International Journal of Engineering Trends and Technology
ISSN: 2231 – 5381 /doi:10.14445/22315381/IJETT-V68I12P205
Volume 68 Issue 12, 26-30, December 2020

Production and Application of Crosslinking-Modified Starch as Fat Replacer: A Review

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Abstract — *Consumption of food products with high fat and calories has various long-term risks, including cancer, obesity, hypertension, heart disease, and type-2 diabetes. Fat replacer is an innovation developed in the last few decades that can be used as a substitute for fat, namely in fat-substitutes and fat-mimetics that play a role in resembling the physical and sensory characteristics of conventional fat. Starch has unique physicochemical properties and is suitable as a substitute for fat. Modification of crosslinking starch can improve native starch properties while also having a lower calorific value because it has low digestibility. Applications of crosslinked-starch as a fat replacer can be used to produce cream, ice cream, mayonnaise, muffin, and other products. Therefore, crosslinking modified starch is interesting to continue to be developed, especially as a fat replacer in various food products.*

Keywords — *Fat replacer, fat mimetic, fat substitutes, crosslinked-modified starch.*

I. INTRODUCTION

Consumption of food products with high fat and calories has various risks, including long-term effects of causing degenerative diseases, such as cancer, hypertension, heart disease, obesity, and type 2 diabetes [1]. In addition, regular and high-intensity consumption of foods containing saturated fat can increase blood cholesterol levels, especially increasing low-density-lipoprotein (LDL) levels, which can lead to the risk of coronary heart disease (CHD) [2]–[5]. Along with the times, the number of obesity in the world tends to continue to increase [6]. The various kinds of negative impacts that can be caused by the consumption of high-fat food products make people need to be aware of the importance of maintaining health, including through the consumption of low-calorie fat products monoacylglycerols and diacylglycerols [7], [8]. The use of food products containing polyunsaturated fat (PUFA) from vegetable oils such as soybean oil and sunflower oil has also been shown to reduce the risk of coronary heart disease [9], besides that consumption of food products that contain low fat and high carbohydrates can lowering serum cholesterol [10].

Another effort that can be made to avoid foods that contain high fat is to replace the source of fat using other components. Fat replacer is an innovation developed in the last few decades, which is used as a substitute for fat, divided into two types, namely fat substitutes and fat mimetics. Fat substitutes are materials with molecules with the same physical and functional characteristics as fats in general; some are olestra derived from polyester sucrose, dialkyl dihexadecylmalonate (DDM), and esterified propoxylated glycerols (EPGs). Meanwhile, fat mimetics have characteristics similar to conventional fat's physical and sensory characteristics using several sources, namely protein and carbohydrates [3], [11].

Carbohydrates are a component that can be used to replace fat partially or completely, such as gums, maltodextrin, polydextrose, cellulose derivates, and starch. These components can stabilize water in the form of a gel matrix to increase viscosity and provide a creamy sensation that resembles products with the use of fat [11]. Starch has properties that can be used as a substitute for fat because it can form a denser texture. Still, natural starch is not suitable for various kinds of food product processing, such as in processes using low pH, high temperature, and freezing. Therefore, modification of starch, including the crosslinking method, can improve starch characteristics and lower calorific value due to low digestibility [12], [13].

Modified starch using the crosslinking method results from modification using chemicals to replace the OH-groups with other functional groups such as an ether group, an ester group, or a phosphate group [12]. Crosslinking modified starch provides changes in natural starch characteristics by increasing its solubility, mechanical shear forces, and stability when it is a paste [14].

II. CROSSLINKING MODIFIED STARCH PREPARATION

Crosslinking is a method that is often used to increase the ability and utility of starch by using the addition of a crosslinking agent [15], [16]. Synthesis or modification of starch by the crosslinking method occurs when the bonds between starch molecules become stronger in chemical bonds where the chemical bonds form bridges using polymer chains [17]. The composition and concentration of the reagent, the starch source, the reaction time, temperature, and pH are the factors that determine the success of the crosslinking method [18], [19].

In general, the crosslinking method can be conducted by a dual modification to improve product characteristics. In its use as a fat replacer, a dual modification method that can be applied is a combination of the crosslinking method and the oxidized method [20]. The use of single treatment or crosslinking results in a tendency for starch to be more difficult to gelatinize, the granules to break, and tend to be easier to setback or retrogradation when cooled. Crosslinking-modified starch can fulfill the required functional properties in the product. However, starch still has some undesirable properties, such as ease of retrogradation, which causes a decrease in viscosity of starch paste and shear resistance [16]. Therefore, a further double modification is needed to improve the starch's characteristics to match better the desired characteristics [20], [21].

