

A REVIEW: FORMATION, BENEFICIAL AND APPLICATION OF RESISTANT STARCH**TỔNG QUAN: PHƯƠNG PHÁP SẢN XUẤT, LỢI ÍCH VÀ ỨNG DỤNG CỦA TINH BỘT TRƠ****Trinh Khanh Son**

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ABSTRACT

This review introduces basic information of resistant starches including their type and structure. There are four types of RS which contain different structure, physiologically beneficial effect and formation. Theoretically, there are three ways of resistant starch formation: (a) chemical modification, (b) physical modification and (c) enzymatic modification. RS2 can be isolated from specific species of plant sources or enzymatic modification. RS3 was produced under the re-association of linear chains of starch. Furthermore, RS4 was formation under chemical modification. Actually, RS is a component of dietary fiber which has various beneficial physiological effect such as laxation and/or blood cholesterol attenuation, and/or blood glucose attenuation, obesity and weight management. Besides, RS is fermented in large intestine and produce short-chain fatty acids that help prevent abnormal colonic cell population and colon cancer. Resistant starch productions by various authors are introduced. Finally, applications of resistant starch are showed to give food manufacturers various selections for using it in industry.

Keywords: *chemical modification; enzymatic modification; food manufacturing; physical modification; resistant starch.*

TÓM TẮT

Bài tổng quan này giới thiệu một số thông tin cơ bản về tinh bột trơ bao gồm các loại tinh bột trơ và cấu tạo của chúng. Về mặt lý thuyết, có ba hướng cơ bản trong việc sản xuất tinh bột trơ: (a) nhóm phương pháp biến tính bằng tác nhân hóa học, (b) nhóm phương pháp biến tính bằng phương pháp vật lý và (c) nhóm phương pháp biến tính bằng enzyme. Các thông tin về việc sản xuất tinh bột trơ bằng các nhóm phương pháp trên do các tác giả khác nhau thực hiện sẽ được giới thiệu. Bên cạnh đó, các lợi ích về mặt sinh lý của tinh bột trơ cũng được giới thiệu. Cuối cùng, một số ứng dụng của tinh bột trơ sẽ được liệt kê nhằm giúp các nhà sản xuất thực phẩm có sự lựa chọn cho việc sử dụng tinh bột trơ trong công nghiệp.

Từ khóa: *tinh bột trơ; biến tính bằng tác nhân hóa học; biến tính bằng phương pháp vật lý; biến tính bằng enzyme; sản xuất thực phẩm.*

1. DEFINITION OF RESISTANT STARCH

Englyst and others [1,2] described resistant starch (RS) as a fraction that resisted hydrolysis by pullulanase and α -amylase in *in vitro* after 120 min of incubation. Furthermore, in *in vivo*, the gut microflora could more or less ferment the starch, thus RS was defined as the fraction that could not be digested in the small intestine. Generally, RS is the difference

between total starch and the sum of RDS and SDS [3]:

$$RS = TS - (RDS + SDS) \quad (1)$$

Resistant starch is sub-divided into four categories: RS₁, RS₂, RS₃, and RS₄ that are normally called type I, II, III, and IV resistant starches.

Type I is physically inaccessible resistant starch that is heat-stable in most normal cooking processes and used as an ingredient in various conventional foods. RS_1 is the difference between the glucose released by the enzyme digestion of a non-homogenized sample and that of a homogenized food by chemical measurement. In general, RS_1 becomes less resistant to hydrolysis by milling or chewing process [5].

Type II is in a certain granular form. The digestive enzymes, like various amylases, have limited access to the compact structure in a radial pattern of starch granules such as raw potatoes, green bananas, some legumes, and high amylose corn. RS_2 is the difference between the glucose released by the enzyme digestion of a boiled homogenized food sample and that of an un-boiled, non-homogenized one. Both RS_1 and RS_2 are digested very slowly and incompletely in the small intestine [3]. The resistance of RS_2 is reduced by food processing and cooking [4].

