Modified Preparation and Application of Starch Octenyl Succinate

Cheng Shi, Shuming Zhong, Ruirui Zhang, Zijie Liu, Yanzhen Yin*

Qinzhou Key Laboratory of Biowaste Resources for Selenium-enriched Functional Utilization, Beibu Gulf University, Qinzhou 535011, China

*Corresponding author: yinyanzhen@bbgu.edu.cn

Keywords: Octenyl succinate starch ester, Preparation method, Function, Application.

Abstract: Octenyl succinate starch ester has outstanding advantages in the preparation of medicinal and food functional materials. Its preparation methods and application research have received extensive attention from researchers. In this paper, the water phase method, organic phase method and dry method commonly used in the preparation of starch octenyl succinate are summarized, and the representative work of starch octenyl succinate in food, pharmaceutical and new functional materials is summarized, which can provide support for further optimizing the preparation process of starch octenyl succinate and exploring new application fields.

1. Starch

Starch is the product of plant photosynthesis. It is a natural polymer compound of polysaccharides formed by glucose polycondensation. It is a natural, renewable and biodegradable polymer with the most abundant sources in nature. It will not pollute the environment. It is not only used to store energy to meet the growth and development of plants, but also plays an important role in human life [1]. It is deposited in seeds, tubers, roots and fruits of plants in the form of particles. It is one of the most abundant carbohydrates in the biosphere [2]. Starch has a semi crystalline structure and consists of two main molecules: linear or slightly branched amylose and highly branched amylopectin. The crystal region is mainly formed by Amlopectin in a double helix structure, which is dense and not easy to be affected by external forces and chemical reagents. The amorphous region is mainly formed by amylose in a loose structure, which is easy to be affected by external forces and chemical reagents. The amylose and branched chain contents of starch from different sources vary greatly. Natural starch is usually a mixture of 10 ~ 20% amylose and 80 ~ 90% amylopectin.

Starch is extracted and refined by wet grinding, sieving and drying. Commercially, corn starch, cassava starch, wheat starch, potato starch and rice starch are widely used [3]. There are a lot of reactive hydroxyl groups in starch molecular chain, which provides a structural basis for starch modification. Based on the inherent characteristics of natural starch, modified starch is treated by physical, chemical or enzymatic methods to introduce new functional groups into starch molecules or change the size of starch molecules and properties of starch granules, thus changing the natural characteristics of starch and making it more suitable for certain application requirements. Nowadays, there are more and more varieties and uses of modified starch, which are widely used in various fields, which brings great convenience to our life and work [4]. At present, the chemical modification of starch mainly involves the esterification, etherification or oxidation of effective hydroxyl groups on glucose monomers [5]. As modified starch is not only widely sourced, cheap and easily available, but also has good degradability and biocompatibility, it is one of the modified natural polymers with the best application prospect. Various modification technologies can endow cassava starch with unique solubility, rheology and other characteristics [6,7], making it widely used in membrane materials [8], biomaterials [9], functional feed [10], The development and application of modified starch have attracted great attention of researchers.

2. Octenyl succinate starch ester

Among esterified starches, starch octenyl succinate (OSA starch for short) is a kind of emulsifying thickener with high safety. It has been certified by FAO and World Health Organization (FAO/WHO) that it can be added to food, and its application range is not limited. It is also the only modified starch that can be used as food additive in China [4, 5], which has outstanding advantages in preparing medicinal and food functional materials. Starch octenyl succinate is white powder, nontoxic and odorless, and can be dissolved in hot water, and can be dissolved in cold water after pregelatinization treatment. It is a transparent liquid and has good stability in acid and alkali solutions [11]. Under alkaline conditions, octenyl succinic anhydride (OSA) reacts with active hydroxyl groups on starch molecules to form OSA starch. In the reaction, the five membered ring of anhydride is opened, one end of which dehydrates and condenses with the hydroxyl group of starch molecule to form ester bond, while the other end generates carboxylic acid, and the pH in the system will continue to decline. Therefore, it is necessary to continuously add alkaline reagents such as sodium hydroxide to neutralize the generated carboxylic acid, so as to control the system to maintain weak alkaline conditions and promote the reaction to esterification. Hydrophilic starch is hydrophobic due to the existence of Octenyl, which leads to the amphiphilic of octenyl succinate starch ester. The esterification mechanism of OSA starch is shown in Figure 1.