The dual modified crosslinked method, which is continued with oxidized, produces starch that is not prone to retrogradation. In this condition, starch granules still have a good three-dimensional space, so that they have better water trapping ability than native starch. This starch can be used or mixed in products (as a fat replacer), which produce or create an impression similar to fat [20]. The characteristics that are almost similar to these fats also come from solid non-fat (SNF) contribution, which can be seen through the increase in viscosity. One of the functions of a fat replacer is that it can bind water, which causes an increase in viscosity. However, not all solid non-fats will produce an impression similar to fat because sensationally, this impression may still be obtained, but the creamy sensation is not there. SNF tends to be difficult to swallow. Therefore, this starch modification becomes a solution to replace fat [21]–[23].

III. REAGENTS FOR CROSSLINKING MODIFICATIONS

A. Phosphorus Oxychloride

The reaction between starch and phosphorus oxychloride is fast to produce starch phosphate. This crosslinking reaction depends on the pH used where high pH is an efficient pH for the crosslinking reaction, namely at pH 11 [24]. The time that is owned by phosphoryl chloride in the reaction is not enough to diffuse into starch so that when reacted, it needs to be conducted quickly and immediately to produce phosphorus dichloride, which will diffuse into starch granules to get optimal results from crosslinking modification [25], [26].

B. Sodium Trimetaphosphate

Sodium trimetaphosphate (STMP) is a chemical reagent whose use is still safe for starch, but the reaction between the reagent and starch is slow, so that sodium sulfate can be added to increase the pH to speed up the reaction rate [25].

C. Adipate

The crosslinking reaction between starch and adipate reagent was rapid with an optimum pH of about 8 with anhydrous acetic acid to maintain the pH of the starch solution. There is a hydroxyl acetylation reaction during the crosslinking reaction as a double modification process [25].

D. Epichlorohydrin

The crosslinking reaction between starch and epichlorohydrin reagent (1-chloro-2, 3-epoxypropane) occurs in a multifunctional manner where one crosslink bond consumes one or two other bonds to form diester and diglycerol. To react starch with epichlorohydrin, a lower reagent concentration is needed and then reacted at 40 °C for 17 hours. The reaction is stopped with the addition of 3% HCl with a final pH of 5.25, and then it can be filtered and dried [27].

IV. APPLICATION OF CROSS-LINKING MODIFIED STARCH AS A FAT REPLACER

A. Low-fat cream

The increasing cases of obesity in the world have led to changes in consumer behavior in the use of food products consumed in everyday life. This makes the consumption of food products with low sugar, salt, and fat content, one of which is low-fat cream [28]. Phosphorus oxychloride (POCl3) can be used as a chemical in the crosslinking method. The resulting swelling power in modified starch is lower than that of natural starch. The swelling ability of modified starch due to hydrogen bonds and covalent crosslinking bonds, which are getting stronger, can hold the granules from breaking quickly during the gelatinization process. Generally, crosslinking modified starch with high amylose content is suitable for solving products' viscosity problems during the healing process [29].

The modified high-amylose rice starch resulted in a smaller particle size than cream with low-amylose rice starch with 6.94 μm and 8.23 μm after heating. The resulting texture is softer with starch, which has a smaller particle size and greatly affects the higher starch concentration. A tougher cream texture also evidences this with natural starch, indicating its high ability to hold water [28]. During the storage period, the cream texture with the addition of modified rice starch becomes harder; this can be due to the retrogradation of the amylose fraction [30].

B. Low-fat ice cream

Ice cream is a food product that is liked by the wider community because of its delicious taste. This dairy product contains high fat, which comes from one of its constituent components, namely milk. Babu and Parimalavalli [31] reported that modified sweet potato starch to ice cream did not significantly affect the protein content of ice cream. The addition of fat replacer using modified sweet potato starch showed a decrease in the overrun value at a concentration of 2%. Overrun is a value that indicates a volume development due to mechanical forces in agitation or stirring, where ice cream with a low overrun value tends to cause a tougher texture [32]. According to Warren and Hartel [33], overrun can affect the size of the air cells contained in ice cream products during the freezing and storage process.

The use of modified sweet potato starch as a substitute for fat in ice cream products impacts reducing the melting rate. This can be affected by the weakening of ice cream's structural texture due to the lower amount of fat [31]. The addition of fat replacer from modified sweet potato starch as much as 1% gave an increase in the ice cream product's hardness but decreased when the addition was made to 2%.

