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Approaching Formaldehyde Reduction using Chestnut as Bio Scavenger

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Limitation of formaldehyde emission in glutaraldehyde tanned leather is an important matter to be noticed. According to the reason that glutaraldehyde can be decomposed under several conditions and produce carcinogenic formaldehyde. Global regulations set the permission level of formaldehyde in the leather to only 20-300 ppm (depending on the leather article). The use of bio scavenger is an alternative for reducing formaldehyde in the skin. This research used chestnuts as formaldehyde bio scavengers. Variations chestnut levels to be applied are 1, 3, and 5%. The skin without the addition of chestnuts was prepared as a control. Based on the results obtained, there was a decrease in formaldehyde levels in the leather after the addition of chestnuts. The optimal level of chestnuts needed to reduce formaldehyde levels in glutaraldehyde tanned leather is 5%. The use of chestnuts can be an alternative additive in the production of glutaraldehyde tanned leather which is more environmentally friendly, due to reduction of the potential formaldehyde release.

Keywords: Formaldehyde; chestnut; additive

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Nowadays, leather industrial development demands are not limited to product quality oriented but also the quality of the processing. The quality of the manufacturing process is regulated in various national and international regulation. In principle, the expected quality of the production process is a production process that takes into account the impact on the environment and health. This is a challenge for the leather tanning industry. Aspects of environmental and health impacts are often related to the utilization of chemicals in the tanning process. The emergence of emissions, limitation of chemical absorption, and the use of toxic and hazardous chemicals are real challenges that must be solved.

The utilization of vegetable and aldehyde tanning agent are often applied as an alternative to substitute chromium. Based on environmental aspect, the use of vegetable tanning agent (VTA) certainly be a solutive option. However, so far, the use of VTA as main tanning has not shown satisfactory results espescially in terms of softness and efficiency. In this regard, aldehyde tanning agent is still preferable when compared to VTA which requires a long time in the impregnation process, costly, and low quality of leather [1]. Nowadays, industrial and modified glutaraldehyde has begun to be widely applied in the free-chrome tanning process. The use of these aldehydes has advantages as a substitute for chromium, mainly because it is more economical in terms of cost, and can be applied in the manufacture of leather articles that require soft physical characteristics. However, these materials are known to decompose under some conditions and produce carcinogenic formaldehyde [2]. Limitation of formaldehyde emissions is essential because in global trade the permissible levels of formaldehyde are only 20-300 ppm depending on the leather article [3]. Research on the potential of various materials to prevent formaldehyde release or often called bio-scavenger has been carried out in various fields. However, observations regarding the potential release of formaldehyde on glutaraldehyde tanned skin and prevention efforts using more varied organic materials have not been carried out.

The addition of tannins extracted from white oak bark had an effect on reducing formaldehyde emissions produced by the use of urea-formaldehyde resin in the manufacture of fiberboard panels. Research using 1.2% tannin from mangrove wood has also been shown to have an effect on reducing the formaldehyde content on particle board [4-5]. In the field of leather manufacturing, the use of 4% mimosa had a better effect on reducing formaldehyde levels when compared to quebracho and tara [6]. However, the use of mimosa is known to to affect skin density, so that it can indirectly reduce skin elasticity. This is certainly not profitable in making softy leather. Therefore, it is necessary to identify the potential use of other types of VTA that do not have a negative effect on leather

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softness. Chestnut can be the option due to the different type of tannin and lower molecular weight. Chestnut trees are tannin-rich, with high levels of both procyanidins (condensed tannins) and ellagitannins (hydrolysable tannins) [7]. Utilization of tannin from chestnut flour has succeeded in reducing the formaldehyde content in the manufacture of Medium Density Fiberboard (MDF) [8]. There is a fundamental chemical structure difference between wood and skin, yet there is no study that has identified the effect of tannin on the potential for formaldehyde release in glutaraldehyde tanned leather. The aim of this work are to observe the formaldehyde release and identify the use of chestnut (*Castanea sativa*) as a formaldehyde bio scavenger on glutaraldehyde tanned leather.

MATERIALS AND METHODS

Materials

Glutaraldehyde tanned leathers were prepared from pickle sheepskins, purchased from local tannery in Yogyakarta. Glutaraldehyde (Rellugan GT-50) was used as main tanning agent. Chestnut (*Castanea sativa*) (SODA) as formaldehyde bio-scavenger applied in three variations (1, 3, 5% w/w).

