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## Utilization of Waste from Puffer Fish Skin as Alternative Raw Materials for Leather Tanning

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### Abstract

Industrial development in the field of leather is increasing lately, but this increase is less supported, especially because of the inadequacy in raw materials. Tanneries in Indonesia began to experience the scant of raw materials, especially raw materials of conventional skin. Actually, the lack of raw leather materials can be resolved by finding some alternatives, e.g. fish skins. In general, skin consists of 3 layers, i.e. the epidermis, dermis and hypodermis, though there are differences in thickness due to different habitats. Therefore, this study aims to know the histological structure and strength through some physical tests of puffer fish as an alternative material for tannery. Hopefully, the efforts to use Puffer fish skin as an alternative material can increase the economy of the community.

The research employs repetition method, with three times experiments. Materials used in these experiments are puffer fish skins, i.e. raw, salted, pickled, and formalin. Each piece was made into histological preparation, and then its tensile strength, elongation, tear strength, and sewing strength were observed. To analyze the data, this research uses ANOVA and if there is a difference, the data will be further analyzed using Post Hoc Test. The results show that, from ANOVA, there are no differences in tensile strength, elongation, and tear strength; whereas, there is a clear difference in sewing strength. From the histological structure and the result of physical tests, puffer fish skins can be used as alternative raw material for leather tanning.

*Keywords:* Histological Structure, Fish Skin, Puffer fish, Tensile Strength, Leather Tanning.

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### 1. Introduction

Manufacture of leather and leather products is one of the eminent National industries. This is reflected in the contribution of the industry towards national income which reaches \$ 6.440 billion. Although the leather industry is seen as an important industry, there are still many issues that still need to be addressed, either by the government, employers, or other stakeholders including higher education institutions. One of the problems often faced by this industry is the lack of raw materials, i.e. fresh skin. Leather raw material domestic supply can meet 70% of the requirement, and the rest is imported from abroad. Slaughtering houses in the country are only able to provide 40% of raw cow skin and 20% of raw sheep/ goat skin. The shortage of raw material plus the import rules have caused many leather craftsmen stopped their businesses and fired the employees. With the

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technology already mastered by the craftsmen, some efforts can be attempted by making diversification of raw materials and products.

Tanning is not something new in Indonesia, especially the use of tanning skins of various land animals, such as buffalos, cows, goats and sheep. The products resulted from the industries include shoes, bags, jackets and so on. Tanning industry is now experiencing production constraints due to the shortage of raw materials from farm animals. Alternatives that can be done are the utilization of fish skin as raw material in tannery. Fish leather is very potential to be developed. Nevertheless, the development is very slow. Fish skin tanning businesses not only add value to skin waste, but also become an alternative raw material in fulfilling the demand of tanning industries in Indonesia. It has been applied to the manufacture of leather-based products, such as bags, jackets, belts, wallets, shoes and sandals.

Until now, the waste of fish skin has not been used optimally and just becomes garbage. In fact, fish skin waste has big potential to develop in leather industry. The use of fish skin as raw materials for leather products also aims to reduce the hunting of wild animals listed in the conservation, and it can also be used as an alternative leather raw material.

Banana puffer fish (*Tetraodon Lunar*) whose existence is quite abundant in Indonesian seas has not been utilized optimally because the fish is considered a deadly poisonous fish. Therefore, the purpose of this study is to determine the tensile strength, elongation, tear strength, sewing strength and histological characteristics of the puffer fish skin in order to make use of it as an alternative raw material in tannery.

## 2. Material and Method

The materials used in the study were 12 pieces of puffer fish skin taken in Rembang. In making the histological preparation, fish skin tissues that will be observed are 3 pieces raw, 3 preserved with salt, 3 with acid (pickled), and the other 3 with formalin, then they are sliced thin (thickness of a few microns), affixed to glass objects, coloured and then covered with a cover glass. Samples that have been processed are more easily observed and will not be damaged in many years, making it easier to learn more (Suntoro, 1983).

