Crystalline Properties of Cassava (*Manihot esculenta* Crantz) Starch and Its Associated Biofoam

Philipus J. Patty*[1] and Synodalia C. Wattimena[2]

[1]*Department of Physics, Universitas Pattimura, Ambon 97233, Indonesia*
[2]*Department of Biology, Universitas Pattimura, Ambon 97233, Indonesia*

Abstract: Making foam using starch as an alternative material to replace a conventional material, polystyrene, is one of the solutions to solve an environmental problem due to the waste of foam made from polystyrene cannot be degraded. This study aims to analyze the crystalline properties of cassava starch and biofoam made from it using X-ray diffraction (XRD) spectroscopy. From the XRD data of cassava starch, the peaks of 2θ were analyzed to determine the type of cassava starch used in this study. The index of crystallinity of both cassava starch and its associated biofoam was calculated from XRD data. XRD data of cassava starch show 4 main peaks of 2θ: 15.0°, 17.0°, 17.9°, and 23.0°, and 3 minor peaks at 11.0°, 20.0°, 26.0°. Based on the main peaks from this XRD data, cassava starch can be categorized as an A-type starch. For cassava starch biofoam, there is only 1 main peak of 2θ at 19.7°, and 5 minor peaks at 11.0°, 15.4°, 21.7°, 23.0°, and 26.4°. The decrease in the crystallinity from the starch to the associated biofoam is shown by the decrease in the index of crystallinity, which decreases from 41.0% in starch to 28.3% in biofoam.

Keywords: Cassava, Starch, Crystallinity Index, XRD.

*Corresponding author: philip.patty@gmail.com

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I. INTRODUCTION

Styrofoam and other products of conventional plastics have become an environmental issue due to the waste they produced. Styrofoam is made from polystyrene, a polymer consisting of styrene monomers. They have been used in many products, such as insulators [1], floatation devices [2], egg cartons [3], food packaging [4], and also for electronics and other fragile packaging. Since styrofoam is made from polystyrene which is difficult to degrade, and they are used in many products as mentioned, they produce waste everywhere to be dealt with and cause an environmental problem.

One of the solutions to the environmental problem due to the waste of styrofoam is by recycling [5]. However, there are some challenging issues in recycling styrofoam. Firstly, styrofoam is difficult to collect, and one of the reasons for that is the material can be blown easily by wind. Secondly, the material is difficult to transport in large quantities since its ratio of weight to volume is very low. Thirdly, The material is easily contaminated, most often by food, hence recycling calls for a labor-intensive cleaning process. Based on these challenging issues, another solution than recycling is needed, and an alternative material to replace polystyrene is one of the best solutions. One of the alternative materials is starch, a polymer that consists of glucose monomers joined by glycosidic bonds. Since starch is a plant material, it is easy to degrade, thus suitable for replacing polystyrene in making foam.

Many researchers have used starch to make foam, biofoam, and study their physical and chemical properties. Some starches used are corn starch [6,7], cassava starch [8], potato starch [9], sago starch [10], and wheat [11], where the researchers tried to do some modifications to make the starch based-biofoam to be comparable to the conventional polystyrene-based styrofoam.

Cassava is one of the traditional Indonesian plants, and cassava starch has been used by many researchers to make biofoam, where they studied the properties of the cassava-based biofoam. Some of the properties of biofoam studied are biodegradability and water absorption [8], tensile strength and water absorption and solubility in the presence of natural fiber and chitosan [12,13], mechanical properties and water resistance in the presence of citric acid and sugarcane bagasse cellulose fiber [14], crystallinity, water absorption as well as surface morphology [15].

In addition to the characterization of cassava-based biofoam, many researchers also studied the properties of cassava starch itself. The properties of cassava starch studied are physicochemical properties [16], chemical and functional properties [17], structural and techno-functional properties [18], and crystalline properties [19,20,21].

