SEM morphology, porosity, swelling and hardness test of foam from dried albumin -gambier tannins

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Abstract. Phenolic foam is a product of natural albumin made from gambier tannins, water, and other additional substances. The interaction of albumin and tannin polyphenols can be considered as complex formation because of the secondary bonds that exist between them. Albumin-based foam is produced by a high-speed mixing system, therefore obtaining a homogeneous emulsion of gas dispersion in the oven-dried liquid. The aim of this study was to examine the morphological structure, porosity, swelling, and hardness of a foam made from several concentrations of dried albumin mixed with gambier tannins. The results showed that there were large, small, regular and cracked pore structures, with an average porosity of 73.16%, swelling of 45.55% and hardness of 22.09 (N/cm²) depending on albumin concentration used.

1. Introduction
Gambier is a group of natural polyphenol compounds which are secondary metabolites of certain plants. Complex phenolic compound like tannins are soluble in polar solvents such as water (especially in hot water), methanol, ethanol, and acetone [1].

The making of natural foam from gambier tannins by the aeration process of its constituent compounds. The final product of this method is known as albumin-tannin foam. When compared with standard cellular solid foam, it has almost the same physical and chemical compositions, with no difference in mechanical and thermal properties. Furthermore, they have the same pore structure, with exception of the larger cell size in the egg white tannin-based foam. This method is not only easy, fast and economical, but also allows the production of solid foams of different cell sizes, which can be controlled by the concentration of albumin-tannin in the initial solution [2].

Studies on the preparation of tannin-based products from gambier extract can be used to make natural foam using egg whites as an additive, hexamine as hardener, and acid as a catalyst. An increase in the amount of gambier extract used can effect the compressive strength of the foam [3], and the presence of natural OH group compounds in the tannins can be chemically altered for the purpose of polymer, synthesis, such as wood adhesives, epoxy resins and in making foam. Extensive research has been carried out in the use of tannins in foam production [2, 4-15], with different results depending on tannins and additives used.

The increase in the use of gambier powder concentration by means of albumin preparation affects several values, such as form density, compressive strength, swelling rate, pH and porosity. The higher
the addition, the denser the resulting foam. Furthermore, SEM results with a magnification power of 150x show that the microscopic structure of the foam is porous. In general, its physical nature is always sturdy and strong during and after storage with the addition of gambier powder.\textsuperscript{[16]}

The interaction between tannin polyphenols and proteins can be considered a complex formation due to the presence of secondary bonds between their structures. It is almost the same as the interaction between tannins and collagen in the skin and in the protein constituent of grapes. Therefore, the interaction of two materials makes the protein insoluble by modifying a certain tertiary structure and foaming hydrogen and van der Waals bond in the protein. In this case, the difference in flavonoid tannin reactions most likely depends on the type and distribution of the different oligomers from certain tannin extracts, the position and number of hydroxyl groups, the average amount of molecular mass, the average weight and solubility of tannin in the reaction medium, and isoelectric point of protein used.\textsuperscript{[17]} Based on this, was making foam study with the aim was to examine the morphological structure, porosity, swelling, and hardness of a foam made from several concentrations of dried albumin mixed with gambier tannins.

2. Methodology
The raw material of this study are albumin and tannins from gambier. The albumin used was obtained from broiler eggs (\textit{Gallus domesticus}), while raw gambier came from Lima Puluh Kota Regency. The additional ingredients used are hexamine, paratoluene sulfonic acid (pTSA) and aquades.

The equipment used are mixer, oven, weighting scale, 80 mesh sieve, digital pH meter from Hana, pressure resistance tester from Cesar GaldabiniGallarate (Italy). Texture analyzer made in the U.S.A, beaker, measuring cup, spatula, analytical balance (presica), pyrometer, and stopwatch.

2.1. Research design
The study was conducted by examining the effect of using different amounts of albumin (A (16%), B (24%), andC (32%)) on the foam manufacturing process, while considering its morphology, pore size, and degrees of swelling and hardness. Furthermore, the production consists of several steps, such as the preparation of dried albumin, preparation of gambier tannins and making foam.

