PHYSICAL CHARACTERISTICS OF PRESERVED AND TANNED PUFFER FISH (*Arothon reticularis*) SKIN

RLM. Satrio Ari Wibowo[1], Rofiatun Nafiah[1]* and Ambar Pertiwiningrum[2)]

[1]Academy of Leather Technology, Yogyakarta
[2]Gadjah Mada University, Yogyakarta

*Corresponding author: alexius_wibowo@yahoo.com

Abstract

In Indonesia, the leather tanning industries have already used big number of raw materials from land animal skins and hides like goats, sheep, cows, buffaloes and reptiles; while they use only a little number of raw materials from fish skin. The use of fish skin as alternative raw material is due to the limited supply of land animal skins and hides. Leather tanning mechanism is basically to put certain substances into the skin fibers. The purpose of this study is to look at the histological structure of puffer fish skins, from the raw and preserved skins until the tanned leather; and then to look at the physical strength, including tensile strength, elongation, tear strength, and sewing strength. This study uses 21 pieces of puffer fish skins consisting of raw and preserved skins, including salted, pickled and formalin. The experiment was done towards vegetable tanned leather, wet blue and formalin tanned leather; each with three-time repetition. To analyze the data, this research uses ANOVA and if there is a difference, the data will be further analyzed using Post Hoc Test. Based on the research result, there is no difference of the skin groups in tear strength. From histological structure, there is no difference between raw and preserved skins, but there is difference in tanning results. Nevertheless, pufferfish skin can still be used as alternative raw material for tanning. From physical tests, including tensile strength, elongation, tear strength and sewing strength, pufferfish skin can be used as raw material for leather products.

Keywords: *Histological Structure, Leather Tanning, Physical Characteristics, Puffer Fish Skin, Skin Preservation*

Introduction

Tanning is not a new thing in Indonesia, especially the use of skin for tanning from various land animals, such as buffalo, cows, goats and sheep. The products resulting from this industry include shoes, bags, jackets and so on. Leather tanning industry is now experiencing production constraints due to the shortage of raw materials from cattle. As alternative, fish skin can be used as raw material for tannery. Fish leather is very potential to be developed but its utilization is very low. Fish skin for tanning business does not only add the value to the waste of skin but it can also become an alternative raw material in leather product industry in Indonesia. So far, waste of fish skin is not used optimally and left only as waste. In fact, fish skin has great potential to be developed in the leather industry. The use of fish skin leather products as raw material also aims to reduce the hunting of wild animals included in the conservation. One example fish skin as waste is the skin of pufferfish.

Puffer fish comes from the family of Diodontidae and is derived from the order of Tetraodontiformes. Tetraodontiformes name is derived from fish tooth morphology, where fish has two large teeth in the upper and bottom jaws, and the teeth are quite sharp [1]. In one side, industrial development in tannery faces limited raw materials but on the other hand, it is also always looking for an alternative and uniqueness or distinctiveness of raw materials; one of which is the skin of the pufferfish. An interesting thing about puffer fish is that it has a round body shape and its skin is thorny. The fish can inflate its body when it faces stress and interference from outside. Besides, the body of pufferfish has black spotted pattern and its body surface is covered with small scales. According to Covington [2] tanning can be defined as an organic material on the skin which is perishable and it can become resistant material against bacterial activities. Tanning will directly change the properties of the skin, especially his performance, grip and smells. Through tanning, leather is expected to have better resistance towards heat, compared to rawhide. The tests to leather quality might include shrinkage temperature and boiling tests. Therefore, the aim of this study is to determine the physical quality of the pufferfish skin; including tensile strength, elongation, tear strength and sewing strength of pufferfish leather, and also to compare the raw skin, preserved skin and tanned leather.

Material and method

The materials used in the study were 21 pieces of puffer fish skin taken from Rembang. In making the histological preparations, fish skin tissues that would be observed were preserved with formalin, then they were sliced thin (thickness of a few microns), affixed to glass objects, coloured and then covered with a cover glass. Samples that have been processed were more easily observed and would not be damaged in many years, making it easier to learn further [3].

Three types of skin preservations were done using salt, acid and formalin. Whereas the tanning processes done were, wet blue with chrome, vegetable tanning with mimosa, and tanning with formalin. This research repeated each experiment three times. This research used ANOVA to analyze the data, and if there was a difference, then it would be further tested using Post Hoc.

