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# Chrome-Free Tanning: Effect of a Combination Tannage Based on Mimosa and Biogenic Silica from Rice Husk

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## Article

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## ABSTRACT

*Chromium (III) sulfate is a popular tanning agent for producing leather. However, chrome tanning wastewater is one of the problems in the leather tanning industry. To prevent this, tanning using vegetable materials can be used in the leather tanning process. One of the natural ingredients that can be used is mimosa. However, mimosa is relatively expensive, so a substitute/combination tanning agent is needed to make tanning costs cheaper. This research aims to determine the effect of using a combination of mimosa and silicic acid from rice husk (RHSA) tanners on the quality of the tanned leather produced. This research uses a completely randomized factorial design with mimosa and RHSA as factors. The analysis shows that the best treatments were 20% mimosa and 20% RHSA. In addition, the analysis shows that the treatment met the standard. The resulting shrinkage temperature was 84 °C, tear strength was 39.98 N mm<sup>-1</sup>, tensile strength was 26.42 N mm<sup>-2</sup> and elongation at break was 41%. Combination tanning also shows no significant difference from conventional tanning and reduces mimosa without decreasing leather quality.*

## KEYWORDS

*mimosa, silicic acid, combination tanning, tanned leather*

## INTRODUCTION

In the leather tanning industry, chromium (III) sulfate is a popular mineral tanning for producing good quality final leather compared with other tanning agents. However, the chrome tanning process will promote wastewater, which is harmful to the environment if not treated properly. A lot of effort has been made to reduce the problems caused by chrome tanning in the leather tanning industry, including establishing wastewater treatment plants [1–4], minimizing chrome [2,3,5–8], and eliminating chrome [9–13]. In this case, minimizing and eliminating chrome in the leather tanning process is the most common

alternative today for lower pollutants produced. In chrome tanning, 30% of the total chromium is disposed of together with wastewater [14]. In addition, the waste contains COD  $0.19 \text{ g L}^{-1}$ , BOD  $0.06 \text{ g L}^{-1}$ , and chromium hexavalent  $0.03 \text{ mg L}^{-1}$  [15,16]. Chromium treatment at the end of pipe treatment requires quite expensive costs [7]. Meanwhile, the costs incurred in tanning with little and no chrome are lower than in the wastewater treatment plant.

The increasing public awareness of environmental sustainability has an impact on the leather tanning process. Tanning processes by eliminating chromium are being widely developed using vegetable tanning materials, non-chrome minerals, aldehyde, oil, and a combination of several leather tanning agents [10–12,17–24]. This is because chromium compounds have carcinogenic, mutagenic, and very toxic properties [25,26].

Combination tanning using vegetables and minerals is one of the steps that can be taken to get good quality tanned leather. One of the vegetable ingredients that can be used is mimosa. Mimosa has 22 – 48% condensed tannin in a dry extract [27]. The principle in the vegetable tanning process is quickly penetrating the tanning agent into the skin collagen with a small molecular size and small binding power [28]. The weakness of vegetable tanning is the stability of the leather to low heat stability and producing stiff, dense, and hard leather [29]. To increase the stability of the leather to heat, the soft and smooth leather can use combination tanning using silica [30,31].

In previous studies, silica in commercial-grade sodium metasilicate was combined with aluminium and tannic acid in goat and sheepskin tanning. In this combined tanning system, silica gives a softness and fluffiness effect of resulting leather [30]. Silicic acid derived from commercial-grade sodium silicate was combined with valonia and mimosa extract in goat tanning could increase thermal stability, mechanical properties, softness, and hydrophilicity, and lengthens the shelf life of resulting leather [31].

Rice husk, a waste from the rice milling process, is one of the natural silica sources which is abundant, cheap, renewable, and environmentally friendly. It contains 15-20% biogenic silica [32,33] which can be extracted into water-soluble silicate compounds. In leather tanning, silica cannot use as a single tanning agent but can use as a combination tanning agent. Therefore, a combination tanning of vegetable materials and biogenic silica from rice husks is a promising approach to producing leather with good characteristics and is more environmentally friendly. Combination tanning techniques using biogenic silica from rice husks have not been widely reported. This research used a combination of mimosa with silicic acid from rice husks (RHSA) in the tanning process for pickle goat pelt. The characteristics of the resulting tanned leather were evaluated and compared with the results of conventional mimosa tanning.

