling the leaves and branches, then pressing it to take the gum out [1, 3]. Based on the percentage of tannin content, gambir has several kinds, such as coin, superior, brown cube, and galamai (black cube) [4]. Heating gambir could increase the solubility of tannin [5] and change catechin into tannin since the catechin loss the water molecules and the monomers are combined into tannin [4].

Nowadays, people are more concerned about the effect of industry on the environment and health [6] that makes them search for the possibility of plant materials [7, 8]. Some research was conducted to find the application of gambir as a leather tanning agent. Kasim, et al. [9] have tanned goat leather using gambir combined with alum that to find the best concentration. His study found that the best result was generated by 3% of alum as a pre-tanning agent and 3% of gambir as a tanning agent because it has the highest degree of tannage and tannin bound. Another study of gambir showed that gambir has different characteristics that caused the different quality of tanned leather [3]. That study collected ten gambir from ten different locations analyzed the characteristics and applied as a tanning agent for leather. The result concluded that the higher the tannin content of gambir the higher the degree of tannage of the leather, and the higher catechin content of gambir the lower tannin bound of the leather.
Sheepskin is relatively small with 0.8 mm thickness [10] and commonly used for the garment (jacket, coat, skirt, and pants). Among other animal skins, sheepskin was softer and more luxurious. To be made into a garment that directly contacts with human skin, it needs to be processed using safe materials to replace chrome. Gambir is a plant-based material that could be used as a natural tanning agent.

Leather tanning is a process to ‘cook’ raw skin into the leather that consists of several stages: soaking, unhairing, liming, deliming, bating, pickling, tanning, dyeing, fatliquoring, and drying. After the pickling stage, pickled sheep leather could be kept at a certain time. Processing pickled sheep leather means that the tanneries could not control the previous pre-pickling stages (usually called beam house stages). The bating stage is a stage in the leather tanning process where non-structural proteins from skins removed by a protease that opens up the structure of the collagen fiber and eases the fiber waves [11, 12]. Mostly, the protease enzyme produced from a microorganism that contains no hazardous materials [13]. By adding more bating agent in the leather making process, more interfibrillar substances could be removed [11] that affect the physical properties [12], the penetration of tanning agent [14], and thermal stability. Therefore, this study determined the effect of rebating in the pickling stage on the leather tanned with gambir.

2. Research method

2.1. Material and method

Raw materials used in this research were processed pickled sheepskins from Sleman, Yogyakarta. Gambir used in this study was a black cube gambir sourced from Sumatera Barat, Indonesia. Black cubegambir (pale catechin) is known as a gambir extract that already proceeds. Chemicals used for the leather tanning process were of commercial grade from a chemical reseller in Yogyakarta.

| Sample Identification | Description |
|-----------------------|-------------|
| Gam-Al                | Alum – gambir tanning combination without rebating |
| Gam-Alx               | Alum – gambir tanning combination with rebating |
| Gam-Glu               | Glutaraldehyde - gambir tanning combination without rebating |
| Gam-Glux              | Glutaraldehyde - gambir tanning combination with rebating |
| Gam                   | Gambir tanning without rebating |
| Gamx                  | Gambir tanning with rebating |

Once received from the seller in Bantul, Yogyakarta, Indonesia, pickled sheepskin was rebated. The rebating formulation as described in Table 2. The percentage of the product was calculated based on the pelt weight. In this process, the sheepskin was added with 8% of salt and 80% of water and ran for 20 minutes in the rotating drum (Otto Specht serial number 80304). After that, 1% of the bating agent for the acid bate was added and ran for 60 minutes.

| Process       | Product          | %  | Duration (min) |
|---------------|------------------|----|----------------|
| Rebating      | Salt             | 8  | 20             |
|               | Water            | 80 |                |
|               | Feliderm Bate AB,| 1  | 60             |
|               | Clariant         |    |                |

