Vegetable Tanning Process of Starry Trigger Fish (*Abalistes Stellaris*) and Its Plotting to Leather Products

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ABSTRACT

The aim of this study was to obtain a optimum concentration of vegetable tanning agent which good for starry trigger fish tanning process, to find out the characteristic of the starry trigger fish leather and to make a plotting of their leather products. The process was done by using three vegetable tanning agents, those were mimosa, quebracho and chestnut. Concentrations of the each tanning agents were varied to 12%, 15% and 18%. The physical characterization of the leather products were tested by using Universal Testing Machine (UTM). The results showed that the highest tensile strength, elongation and tear strength achieved by 18% concentration of each tanning agents. The plotting of leather products for the tanned starry trigger fish skin based on its physical characteristics were leather goods and leather crafts products.

Keywords: Starry trigger fish, Vegetable tanning, Leather products, Eco-friendly

INTRODUCTION

Vegetable tanning is the major tanning methods until the advent of chrome tanning involved (Surdar and Muralidharan, 2017). Each of the tanning process has its own advantages and disadvantages. The common tanning is based in the use of mineral tanning agents and mostly using chromium (III) sulphate, because of the ease of the process (Swarna *et al.*, 2008) and satisfaction in characteristics of the leather products (Afsar and Sekeroglu, 2008). However, mineral tanning contributes to environmental pollution problems. Any concern have been expressed on the toxicity of chromium(III) (Shrivastava *et al.*, 2000). Chromium (III) can possibly turns into chromium (VI) in certain condition (Fathima *et al.*, 2001) that can lead to waste and tanned leather which provide a variety of hazardous effects such as allergic, toxic, mutagenic and carcinogenic (Afsar and Sekeroglu, 2008). Therefore, there is constant search for eco-friendly tanning agents. In recent times, the non-mineral tanning agents involving vegetable tannin are regaining its importance (Swarna *et al.*, 2008).

Vegetable tanning agents are produced from renewable natural resources that its main advantage are labelled as environmentally friendly. The vegetable tanning agents that used for tanning usually leached from wood, bark, leaves, root and others vegetable parts (Swarna *et al.*, 2008) which are easily soluble in water. Historically, each country used the vegetable tannin that was available locally. In Indonesia mimosa, chestnuts and quebracho are common vegetable tannin used for tanning process. Mimosa is produced from wood and bark of *Acacia mearnsii* and *A. Mangium*, quebracho from *Schinopsis balansae* and *lorentzii* plants, chestnut was from *Castanea sativa* plant. Chestnuts is classified as pyrogallol tannins that does not discolour with light, in the other hands, mimosa and quebracho are classified as catechol tannins that usually turn more reddish in light.

Vegetable tanning agents have always been the main alternative for tanning process that are more safe for environment.

Fish is increasingly getting more attention as a raw material of exotic leather. Some works reported the process of fish leather tanning, i.e. *Himantura* stingray (Family Dasyatidae) (Karthikeyan *et al.,* 2009), red snappers (Lutjanus campechanus) (Melawati, 2014), tuna (*Thunnus sp)* (Tomi, 2009). Indonesia is archipelagic nation that has 13,466 islands (Bakosurtanal, 2010) and vast area of water ecosystems. Therefore, indonesia has huge potensial in fisheries. A potensial fish that can be used as raw material in tanning process is starry triggerfish (*abalites stellaris*) that has local name *ikan ayam-ayam*, *ikan togek*, and sometimes called *ikan etong*. The skin of starry triggerfish is very hard and the scales cannot be cleaned with common cleaning tool. Therefore, since only the meat that can be use, usually the fish skin is simply discarded and becomes waste. In our initial survey, the amount of starry triggerfish skin that were discarded as waste in around Tasik Agung beach, Rembang District, Central Java per day reaches about 25 to 50 kg. Considering the unique physical properties of this fish and the facts that the skin in lay as waste, it is necessary to empower starry triggerfish skin into valuable products. One of those is being tanned and plotting them to raw materials of leather products.