## EXPERIMENTAL

### Materials and Methods

This research used a pickle goat pelt from the back part with a size of 15 x 30 cm obtained from a local leather industry, mimosa (Aritan, India), formic acid (Merck), sodium hydroxide (Merck), sodium bicarbonate (Merck), sulfuric acid (Merck), NaCl (UnichemCandi, Indonesia), and sodium formate (Merck). Rice husk was obtained from the rice mill in Karawang Regency, West Java, Indonesia. The equipment includes a 40 x 30 cm tanning drum, toggle drying, horse up, hot plate stirrer, furnace, and test equipment. Moreover, this research used a factorial complete randomized design. The first factor was the dose of RHSA solution with four levels, namely 5%, 10%, 15%, and 20%. The second factor was the dose of mimosa, namely 10%, 20%, and 30%. Each treatment was repeated three times. The parameters observed were ash content, shrinkage temperature, tensile strength, tear strength, elongation at break, leather morphology, and leather organoleptic. The other parameters observed were RHSA content and particle size.

### Preparation of Silicic Acid from Rice Husk

The rice husk was ashed using an electric furnace at 500 °C for 5 hours. Rice husk ash and 0.25 M NaOH solution were added to the Erlenmeyer with a ratio of 1:5. Rice husk ash was stirred at a constant speed. The extraction process was carried out for 60 minutes after the solution boiled. Furthermore, the extract solution and rice husk ash dregs were separated using filter paper [modified 34] to obtain a sodium silicate solution. In the sodium silicate solution, 1% sodium citrate and 10% H<sub>2</sub>SO<sub>4</sub> were added to lower the pH of the silicate solution to pH 3 while producing silicic acid. Then the silicic acid solution was analyzed for its silica content using AAS (Atomic Absorption Spectrophotometry) and for particle size and distribution using a PSA (Particle Size Analyzer). The silicic acid solution from the rice husk (RHSA) was then used as a tanning agent for the mimosa–RHSA combination.

### Combination Tanning of Mimosa – Silicic Acid from Rice Rusk (RHSA)

The tanning process consists of two stages: preparation of pickle skin and tanning. The pickle skin preparation stage comprises soaking, liming, deliming, bating, and pickling. The soaking to deliming stages refers to [35], while the bating to pickling stages refer to [36]. The bating stage follows the best treatment [37]. The tanning stage is carried out through depickling and tanning, which can be seen in Table 1. The leather tanning process used a pelt from the back part of 30 cm x 15 cm size. Each experiment included two pelts for the tanning process.

Table 1. Procedure for combination tanning using mimosa-RHSA dan vegetable tanning

| Processes                                                      |                   | Materials and doses                   | Remarks                                                                                                                               |
|----------------------------------------------------------------|-------------------|---------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|
| Depickling                                                     |                   | Pickle pelt                           | The material doses are based on pickle pelt.                                                                                          |
|                                                                |                   | Water (100%)                          | Mix pickle pelt, water, and NaCl in a drum and run                                                                                    |
|                                                                |                   | NaCl (10%)                            | for 30 minutes. Add sodium bicarbonate (3 x 10                                                                                        |
|                                                                |                   | Sodium bicarbonate (0.5%)             | minutes) and run the drum for 30 minutes. Test the pelt until getting the pH 4.5 – 4.8                                                |
| Experiment                                                     | Tanning 1         | Mimosa (X %)                          | Add mimosa to a drum and run for 3 hours. Then,                                                                                       |
|                                                                |                   | Formic acid (0.5%)                    | add formic acid and H <sub>2</sub> SO <sub>4</sub> to decrease the pH of the                                                          |
|                                                                |                   | H <sub>2</sub> SO <sub>4</sub> (0.2%) | pelt to 3.                                                                                                                            |
|                                                                | Tanning 2         | RHSA Solution (Y %)                   | Add RHSA solution to drum and run for 3 hours.                                                                                        |
|                                                                |                   | Sodium bicarbonate (1.2%)             | After that, add sodium bicarbonate and run the                                                                                        |
|                                                                |                   | Sodium formate (2%)                   | drum for 1 hour. Add sodium formate and run the drum for 30 minutes. Drain the water in the drum and wash the pelt with water (200%). |
| Control                                                        | Vegetable tanning | Mimosa (40 %)                         | Add mimosa and run the drum for 4 hours. Then,                                                                                        |
|                                                                |                   | Formic acid (0.5%)                    | add formic acid until getting pH 3.5 in the pelt. Drain the water and wash the pelt with water (200%).                                |
| The leather is tested physically, mechanically, and chemically |                   |                                       |                                                                                                                                       |

### Analysis of Silica Content and Size

Silica content was tested using the AAS method [38]. Meanwhile, the particle size of silica was tested using PSA [39]. The concentrated solution sample was diluted  $10^{-3}$  so that it was read on the PSA tool. The sample was shaken using a vortex mixer for 1 minute. The sample was then put into a clean cuvette until the sample filled 2/3 of the cuvette used. After that, the cuvette was inserted into the tool. Before being measured, the samples were put at a room temperature of 25 °C. Finally, the tool could be read.

