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THE PROSPECT OF SHRIMP SHELL WASTE AS RAW MATERIAL IN THE GELATIN PRODUCTION

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ABSTRACT

Gelatin has been widely used in the food and pharmaceutical industries, e.g. as clarifier, thickener, emulsifier as well as foaming agent. Most commercial gelatins are produced from cow bone and skin as well as pig bone and skin. In the future this might become a serious problem because of the increasing demand of beef bone and skin for food as well as the “un-halal” aspect of “pig” gelatin. This condition reflects the need of study to produce gelatin from other sources such as shrimp shell waste. Shrimp shell consists of 25-40% protein, where the protein itself comprises of 60-75% collagen that can be converted to gelatin. Generally, gelatin is made through 3 steps, i.e. preparation of the raw material, demineralization and extraction. This research was aimed to study the effects of HCl solution concentration in the demineralization step, as well as the extraction temperature and extraction time to the yield of gelatin. Fourier Transform Infra Red (FTIR) was used to confirm the presence of gelatin in the final product. The results showed that the highest yield (32,1%) was produced using 9% HCl solution in the demineralization step, as well as the extraction temperature of 70°C and the extraction time of 3 hours in the extraction step. The characterization using FTIR shows that the gelatine produced from shrimp shell has the fungsional group of O-H (3600 cm^{-1}), C-H (2970 cm^{-1}), C=O (1690 cm^{-1}) and secondary N=H (1540 cm^{-1}) which are similar to the commercial gelatine made from cow skin. Various tests were also conducted, including moisture content (=14%), ash content (=10, 2%), protein content (=75, 8%), pH (=5), melting point (=32, 1°C), viscosity (=2, 8 cP) and Bloom gel strength (=76, 9 g). The results indicate the high quality of the produced gelatin, which is similar to commercial gelatin. Therefore, the use of shrimp shell waste as raw material in the gelatin production is quite potential.

Keywords: gelatin, hydrochloric acid, shrimp shell waste.

INTRODUCTION

Gelatin is a denaturalized protein that is derived from collagen and usually extracted from cattle bones and skins as well as pig skins. It is a transluscent brittle solid substance, colourless or slightly yellow, nearly tasteless and odourless. Every year, around 200.000 metric tonnes of gelatin is used in many kinds of industries (1). Beside in the form of sheet, nowadays gelatin is also available in granular powder (2). Producing gelatin from cattle has 2 main problems. The first problem is the aspect halal in slaughtering process of the cattle, while the second problem might be the spreading of mad cow disease or Bovine Spongioform Encephalopathy (BSE). Meanwhile gelatin produced from pig skins is not halal for Moslem and it is also not acceptable for Judaism (3). As the increasing of human population, in the future the demand of gelatin might also increase. Therefore, exploring the alternative raw materials to produce gelatin should be conducted.

A number of researchers have studied on the use of mammalians, poultries as well as fishes as the raw materials to produce gelatins. Badii and Howell (3) used horse mackerel skin , while Takeshi T. and Nobutaka S. (4) tried some fish products such as skin collagen of bullhead shark (*Heterodontus japonicus*), bone collagen of skipjack tuna (*Katsuwonus pelamis*), and fin collagen of Japanese sea-bass (*Lateolabrax japonicus*). The other researchers were Irwandi *et al*. (5) who used kerapu (*Epinephelus sexfasciatus*), jenahak (*Lutjianus argentimaculatus*), kembung (*Rastreligger kanagurta*) and kerisi (*Pristipomodes typus*). In addition, H.Y. Liu *et al*. (6) have succeeded in using Channel Catfish (*IctalurusPunctatus*) head bones. More over, Mariod *et al*. (7) have prepared gelatines from two Sudanese insects, i.e. melon bug (*Aspongubus viduatus*) and sorgum bug (*Agonoscelis pubescens*).

As the growing interest in developing alternative raw materials, the use of sea animals’ by-product might be prospective. One of them is the shrimp shell waste.
Every year Indonesia exports around 80.000 tons of shrimp meat, where the solid waste of the shrimp can be converted to gelatin. Accordingly, the conversion of shrimp shell waste to gelatin would enhance the economic value of the waste and also solve the environmental pollution problem.