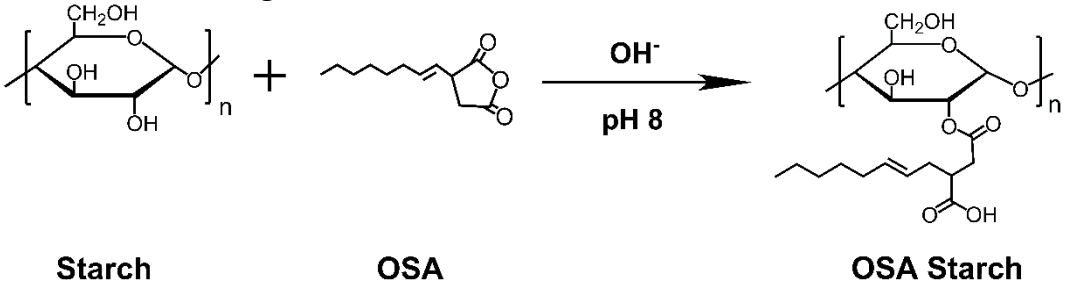

Figure 1 The esterification reaction mechanism of starch octenyl succinate

3. Preparation of octenyl succinate starch ester

At present, the preparation methods of starch octenyl succinate mainly include water phase method, organic phase method and dry method. In addition, the starch is pretreated first and then esterified.

In the aqueous phase method, water is used as medium to prepare starch emulsion with a certain concentration, OSA is slowly dripped into the starch emulsion, then the reaction system is adjusted to be slightly alkaline with alkali solution, and the reaction is stirred at a certain temperature. After a certain period of reaction, it was adjusted to neutrality with hydrochloric acid. Finally, the reaction solution was alternately washed with water and ethanol, dried and crushed to obtain OSA starch samples. Liu et al. [12] prepared a series of waxy corn starch esters with substitution degree by aqueous phase method, and found that OSA groups were unevenly distributed in the amorphous region of the whole particle, and the strength of the central cavity of the particle increased obviously. The advantages of aqueous phase process are mild conditions and simple operation, and the products obtained are relatively pure. However, because the reaction is a heterogeneous reaction between starch granules and anhydride liquid, the low solubility of OSA in water often leads to low reaction efficiency and low degree of substitution.

Organic phase method uses inert organic solvents (such as ethanol, benzene, acetone, dimethyl sulfoxide, etc.) instead of water as reaction medium, and adds OSA and starch to react. At the same time, organic base or inorganic base is used to adjust the micro-alkali environment of the reaction system, and stirring is continued; after the reaction is finished, it is neutralized with acid, and then washed, filtered, dried and crushed with ethanol to obtain OSA starch products. Viswanathan [13] first reported the research work of using pyridine instead of water to prepare OSA in non-aqueous medium. In this work, pyridine was used as a reaction solvent, which increased the initial reactivity of starch granules and also served as a catalyst for OSA starch reaction to form succinyl-pyridinium

intermediate, which was easier to react with starch hydroxyl than unactivated OSA molecules. Wang et al. [14] recently used this method to prepare delivery carriers for bioactive food ingredients, and finally obtain products with high degree of substitution to make matrix tablets, which can transport bioactive food ingredients to the colon and prevent enzyme degradation in the early stage of digestion. The advantages of organic phase production are high reaction efficiency and high degree of substitution of products, but the cost is high. Organic solvents do some harm to the environment and human health. Therefore, the products obtained by this method are greatly limited in application.

The dry method is to mix starch with alkali solution (such as Na3PO4, Na2CO3, etc.) to keep the starch in a semi-dry state, and add OSA under heating condition for uniform mixing reaction. Kim et al. [15] prepared glutinous rice starch octenyl succinate by heating the mixture of starch and OSA at high temperature under the condition of low pH. The production method has the advantages of simple process, low product cost, high reaction efficiency, high product substitution degree and low environmental pollution. However, the materials cannot be fully mixed evenly, which may lead to severe local reaction and high impurity content of the product.

In the esterification process, because starch is a polycrystalline system, it is difficult for OSA groups to enter the starch due to the tight crystalline region, and most of the modified OSA groups are distributed on the surface of starch. Pretreatment of starch can expose more active hydroxyl groups and reduce crystallinity of starch, improve reaction efficiency and degree of substitution, and improve product performance. Zhengmao Zhang et al. [16] pretreated corn starch by mechanical activation, and then cross-linked and esterified, and concluded that the degree of substitution and anti-coagulation of starch products obtained by composite modification were better than those obtained by single modification. Huang et al. [17] adopted α- Amylase pretreated corn starch had larger specific surface area and increased reaction pores. The substituents of enzymatic pretreated OSA starch were distributed in the amorphous and crystalline regions of the granules.