### Analyses of Physical and Chemical Properties of the Leather

The observed variables of physical properties were tear strength (SLP 7), tensile strength (SLP 6), elongation (SLP 6), shrinkage temperature (SLP 18), and chromium oxide content (SLC 7). The sample was conditioned at  $23 \pm 2$  °C and  $50 \pm 5\%$  relative humidity (RH) prior to the test. The conditioning process was carried out for 48 hours [40].

### Scanning Electron Microscopy (SEM)

Before and after being given the treatment, the skin was cut into small pieces (6.5 cm x 1 cm), placed in a test tube with pure water to coat the pieces, and followed by freeze-dried. Two sample parts with a thickness of 1.5 mm were cut from each dry sample. Silver paint was applied around the sample. Samples were coated in gold with Scancoat Six sputter-coated. Samples were observed using a Quanta 200 FEG Environmental Scanning Electron Microscope. Zooms were performed 50, 250, 500, and 1,000 times [42].

### Analysis of Colors

Measurement of tanned skin colour used a Colorimetric tool. Colour measurements include L, a, b, h, and c, which were recorded by the control and treatment samples. L represents whiteness on a scale of 0 – 100. The higher the value, the brighter the colour. The total colour difference ( $\Delta E$ ) and hue difference ( $\Delta h$ ) were calculated using the following equation:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (1)$$

$$\Delta h = \tan^{-1}(b/a) \quad (2)$$

Where  $\Delta E$  is the overall difference of all colours,  $\Delta L$  is the difference in brightness,  $\Delta a$  and  $\Delta b$  are the differences in the values of a and b. 'a' represents the red and green axes if 'a'>0 is red and 'a'<0 is green. Meanwhile, if 'b'>0 is yellow and if 'b'<0, then it is blue, and C represents the chromaticity of the colour, which is meant by intensity. The change in brightness is ' $\Delta L$ ', a positive value on  $\Delta L$  indicates the sample became brighter [22].

### Leather Organoleptic Test

The organoleptic test used several parameters: softness, fullness, grain smoothness, general appearance, and dye uniformity. Panellists measured the brightness level of the colour with a value of 1 – 10. A value of 1 is the worst value, while 10 is the best value. This applies to other parameters. The results were then averaged on each parameter. The panellists used were 1 experienced tanner and 2 trained panellists.

## RESULTS AND DISCUSSION

### Characteristics of Silicic Acid from Rice Husk

Table 2 shows the characteristics of the RHSA solution produced in this research. The resulting RHSA solution has an average particle size of 138.83 nm with a Si content of 3,962 mg L<sup>-1</sup>. According to several studies, silica extracted from rice husk ash has an amorphous form [42,43]. The average particle size of RHSA produced is larger than that of biogenic silica nanoparticles from rice husk, which is 5 – 50 nm [27,34,44], but smaller than the average particle size of silicic acid derived from commercial-grade sodium silicate (366.19 nm) [31]. This RHSA solution was further used as a leather tanning agent. RHSA's small particle size is expected to enter the skin tissue well in tanning.

Table 2. The characteristics of silicic acid solution from rice husk

| Parameter                        | Value  |
|----------------------------------|--------|
| Si content (mg L <sup>-1</sup> ) | 3,962  |
| Si Size (nm)                     | 138.83 |

### Ash Content

Ash content indicates the presence of mineral content in the leather produced. In the combination tanning of mimosa and RHSA, silica is used. The tanning process using minerals will certainly increase the ash content of the tanned leather. Analysis of the ash content in the tanning combination of mimosa and nano-silica can be seen in Table 3.

Table 3. The chemical and physical leather properties of combination tanning of mimosa–RHSA

| Mimosa | RHSA | Ash Content (%)         | Shrinkage Temperature (oC) |
|--------|------|-------------------------|----------------------------|
| m10    | S5   | 2.35±0.15 <sup>b</sup>  | 69.23±0.87 <sup>a</sup>    |
|        | S10  | 2.64±0.16 <sup>c</sup>  | 71.17±1.04 <sup>b</sup>    |
|        | S15  | 2.90±0.02 <sup>de</sup> | 73.33±0.58 <sup>c</sup>    |
|        | S20  | 3.18±0.07 <sup>f</sup>  | 73.50±0.50 <sup>c</sup>    |
| m20    | S5   | 2.59±0.20 <sup>c</sup>  | 81.00±1.00 <sup>d</sup>    |
|        | S10  | 2.70±0.06 <sup>cd</sup> | 83.00±1.00 <sup>e</sup>    |
|        | S15  | 3.02±0.08 <sup>ef</sup> | 83.67±1.15 <sup>ef</sup>   |
|        | S20  | 3.16±0.09 <sup>f</sup>  | 84.00±1.00 <sup>efg</sup>  |

