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Characteristic of Chrome-Tanned and Vegetable-Tanned Goat Garment Leathers

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ABSTRACT. *Chrome tanning material is still widely used in the tanning process for garment leather production. Its use began to be reduced to overcome its negative environment impact. Vegetable tannin of a mimosa and tara combination was used in this study to substitute chrome tanning material. Garment made from vegetable-tanned leather with a ratio mimosa to tara of 5:13 was compared to garments made from chrome-tanned leather, both the production methods and resulting leather characteristics. To obtain garment leather characteristics, chrome-tanned leather requires auxiliary materials and two fatliquoring steps. Vegetable-tanned leather requires more auxiliary materials and fatliquoring steps (3 steps). Physical test results show that chrome-tanned leather gives better tensile strength, elongation, tear strength, and softness that meet with SNI (Standar Nasional Indonesia or Indonesian National Standard). Meanwhile, garments from vegetable-tanned leather exhibit elongation, tear strength, and softness that meet with SNI. However, adding auxiliary materials and fatliquoring steps in the garment-making process from vegetable-tanned leather is still unable to produce the softness, smoothness, and elasticity of a garment from chrome-tanned leather.*

Keywords: Garment, vegetable-tanned leather, chrome-tanned leather

INTRODUCTION

Skin is a by-product of animal husbandry, which can become waste if not treated properly. Processing skin into various leather products can increase the selling value. One of the processing skin steps is tanning, which plays a main role in making leather's character. The tanning process requires a material with good astringency properties to produce skin with a stable fibre and structure to prevent being putrefied by bacteria (Unango *et al.*, 2019).

Recently, chrome tanning material is still widely used in leather tanning process due to its excellent character produced, as high hydrothermal stability, good softness, lighter, comfortable feel, and high strength properties (Örk *et al.*, 2014; Liu *et al.*, 2016; Maina *et al.*, 2019; Ahmed & Maraz, 2021). Those characteristics cause chrome tanning materials to be used to produce soft leather. However, using chrome as a tanning material is of particular concern for environmental issues. After all, it can be oxidized from trivalent chromium to a hexavalent with toxicity (Liu *et al.*, 2016) which can be harmful to humans, soil, and water ecosystems (Nigam *et al.*, 2015). This has led to the Environmental Governing Council imposing restrictions on the use of chromium, especially concerning chromium waste (Vaiopoulou & Gikas, 2020). In Indonesia, this regulation is written in a ministerial decree which states that the maximum limit for total chrome content in leather tannery waste is 2.0 mg/L (Keputusan Menteri Lingkungan Hidup, 1995).

Garment leather, as one of soft leathers, is mostly made from chrome-tanned leather. Restriction on chrome usage results in developing garment leather production using various tanning materials. Previous studies have explored various combination tanning methods, including the use of white minerals with natural tannins (Pradeep *et al.,* 2021), chromium combined with vegetable tannin (Örk *et al*., 2014), and tara with phosphonium (Aravindhan *et al*., 2015). These researches prove that combination tanning using natural tannin is suitable to substitute chrome in the leather process regarding to its ecofriendly (Bhavya *et al*., 2020), although it results in different characteristics of leather. Vegetable tannin produces tough and stiff leather, so it is usually used for leather that requires less elasticity, such as shoe uppers, furniture, and garments (Griyanitasari *et al.,* 2018; Falcão & Araújo, 2018; Abdulla-Al-Mamun *et al.,* 2023). However, the natural look and feel obtained increase their use in the production of garment leather (Örk *et al*., 2016). The study used combination tanning using aldehyde to provide the softness character of the leather. Aldehyde tanning is well known to produce good filling and soft leather (Purnomo, 2016). Combination tanning may lead to better characteristics of leather (Örk *et al.,* 2016), even characteristics of a combination of vegetable-tanned leather and aldehyde-tanned leather. Besides, the using of sulfited oil in leather can enhance the softness, so it is expected to produce garment leather that requires good softness (Purnomo *et al*., 2020).