Tests for tensile strength and elongation were done based on SNI 06-1795 -1990 [10]; sewing strength based on SNI 06-1117-1989 [4] and tear strength based on SNI 06-1794-1990 [11].

Results and discussion

The 4th International Symposium for Sustainable Humanosphere (ISSH)
A Forum of Humanosphere Science School (HSS)
Bandung, 22 – 23 December 2014

Tanning goal is to transform raw skin easily damaged by the microorganisms, physical and chemical activities into the skin more resistant to these effects. The principle of tanning is the inclusion of certain material (tanning substances) in the skin fiber and causes a chemical bond between tanning substances and skin fiber.

The results of tensile strength, elongation, tear strength, and sewing strength tests can be seen in the following table:

Table 1. Raw Skin - Skin Preservation - Tanning

	Tensile Strength (Kg/cm2)	Elongation (%)	Tear Strength (Kg/cm)	Sewing Strength (Kg/cm)
Raw Fish	146,38	114,15	43,55	110,71
Skin Preservation	133,16	98,57	44,24	124,73
Tanning	103,30	72,32	37,95	79,98

The results of the four tests above, if put into diagram as seen in **Figure 1** below, show that the results of the tests were higher because there was no chemical substance put into the skin. Whereas, the decrease of the four tests results were caused by the chemical substance, in which there was already chemical reaction between skin collagen and the chemical substance so that the strength of the tanned leather became lower compared to raw and preserved skin.

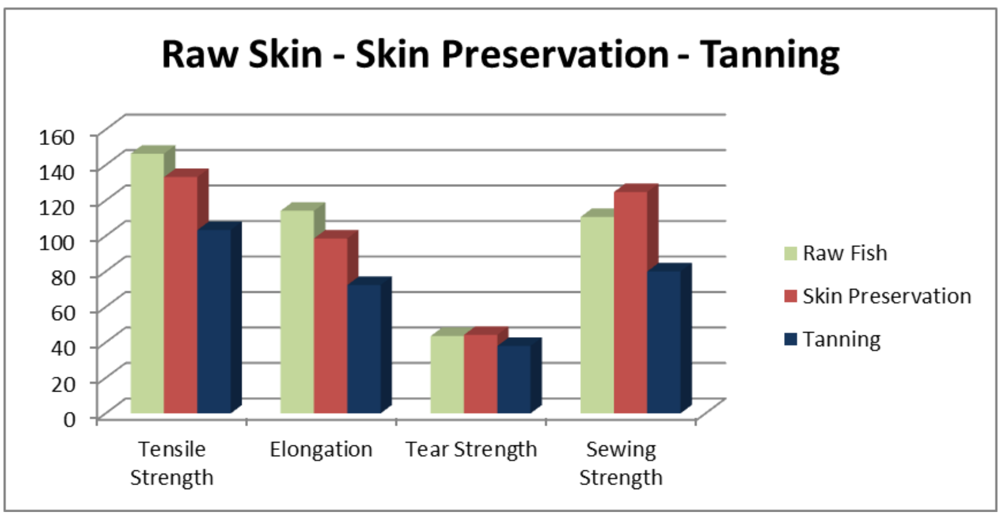


Figure 1. Physical testing results of raw skin, preserved skin and tanned leather

Figure 1 shows that the physical treatment of skin tanning produces lower yields than rawhide and skin preservation. These occur in tensile strength, elongation, tear strength and sewing strength.

One important factor influencing the physical character of tanned leather is the raw skin structure. Tensile strength is one element that needs to consider in assessing leather quality. It is alleged that the effect of tanning substances put into the skin is very influential on the physical strength of skin. Judoamidjojo [5] states that the tanning substances, which are more perfectly bound to collagen skin, make the leather more stable and limp but it has a lower physical strength due to the shortening of the fibers of collagen; compared to the raw skin.

During the tanning process, there are some steps to go through. First step is the reaction between hydroxyl groups in vegetable tannin and collagen structure. Second is the bound reaction from tanning and other substance molecules until all empty spaces in the collagen chains are filled completely during tanning processes, with osmotic swelling of fibril structure due to acid surrounding. Tanning results can be perfect if collagen can absorb a half of the tanning substances used.