Based on XRD data, starches can be classified as type A, type B, and type C, where XRD data of type A starch shows peaks of 2θ at 15°, 17°, 18°, and 23°, type B starch at 5.6°, 15°, 17°, 20°, 22°, and 24°, and type C starch, a combination of type A and type B, at 5.6°, 15°, 17°, and 23° [22]. Using this classification, cassava starch has been categorized as type A starch [15,19,23]. However, other researchers showed that cassava is type B starch [21], and some others are type C starch [24,25]. It is of interest, then, to study the properties

of cassava starch from Indonesian cassava plants based on the XRD data to know its type as well as the properties of biofoam made from it.

This study aims to characterize the crystallinity properties of cassava starch and also biofoam made from the starch using XRD spectroscopy. From the XRD data of cassava starch, the type of starch can be determined, and the index of crystallinity of the starch can be calculated. From the XRD data of biofoam, the index of crystallinity can be determined, from which one can observe how the crystallinity changes from starch to biofoam.

II. METHOD

The cassava starch was prepared from cassava roots taken from a local garden in Ambon Island, Indonesia. From the starch, the biofoam was prepared, and both starch and biofoam were observed under an XRD spectrophotometer to analyze their crystallinity properties.

A. Starch and Biofoam Preparation

For starch preparation, first, the cassava was peeled, washed, and then ground using a grinder. After grinding, the paste of cassava was mixed with distilled water with a ratio of 1:3, and the slurry was filtrated through a double layer of cheesecloth. The filtered slurry was then allowed to rest for two hours for the process of sedimentation. The liquid at the top was decanted and discarded. The process of filtration was done twice. The sediment then was dried in the oven at 45° C for 48 hours and stored in a container for further analysis.

B. Crystalline Analysis

For crystallinity properties analysis of starch and its associated biofoam, an XRD spectrophotometer was used. For this purpose, XRD Rigaku MiniFlex 2 was used. The monochromator is Cu-Kα radiation with $\lambda = 1.5405$ $\mathring{A}$ at a power of 30 kV, 15 mA under an angle of 2θ ranging from $3^\circ - 145^\circ$ with an interval of 0.02°. For XRD measurements, the sample of cassava starch was used directly without any treatment, but a sample of cassava starch-based biofoam was ground to find a powder using a mortar and pestle. The raw data of XRD was truncated between 10° to 30° of 2θ, since at 2θ larger than 30° there were no peaks observed. The data was also smoothed by applying a Savitzky-Golay filter with the polynomial degree of 3 and 40 points for clarity.

The index of crystallinity I_C of cassava starch and its associated biofoam was determined by analyzing the XRD data of both samples and was calculated using Eq. (1) [20]

$$I_C = \frac{A_C}{A_C + A_A}, \quad (1)$$

where A_C and A_A are the areas of crystalline and amorphous parts, respectively. The crystalline area A_C was determined by integrating the area under the peaks of XRD data, while A_C + A_A was by integrating the whole area of the XRD data.

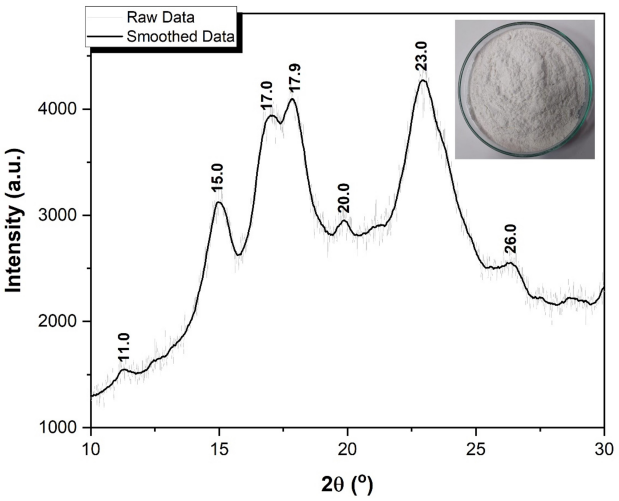

FIG. 1: XRD data of cassava starch and the image of the starch (inset).

