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The Use of Glutaraldehyde Tanning Materials for Goat Skin Tanning

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ABSTRACT

Tanning process using free chromed material is needed to reduce toxic content in leather. The aims of this study is to increase byproducts of livestock by goat skin tanning with free chrome tanning materials. This study used glutaraldehyde as tanning materials. Goat skins were tanned become upholstery leather, and then physical quality was determined. The materials of this study were pickle goat skin. Physical testing conducted in Balai Besar Kulit, Karet dan Plastik (BBKKP) Yogyakarta. The results were analyzed descriptively using SPSS version 17.0 for Windows. Statistical analysis showed that the value of tensile strength, elongation, tear strength, sewing strength, scrub resistance of paint to dry and wet were 166.025 ± 72.315 kg/cm²; 69.910 ± 9.107%; 26.785 ± 6.031 N/cm; 115.120 ± 18.681 kg/cm; 0.775 ± 0.353; 0.775 ± 0.353 respectively. This study showed that the physical quality of upholstery leather which tanned using free chrome tanning materials have the physical qualities that met with SNI standard for leather upholstery.

Key words: Glutaraldehyde, Goat skin, Tanning materials

Introduction

Skin is by-product of livestock. Tanning is one of the ways to increase the value of the skin. By the tanning, skin changed to be leather. The price of leather is more expensive than skin. Now days, the need of finish leather for upholstery, especially for car upholstery in Indonesia is increasing, but these needs can't be fulfilled by domestic manufacturers.

According data from the Association of Indonesia Tanning in 2010 there are only six tannery companies to produce leather upholstery of 67 tannery companies there. The leather-based industry especially leather products industry (footwear, garment, upholstery and leather goods) is highly fashion oriented (Covington, 2009). This indicates the potential market opportunities for development the upholstery tanning industry.

Tanning industry is still a lot of use of chrome tanning materials as main tanning material, because the skin which tanned with chrome has advantages that today are difficult to replace with other tanning materials. This tanning materials gives nature a very flexible, supple, limp, flexible and most prominent. The leather which tanned with chrome has resistance high hydrothermal heat that can reach 140°C and can be applied to all articles of skin, especially for skin that require a degree of high enervation (Purnomo, 2016). Chrome tanning is currently the preferred technique being more rapid process for leather production. It is also more versatile and imparts a better combination of chemical and physical properties to leather than vegetable tanning, thereby producing a softer and better quality (Tariq *et al*., 2009). But, tanning using chrome (III) allegedly will be formed of chrome (VI) is carcinogenic that can endanger human healthy and environmentally unfriendly (Kasmudjiastuti *et al*., 2016).

Todays, green leather on leather tanning industry began to be developed in line with the environmental issues that include chrome as heavy metals should be restricted usage and effluent standards. Every country has the effluent standards vary, but generally refers to the amount that is approaching. Especially for developing countries to chrome exhaust standard III valence of 1.5 to 5 mg/L and chrome VI valence of from 0.1 to 0.5 mg/L or 0 mg/L on leather. Chrome tanning substance is a substance with III valence tanner that is slightly toxic, so its use is still allowed, but the liquid effluent or solids must be handled in accordance with the laws and regulations (Purnomo, 2015). Chakraborty *et al*. (2008) also explains that tanning using chrome tanning agent is still the most widely used, but the waste of chromium to date have not dealt with the right systems to allow for the change of chrome (III) to chrome (VI).

Nowadays the term wet white, it's produced from leather tanned with aldehyde component (glutaraldehyde) or synthetis. The type

of glutaraldehyde tanning material was developed as a replacement for chrome tanning because enervation produced approaching enervation chrome tanning materials. But, still needs deeper study on the toxicity of glutaraldehyde as a substitute for chrome tanning materials to be regarded as environmentally friendly tanning materials. Yasmeen (2016) said that new cross-linked chitosan magnetic beads modified with cysteine-glutaraldehyde schiff's base (Chi-CG) were utilized as a possible adsorbent for the elimination of Cu(II) and Cr(VI) from aqueous solutions.