MATERIALS AND METHODS

Materials

Starry triggerfish were collected from the local market in Rembang. The skin was peeled by using knife to remove the remnants of the flesh, then washed thoroughly. The cleaned starry triggerfish skin was then weighed and ready for the next process. Three commercial grade vegetable tanning agents, i.e. Mimosa, Chestnuts, Quebracho were chosen for the tanning studies. The chemicals used for leather processing have been commercial grade.

Methods

The tanning process for starry triggerfish were done in several steps. Soaking was done using 500% water, 2% alcem oda, 1.5% preventol ZR, 1.5% H_2O_2 and run for 2 hours. Liming process was done using 300% water, 6% lime, 3% Na_2S and run for 2 hours one times and 5 minutes for 5 times. Reliming process was done using 200% water for 2 hours. Deliming process was done using 150% water, 3% ZA and runs for 1 hours. Bating was done by addition of 3% oropon and runs for 90 hours. Degreasing process was done using 200% water, 2% peltek BH and runs for 1 hours. Bleaching process was done using 200% water, 5% NaCl, 1% $KMnO_4$, runs for 1 hours and drained, then 200% water, 5% NaCl, 3% sodium metabisulphite were added and run for 30 minutes 3 times. pH value was adjusted using oxalic acid. Pickel process was done using 100% water and 10% NaCl runs for 15 minutes, then 2.5% FA was added and run for 20 minutes 3 times, then 1.5% novaltan PF added and run for 1 hour, then 0.5% sulphuric acid added and run for 15 minutes 3 times.

The studies were focused in tanning process with varying the vegetable tanning agents, ie. mimosa, chestnuts, quebracho and the concentration, ie. 12%, 15% and 18%. All processes were done using 80% corian pickle, tanning agents and run for 7 minutes. Wetting back process was done to complete the tanning. Neutralization was done by using 150% water, 1.5% eurekanol and run for 30 minutes, then adding 0.8% baking soda and run again for 15 minutes 3 times. Fatliquoring was then done by adding 100% water, fatliquoring agents and run for 1 hour. Fixation was done by using 1.5 formic acid and run for 20 minutes 3 times.

Measurement of the tensile strength

The test was conducted by using Universal Testing Machine (Gester GT-K01) using methods SNI 06-1795-1990. Specimens were prepared by cutting the fish skin in the size of 11 × 3 cm using speciment cutter. The thickness and width of the specimen were measured along the skin and taken for further calculation. Measurement was made with a precision of 0.01 mm. The side end of each of the sample was placed in the clamp, then the stretching was conducted in specific rate. The tensile strength was calculated as the maximum load required to stretch the specimen until its broken.

Measurement of the elongation

The test was conducted by using same instruments with the tensile measurement (Gester GT-K01) using methods of SNI 06-1795-1990. The value of elongation was obtained through calculation of the difference between final and initial sample length divided by the initial sample length, and then expressed as a percent.

Measurement of the tear strength

The test was conducted based on SNI 06 - 1794-1990 methods using universal testing machine. For this test, the skin was cut with the size of 10 × 2 cm then make a hole inside the specimen with the diameter of 0.2 cm within 2 cm from the side end. After that, create a wedge of hole extended to others side so that the sample cut and shaped as tongue pieces. The specimen thickness was measured and then the two parts of the tongue mounted on the clamp. The tear strength was calculated as maximum load required to stretch the sample until it was torn apart.

Plotting the fish leather products

Based on the testing results that has been done above, the leather was plotted to several product that most suitable to its characteristic.

RESULTS AND DISCUSSION

The effect of the amount of material on the quality of leather tanning generated from each type of tanning agents (mimosa, quebracho and chestnut) had been studied to find out its plotting to leather products.