The research employs repetition method, with three times experiments. In every experiment, this research observes its histological structure and does some physical tests, including tensile strength, elongation, tear strength, and sewing strength. To analyze the data, this research uses ANOVA and if there is a difference, the data will be further analyzed using Post Hoc Test. Tensile strength and elongation tests are based on SNI 06-1795 -1990; whereas, sewing strength test is based on SNI 06-1117-1989 and Tear Strength Test on SNI 06-1794-1990.

## 3. Results and Discussion

### 3.1. Histological Structure of Puffer Fish Skin

Generally, skin fish contains of 69.6% water, 26.9% protein, 2.5% ash and 0.7% fat. Quality requirements of fish skin; stingray for example, according to SNI 6-6121-1999 must be 1 mm thick, has minimum shrinkage temperature of 70°C, a minimum tensile strength of 2000 N, tear strength

of at least 300 N, the maximum water content of 20%, a maximum oil content of 12% , skin condition is strong and not wrinkle (Grace, et al, 2008). Fish skin basically has fingertip or distinctive natural markings that differ from each other.

Yato (2001) states that the connective tissue is generally collagen proteins, as found in the skin tissue system. There are at least 12 types of collagen that can be identified at a particular location. Type I collagen is the predominant collagen in animal skin, especially cows, as well as fish skin in general, although there is type V collagen content in small quantities, in which collagen type I is a three-spun fibers (alpha helix) of the polypeptide chain. In general, the cow skin collagen is same with collagen of fish skin, only the content of hydroxy proline in fish skin collagen is less than that in cow skin. Nevertheless, collagen thermal stability depends on the degree of cross-linking which is determined by the amino acids formed on the hydroxy proline; thus causing heat resistance of fish skin is lower than than vertebrata animal skins, such as cows.

The thickness of the skin is not the same in various different parts of the body. The skin thickness might be caused due to the thickness of one or two parts of the skin; for example in the area of intra thick scapular which is up to more than 0.5 cm; whereas in the eyelid only 0.5 mm thick. The average skin thickness is 1-2 mm.

The epidermis is the layer of the skin wide. The epidermis of the skin is always wet, which is caused by mucus. Mucus is produced by a gland cells inside the epidermis (Omar, 1987). In the mucus on this layer, there is a cup-shaped gland cell producing a substance (a kind of glycoprotein) called *mucin*. If these substances come into contact with water, it will turn into mucus, and make the epidermis of skin always wet. Fish which do not have scales produce more mucus than fish with scales. The function of much produced by fish itself is to reduce friction with the body of water that makes the fish can swim faster (Omar, 1987). While the dermis is the skin layer which is thicker than the outer one. The dermis contains blood vessels, nerves, and connective tissue. This layer also plays a role in the formation of fish scales on that with scales.

In the dermis of puffer fish skin appearing in the image, there is Chromatophore. Chromatophore is one of the specific cells with the function, i.e. giving the colour to the skin, such as yellow or brown. Moreover, in the epidermis there is a basin, which is formerly as the place for thorn follicles of the puffer fish skin; but in the preparations observed there is no thorn since during the microtome process, the microtome knife is not capable to cut the puffer fish thorn because of the structure of the thorn which is very hard.

Long, et al (1996) 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.

