

Chemical Modification of Starch For The Production of Resistant Starch Type-4 (RS4): A Review

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Abstract — Starch digestibility is closely related to its physiological effects in contributing to calorie needs and blood sugar. Various types of starch modifications have been introduced to control calorie intake. Modification of resistant starch (RS) can be an alternative for controlling calorie and glucose intake. The RS can be obtained by chemically modifying starch to resistant starch type 4 (RS4). RS4 is starch that cannot be hydrolyzed into D-glucose through digestion in the small intestine but will be fermented in the colon. This review describes various production methods, physicochemical characteristics, and applications of RS4 in the food industry. RS4 can be produced from various types of chemically modified starch, including by cross-linking, esterification, transglycosylation, and hydroxypropylated methods. Each method has a different effect on the characteristics of RS4, and this can be adjusted to the starch characteristics needed by the food industry. In addition to producing RS4 with low digestibility, chemically modified starch also has better functional properties according to the type of modification and functional groups added to the starch molecule, so that it can act multifunctional.

Keywords — chemical modification, modification method, resistant starch type 4, starch digestibility, starch modification.

I. INTRODUCTION

Starch is the main source of calories by contributing about 40% of the body's energy needs [1]. Starch is digested starting from the organs of the mouth, stomach, and small intestine using the digestive enzymes α amylase and dextrinase, maltase, α glucosidase, and amyloglucosidase[2]. Starch will be converted into glucose, then absorbed by the small intestine, and then metabolized to produce energy at the cellular level. On the other hand, the starch eaten can affect the glycemic response, which can increase the risk of type 2 diabetes. This is due to excessive glucose content in the blood due to excessive consumption of starch-rich foods [1]. Based on its digestibility and physiological effects, starch is classified into slowly digestible starch (SDS), resistant starch (RS), and rapidly digestible starch (RDS). RDS will be digested faster than others, increasing blood sugar levels and insulin levels, while SDS will be digested more slowly in the small intestine. While RS is a starch that

cannot be hydrolyzed into D-glucose through the digestion process and will be fermented in the colon by microbes to produce short-chain fatty acids (SCFAs), this can be useful for preventing colon cancer [2], [3].

Resistant starch can be classified into five types including (a) RS1, resistant starch, which is physically indigestible since it is trapped by the protein complex, cell wall building blocks, and other material protectors; (b) RS2, is a standard starch granule with polymorph types of B and C; (c) RS3, is retrograded starch after going through the gelatinization process; (d) RS4, is a chemically modified starch with the addition of a functional group, for example through esterification, cross-linking, and transglucosylation; and (e) RS5, is a starch consisting of at least two different components that form starch complex compounds, such as amylose-lipid complex and maltodextrin-resistant [4]. Starch digestibility resistance depends on the type and modification used [5]. Chemically modified starch can inhibit the digestive process by blocking access to enzymes in starch [6]. This chemically modified starch only produces a small amount of energy, so some researchers also use it as a fat replacer [7], [8].

In the widespread use of starch, starch modification is a crucial point. Starch modifications that have been used in the food industry include chemical, biochemical, and physical modifications [9], [10]. Chemical modification resulting in RS4 can manipulate the digestibility of starch by forming a steric barrier at the site of enzymatic action. For example, the addition of a hydrophobic group in the form of octenyl succinate (OS) on the starch molecule, so that it can block starch from amyolytic enzymes [2], [11]. This review discusses various further studies on the chemical modification of starch to RS4. Chemical modifications of starch are the method of esterification, cross-linking, transglucosylation, and hydroxypropylation.

II. METHOD OF CHEMICAL MODIFICATION OF STARCH

A. Esterification Using Acids and Octenyl Succinate Anhydride (OSA)

The RS4 production method can be carried out by the esterification using organic acids, including citric acid, formic acid, malic acid, acetic acid, tartaric acid, and polylactic acid [2], [3]. The use of citric acid in the starch modification



method is one of the most frequently used chemical methods to produce RS4. This is due to this method is considered effective for producing resistant and stable starch to high temperatures [12]. In this method, dehydrated citric acid will form anhydrous and carboxyl groups (COOH). Then proceed with the esterification process using a hydroxyl group (OH-) on the starch polysaccharide chain and form starch citrate adduct [13]. Further heating can cause the starch to form cross-links, so that esterification using citric acid has a starch-resistant effect on amylase and reduces digestibility by pancreatic enzymes [14], [15].

The mechanism of starch modification through esterification using citric acid is as follows. When heating, citric acid dehydrates and forms an anhydrous which when in contact with starch in an environment with low humidity; this anhydrous reacts by adding a citrate group to the starch molecule by forming covalent bonds. Furthermore, citric acid and anhydrous will enter the starch granule through the canal and cavitation, destroying the microstructure of the crystalline and amorphous parts of starch, then forming intermolecular covalent cross-links on carboxylic groups by hydrogen bond substitution [16].