The advantage of retaining with glutaraldehyde is the uniform and better filling effect than reduced chromed or chrome 33.33%, giving a very soft and soft effect, giving a flat effect on the base of dyeing without reducing the sharpness of the color, increasing the sweat resistance (Purnomo, 2008). Based on the description above, needed a study which evaluating the physical quality of the leather tanned with glutaraldehyde tanning materials (free-chrome tanning agent) to increase the value of by-product of livestock.

Materials and Methods

The sample used in this study as much as 8 sheets of pickled goat skin for glutarldehyde tanning materials (9 square feet respectively), every treatment consist of 2 sheets of pickled goat skin and repeated 4 times. The tools are indicator pH, tanning drum (RPM : 10-12), post tanning drum (RPM: 15-20), sammying and setting-out machine (type: GJ5P-150, product: 3H Machine Co., Ltd.), vacuum dryer machine (type: GGZK-LT, product: Nantong Sirui Engineering Co. Ltd.), stacking machine (type: Double GLRZ, product: Rugao Dongxing Machinery Co., Ltd.), and toggling machine.

The chemicals are: H_2O, HCl, HCOOH, NaCOOH, $NaHCO_3$, NH_3, BCG indicator, anionic wetting agent (product name: Peramit ML-N, product: Pulcra Chemicals, Geretsried Germany), natrium naphthalene (product name: Tanigan PAK, product: Lanxess High Performance Composite Materials Co., Ltd., Jiangsu China), glutaraldehyde tanning agent (product name: Rellugan GT-50, product: BASF, Florham Park, USA), chrome syntan (product name: Rokytan RHP, product: Tytan Organics Pvt. Ltd., Mumbai India), allumunium sulfat (product name: Novaltan AL, product: Zschimmer and Schwarz, Lahnstein Germany), naphthalene sulfonat (product name: Tysyntan-TFS, product: Tytan Organics Pvt. Ltd., Mumbai India), resin dicyandiamide/ resin melamin (product name: Ukatan AG, product: Schill and Seilacher, Boblingen Germany), resin acrylic (product name: Tysyntan-TFS, product: Tytan Organics Pvt. Ltd., Mumbai India), sulphited fish oil (product name: Derminol SPE, product: Cybex Exim Solutions Ltd., Noida India), phenolic syntan (product name: Tanicor SGN, product: Stahl, Berlin Germany), quebracho, tara, Dispersing agent (product name: Tanigan PR, product: Lanxess High Performance Composite Materials Co., Ltd., Jiangsu China), lecithin oil (product name: Derminol® NLM, product: Stahl, Echterdingen Germany), anionic flouro polymer (product name: Derminol LUB, product: Stahl, Echterdingen Germany), synthetic oil (product name: Derminol® OCS, product: Clariant, Echterdingen Germany), emulsifier (product name: Tannit LSW, product: Boehme, Geretsried Germany), resin cationic (product name: Sincal DR, product: Zschimmer & Schwarz, Lahnstein Germany)**,** anti mold (product name: Preventol® CR plus L-N, product: Lanxess High Performance Composite Materials Co., Ltd., Jiangsu China).

Method

Tanning. Pickled goat skin was tanned using glutaraldehyde tanning materials. Tanning procedure refers to (Purnomo, 2015). The use of chrome has negative effects on the environment that can destabilize the nutrient, so it is necessary to minimize the use of chrome tanning materials in the tanning process and to increase the physical quality of leather (Anggriyani and Laili, 2017). The tanning process can be seen in Figure 1.

Post tanning. Before wet-processing of pasca tanning, the pickled skin was shaved with a thickness of 0.9-1.0 mm (thickness standard of upholstery). Post tanning process includes retanning, fatliquoring, dyeing and fixing. Mechanical actions are: sammying setting-out, hang-drying, staking and toggling. Post tanning procedure refers to (Purnomo, 2017).

