The effect of level concentration *Ceriops tagal* on leather tanning of barramundi (*Lates calcarifer*) fish skin on chemical, mechanical and leather morphology properties

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Abstract. Vegetable tanning is the most classical tanning process to give leather the most natural and environmental friendly characteristics. The aim of this study is to investigate the effects of concentrations of *Ceriops tagal* as vegetable tanning material on chemical, mechanical, and leather morphology properties. The experiments were conducted by tanning the Barramundi fish skin using 15, 20 and 25% of *Ceriops tagal* followed by Aluminum 4%. The chemical, mechanical properties of the leather were analyzed and microscopic observation was also conducted. Microscopic observation with the scanning electron microscope (SEM) has been performed to investigate the grain characteristics and fibre structure of the tanned leather. The results of this study indicated that *Ceriops tagal* concentration affected on chemical and mechanical properties. The optimum result of this research was shown at the usage of 25% *Ceriops tagal*. The results of analysis on the Barramundi fish skin showed the following properties: The chemical properties were tannin bound content of 31.1%; hide substance content of 37.68%; and degree of tannage of 82.96%. Their mechanical properties were tensile strength of (14.31±3.73 N/mm²); elongation at break of (62.68±9.33%); and tear strength of (587.85±141.25 N/cm).

1. Introduction
Tingi trees (*Ceriops tagal*) is one potential source of tannins and these include type of mangrove tree the source of which tannins contained in the bark. *Ceriops tagal* bark was potential as tanning agent due to high tannin concentration [1]. The bark powder containing tannin content of 42.21%; non-tannin content of 54.44%; water content of 3.35% and total solid of 96.65% [2]. The FTIR (Fourier transform infrared spectroscopies) spectral data indicated that *Ceriops tagal* tannin was similar with wattle (mimosa) contained hydroxyl, aromatic and ester group [3]. The bark of *Ceriops tagal* as sustainable source for tanning agent as vegetable tanning materials and it is effective for use as a vegetable tanning material by adding alum. The use of alum in tanning using *Ceriops tagal* can increase fixation and penetration of vegetable tanning material into the skin fiber [4]. The used of
Ceriops tagal powder 15 – 25% following by aluminum 4% gives the goods results for lining leather from goat skins [2]. Ceriops tagal can also be used as a tanning agent and also be used as a re-tanning agent, the optimum re-tanning of tilapia skins at a concentration of 15% [5].

Vegetable tanning could play a dominant role in the future of leather industry. The leathers processes through vegetable tanning have distinct advantages such as comfort, natural substance, and environmental friendly [6]. Tannins are the most important substances in the plant, found in the wood, bark, leaves and roots fruits, which occurs naturally [7] and is used as tanning agent [1]. Tanning is the most important step in leather production. During tanning, collagen will fix the tanning agent to its reactive sites, as a result stopping the putrefaction phenomenon.

Leather can be produced from the skin of any animal, bird, reptile or fish. Fish skin is a byproduct of food production processes, and would be thrown away if not used for leather. Therefore, it can be used as a raw material for leather products. Fish skin has unique scaly patterns and color designs, which are difficult to be imitated by man [8]. Each skin is as unique for each fish and you can see the prominent scale pockets in the finished leather. Fish skin is physically different form cow hides, so it is turned into leather by a process with differences such as descaling rather than dehairing and using lower temperatures. Now there are many different types of fish skin i.e stingray, salmon, snapper varieties and barramundi. Fish leather is used for handbags, shoes, furniture upholstery, and car interiors.

The barramundi (Lates calcarifer) have large scaled with previous names: bara, giant perch and silver barramundi [9]. The barramundi makes great leather, with a very unusual and unique pattern once the scales have been removed and the scale pockets to produce a unique.

The aim of this study is to investigate the effects of concentrations of Ceriops tagal as vegetable tanning material on chemical, mechanical, and morphology properties in quality of the Barramundi (Lates calcarifer) fish skin.

2. Materials and Methods

2.1. Materials

The barramundi fish skin as raw material was obtained from company of fish fillet in Probolinggo Indonesia, wetting agent, sodium sulfide, lime, degreasing agent, bating agent, salt (NaCl), formic acid, sulfuric acid, sodium bicarbonate, Ceriops tagal powder from Indonesia; mimosa powder ME Brand Extract from Czechoslovakia; phenolic syntan, glutaraldehyde, white syntan, sulphited oil, and anti-mold were used in this study.

The equipment used were rotary drum (Otto Specht No.Seri 80304), horses, hand staking. Kubelka glass apparatus, tensile strength tester (Zwick Roell ZO20 tipe KAP – TC serial 07 4170 made in Germany) and Scanning Electron Microscope (JEOL JSM-6360LA) was used for the chemical and microscopic test.