| Mimosa                | RHSA | Ash Content (%)         | Shrinkage Temperature (oC) |
|-----------------------|------|-------------------------|----------------------------|
| m30                   | S5   | 2.61±0.16 <sup>c</sup>  | 83.00±1.00 <sup>e</sup>    |
|                       | S10  | 2.73±0.10 <sup>cd</sup> | 83.83±1.04 <sup>ef</sup>   |
|                       | S15  | 3.10±0.07 <sup>ef</sup> | 85.33±0.58 <sup>fg</sup>   |
|                       | S20  | 3.17±0.07 <sup>f</sup>  | 85.33±1.53 <sup>fg</sup>   |
| Conventional (mimosa) |      | 1.94±0.13 <sup>a</sup>  | 85.67±0.76 <sup>g</sup>    |
| BIS – 576 [45]        |      |                         |                            |
| SNI 0234:2009 [46]    |      | Max. 2                  |                            |

m: mimosa (10, 20 dan 30 %); S: RHSA (5, 10, 15 dan 20 %); <sup>a</sup> Means in the same column with different superscripts describe significant data using the DMRT test 5%

Analysis of variance shows that mimosa and RHSA had a significant effect on the ash content of the leather. However, these two factors did not show any interaction. The analysis results show that the highest ash content was found in the m30S20 treatment, i.e.,  $3.17 \pm 0.07\%$ , and the lowest ash content was found in the m10S5 treatment, i.e.,  $2.35 \pm 0.15\%$ . Further analysis shows that all treatments were significantly different from conventional tanning ash content. Table 3 shows that the ash content of the leather in each treatment had levels above 2%. Referring to SNI 0234:2009, the leather produced did not meet the established standards; however, based on BIS – 576 (The Bureau of Indian Standards), the ash content of the leather was not determined.

Table 3 shows that each increase in RHSA dose caused an increase in the ash content of the resulting tanned leather. This is inversely proportional to the conventional treatment (40% mimosa), which showed a low ash content, i.e., 1.94%. The increase was due to the presence of silica in the leather. The bonds between silica and active groups on collagen were a factor in the increase in leather ash content. Besides, it was influenced by the tannins contained in mimosa. Tannin can naturally bind minerals [42]. Silica, which is also a group of minerals, is thought to bind with tannins, thereby increasing the ash content of tanned leather. The mineral content found in the skin could also be caused by calcium, potassium, and iron [24]. In addition, there were other minerals in the form of salts such as sulphates, chlorides, carbonates, and phosphates, but these ingredients were very small, allowing them to increase the ash content of the leather. This was because, before the tanning stage, the skin has undergone a lot of washing processes and removal of materials that could inhibit tanning.

### Shrinkage Temperature

Leather tanning causes an increase in the shrinkage temperature of the tanned leather. This is due to a reaction between the tanning agent and skin collagen so that new bonds are formed. The results for the



tanning combination of mimosa – RHSA can be seen in Table 3. Analysis of variance shows that mimosa and RHSA had a significant effect on the shrinkage temperature of the resulting tanned leather but showed no significant interaction. Further test results show that all treatments indicated a significant difference from conventional treatment (Table 3).

The analysis results show that the lowest shrinkage temperature was found in tanning m10S5 with a shrinkage temperature of  $69.23 \pm 0.87$  °C. In contrast, the highest shrinkage temperature was found in the m30S15 and m30S20 treatments with a shrinkage temperature of  $85.33 \pm 0.58$  °C and  $85.33 \pm 1.53$  °C. Meanwhile, the shrinkage temperature in the conventional treatment was  $85.67 \pm 0.76$  °C. The results of the further analysis show that the m20S20, m30S15, and m30S20 treatments were not significantly different from the conventional treatment, while the other treatments showed significant differences (Table 3).

Further analysis shows that the higher the dose of mimosa used, the higher the shrinkage temperature. According to [27], the increase in shrinkage temperature in tanning using vegetable materials is due to a reaction between vegetable tanning materials and skin collagen, more precisely in the carboxyl group, to form hydrogen bonds and covalent bonds also. This bond causes the leather to experience an increase in its shrinkage temperature, but not as high as using a chrome tanning agent. The content of tannins (polyphenolic compounds), which have many hydroxyl groups and other groups (such as carboxyl), can form hydrogen bonds with collagen [47–49], one of the tanning materials which contains a lot of tannins is mimosa.

Meanwhile, further analysis on increasing the dose of RHSA solution shows increased shrinkage temperature. According to [6], silica can bond with collagen through hydrogen bonds. However, silica cannot be used as a sole tanning agent because it produces leather with poor shrinkage temperature and strength properties. This bond causes tanning using silica to not provide a significant increase in temperature. Other studies stated that using sodium silicate above 10% did not increase the temperature of shrinkage on the skin; the maximum temperature of shrinkage obtained was 67 °C [50].