This can occur because the ability to freeze in the serum phase makes the hardness value obtained negatively correlated with the viscosity value. In addition, the addition of 1% modified sweet potato starch provides the best quality in the sensory assessment of the product [31].

C. Low-fat mayonnaise

Mayonnaise is an oil-in-water emulsion with a semi-solid form obtained from a mixture of oil, egg yolk, salt, vinegar, and spices, in general mustard [34]. The use of modified starch-based fat replacers can reduce fat and its ability to provide a creamy texture, create the desired tasteless sensation, and increase product viscosity. This is because starch molecules can trap water, making the final texture of the product softer [35]–[37].

The addition of a fat replacer based on modified rice starch with dual modifications, namely crosslinking with hydroxypropylated, decreased the viscosity of the mayonnaise product linearly. The use of modified starch at a concentration of 20% provides benefits in viscosity retention [38]. The addition of a fat replacer at a concentration of 20% is considered optimal by providing a more shiny appearance and yellowish-white color. In addition, there was a decrease in the value of Freeze-thaw stability (syneresis) by 50% for 4 days of storage [38]. Carcelli et al. [34] reported that the formation of mayonnaise with a 25% fat reduction formulation obtained a product that good quality without changing the mayonnaise's taste.

The mayonnaise microstructure with the full use of fat is considered the expected structure in the manufacture of mayonnaise products where the small droplets formed are close together and interact strongly with other droplets. The decrease in the amount of fat is seen by the presence of space between the droplets, which is shown on the mayonnaise's microstructure with lower fat content. The microstructure of the addition of fat replacer described gel formation in the continuous phase of the mayonnaise product in thickening the mayonnaise structure [34].

D. Muffin

Muffins are high-calorie food products that are popular with consumers due to their sweet taste and soft texture. Apart from using starch, in general, the fat replacer used in muffin making still comes from carbohydrates, namely maltodextrin. Modified starch can increase water absorption capacity and reduce the possibility of syneresis [39], [40]. Muffin dough, which produces a low specific gravity value, indicates that the air generation rate with a higher air retention capacity is in the dough. The lowest specific gravity value indicates the best retention. The volume of muffins during roasting using a fat replacer made from modified cassava starch decreased. After reducing the constituent fat in making muffins, the final texture of the product becomes chewier with increasing springiness and chewiness values. During the storage process, the muffin texture becomes more compact by replacing fat with crosslinking modified cassava starch [41]. Crosslinking modified starch with high swelling ability suppresses the formation of insoluble structural networks during the cooling process of the paste to slow down starch retrogradation and keep muffins soft during storage [20], [42].

TABLE 1. APPLICATION OF CROSS-LINKING MODIFIED STARCH IN VARIOUS FOOD PRODUCTS

No	Types of products	Product Characteristics	References
1	Low-fat cream using rice starch	- Starch granule size 2.83 to 4.36 µm - Lower swelling ability and higher syneresis ability than native starch - The total energy in the cream product decreases as the fat content decreases - The texture of the cream is denser (hard) at a starch concentration of 15% - Best texture, creaminess, and sensory when using 5% modified starch	[28]
2.	Low-fat ice cream using sweet potato starch	- Fat and protein content did not change significantly - The decreased overrun value indicates a texture that tends to harden at the addition of 2% fat replacer - Melting point decreased - The good flavor when adding 1% fat replacer - The texture is harder	[31]
3.	Low-fat mayonnaise using corn starch	- Mayonnaise has a good consistency and emulsion stability - The texture is harder	[34]
4.	Low-fat mayonnaise using rice starch	- Lower viscosity - Lower syneresis - Shinier appearance, yellowish-white color on the addition of modified starch 20%	[38]
5.	Low-fat muffins use cassava starch	- The texture is softer and chewy when the addition of modified cassava starch is> 8%	[41]

V. CONCLUSIONS

Carbohydrates are components that can replace the use of fat in food as a fat replacer. The modified starch by the crosslinking method has the advantage of maintaining viscosity by producing a non-fat solid component that resembles the characteristics of fat. In addition, its ability to trap water can provide a stable and desirable viscosity. Starch modification can also provide tastelessness and creaminess characteristics so that it does not interfere with the final product's taste. However, the use of modification with a single method has a weakness, so that a combination of modifications is needed to improve the characteristics of the modified starch.

ACKNOWLEDGMENT

The authors would like to thank the Rector of Universitas Padjadjaran and The Ministry of Education and Culture of the Republic of Indonesia for the support provided.

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