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Utilization of Modified White Corn Starch in Producing Marshmallow Cream

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Abstract

The purpose of this study was to determine the effect of the white maize starch by oxidation and acetylation-oxidation modification on gel formation and character of the resulting gel and applying a modified white corn starch in manufacturing of marshmallow cream. White corn varieties Srikandi, Pulut and Canggal are used as raw materials to produce starch. Starch modification is conducted by oxidation and acetylation-oxidation. Quality analysis of the modified starch is freeze thaw stability, smallest gel formation concentration and gel strength. Corn starch, both native and modified applied in manufacturing of marshmallow cream. The results showed that the treated starch acetylation-oxidation provide the best freeze thaw stability with the least water released than native starch and modified starch oxidation. Starch modified by oxidation tend to have the highest Least Gelling Concentration (LGC). Gel produced from modified starch both oxidation and acetylation-oxidation have gel strength greater than the native starch. Marshmallow cream that uses a modified starch by acetylation-oxidation, have the best received power in testing organoleptic by the panelists. Use of modified starch does not give a noticeable difference in color of the product, but it gives texture and the best spread power compared to products using original starch.

Keywords: Oxidation, acetylation-oxidation, marshmallow cream, white corn, starch

Abstrak (Indonesian)

Penelitian bertujuan untuk mengetahui pengaruh modifikasi pati jagung putih secara oksidasi dan asetilasi oksidasi terhadap pembentukan gel dan karakter gel yang dihasilkan serta aplikasi pati jagung putih termodifikasi dalam pembuatan marshmallow cream. Bahan baku yang digunakan adalah jagung putih varietas Srikandi, Pulut dan lokal yang diekstrak patinya. Modifikasi pati dilakukan secara oksidasi dan asetilasi-oksidasi. Pati termodifikasi dianalisa freeze thaw stability, konsentrasi pembentukan gel terkecil dan kekuatan gel. Hasil penelitian menunjukkan bahwa pati yang mengalami perlakuan oksidasi-asetilasi memberikan stabilitas freeze thaw terbaik dengan sedikitnya air yang terlepas dibanding pati alami dan pati termodifikasi secara oksidasi. Pati yang mengalami modifikasi secara oksidasi cenderung memiliki index konsentrasi pembentukan gel terendah (Least Gelling Concentration / LGC) tertinggi. Gel yang dihasilkan pati termodifikasi baik secara oksidasi maupun asetilasi memiliki kekuatan gel lebih besar dibandingkan pati aslinya. Marshmallow cream yang menggunakan pati termodifikasi secara oksidasi asetilasi, memiliki daya terima terbaik dalam pengujian organoleptik oleh para panelis, Penggunaan pati termodifikasi tidak memberikan perbedaan yang nyata dalam hal warna produk, namun memberikan tekstur dan daya oles yang terbaik dibandingkan dengan produk yang menggunakan pati asli.

Kata kunci: Oksidasi, asetilasi oksidasi, marshmallow cream, jagung putih, pati

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INTRODUCTION

Gelatin is including essential ingredient in the manufacture marshmallow, because of its ability to produce and support the foam formed and form a film that captures air bubbles are formed [1]. The type of gelatin used for products such as marshmallow confectionary is gelatin with medium to low viscosity. Gelatin generally used for confectionary products are gelatin type A, because it has a low viscosity. Gelatin type A usually comes from young bones and skin, the skin and bones could be from cows that age is still relatively young, and pigskin [2]. The use of gelatin derived from animal skin is a problem for vegetarians, while pork skin gelatin as a raw material to cause problems for consumers who are Muslims [3]. The role of gelatin in the manufacture of marshmallow cream can be replaced by a polysaccharide that has the ability to form a gel in the cooling process [4]. The ability to form a gel in the starch can be used to replace the role of gelatin in confectionery products, especially marshmallows. In the gel confectionery products, a high viscosity during the cooking process is not desirable, therefore, to use modified starch.

Acetylation and oxidation methods are examples of methods used to chemically modify starch. The process of oxidation of starch, resulting in depolymerization and the formation of carboxyl and carbonyl functional group. While the process of acetylation, causing esterification of hydroxyl functional groups on the starch and the stability of the sol [5]. The starch undergo oxidation has weakened granules so that it will be fragmented during the cooking process and will not increase the viscosity so that it can be applied to confectionery products, especially products that require gel with low rigidity [6]. The use of oxidation-acetylated starch in confectionery products as a substitute for gelatin role will be very beneficial, given the potential for significant Muslim consumers, regarding halal gelatin.