III. RESULTS AND DISCUSSION

A. Type of Cassava Starch Identification Based on XRD

Fig. 1 shows the XRD data of cassava starch and the image of the starch (inset). For convenience, the data were smoothed as explained in the methodology, and both raw and smoothed data are shown in the figure. There are 4 main diffraction peaks of 2θ: 15.0°, 17.0°, 17.9°, and 23.0°, and 3 minor peaks at 11.0°, 20.0°, 26.0°. Based on the main peaks from this XRD data, Cassava starch can be categorized as an A-type starch. This result is consistent with the previous data which also found cassava starch as an A-type starch [15,19,23].

XRD data in Fig. 1 indicates that cassava starch granules, like all other starch granules, consist of both crystalline and amorphous parts, thus semi-crystalline. The granule contains two major polysaccharides, amylose, and amylopectin. Amylose is a linear polymer of α-(1→4)-linked D-glucose units containing a very small number of α-(1→6) linked branches, while amylopectin is a high branch molecule with α-(1→4)-linked D-glucose backbone and α-(1→6) linked branches. The chain of amylose molecules is long, consisting of hundreds to thousands of glucosyl units [26], while the chain of amylopectin molecules is short [27] and contains very extensive branches, thus a very complex molecular structure. The short-chain amylose molecules form double helices which crystalize in crystalline parts of the granule [28]. It has been shown previously that a starch granule consists of rings of crystalline and amorphous parts alternately as shown in Fig. 2 A. The diameter of cassava granules is in the range of 3 to 16 μm [21,29]. Crystalline ring parts, which contribute to the peaks in XRD data, contain double helices of amylopectin (Fig. 2 B). For an A-type starch like cassava, the double he-

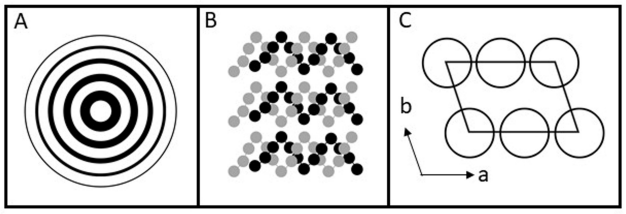

FIG. 2: A. Rings of crystalline (black) and amorphous (white) parts alternately in a granule. B. Double helices of amylopectin in crystalline parts. C. Double helices were packed in a monoclinic unit cell (Top view) with lattice parameters a = 2.12 nm, b = 1.17 nm, c = 1.07 nm, and γ = 123.5 [30] in an A-type starch-like cassava starch.

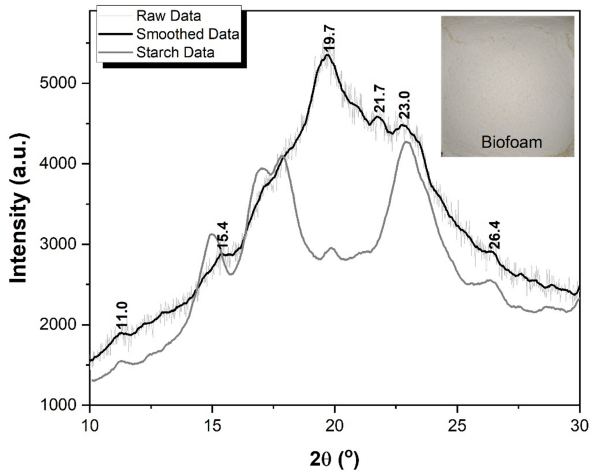

FIG. 3: XRD data of cassava starch-based biofoam and the image of biofoam (inset). For comparison, the XRD data of cassava starch has been added.

lices were packed in a monoclinic unit cell with lattice parameters a = 2.12 nm, b = 1.17 nm, c = 1.07 nm, and γ = 123.5 [30] as shown in Fig. 2 C.

Other studies found that cassava starch is a B-type starch [21], where the peaks were observed at 2θ of $5°$, $15.3°$, $17.23°$, and $22.71°$. Compared to the results of our study, there is an extra peak at $5°$ and the absence of a peak at $18°$. Other studies categorized cassava starch as a C-type starch, where the 2θ peaks were observed at $15°$, $17°$, and $22.7°$ [25]. Compared to the results of our study, there is an absence of peak $18°$. The results that some cassava starches like in this study are type A, some are type B and C indicate the variety of the cassava starch. The variety can be caused by geographical origin, where the environment affects the structure of cassava starch, and genetic variation due to different varieties.