2.2. Research implementation
2.2.1. Preparation of gambier tannins.Gambier is mashed, aquades (1:10) are added, then the extraction process is performed at $\pm 80^\circ$C for 15 minutes and filtered using filter paper. The extract is then dried on a rotary vacuum evaporator and crushed until it passes through an 80 mesh sieve to obtain a powdered form.\textsuperscript{[3]}

2.2.2. Preparation of dried albumin. Chicken eggs that have been separated between egg whites and yolks are placed on a stainless pan and dried on a bath at $\pm 60^\circ$C for 48 hours. After the drying and slab-shaping process, they are mashed into powder until the particles are able to pass through the 80 mesh sieve.\textsuperscript{[3]}

2.2.3. The process of making foam. The form manufacturing process is by preparing albumin (according to treatment), and mixing with tannin (14%), water and additional additives (pTSA, hexamine). The mixture is stirred $\pm 1000$rpm for 15 minutes to foam homogeneous liquid foam. Thereafter, the drying process is performed using an oven at a temperature of $\pm 100^\circ$C for 2 hours.

2.3. Analysis and observation
2.3.1. Observation of the scanning electron microscope (SEM). The morphology of the foam surface was observed using a Scanning Electron Microscope (SEM) test, type S-3400N Hitachi with a magnification of 100 times. The sample preparation was carried out by the technique of coating its surface with dry gold (Au), the diameter was 1cm and the maximum height was 5 mm. The operating conditions are a voltage of 10.0 kV and current of 0.5 mA.
2.3.2. Characteristics of the pore structure \cite{17}. The porosity of a foam is defined as the ratio of its density ($\rho_{\text{foam}}$) and that of the main additives ($\rho_{\text{ingredient}}$). It is calculated as follows (1):

$$\varepsilon = 1 - \frac{\rho_{\text{foam}}}{\rho_{\text{ingredient}}}$$  \hspace{1cm} (1)$$

The Hitachi S-3400N scanning electron microscope was used to observe the microstructure of the foam and the average cell diameter, which was estimated from several photographs.

2.3.3. Swelling test\cite{18}. Samples measuring 30x30x30 mm were weighed and immersed in water for a day and night at room temperature (26-27°C). Thereafter, it was removed from the solvent and was reweighed in drying order to obtain the difference between before and after immersion. The weight obtained was recorded, and the cross bond determination was performed by the inflation test which was calculated using equation (2):

$$S = \frac{m_2 - m_1}{m_2 \times 100\%}$$  \hspace{1cm} (2)$$

$S$ = swelling degree (%), $m_2$ = mass of foam after immersion in solvent (grams), $m_1$ = mass of foam before immersion in solvent (gram).

2.3.4. Hardness test. The hardness test used a digital equipment Texture Analyzer type CT3 Brookfield manufactured in the U.S.A, and it worked by placing the object in its place. The values are then displayed on the digital screen for further recording, according to the hardness measurement.

3. Result and discussion

3.1. Observation of the scanning electron microscope (SEM).

After observing with a SEM photo tool of 150x magnification (figure 1), it can be seen that the foam has a porous structure and that there are differences in the shape, distance and size of the pores produced. From the resulting image, it appears to have a large and small round shape, random/shapeless, orderly, irregular and cracked.

It can be seen from the SEM image of treatment C that the pore structure of the foam is denser and smaller, while that of A and B is better and orderly. On this basis, it can be seen that the use of an increasing amount of albumin with constant water and gambier tannins will make the resulting foam denser and the pore structure smaller and denser, caused of increasing amount complex bonds formed between tannis and albumin with shorter chain links structures. According to \cite{2}, changes in concentration of the use of gambier extract and albumin will result in different final foam products in terms of density, porosity, shape and cell size.

The result of previous studies \cite{9}, showed that SEM images of tannins-albumin-based foams had a porous cellular structure. Some foams are colored yellow or dark brown depending on the basic catalyst used. The porosity of albumin-tannin foam samples showed opened cell structures. Under the same condition, there is no significant difference in porosity between foam obtained with different formulations. While that foam obtained provide the same colored with gambier tannin used.
3.2. Foam porosity Characteristic of pore structure.