Rebated sheepskins were then subjected to the formulation shown in Table 3. This formulation was modified formula from Musa et al. [7]and Sreeram et al. [15]. Similar to Table 2, the percentage of the product in Table 3 was calculated based on the pelt weight.
Table 3. Formulation of the tanning process

| Process                      | Product                                      | %  | Duration (min) |
|------------------------------|----------------------------------------------|----|----------------|
| Repickle                     | Salt                                         | 10 | 10             |
|                              | Water                                        | 80 |                 |
| Pertaining                   | Sodatan SB, Selic chemical company           | 2  | 30             |
|                              | Sodatan TSN, Selic chemical company          | 2  | 30             |
|                              | Tanmit LSW, Dr Bohme                         | 0,5| 30             |
| Tanning                      | Gambir extract                               | 25 | 4 x (30 Ø 15)  |
| Tanning combination          | Alum/glutaraldehyde                          | 6  | 60             |
| Drained, aged, and shaved    |                                              |    |                |
| Wetting back                 | Water                                        | 200|                 |
|                              | Wetting agent                                | 0,5| 30             |
|                              | Oxalic acid                                  | 0,3|                 |
| Neutralization               | Water                                        | 150|                 |
|                              | Novaltan PF                                  | 2  | 60             |
|                              | Sodatan TSN, Selic chemical company          | 1  |                 |
|                              | Sodium Formate (HCOONa)                      | 2  | 2 x 30         |
|                              | Baking Soda (NaHCO₃) (Optional)              | 0,5| 2 x 15         |
| Retanning                    | Acrylic Syntan (R40), Abhilash chemicals Pvt., Ltd., India | 6  | 60             |
|                              | 40 ºC water                                  | 70 |                 |
| Fatliquoring                 | Water 50 ºC                                  | 40 | 40             |
|                              | Tannit LSW, Dr. Bohme                        | 2  |                 |
|                              | Seroil LL, Quimser S.A                       | 2  |                 |
|                              | Garboil BS, Selic chemical company           | 6  | 30             |
|                              | Coriol FBD                                   | 4  |                 |
|                              | Leathermol BLM, Allied chemicals international company limited | 2  |                 |
| Fixating                     | Formic acid (HCOOH)                          | 1,5| 2 x 30         |
| Antifungal                   | Antifungal agent                             | 0,05| 30           |
| Masking                      | Catalix GS, Clariant                         | 1  | 15             |

2.2. Analytical procedures

2.2.1. Physical properties. The softness, tear strength, tensile strength, and elongation were determined. Measurement of softness used 20 mm diameter of the sample. Measurement of the physical properties was performed as per standard procedures [16-17].

2.2.2. Chemical properties. Chemical properties tests of crust leather were used to investigate the tannin bound and degree of tannage that were calculated using equations 1 and 2.

\[
\text{Tannin bound} = 100\% - (\text{water content} + \text{fat content} + \text{water soluble substances} + \text{insoluble ash} + \text{hide substances})\% \tag{1}
\]
Degree of tannage = \frac{\text{tannin bound}}{\text{hide substance}} \times 100\% \tag{2}

2.2.3. Hydrothermal stability. Using DSC-60, the thermal denaturation of each sample was determined. The heating rate was maintained at 10°C/min. The sample weighed around 5 mg.

2.2.4. Organoleptic properties. All of the samples were assessed for general appearance, grain smoothness, and fullness by hand and visual examination of three experienced tanners. Those tanners gave a score for each parameter on a scale of 0 – 10 points. Higher points mean better property.

2.2.5. Scanning electron microscopy. Scanning Electron Microscopy SEC type SNE 3200 M was used to analyze samples before and after acid bating addition and crust leather samples. Samples were cut into specimens without pre-treatment and were coated with gold. The grain surface and cross-section were obtained by SEM operation at an accelerating voltage of 15 kV.

3. Results and discussions

3.1. Physical properties

From Figure 1, it was observed that leather tanned with glutaraldehyde-gambir was the softest leather. Glutaraldehyde followed by gambir leather without rebating has a higher value of softness than that with rebating, while alum-gambir leather without rebating has a lower value of softness than that with rebating.

