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The use of protein binder from shaving waste for leather finishing: Judging from the physical, chemical, and morphological properties of lizard skin leather

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Abstract. Shaving waste is the tanned hides/skins shavings produced by the leather tanning industry. The waste is very polluting the environment because it contains chromium, difficult to degrade, large in volume and light in weight. Therefore it is difficult to handle for the leather tanning industry. The purpose of this study was to deal with the problem of shaving waste which was very polluting the environment and to evaluate the effect of the application of protein binders made from the shaving waste on physical, chemical, and morphological properties of the lizard skin leather. The shaving waste was hydrolysed using NaOH and separated by filtering the results of the hydrolysis. Filter results were tested as protein binder and used for lizard skin leather finishing. The lizard skin leather was then finished with a variation of the protein binder 1:1, 1:3, and 1:5. Then, the leather was tested physically, chemically, and morphologically. The results of the organoleptic test showed that all variations were almost the same and met the requirement of Indonesian Standard on the quality of chrome-tanned snake finished leather (SNI 06-4586-1998). For the physical properties, all parameters met the requirement of SNI, except for elongation. Chemical tests results showed that all of the parameters met the requirement. Morphologically, it showed that the greater the ratio between the protein binder and water, the smoother the morphology of the surface.

1. Introduction

Shavings waste are tanned hides/skins shavings which are solid leather tanning industries containing chrome. This solid waste is very large and light in volume, which is about 99-100 kg per ton of processed skin. However, this shaving waste contains a lot of protein that can still be used. Shaving waste is a collection of very fine collagen protein fibres with properties that are not easily damaged by chemical, physical, or microorganism treatment [1].

Collagen is a material that has the strength of a range and structure in the form of fibres. One substance derived from collagen is gelatine. If collagen was boiled, the structure becomes permanently damaged and produces gelatine [2]. The protein is an important bone constituent where fibres are arranged to form a certain angle so that it can withstand tearing from various departments. About the dry weight of cartilage is collagen, so cartilage becomes strong. One substance derived by collagen is gelatine. Shaving waste hydrolysis is one way to destroy shaving waste which would then be separated between chromium contained in shaving waste and collagen protein which can be used for protein

binders in skin finishing. Various methods/isolation of collagen protein from shaving waste include thermo-hydrolysis method. Acid hydrolysis, alkaline hydrolysis, and enzymatic hydrolysis. According to Catalina *et al*. [3] the assylamide bonds of collagen tissue are easily hydrolysed by alkali at high temperature and alkalis would be neutralized by the new carboxyl collagen produced by collagen acylamide damage, so that alkalis would be released during hydrolysis. Alkaline hydrolysis of collagen tissue is much easier and more perfect than pyrolysis caused by alkaline catalysts, and at the same time the molecular weight of isolated collagen protein is much smaller than the protein produced by pyrolysis caused by alkali hydrolysis [4].

The collagen component is hydrolysed from the skin waste by alkali would dissolve in aqueous solution, but the chrome salt in the skin waste would still not dissolve in alkaline conditions, so the separation of collagen protein and chrome salt was needed [5]. Collagen is a material that has the strength of a range and structure in the form of fibres. This type of protein is widely found in high-level vertebrates. Nearly a third of the protein in vertebrate bodies is collagen. The larger the animal, the greater the total protein portion which is the main fibre component in the bones, teeth, cartilage, inner layer of skin (dermis), tendons (tendon) and cartilage. One substance derived from collagen is gelatine. If collagen was boiled, the structure becomes permanently damaged and produces gelatine. Due to the presence of a large number of hydrophilic side chains (like water) in gelatine, in water solution forms an irregular network [2]. This collagen is included as collagen binding network consisting of fibre, this structure is then composed of collagen fibrils, which look like transverse lines. According to Catalina, *et al*. [3], acylamide bonds from collagen tissue are easily hydrolysed by alkali at high temperatures, and alkalis would be neutralized by the new carboxyl collagen resulting from collagen acylamide damage, so that alkalis would be released during hydrolysis. Alkaline hydrolysis of collagen tissue is much easier and more perfect than pyrolysis caused by alkaline catalysts, and at the same time the molecular weight of isolated collagen protein is much smaller than the protein produced by pyrolysis caused by alkali [4]. The results of alkaline protein hydrolysis of the collagen depend on the type and amount of alkali, temperature and hydrolysis time. Chromium content, ash content and molecular weight also depend on the type and amount of alkali, temperature and hydrolysis time [5].