In general, aqueous phase method, organic phase method and dry method have their own advantages and disadvantages in the preparation of OSA. For specific synthesis and preparation, appropriate preparation methods can be selected according to the requirements of preparation efficiency, product substitution degree or solvent system. In addition, mechanical activation pretreates starch and then modifies it to prepare OSA, which provides more preparation process options for the development of modified starch to meet the needs of different industries.

4. Application of octenyl succinate starch ester

OSA starch has double functions of emulsification and thickening, which can improve the texture and structural stability of materials. OSA starch is often used as emulsifier in food, medicine and industrial products. As a clouding agent in beverages, microcapsule wall materials and biodegradable materials.

OSA starch is an interesting food application ingredient, because it has gelatinization characteristics, slow digestibility and other functional characteristics, and also has emulsification. Generally speaking, OSA starch is a low-cost fat-free component with certain resistance to digestion, so its application is beneficial to the formulation of functional foods, aiming at meeting the needs of obesity and diabetes prevalence for healthier products and heart disease in the world. Balic et al. [18] used OSA starch as a fat substitute in bread dough, and obtained products with similar characteristics to control bread. Chivero et al. [19] formulated an emulsion similar to mayonnaise, replacing mayonnaise with commercial OSA starch.

In the pharmaceutical industry, starch octenyl succinate partially degraded by enzyme can be used as the matrix carrier of tablets, which can endow tablets with good dispersibility in water. Wolf et al. [20] found that after people take OSA modified starch, the glucose concentration in blood is reduced compared with the original starch, which can reduce the burden in the gastrointestinal tract and prevent the blood sugar in the body from being too high. It can also reduce gastrointestinal dyspepsia caused by high blood sugar in the body, thereby reducing the risk of diabetes. In addition, the product is non-toxic and has no adverse reactions. Therefore, it is widely used in the pharmaceutical industry.

Octenyl succinic acid esterified starch is the most suitable wall material for microencapsulation. It is used to wrap water-insoluble substances, such as beverage emulsion, aromatics and cosmetic oil. The wall material and core material are made into emulsion liquid under emulsifying effect of emulsifier, and then spray drying is used to make the wall material wrapped on the core surface to form a semitransparent or sealed capsule [21]. In addition, as people pay more attention to the big health industry, expanding the application of starch octenyl succinate in the field of big health functional materials is an application field worth exploring in the future.

5. Conclusions

The preparation methods of starch octenyl succinate mainly include water phase method, organic phase method and dry method. In addition, the composite modification method of starch pretreatment and then esterification is an effective supplement to the traditional preparation methods. Water-phase method, organic-phase method and dry method have their own advantages and disadvantages in preparing OSA, so we can choose the appropriate preparation method according to the requirements of preparation efficiency, product substitution degree or solvent system. In the application of octenyl succinate starch ester, it is mainly used as emulsifier in food, medicine and industrial products, turbidity agent in beverage, microcapsule wall material and biodegradable material. In addition, expanding the application of octenyl succinate starch ester in the field of health functional materials is an application direction worthy of attention in the future.

Acknowledgments

Financial support from National Natural Science Foundation of China (51663020), Natural Science Foundation for Distinguished Young Scholars of Guangxi Province (2017GXNSFFA198007) and Project of Guangxi Colleges and Universities for the Promotion of Foundation Ability of Young Teachers (2019KY0469). The authors also acknowledge Guangxi Colleges and Universities Innovation Research Team.

References

[1] Li Z, Wei C X. Morphology, structure, properties and applications of starch ghost: A review [J]. International Journal of Biological Macromolecules, 2020, 163: 2084-2096.

[2] Defloor I, Dehing I, Delcour J A. Physico-Chemical Properties of Cassava Starch. Starch-Stärke 1998; 50:58-64.

[3] Kringel DH, EL HSLM, Zavareze EDR, et al. Methods for the Extraction of Roots, Tubers, Pulses, Pseudocereals, and Other Unconventional Starches Sources: A Review [J]. Starch/Stärke, 2020, 72 (11- 12): 1900234.