The garment is one of the leather products expected to have a softness characteristic. This study was conducted to investigate the effectiveness of using vegetable-tanned leather to substitute chrome-tanned leather, which is generally used in garment leather production. This can reduce the use of chromium in the leather-making process, thereby also reducing the chromium content in leather tannery waste so that the process is more environmentally friendly. The production methods, including materials and steps that may affect the softness of the leather, such as the use of glutaraldehyde, sulfited oil, and fatliquoring method, and the characteristics of resulting leathers were observed.

MATERIALS AND METHODS

Materials

Materials used in this study were six sheets of pickled goat skins. The chemicals used were NaCl, CH_3COOH, NaCOOH, HCOOH, $NaHCO_3$, Na_2CO_3, $C_2H_2O_4$, NH_3, CH_3COONa, acid dyestuff, BCG indicator, wetting agent (Peramit MLN from Pulcra Chemicals), polycarboxylate (Novaltan MAP from Zschimmer and Schwarz GmbH and Co KG), chrome tanning agent (Chromosal B from Lanxess), cationic oil (Catalix GS from Clariant), self-basifying agent (Feliderm MGO from Clariant), dispersing and levelling agents (Coralon OT from Clariant), Tara (Sodatan TVT), Mimosa (Mimosa ME from PT Galic Bina Mada), sulfited fish oil (Derminol SPE from Stahl Leinfelden GmbH), batting agent (Feliderm Bate AB from Stahl Leinfelden GmbH), glutaraldehyde tanning agent (Relugan GT 50 from BASF), sodium salts (Tanigan PAK from Lanxess), penetrating agent (Dermagen GP from Stahl Leinfelden GmbH), resin acrylic (Drasil SM/S from Pulcra Chemicals), sulfited marine oil (Eurekanol SFO from Allied Chemicals International Co., Ltd.), synthetic oil (Lipoderm Liquor SAF from BASF), synthetic oil and softening agent (Derminol OCS from Stahl Leinfelden GmbH), lecithin oil (Sedaflor LC 13 from Pulcra Chemicals), cationic resin (Retingan R4B from Lanxess), and microbiocide (Preventol CR from Lanxess).

Leather Preparation Process

The tanning process was conducted in two processes, the chrome tanning and vegetable tanning processes. Tanned leathers, wet blue and vegetable-tanned leather, were then treated in post-tanning. The post-tanning process was performed, including the wet and mechanical processes. The stages of the leather processing are detailed in Table 1 and Table 2. The goat leather was shaved before the wet process with a 0.4-0.6 mm thickness.

Table 1. Stage of leather process from chrome-tanned goat leather

Process Flow	%	Chemical	Process Control		
			Time (min)	pH	°C
Tanning					
Wetting back	100	Water			
	15	NaCl			
	1	Peramit MLN	15		
	0.5	HCOOH	5×10	2.8	
Drain					
Re-Pickling	75	Water			
	7.5	NaCl	5	2.5	
Pre-Tanning	3	Novaltan MAP	120		
Tanning	10-25	Pickle Water		2.5	
	4	Chromosal B			
	1	CH_3COONa			
	2	Catalix GS	10		
Basifying	0.4	Feliderm MGO	420	3.8	
	0.1	$NaHCO_3$	30	3.9 – 4.1	
Anti-Fungal	0.2	Preventol Cr	30		
Sammying					
Post-Tanning					
Wetting back	200	Water			
	0.5	CH_3COOH		3.8 – 4.0	
	0.75	Peramit MLN	30		
Rebatting	2	Feliderm Bate AB	60		
Drain					
Retanning I	100	Water			
	3	Chromosal B	30		
	3	Relugan GT 50	60		
		Drain			
Neutralizing	150	Water			
	1.5	Tanigan PAK	10		
	0.5	NaCOOH	10		
	0.5	$NaHCO_3$	20		
	0.5	$NaHCO_3$	20	5.5 – 5.8	
Drain, wash with running water 15 minutes					
Retanning II	100	Water			
	3	Drasil SM/S	30		
	4	Eurekanol SFO	60		
Drain, wash					
Fatliquoring I	200	Water	5		70-80
Drain ½ volume of water					
	75	Water			60-70
	8	Eurekanol SFO			
	4	Lipoderm Liquor SAF			
	0.5	Peramit MLN	60		
Dyeing	1	Dermagen GP	30		
	3	Acid Dyestuff	30		
	0.5	NH_3	20		
Fixing	100	Water			
	0.5	Formic acid	10		