Type III, the most resistant starch fraction, consists of re-associated amylose formed during cooling of gelatinized starch, and is contained in moist-heat-treated foods. Pancreatic amylases cannot hydrolyze RS_3 at all. This type of RS remains intact despite dispersion by boiling and enzymatic digestion [3]. Only KOH or dimethyl sulfoxide (DMSO) can disperse this RS_3 [5]. In the formation of RS_3 , starch granule is completely hydrated resulting in the leaching of amylose molecules into the solution as a random coil polymer. These coils re-associate as double helices and are stabilized by hydrogen bonding on cooling [6]. There are six glucose residues per turn, in a 20.8 Å repeat, of each strand in the helix. This double helix model is left-handed and parallel-stranded helices [3]. By using DSC, a melting point or endothermic peak of an RS_3 was found to be at least about 140°C. Four sequential stages (gelatinization, nucleation, propagation, and heat-treatment) are used to increase RS_3 content in samples [7]. To prevent substantial production of lower melting amylopectin crystals, lower melting amylose crystals, and lower melting amylose-lipid

complexes, this procedure uses crystal nucleation and propagation temperatures. The nucleating and propagating temperatures used are higher than the melting point of the amylopectin crystals and any amylose-lipid complexes, respectively. The high melting temperature of this RS_3 allows its application in bakery products [3].

Thus, the relationship among various starch fractions based on the action of digestive enzymes can be expressed as follows:

$$RS_1 = TS - (RDS + SDS) - RS_2 - RS_3 \quad (2)$$

$$RS_2 = TS - (RDS + SDS) - RS_1 - RS_3 \quad (3)$$

$$RS_3 = TS - (RDS + SDS) - RS_1 - RS_2 \quad (4)$$

Except α -(1→4) or α -(1→6) bond, some novel chemical bonds are found in RS_4 fraction (Sajilata and others 2006). These new linkages could be formed by cross-linking with various types of chemical reagents [4].

Commercially available resistant starches include Hi-maize[®] (RS_2), Novelose 330[®] (RS_3), and CrystaLean (RS_3).

2. FORMATION OF RESISTANT STARCH

Chemical, physical, and enzymatic treatments can be used to prepare RS.

2.1 Chemical modifications

A distarch phosphate is prepared by cross-linking with phosphorous oxychloride or sodium trimetaphosphate (STMP). The primary (6-OH) and secondary hydroxyls (2-OH and 3-OH) in starch are able to react with multifunctional reagents resulting in cross-linked starches. Cross-linking starches that contain high amount of RS were reported [8]. Phosphoryl chloride ($POCl_3$), sodium trimetaphosphate, sodium tripolyphosphate (STPP), and epichlorohydrin were used to prepare these cross-linked resistant starches. In that study, RS_4 level reached 75.7, 85.6, and 75.8% at 2.0% (sb) and 2.0% (sb), respectively, of STMP/STPP (11.9:0.1, w/w) [9].

The citrate resistant starch production was reported by Xie and Liu [10], in which waxy corn citrate starch with RS content of

87.5% was prepared by the reaction at 140°C for 7h. Citrate groups prevented starch granules from swelling resulting in the resistance to enzymatic hydrolysis.

RS₄ has been prepared from various starch sources such as potato, banana, corn, wheat, and so on. Currently, phosphated distarch phosphate made from high amylose maize is utilized as a food additive (E1413) in the EU [3].

2.2 Physical modifications

Heat treatment is one of the popular methods for the formation of RS. For RS₃ formation, the granular starch is completely gelatinized resulting in random coil polymer of leached amylose in solution. During cooling process, the polymer chains re-associate as double helices, stabilized by hydrogen bonds. There are six glucose units per turn in a 20.8 Å repeat in the helix of each strand. Further retrogradation causes the double helices to pack in a hexagonal unit cell [11, 12]. High RS₃ content can be obtained by retrogradation in which gelatinized starches are stored under various temperature conditions [13, 14]. Kim and Kwak [13] reported the increase of RS content up to 12.44% by autoclaving-cooling cycles (120°C/1h - 40°C/overnight). Besides, Berry [14] reported the formation of around 10% RS by autoclaving (134°C) and storage at 4°C for 2 days. Other authors [15] applied both annealing and heat-moisture treatment to partially acid-hydrolyzed high-amylose maize starch to reach the maxima of total RS and boiling-stable RS (79.2 and 63.2%, respectively). In addition, a previous study by Jacobasch and others [16] reported an increase in yield of RS (771 g/kg) by heat-moisture treatment of Novelose 330.