B. Change of Crystallinity from Starch to Biofoam

To see the change of crystallinity from cassava starch to cassava starch-based biofoam, XRD data of the starch and the associated biofoam were compared. Fig. 3 shows the XRD

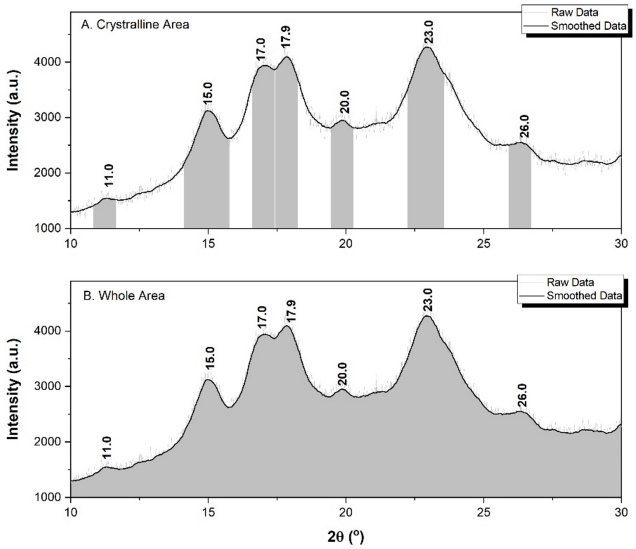

FIG. 4: A. Integration of crystalline area (shaded area) of cassava starch. B. Integration of crystalline and amorphous areas (shaded area) of cassava starch.

data of cassava starch-based biofoam and the image of the biofoam (inset). For convenience, the data were smoothed as explained in the methodology, and both raw and smoothed data are shown in the figure. For comparison, the XRD data of the starch from Fig. 1 is also shown. The figure shows that XRD data of the biofoam contains only 1 main peak of 2θ: $19.7°$, and 5 minor peaks, $11.0°$, $15.4°$, $21.7°$, $23.0°$, and $26.4°$. There are 3 feature differences between XRD data of cassava starch and its associated biofoam. Firstly, the main peaks of $17.0°$ and $17.9°$ in starch XRD data disappeared in associated biofoam XRD data. Secondly, the main peaks of $15.0°$ and $23.0°$ in starch XRD data became minor peaks in associated biofoam XRD data. Thirdly, the minor peak of $20.0°$ in starch XRD data became the main peak in associated biofoam XRD data. In addition, the minor peaks of $11.0°$ and $26.0°$ in starch XRD data appear as minor peaks in associated biofoam XRD data. A similar change of XRD peaks from cassava starch to the associated biofoam incorporated with grape stalks has also been observed [25].

The change from 4 main peaks in cassava XRD data to 1 main peak in associated biofoam XRD data indicates that there is a decrease in crystallinity when cassava starch was processed to become biofoam. Quantitatively, the crystallinity is measured by an index of crystallinity.

The index of crystallinity of cassava starch was determined using Eq. (1). The crystalline area was determined by integrating the area under the curve of the peaks, while the whole area, crystalline plus amorphous areas, was by integrating the area under the curve of the whole data. Fig. 4 A shows the crystalline area integrated (shaded areas) and the results of the integration are summarized in Table I. The total crystalline area was found to be 22,015.4 a.u.. To determine the whole area, the integration was conducted from the minimum to the maximum of 2θ. Fig. 4 B shows the whole area integrated (shaded area) and the results of the integration are summa-