Chromium content in collagen protein depends on the pH of the alkaline solution. Finishing is the final stage of skin tanning which aims to enhance the beauty of the skin, protect the skin from physical activity, and cover skin defects. In the finishing process the skin is given three outer layers, namely a layer of base coat, medium coat, and top coat. The chemicals used in the finishing process consist of fillers, adhesives, gloss, softeners, and dyes. The adhesive material or commonly called the binder is the most widely used material in the finishing process, because it is used when making all finishing layers. Binder is one of the adhesive and glossy materials used for finishing. The number of types of binders needed is the material used to make the binder must also be multiplied by references. Binder material that can be used is essentially material that can be bonded. Substances that can be attached to are protein types of casein and albumin [6]. Usually tanners use a patent binder whose quality is already known. But along with the increasing needs of life and soaring prices of chemicals, tanners began to try natural binders with almost the same quality, or even better. Binders are made from ingredients that contain proteins such as milk, eggs, skin and others. The purpose of this study was to deal with the problem of shaving waste which was very polluting the environment and to evaluate the effect of the application of protein binders made from the shaving waste on physical, chemical, and morphological properties of the lizard skin leather.

2. Materials and Methods

2.1. Materials

The material used in this study was lizard skins, while the chemicals used were chrome-tanned leather shaving waste, NaOH, H_2SO_4, and formalin. The chemicals for leather finishing were binder, lack, thinner, pigment, LD, urethane, acrylic, cationic, pH paper.

2.2. Equipment

The equipment used in this study were machines for tanning and leather finishing, such as rotating tanning drum, spray gun, air-pressure compressor, as well as buckets and wooden stirrer. Equipment for physical testing of tensile strength, elongation, and tear-strength used Zwick / Roell 2020, thickness gauge. Softness Tester (ST 300, England), an instrument for degree of tannage testing, and a Scanning Electron Microscope.

2.3. Method

shavings wastes 200 grams in weigh were put in 100 ml NaOH with the concentration of 3%, then put in a waterbath with a temperature of 80-90°C and stirred for 3 hours. Then, the filtering used sheet filter paper until the filtrates were drained. Filter results were collagen proteins which were then neutralized and preserved with 5 drops of formalin then it concentrated and could be used for protein binders. Protein binder was then applied onto the leather for finishing with variations of 1:1; 1:3, and 1:5 (binder viscosity 12.8 cp). The leathers were then tested according to the Indonesian Standard for chrome-tanned freshwater snake finished leather. In addition, morphology of the selected leather sample was evaluated with Scanning Electron Microscope (SEM).

3. Results and Discussion

3.1. Properties of the lizard skin finished leather

Shavings waste that would be processed for protein binder were taken from one of the companies in Yogyakarta. The shavings waste before hydrolysis was first examined for water content, chrome content, and protein content. The evaluation of the shaving waste showed that the water content of shaving waste was 41.67%, while the protein content was 58.49%. Chrome content in shaving waste was 25,518.52 ppm. It indicates that the protein content of shaving waste was still high as well as the chrome content, thus both could be processed further to separate between chromium and collagen protein. According to Jiang *et al*. [5], the collagen component was hydrolysed from leather waste by alkali would dissolve in water, but the chrome salt in the leather waste would not dissolve in alkaline conditions, so the separation of collagen protein and chrome salt was needed.

Table 1. The organoleptic results of lizard skin leather

Test parameters	Code	Test results
Scales/colors	B_0	Pretty good
	B_1	Pretty good
	B_2	Pretty good
	B_3	Pretty good
Skin Conditions/Nerf Release	B_0	Contains, tough and quite limp
	B_1	Contains, tough and quite limp
	B_2	Contains, tough and quite limp
	B_3	Contains, tough and quite limp
Meat section/Elasticity	B_0	Clean
	B_1	Clean
	B_2	Clean
	B_3	Clean
Skin Shape	B_0	Symmetrical
	B_1	Symmetrical
	B_2	Symmetrical
	B_3	Symmetrical