2.3 Enzymatic modifications

Debranching enzymes (isoamylase, pullulanase) have been used to form linear short chain α -glucans. Typically, at least 95% starch is debranched by weight to form linear chains which have average chain length of 14–20 glucose residues and less than about 0.2% α -1,6-D-glucosidic linkages. The

debranched starch enhances the recrystallization by allowing the starch to stand and retrograde, resulting in highly crystalline short chain amylose as RS₃ which constitutes around 70–75% of samples [17].

Digestion-resistant starch was prepared by using recombinant amylosucrase from *Neisseria polysaccharea* [18] with sucrose as donor. Branch chain elongation was found during enzymatic reaction. In addition, insoluble RS value increased from 6.9% of waxy and 7.7% of normal corn starches to 22.3 and 20.7%, respectively. Higher melting temperature of enzymatically modified starches was observed compared to the corresponding native starches. Furthermore, both pasting temperature and peak viscosity of modified starches increased compared to those of native starches.

3. PHYSIOLOGICALLY BENEFICIAL EFFECTS OF RESISTANT STARCH

RS may be considered as a component of dietary fiber [19]. A definition of dietary fiber proposed by AACC [20] is as follows: “Dietary fiber is the edible parts of plants or analogous carbohydrates that are resistant to digestion and absorption in the human small intestine with complete or partial fermentation in the large intestine. Dietary fiber includes polysaccharides, oligosaccharides, lignin, and associated plant substances. Dietary fibers promote beneficial physiological effects including laxation, and/or blood cholesterol attenuation, and/or blood glucose attenuation”.

RS is not digested in the small intestine and has few interactions with other components of the upper gastrointestinal tract. It is fermented in the large intestine and produces carbon dioxide, methane, hydrogen, organic acids, and short-chain fatty acids (SCFA) such as butyrate, acetate and propionate [4]. SCFA helps prevent the development of abnormal colonic cell population. Besides, the butyrate formation in the large intestine leads to colon cancer prevention [5]. Furthermore, colonic blood flow and fluid and electrolyte uptake are stimulated by SCFA [21].

RS shows not only positive effect on hypocholesterolemia such as lower plasma cholesterol and triacylglycerol (Sajilata and others 2006) but also the inhibition of fat accumulation [22]. Rich-RS foods have beneficial effects on diabetes and impaired glucose tolerance, and can be applied to the treatment of obesity and weight management as well [4]. RS reduces gall stone formation [23]. The potential benefits of RS in ameliorating the symptoms of inflammatory bowel diseases such as ulcerative colitis have also been examined [4].

4. APPLICATIONS OF RESISTANT STARCH

The industrial applications of RS are mainly based on two reasons: (a) potential physiological benefits and fiber-fortification, and (b) unique functional properties, yielding high quality products not attainable with traditional insoluble fibers. RS can be used in grain-based low and moderate moisture foods. Because of low water holding capacity, RS is a functional ingredient that provides good handling in processing and improves texture,

crispness, and expansion in the final product [24].

RS is used as a source of dietary fiber in bakery products such as bread and muffins and breakfast cereals. According to the starch selected, desired fiber level, structure-function relationship, and the amount of RS used could be varied. In bakery products, RS₃ can be used as a low-calorie substitute because of its baking properties (surface cracking, pleasant aroma, golden brown color, and cookie spread) [25].

Replacing 30% of flour with 4 cycled autoclaved-cooled RS₃ corn starch, cross-linked RS₄ maize starch and annealed and cross-linked RS₄ maize starches resulted in sponge cakes of high quality, while for yellow layer cakes, the replacement level was found to be 12.5% [26, 27]. RS (20%) from high amylose corn starch exhibited excellent properties in tablet coating [28]. Cross-linked RS₄ prepared from some starches has been used in formulations needing pulpy texture, smoothness, flow ability, low pH storage, and high temperature storage [29].

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