Process Flow	%	Chemical	Process Control		
			Time (min)	pH	°C
	0.5	Formic acid	10		
Fatliquoring II	75	Water			80
	3	Eurekanol SFO			
	4	Derminol OCS			
	1.5	Sedaflor LC-13			
	0.25	Peramit MLN	60		
Fixing	0.5	HCOOH	15		
	0.5	HCOOH	15		
	0.5	HCOOH	15	Min. 2.5	
	0.2	Retingan R4B	15		
	0.2	Preventol CR	15		
Drain					
Wash					
Drain					
Setting out					
Hang drying					
Conditioning					
Staking					
Toggling					
Milling					

Table 2. Stage of leather process from vegetable-tanned goat leather

Process Flow	%	Chemical	Process Control		
			Time (min)	pH	°C
Tanning					
Wetting back	150	Water			
	12	NaCl	10	3	
Pre-Tanning	100	Water			
	5	NaCl	15		
	1	HCOOH	2×10	3	
	3	Relugan GT 50	45		
Fixation	1.5	$NaHCO_3$	4×10		
	1	$NaHCO_3$	3×10		
	0.5	Na_2CO_3	3×10	6 – 8	
Drain					
Shaving					
Tanning	50	Water			
	3	Na_2SO_4	30		
	4	Coralon OT	45		
	3	Derminol SPE	30		
	5	Tara	60		
	3	Derminol SPE	30		
	5	Mimosa	60		
	3	Derminol SPE	30		
	5	Mimosa	60		
	3	Derminol SPE	30		
	3	Coralon OT	30		
	3	Mimosa	60		
Drain					
Wash					
Drain					
Fatliquoring	50	Water			60-70

Process Flow	%	Chemical	Process Control		
			Time (min)	pH	°C
	4	Provol 100	60		
Fixing	2	$C_2H_2O_4$	15		
	2	HCOOH	15	3 – 3.5	
	0.2	Preventol Cr	15		
Setting Out					
Vacuum Drying					
Hang-Drying					
Post-Tanning					
Wetting back	200	Water			
	0.5	CH_3COONa		3.8 – 4.0	
	3	Peramit MLN	60		
Drain					
Retanning	100	Water			
	3	Relugan GT 50	30		
	3	Relugan GT 50	60		
		Drain			
Neutralizing	150	Water			
	1.5	Tanigan PAK	10		
	0.5	NaCOOH	10		
	0.5	$NaHCO_3$	20		
	0.5	$NaHCO_3$	20	5.8 – 6.0	
Drain					
Fatliquoring I	200	Water	5		70-80
Drain ½ volume of water					
	0	Water			60-70
	11	Eurekanol SFO			
	4	Lipoderm Liquor SAF			
	3	Derminol OCS			
	2	Peramit MLN	60		
Fatliquoring II					
Drain ½ volume of water					
	100	Water			60-70
	12	Eurekanol SFO			
	4	Lipoderm Liquor SAF			
	1.5	Peramit MLN	60		
Dyeing	1	Dermagen GP	30		
	3	Acid Dyestuff	30		
	0.5	NH_3	20		
Fixing	0.5	Formic acid	10		
	0.5	Formic acid	10	Min. 3.5	
Drain, wash					
Top Fatliquoring	0	Water			80
	5	Eurekanol SFO			
	6	Derminol OCS			
	2.5	Sedaflor LC-13			
	0.5	Peramit MLN	60		
Fixing	150	Warm water			
	0.5	HCOOH	15		
	0.5	HCOOH	15		
	0.5	HCOOH	15	Min. 2.5	
	0.2	Retingan R4B	15		
	0.2	Preventol CR	15		