Remarks:
B_0 = Lizard skin leather finished with 1:3 common protein binder
B_1 = Lizard skin leather finished with 1:1 research protein binder
B_2 = Lizard skin leather finished with 1:3 research protein binder
B_3 = Lizard skin leather finished with 1:5 research protein binder

The used of protein binder obtained from a hydrolysis with 3% NaOH proposed properties that suitable for the application of leather finishing. Visually, the leathers finished with variations of the protein binder had similar organoleptic properties with those finished with common protein binder used in the tanneries. Table 1 exposes the organoleptic properties of the lizard skin leather after the application of the protein binder. Based on the organoleptic test results, the lizard skin leather finished with all variations of the protein binder could met the requirements in Indonesian Standard of SNI 06-4586-199, and the it was seen that the protein binder obtained from the shaving waste has similar organoleptic properties with common protein binder purchased in the market.

The testing of physical parameters of the lizard skin finished leather with protein binder from shavings waste reveals several properties that could be used to evaluate the quality of the leather (Table 2). It could be seen that most of physical properties of the finished leather comply the Indonesian standard of chrome-tanned freshwater snake finished leather. However, the elongation value of the leather finished with shavings waste derived protein binder with a ratio of 1:1 reached 43%, while the standard requires a maximum of 30%.

Table 2. The physical properties of the lizard skin finished leather.

Test Parameters	**Code**	**Test Result**	SNI 06-4586-1998
Thickness, mm	B_0	0.48	
	B_1	0.60	Min 0.2 (flat)
	B_2	0.52	
	B_3	0.70	
Scratch resistant paint cover			
Dry	B_0	Not fade (4/5)	Not fade (4/5)
	B_1	Not fade (4/5)	
	B_2	Not fade (4/5)	
	B_3	Not fade (4/5)	
Wet	B_0	A little faded (4)	A little faded (3/4)
	B_1	A little faded (3/4)	
	B_2	A little faded (3/4)	
	B_3	A little faded 3/4)	
Tensile strength, N/cm^2	B_0	1738.78	
	B_1	2213.3604	Min 1000
	B_2	1776.24	
	B_3	2007.49	
Elongation,%	B_0	29.71	
	B_1	43.00	Max 30
	B_2	27.20	
	B_3	4.89	
Tear strength, N/cm	B_0	190.55	
	B_1	262.63	Min 150
	B_2	222.23	
	B_3	262.82	

Remarks:
B_0 = Lizard skin leather finished with 1:3 common protein binder
B_1 = Lizard skin leather finished with 1:1 research protein binder
B_2 = Lizard skin leather finished with 1:3 research protein binder
B_3 = Lizard skin leather finished with 1:5 research protein binder

Furthermore, it was necessary to conduct a chemical properties evaluation on the lizard skin leather which was finished with the protein binder derived from the waste, compared to its with common

protein binder. Data of chemical test results as in Table 3 shows that the water content and pH meet the standard, while the ash content did not meet the requirements. This was likely because the washing time was less clean. Fat content of the finished leather in treatment B_3 did not meet the requirements because it was slightly above the specified standard (6.30) while the specified standard was 2.0-6.0.

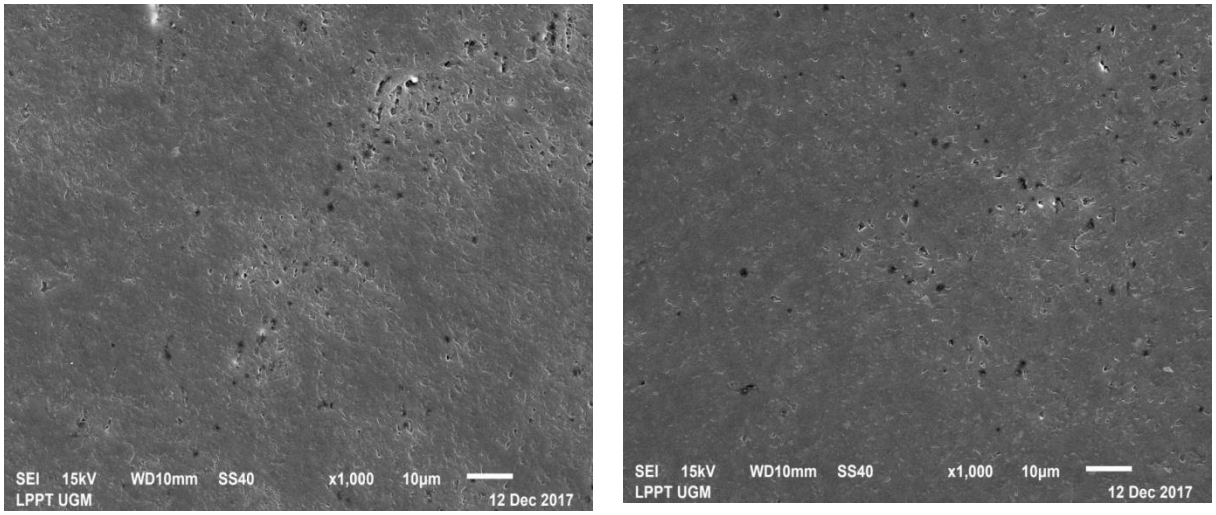
Table 3. The chemical properties of the lizard skin finished leather.