Therefore, the aims of this paper are to determine the effect of the white corn starch modification by oxidation and acetylation-oxidation on gel formation and character of the resulting gel; and applying a modified white corn starch in the manufacture of marshmallow.

MATERIALS AND METHODS

Materials

The white corn Canggal and Srikandi varieties is supplied from the Food Plant Research Institute Ungaran, Semarang, Indonesia and Pulut varieties from Agriculture Office of Gorontalo, Indonesia.

The chemicals used to starch modification are sodium hydroxide, sodium hypochlorite, sulfuric acid and distillated water the materials used to make marshmallow cream are sugar, corn syrup and egg white.

Isolation and modification of corn starch

Isolation of corn starch use the method of Chi et al. [7]. Oxidation of corn starch performed using methods of Aini and Hariyadi [6]. Acetylation-oxidation process conducted by using acetylation by Garg and Jana [8] and continued with the process of oxidation.

Analysis of corn starch

Analysis performed on corn starch include least gelation concentration (LGC) [9], syneresis or freeze thaw stability [10] and the gel strength [11].

Production of marshmallow cream

Marshmallow cream was produced in the following manner: 20 g of corn starch was dissolved in 100 mL of water then heated to form a starch gel. Furthermore, starch gel is heated with a sugar solution that made from 100 g of sugar, 40 mL of corn syrup, and 20 mL of water. Meanwhile, 80 g of egg whites whipped until fluffy and then blended with starch gel. The mixing of the dough is done at 40°C to form marshmallow cream. The dough was left at 30°C for 16 hours before sensory analysis.

Sensory analysis of marshmallow

Sensory analysis was conducted by 25 trained panelists, with four samples of marshmallow cream (without the addition of starch, with the addition of native starch, with the addition of modified starch by oxidation process, and with the addition of modified starch by acetylation-oxidation process). Testing was performed by Hedonic Test in a scale of 1-5 and Ranking Test. The hedonic test was performed to support the results of the ranking test due to the best formula may not be accepted by consumers. The hedonic test is carried out on the parameters of color, texture and topical power. Ranking test is conducted by sorting formula based on the favorite level of the overall.

RESULT AND DISCUSSION

Characteristics of modified white corn starch

Gelation characteristics

Table 1 shows the characteristics of white corn starch. At low starch concentration, the lower of LGC has the better gelation ability. The lowest LGC index

was observed in the starch samples derived from Pulut varieties that have amylose content was smaller than the two other varieties (Srikandi and Canggal). Increasing concentrations of starch will increase hardness and strength of the gel, due to the higher the starch concentration will produce more rigid of gel.

Table 1. The gelling characteristics of native and modified white corn starch

Corn variety	Type	Starch concentration (%)						LGC
		2	4	6	8	10	12	
Pulut	Native	V	G	G	FG	FG	FG	4
	Oxidation	V	V	G	G	FG	FG	6
	Acetylation -oxidation	V	G	G	G	FG	FG	4
Canggal	Native	V	V	G	FG	FG	FG	6
	Oxidation	V	V	G	G	G	FG	6
	Acetylation -oxidation	L	V	G	G	G	FG	6
	Native	V	V	G	G	FG	FG	6
	Oxidation	L	V	G	G	FG	FG	6
	Acetylation -oxidation	L	V	G	G	G	FG	6

Abbreviation: LGC= Least gelation concentration; L = liquid; V = viscous; G = gel; FG = firm gel

Pulut starch has high content of amylopectin with the lowest LGC index. The highest LGC index in the sample has amylose content and modified by oxidation. This is consistent with Luo et al. [13] that the lowest LGC index in the sample has a high content of amylopectin. In this study, the highest LGC index in samples has a high amylose content and modified by oxidation. Gel strength of amylopectin provides rigidity starch due to their part crystalline, which this crystalline area is good both during the development of granular or liquid media solution among granules, may contribute to increasing the strength and their rigidity of starch gel [14].

Starch is being subjected to chemical modification i.e. oxidation. It is tend to have the highest index of LGC, as according to Zhang et al. [15]. The presence of carboxyl and carbonyl has tended to stretch by intramolecular, which limit the interactions between amylose molecules that undergoes oxidation. In modified starch by acetylation-oxidation, LGC index tend to be equal to starch by oxidation is "6". It indicates the gel formation was started at a concentration 60% g/l of starch but differ in provide the characteristics of resulting gel.