Seen from the physical test, the preserved and raw skins are not so different because of the lack of tanning substances that go into the collagen fibers of the skin; although in preservation, acid and formalin have been added. But, it is not so influential to physical quality of the skin. Actually, fresh fish skin can be directly tanned; but based on economic considerations, it is rarely done. Skin needs to be preserved so that it can be saved and brought into the tannery. Basically, treatment to fresh raw skin; either physically, mechanically or chemically; aims to maintain both structure and chemical composition. Preservation principle is the reduction of the water content of fresh skin so that the skin moisture content is less than the minimum threshold required for microbial growth and development.

Table 2. Test Results (Raw Skin – Skin Preservation- Tanning)

Descriptives

		N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
						Lower Bound	Upper Bound		
Tensile Strength	Raw Skin	3	180.8033	12.68264	7.32233	149.2979	212.3088	166.43	190.42
	Skin Preservation	3	133.1600	12.84342	7.41515	101.2552	165.0648	118.69	143.22
	Tanning	3	103.3033	6.62740	3.82633	86.8400	119.7667	98.58	110.88
	Total	9	139.0889	35.19057	11.73019	112.0390	166.1388	98.58	190.42
Elongation	Raw Skin	3	88.9400	5.54704	3.20258	75.1604	102.7196	82.78	93.54
	Skin Preservation	3	98.5700	13.72348	7.92326	64.4790	132.6610	90.26	114.41
	Tanning	3	72.3156	1.27719	.73738	69.1429	75.4883	71.14	73.68
	Total	9	86.6085	13.69249	4.56416	76.0835	97.1335	71.14	114.41
Tear Strength	Raw Skin	3	48.2933	12.24355	7.06882	17.8787	78.7080	40.43	62.40
	Skin Preservation	3	44.2422	1.49452	.86286	40.5296	47.9548	43.17	45.95
	Tanning	3	37.9522	.50673	.29256	36.6934	39.2110	37.45	38.46
	Total	9	43.4959	7.64611	2.54870	37.6186	49.3732	37.45	62.40
Sewing Strength	Raw Skin	3	172.8733	22.23725	12.83868	117.6329	228.1137	152.07	196.31
	Skin Preservation	3	124.7311	10.83972	6.25832	97.8037	151.6585	116.46	137.00
	Tanning	3	79.9822	1.59140	.91879	76.0290	83.9355	78.88	81.81
	Total	9	125.8622	42.09803	14.03268	93.5028	158.2216	78.88	196.31

Table 3. Results of ANOVA

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
Tensile Strength	Between Groups	9167.558	2	4583.779	37.193	.000
	Within Groups	739.450	6	123.242		
	Total	9907.008	8			
Elongation	Between Groups	1058.405	2	529.202	7.192	.025
	Within Groups	441.469	6	73.578		
	Total	1499.874	8			
Tear Strength	Between Groups	162.914	2	81.457	1.604	.277
	Within Groups	304.790	6	50.798		
	Total	467.704	8			
Sewing Strength	Between Groups	12948.895	2	6474.448	31.607	.001
	Within Groups	1229.055	6	204.842		
	Total	14177.950	8			

Results of comparison between tensile strength, elongation, tear strength, and sewing strength (raw skin, preserved skin and leather) give significant values of 0.000; 0.025; 0.277; and 0.001. It means that there is a difference in tensile strength, elongation, and sewing strength. Whereas the tear strength with the significant value of 0.277 > 0.05 shows that there is no difference in tear strength between the skin groups. The difference in tensile strength, elongation, and sewing strength in detail can be seen in Post Hoc out put. Tear strength is the maximum strength needed to tear the object and it is stated in Newton/cm of the skin thickness. According to SNI 06-6121-1999, the minimum tear strength in stingray skin is 300 N/cm. There is no real difference in the significance of 95 %, showing that adding the mimosa does not give significant influence towards the tear strength.

In leather industry, chrome leather has good position in the market, especially for shoe upper, gloves, jacket, etc. The bound between chrome and protein, which is called cross link and formed during the tanning process, will change the skin character into more resistant to physical and chemical influences. As vegetable tannin, chrome tanning substances also have certain characteristics related to the size of molecules. Chrome tanning results in leather which is soft and smooth, more resistant to heat, higher tensile strength, and better results after dyeing. Therefore, chrome leather is more suitable for shoe upper.