Test Parameters	Code	**Test Result**	SNI. 06-4586-1998
Vaporizing substances, %	B_0	13.48	Max 18
	B_1	12.43	
	B_2	13.92	
	B_3	11,90	
Ash Content, %	B_0	3.10	Max 2.0
	B_1	4.12	
	B_2	4.02	
	B_3	4.16	
Fat/Oil content, %	B_0	2.77	2.0 – 6.0
	B_1	3.95	
	B_2	3.14	
	B_3	6.30	
pH	B_0	4.64	3.5 - 7
	B_1	4.73	
	B_2	4.72	
	B_3	4.89	

Remarks:
B_0 = Lizard skin leather finished with 1:3 common protein binder
B_1 = Lizard skin leather finished with 1:1 research protein binder
B_2 = Lizard skin leather finished with 1:3 research protein binder
B_3 = Lizard skin leather finished with 1:5 research protein binder

3.2. SEM result of lizard skin

SEM test results from lizard skin finished leather could be associated with the results of physical tests. The lizard skin leather finished with a protein binder with a ratio of 1:1 and at 1000 magnification provides an image which indicates the binder was well blended and blends with the skin. The dry paint resistance was 4/5, which was the limit number, not fade for dry rub paint resistance. While for the wet paint resistance was 3/4 where the number was also the limit number did not fade from the rubbing resistance of the wet lid paint. The following was a SEM image of lizard skin with the use of protein binders for skin finishing was 1:1.



B1 B3

Figure 1. SEM image of 1000x magnification lizard skin finished leather

From SEM images of lizard skin leather (Figure 1) with a 1:3 ratio of protein binder, it looks smoother and evenly distributed and when linked to the results of physical tests, everything was the same as SEM images with the use of 1:1 protein binder for dry paint was 4/5 while for the wet paint resistance was 3/4. Of the three SEM images, the most subtle skin morphology was the one that uses research binders with various variations, but the morphology was almost the same.

4. Conclusions

Shavings waste could be used for protein binders. Protein binders which applied for skin finishing has results organoleptic, physical and chemical tests on skin that meet the requirements of the Indonesian standard. From the results of the skin morphology test at 1000 magnification, it appears that the skin was very evenly distributed with different variations of the protein binder.

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References

[1] Sutyasmi S 2012 Daur ulang limbah shaving industri penyamakan kulit untuk kertas seni *Maj. Kulit, Karet dan Plast.* **28** 113–21 (in Indonesian)
[2] Katili A S 2009 Struktur dan fungsi protein kolagen *J. Pelangi Ilmu* **2** 19–29 (in Indonesian)
[3] Catalina M, Attenburrow G, Cot J, Covington A D and Antunes A P M 2006 Isolation and characterization of gelatin obtained from chrome-tanned shavings *II IULTCS Eurocongress: Innovation and New Technologies for the Future of Global Leather Industry* (Istanbul: IULTCS)
[4] Pati A, Chaudhary R and Subramani S 2014 A review on management of chrome-tanned leather shavings: A holistic paradigm to combat the environmental issues *Environ. Sci. Pollut. Res.* **21** 11266–82
[5] Jiang H, Liu J and Han W 2016 The status and developments of leather solid waste treatment: A mini-review *Waste Manag. Res.* **34** 399–408
[6] Sharphouse J H 1971 *Leather Technician's Handbook* (London: Leather Producers' Association)