Organoleptic test

The results of organoleptic test results were shown in Table 1 and Figure 1

Table 1. The results of organoleptic observations

Observation	Mimosa	Chesnuts	Quebracho
Nerf deliverance	Attached	Attached	Attached
Leather condition	Flexible and filled	Flexible and filled	Flexible and filled
Color	Even	Even	Even
Torn strength	Not torn	Not torn	Not torn
Elasticity	Less elastic	Less elastic	Less elastic
Flesh appearance	No flesh left	No flesh left	No flesh left
Cross section	Similarly cut	Similarly cut	Similarly cut

There was no difference of organoleptic appearence of leather tanned by those three of tanning agents. The unique appearence was the typical hard scales which remained thicker and more artistic.

Figure 1. Starry triggerfish leather processed with (A) mimosa, (B) quebracho and (C) chesnuts.

As expected, since the mimosa and quebracho were classified as catechol tannin, the resulting leather were more reddish that make it harder to gives proper dyes. These characteristics were slightly different with the chesnuts (pyroganoll tannins) leather processing that gives less colour in its products.

Physical test

The physical properties of leather produced greatly affects its application on a product. Leather which is tanned with vegetable tanning agents in organoleptis seems to be more rigid and thicker. As in cow or buffalo leather using vegetable tanning agents usually ~~is~~ becomes thicker. Vegetable tanned leather are generally used for the soles of shoes or belts and certain leather goods that do not require high elasticity. A good physical quality of leather will improve product quality. The physical properties which is very dominant in determining the quality of a product are the leather tensile strength, elongation and tear strength. In general, the use of processed skin requires a good tensile strength and elongation. For art leather products or leather crafts the characteristic of texture and beauty of the leather texture are more important rather than the specific physical properties. To determine the physical properties of tanned leather is influenced by many factors, such as the type of tanning materials, thr quality of raw material of leather, preservation of leather, liming, lime waste, erosion protein, tanning or anointment, also at the stage of completion such as stretching, humidification and extension. The of physical testing of starry trigger fish skin tanned by using vegetable tanning materials, mimosa, quebracho and chestnut are shown in Table 2.

Effect of concentration and tanning agents on tensile strength

The results of tensile strength test using vegetable tanning agents of mimosa 12%, 15% and 18% were 46.67 kg/cm^2, 76.92 kg/cm^2 and 80.00 kg/cm^2 respectively. Tensile strength test with chesnuts 12%, 15% and 18%, resulting in 107.69 kg/cm^2, 192.72 kg /cm^2 and 195.00 kg/cm^2 respectively. Quebracho 13%, 15% and 18% resulting in tensile strenth of 61.33 kg/cm^2, 69.33 kg/cm^2 and 73.85 kg/cm^2 respectively. The values of tensile strength increased as long as the increased of tanning agents concentration. The highest value of tensile strenth was obtained by using chestnuts tanning agent, however, these value was lower than that of stingray skin which was 2000 N/cm^2.

The increase of tensile strength value presumably was due to the reactivity of tanning agents to the collagen fibers. The presence of –OH functional group in vegetable tanning agents that reacted completely with NH_2 functional groups from collagen can alter the properties of leather collagen. More tanning agents added would gives higher crosslink density into leather, thus gives better tensile strength.

Table 2. The result of physical test

Vegetable tanning agents	Type of Test		
	Tensile strength (kg/cm^2)	Elongation (%)	Tear strength (kg/cm)
Mimosa12%	46.67	16.02	20.00
Mimosa15%	76.92	21.67	26.91
Mimosa18%	80.00	25.09	38.80
Chesnuts 12%	107.69	19.89	24.00
Chesnuts 15%	192.73	31.78	26.67
Chesnuts 18%	195.00	34.10	35.20
Quebracho 12%	61.33	14.19	17.69
Quebracho 15%	69.33	20.34	18.40
Quebracho 18%	73.85	26.81	23.60