An important factor influences the physical characters of tanned leather is the raw skin structure. The tensile strength is one factor that needs to consider in assessing the quality of leather.

Tabel 4. Results of Post Hoc

Multiple Comparisons

LSD

Dependent Variable	(I) kel_6	(J) kel_6	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
Tensile Strength	Raw Skin	Skin Preservation	47.64333*	9.06428	.002	25.4638	69.8228
		Tanning	77.50000*	9.06428	.000	55.3205	99.6795
	Skin Preservation	Raw Skin	-47.64333*	9.06428	.002	-69.8228	-25.4638
		Tanning	29.85667*	9.06428	.017	7.6772	52.0362
	Tanning	Raw Skin	-77.50000*	9.06428	.000	-99.6795	-55.3205
		Skin Preservation	-29.85667*	9.06428	.017	-52.0362	-7.6772
Elongation	Raw Skin	Skin Preservation	-9.63000	7.00372	.218	-26.7675	7.5075
		Tanning	16.62444	7.00372	.055	-.5131	33.7619
	Skin Preservation	Raw Skin	9.63000	7.00372	.218	-7.5075	26.7675
		Tanning	26.25444*	7.00372	.010	9.1169	43.3919
	Tanning	Raw Skin	-16.62444	7.00372	.055	-33.7619	.5131
		Skin Preservation	-26.25444*	7.00372	.010	-43.3919	-9.1169
Tear Strength	Raw Skin	Skin Preservation	4.05111	5.81941	.512	-10.1885	18.2907
		Tanning	10.34111	5.81941	.126	-3.8985	24.5807
	Skin Preservation	Raw Skin	-4.05111	5.81941	.512	-18.2907	10.1885
		Tanning	6.29000	5.81941	.321	-7.9496	20.5296
	Tanning	Raw Skin	-10.34111	5.81941	.126	-24.5807	3.8985
		Skin Preservation	-6.29000	5.81941	.321	-20.5296	7.9496
Sewing Strength	Raw Skin	Skin Preservation	48.14222*	11.68596	.006	19.5477	76.7367
		Tanning	92.89111*	11.68596	.000	64.2966	121.4856
	Skin Preservation	Raw Skin	-48.14222*	11.68596	.006	-76.7367	-19.5477
		Tanning	44.74889*	11.68596	.009	16.1544	73.3434
	Tanning	Raw Skin	-92.89111*	11.68596	.000	-121.4856	-64.2966
		Skin Preservation	-44.74889*	11.68596	.009	-73.3434	-16.1544

*. The mean difference is significant at the .05 level.

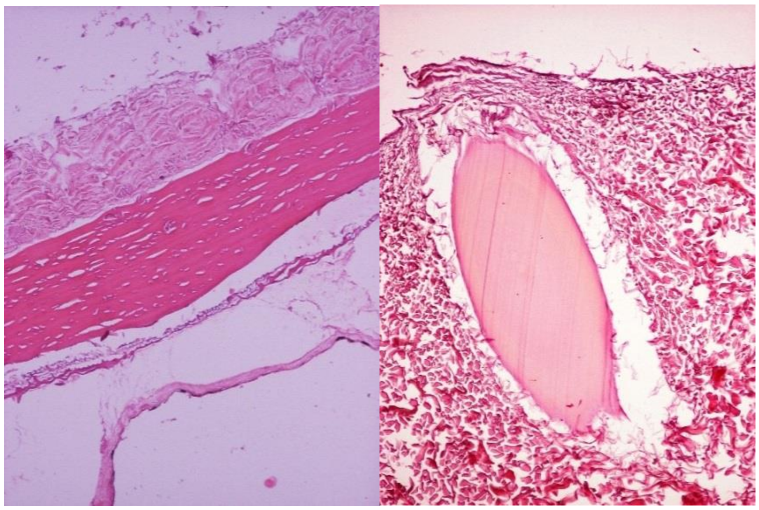
Value of 0.002 < 0.05, meaning that there is a difference in tensile strength of both. Comparison results between raw akin and leather give significant value of 0.000 < 0.05, showing that there is a difference of both. Moreover, comparison results between preserved skin and leather give significant value of 0.017 < 0.05, meaning that there is also difference in both. The data in elongation prove also similar results; in which they give significant value of 0.010 < 0.05, showing that there is a difference in both.