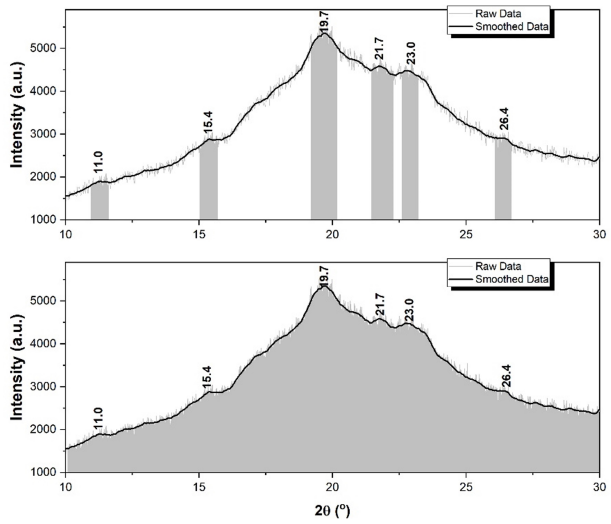

FIG. 5: A. Integration of crystalline area (shaded area) of cassava starch-based biofoam. B. Integration of crystalline and amorphous areas (shaded area) of cassava starch-based biofoam.

rized in Table 1, where the total of the whole area was found to be 53,559.8 a.u.. The index of crystallinity of cassava starch was found to be 41.0%. This index is approximately the same as what was found previously [19].

TABLE I: The crystalline and whole area of cassava starch XRD data calculated from the shaded area in Fig. 4

No	Shaded Area	Peaks	Area (a. u.)
1	Crystalline	11.00	1238.8
		15.00	4561.3
		17.00	3175.7
		17.99	3259.9
		20.00	2374.7
		23.00	5336.2
		26.00	2068.8
		Total	**22015.4**
2	Whole		**53559.8**

The index of crystallinity of cassava starch-based biofoam was determined using Eq. (1). Fig. 5 A shows the crystalline area integrated (shaded areas) and the results of the integration are summarized in Table II. The total crystalline area was found to be 18,297.3 a.u.. To determine the whole area, the integration was conducted from the minimum to the maximum data. Fig. 5 B shows the whole area integrated (shaded area) and the results of the integration are summarized in Table II, where the total of the whole area was found to be 64,563.6 a.u.. The index of crystallinity of cassava starch-based biofoam was found to be 28.3%.

The results of the index of crystallinity of cassava starch

TABLE II: The crystalline and whole areas of cassava starch-based biofoam XRD data calculated from the shaded area in Fig. 5

No	Shaded Area	Peaks	Area (a. u.)
1	Crystalline	11.00	1200.9
		15.40	1676.9
		19.70	6321.1
		21.70	3766.5
		23.00	3483.5
		26.40	1848.4
		Total	**18297.3**
2	Whole		**64563.6**

and its associated biofoam show that the index of crystallinity decreases as starch was processed into biofoam. The decrease may be caused by the fact that in the process of gelatinization during thermal processing from starch to foam [27], the structure of the granule is destroyed partially or totally, which eventually results in an amorphous matrix [28]. This amorphous matrix can explain why the index of crystallinity decreases, thus the change of the peaks in XRD data from cassava starch to its associated biofoam. It also has been shown that the mechanical treatment of starches results in a decrease in the index of crystallinity [20].

IV. CONCLUSION

In this study, the crystallinity of cassava starch and biofoam made from it was analyzed using XRD spectroscopy. For cassava starch, there are 4 main diffraction peaks of 2θ: peaks at 15.0°, 17.0°, 17.9°, and 23.0°, and 3 minor peaks at 11.0°, 20.0°, 26.0°. Based on the main peaks from this XRD data, cassava starch can be categorized as an A-type starch. An A-type starch consists of crystalline and amorphous parts arranged as radial rings alternately in a granule, where a crystalline ring contains double helices of highly branch amylopectin molecules, packed in a monoclinic unit cell. For cassava starch biofoam, there is only 1 main peak of 2θ: 19.7°, and 5 minor peaks at 11.0°, 15.4°, 21.7°, 23.0°, and 26.4°. The crystallinity of cassava starch decreases after being processed into biofoam. This is indicated by the decrease in the number of main peaks from 4 to 1, as well as the index of crystallinity, which decreases from 41.0% in starch to 28.3% in biofoam.

