Hydrolysis of leather shavings waste for protein binder

I F Pahlawan, S Sutysmi and G Griyanitasari

Center for Leather, Rubber, and Plastics, Ministry of Industry, Yogyakarta, Indonesia

E-mail: iwan.fp@kemenperin.go.id

Abstract. The objective of the research is to treat the leather shaving scrap to reuse it in the leather production as protein binder. The treatment was conducted by hydrolysed the scraps with sodium hydroxide in 90°C with different concentration (1%, 2%, and 3%) and time of hydrolysis (1 hour, 2 hours, and 3 hours). The hydrolysis resulted in two forms of substance, liquid and solid. The liquid substance, which is collagen protein, was then observed for its viscosity, protein content and chrome content. Furthermore, analysis of amino acid was conducted by liquid chromatography-mass spectrometry (LCMS). The result showed that the treatment with 3% sodium hydroxide for 3 hours could produce the best protein binder with 6.64% protein content, 47.55 ppm chrome content, and the viscosity at 16.9 cp. The protein binder contains the amino acid, such as arginine, glycine, aspartic acid, glutamic acid, proline, lysine, and valine. The binder has the potential to replace the common binder, which mainly from casein, used in the leather producers. It is important to know the quality of leather finished by the protein binder. Thus, further study could be explored to apply the binder for various leather finishing applications.

1. Introduction

Agro-industry deals with the processing of agricultural product, either from plant or animal, to increase the value of agriculture product. Leather tanning industry, as an animal-based processing industry, has a contribution to the development of agro-industry. The technology in animal product processing has transformed the wasted raw hides or skins into exclusive leather and leather goods. Among all technology in the leather tanning process, the use of chrome tanning agent is the most favorite tanning agent used in the tanneries [1]. Chrome tanning agent has more advantages than other tanning agents, in term of thermal stability as well as physical properties. Unfortunately, chrome-contained waste has been a major concern in the tanneries for years. Globally, leather tanning industry generated chrome-contained solid waste 600,000 metric tons every year [2]. The effort to minimize the waste or reuse it would be a breakthrough for the leather tanning industry.

Chrome waste exists from the use of chrome tanning agent in the tanning process. Chrome waste includes in the wastewater, sludge, shaving scraps, buffing dust, etc. Several studies have been investigated in processing the by-product of leather tanning process which contains chrome. Chrome leather wastes have been modified into new materials or used it as a component for producing new materials, such as composites for shoes in-soles [3]; particle board [4]; and art paper [5]. Most of previous researches focused on how to utilize the chrome leather waste for producing new products for other industries. Meanwhile, the leather tanning industry needs improvement to gain more profit. The
industry waste seems to be potential to be explored for its application back in the industry, whether for whole process or partly.

As the concept of Reduce, Reuse, Recycling (3R), it is essential to reuse the waste generated from the industry in the industry. Benefits could reaches broader aspects not only environmental aspect, but also economical aspect as well as social aspect. Thus, leather tanning industry could sustain and contribute to greener environment. Thus, the objective of the research is to treat the leather shaving scraps to reuse it in the leather production as protein binder.

2. Materials and Methods

2.1. Materials

This study used leather shavings waste as main material, where those were obtained from two tanneries located in Piyungan Leather Tanning Industrial Estate, Bantul, Yogyakarta. The waste was scraps obtained from the adjustment of wet blue leather thickness by using leather shavings machine before entering the post-tanning process. Sodium hydroxide was procured from local supplier. The equipment used during the research included water bath, beaker glass, plastics filter, paper filter, thermometer and stirrer.

2.2. Methods

2.2.1. Leather shavings characterisation

Leather shavings scrap were prepared for analysis of water content, protein content, and total chrome content. The chrome content was the total chrome contained in the shaving waste. It was determined using Atomic Absorption Spectroscopy (AAS) technique. While, the protein and water content in the shaving waste was determined using Kjeldahl and oven method, respectively, according to AOAC [6].

2.2.2. Leather shavings hydrolysis

The shaving scraps was added and stirred with sodium hydroxide solution with ratio 1:5. The concentration of sodium hydroxide was varied 1%, 2%, and 3% (w/w). Then, it was heated in a water bath (Memmert) at the temperature of 90°C. The hydrolysis time was also varied for 1, 2, and 3 hours. The hydrolysate was, then, separated between collagen protein and chrome through filtering process with 200 mesh filter paper. Sulphuric acid was added to adjust the pH of collagen protein at 7. Subsequently, formaldehyde was added to the collagen protein as the preserving agent.

2.2.3. Physical and chemical properties

The physical properties of the hydrolysates were examined by the viscosity of the collagen protein obtained from the hydrolysis. The measurement was done by a viscometer. The hydrolysates were also investigated for its chemical properties, i.e. chrome content and protein content.

2.2.4. Amino acids analysis

The amino acid measurement in the collagen protein was determined with Liquid Chromatography-Mass Spectrophotometer (LC-MS).

3. Results and Discussion

Leather shavings wastes taken from the tanneries were observed for its characteristics. The wastes were collected from the tanneries which applied full-chrome tanning process for producing wet blue leather. Consequently, the total chrome content was majority in the wastes. Table 1 exposes the properties of leather shavings scrap before treated.