In sewing strength, the comparison results between raw and preserved skins give significant value of 0.006 < 0.05, between raw skin and leather 0.000 < 0.05, and between preserved skin and leather 0,009 < 0,05; meaning that there is also a difference in sewing strength of the groups.

According to Sharphouse [8], too much mimosa will cause the accumulation of mimosa in the skin which can reduce the strength of the skin, since the skin becomes brittle. The low elongation obtained with mimosa tannin is as a result of the mimosa tannin that change a single fiber into a compact structure of the skin. The empty skin structure due to protein loss will be filled by a hydroxyl group of tanning substance, where hydroxyl is bound to the NH3 group and COO of collagen structure. Mann [6] adds that the astringent tannins will make the inner part of skin not well tanned since the pore is covered by quick surface shrinkage. This condition will cause a state of "case hardening" (dryness of the surface) which causes stiffness of the skin. Mimosa is a source of tannin with high astringent character.

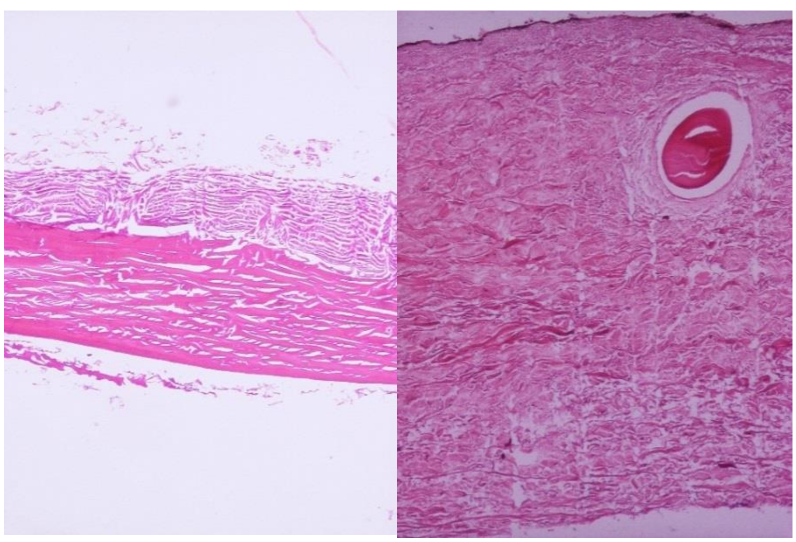
The amount of cross-linkage formed will determine the shrinkage temperature of aldehyde-tanned leather. The more oxymethylene bridge, the higher shinkage temperature will be. The increase of shrinkage temperature is very significant to the amount of aldehyde-bound, while the aldehyde bound depends on the pH liquid of tannin [4].

Hysthological Structure of Pufferfish Skin



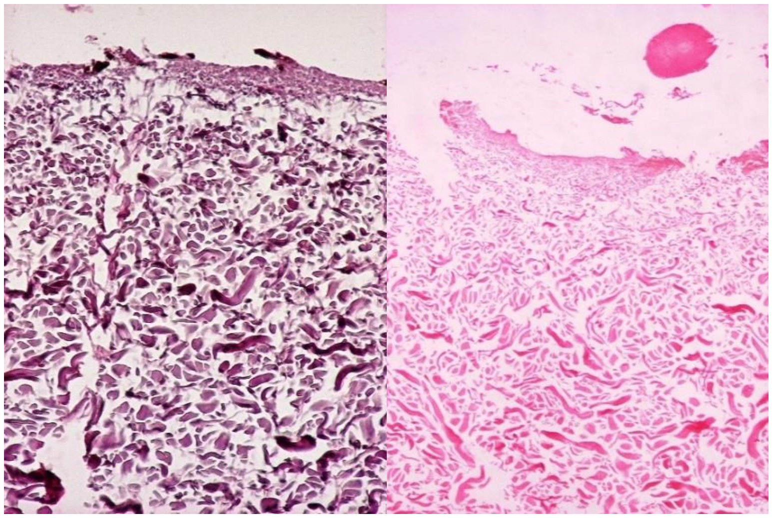
(a) **(b)**

Figure 2. Microstructure of Pufferfish (a) Longitudinal section of epidermis, and dermis; magnification 40 x, Colouration: HE (b) Thorn seen in surface between epidermis and dermis magnification 400 x colouration HE