The same rigid gel was formed by the oxidation of starch and native starch, but softer than the other starch. Meanwhile oxidized starch has a gel that more rigid and harder than the two other starches that look soft and sticky.

Gel strength

Marfill et al. classifies the gel strength measurements into two types [16]. The first type is measurement hardness or violence gel that shows damage (resistant) of gel when pressed (compression) or indicate the magnitude of the load for deforming the gel before damage or breakdown of the gel. The second type is a measurement of breaking strength or power gel rupture, the gel elasticity limit or show magnitude resistance to deformation gel (gel to tear or rupture). The use of different white corn varieties produces different gel strengths. Gel strength is affected by the content of amylose, fat, sugar, protein, mineral and salt.

Starch derived from Srikandi varieties with oxidation modification treatment, gives the highest hardness gel (i.e. 45.3 gf) compared to other starch (Figure 1). The higher the amylose content of starch, it will produce a high gel strength. With such high amylose content of the amylose, tendency to form aggregates is larger, then the formed gel is stronger.

During expansion, amylose tends to dissolve and escape into water media, reassociation between the hydrogen bond and configurate gel. It is called retrogradation or setback. Pasta becomes cloudy and opaque when it is cooled, and ultimately will release water to form elastic consistency. Due to the configuration of amylopectin, reassociation be low and gelation capability decreased, so that the sol or paste made from waxy maize starch become soft and clear. High degree of linearity at high amylose starch will produce pasta that is more rigid and opaque [17]. The higher the amylose content in the starch, the crystals formed will widen, resulting in higher gel strength.

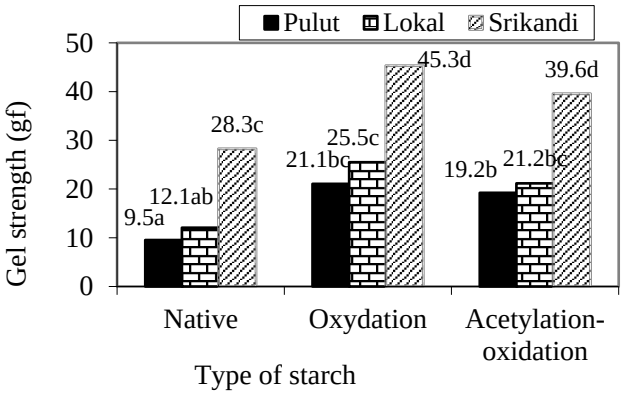

Figure 1. Gel strength of modified white corn starches

Gel strength of gel produced from modified starch is greater than from native starch. According to [15]), the replacement of carboxyl and carbonyl result in hydration and swelling of the starch, gelatinization temperature of oxidized starch is rising, but enthalpy unchanged. Oxidation at low chlorine concentration (1%) produce starch with higher peak and final starch

viscosities and lower breakdown. Carboxyl groups form crosslinks hemiacetal that strengthen the integrity of the starch. Although amylose and amylopectin are degraded at a higher level of oxidation, depolymerization of starch molecules will be override occurred crosslinking.

Modification of starch by acetylation cannot prevent the decline or increase viscosity in starch paste cooling process. Existence of acetylation is only able to prevent the decline and increase in viscosity rapidly, with the properties of the stability pasta better than native starch paste

Syneresis (freeze thaw stability)

Syneresis or freeze thaw stability, the most important properties of starch, is the release of water from the pasta during the cooling process. In general, a low syneresis appears in the first period of freeze thaw, then syneresis will be higher in the next period (Figure 2). This phenomenon occurred because the reassociation of starch chain, which started with the nucleation followed by the propagation to form perfect crystals [18].

In the first period, more water was released from native starch compared to modified starch. Native starch release water 5.75 to 10.25%, compare to 3.70 to 5.64% of the oxidation modified starch, and 1.50 to 3.35% of acetylation modified starch. Release of water will be higher in the periods of subsequent freeze thaw. This phenomenon happens because starch chain reassociation, which begins with the nucleation and continued with propagation to form a perfect crystal.

In the second period, Srikandi starch shows the highest water released than the other two types of starch. Instead acetylation-oxidation modified starches provide the best freeze thaw stability with the least water released. Amylose content related to the ability of native starch to syneresis. In modified starch removal of water also affected by the amylose content. However, according to Sangseethong [19], there are other factors that affect water released namely their carboxyl group, has an important role in stabilize amylose molecules and minimize the occurrence of retrogradation.