Another RS4 synthesis path that can be used in the esterification process is by using octenyl succinate anhydride (OSA). The modification process was carried out in a semi-alkaline liquid medium on starch granules [17]. Basically, this method has almost the same principle as the esterification method using acids, namely by reducing the hydrogen bonds between the starch chains by forming an alkoxide functional group with an OH group through a covalent bond of glucose monomer substitution, which can be accessed to give the desired quality to the starch substrate [11]. In addition, producing modified starch with OSA, besides producing RS4, the modified starch also has properties that can stabilize the emulsion system in various food and cosmetic products [10], [11].

The FDA approved OSA modified starch is to use a maximum of 3% w/w of the OSA starch base. The theoretical allowable degree of substitution about 0.02, which is served with the overall reaction of OSA with starch. The proportion of the degree of substitution shows the value of the efficiency, which is the proceeds of the resulting degree value compared to the value of the permitted degree of substitution [17].

B. Crosslinking Methods

RS4 is characterized as insoluble fiber and does not experience swelling in water media [18]. Cross-linked starch can be used to stabilize the granule structure of starch and to avoid swelling. However, at another level, cross-linked starch can also be used as a thickener in food, but this is not sufficient to produce a resistant effect to amylase. Therefore, by escalating the degree of cross-linking of the starch, it is hoped that it can inhibit the entry of amylase molecules (21–160 kDa) into the starch granules [19]. Usually, this can be conducted by modifying it by adding a polyfunctional

reagent in the form of phosphoryl chloride (POCl_3) and sodium trimetaphosphate (STMP) [20], [21].

Based on research conducted by Woo and Seib[21], it was found that several levels of RS4 were generated through the cross-linking mechanism with POCl_3 , STMP, and epichlorohydrin. The results showed that the highest amount of RS4 was produced by cross-linking starch with POCl_3 .

C. Transglucosylation (TG) Methods

Transglucosylated starch is a chemically modified starch where starch contains glycosidic bonds that cannot be broken by the enzymes produced by the host microorganisms in the digestive tract, causing a decrease in starch digestibility [22]. In the glycosylation stage, the complex of substrate and enzyme will be shaped, then initiating the formation of intermediate oxazolinium ions. The properties of the acceptors determine the type of reaction or chemical reagents used. The reaction continues in the direction of hydrolysis when the acceptor is water; whereas transglucosylation (TG) will occur when the acceptor is a sugar molecule, which leads to oligosaccharides with longer chain lengths making it difficult to hydrolyze by digestive enzymes [23].

D. Hydroxypropylation (HP) Methods

Hydroxypropylation is a chemical modification that produces starch ether when starch reacts with propylene oxide. The hydroxypropyl group ($-\text{CH}_2\text{CHOHCH}_3$) will be damaged when the hydrogen bonds in starch are weakened so that it is more easily accessible to water [24]. Based on research conducted by Zhao et al. [25], hydroxypropyl substitution is located in the lamellar amorphous group (branch area) and the amorphous part between the side chain crystals (lamellar crystals). This is due to the lamellar amorphous part is the most flexible and easily accessible part of the chemical compound. Meanwhile, on the internal side of the chain, the amylopectin molecule has a more compact structure so that not many parts are substituted by hydroxypropyl. Hydroxypropyl inserted into the starch chain is adequate for disturbing the intra- and inter-molecular hydrogen bonds, furthermore weakening the granule of the starch, then cause an increase movement of the starch chain free in the amorphous region. Hydroxypropylated starch is important in food applications because of its low-temperature storage stability, high clarity of pasta, and relatively low pasting temperature required for food products [26].

III. PHYSICO-CHEMICAL PROPERTIES OF RS4

Different types of chemical modifications to starch will have different impacts on the physicochemical characteristics of the resulting RS4. The modifications such as hydroxypropylation and acetylation will increase swelling, whereas cross-link modification will reduce swelling and solubility of starch from various starch sources tested [27]. The following is a summary of several studies that show the different effects of chemical modification on the physico-chemical and morphological properties of RS4.