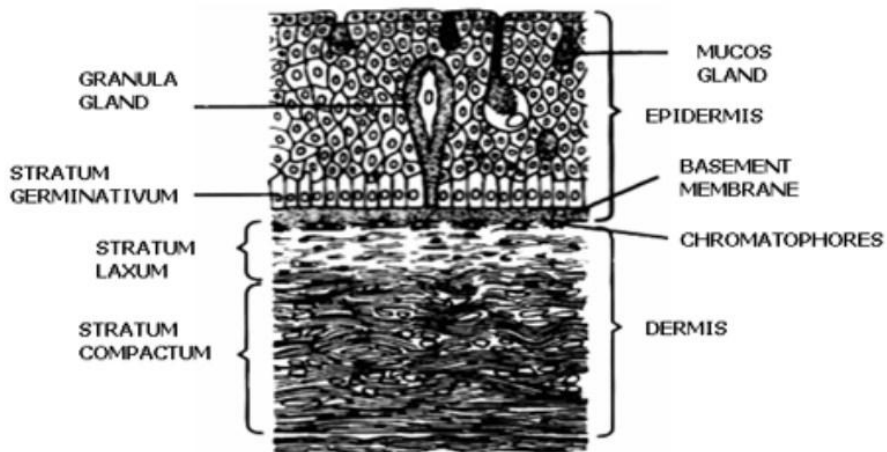


Fig 1. Longitudinal Section of Fish Skin (Junaidianto, 2009)

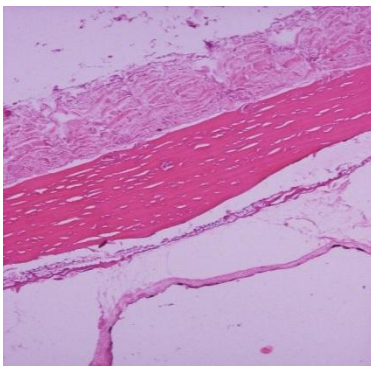


Fig 2. Microstructure of Puffer Fish Skin Thickness  
Colouration: H&E Magnification: 100x

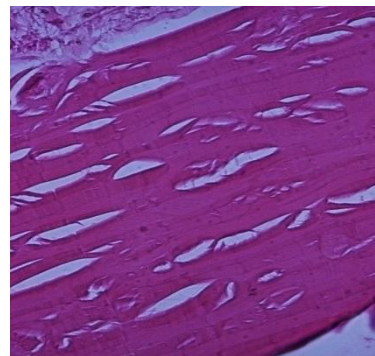


Fig 3. Microstructure of Puffer Fish Skin Dermis  
Colouration: H&E Magnification: 250 x

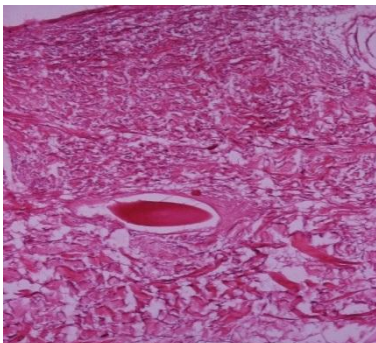


Fig 4. Microstructure of Salted Puffer Fish Skin  
Dermis Colouration: H&E Magnification: 200x

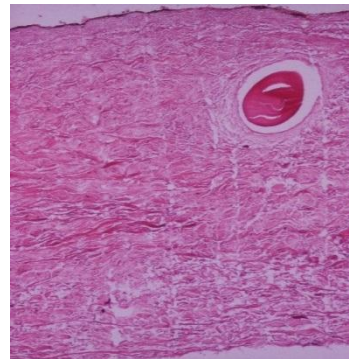


Fig 5. Microstructure of Puffer Fish Skin with thorn seen,  
Colouration: H&E Magnification: 250x

Epidermal tissues join the hypodermic tissue forming an organ of the fish skin. Fish skin along with the muscle, meat, and bones form a useful system for the movement of fish and also as protective internal organs of the fish which are soft (Darjono, et al, 2001).

Hawkes (1974) states epidermis and dermis of the fish have a complete structure with protectors. Surface of the epidermis is protected by mucus that prevents from microbes, usually patterned on the surface of keratinocytes. Set of filaments are spread throughout the keratinocytes but not to the ribosomes, endoplasmic reticulum, and the Golgi apparatus.