Methods

Leather Preparation

Leather tanning process was conducted using pickle sheepskins as raw material. Modification of the retanning material in the form of chestnuts with a concentration variation of 1, 3, 5% (w/w) was applied as a formaldehyde bio scavenger. The stages and details of the formulation of the tanning process can be seen in Table 2.

Characterization

The identification of the formaldehyde level conducted in chemicals as initial identification, leather, and spent tanning liquor. The identification was carried out using UV-Vis Spectrophotometry method. Functional group characterization was carried out using FTIR to determine changes in functional groups in the leather.

Table 1. Tanning Formula and Stage Processing.

Process	Chemical (%)	Time (minutes)
Tanning	100 % H_2O	
	15% NaCl	90’
	3% Glutaraldehyde (Rellugan GT 50)	
	1% NaHCOO	3x10’
	1,5% $NaHCO_3$	3x10’
Drain		
Post Tanning		
Retanning	100% H_2O	
	3% Acrylic Resin (Tergotan ESN)	
	3% Melamin Resin (Sertan RD)	60’
	1,5% Naphtalene Syntan (Coralon OT)	
Bio Scavenger addition		
	1,3,5 % Chestnut	60’
Fixation	1,5% Oxalic Acid	3x15’
Drain-Wash		

Table 2. Initial Identification of Formaldehyde Content.

Chemical	Formaldehyde Content (%)
Glutaraldehyde (Relugan GT 50)	18.22%
Acrylic Resin (Tergotan ESN)	0.01%
Melamin Resin (Sertan RD)	0.04%

RESULTS AND DISCUSSION

FTIR Characterization

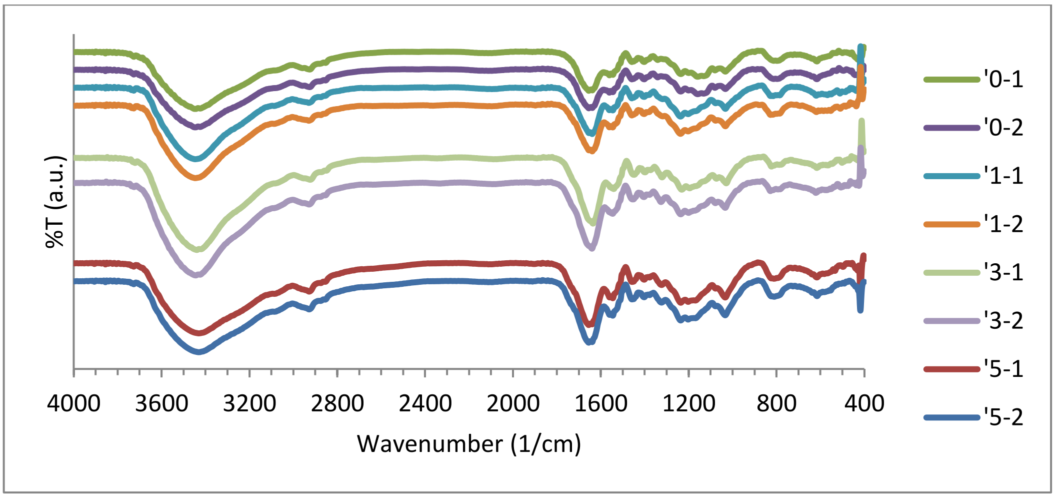

Figure 1. Infrared spectra (a) (control) 0-1, (b) (control) 0-2, (c) (1% chestnut)1-1, (d) (1% chestnut) 1-2, (e) (3% chestnut)3-1, (f) (3% chestnut) 3-2, (g) (5% chestnut)5-1 dan (h) (5% chestnut) 5-2.

