The addition of biosilica and coconut oil to improve the characteristic of starch-based biofoam packaging

K Wahyuningsih¹, E S Iriansi* and B Amalia²

¹Badan Penelitian dan Pengembangan Pertanian, Ministry of Agriculture, Jl. Tentara Pelajar No.12, Cimanggu, Bogor, Jawa Barat 11161, Indonesia
²Badan Penelitian dan Pengembangan Industri, Ministry of Industry, Jl. Balai Kimia No. 1, Pasar Rebo, Jakarta 13710, Indonesia

Corresponding author: evisavitri1601@gmail.com

Abstract. Biofoam (biodegradable foam) is food packaging made of starch with biodegradable characteristic that environmentally friendly. To produce starch-based biofoam with good physical characteristic, requires large amount of starch (30% to 60%) in the formula. To be economical and to reduce the use of starch, it is needed to add filler material. This research aimed to investigate the effect of biosilica and coconut oil addition on the characteristic of cassava starch-based biofoam. Biosilica used as biofiller was extracted from rice husk. In this research, biofoam control (without filler), filled with commercial silica, filled with biosilica and filled with biosilica plus coconut oil were compared. Products were characterized on physical properties namely moisture content, density, color (Chromameter), contact angle (3D Optic Microscope), crystallinity (X-Ray Diffraction) and surface morphology (Scanning Electron Microscope). Meanwhile mechanical properties were measured on compressive strength and tensile strength (ASTM). The result indicated that cassava starch-based biofoam which filled with biosilica and coconut oil were increased its physical and mechanical properties. This type of biofoams have moisture content up to 13.82%, density 17.39%, more mechanical properties and more water resistance. Its compressive strength has increased up to 146% and the tensile strength to 56% compared to control.

1. Introduction
The people’s awareness to use food packaging which is environmentally friendly and safe for health has been increasing. This trend made food packaging producers were competing each other to conduct research in developing the suitable product. Starch-based biodegradable foam (biofoam) is one type of packaging made of environmentally friendly and potential to develop biopolymer. Researchers have investigated and developed starch-based biofoam for packaging, such as using sweet potato starch (Ipomea batatas) [1], oca sweet potato starch (Oxalis tuberosa) [2], cassava starch [3-10], the mixture of corn starch and potato starch [11,12] and sago starch [13]. Various formula of starch-based biofoam have been developed using various composition of starch, from 30% to 62%, average was 44%. With such amount, it will induce a competition of using starch between food vs. packaging industry. Therefore, it requires solution to the problem to make sure that the need of starch both in foodstuff and biofoam packaging are fulfilled.

The efforts to minimize the use starch in packaging formula is by add filler. Filler addition into a product polymer can also increase the physical and mechanical properties. The development of starch-
based biofoam has been conducted by adding filler, both from mines and biological resources. Some materials used as filler or bio-filler were calcium carbonate, bio-calcium carbonate from *Halimeda macroloba* [6], kaolin [12], magnesium silicate [4], dan rubber seed sell [5]. The use of bio-filler from biodegradable resources could be widely developed by using agricultural biomass. One of the agricultural biomasses which is abundant in Indonesia is rice husk. According to Kordatos et al. [14] rice husk had 80 – 90% silica content. Therefore, it has potential to be used as bio-filler in starch-based biofoam. Silica is materials that has good physic-chemical properties, good stability, and has heat resistance at high temperature [15]. The use of silica as filler could increase the physical and chemical properties, performance, and capability of the resulted products. As stated by previous study Thuong [16], the addition of silica filler could increase mechanical properties of natural rubber compound in superior way; tensile strength increased up to 7 times and loss modulus increased up to 25 times.

Performance of physical and chemical properties of starch-based biofoam could also be improved by adding oil into formula. The addition of hydrophobic material such as latex, beeswax, and 10% palm oil into formula of starch-based biofoam increased water resistance and compressive strength [17]. Previous study, showed that the addition of oregano oil into starch-based biofoam formula affected its physical and mechanical characteristics [1]. The color of biofoam became reddish-yellowish and the elongation value decreased significantly compared to biofoam without oregano oil. Coconut oil is one of inexpensive and easy to obtain in Indonesia, for that it has potential to be used as ingredients in the starch-based biofoam. Based on the previous results, this research was aimed to investigate the physic-chemical and mechanical properties of cassava starch-based biofoam which formulated with the addition of biosilica extracted from rice husk and the addition of coconut oil.