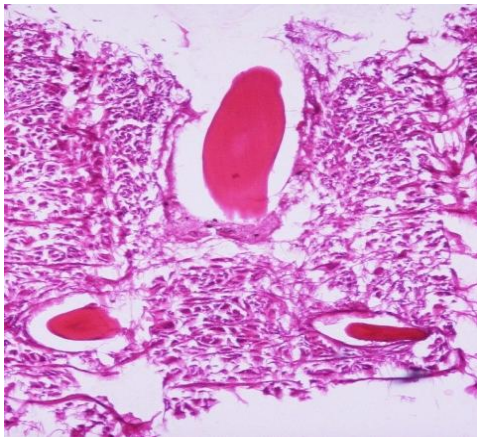


Fig 6. Microstructure of Pickled Puffer Fish Skin  
Colouration: H&E Magnification: 200x

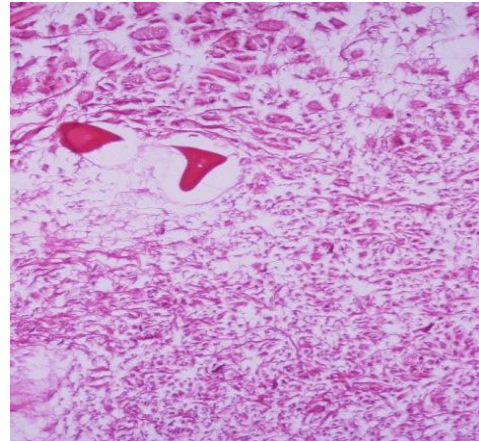


Fig 7. Microstructure of Formalin Puffer Fish Skin  
Colouration: H&E Magnification: 250x

### 3.2. Testing Results

The comparison between tensile strength, elongation, tear strength, and sewing strength of the skin groups (raw, salted, pickled, and formalin puffer fish skins) show significant values: 0.074; 0.228; 0.747 > 0.05. It means there are no differences in tensile strength, elongation, and tear strength of the skin groups. Whereas in sewing strength, it gives the significant value of 0.001 < 0.05, meaning that there are difference in the sewing strength of the skin groups.

Table 1. Testing Results of Puffer Fish Skin

		ANOVA				
		Sum of Squares	df	Mean Square	F	Sig.
Tensile Strength	Between Groups	8501.185	3	2833.728	3.395	.074
	Within Groups	6677.940	8	834.743		
	Total	15179.125	11			
Elongation	Between Groups	1521.902	3	507.301	1.782	.228
	Within Groups	2278.083	8	284.760		
	Total	3799.985	11			
Tear Strength	Between Groups	51.274	3	17.091	.415	.747
	Within Groups	329.136	8	41.142		
	Total	380.410	11			
Sewing Strength	Between Groups	13838.453	3	4612.818	16.220	.001
	Within Groups	2275.175	8	284.397		
	Total	16113.628	11			

The Difference in the sewing strength of the skin groups in detail can be seen in the following output of Post Hoc.