Figure 1 showed the presence of an amide group I, an amide group II, an amide group III, a methylene group and a hydroxyl group. The absorption band of the amide I group was detected at wave numbers 1639-1656 cm^{-1} as a stretching vibration of the carbonyl group (C=O) [9-10]. The amide group II was observed at wave numbers 1545-1546 cm^{-1} as C-N stretching vibrations and overlapping with N-H bending vibrations [11-13]. The absorption band of the amide group III appears in the wave number region of 1235-1237 cm^{-1} as a stretching vibration of the carboxylate group [14]. The absorption of the methylene group is not very visible but appears at wave numbers 1450-1460 cm^{-1} and 2925-2929 cm^{-1} as asymmetric bending and stretching vibrations [15] [10]. The vibration of the hydroxyl group was observed in the wave number range of 3424-3446 cm^{-1} [16].

The use of glutaraldehyde as a tanning agent did not produce new absorption bands. This is because glutaraldehyde contains –CH and C=O bonds which are also present in the initial skin. The use of chestnuts also did not result in new absorption bands. This happens because chestnuts, which are natural tanning materials, generally have absorption in the wave number region of 1034-1080 cm^{-1} and 3400 cm^{-1}, where it is known that the absorption band in this area overlaps with the stretching vibrations of –CO and –OH from the skin [9, 17]. However, the hydroxyl group of vegetable tanning agent causes an increase in the absorption intensity of –OH both at wave numbers 1639-1656 cm^{-1} and 3423-3446 cm^{-1}. The greater the number of chestnuts used, the greater the intensity of this –OH absorption band.

Identification of Formaldehyde Level

Based on the formaldehyde level identification, it is known that formaldehyde release occurs in glutaraldehyde tanned leather with an average value of 0.301% (3010 mg/kg). It proves that there is formaldehyde emission from glutaraldehyde tanned leather. According to Covington (2009), although so far it is believed that it can be used as an alternative that is more environmentally friendly, it is known that glutaraldehyde has the potential to cause emissions as well as formaldehyde [18]. This level is far above the maximum level required by the American Apparel and Footwear Association (2014), which is 20-300 ppm [3].

Table 3. Formaldehyde Levels in Leather.

Treatment	Formaldehyde Level (average, %)	Formaldehyde Level (average, mg/kg)	Formaldehyde Reduction (%)
Control	0,301	3010	0
Chestnut 1%	0,234	2340	22,26
Chestnut 3%	0,217	2175	27,74
Chestnut 5%	0,172	1725	42,69

Table 4. Formaldehyde Levels in Spent Tanning Liquor.

Treatment	Formaldehyde Level (mg/L)
Control	7.35
Chestnut 1%	17.11
Chestnut 3%	19.43
Chestnut 5%	22.76

Decreasing level of formaldehyde occurred after the addition of chestnuts at all treatment variations (1.3 and 5% levels) (Table 3.). This is influenced by the phenol content in chestnuts which affects the reduction of formaldehyde. The mechanism of formaldehyde reduction by tannin is influenced by the reaction between the phenol group (-OH) in tannin and formaldehyde [19]. As described by Sprengling and Freeman (1950), theoretically the phenol group can react with formaldehyde only in the ortho and para positions [20]. The use of chestnuts at the 5% level showed the most significant trend of decreasing formaldehyde levels, namely 42.69%. This was consistent with the increase in the phenol content of the leather with the addition of chestnuts, as confirmed by the skin characterization (FTIR).

The decreasing of formaldehyde levels in the leather was followed by changes in formaldehyde levels in the waste. Table 4. showed that after adding chestnuts there was an increase in formaldehyde levels in the waste solution. This can be explained because the effect of the acid from chestnuts resulted in a decrease in the reactivity of glutaraldehyde tanning agents on the skin and the tendency to hydrolyze formaldehyde resin derivatives. This is caused by the structure of chestnuts which are esterified components of gallic acid and glucose [18], and have a tendency to acidic pH (3.5) [21]. Thus resulting in an increase in dissolved formaldehyde levels in the waste influenced by the hydrolysis of formaldehyde derivatives due to an acidic pH [19].

CONCLUSSION

This study showed that there is formaldehyde emission in glutaraldehyde tanned leather. Based on the formaldehyde level identification, it is known that formaldehyde release occurs in glutaraldehyde tanned leather with an average value of 0.301% (3010 mg/kg). Chestnut can be an alternative additive in the manufacture of glutaraldehyde tanned leather which is more environmentally friendly, because it can reduce the potential for formaldehyde levels. The optimal level of chestnut needed to reduce formaldehyde levels in glutaraldehyde tanned leather is 5%.

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