![Figure 1. Presentation of softness and tear strength of the leather samples](image)

Crust leather from control leather and experimental leather showed different tear strength and given in Figure 1. Leather samples of alum followed by gambir showed the highest tear strength, while leather samples tanned with glutaraldehyde followed by gambir showed the lowest. From the same figure, it is observed that rebating slightly increased the tear strength of gambir followed by alum tanned leather. On the other hand, rebating decreased the tear strength of gambir-glutaraldehyde and control leather samples. Tear strength could be defined as the toughness of the leather because it is strongly correlated with the ability of leather to ‘survive’ from the tear [18]. Sizeland et al. [18] also found that tear strength is influenced by the strength perpendicular to the axis of fibril collagen which is affected by the strength of the cross-link.
Figure 2. Presentation of tensile strength and elongation of the leather samples

Leather tanned with gambir-glutaraldehyde showed the highest tensile strength, while the elongation was the opposite. Graphical presentation in Figure 2 also revealed that the tensile strength value of the leather tanned with gambir and glutaraldehyde were the highest. However, this combination showed the lowest elongation. Gambir-glutaraldehyde tanned leather with rebating showed higher tensile strength value than that without rebating, while the other samples were the opposites. Elongation test results revealed that rebating decreased the elongation value of gambir-glutaraldehyde and control leather, whereas in the gambir-alum leather was almost equal.

Adding more bating agent in the leather making process could have two different effects, first, it can increase the quality of the leathers, and the second is the collagen could be overworked caused by the hydrolyzing effect of the bating agent on the collagen [11]. This study [11] also found that after the bating stage, the fibers were separated and opening up. When the skin was added with the more bating agent, the opening up was bigger and there were some fibers splitting-up.

3.2. Chemical properties
The chemical analysis result is given in Table 4. The hide/skin substance value is the quantification of the collagen (the skin protein). In the bating stage, non-fibrous protein, including collagen types that do not form collagen fibrils, were also removed [11]. Rebating means removing more interfibrillar protein in the skin.

Table 4. Analysis results of the chemical properties testing

| Parameter          | Uji   | Gam-Al | Gam-Alx | Gam-Glu | Gam_Glux | Gam  | Gamx |
|--------------------|-------|--------|---------|---------|----------|------|------|
| Moisture (%)       | 11.66 | 11.02  | 13.57   | 11.78   | 12.92    | 11.17|
| Insoluble ash (%)  | 1.110 | 2.020  | 1.39    | 1.085   | 1.250    | 1.430|
| Fats/oils (%)      | 18.99 | 17.23  | 12.27   | 11.30   | 14.79    | 14.42|
| Hide substance     | 52.15 | 56.31  | 55.84   | 56.01   | 52.55    | 56.62|
| Tannin bound (%)   | 14.29 | 12.51  | 14.55   | 18.65   | 17.31    | 14.85|
| Degree of tannage (%) | 27.42 | 22.22  | 26.06   | 33.3    | 32.95    | 26.22|

From the same table, it was observed that the tannin bound and the degree of tannage were linear. Leather tanned with gambir followed by glutaraldehyde (rebated) showed the highest tannin bound and degree of tannage, whereas leather tanned with gambir followed by alum (rebated) showed the lowest. Rebating increased the tannin bound and the degree of tannage of gambir-glutaraldehyde leather, while in the gambir-alum and control leather decreased. The percentage of the degree of tannage presents the
tannin content in the leather that it could determine the stabilization of the chemicals in the collagen and affect the properties of the finished leather [19].

3.3. Hydrothermal stability

Hydrothermal stability is one of the methods to measure the efficiency of the tanning process based on phase transition and the denaturation process of the collagen using differential scanning calorimetry (DSC) [20]. All of the samples in this study had two peaks (Figure 3).

From the Figure 3, all of the samples undergo thermal denaturation and it was showed that rebating have an impact on the collagen stability of leather tanned with gambir-alum (Figure 3(a)), gambir-glutaraldehyde (Figure 3(b)), and gambir (Figure 3(c)). Compared with the literature [21], the thermogram peaks of all samples in this study were broader and narrower. It is showed that gambir, with or without tanning agent combination, has low tannin diffusity that caused diverse cross-linking [22]. DSC peak showed the unique population of the collagen molecules [22, 21]. The broader the peak the broader the distribution of collagen molecules that have hydrothermal stability. Moreover, the two peaks of all the samples revealed that the collagen molecules distribution across the thickness of the leather has unequal thermal stability [22].
Each peak has the temperature of denaturation called $T_{\text{max}}$, where the hydrothermal stability of the collagen was presented. On the other hand, the shrinkage temperature ($T_s$) that usually used as the ‘cook proof’ in the leather tanning industry is the onset temperature ($T_i$) in the DSC [22]. From Table 5, the first onset temperature varied between 65.9 and 99.06°C. Rebated gambir-alum tanned leather was higher than that of unrebated leather. However, gambir-glutaraldehyde and control leather showed opposites. Surprisingly, the unrebated gambir tanned leather revealed the highest onset temperature. For the second onset temperature, the gambir-glutaraldehyde tanned leather showed the highest value.