Table 2. Post Hoc Test

**Multiple Comparisons**

LSD

Dependent Variable	(I) Group	(J) Group	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Tensile Strength	Raw Fish	Salted Fish	34.42000	23.59015	.183	-19.9790	88.8190
		Pickle Fish	75.10000*	23.59015	.013	20.7010	129.4990
		Formalin Fish	33.41000	23.59015	.194	-20.9890	87.8090
	Salted Fish	Raw Fish	-34.42000	23.59015	.183	-88.8190	19.9790
		Pickle Fish	40.68000	23.59015	.123	-13.7190	95.0790
		Formalin Fish	-1.01000	23.59015	.967	-55.4090	53.3890
	Pickle Fish	Raw Fish	-75.10000*	23.59015	.013	-129.4990	-20.7010
		Salted Fish	-40.68000	23.59015	.123	-95.0790	13.7190
		Formalin Fish	-41.69000	23.59015	.115	-96.0890	12.7090
	Formalin Fish	Raw Fish	-33.41000	23.59015	.194	-87.8090	20.9890
		Salted Fish	1.01000	23.59015	.967	-53.3890	55.4090
		Pickle Fish	41.69000	23.59015	.115	-12.7090	96.0890
Elongation	Raw Fish	Salted Fish	-25.21333	13.77825	.105	-56.9860	6.5594
		Pickle Fish	-7.90000	13.77825	.582	-39.6727	23.8727
		Formalin Fish	4.22333	13.77825	.767	-27.5494	35.9960
	Salted Fish	Raw Fish	25.21333	13.77825	.105	-6.5594	56.9860
		Pickle Fish	17.31333	13.77825	.244	-14.4594	49.0860
		Formalin Fish	29.43667	13.77825	.065	-2.3360	61.2094
	Pickle Fish	Raw Fish	7.90000	13.77825	.582	-23.8727	39.6727
		Salted Fish	-17.31333	13.77825	.244	-49.0860	14.4594
		Formalin Fish	12.12333	13.77825	.405	-19.6494	43.8960
	Formalin Fish	Raw Fish	-4.22333	13.77825	.767	-35.9960	27.5494
		Salted Fish	-29.43667	13.77825	.065	-61.2094	2.3360
		Pickle Fish	-12.12333	13.77825	.405	-43.8960	19.6494
Tear Strength	Raw Fish	Salted Fish	4.74000	5.23718	.392	-7.3370	16.8170
		Pickle Fish	2.28000	5.23718	.675	-9.7970	14.3570
		Formalin Fish	5.13333	5.23718	.356	-6.9436	17.2103
	Salted Fish	Raw Fish	-4.74000	5.23718	.392	-16.8170	7.3370
		Pickle Fish	-2.46000	5.23718	.651	-14.5370	9.6170
		Formalin Fish	.39333	5.23718	.942	-11.6836	12.4703
	Pickle Fish	Raw Fish	-2.28000	5.23718	.675	-14.3570	9.7970
		Salted Fish	2.46000	5.23718	.651	-9.6170	14.5370
		Formalin Fish	2.85333	5.23718	.601	-9.2236	14.9303
	Formalin Fish	Raw Fish	-5.13333	5.23718	.356	-17.2103	6.9436
		Salted Fish	-.39333	5.23718	.942	-12.4703	11.6836
		Pickle Fish	-2.85333	5.23718	.601	-14.9303	9.2236
Sewing Strength	Raw Fish	Salted Fish	62.16667*	13.76946	.002	30.4142	93.9191
		Pickle Fish	5.21667	13.76946	.715	-26.5358	36.9691
		Formalin Fish	77.04333*	13.76946	.001	45.2909	108.7958
	Salted Fish	Raw Fish	-62.16667*	13.76946	.002	-93.9191	-30.4142
		Pickle Fish	-56.95000*	13.76946	.003	-88.7024	-25.1976
		Formalin Fish	14.87667	13.76946	.311	-16.8758	46.6291
	Pickle Fish	Raw Fish	-5.21667	13.76946	.715	-36.9691	26.5358
		Salted Fish	56.95000*	13.76946	.003	25.1976	88.7024
		Formalin Fish	71.82667*	13.76946	.001	40.0742	103.5791
	Formalin Fish	Raw Fish	-77.04333*	13.76946	.001	-108.7958	-45.2909
		Salted Fish	-14.87667	13.76946	.311	-46.6291	16.8758
		Pickle Fish	-71.82667*	13.76946	.001	-103.5791	-40.0742

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

The result of comparison between raw and pickled puffer fish skins gives the significant value of  $0,013 < 0,05$ , meaning that there is a difference in Tensile Strength of the two types of skins; and between raw and salted puffer fish skins gives the significant value of  $0,002 < 0,05$ , meaning that there is also a difference. Furthermore, the result of the comparison between raw and formalin puffer fish skins gives the the value of  $0,001 < 0,05$ , showing that there is a difference; and last but not least, between salted and pickled which gives the value of  $0,003 < 0,05$ , meaning there is also a difference in both types of skins. This matter is caused by the difference in preservation methods, in which the skin has various elasticities and thicknesses. It means that in order to have an optimum sewing strength, the elasticity and the thickness of skins must be fixed during the tanning process.