2.2. Tanning experiments

The tanning experiments were carried out on processed barramundi fish skin using Ceriops tagal powder. The tanning trials were carried out using mimosa as a matched pair control as comparison for experimental leathers. The tanning process mentioned in Table 1 is followed for both experimental and control leathers.

| Process       | %  | Product   | Duration (min) | Remarks |
|---------------|----|-----------|----------------|---------|
| Washing       | 300| Water     | 15             | Drain   |

Table 1 Formulation of tanning process
| Process                        | Temperature | Time      | Solution                                          | Treatment                                                                 |
|-------------------------------|-------------|-----------|---------------------------------------------------|---------------------------------------------------------------------------|
| Soaking                       | 300         | 1         | Water, Wetting agent                              | Drain                                                                     |
| Washing                       | 300         |           | Water, Lime                                       | Drain                                                                     |
| Removal of scales and liming  | 300         | 2, 6      | Water, Sodium sulfide, Lime                       | Run 30' stop 30' run 5' Stop 30' (3X) 15'/hour (3X), Over night          |
| Fleshing and Removal of scales|             |           |                                                   |                                                                           |
| Reliming                      | 300         | 2         | Water, Lime                                       | Over night                                                                |
| Washing                       | 300         |           | Water, Lime                                       | Drain                                                                     |
| Deliming, bating, degreasing  | 200         | 2, 0.5, 2 | Water, Ammonium chloride, Bating agent, Degreasing agent | 90 Drain                                                                  |
| Washing                       | 300         |           | Water, Lime                                       | Drain                                                                     |
| Pickling                      | 100         | 10, 1, 1  | Water, Salt/Natrium Chloride, Formic acid, Sulfuric acid | 15, 3 X 15, 3 X 15 + 180 Over night                                      |
| Tanning                       | 15          | (15, 20, 25) | Mimosa/ Wattle Control, C.tagal (Experimental) | 3 X 30 + 90 3 X 30 + 90                                                   |
| Fixation                      | 4           |           | Alum, Sodium bicarbonate                          | pH 3.5                                                                   |
| Neutralization                | 1           |           | Sodium bicarbonate                                | pH 5                                                                     |
| Washing                       | 300         |           | Water                                              |                                                                           |
| Retanning                     | 100         | 3, 3, 3   | Water 50°C, White syntan, Phenolic syntan, Glutaraldehyde | 30, 15, 60 Drain                                                         |
| Fatliquoring                  | 100         | 3         | Water 50°C, Lipoderm liquor SAF, Sandolix WWL     | 60                                                                        |
| Fixing                        | 0.5         |           | Formic acid                                       | 30 pH 3.5                                                                |
| Washing                       | 300         |           | Water                                              | Drain and pile overnight, and staked                                    |

2.3. Chemical properties
The chemical analysis of the leather viz. for water content, oil content [10], water soluble matter content [11], insoluble ash content, [12] degree of tannage, [13] tannins bound content, [14] hide substance content [14] were carried out for experimental and control.

Calculation of degree of tannage:

\[
\text{Degree of tannage} = \frac{\text{Tannin bound content}}{\text{Hide substance content}} \times 100\%
\]  

(1)

\[
\text{Tannin bound content} = 100\% - \left[\text{water content + oil content + water soluble matter + insoluble ash content + hide substance}\right] \%
\]  

(2)

2.4. Physical Properties

Physical properties such as tensile strength, elongation at break and tear strength were measured as per standard procedure [15,16].

2.5. SEM (Scanning Electron Microscope) analysis of leather samples

Cross section of experimental and control crust leather was observation by JEOL JSM-6360LA scanning electron microscope (SEM). The SEM analysis was conducted at 500X and 1000X magnifications.

3. Results and Discussion

3.1. Chemical properties

The chemical properties of Barramundi fish skin are given in Table 2. The chemical measurements viz. for water content, oil content, water soluble matter content, insoluble ash content. The tannins bound content, hide substance content, and degree of tannage shown in Figure 1 to 3.

| No. | Test Parameters        | Experiments | Control |
|-----|------------------------|-------------|---------|
|     |                        | C.tagal 15% | C.tagal 20% | C.tagal 25% |
| 1.  | Water content, %       | 15.53       | 15.26    | 15.76       | 15.50 |
| 2.  | Oil content, %         | 8.54        | 8.06     | 7.22        | 7.97  |
| 3.  | Water soluble matter content, % | 2.31 | 2.09 | 1.20 | 0.86 |
| 4.  | Insoluble ash content, % | 7.91 | 7.55 | 7.04 | 6.18 |
| 5.  | Hide substance content, % | 44.11 | 41.14 | 37.68 | 40.55 |