### **Mechanical properties of combination tanning leather**

Leather tanning provides increased mechanical properties of tanned leather. Some of the mechanical properties of the skin that experience some changes are tear strength, tensile strength, and elongation. Table 4 shows that the tanning of the combination of mimosa and nano-silica affected the quality of the leather's tear strength, tensile strength, and elongation. The increase in mechanical properties of leather has implications for applying leather in various products.

The results of the analysis of variance showed that mimosa and RHSA had a significant effect on the tear strength of the resulting leather. Still, these two factors did not show any significant interaction. Table 4 shows that the m10S5 treatment had the lowest skin tear strength, namely  $29.83 \pm 1.79 \text{ N mm}^{-1}$ , while the highest tear strength was in the m30S20 treatment, namely  $40.25 \pm 1.49 \text{ N mm}^{-1}$ . The tear strength in this research showed a significant difference from conventional treatment (Table 4). In conventional tanning, the tear strength of the leather was  $42.05 \pm 2.38 \text{ N mm}^{-1}$ . The m20S20, m30S15, and m30S20 treatments showed no significant difference from the conventional treatment. Meanwhile, the other treatments showed a significant difference from the conventional treatment. Thus, when viewed from the tear strength, combination tanning of mimosa – RHSA can reduce the use of mimosa by 20% compared to conventional tanning.

Table 4. Mechanical properties of mimosa – RHSA combination tannage

| Mimosa                | RHSA | Tear strength ( $\text{N mm}^{-1}$ ) | Tensile strength ( $\text{N mm}^{-2}$ ) | Elongation at break (%) |
|-----------------------|------|--------------------------------------|-----------------------------------------|-------------------------|
| m10                   | S5   | $29.83 \pm 1.79^a$                   | $30.89 \pm 2.53^c$                      | $52.67 \pm 5.07^c$      |
|                       | S10  | $31.71 \pm 1.47^{ab}$                | $30.46 \pm 2.98^c$                      | $46.45 \pm 4.33^b$      |
|                       | S15  | $32.51 \pm 0.74^{ab}$                | $29.10 \pm 0.05^{bc}$                   | $38.44 \pm 2.04^a$      |
|                       | S20  | $34.49 \pm 1.67^{bc}$                | $28.81 \pm 1.32^{ab}$                   | $38.00 \pm 0.50^a$      |
| m20                   | S5   | $33.11 \pm 1.91^b$                   | $28.82 \pm 1.62^{bc}$                   | $53.56 \pm 4.19^c$      |
|                       | S10  | $34.47 \pm 0.84^{bc}$                | $27.08 \pm 0.73^{ab}$                   | $43.17 \pm 3.92^{ab}$   |
|                       | S15  | $36.54 \pm 1.11^{cd}$                | $26.38 \pm 2.24^{ab}$                   | $41.56 \pm 1.17^{ab}$   |
|                       | S20  | $39.98 \pm 1.41^{ef}$                | $26.42 \pm 1.13^{ab}$                   | $41.00 \pm 2.65^{ab}$   |
| m30                   | S5   | $36.07 \pm 0.39^{cd}$                | $28.77 \pm 2.70^{bc}$                   | $58.22 \pm 1.35^c$      |
|                       | S10  | $38.47 \pm 2.45^{de}$                | $25.75 \pm 1.91^{ab}$                   | $52.83 \pm 4.09^c$      |
|                       | S15  | $40.06 \pm 1.89^{ef}$                | $24.68 \pm 0.73^a$                      | $43.61 \pm 4.09^{ab}$   |
|                       | S20  | $40.25 \pm 1.49^{ef}$                | $23.91 \pm 1.25^a$                      | $42.78 \pm 2.51^{ab}$   |
| Conventional (mimosa) |      | $42.05 \pm 2.38^f$                   | $25.22 \pm 1.04^a$                      | $41.55 \pm 2.17^{ab}$   |
| BIS – 576 [45]        |      | Min. 29.42                           | Min. 19.61                              | 40 – 65                 |
| SNI 0234:2009 [46]    |      | Min. 29.42                           | Min. 22.06                              | Max. 70                 |

m: mimosa (10, 20 dan 30 %); S: RHSA (5, 10, 15 dan 20 %); <sup>a</sup> Means in the same column with different superscript describes significant data using the DMRT test 5%.