A. Degree of Substitution (DS)

The degree of substitution depends on the source or type of starch and the reaction conditions chosen. In research with the esterification method using citric acid, the degree of substitution raised from 0.036 to 0.141, along with the addition of citric acid levels from 10% to 60% of the total amount of dry starch. When the change in the degree of substitution changed from 0.123 to 0.273, the resistant starch content raised significantly from 61.7% to 86.5%. This shows that the escalate in the content of resistant starch is directly proportional to the value of the degree of substitution and addition of citric acid. This is due to the occurrence of esterification among starch and citric acid, which forms a cross-linking structure that has a high hydraulic hydrant so that it can inhibit amyolytic enzymes to digest starch [28]. Similar to the study of modification using OSA, the added OSA concentration is direct to the degree of substitution [17]. In the study conducted by Remya et al. [29], esterification, which experienced a raise in the degree of substitution with increasing levels of added OSA, the value of the degree of substitution in modified starch using this method was about 0.0033 to 0.020 for potato starch and 0.0101 to 0.0338 for cassava starch. Meanwhile, the degree of substitution using hydroxypropylation also shows the same pattern, another thing that causes this increase is also influenced by the treatment used in the synthesis process of RS4. In the study conducted by Chun et al. [30], a combination modification was carried out between the addition of hydroxypropylation and continued high hydrostatic pressure (HPP) which showed that the degree of substitution raised with the length of the modification process from 5 to 20 hours.

B. Chemical Bonds

In the synthesis of RS4, several studies have also conducted the chemical bond analysis to detect or identify changes in compounds and detect the functional groups using the FTIR method. The generally observed frequency area is in the 3000-3600 cm^{-1} region, whereas to show the absorption of starch hydrogen bond groups and the absorption is in the frequency region of 2800-3000 cm^{-1} . This is due to the presence of a vibrational range in the $-\text{CH}$ bond. The result of resistant starch using citric acid produced a peak area at 1740 cm^{-1} . This absorption is associated with the vibrational range of the C – O carbonyl group bonds, the peak of 1740 cm^{-1} which is getting stronger, is directly proportional to the increase in the value of the degree of substitution along with the concentration of acid added to the starch modification treatment using the acid method [28]. The modification of Raja banana starch also shows the highest frequency area at 3271.42 cm^{-1} ; this is related to hydrothermal treatment and esterification, which indicates the establishment of covalent bonds between C – O groups in starch and citric acid [16]. Meanwhile, it was confirmed that the modification using OSA produced 2 new peaks at 1724 and 1572 cm^{-1} in the modified potatostarch and cassava

starch. The absorption at 1572 cm^{-1} was caused by the vibrational range of the carboxylate group RCOO^- and a peak at 1724 cm^{-1} which indicated the vibrational range of the C = O group of the OSA group [29].

C. Chemical Bonds

The crystalline structure of starch will change when heated in water. The crystal structure will bind to water molecules by forming hydroxyl groups from amylose and amylopectin using hydrogen bonds which will cause swelling of the granules and solubility [27]. A study using canna starch with the citric acid modification method showed alteration in the crystal structure of type B with changes in the diffraction of 20 peaks with the highest peaks at 17° and double peaks at 22° and 24° [31]. Meanwhile, Raja banana starch decreased the dominance of type A crystal structure with the highest peaks at 23.0°, 17.5, and 15.0, the relative crystallinity of unripe plantain changed by almost 28.76% due to modification and heating treatment so as to increase the detected crystal peak at 5° which shows the forming of a type B crystal structure pattern [16]. The peaks of modified starch crystals using citric acid decreased significantly to be smaller and almost lost. This is inversely proportional to the increase in the degree of substitution and the concentration of acid added at the time of modification of canna starch using the acid method [28]. This change in the crystal structure is also shown by hydroxypropylation treatment with a combination of high hydrostatic pressure treatment. The modification of starch shows that the crystalline structure of type A starch changes to the crystal structure of type B caused by modification of hydroxypropylation [30]. Meanwhile, a different thing was shown by the treatment using the octenyl succinylated esterification method, which showed that there was no change in the crystal pattern after observation. However, the results showed that there was a decrease in the percentage of relative crystallinity. This is due to the reaction of OSA, which is performed in an alkaline, which can influence the crystal structure and facilitate the reaction of starch and large OSA groups [29].

D. Swelling Power

Swelling and solubility are proof of the strong interactions among the starch chains and the amorphous sites and the crystal domains. This interaction is affected by the presence of amylose and amylopectin ratios and their characteristics related to weight, distribution, molecular conformation, and degree and length of branching [27]. Starch modification using OSA can increase the swelling power of starch. This has been reported from several studies which show that the addition of a large OSA group has the effect of weakening the intermolecular hydrogen bonds; this has an effect on the ability of starch to bind water. For example, in potato starch, the initial water-binding capacity of 80.2% and the water-binding capacity of cassava starch initially was 72.1%, then decreased after modification using the OSA esterification method, namely in the range 70.4-72.4% for potato starch and 58.0-59.8% in cassava starch [29].