The test results from these parameters are used to calculate degree of tannage. Degree of tannage of skin was related to the bound tannin content and hide substance content. The ratio tannin bound content / hide substance content is called the degree of tannage and is of practical value to the tanner in determining the quality of leather. The calculation of the degree of tannage is to determine tannins which is bound by the skin compared with skin proteins that have not bounded with tannins (raw skin). So, the degree of tannage is affected by tannins bound and hide substance (raw skin). The tannin bound content, hide substance content and degree of tannage with variation of Ceriops tagal concentration (15; 20; 25 %) successively shown in the Figure 1, 2 and 3.

Tannin will be absorbed and bound tightly by collagen of raw skin during tanning. The tannins bound in the skin is affected by the amount of tannins that can diffuse into the skin tissue [17]. High concentration of tanning material outside skin may increase the diffusion of tanning material. Therefore, the higher the concentration, the amount of tanning material cause tannins into the skin tissue is more so the amount of tannin bound by collagen increased. The higher the concentration of Ceriops tagal used, the greater tannin bound to the skin tissue. The highest tannin bound content was
31.10% observed on the skin tanned by *Ceriops tagal* 25%, whereas the lowest was reached on the skin tanned by *Ceriops tagal* 15% i.e 21.60% (Figure 1). Hide substance is protein that has not bounded with tannin. The more tannin which are bound, the number of hide substance in the skin will decrease, so the number of comparisons of tannins bound and hide substance will be even greater. On the contrary, the highest hide substance was 44.11% observed on the skin tanned by 15% *Ceriops tagal*, whereas the lowest was reached on the skin tanned by *Ceriops tagal* 25% i.e 37.68% (Figure 2).

![Figure 1. Tannins bound content of skin using control and *Ceriops tagal* (15, 20, 25%)](image1)

![Figure 2. Hide substance content of skin using control and *Ceriops tagal* (15, 20, 25%)](image2)

![Figure 3. Tannin bound content of skin using control and *Ceriops tagal* (15, 20, 25%)](image3)

Increasing the degree of tannage depends on the number of tannin which is bound by collagen skin. The more tannins that bound the amount of a substance in the skin raw will decrease, so that the ratio
of the amount of tannin which is bound by the amount of the raw skin will be even greater [17]. The higher the concentration of Ceriops tagal, the greater degree of tannage. The highest degree of tannage was resulted by the experimental using 25% Ceriops tagal i.e 82.96 %, with tannins bound are 31.10% and hide substance are 37.8%. The results of degree of tannage for experimental of 25% Ceriops tagal tanned is more than control (71.37%). Therefore, they met the standard, i.e. minimum of 50% [18] (Figure 3).

3.2. Physical properties

The effects of Ceriops tagal concentration on physical properties of Barramundi fish skin are given in Table 3. The physical properties measurements viz. for tensile strength, elongation at break, and tear strength. The strength properties of leather are almost most important deciding about quality of manufactured leather. The strength value of Ceriops tagal tanned leather have been found to meet the standard [19], because there is not yet standard about bony fish skin include Barramundi fish skin. Therefore, the reference of standard for this study with the standard [19], even though less suitable, because different histological structure of fish skin with goat skin making it difficult to compare.

Table 3 Physical strength characteristics of the Barramundi fish skin tanned using C.tagal (Experimental) and mimosa (control)

| Property                | C.tagal (15%) | C.tagal (20%) | C.tagal (25%) | Mimosa (control) | SNI 0253: 2009 |
|-------------------------|--------------|--------------|--------------|------------------|----------------|
| Tensile strength, N/mm² | 12.41±4.77   | 12.58±2.87   | 14.31±3.73   | 16.60±4.11       | Min.16         |
| Elongation break, %     | 63.16±12.65  | 57.83±8.01   | 62.68±9.33   | 66.07±10.94      | Max.55         |
| Tear strength N/cm      | 513.59±190.45| 430.45±144.62| 587.85±141.25| 770.39±365.75    | Min. 150       |

3.3. Tensile strength (N/mm²)

The tensile strength of Barramundi fish skins obtained from this experimental were in the range of 12.58±2.87 to 14.31±3.73 N/mm² (Table 3). The highest tensile strength was given by the experimental using 25% Ceriops tagal are 14.31±3.73 N/mm², while the lowest was given by the experimental using 15% Ceriops tagal are 12.41±4.77 N/mm². However, the tensile strength for control (Mimosa) skin is more than the experimental of Ceriops tagal, i.e 16.60±4.11 N/mm². Therefore, they met the standard [19], i.e minimum of 16 N/mm².