Starch derived from Srikandi varieties has the lowest level of stability with the increasing number of water released. The acetylation-oxidation modification step produces the higher levels of stability against retrogradation than native starch and oxidized starch. Retrogradation process has several effects such as increased viscosity, turbidity formation, formation of the layer is not soluble in hot pasta, the formation of insoluble particles, gel formation, and the occurrence of syneresis [20].

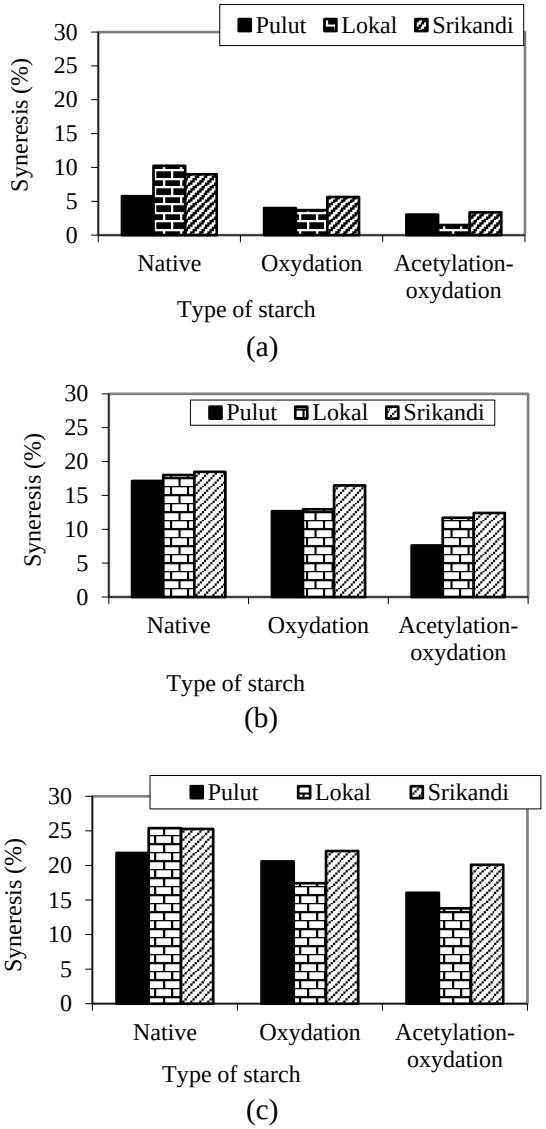

Figure 2. Syneresis of starch at different period: a) 1st period, b) 2nd period; c)3rd period

Starch retrogradation occurs when the starch molecules start reassociation to form the structure. Starch gel is unstable and non-equilibrium systems that cause structural changes during storage [21]. Syneresis on starch derived from Srikandi varieties larger than the other two types of starch, regard to differences in levels of amylose. During freeze thaw period, the texture of the entire pasta starch changes from soft gel into a gel with porous texture and spongy structure.

Retrogradation in starch gel increases along with longer storage periods. Characteristics retrogradation gel starch was indirectly affected by rearrangement of the structure of starch chain, with parts of amorphous and crystalline starch that not yet gelatinization, which

then switch affects the breakdown granules during gelatinization and the interactions that occur between chains of starch during storage gel [14, 20].

Sensory properties of marshmallow cream

Starch from Srikandi varieties was selected in the application as a substitute for gelatin in marshmallow cream. This is based on its ability to form a gel and the best starch gelation properties because of the higher amylose content. Both types of modification are oxidation and acetylation-oxidation used in the manufacture of marshmallow cream to determine the influence of properties in the reception panelist. Both oxidation and acetylation-oxidation process provide different the functional properties of starch, so it will affect the final product.

Quality evaluation of a product can be performed by physical, chemical and nutritional test. However, it is nothing if the food product is not edible because organoleptic properties are not appetizing. Thus, the organoleptic testing is a necessity for food commodities. Testing the organoleptic quality of food commodities is not only taste it, but also the shape, size, color, texture, and aroma plays a very important.

Table 2 shows the result test of sensory properties value of marshmallow cream. White color on marshmallow cream did not differ from each other by a score reception 3.08 to 3.32 (neutral). Both native and modified starch has a high degree of whiteness. Therefore, application of modified corn starch to the marshmallow cream will continue to give the white color in the final product, which could not be distinguished by the panelists.