It can be shown that the chrome content of the sample reach more than 20,000 ppm. It indicates that the samples originated from full-chrome leather. In addition, it is a common range for chrome-tanned leather [7]. The figures in Table 1 will be the basis for further treatments of the waste to obtain the protein binder.
Tabel 1. The shavings scrap characteristics.

| Properties            | Samples  |
|-----------------------|----------|
| Chrome content (ppm)  | 23,176.14|
| Protein content (%)   | 52.26    |
| Water content (%)     | 43.67    |

3.1. Physical property

Visually, the hydrolysis of the waste creates changes in the form of sample. Heat and agitation affect the hydrolysate to coagulate with specific viscosity. Figure 1 shows the viscosity of the protein hydrolysates with different concentration of sodium hydroxide and time of hydrolysis. The viscosity of the hydrolysates ranged between 3-14 cp after 1 hour of hydrolysis for all treatment. After 2 hours of hydrolysis, the treatment of 2% and 3% sodium hydroxide created a sharp increase for the hydrolysates’ viscosity, while the treatment of 1% sodium hydroxide increase the viscosity slightly. The gap of the sample’s viscosity was decrease after 3 hours of hydrolysis. The Figure 1 indicates the longer hydrolysis time could increase the viscosity of the hydrolysate.

![Figure 1. Viscosity of the hydrolysates.](image)

The graph shows that time makes the hydrolysates more viscous. Hydrolysis of leather shaving scraps with the alkaline 1% presents the gradual increasing of hydrolysate’s viscosity. The other treatments, however, seem to be more reactive in increasing the viscosity. In two hours, 2 and 3% of NaOH could tighten the empty space around the protein. Hence, the amino acids chain would not be broken. It could indicates the condition of protein when the hydrolysis applied with specific temperature and time [8]. As the hydrolysate was obtained from leather scraps, it contains collagen protein which most of it composed by hydroxyproline. According to Zhang et al. [9] the changes in the collagen protein viscosity are caused by the denaturation process where the triple helical structure of the collagen is breakage. The treatment shows that time of hydrolysis in a steady temperature created the hydrolysates at a close range of viscosity.

3.2. Chemical properties

As physical property, chemical properties were investigated to examine the hydrolysates. It is important to observe the chrome content after the treatment of hydrolysis. The chrome content of the hydrolysates seems to gradually decrease, as shown in Figure 2. It can be shown that extend the
hydrolysis time could decrease the chrome left in the hydrolysates. The graph shows that the decreasing of the chrome content is ranged between 35.9% and 60.6% during the time of hydrolysis for all treatments. The trend shows that the hydrolysis with 1% NaOH resulted lowest reduction for chrome content in the hydrolysate.

Wionczyk et al. [10] stated that the alkaline hydrolysis has created insoluble trivalent chromium from soluble state of its hydroxocomplexes. Furthermore, the temperature used for hydrolysis at 90°C foster the chrome to be dissolved. It confirms the argument of Ting-da et al. [11] in determining the temperature that affect the chromium content in the chrome-contained leather waste.

While the chrome reduction seems linear, the protein content of the hydrolysates shows different trend. The range of protein content of the hydrolysates is 4.50-6.76, where the hydrolysis time of 3 hours resulted in protein content at 6% (Figure 3). It is interesting to compare the protein content with different time of hydrolysis, between 1 hour and 3 hours.
Figure 3 indicates that the hydrolysis will create a reaction that brings to a steady range of protein content. The hydrolysis of chrome-containing leather waste related to a fractionation of protein in aqueous condition. Typically, hydrolysis in alkaline condition is influenced by the type of alkali used for hydrolysis, pH condition, as well as temperature and time of hydrolysis [12]. Ting-da et al. [11] argued that the time of hydrolysis will improve the extraction of protein with lower molar mass. In order to confirm it further an analysis could be observed through amino acids analysis.

3.3. Amino acids analysis

The collagen protein derived from leather shaving waste was determined its amino acid qualitatively and quantitatively. Table 2 expresses the amino acid detected in the protein binder with LC-MS instrument. It can be shown that amino acid of arginine is the majority in the hydrolysates, followed by glycine, aspartic acid, glutamic acid, proline, lysine and valine.

It is contrary with the finding of Mu et al. [13], which argued that alkaline amino acids, such as arginine and histidine, resist to protein hydrolysis. Thus, they are common in the un-hydrolysed substrates. It is possible to happen due to the filtration condition during the treatment, which makes the substrates flow through the filtrate and contaminate the hydrolysates.

| Amino acid     | Result   | Unit    |
|----------------|----------|---------|
| Aspartic Acid  | 5,057.00 | mg/kg   |
| Serine         | 34.80    | mg/kg   |
| Glutamic Acid  | 3,160.60 | mg/kg   |
| Glycine        | 7,338.30 | mg/kg   |
| Threonine      | 8.10     | mg/kg   |
| Cystein        | 34.80    | mg/kg   |
| Alanine        | 29.80    | mg/kg   |
| Tyrosine       | 8.10     | mg/kg   |
| Proline        | 3,022.90 | mg/kg   |
| Methionine     | -        | mg/kg   |
| Valine         | 1,491.90 | mg/kg   |
| Isoleucine     | 522.70   | mg/kg   |
| Leucine        | 651.40   | mg/kg   |
| Phenylalanine  | 837.00   | mg/kg   |
| Histidine      | 439.50   | mg/kg   |
| Lysine         | 2,658.10 | mg/kg   |
| Arginine       | 9,137.30 | mg/kg   |

4. Conclusion

The leather shaving wastes is potential to reuse in the leather production process. According to several properties resulted, hydrolysis of the waste with NaOH 1% for 3 hours could be used for protein binder in leather finishing process. However, it is important to evaluate the resulted leather when use this protein binder. Thus, further investigation could be explored the application of protein binder derived from leather shavings scrap in leather finishing process.

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