2. Materials and methods

2.1. Materials

Materials were cassava starch, commercial silica powder (ZEOSIL 175MP), rice husk, sizing agent, magnesium stearate, polyvinyl alcohol, water, abaca (*Musa textilis*) fiber, coconut oil, NaOH technical grade, HCl technical grade, tween 80.

2.2. Methods

2.2.1. Biofoam production by thermopressing. Biofoam was made using thermopressing method according to Iriani *et al.* [18] in the Laboratory of Indonesian Center for Agricultural Post Harvest Research and Development. Dried materials were weighed with the formula: starch 15 g, filler 6 g, magnesium stearate 3 g, polyvinyl alcohol 6 g, abaca fiber 6 g and water 24 ml then mixed until homogenous. The filler used are commercial silica powder and biosilica powder. Biosilica powder was extracted from rice husk which produced using sol-gel method [19] in Biosilica Pilot Plan-Indonesian Center for Agricultural Post Harvest Research and Development Kerawang. The process are the addition of coconut oil and tween, as amount of 10 and 1% of the starch weight respectively, followed with adding water and mixing. In total, 65 g of resulted mixture then molded in tray or bowl-shaped thermopressing at approximately 160-200°C for 5 minutes. All the types of biofoam produced in this research were replicate for three times. To improve water resistance, sizing agent was spread on the surface of the biofoam.

2.2.2. Biofoam characterization. The physical properties of the biofoam were characterized at (1) moisture content (AOAC 2012); (2) color (chromameter); (3) density; (4) contact angle (3D–Optic Microscope); and (5) surface morphology (Scanning electron microscope/SEM). SEM analysis was carried out with the Zeiss EVO MA10 Scanning Electron Microscope. A small piece (2 mm x 2 mm) of sample was fitted in cross section visualize bronze by using double-site tape. The surface of samples was coated with gold before imaging and observed with an accelerating voltage of 16.00 kv
and the working distance (WD) of 26.5–27.5 mm. The mechanical properties were characterized at (1) tensile analysis (ASTM D638–14) and compression strength (ASTM D695-15); (2) crystallinity, using by X-Ray Diffraction/XRD Bruker D8 Advance was Ni-filtered Cu Kα (λ = 1.54060) radiation (40 kV and 35 mA). The biofoams were mounted on a sample holder, and the pattern was recorded in the reflection mode at an angle 2θ over a range of 5.000° to 80.009° at a speed of 2.5°/min.

3. Results and discussion

To improve the product performance of cassava starch-based biofoam, biofiller namely biosilica from rice husk and additive material namely coconut oil were added. Figure 1 shows the resulted biofoam that are biofoam control (without filler addition), biofoam with the addition of commercial silica powder, biosilica powder and combination of biosilica with coconut oil.

![Figure 1. The appearance of biofoam](image)

Table 1. Physical properties of starch-based biofoam packaging

| No | Parameters                  | Biofoam (control) | Biofoam+ commercial silica | Biofoam+ biosilica | Biofoam+ biosilica+ coconut oil |
|----|-----------------------------|-------------------|---------------------------|-------------------|---------------------------------|
| 1  | Moisture content (%)        | 8.03±0.05         | 8.68±0.16                 | 8.91±0.17         | 9.14±0.02                       |
| 2  | Density (g/cm³)             | 0.23±0.01         | 0.24±0.00                 | 0.36±0.01         | 0.27±0.02                       |
| 3  | Colour: Hue = Hunter’s color, L = lightness, a = redness, b = yellowness |
|    | L                           | 81.73±1.492       | 85.11±1.914               | 75.54±5.750       | 80.89±1.507                     |
|    | a                           | 1.92±0.457        | 0.85±1.676                | 1.22±1.325        | 2.37±0.787                      |
|    | b                           | -1.66±0.611       | -4.28±1.072               | 2.41±1.513        | 2.38±0.842                      |
|    | Hue                         | 319.84±6.201      | 276.9±19.955              | 58.38±38.160      | 45.53±9.021                     |

Hue = Hunter’s color, L = lightness, a = redness, b = yellowness
Results are expressed as mean of three determinations±standard deviation.