In tensile strength, figure 8 below shows that the four groups of the puffer fish skin observed fulfil the requirement of SNI 0250-1989- A for skin, i.e. the tensile strength must be minimum 100 kg/cm<sup>2</sup>, and all groups have no differences, so they can be alternative for leather product raw material. The tensile strength values of all skin groups meet the cosumer acceptance; i.e. puffer fish skin fulfilling the quality standard will result also on qualified, durable, robust, and comfortable-to-wear leather products. Tensile strength is maximum amount of force needed to pull the skin until it breaks; stated in N/cm<sup>2</sup>.

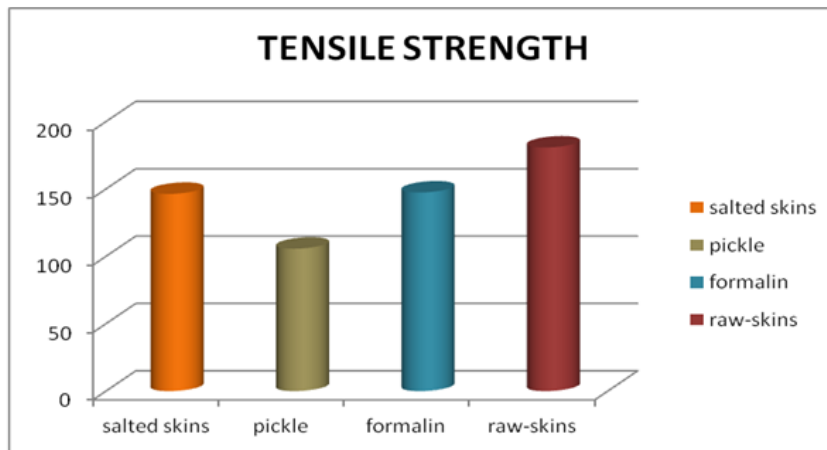


Fig 8. The Comparison on Tesnsile Strength of Raw, Salted, Pickled, and Formalin Puffer Fish Skin

Skin elongation is the amount of additional length resulted from the skin stretched until it breaks; divided by the original length. It is stated in percentage (Anonymous, 1990). In general, the flexible leather has a high tensile strength, because when it receives the maximum pull force to break, it will be more elastic and give bigger additional length (Purnomo, 1985). Results in puffer skin research show the elongation of raw skin is 88.94%; salted puffer fish skin 114.15%; pickled puffer fish skin 96.84% and formalin puffer fish skin 84.72%. Whereas, SNI 0250-1989-A states that the minimum requirement for elongation is 50%. It means that puffer fish skin well fulfill the



standard of material for leather products.

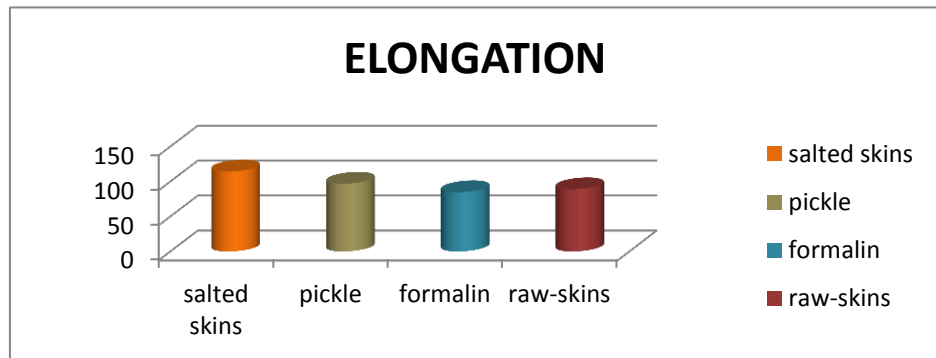


Fig 9. The Comparison on Elongation of Raw, Salted, Pickled, and Formalin Puffer Fish Skin

Results of the research in tear strength show that, in the measurement of N / cm (1 kgf = 9.8066), the raw puffer fish skin is 473.561 N / cm; salted puffer fish skin is 427.08 N / cm; pickled puffer fish skin 484.96 N / cm, and formalin puffer fish skin 423.25 N / cm. All have complied with SNI for leather goods.