It can be seen from the result of table 1 that there are differences in the values of foam porosity. A decrease in value occurs along with the increase in the amount of albumin used. The highest porosity value was 81.80% in treatment A, while the lowest was 66.69% in treatment C. Its happens because on foaming process the dried albumin used is not occur perfectly because the water used fixed/not increase with albumin used. Its has been known, that albumin used in dry form and to restored albumin foaming process while stirred, need the water its been lost, so tannin used.

The porosity value was obtained from the calculation of the ratio between the density of the foam sample and its main additive, such as albumin and dried gambir extract [9]. Furthermore, the foam pores were closer to each other because of the large porosity value obtained from the morphological SEM image.

According to [2], that change in the amount of albumin use would change the resulting value of porosity, cell size, stirring speed, surfactant addition, stirring and cooking time. To increase the foaming speed and pore formation, it is necessary to use other additives such as hexamine as a
hardener and pTSA as catalyst, for resulting foam to remain stable after cooking. The porosity, swelling and hardness values of foam can be seen in Table 1.

Table 1. Value of porosity, swelling and hardness

| Treatment (albumin used) | Porosity (%) | Swelling (%) | Hardness (N/cm²) |
|-------------------------|--------------|--------------|------------------|
| A (16%)                 | 81.8         | 59.32        | 17.81            |
| B (24%)                 | 70.99        | 63.46        | 20.37            |
| C (32%)                 | 66.69        | 67.86        | 28.09            |
| Average                 | 73.16        | 45.55        | 22.09            |

3.3. Foam swelling.
The swelling degree of tannin-albumin foam in various treatment are shown in Table 1, and the swelling value ranges from 59.32-67.86%. The highest was obtained in treatment C of albumin using 32%, while the lowest was in A using 16%. Stated that from the result of the swelling value obtained, the presence or absence of a cross bonds between the constituent materials in the foam synthesis can be seen. Various positive compositions suggest the presence of cross bonds, and it allows the tannin-albumin foam to swell because the water’s molecules used as solvents can penetrate the tissue.

According to [18], the greater swelling degree showed that the synthesized foam contains a small amount of cross bonds, and it is easily penetrated by solvents. Therefore, it can be seen that the used of albumin 16% has the lowest swelling degree, having a cross bond between the constituent components in the higher foam, and vice versa.

The cross bond that occurs in the constituent components of the foam is the same as that which occurs in the tanning process. Foam is formed by trapping gas bubbles in a liquid or solid. Tannin has a property that if it is dissolved in water, it will foam a colloidal system. Colloidal is a form of a mixture (dispersion system) of two or more substances that are heterogeneous but has a dispersed particle size that is big enough (1-1000 nm).

3.4. Foam hardness test.
The average hardness values are represented in Table 1, and the lowest was obtained in treatment (A) of 17.81 N/cm², while the highest was in (C) of 28.09 N/cm². The increase in value was due to the increasing amount of albumin used, although gambier and water were constant. Therefore, the liquid emulsion formed because thicker and it created a denser and harder foam when it was fried.

If the hardness test is associated with the mechanical strength value of the produced foam and the results of the regression analysis, it will show a relatively close relationship between them (r = 0.995), where the two variables will depend on the amount of albumin and gambier used. From graph 2 it can be seen that harder of foam produced cause the higher compressive strength value of its, and vice versa. The hardness value of foam was influenced by the constituent components in its manufacture. As with the foam swelling, the hardness value was also influenced by the addition of the albumin concentration used.

The hardness test and mechanical strength value of the foam are needed when will be applied in various needs. The foam having high hardness test and mechanical strength, according to [19], is very useful because of their rigidity levels and precise if use for construction applications, such as a substitute wood furniture components and decorative panels automobile.
Figure 2. Graph of foam hardness value associated with mechanical strength value

4. Conclusion
The results showed that the SEM morphology, porosity value, swelling and hardness degree of the foam were influenced by the use of dried albumin. The porosity value of foam ranged 66.69 to 81.80%, swelling is 59.32-67.86% and the hardness value at 17.81-28.09 N/cm². Furthermore, it showed porous structures with differences in the shape, distance, and size. In addition, the produced foam became harder and denser with an increased amount of albumin.

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