Table 4 shows that each addition of mimosa and RHSA concentrations caused an increase in the tear strength of the leather. In addition, all treatments showed the quality that complied with The Bureau of

Indian Standards as upper leather (IS-576) and SNI 0234:2009, namely having a minimum tear strength value of  $29.42 \text{ N mm}^{-1}$ . According to [51], the number of tannins bonded to the carboxyl group on collagen affects the tear strength of the leather. Thus, the low tannin used in tanning also affects the low tear strength. [52] also showed a similar result, where the higher the mimosa used, the greater the tear strength of the resulting tanned leather. According to [27] tanning using silica increases leather strength, but the increase is very low. In several other combination studies, the use of silica in the leather tanning process helped improve the mechanical properties of the leather formed [30,50].

Tensile strength is defined as the maximum stress that a material can bear before breaking. The results of the analysis can be seen in Table 4. Table 4 shows that the lowest tensile strength of the mimosa-RHSA combination leather was found in the m30S20 treatment of  $23.91 \pm 1.45 \text{ N mm}^{-2}$ , while the highest tensile strength was found in the m10S5 treatment with a tensile strength of  $30.89 \pm 2.53 \text{ N mm}^{-2}$ . However, the quality of the leather produced from all treatments met the quality of upper leather from The Bureau of Indian Standards (IS-576) and SNI 0234:2009, namely the minimum tensile strength was  $19.61 \text{ N mm}^{-2}$  and  $22.06 \text{ N mm}^{-2}$ . The results of the analysis of variance showed that both mimosa and RHSA had a significant effect on the tensile strength of the leather but did not show any interaction between the two factors. Meanwhile, further analysis showed that the tensile strength in the conventional treatment was not significantly different from the m30S20, m30S15, m30S10, m20S15, m10S20, m20S10, and m10S10 treatments. Meanwhile, the other treatments were significantly different from the conventional treatment.

Table 4 shows that the higher the dose of mimosa and RHSA used affects the tensile strength of the resulting leather. The tensile strength of the leather was decreased due to silica coating the collagen fibres, making it difficult for the mimosa tanning material to bind to the collagen fibres. According to [53], silica does not have a specific effect on improving the quality of tanned leather because silica only coats the skin's collagen fibres. This is in line with [21], stating that adding aluminium to the tanning of a combination of vegetable tanners and aluminium decreases the tensile strength of the resulting leather. According to [24], other factors affecting the tensile strength of leather are the grain direction, thickness, and location of leather sampling. Meanwhile, the presence of non-collagen proteins in the pelt will also affect the tensile strength of the leather, this is because non-collagen proteins can inhibit tanning agents from penetrating the pelt [54].

Elongation at the break of the leather shows that there was an extension of the leather to the force that caused the leather to break. The results of the elongation analysis of combination tanning of the mimosa-RHSA can be seen in Table 4. Table 4 shows that with increasing doses of RHSA, the elongation of the

leather decreased. The treatment with the lowest elongation was found in m10S20, namely  $38.00 \pm 0.50\%$ , while the treatment with the highest elongation was found in the m30S5 treatment of  $58.22 \pm 1.35\%$ . Meanwhile, conventional tanned leather has a value of  $41.55 \pm 2.17\%$ . Based on The Bureau of Indian Standards as upper leather (IS-576), some treatments did not meet the standards, which had values below 40 – 65%, including m10S20 and m10S15. However, if referring to SNI, all treatments still met the standards.

Table 4 shows that the m10S20, m10S15, m20S20, m20S15, m30S20, m20S10 and m30S15 treatments were not significantly different from the conventional treatment, while the other treatments showed significant differences. The analysis results show that increasing the dose of mimosa caused an increase in leather elongation. This was also seen in [52], where increasing the dose of mimosa increased the elongation of the leather. Meanwhile, increasing the dose of RHSA caused a decrease in leather elongation. This is in line with [6], increasing the dose of silica in combination with tanning causes a decrease in the elongation of tanning leather.

### **Determination of The Best Treatment**

The best treatment was determined by comparing the results of all combination tanning treatments of mimosa–RHSA with the results of conventional tanning to show no significant differences in shrinkage temperature, tear strength, tensile strength, and elongation of the leather. In addition, the best treatment was also determined by looking at how much the use of mimosa can be reduced in conventional tanning. The analysis results show that the m20S20, m30S15, and m30S20 treatments produced leather quality that was not significantly different from the conventional tanning results for the characteristics of wrinkle temperature, tear strength, tensile strength, and elongation. Of the three treatments, m20S20 was considered the best treatment because it reduced the use of mimosa by 20%.

### **Leather Organoleptic**

The test results show that the leather produced from the combination tanning of mimosa – RHSA had organoleptic properties, which were superior to conventional tanning (Table 5). On softness, grain smoothness, and colour uniformity parameters, the best treatment had a higher value than the conventional one. However, in the fullness parameter, the leather from conventional tanning was higher than the best combination tanning treatment.