E. Gelatinization

Gelatinization occurs when starch granules swell to several times their initial size, rupture, and simultaneously the amylose is released and established a three-dimensional network [27]. Modification using cross-linking can hinder cooperative melting of crystals in starch which can lead to an escalation of several degrees of gelatinization temperature [21]. The modified treatment using the citric acid method can reduce the degree of relative crystallinity caused by esterification by the acid initiating a characteristic change of the double helix arrangement. This then affects the formation of substitution citrate covalent bonds, which change the shape of the chain, causing an increase in the amorphous area of starch [16]. All of the tested OSA modified starches showed higher gelatinization temperatures (To, Tp and Te) compared to native starch. The increase in gelatinization temperature is directly proportional to the increase in the value of the degree of substitution. However, several studies resulted in a decrease in gelatinization temperature, which was probably caused by the impairment of the interactions between starch macromolecules by the OS group [29]. Meanwhile, research using hydroxypropylated starch experienced lower enthalpy (ΔH) and gelatinization temperature compared to native starch; this is also correlated to the degree of substitution [30].

F. Pasting Properties

As the starch undergoes gelatinization, the starch granules expand several times from their original size. The Visco-Amylo-Graph from the Rapid Visco-Analyzer (RVA) can be used to determine the effect of the modified treatment. The top shape of the curve reflects the processes involved in the pasta cycle. The high peak of the curve indicates the competence of the starch granule to swell freely before the physical shape of the starch granule breaks [27]. The paste curve produced from modified starch using the citric acid method shows a horizontal curve. This indicates that all acid esterified starch samples had a low degree of substitution, did not expand or form a paste during the RVA test. In addition, there was also a decrease in the viscosity of acid-modified starch, which is a characteristic of significant amorphous area damage [28]. Meanwhile, the paste curves of all resistant starches that were modified using the cross-linking method showed no more than 8% solid starch in the starch slurry [21]. Meanwhile, the modifications made using OSA show a lessen in the peak viscosity indicated by the peak of the curve along with the gradual increase in the degree of substitution. However, several other results showed that there was a rise in the peak viscosity in the modified cassava starch samples using OSA [29].

III. RS4 APPLICATIONS IN VARIOUS FOOD PRODUCTS

The various modification methods of RS4 and their applications in food products can be seen in Table 1.

TABLE 1. THE VARIOUS MODIFICATION METHODS OF RS4 AND THEIR APPLICATIONS IN FOOD PRODUCTS

N o	Modificati on	Characteristic	Application	Refere nces
1	Esterificati on	Has lower gelatinization and retrogradation temperatures, lower gelling ability, and higher paste clarity.	Used in frozen and refrigerated food products as an emulsifier and stabilizer in encapsulation.	[32]– [34]
2	Cross- linking	Has higher granule stability against high shear, high temperature, swelling, and acidic conditions.	Used as a thickener and texturizer in gravies, sauces, soups, bakeries, and dairy products.	[32], [33]
3	Etherificati on(Hydrox ypropylatio n)	Increases freeze-thaw stability, reduces syneresis, improves viscosity and clarity of starch paste.	It is widely used in food products such as puddings, fruit pie fillers, sauces, dips, and gravies.	[25], [30], [32]

Based on the physico-chemical properties of RS4, several food industries take advantage of the functional properties in various food products, especially those with functional health aspects. For example, the use of cross-linked starch as probiotic microencapsulation support in foodstuffs due to its ability that amyolytic enzymes cannot digest, several bacteria that have been successfully encapsulated with this resistant starch include *Lactobacillus casei*, *Lactobacillus brevis*, and *Lactobacillus plantarum*[34]. In the modification of the cross-linking of banana flour starch phosphate using sodium trimetaphosphate, the resistant starch can be used as a potential raw material for the expansion of gluten-free food, which is applied to bakery products and cookies [35]. In addition, RS4 has a function as dietary fiber, so that the colloidal nanoparticles of RS4 from cross-linking and acid hydrolysis could be widely applied to produce beverages rich in dietary fiber [18]. RS4 can also function as a texture improver when added to various types of baked goods, which aims to provide a sweet taste and soft texture to breadcrumbs [36]. In addition, RS4 also has the ability to increase emulsifying capacity and slow down lipid oxidation effectively in food products [33].

IV. CONCLUSIONS

RS4 can be produced through several methods, and each method has a different effect on the characteristics of RS4. This is related to differences in functional groups added during the modification process of RS 4. These differences can be seen from several parameters such as the degree of substitution, the presence of certain types of chemical bonds, the crystallinity structure, pasting properties, gelatinization, and swelling power. The different characteristics of RS4 determine the application of RS4 in various food industries. Therefore, it is necessary to adjust the selected method, which produces resistant starch with the required characteristics and functional properties, for example, as an emulsion, stabilizer, texture forming, or as microencapsulation matrix support.

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