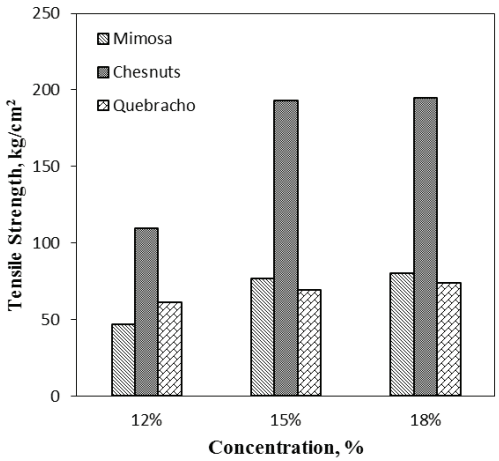

Figure 2. Graphical representation of leather tensile strength

Effect of concentration and tanning agents on elongation

Elongation of leather was the length of leather when it was stretched until broken. It was divided by its original length and expressed as a percent. Elongation strength showed the ability of the skin from getting broken. The good strength of leather due to good quality of stretching was indicated by the size of the broken site and the increase of value of elongation. The results of elongation test of starry trigger fish leather tanned by using vegetable tanning agents showed that, mimosa of 12, 15 and 18% were 16.02, 21.67 and 25.09% respectivelly. chesnut of 12, 15 and 18 were 19.89, 31.78 and 34.10% respectively. While elongation of leather tanned with, quebracho of 12, 15 and 18% were, 14.19, 26.81 20.34% respectively.

The results of elongation test for starry triggerfish leather ranged from 14% to 34%. These results were in association with the quality requirements of crust tanned goat/sheep leather, that has a maximum value was 50% (SNI 06 - 3635-1994). Figure 3 above showed that elongation of leather has increased along with the increase of the tanning agents concentration. The value of elongation was related to the leather elasticity. Leather became weak because of the reduction in liming and elastin protein skin erosion. Elastin is a fibrous protein that forms highly elastic fibers because it has a chain of amino acids that form the corner (Judoamidjojo, 1974). These angles become straight when there is a stress

force and will return to normal when the force is removed. The loss of elastin in skin proteins can reduce the elasticity of the skin. Skin elongation is also affected by the high fiber protein composition. The degree of elongation and enervation is also influenced by the process of completion as toggling, relaxation and smoothing (Purnomo,1985).

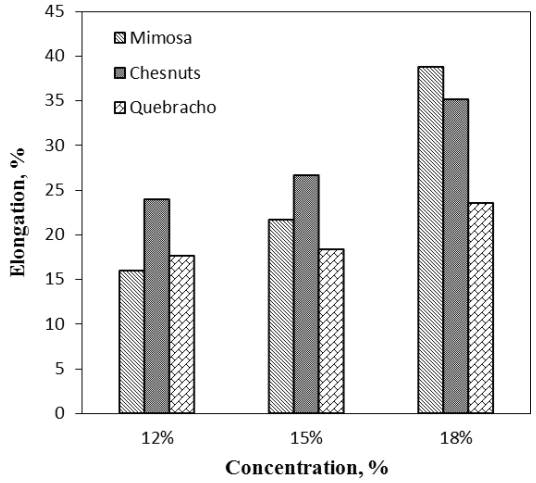

Figure 3. Graphical representation of leather elongation

Effect of concentration and tanning agents on tear strength

Tear strength indicated the maximum limit of the skin to be torn.The skin that was tanned with high levels tanning agents would have a high tear resistance (Fahidin, 1977).

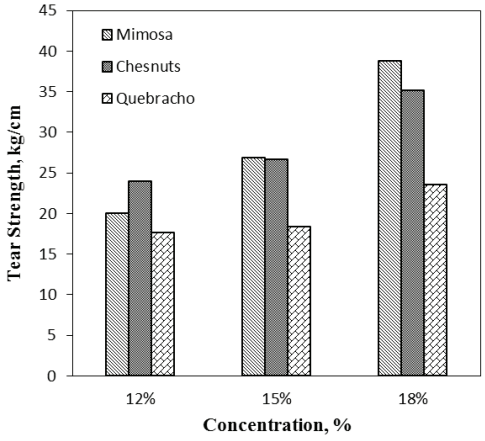

Figure 4. Graphical representation of leather tear strength

Figure 4 showed that the tear strength of starry triggerfish tanned with mimosa of 12%, 15% and 18% ranged between 20 to 38 kg/cm, chesnut ranging from 24 to 35 kg/cm and quebracho ranging from 17 to 23 kg/cm. The tear strength values was increased along with the increased of tanning agents concentration. Th higher concentration of tanning agents used mean that the active ingredients that crosslink to the protein collagen fibers of the skin is also higher. Then, the crosslink will be more dense and the skin becomes more resistant, stronger and lower possibility from getting broken.