Table 5. The organoleptic result of the best treatment combination tanning of mimosa–RHSA and conventional vegetable tanning

|                | Parameters  |             |                  |                    |                |
|----------------|-------------|-------------|------------------|--------------------|----------------|
|                | Softness    | Fullness    | Grain smoothness | General appearance | Dye uniformity |
| Best treatment | 6.83 ± 0.29 | 6.67 ± 0.58 | 7.00 ± 0.00      | 7.00 ± 1.00        | 7.00 ± 0.00    |
| Conventional   | 5.66 ± 0.58 | 7.66 ± 0.58 | 6.67 ± 0.29      | 7.00 ± 1.00        | 6.16 ± 0.29    |

The silica in the tanning combination of mimosa - RHSA gives a softening effect to the leather. This is due to the natural gelling properties of silica [6]. These properties also cause silica to increase the smoothness of tanned leather. In addition, silica fills the voids in the skin fibres. However, the best treatment had an impact on the fullness of the leather. This was because the reduced dose of mimosa and silica could not cover it. The analysis results in Table 5 show that leather from conventional tanning has higher fullness properties.

### Leather Morphology

The results of the morphological analysis of conventional tanned leather (40% mimosa) and the best treatment show that there were differences in the structure of the skin collagen fibres (Figure 1). Figure 1 shows that the fibres in conventional tanning looked like they were not compact and rough, but the distance between the fibres looked tight. Meanwhile, the best treatment showed that the collagen fibres looked compact, and the size of the fibres looked bigger.

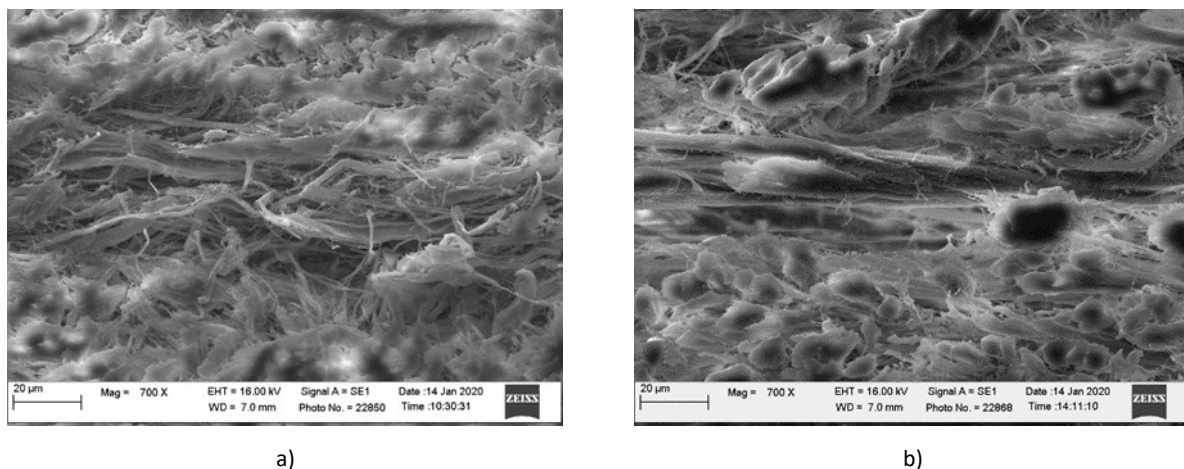


Figure 1. Micrograph scanning electron: a) Mimosa tanning (mimosa 40%) dan, b) Best combination tanning of mimosa 20% – RHSA 20%.

The difference in fibre in conventional tanning and the best treatment was due to using RHSA as an additional tanning agent. Silica in the RHSA solution can coat the collagen fibres so that the fibres look more compact. The silica content in the leather also increases the softness properties. Figure 1 shows that the density between the fibres affected the fullness properties of the leather produced the better as shown in Table 5. However, a fullness that is too high causes the leather to be hard.

### Colour Measurements of Conventional and Experimental Leather

The process of tanning leather using vegetable materials will affect the tanned leather produced. The resulting leather has a colour that tends to be dark. Table 6 shows that the discolouration ( $\Delta E$ ) in the best treatment was lower than the skins resulting from conventional tanning. The results of the analysis of variance and Duncan multiple range tests (DMRT) show that there was a significant difference between the best treatment with conventional tanning (40% mimosa) and no significant difference with conventional tanning (20% mimosa). The low discolouration in the best treatment was due to the reduced dose of mimosa used in the leather tanning process. This is also supported by the data in Table 6, which states that conventional tanning (20% mimosa) is significantly different from conventional tanning (40% mimosa). Thus, the colour resulted from the best treatment, and conventional tanned leather (20% mimosa) was lighter than that of conventional tanned leather (40% mimosa) (Figure 2).