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[1] Y Zhang and S.Y. Lie, "The application of broken expanded polystyrene particles in thermal insulation coating material," *IOP Conf. Ser.: Mater. Sci. Eng*. vol. 770, p. 012022, 2020. doi:10.1088/1757-899X/770/1/012022

[2] M. Niaounakis, "The Management of marine plastic debris," William Andrew Applied Science Publisher, New York, 2017. https://doi.org/10.1016/B978-0-323-44354-8.00001-X

[3] A. Kudzal, Z. Zhang, and J. Lagassey, "Axiomatic design of an improved egg carton manufacturing proccess," *Proceeding of the 8th International Confefrence of Axiomatic Design*, Camous de Caparica, 2014 .

[4] E. Drago et al., "Innovations in Smart Packaging Concepts for Foods: An Extensive Review," *Foods* vol. 9, no.11, p. 1628, 2020. doi.org/10.3390/foods9111628.

[5] A. Salisu and Y.S. Maigari, "Polystyrene and its recycling: A review," *Proceeding of Materials Science and Technology Society of Nigeria (MSN)*, Kaduna State, 2021.

[6] P. Luna et al., "Biodegradable foam based on extracted fraction from shorgum-by profuct," *IOP Con. Ser.: Earth Environ. Sci.*, vol. 749, p. 012057, 2021. doi:10.1088/1755-1315/749/1/012057.

[7] R. Mirdayani and A. Amalia, "Characteristics of edible films based on corn starch and protein isolates from liquid waste extraction of tofu processing industry," *Jurnal Kimia Sains dan Aplikasi*, vol. 23, no. 6, pp. 216-221, 2020. doi.org/10.14710/jksa.23.6.216-221.

[8] S. Sumardiono et al., "Characteristics of biodegradable foam (bio-foam) made from Cassava flour and Corn fiber," *IOP Con. Ser.: Matter. Sci. Eng*., vol. 1053, p. 012082, 2021. doi:10.1088/1757-899X/1053/1/012082.

[9] N. H. P. Rodrigues et al., "Starch-Based Foam Packaging Developed from a By-Product of Potato Industrialization (Solanum tuberosum L.)," *Appl. Sci*., vol. 10, no. 7, p. 2235, 2020. doi.org/10.3390/app10072235.

[10] E. R. M. Saleh, K. A. Rakhman, and S. Samad, "Synthesis of biofoam from Sago waste as a biodegradable food storage candidate," in *First Asian PGPR Indonesian chaper international e-conference 2021, KnE Life Sciences* vol. 2022, pp 162-169, 2022. Doi.10.18502/kls.v7i3.11117.

[11] A. Aygun, M. K. Uslu, and S. Polat, "Effect of strach sources and supplementary materials on starch based foam trays," *J. Polym. Environ*., vol. 25, pp. 1163-1174, 2017. doi 10.1007/s10924-016-0886-0.

[12] N. Kaisangsri, O. Kerdchoechuen, and N. Laohakunjit, "Biodegradable foam tray from cassava starch blended with natural fiber and chitosan," *Industrial Crops and Products*, vol. 37, no. 1, pp. 542-546, 2012. doi.org/10.1016/j.indcrop.2011.07.034.

[13] E. S. Iriani, K. Wahyuningsih, and E. Octavia, "The Effect of Surface Modification by Sizing Agent on the Water Absorption Capacity of Cassava Starch-based Biofoam Packaging," *Macromolecular Symposia*, vol. 391, no. 1, p. 1900133, 2020. doi.org/10.1002/ masy.201900133.

[14] N. Khanoonkon et al., "Development of biofoam trays from cassava starch blended with citric acid modified starch and sugarcane bagasse cellulose fiber," *Journal of Food Science and Agricultural Technology*, vol. 6, pp. 40-45, 2022.

[15] S. Amaraweera et al., "Preparation and characterization of dual-modified cassava starch-based biodegradable foams for sustainable packaging applications," *ACS Omega*, vol. 7, no. 23, pp. 19579 – 19590, 2022. doi.10.1021/acsomega.2c01292.