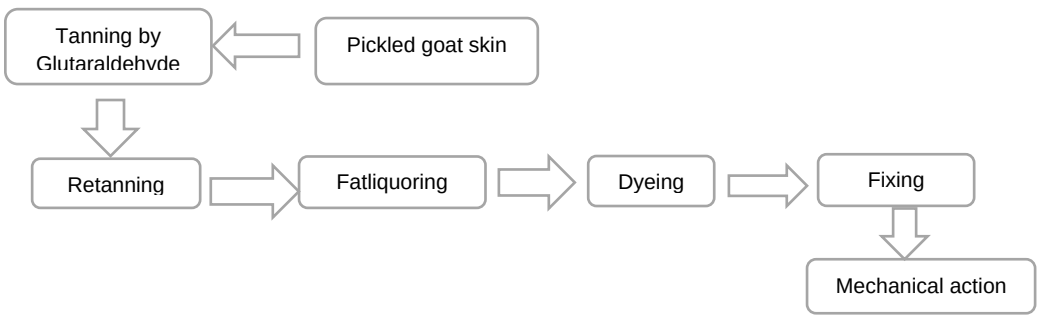

Figure 1. Diagram of Leather processing.

Physical quality test. Physical testing conducted in Balai Besar Kulit Karet dan Plastik (BBKKP) Yogyakarta. Physical testing refers to SNI 06-1795-1990 (tensile strength and elongation test), SNI 06-1794-1990 (tear strength test), SNI 06-0117-1989 (sewing strength test), SNI 06-0996-1989 (scrub resistance of dry and wet paint test).

Data analyzed. Data was analyzed using Descriptive Analysis with SPSS version 17.0 for Windows (IBM USA, 2009).

Result and Discussion

The physical quality test result of upholstery leather are presented in Table 1. This results show that tensile strength, elongation, tear strength, and the sewing strength meet with SNI for upholstery's standard (SNI No. 06-07776-1989) which is shown in Table 2. Table 1 shows that the tensile strength of upholstery in this study is 166,025 ± 72,315 kg/cm². Based on the SNI reference No. 06-07776-1989, this result meets with the standards of SNI upholstery physical quality (minimum 125 N/cm²). This study shows that leather tanned with glutaraldehyde tanning materials has tensile strength higher than leather tanned with chrome tanning materials (Chakraborty *et al*., 2008).

Syntan serves as a filler material in the process of retanning, so this leather is more solid. Syntan accelerate the reaction between glutaraldehyde (CHO-CH_2- CH_2- CH_2-CHO) with a group of NH_2 of skin collagen (Purnomo, 2016). The addition of syntan as much as 3% in the retanning process causes increasing the skin leather tensile strength. Tensile strength is also affected by the use of sulphated oil. The adding of sulphated oil serves as a lubricant fibers of the skin to pull the skin becomes more resistant. The use of sulphated oil for upholstery leather is 2 – 3% from wet blue or wet white weight (Thanikaivelan *et al*., 2005).

This study showed the elongation of upholstery skin leather is 69,910±9,107%. Based on the SNI reference No. 06-07776-1989, this result meets with the standards of SNI upholstery physical quality (minimum 40%), and this result is inversely with tensile strength (Samiadi and Bulkaini, 2005). But, the leather is too elastic. This is not recommended for the manufacture of leather upholstery especially for automotive upholstery and footwear article (Palop, 2000). The high value of elongation is influenced by the addition of oil on the fatliquoring and top fatliquoring process. We used sulphited oil as much 21%, this is serves as a lubricant the fibers of the skin to make the skin becomes more resistant to tensile and keep the skin fibers to prevent sticking so the skin becomes more elastic. Leather upholstery does not require a high elongation so the percentage of sulphited oil must be decreased.

This research showed the tear strength of upholstery skin leather is 26,785 ± 6,031 N/cm. Based on the SNI reference No. 06-07776-1989, this result meets with the standards of SNI upholstery physical quality (minimum 20 N/cm). Tear strength is a very important requirement for the standard of upholstery leather. Good quality of upholstery leather is having a high tear strength. In this study, the tear strength was affected by the tanning materials. Aldehyde tanning material is able to form crosslinks with the skin collagen (Purnomo, 2016). We use glutaraldehyde tanning materials, it is the other type of aldehyde compound (Bossche *et al*., 2007).

Table 1 shows the sewing strength test is 115,120 ± 18,681 kg/cm. Based on the SNI reference No. 06-07776-1989, this result meets the standards of SNI upholstery physical quality (minimum 50 kg/cm). The minimum requirement of sewing strength for upholstery is 100 kg/cm with a thickness of less than 2 mm (Anonymous, 2009). Tear strength directly proportional with the sewing strength.