Texture value of marshmallow cream ranges from 2.48 (dislike) to 3.96 (tend to like). Texture of marshmallow cream without addition of starch had a lowest score of 2.48, while the addition of modified starch acetylation-oxidation provides the best texture (3.96). Characteristics of acetylated-oxidation starch paste suitable as a substitute of gum in chewing. The shelf life of gum confection made from starch increase due to great stability and resistance to stirring. According to Salem et al. [22], the modified starches by acetylation-oxidation also gives the characteristic taste and appearance better than acid-modified starch.

The ability to smear of marshmallow cream is expressed as a convenience product to spread on the surface of the field. Application in the food, marshmallow cream can act as a substitute for butter on bread, as well as filling in the biscuit.

Table 2. Sensory properties score of marshmallow cream

Marshmallow cream	Spreadable	Color	Texture	Preference
Without starch	2.8[a]	3.08[a]	2.48[a]	1.36[a]
With native starch	3.36[b]	3.12[a]	3[b]	2.34[b]
With oxidation starch	3.64[c]	3.28[a]	3.64[c]	2.58[b]
With acetylation-oxidation starch	3.96[c]	3.32[a]	3.96[c]	3.72[c]

Note: the numbers in one column followed by the same letter (a, b, or c) show no significant difference at the 5% in the statistical test

Topical power of marshmallow cream ranged from 2.8 (likely neutral) to 3.96 (tend to like). Topical power closely related to rheologic properties (i.e. flow properties) of the gel-forming material, the thickness (viscosity) and the moisture content of the product [23]. The modified starch is a gelling material with a low viscosity level. Oxidized starch gives marshmallow cream viscosity higher than acetylated-oxidation starch, which has a better fluidity then easily applied. Therefore, the best acceptance of panelist is the product that use of acetylation-oxidation starch.

The appearance of marshmallow cream was significantly different between with the addition of native starch and without the addition of starch. Products with the addition of oxidized starch is not a significantly different products with added acetylated-oxidized starch. Scores of flatness spreads ranged between 2.8 (tend to be neutral) to 3.96 (tend to like). Ease smeared closely related to flow properties of the gel-forming material, the viscosity and the moisture content of the product. Artamonova et al. [24] state that the modified starch is a gelling material with a low viscosity level. Oxidized starch gives viscosity of marshmallow cream higher than the acetyl-oxide starch, which has better fluidity so easily applied. Therefore, the best product is using acetyl-oxide starch.

CONCLUSION

Starch is being subjected to acetylation-oxidation provide the best freeze thaw stability with the least water released than native starch and modified oxidation starch. Starch modified by oxidation tend to have the highest LGC index. Gel produced from modified starch has gel strength greater than from native starch. Marshmallow cream that uses a starch modified by acetylation-oxidation, have the best received power in testing organoleptic by the panelists. Use of modified starch does not give a noticeable

difference in color of the product, but it gives the best texture and spread power compared to products using native starch.

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REFERENCES

[1] E. Kirtil, A. Aydogdu, and M. H. Oztop, "Investigation of physical properties and moisture sorption behaviour of different marshmallow formulations," *Acta Hortic.*, no. 1152, pp. 243–248, Mar. 2017.

[2] Y. Demirhan, P. Ulca, and H. Z. Senyuva, "Detection of porcine DNA in gelatine and gelatine-containing processed food products—Halal/Kosher authentication," *Meat Sci.*, vol. 90, no. 3, pp. 686–689, 2012.

[3] A. A. Karim and R. Bhat, "Gelatin alternatives for the food industry: recent developments, challenges and prospects," *Trends Food Sci. Technol.*, vol. 19, no. 12, pp. 644–656, Dec. 2008.

[4] R. C. Prestes, E. Beleski, and B. Carneiro, "Hydrolyzed collagen, modified starch and guar gum addition in turkey ham," *Ciência Rural*, vol. 42742, no. 7, pp. 1307–1313, 2012.

[5] C. I. K. Diop, H. L. Li, B. J. Xie, and J. Shi, "Effects of acetic acid/acetic anhydride ratios on the properties of corn starch acetates," *Food Chem.*, vol. 126, no. 4, pp. 1662–1669, 2011.

[6] N. Aini and P. Hariyadi, "Gelatinization properties of white maize starch from three varieties of corn subject to oxidized and acetylated-oxidized modification," *Int. Food Res. J.*, vol. 17, no. 4, pp. 961–968, 2010.

[7] H. Chi *et al.*, "Effect of acetylation on the properties of corn starch," *Food Chem.*, vol. 106, no. 3, pp. 923–928, Feb. 2008.