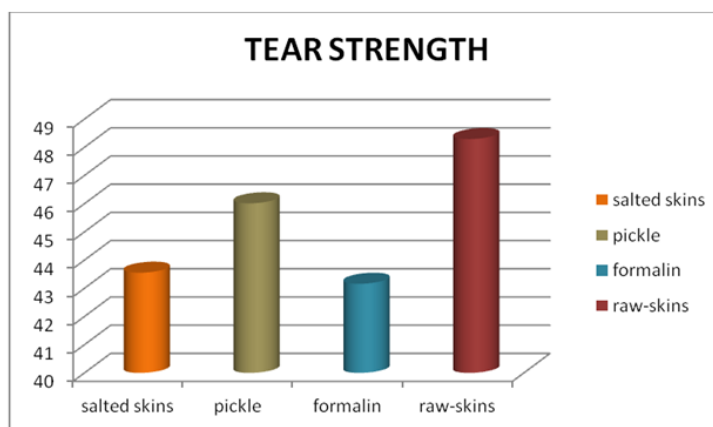


Fig 10. The Comparison on Tear Strength of Raw, Salted, Pickled, and Formalin Puffer Fish Skin

Sewing strength is equivalent to the tensile strength and tear strength. If the tensile strength and tear strength are high, the sewing strength is also high. Sewing strength is affected by the thickness of the skin, collagen protein content and density, the angle of collagen fibers connection and thickness of korium (Kanagy, 1977). Anonymous (1981) stated that the sewing strength of goat leather (glace) is a minimum of 50 kg / cm. Results of research confirms that puffer fish skin fulfill the standards of sewing strength.

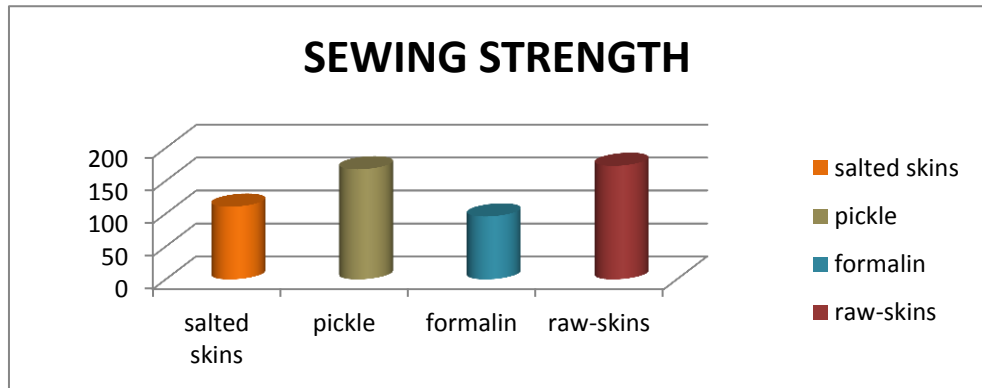


Fig 10. The Comparison on Sewing Strength of Raw, Salted, Pickled, and Formalin Puffer Fish Skin

From all physical tests conducted above, the four types of groups: raw, salted, pickled, and formalin, meet the requirement of material for leather tanning. Therefore, puffer fish skin can be used as alternative for leather tanning raw material. The puffer fish skin can be tanned and is one of the value-added alternatives for fishermen, because it can be processed into finished goods such as wallets, bags, jackets, belts, shoes, and other leather products that have economic values. Through the good tanning method, the economic value generated from a sheet of skin can be fully utilized for a wide range of interesting products with re-use approach. Development of such products is expected to increase the added value of fishing industry waste, as eminent commodities of marine and fisheries sector.

#### 4. Conclusion

1. Puffer fish skin, when seen from its histological structure, can be used as an alternative material in tannery.
2. Results from physical test such as tensile strength, elongation, tear strength and sewing strength show that puffer fish skin can be used as raw material for leather products.
3. The experiment should be re-tested with more samples.

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