Table 1 shows that biofoam modified with the addition of silica filler had higher moisture content compared to control; it increased from 8.10 to 13.82%. This was due to silica is hydrophilic, able to absorb liquid in the mixture, thus water can’t evaporate during hot press process. This result was in agreement with previous report which showed the addition of filler would improve the moisture content. Starch-based biofoam filled with kaolin increased moisture content 5.42% [12]. Moo-tun et al. [4] also reported that starch-based biofoam with the addition of magnesium silicate and calcium carbonate as filler increased water moisture of the biofoam. Its due to magnesium silicate material and calcium carbonate were more hygroscopic than starch.
Figure 1 shows the addition of silica change biofoam color became brighter compared to without silica. The L value in biofoam produced with silica was higher compared to biofoam without silica filler. However, the addition of coconut oil decreasing L value and increasing a and b values, therefore it became darker, yellowish, or reddish compared to biofoam without coconut oil addition. As the result, color intensity (a and b) became more reddish or yellow-brownish [20]. According to Cruz-tirado et al. [1], the decrease of L was induced by phenolic material in oil that absorb light at low wavelength.

Density is important parameter in physical characteristic of packaging, since its closely relates to thermal properties. Moo-tun et al. [4] mentioned that high density has high thermal conductivity, then it could be use as packaging. The density of starch-based biofoam was 0.175 – 0.30 g/cm³, therefore it had thermal conductivity that could be use as disposable food packaging. The result on Table 1 shows that biofoam without filler has density value 0.23 g/cm³, while the highest density was found in biofoam filled with biosilica (0.36 g/cm³). Both filler, commercial silica and biosilica can not be dissolved in water, so it underwent agglomeration in the mixture of biofoam and increased its density.

The biofoam morphological structure on Figure 2 shows that particles of both silica and biosilica powder tend to group, not equally distributed into biofoam matrix. According to Moon-tun et al. [4], the addition of 15% filler magnesium silicate, not water-soluble, cause poor process of material dispersion and distribution in biofoam material as the result of agglomeration. Therefore, the process of starch expansion during baking process was not optimal, then the biofoam density increased. Chiarathanakrit et al. [6] reported that the addition of 10% CaCO₃ isolated from macroalgal H. macroloba increased the density of starch-based biofoam. Adding kaolin filler to the formula of starch-based biofoam also increase the density [12]. In the other hand, addition of coconut oil also increase 13.82% density compared to biofoam control (without coconut oil addition). The interaction between oil (lipid) and starch (carbohydrate) cause slowing down of vapor rate during hot press process, thus it raising biofoam density [1]. The increasing density of silica and coconut oil addition causing biofoam structure to be more compact, more solid, and less porous as shown on Figure 2. Limited interaction between water and starch, made plasticization process went slower. The increase of mixture viscosity during the formulation also occurred, then it decreased the capacity of biofoam matrix expansion by producing cell structure which had lower porosity [4].
Figure 2. Morphology of biofoam: (a) biofoam control, (b) biofoam + commercial silica, (c) biofoam + biosilica, (d) biofoam + biosilica + coconut oil

The filler and oil addition into biofoam formula causing change of biofoam contact angle, so did the biofoam layer using sizing agent. The higher contact angle was shaped between water particle and biofoam surface, the more increasing hydrophobic characteristic of biofoam was. According to Stansess et al. [21], material would have hydrophobic characteristic if it had contact angle >90°, and for over 120° it would be called superhydrophobic. Figure 3 shows that the addition of biosilica as filler and oil was able to increase contact angle from 60° to 87° or 45% compared to biofoam control. Meanwhile layering using sizing agent had contact angle between biofoam surface and water surface over 90°. It indicated that the addition of silica, oil and layering sizing agent on biofoam could increase the hydrophobic characteristic of the biofoam. Kasemsiri et al. [17] stated that the addition of hydrophobic materials such as latex, beeswax and 10% palm oil could increase water resistance of starch-based biofoam. Palm oil is popular, cheap, and abundant additive material that is water resistant [22]. The addition of composite such as filler and fiber to reduce the amount of starch use evidently
could decrease biofoam hydrophilicity [4]. It is also supported by the result of surface morphology observation in Figure 2 (b2) and 2 (c2); the addition of both commercial silica and biosilica filler could make porous on biofoam surface tightly covered by silica material, so it delaying the water molecule adsorption process into biofoam. Similarly, the layering of starch-based biofoam using sizing agent such as ketene dimer could also reduce water adsorption up to 83.26% [3].