[16] S. M. Chisenga et al., "Characterization of physicochemical properties of starches from improved cassava varieties grown in Zambia," *AIMS Agriculture and Food*, vol. 4, no. 4, pp. 939-966, 2019. doi.10.3934/agrfood.2019.4.939.

[17] O. O. Oladunmoye et al., "Chemical and functional properties of cassava starch, durum wheat semolina flour and their blends," *Food Science & Nutrition*, vol. 2, no.2, pp. 132– 138, 2014. doi: 10.1002/fsn3.83.

[18] R. Dariva et al., "Structural and Techno-Functional Properties of Cassava Starches and Application on Cheese Bread," *Biointerface Research in Applied Chemistry*, vol. 11, no. 1, pp. 7400-7409, 2021. doi.org/1033263/BRIAC111.74007409.

[19] H. F. Sangian et al., "A comparative studies of the structure, crystallinities, Miller indices, crystal parameters, and particle sizes of microwave- and saline water-treated cassava starch," *BioResources*, vol. 14, no. 4, pp. 8212-8228, 2019. doi.10.15376/BIORES.14.4.8212-8228.

[20] K. Dome et al., "Changes in the crystallinity degree of starch having different types of crystal structure after mechanical pretreatment," *Polymers*, vol. 12, no. 3, p. 641, 2020. doi:10.3390/polym12030641.

[21] K.A. Dolas et al., "Effect of starch modification on physicochemical, functional and structural characterization of cassava starch (*Manihot esculenta* Crantz)," *Food Research*, vol. 4, no. 4, pp. 1265 – 1271, 2020. doi.org/ 10.26656/fr.2017.4(4).075.

[22] Z. Xie et al., "Effect of drying processes on the fine structure of A-, B-, and C-type starches," *Starch*, vol. 70, no. 3-4, p. 1700218, 2018. doi.org/10.1002/star.201700218.

[23] T. de S. Rocha, A. P. de A. Carneiro, and C. M. L. Franco, "Effect of enzymatic hydrolysis on some physicochemical properties of root and tuber granular starches," *Food Sci. Technol*., vol. 30, no. 2, pp. 544-551, 2010. doi.org/10.1590/S0101-20612010000200039.

[24] C. L. Luchese, J. C. Spada, and I. C. Tessaro, "Starch content affects physicochemical properties of corn and cassava starch-based films," *Industrial Crops and Products*, vol. 109, pp. 619-626, 2017. doi.org/10.1016/j.indcrop.2017.09.020.

[25] J. B. Engel, A. Ambrosi, and I. C. Tessaro, "Development of biodegradable strach-based foam incorporated with grape stalks for food packaging," *Carbohydrate Polymers*, vol. 225, p. 115234, 2019. doi.org/10.1016/j.carbpol.2019.115234.

[26] S. Hizukuri et al., "Molecular structure of rice starch," *Carbohydr. Res*., vol. 189, pp. 227-235, 1989. doi.org/10.1016/0008-6215(89)84099-6.

[27] E. Bertoft et al., "Internal unit chain composition in amylopectins," *Carbohydr. Polym*., vol. 74, no. 3, pp. 527 – 543, 2008. doi.org/10.1016/j. carbpol.2008.04.011.

[28] A. Imberty et al., "Recent advances in knowledge of starch structure," *Starch/Strake*, vol. 43, no. 10, pp. 375 – 384, 1991. doi.org/10.1002/star.19910431002.

[29] M. E. M. Segura and E. E. P. Sira, "Characterization of native and modified Cassava starches by scanning electron microscopy and X-ray diffraction technoques," *Cereal Food Worlds*, vol. 48, no. 2, pp. 78 – 81, 2003.

[30] S. Perez and E. Bertoft, "The molecular structures of starch components and their contribution to the architecture of starch granules: A comprehensive review," *Starch/Starke*, vol. 62, no. 8, pp. 389 – 420, 2010. doi.org/10.1002/star.201000013.