Table 6. The leather colour comparison using a colourimeter in the best treatment and conventional vegetable tanning

|            | Best treatment     | Conventional (mimosa 20%) | Conventional (mimosa 40 %) |
|------------|--------------------|---------------------------|----------------------------|
| $\Delta L$ | $-13.41 \pm 0.26$  | $-16.18 \pm 0.41$         | $-20.59 \pm 0.24$          |
| $\Delta a$ | $14.02 \pm 0.31$   | $13.44 \pm 0.35$          | $13.03 \pm 0.19$           |
| $\Delta b$ | $20.57 \pm 0.42$   | $19.87 \pm 0.28$          | $21.37 \pm 0.53$           |
| $\Delta C$ | $18.42 \pm 0.46$   | $17.65 \pm 0.31$          | $19.10 \pm 0.54$           |
| $\Delta H$ | $-16.75 \pm 0.27$  | $-16.24 \pm 0.28$         | $-16.19 \pm 0.20$          |
| $\Delta E$ | $28.28 \pm 0.58^a$ | $28.94 \pm 0.58^a$        | $32.41 \pm 0.57^b$         |

L: represents whiteness; a: red and green; b: blue and yellow; C: chromaticity/intensity; H: hue; E: total colour change;

<sup>a</sup> Means in the same raw with different superscript describe significant data using DMRT test 5%.

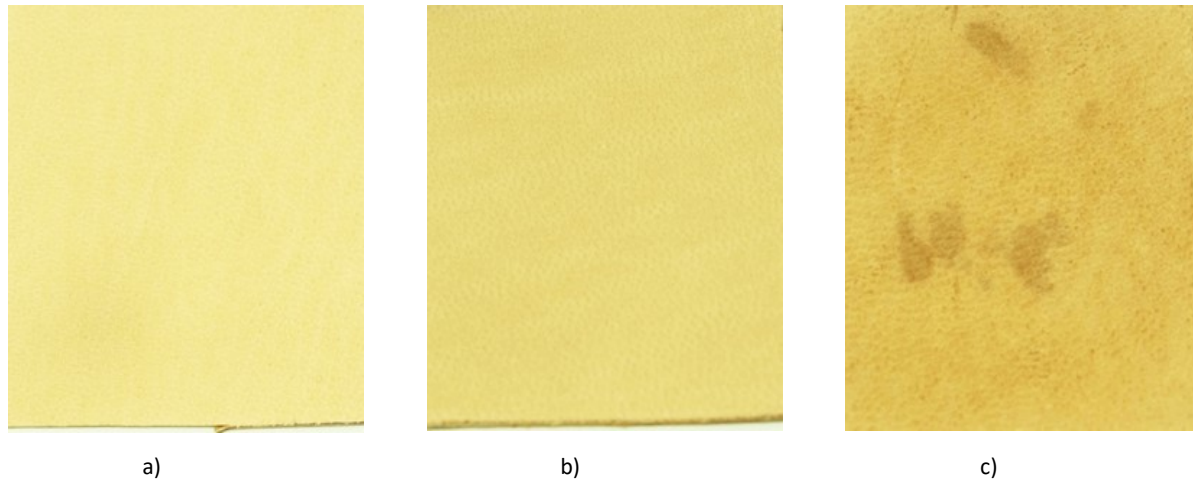


Figure 2. The leather colour comparison a. The best treatment; b. Mimosa 20%; dan c. Mimosa 40%

## CONCLUSION

Biogenic silica from rice husk in the form of silicic acid (RHSA) was used as a tanning agent in the combination tanning process. The combination of 20% mimosa and 20% RHSA increased physical and mechanical leather properties and was the best experiment. Statistically, the quality of the best experiment is equal to conventional mimosa tanning. The combination could reduce the dose of mimosa in conventional mimosa tanning and the quality not significantly from conventional tanning using full mimosa. The value in the organoleptic test was no different with the mimosa, but the colour was brighter than the mimosa tanning.

### *Author Contributions*

Preparation and creation of the published work, specifically writing the initial draft (including substantive translation), conducting a research and investigation process, specifically performing the experiments, and collecting data – Nugraha AW; Head of the research project, supervision of students and oversight of study, preparation, and creation of the published work by those from the original research group, specifically critical review, commentary, and revision of writing – Suparno O; Supervision of students and oversight of study, preparation, and creation of the published work by those from the original research group, specifically critical review, commentary, and revision of writing – Indrasti NS; Design and development of methodology; supervision of student and oversight of the study, creation of models, preparation, and creation of the published work by those from the original research group, specifically critical review, commentary, and revision of writing – Hoerudin H.

### *Conflicts of Interest*

The researcher states that there is no conflict of interest with any party in the content of the articles written.

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