Process Flow	%	Chemical	Process Control		
			Time (min)	pH	°C
Drain					
Wash					
Drain					
Setting out					
Hang drying					
Conditioning					
Staking					
Toggling					
Milling					

Note: The amount of chemical in post-tanning process was added to 50% of the actual goat leather weight

Physical Test and Hand Assessment of Leathers

Physical properties of leathers, including tensile strength, elongation, tear strength, and softness, were determined using standard procedures for leather physical tests (SNI 06-1794-1990 and SNI 06-1795-1990). Garment leather tanned with chrome tanning material and garment tanned with vegetable tannin were examined. Hand assessment was done to examine organoleptic properties such as grain smoothness, fullness, and elasticity of leathers. Four experienced tanners measured the level of organoleptic properties with a range of 1-5 points for each property. A higher value represents the better property. The results were then averaged for each property.

RESULT AND DISCUSSION

The tanning process using chrome salts as the main tanning material is almost certain to produce a soft leather (Ahmed *et al*., 2021). Meanwhile, the tanning process using vegetable tannin tends to produce stiff and tough leather. The percentage of vegetable tannin as the main tanning material used in this study is greater than that of chrome salts (Table 3). This is applied because the vegetable tanning process generally uses 20-25% of tannins on the pelt weight (Thorstensen, 1993; Jones, 2000). It is well known that vegetable-tanned leather exhibits fullness character (Sutyasmi *et al*., 2016). Therefore, three aspects to consider in producing garment leather from vegetable tannin are fullness, strength, and softness (Sreeram *et al*., 2010). However, more vegetable tannin used in leather process reduces softness and strength characteristics (Sreeram *et al*., 2010). Hence, the use of vegetable tannin in this study was less than 20%. In addition, restriction on the use of chromium is also a reason for the amount of chromium not being as much as that of vegetable tannin, which is 4-8% (Anggriyani *et al*., 2002).

Table 3. Percentage of material used in garment leather production

Material	Garment from chrome-tanned leather	Garment from vegetable-tanned leather
Main tanning material	7% Chromosal B	5% Tara 13% Mimosa
Aldehyde	3% Relugan GT 50	9% Relugan GT 50
Sulfited oil	15% Eurekanol SFO	12% Derminol SPE 28% Eurekanol SFO

Furthermore, garment leather using vegetable tannin requires more auxiliary materials to increase the softness to achieve the character of garment leather. In this case (Table

3), they were glutaraldehyde and sulfited oil which have the ability to increase the softness of leather (BASF, 2007; Allied Chemicals International Co., Ltd., 2016). Both were used in larger quantities for leather making process from vegetable-tanned leather (9% aldehyde and 40% sulfited oil) than for leather making process from chrome-tanned leather (3% aldehyde and 15% sulfited oil). In this study, chrome-tanned leather requires oil for retanning (4% Eurekanol SFO) and fatliquoring steps (11% Eurekanol SFO), while vegetable-tanned leather uses oil for tanning (12% Derminol SPE) and fatliquoring steps (28% Eurekanol SFO). Oil helps open up fiber structure making the tanning or retanning agents more easily penetrate the skin. In fatliquoring step, oil prevents fiber sticking by lubricating the fiber structure so the skin becomes more resistant to tensile and more elastic (Rachmawati & Anggriyani, 2018). The effectiveness of this step depends on the level to which the oil penetrates the structure of skin. Sulfited oil contains sulfonate and hydroxy sulfonate groups which makes it stable to acids, hard water salts, and metal ions (Covington, 2020). Those groups are able to penetrate well down into the skin leading to increased leather softness and strength (Purnomo *et al*, 2020; Covington, 2020). Hence, the percentage of sulfited oil for leather process from vegetable-tanned leather is greater to complement the tough characteristic of resulting leather.