The results of strength tests showed that the use of 18% mimosa, chestnuts and quebacho tanning agents generated highest tear strength value. The higher concentration resulting in more absorbance of the tanning agents during the process, because high

ionization properties of collagen in protein fibers in a wide range of pH. The ionization power prevent the leather from getting shrinkage and make the water contents stable that produce a dense and strong leather (O'Flaherty, 1978).

The greater mimosa concentration will strengthen the structure of the leather (Untari, 1995). The value of the tear strength in line with the levels of tanning agents contained in its leather. Tear strength of leather is also affected by the skin structure changes and high protein fibre composition in the skin. The fibers of the skin is contracted at the limming and fleshing process so will make the tear strength lower. Tear strength will further increase when collagen fibers hold a bond with the tanning material (Purnomo, 1985).

Plotting of leather products

Based on the results of all tests and considering the characteristics of vegetables-tanned of the leather, starry trigger fish leather was suitable for leather goods and leather craft which do not need any specific physical properties, such as handbags, wallets, belts, passport casses. The thick and hard scales of starry trigger fish skin were the artistic and unique properties as raw materials to produce beautiful leather goods and leather crafts. The pictures bellow were the leather product prepared with vegetables-tanned starry trigger fish leather.

Bags

Ladies handbag made of pull up leather with a combination of starry trigger fish leather designed with elements geometric associated with zigzag stitches. The small size of the fish leather, make combination was needed for dealing with larger leather products.

Figure 5. Ladies bag 1

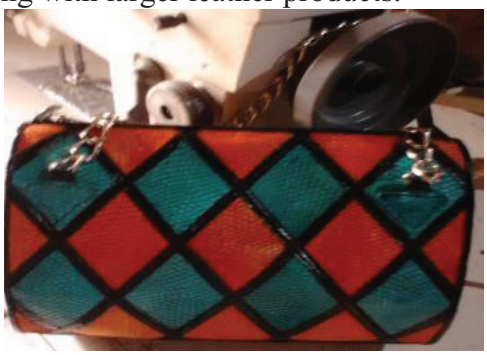

Figure 6. Ladies bag 2

Ladies purse

Handpurse created with starry tigger fish leather combined with goat leather

Figure 7. Ladies Purse

Men wallet and passport case

Handheld Wallets for men with smaller size, it had small container to keep money and card safe. Also the leather could made to passport case to keep passport and card with similar size.

Figure 8. Man wallet

Figure 9. Passport case

Key holder and coins wallet

Key holder was used to keep key and certificate of vehicle number (STNK) with a combination of black calf glaze leather.The coin wallet was used to save the coins.

Figure 10. Key holder

Figure 11. Coin wallet

Derby model shoes

Derby Shoes which was semi-formal shoes made with a combination of starry trigger fish leather.

Figure 12. Derby shoes

Figure 13. Leather case for 7 inches tablet

7 inch Tablet Leather Case

This-tablet case was made from the trigger fish leather combined with boks cow leather

CONCLUSIONS

The best formula in this research for processing trigger fish skin with vegetable tanning agents was 18% of mimosa, chesnuts and quebracho. The resulting leather that processed with chesnuts had lighter colour compared to mimosa and quebracho which are more reddish. With this concentration, the leather had physical characteristics with appropriate values of tensile strength, elongation and tear strength that suitable for plotting in leather goods and leather craft. The small size of the leather, make it more prefered to be used in combination, espesially in larger leather products.

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