Table 5. Hydrothermal stability data of the samples using DSC

| Sample  | $T_{\text{onset}}$ (°C) | $T_{\text{onset}}$ (°C) | $T_{\text{max}}$ (°C) | $T_{\text{max}}$ (°C) |
|---------|-------------------------|-------------------------|-----------------------|-----------------------|
| Gam-Al  | 65.9                    | 269.34                  | 101.94                | 305.79                |
| Gam-Alx | 94.81                   | 259.27                  | 121.62                | 283.73                |
| Gam-Glu | 94.81                   | 259.27                  | 121.62                | 283.73                |
| Gam-GLux| 90.19                   | 273.75                  | 112.01                | 292.25                |
| Gam     | 99.06                   | 205.97                  | 114.9                 | 289.2                 |
| Gamx    | 77.17                   | 269.31                  | 96.65                 | 306.72                |

The higher the denaturation temperature ($T_{\text{max}}$), the more stable the skin collagen. Rebated gambir-alum tanned leather showed higher $T_{\text{max}}$ than the unrebated one, while other samples showed the opposites. Gambir-alum leather with rebating showed the same DSC parameters value with gambir-glutaraldehyde leather without rebating. In the tanning process, aluminum salt performed weaker and longer covalent bond with the collagen, unstable, and easily hydrolyzed [20].

3.4. Organoleptic properties
The combination tanning agent affected the color of the crust leather. From Figure 4, it is seen that the grain surface of gambir-glutaraldehyde leathers were the smoothest ones with less looseness than others. While the gambir leather with rebating was the darkest and unclear surface.
The organoleptic properties of crust leathers from the experiment were presented in Figure 5. From the graphical presentation, the gambir-glutaraldehyde leather without rebating was the softest. It was similar to the softness testing results. From the same figure, it is shown that unrelated gambir-glutaraldehyde leather exhibited better fullness than other samples, whereas rebated gambir-glutaraldehyde leather exhibited better grain smoothness and general appearance.

3.5. Scanning electron microscopy analysis
The scanning electron micrograph of the samples is shown in Figure 6(a)-(f) to investigate the grain characteristics. It is seen that the grain surface of crust leather at a magnification of X 80 was clean without tannin deposition. The pores of all the leather samples were visible but the gambir-glutaraldehyde tanned leather. The grain surface of gambir-glutaraldehyde (Figure 6(c) and 6(d)) tanned leather was smoother than others. The pores of Gam-Alx leather (Figure 6(b)) were smaller and neater than Gam-Al. The grain surface of gambir-Alum tanned leather (Figure 6(a) and (b)) also looks smoother than gambir tanned leather (control).
Figure 6. Scanning electron micrograph of the grain surface (80 X) of leather samples: (a) Gam-Al; (b) Gam-Alx; (c) Gam-Glu; (d) Gam-Glux; (e) Gam; (f) Gamx

4. Conclusions

Gambir (*Uncaria gambir*) is a traditional plant from West Java, Indonesia which contains tannin to offer environmentally benign leather tanning methodology. This study reported that rebating using acid bate before repickling increased softness, tear strength, and hydrothermal stability of gambir-alum tanned leather. Alum has a weaker covalent bond with skin collagen that rebates helped the fiber to split up to strengthen the interaction with skin collagen. Even though gambir-glutaraldehyde tanned leather showed the best organoleptic properties, rebating only increased its tensile strength, degree of tannage and tannin bound. The broad DSC peak revealed that the distribution of tanning agent molecules of all samples was ununiformed. In this study, rebating could increase and decrease the quality of leather.
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