Aldehyde tanning materials, either formaldehyde or glutaraldehyde, are well known to produce plump leather (Covington, 2020). This plump property gives garment leather the desired character. Similar to the percentage of sulfited oil, the percentage of aldehyde for the leather process from vegetable-tanned leather is larger to get the desired garment leather characteristic.

Besides auxiliary materials, the fatliquoring method is important in increasing leather softness. The use of oil in the garment-making process from vegetable-tanned leather begins at the tanning step to help penetrate vegetable tanning molecules. Oil disperses vegetable tanning molecules so they penetrate easily into the skin. Fatliquoring was also carried out in the post-tanning process through three steps. The first and second steps were done before dyeing, while the third was done after dyeing as top-fatliquoring. A short-float method, which consumes 0% water, was used in the first and top-fatliquoring steps. This method does not use water at all. Water for the process is only sourced from wet skin. Generally, the short-float method is used for manufacturing soft leather (Purnomo *et al.*, 2020). Little water increases the ratio between oil and skin so the oil is more easily transported into the skin.

Unlike the garment-making process from vegetable-tanned leather, the process from chrome-tanned leather involves two fatliquoring steps. This is due to the basic character of chrome-tanned leather already having a softness so a smaller amount of oil is needed to achieve the desired garment characteristic. Both steps were carried out using a medium-float method with 75% water dosage. More water decreases the ratio between oil and skin so the oil does not penetrate too deep into the skin.

The leather produced is then physically analyzed and compared with SNI for garment's standard (SNI 4593:2011) (Table 4). The data show that garments made from chrome-tanned leather exhibits tensile strength (14.7263 ± 2.3931 N/mm^2), elongation (50.5130 ± 7.9329 %), tear strength (23.8759 ± 1.5411 N/mm), and softness (5.9600 ± 0.3209 mm) that meet with SNI (Table 4.). Meanwhile, test results of garments from vegetable-tanned leather meet with the standard for elongation (33.2018 ± 8.3706 %), tear strength (26.6715 ± 8.0992 N/mm), and softness (5.4400 ± 0.4336 mm). Its tensile strength does not meet the standard with a 12.3285 ± 1.4948 N/mm² result. Almost all test results for garments tanned with chrome are higher than those tanned with vegetable tannin. This indicates that chrome-tanned leather gives better physical test results than vegetable-tanned leather (Ork *et al*., 2014). However, the addition of auxiliary materials such as aldehyde and sulfited oil in the process from vegetable-tanned leather is still unable to generate better characteristics than chrome-tanned leather, except for its tear strength. The ability of tanning material to form crosslinks with the skin collagen makes the skin more difficult to tear. Vegetable tannin contains polyphenolic molecules that can bind with the skin via hydrogen and covalent bonds at once and then form crosslinks (Combalia *et al*., 2016; Rosiati & Udkhiyati, 2022; Xiao *et al*., 2023). This creates a strong interaction between the skin and vegetable tanning, making it difficult to torn.

Table 4. Physical properties of garment leathers

Physical Test	SNI 4593:2011	Garment from chrome-tanned leather	Garment from vegetable-tanned leather
Tensile strength (N/mm²)	Min. 14	14.7263 ± 2.3931	12.3285 ± 1.4948
Elongation (%)	Max. 60	50.5130 ± 7.9329	33.2018 ± 8.3706
Tear strength (N/mm)	Min. 12.5	23.8759 ± 1.5411	26.6715 ± 8.0992
Softness (mm)	5 – 7.5	5.9600 ± 0.3209	5.4400 ± 0.4336

Hand assessment was done to compare organoleptic properties of leathers. It is observed in Figure 1. that garment leather tanned with vegetable tannin exhibits better fullness compared to garment leather tanned with chrome tanning material. Vegetable tannin is known to have a higher molecular weight than chrome tanning material (Ding *et al*., 2019). This makes vegetable tannin polymers bonded with skin more compact than chrome polymers. Thus, vegetable tannin produces a better filling effect for leather (Ding *et al*., 2019).