Figure 3. Contact angle between of surface water with biofoam (a) biofoam control; (b) Biofoam + commercial silica; (c) Biofoam+biosilica+coconut oil; (d) Biofoam+biosilica+sizing agent

Figure 4. Diagram of mechanical properties of cassava starch-based biofoam incorporated biosilica and coconut oil. Results are expressed as mean±range of twice determinations.
Mechanical properties of packaging are one of several factors determining the strength of packaging to sustain and hold the content. Figure 4 shows that the compressive and tensile strength biofoam added with commercial silica increased approximately 27% compared to biofoam without filler addition (control). It is indicated that silica could increase the mechanical characteristic of the biofoam. However, it did not occur when using biofiller made of rice husk. Biofiller, biosilica extracted from rice husk, added into the formula caused the decreasing compressive and tensile strength approximately 23% compared to biofoam control. It was caused by uneven biosilica distribution into biofoam matrix. Biosilica particles tend to agglomerate forming bigger particle structure, so addition reaction between matrix surface and filler (biosilica) lessened. Biosilica has polar and hydrophilic surface [23], bigger particle size, was easy to aggregate, so it was not easy to disperse evenly in rubber matrix and caused elastic characteristic of rubber compound less maximum [24-26].

Based on the observation of biofoam morphology using SEM shown on Figure 2 (b1 and c1), it could be seen that silica or biosilica particles were not distributed evenly into biofoam matrix. In the other hand, biofoam morphology with biosilica and coconut oil treatment shown on Figure 2 (d1) indicated biosilica distributed evenly into biofoam matrix. The addition of coconut oil supported the process of biosilica expansion during baking and molding process using hotpress machine, then biosilica could disperse evenly into biofoam matrix and increase the mechanical properties. Diagram on Figure 4 showed that the addition of coconut oil into the biofoam formula using biosilica could increase compressive strength up to approximately 146% compared to compressive strength of biofoam control. Also, the tensile strength increased 56% compared to biofoam control. Coconut oil was able to perform as coupling agent for biosilica, so it could decrease agglomeration between biosilica particles forming the smaller particle structure. The small size of biosilica particle enabled biosilica distributed evenly into biofoam matrix, so the more compatible reaction occurred forming biofoam with the stronger and the better mechanical properties.

Observation using XRD method showed that filler and oil addition into starch-based biofoam formula did not cause any change on crystallin structure. Figure 5 shows that crystalline peaks of starch-based biofoam emerged at 2θ approximately 22°. The addition of filler caused the biofoam intensity of crystalline structure increase compared to biofoam control (without filler addition). Similarly, the addition of coconut oil increased the biofoam intensity of crystalline structure, which was higher than other biofoam. Crystalline area emerged at crystalline peaks 2θ 13° - 22°. It was caused by the interaction of lipid in oil with amylose in starch forming lipid-amylose linkage and amylose crystallization forming type-V crystalline structure. Cruz-tidaro et al. [1] produced sweet potato starch-based biofoam (Ipomoea batatas) added with essential oil with type-V crystalline structure.
structure for the peaks at $2\theta = 21.5^\circ$. Materials with this structure showed hydrophobic characteristic. It is supported by the data of contact angle on Figure 3(c); biofoam with coconut oil addition had the bigger contact angle compared to biofoam without oil addition.

4. Conclusion
Biosilica extracted from rice husk can be used as filler to decrease the large amount use of cassava starch in the biofoam (biodegradable foam) formula. The research showed that the addition of biosilica filler caused the increase of moisture content up to 13.82% and density 17.39% compared to biofoam without filler addition (control). However, the mechanical properties and water resistance increased after coconut oil addition into the biofoam formula. Compressive strength increased 146% and tensile strength 56% compared to biofoam without coconut oil addition.

Acknowledgements
The authors would like to greatly thank Center for Excellence-Ministry of Research, Technology and Higher Education of the Republic of Indonesia (Contract Num. B.3204.1/HK.230/H.10/09/2019 – 678/BPPI/BBKK/IX/2019) for research funding. Special thanks was also acknowledged to Ema Sri Mulyani and M. Ghoussul Adom for technical assistant in the laboratory. All authors contributed equally to this work.

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