(a) **(b)**

Figure 3. Microstructure of preserved pufferfish skin (a) Longitudinal section of pufferfish skin with epidermis, and dermis magnification 40 x colouration HE (b) thorn seen magnification 100 x colouration HE



(a) **(b)**

Figure 4. Microstructure of tanned leather (a) longitudinal section with collagen magnification 100 x colouration HE ; (b) loose thorn in the surface, magnification 100 x colouration HE

Long et al [5] suggest that naturally, the structure of fish skin dermis can make its tensile strength is quite high due to the parallel trans structure. The dermis is composed and organized as parallel fiber layers which tend to form an angle (helically oriented) in the opposite direction.

Figure 2 shows that the composition of puffer fish skin structure is still complete, compared to tanned pufferfish leather. The incomplete structure of tanned leather is caused by the loss of protein, except collagen, and then replaced by tanning substances during tanning processes. Figure 3 shows that seen through cross section of skin histology, the structure of preserved skin is still complete, but less compact compared to raw skin, due to the water loss as an effect of acid put into the skin.

Conclusion

From the discussion above, it can be concluded that there is a difference between raw skin, preserved skin and tanned leather in tensile strength, elongation and sewing strength. Based on the research result, there is no difference of the skin groups in tear strength. From histological structure, there is no difference between raw and preserved skins, but there is difference in tanning results. Nevertheless, pufferfish skin can still be used as alternative raw material for tanning. From physical tests, including tensile strength, elongation, tear strength and sewing strength, pufferfish skin can be used as raw material for leather products. Thus, it should be tested with different types of each tanning.

Bibliography

[1] BPOM Badan Pengawas Obat dan Makanan. 2006. Ikan buntal (Puffer Fish) ikan nikmat yang beracun. InfoPOM, 7(6):5-10.

[2] Covington, A.D. 2009. *Tanning Chemistry : The Science of Leather*. RSC Publishing : Northampton.

[3] Suntoro, S. H. 1983. *Metode Pewarnaan (Histologi & Histokimia)*. Bhratara Karya Aksara. Jakarta.

[4] SNI-06-1117-1989. Cara Uji Kekuatan Jahit Kulit. Dewan Standardisasi Nasional. Jakarta.

[5] Judoamidjojo RM. 1981. *Teknik Penyamakan Kulit untuk Pedesaan*. Bandung: Angkasa

[4] Purnomo, E. 2009. *Upholstery=Car Automotif Leather Seat*. Akademi Tekonologi Kulit: Yogyakarta.

[5] Long, J. H., Hale, M.E. Henry, M.J.M.C, Wesneat, M.W. 1996. Functions of Fish Skin: Flexural Stiffness And Steady Swimming Of Longnose Gar Lepisoteus Osseus. *The Journal of Experimental Biology* 199, 2139–2151, Department of Biology, Vassar College, Poughkeepsie, NY 12601 dan Department of Organismal Biology and Anatomy, University of Chicago, Chicago, IL 60637 dan 3Center for Evolutionary and Environmental Biology, Field Museum of Natural History, Chicago, IL 60605, USA.

[6] Mann. 1981. Rural Tanning Technique. Food and Agriculture Organization of The United Nations. Rome.

[7] Omar. 1987. Struktur Dasar Kulit Ikan. Fakultas Perikanan dan Ilmu Kelautan. IPB, Bogor.

[8] Sharphouse, J.H. 1971. Leather Technician's Hand Book. Leather Products Association London

[10] SNI-06-1795-1990. Cara Uji Kekuatan Tarik dan Kemuluran Kulit. Dewan Standardisasi Nasional. Jakarta.

[11] SNI-06-1794-1990. Cara Uji Kekuatan Sobek dan Kekuatan Sobek Lapisan Kulit. Dewan Standardisasi Nasional. Jakarta.

[12] SNI-06-6121-1999 Kulit Ikan Pari Untuk Barang Kulit. Dewan Standardisasi Nasional. Jakarta.

[14] Thortensen, T.C. 1976. *Practical Leather Technology*. Robert Ekreiger Publishing Company: Huntington New York.

[15] Triatmojo, Suharjono. 2012. *Teknologi Pengolahan Kulit Sapi*. PT Citra Aji Parama: Yogyakarta.