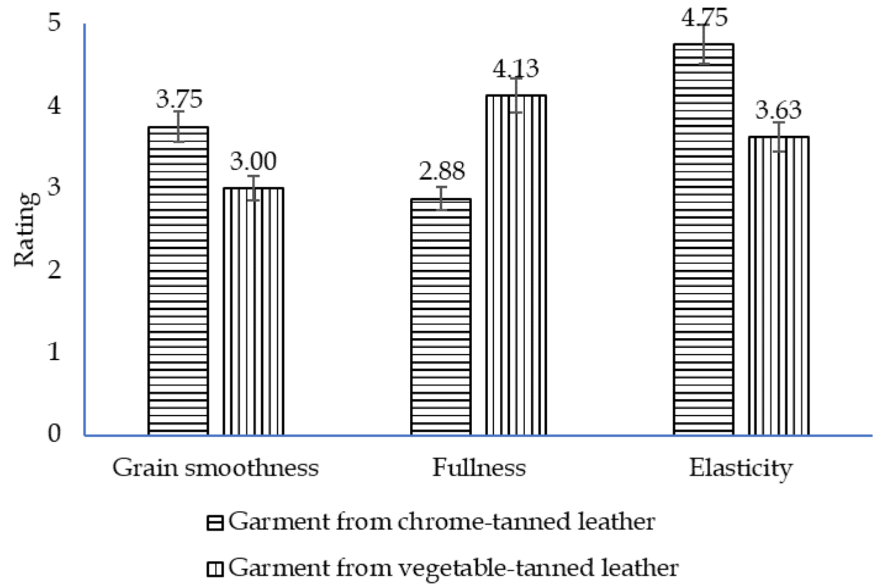

Figure 1. Organoleptic properties of garment leathers

The grain smoothness and elasticity of the garment tanned with chrome are 3.75 and 4.75, respectively. Those values are higher than those of garment leather tanned with vegetable tannin, which are 3.00 and 3.63. Based on physical and organoleptic test results, it is found that more percentages of auxiliary materials, such as aldehyde and sulfited oil (9% aldehyde and 40% sulfited oil) used for garment process from vegetable-tanned leather are unable to produce the softness, smoothness, and elasticity like a garment from chrome-tanned leather.

CONCLUSION

Garment made from vegetable-tanned leather with a ratio mimosa to tara of 5:13 was compared to garments made from chrome-tanned leather, both the production methods and the character of resulting leathers. twos. Chrome-tanned leather requires auxiliary materials and two fatliquoring steps to obtain garment leather characteristics. Vegetable-tanned leather requires more auxiliary materials and fatliquoring steps. Physical test results show that chrome-tanned leather gives better tensile strength (14.7263 ± 2.3931 N/mm^2), elongation (50.5130 ± 7.9329 %), tear strength (23.8759 ± 1.5411 N/mm), and softness (5.9600 ± 0.3209 mm) that meet with SNI. Test results of garments from vegetable-tanned leather meet with the standard for elongation (33.2018 ± 8.3706 %), tear strength (26.6715 ± 8.0992 N/mm), and softness (5.4400 ± 0.4336 mm). Its tensile strength does not meet the standard with a 12.3285 ± 1.4948 N/mm^2 result. More auxiliary materials and fatliquoring steps in the garment-making process from vegetable-tanned leather are still unable to produce the softness, smoothness, and elasticity of a garment made from chrome-tanned leather. It is recommended for further research to combine vegetable tannins with other tanning agents in garment-making process to increase their tensile strength.

CONFLICT OF INTEREST

We certify that there is no conflict of interest with any financial, personal, or other relationships with other people or organizations related to the material discussed in the manuscript.

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