Aldehyde tanning materials especially glutaraldehyde not yet fully applied in the upholstery tanning industry compared with chrome tanning materials. Chromium is one of the tanner substances that is widely used in leather processing, because it has several advantages including finished leather (leather) is more subtle, more resistant to heat, and more resistant to tearing (Takigawa and Yoko, 2006). The physical quality of goat skin upholstery tanned with chrome tanning materials have been investigated by Chakraborty *et al*. (2008) which is shown in Table 3.

Although, chrome tanning is the most profitable tanning system but the chrome waste problems can't be resolved, especially carcinogenic hazard from chrome (VI). Chrome (Cr) is a kind of heavy metal which the exhausted should be limited because it have bad effect of inhalation, oral, and dermal exposure of humans and animals (Simons *et al*., 2000). Every country has different standard of chrome wasted. In developing countries, the waste from Cr (III) in tanning industry minimal 1.5-5 mg/L, and Cr (VI) minimal 0.1-0.5 mg/L (Purnomo, 2015). Erdem (2006) stated that commercial chrome

Table 1. Physical quality test of upholstery leather tanned with glutaraldehyde tanning materials

Physical test	Result
Tensile strength	166,025 ± 72,315 kg/cm²
Elongation	69,910 ± 9,107%
Tear strength	26,785 ± 6,031 N/cm
Sewing strength	115,120 ± 18,681 kg/cm
Scrub resistance of dry paint	0,775 ± 0,353
Scrub resistance of wet paint	0,775 ± 0,353

Table 2. SNI No. 06-07776-1989

Physical test	Result
Tensile strength	Minimal 125 N/cm²
Elongation	Minimal 40%
Tear strength	Minimal 20 N/cm
Sewing strength	Minimal 50 kg/cm

Table 3. Physical quality of upholstery leather tanned with chrome tanning materials

Physical test	Result
Tensile strength	158,5985 kg/cm²
Elongation	45,21%
Tear strength	25,10 N/cm

tanning products are generally used in powder form. They contain about 25% Cr_2O_3 of 33% basicity. Basic chrome sulphate liquors are also used. These liquors are prepared by reducing the Na/K chromates in the presence of sulphuric acid. However, the mineral tanning also contributes to the problem of environmental pollution, especially in developing countries. Thus, it is necessary to use non-mineral tanning process to support environmentally friendly in the manufacture of leather (Suparno *et al*., 2002).

Glutaraldehyde is an excellent tanning material which is capable of cross-linking proteins due to its bifunctional nature. When used as a tanning agent in itself, it can produce a good leathering effect and has a dark yellow color and can be natural dyes (Darmawati *et al*., 2017). Glutaraldehyde has been found to have a softening effect on leather and also has the ability to make the leather more receptive to subsequent chemical treatments for water-repellency and other specific effect (Dettmer *et al*., 2011). Glutaraldehyde, still commonly used as pre-tanning agent of shrunken leather and re-tanning agent of glove leather (Rachmawati and Udkhiyati, 2017). Glutaraldehyde is the type of aldehyde that resulting from crosslinking between glutaraldehyde (CHO-CH_2- CH_2- CH_2-CHO) with NH_2 groups of the skin collagen (Chakraborty *et al*., 2008).

Glutaraldehyde has shrinkage temperature less than 90°C (Vitolo *et al*., 2003). It is happens because much of oxymethylene bridges resulting crosslinking, so it is caused wrinkle temperature rised. Crossed-Linkage determines the temperature of skin wrinkle. The rising of wrinkle temperatures significantly with the number of aldehyde bound, while aldehyde bound depending of pH tanning process (Purnomo, 2016). This study is consistent with the study results from Chakraborty *et al*. (2008), the goat skin which tanned with glutaraldehyde tanning materials shows wrinkle temperature at 88°C.

Conclusion

In order to reduce the negative effects of chrome in the tanning industry, alternative tanning materials are needed. Glutaraldehyde is ideal to be used as an alternative of chrome as a tanning material in term of upholstery leather physical qualities. Physical qualities of upholstery meet with SNI standards.

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