Shrimp shell consists of 25-40% protein, 15-20% chitin and 45-50% calcium carbonate (8) where the protein itself comprises of 60-75% collagen, 4-5% elastine and 20-35% keratine (9). Among all of the protein, only collagen can be converted to gelatin, because collagen has hydroxyproline which acts as gel builder (10). The conversion steps of collagen to gelatin are random breaking of some peptide bonds, breaking of helix side bond and the configuration modification to reach the chain stability (11). Due to the strong complex bond built by protein, chitin and calcium, demineralization process should be conducted to break the bond.

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MATERIALS AND METHOD

This research consisted of four steps, i.e. 1) material preparation 2) demineralization 3) solvent extraction, and 4) characteristics analysis of gelatin. Characteristics that will be analyzed include water content, protein content, ash content, and melting point, viscosity of the solution and gel strength.

Materials preparation

Shrimp shell was obtained from PT. Bumi Menara Internusa, Surabaya. Upon arrival at the laboratory, the visible fat was mechanically removed, while the shrimp shell was washed with warm water and slight ethanol before stored in the freezer until it was used for the experiments. Prior to be used, the shrimp shell was allowed to reach room temperature, and dried under the heat of the sun, crushed and sieved until (-40/+60 mesh). Chemicals used in this experiment, i.e. hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3), oxalic acid ($H_2C_2O_4$), Na borax and NaOH were supplied by PT. Berkat Jaya, Surabaya.

Demineralization

The shrimp shell powder was soaked in a HCl solution for 24 hours at room temperature with a ratio of shrimp shell powder and HCl solution was 1:6 (m/v). In this study, the concentrations of HCl solution used were 3, 5, 7, and 9 % to study the effect of acid concentration on the yield of gelatin. After that, the solid was separated from the acid solution, and then washed with distilled water until the shrimp shell powder obtained the pH of 5.

Solvent extraction

The shrimp shell powder was extracted with demineralized water at a ratio of 1:4 (w/v). Extraction performed at 60, 65, 70, 75, and 80°C for 1, 2, 3, 4, 5, 6, 7 and 8 hours until a constant yield of extract. The solution was filtered from shrimp shell solids with Whatman filter paper No.42, and then dried by vacuum oven until constant weight is obtained. Finally, gelatin powder was weighed.

Characteristics Analysis

Gelatin powder which is the largest yield of all operating condition was analyzed by FTIR. Besides, some tests were conducted, consisted of moisture content, ash content, protein content, pH, melting point, viscosity of the solution and gel strength.

RESULTS AND DISCUSSIONS

The effects of HCl concentration, extraction temperature and extraction time to the yield of gelatin are shown in Figure-1:

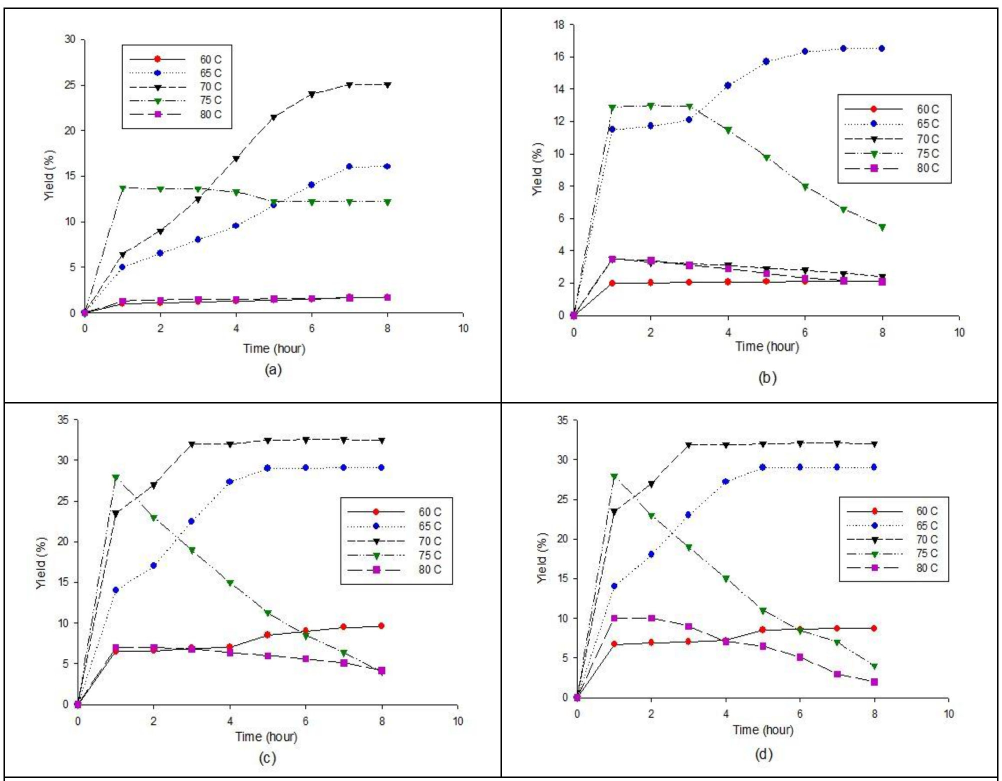

Figure-1. The effect of extraction time and extraction temperature to the yield of gelatin for (a) 3%HCl, (b) 5% HCl, (c) 7% HCl, (d) 9% HCl.

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At the extraction temperature of 60-70° C and at the same extraction time, the increasing of yield occurs as the increasing of the acid solution. This is because the higher concentration of acid will be more effective, so that the yield can be increased in a relatively short extraction time. In the extraction temperature of 75-80°C and at the same extraction time, there is a sharp decrease of yield as the increasing of acid concentration. This is due to the increasing number of peptide bonds in the chain termination collagen. With the breaking of many bonds in the peptide chain and inter-chain helical collagen, gelatin hydrolysis process does not require heating to high temperatures. Excessive heating will cause damage that can reduce the yield of gelatin.

At the same acid concentration and extraction time, there is an increased yield at a temperature of 60-70°C and a decrease in the yield at a temperature of 75-80°C. Heating at 60-70°C which is above the shrinkage temperature of collagen can help the decomposition of the triple helix collagen fibers into gelatine and increase the diffusivity of gelatine in water so that the yield can be increased. However, the extraction temperature which is too high such as 75 and 80°C can result in thermal denaturation of proteins. Consequently, the gelatin becomes insoluble in water and will separate from the extract during filtration and reduces the yield of extraction (12). The extraction conducted at the damage temperature of gelatin, which is 80ºC (13), will cause damage in a shorter time than the lower extraction temperature (12).

At the same temperature and acid concentration, at the beginning of extraction the yield of gelatin increases. Then in the next time interval, the yield will be constant for the extraction temperature of 60-70°C. This is because at the beginning of extraction, which is the first time the skin is contacted with solvent, shrimp peel located on the surface of solids will be directly hydrolyzed and the formed gelatin will be extracted immediately. At the next time interval, the extraction comes from the inside solids. Therefore, the extraction rate is lower than at the beginning of extraction. After a certain time interval, the extract yield tends to be constant because the solution has reached a point of equilibrium so that the solvent can no longer extract (14). At 75 and 80°C, the longer the extraction time, the yield will decrease due to the increasing excess of heat energy that goes into the extraction system which can increase the protein breakdown. From the research, the conditions that produce the highest yield is soaking with 9% HCl and extraction temperature of 70°C for 3 hours.

Fourier Transform Infra Red (FTIR) analysis in this study is used to validate that the substance is really obtained in the extraction of gelatin. The results are shown at Figure-2 as follows:

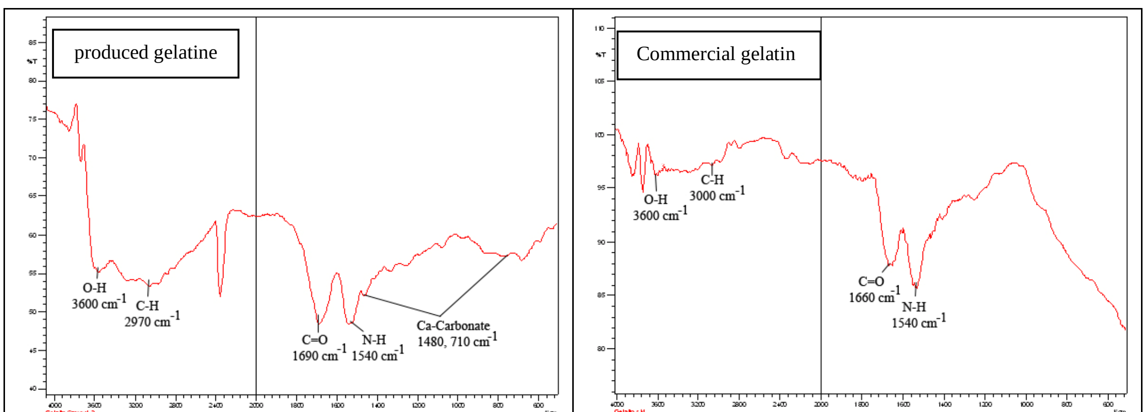

Figure-2. FTIR Analysis of Produced Gelatin and Commercial Gelatin.

Gelatin is a protein compound with distinctive marker amino acids, namely hydroxyproline and glycine. Thus, the gelatin will have an OH group of hydroxyproline, C=O and NH as a marker peptide bonds, and CH as the identity of the carbon chain. For comparison, commercial gelatin type A made from cow bone was used.

FTIR analysis of the results showed that both the extracted gelatin and commercial gelatin made from cow bone has functional groups OH, CH, C=O, and NH secondary. In the produced gelatin, the OH peak appears at wave number 3600 cm^{-1} while the commercial gelatin at wave numbers 3569 cm^{-1}. The OH peak is generally found in the range of wave numbers 3600-3200 cm^{-1} (15). The peak of C=O of gelatin extracted appears at wave numbers 1692 cm^{-1} while the commercial gelatin at wave number 1697 cm^{-1}. The peak of C=O which is a typical marker proteins are generally found in the range of wave numbers 1800-1650 cm^{-1} (15). The NH peak of gelatin product is in 1544 cm^{-1} while the commercial gelatin contained in the 1535 cm^{-1}. This is consistent with the literature in which the FTIR spectra of secondary NH group functions as a marker cluster gelatin chain amino acids contained in the wave number range of 1600-1460 cm^{-1} (15). The CH visible peak overlap on the graph spectra gelatin and gelatin extracted commercially respectively located at wave numbers 2973 cm^{-1} and 2971 cm^{-1} can be identified as the carbon chain of the gelatin molecules. The CH peak wave numbers are in the range of 3000-2840 cm^{-1} (15).

The characteristics of extracted gelatin at the highest yield and the commercial gelatin are shown in Table-1.

Table-1. Characteristics of gelatin

Characteristics	Gelatine produced in this research	Commercial gelatin
Moisture	14%	8.4%
Ash	10.2%	0.9%
Protein	75.8%	90.7%
Melting point	32.1°C	31.4°C
pH	5	5
Viscosity	2.8 cP	2.7 cP
Bloom gel strength	76.9 g Bloom	100.3 g Bloom

On the analysis of the characteristics of gelatin, gelatin produced a maximum yield still not meet the ISO standard gelatin in ash content parameters. The ash content is quite large, indicating demineralization process is less effective. Shrimp shell as a material that has a high calcium levels are also a factor that complicates demineralization (8). Therefore, it is necessary to add the salt precipitation process to the extract solution or conducting additional demineralization to remove the minerals on the shrimp shells to obtain product that meet the standards of gelatin.

CONCLUSIONS

The results show that the higher the concentration of acid solution produces the higher yield, but it can make gelatin more susceptible to thermal damage. The higher the extraction temperature produces the higher yield but decreases at damage temperatures of the gelatin. The longer the extraction time, yield increases to approximately constant, but decreases if the extraction is conducted at temperature damage. The operating condition which produces the highest yield is soaking with 9% HCl solution, extraction temperature of 70ºC, and extraction time of 3 hours. Characteristics of gelatin obtained as the largest yield has met Indonesian National Standard (SNI) on water content and pH value, while the ash content is not yet meet the standards. Therefore, further research might be conducted to decrease the ash content and to increase the protein content.

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