[8] S. Garg and A. K. Jana, "Characterization and evaluation of acylated starch with different acyl groups and degrees of substitution," *Carbohydr. Polym.*, vol. 83, no. 4, pp. 1623–1630, 2011.

[9] M. O. Aremu, O. Olaofe, and E. . Akintayo, "Functional Properties of Some Nigerian Varieties of Legume Seed Flours and Flour Concentration Effect on Foaming and Gelation Properties," *J. Food Technol.*, vol. 5, no. 2, pp. 109–115, 2007.

[10] O. S. Lawal and K. O. Adebowale, "Physicochemical characteristics and thermal properties of chemically modified jack bean (Canavalia ensiformis) starch," *Carbohydr. Polym.*, vol. 60, no. 3, pp. 331–341, May 2005.

[11] D.-H. Kim, S.-K. Na, and J.-S. Park, "Preparation and characterization of modified starch-based plastic film reinforced with short pulp fiber. I. Structural properties," *J. Appl. Polym. Sci.*, vol. 88, no. 8, pp. 2100–2107, May 2003.

[12] F. Han, M. Liu, H. Gong, S. Lü, B. Ni, and B. Zhang, "Synthesis, characterization and functional properties of low substituted acetylated corn starch," *Int. J. Biol. Macromol.*, vol. 50, no. 4, pp. 1026–1034, May 2012.

[13] F. Luo, Q. Huang, X. Fu, L. Zhang, and S. Yu, "Preparation and characterisation of crosslinked waxy potato starch," *Food Chem.*, vol. 115, no. 2, pp. 563–568, Jul. 2009.

[14] N. L. Vanier *et al.*, "Physicochemical, crystallinity, pasting and morphological properties of bean starch oxidised by different concentrations of sodium hypochlorite," *Food Chem.*, vol. 131, no. 4, pp. 1255–1262, Apr. 2012.

[15] Y.-R. Zhang, X.-L. Wang, G.-M. Zhao, and Y.-Z. Wang, "Influence of oxidized starch on the properties of thermoplastic starch," *Carbohydr. Polym.*, vol. 96, no. 1, pp. 358–364, 2013.

[16] P. Marfill, A. Anhe, and V. Telis, "Texture and Microstructure of Gelatin / Corn Starch-Based Gummy Confections," *Food Biophys.*, vol. 7, pp. 236–243, 2012.

[17] J. Singh, L. Kaur, and O. J. McCarthy, "Factors influencing the physico-chemical, morphological, thermal and rheological properties of some chemically modified starches for food applications—A review," *Food Hydrocoll.*, vol. 21, no. 1, pp. 1–22, Jan. 2007.

[18] D. Trivedi, R. J. Bennett, Y. Hemar, D. C. W. Reid, S. K. Lee, and D. Illingworth, "Effect of different starches on rheological and microstructural properties of (II) commercial processed cheese," *Int. J. Food Sci. Technol.*, vol. 43, no. 12, pp. 2197–2203, Dec. 2008.

[19] K. Sangseethong, N. Termvejsayanon, and K. Sriroth, "Characterization of physicochemical properties of hypochlorite- and peroxide-oxidized cassava starches," *Carbohydr. Polym.*, vol. 82, no. 2, pp. 446–453, 2010.

[20] O. V. López, N. E. Zaritzky, and M. A. García,

"Physicochemical characterization of chemically modified corn starches related to rheological behavior, retrogradation and film forming capacity," *J. Food Eng.*, vol. 100, no. 1, pp. 160–168, 2010.

[21] L. Copeland, J. Blazek, H. Salman, and M. C. Tang, "Form and functionality of starch," *Food Hydrocoll.*, vol. 23, no. 6, pp. 1527–1534, 2009.

[22] S. A. Salem, E. M. Hamad, and I. S. Ashoush, "Effect of Partial Fat Replacement by Whey Protein, Oat, Wheat Germ and Modified Starch on Sensory Properties, Viscosity and Antioxidant Activity of Reduced Fat Ice Cream," *Food Nutr. Sci.*, vol. 7, no. 6, pp. 397–404, 2016.

[23] D. M. Thomson, "Marshmallow Power and Frooty Treasures: Disciplining the Child Consumer through Online Cereal Advergaming," *Crit. Stud. Media Commun.*, vol. 27, no. 5, pp. 438–454, Dec. 2010.

[24] M. Artamonova *et al.*, "Study of the properties of marshmallow with the Sudanese rose and black chokeberry dyes upon storage," *EUREKA Life Sci.*, vol. 3, pp. 15–23, 2017.