3.4. Elongation at break (%)

The experimental shows that elongation at break of the Barramundi fish skin were in the range of 57.83±8.01% to 63.16±12.65% (Table 3). The highest elongation at break was obtained from the experimental using 15% Ceriops tagal are 63.16±12.6 % and the lowest one was given by experimental using 20% Ceriops tagal are 57.83±8.0%. The elongation at break with 25 % Ceriops tagal are 62.68±9.33%. However, the elongation at break for control (Mimosa) skin is more than the experimental of Ceriops tagal, i.e 66.07±10.94 % N. Therefore, they met the standard [19], i.e. maximum of 55%. Generally, application of fish skin only small cut as an action fish skin or not full skin.

3.5. Tear strength (N/cm)
The tear strengths of Barramundi fish skin in this experimental were in the range of 430.45±144.62 N/cm to 587.85±141.25 N/cm (Table 3). The highest value was given by experimental using 25% *Ceriops tagal* i.e 587.85±141.25 N/cm and the lowest was obtained from the experimental with 20% *Ceriops tagal* i.e 430.45±144.62 N/cm. It shows that all of the experimental, the tear strength fulfilled the standard [19]. However, the tear strength for control (Mimosa) skin is more than the experimental of *Ceriops tagal*, i.e 770.39±365.75 N/cm. Fish skin has natural cross-fibre structure, unlike cattle leather for instance, in which the fibres run only in one direction. This natural cross-fibre pattern makes fish skin stronger than “ordinary” leathers.

### 3.6. Microscopic Observation

The scanning electron micrographs has been performed to observation the grain characteristics and fiber structure of the tanned leather are given in Figure 4 and 5. The scanning electron micrographs at the cross section at magnification of 500X and 1000X. The scanning electron micrographs of crust sample from Barramundi fish skin experimental (*Ceriops tagal*) and control (mimosa) showing in the grain surface at magnification of 500X are given in Figure (4a-d), respectively. It is seen that the grain surface of sample from experimental tanning process with *Ceriops tagal* (15, 20, 25%) and control as tanning agents produced a good character of leather such as clean. The scanning electron micrographs of crust sample from Barramundi fish skin experimental (*Ceriops tagal*) and control (mimosa) showing in the grain surface at magnification of 1000X are given in Figure (5a-d), respectively. The fibers of both the experimental and control leathers appeared to be well separated, cleaner, opened up and clearly visible as seen in the photomicrograph. But the *Ceriops tagal* (25%) tanned (Figure 5c) showed better fullness, more compact and more opened up fiber structures compared to the experimental using 15% and 20% *Ceriops tagal* and control. This was due to the tannins bound content and degree of tannage more than the experimental using 15% and 20% *Ceriops tagal* and control.

The tannins bound content are influenced by the amount of tannins that can diffuse into the skin tissue. Increasing the degree of tannage depends on the number of tannin which is bound by collagen skin.

### 4. Conclusion

At the present study, an attempt has been made to produce leathers using a eco-friendly *Ceriops tagal* as vegetable tanning material. It is seen that tanning using (15-25%) *Ceriops tagal* followed by aluminium 4%. It was showed that the concentration of *Ceriops tagal* affects the quality of the Barramundi (*Lates calcarifer*) fish skin. From this study, the treatment to produce the optimal Barramundi fish skin was the tanning with 25% *Ceriops tagal*. The treatment resulted in the Barramundi fish skin that has the best tannins bound content, degree of tannage, and strength properties. The quality of Barramundi fish skin is as follows: tensile strength of (14.31±3.73) N/mm²; elongation at break of 62.68±9.33%; tear strength of 587.85±141.25 N/cm; water content of 15.76%; oil content of 7.22%; insoluble ash content of 7.04%; water soluble matter of 1.20 %; tannins bound content of 31.10%; hide substance content of 37.68%; degree of tannage of 82.96%. Scanning electron microscope observation of experimental leather showed better fullness, more compact and more opened up fiber structures compared to the experimental using 15% and 20% *Ceriops tagal* and control.

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Figure 4: Scanning electron micrographs of (4a) experimental C.tagal (15%), (4b) C.tagal (20%), (4c) C.tagal (25%), (4d) control (mimosa) samples showing the grain surface at magnification of 500X after tanning.

Figure 5: Scanning electron micrographs of (5a) experimental C.tagal (15%), (5b) C.tagal (20%), (5c) C.tagal (25%), (5d) control (mimosa) samples showing the grain surface at magnification of 1000X after tanning.

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