[4] Garcia M A V T, Gaicia C F, Faraco A A G. Pharmaceutical and Biomedical Applications of Native and Modified Starch: A Review [J]. Starch/Stärke, 2020, 72 (7-8): 1900270.

[5] Mahadevan B, Thorsrud BA, Brorby GP, et al. A 3-week dietary safety study of octenyl succinic anhydride (OSA)-modified starch in neonatal farm piglets [J]. Food and Chemical Toxicology, 2014, 72: 83 -89.

[6] Lin Honghui, Zheng Weiwan, Zhao Weixue, et al. Study on synthesis and application of starch octenyl succinate [J]. Food Science, 2008 (08): 314-317.

[7] Padi RK, Chimphango A. Commercial viability of integrated waste treatment in cassava starch industries for targeted resource recoveries. Journal of Cleaner Production, 2020, 265, 121619.

[8] Jumaidin R, Khiruddin MAA, Saidi ZAS, Salit MS, Ilyas R A. Effect of cogon grass fibre on the thermal, mechanical and biodegradation properties of thermoplastic cassava starch biocomposite. International journal of biological macromolecules, 2020, 146, 746- 755.

[9] Orozco-Parra J, Mejía CM, Villa CC. Development of a bioactive synbiotic edible film based on cassava starch, inulin, and Lactobacillus casei. Food hydrocolloids, 2020, 104, 105754.

[10] Yang YJ, Wang BF, Liao XX, Wei AL, Zhang XW. Effects of Cassava Starch Hydrolysate on Cell Growth and Lipid Accumulation of Heterotrophic Microalgae Chlorella protothecoides. Modern Food Science & Technology 2009; 25:1275-1278.

[11] Mohammed KAF. The nutritive value of cassava starch extraction residue for growing ducks. Tropical Animal Health & Production 2018; 19:1-8.

[12] Zhan F, Li J, Youssef M, Li B. Enhancement of foam stability parallel with foamability of the foam stabilized by sodium caseinate-based complex: Octenyl succinate starch acting a dual role. Food Hydrocolloids, 2021, 113, 106479.

[13] Liu W, Li Y, Goff H D, et al. Distribution of octenylsuccinic groups in modified waxy maize starch: An analysis at granular level [J]. Food hydrocolloids, 2018, 84: 210-218.

[14] Viswanathan A. Effect of Degree of Substitution of Octenyl Succinate Starch on the Emulsification Activity on Different Oil Phases [J]. Journal of environmental polymer degradation, 1999, 7 (4): 191-196.

[15] Wang X Y, Li X X, Chen L, et al. Preparation and characterisation of octenyl succinate starch as a delivery carrier for bioactive food components [J]. Food Chemistry, 2011, 126 (3): 1218-1225.

[16] Kim H, Sandhu K S, Lee J H, et al. Characterisation of 2-octen-1-ylsuccinylated waxy rice amylodextrins prepared by dry-heating [J]. Food Chemistry, 2010, 119 (3): 1189-1194.

[17] Zhang Zhengmao, Li Jiliang. Research on mechanical activation-crosslinking-octenyl succinate compound modification of corn starch[J]. Food and Feed Industry, 2016 (1): 22-26.

[18] Huang Q, Fu X, He X W, et al. The effect of enzymatic pretreatments on subsequent octenyl succinic anhydride modifications of cornstarch [J]. Food Hydrocolloids, 2010, 24 (1): 60-65.

[19] Balic R, Miljkovic T, Ozsisli B, et al. Utilization of Modified Wheat and Tapioca Starches as Fat Replacements in Bread Formulation [J]. Journal of Food Processing and Preservation, 2017, 41 (1): e12888.

[20] Chivero P, Gohtani S, Yoshii H, et al. Assessment of soy soluble polysaccharide, gum arabic and OSA-Starch as emulsifiers for mayonnaise-like emulsions [J]. LWT-Food Science and Technology, 2016, 69: 59 -66.

[21] Wolf BW, Wolever TMS, Bolognesi C, et al. Glycemic Response to a Food Starch Esterified by 1-Octenyl Succinic Anhydride in Humans [J]. Journal of Agricultural and Food Chemistry, 2001, 49 (5): 2674- 2678.

[22] Ye F, Miao M, Huang C, Lu K, Jiang B, Zhang T. Elucidation of substituted ester group position in octenylsuccinic anhydride modified sugary maize soluble starch. Journal of agricultural and food chemistry 2014; 62:11696-11705.