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# PROPERTIES AND APPLICATION OF MODIFIED STARCHES IN FOOD PRODUCTION

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*Starch is the most abundant organic compound found in nature after cellulose. The properties of native starch do not always meet the requirements for a multitude of industrial applications. Functional limitations of native starch can be overcome by modifications of physical, chemical and enzymatic methods to broaden its applications. In this article, some common chemical modifications such as esterification, etherification, crosslinking of starch, as well as dual modification of physical and chemical method or chemical and enzymatic method, have been reviewed. This article also highlighted the application of chemical modified starch in food industry.*

*The analysis of literary and Internet sources showed that among the additives used in the food industry, modified starches occupy a special place, and their use in modern food technologies as structure-forming additives allows for the creation of a wide range of products. A review of the literature showed the lack of a sufficient number of works and developments on studying the properties of modified starches and establishing the changes that occur in the starch molecule during processing.*

*Their ability to form pastes was studied, the gelatinizing ability of modified starches was studied according to the organoleptic indicators of the formed pastes.*

*The article establishes the influence of various types of modification on the crystallinity of modified starch and its properties.*

*Analysis of the nature of the diffractograms of potato starch shows that after modification, the relative degree of crystallinity generally changes due to the breaking of existing bonds, as well as the formation of new ones in the process of modification. Since the decrease in the degree of crystallinity leads to a better attack of starch by enzymes, the human body better assimilates products that have undergone the destruction process, but the use of cross-linked and oxidized starches allows you to obtain pastes of the required structure.*

***Key words:*** *modified starches, chemical modification, application, drag forming ability, organoleptic indicators, the process of pasteurization.*

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**Introduction.** Starch is a natural macromolecule compound synthesized in plastids in photosynthetic and non-photosynthetic cells and is the second largest renewable resource after cellulose (Tetlow & Butler, 2023, p.83-129). It has the characteristics of low price, non-toxic, degradable, modifiable, environmentally friendly, and has gradually become an important base raw material for food industry or non-food industry (Lu et al., 2013, p.9882-9821). However, due to its insolubility in cold water, poor dispersibility, poor film-forming ability and inability to form stable adhesive systems, the practical applications of starch in textile, papermaking, pharmaceuticals, food and other industries has been greatly limited (Simi & Emilia Abraham, 2007, p.173-180). Therefore, it is necessary to improve the functional properties of starch by chemical, physical and enzymatic modification to meet the increasing application needs of people, among which chemical modification produce the most diverse and versatile types of modified starch (Chen et al., 2018, p.283-321). The microstructure of starch is a macromolecular cyclic structure composed with glucose groups. There are a large number of alcohol hydroxyl groups in starch molecules, which can react with numerous chemical reagents to produce various types of modified starch (Zia ud et al., 2017, p.2691-2705; Wang et al., 2020b, p.116-292). Starch has been chemically modified in different ways by using chemical agents to reduce or increase the molecular weight of starch in recent years. Chemical modification is the most widely explored modification method due to the non-destructive nature of some selected processes and potential increases in the functionality of the modified starch (Masina et al., 2017, p.1226-1236).

A large number of hydroxyl groups in starch molecules provides active sites for chemical modification. Chemical modification is insertion of new functional group such as carboxyl, acetyl, hydroxypropyl, amine and amide on the starch backbone to give specific properties to the starch. Different chemical modification methods are achieved by decomposition such as acid hydrolysis and oxidation or by derivatization, such as esterification, etherification, crosslinking, and dual modification (Haq et al., 2019, p.12-35.; Lemos et al., 2021, p.218-234).

Esterification of starch refers to the conversion of hydroxyl groups in starch molecules to alkyl or aryl derivatives by inorganic or organic acids. The common esterified starch mainly includes acetate starch (Lin *et al.*, 2017, p.316-326), phosphate starch (Sang & Seib, 2006, p. 167-175.; Ramadan & Sitohy, 2020), starch octenyl succinate (Wang *et al.*, 2020b) etc.

The hydroxyl groups in starch molecules is etherified with reactive substances under alkaline conditions to produce etherified starch, which mainly includes hydroxypropyl starch (Wang et al., 2020a, p.131-149) and carboxymethyl starch (Zhou *et al.*, 2018, p.1700250.; Liang *et al.*, 2021, p.601-606).

Crosslinked starch is synthesized by strengthening intermolecular hydrogen bonds through chemical bonds that form bridges by connecting polymer chains, in which sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), epichlorohydrin (ECH), and phosphoryl chloride (POCl3) are commonly used as crosslinking agents. (Wang *et al.*, 2020b; Sandhu *et al.*, 2021). The functional properties of crosslinked starch are mainly determined by the types of crosslinking agents.

Dual modification of starch involves the combination of physical and chemical modification methods or chemical and enzymatic modification methods for enhancing the functional properties of starch and improving its utilization (Haq *et al.*, 2019, p.12-35). Chemically dual modified starches are widely used as binder, thickeners and emulsifiers in food industry, whereas it can be used as heavy metal absorbents in non-food industry (Zia ud et al., 2017, p.2691-2705). Dual modification of crosslinking and octenylsuccinylation of cassava starch had great effects on the physicochemical and emulsifying properties, which can expand its applications and make it suitable for a wider range of food products such as canned, refrigerated, and frozen foods (Sriprablom et al., 2023).

Modified starch is widely used in food and non-food industry due to its characteristics of low gelatinization temperature, high transparency, high solubility, good freeze-thaw stability and viscosity. With the development of food industry, the demands of chemically modified starches as chelator, cryoprotectant, drying aid, fat replacer, flavor carrier, flavor and color precursor through Maillard reactions, and substrate in fermentations are increasing (Lee & Puligundla, 2017, p.311-316). Acid-hydrolyzed starch is used as gelling agent in gum and cheese loaves, as fat replacer in low-fat ice cream due to it low past viscosity, high gel strength and water solubility, as well as used in slowly digestible cookies for rich in resistant starch (Wang & Copeland, 2015, p.1081-1097). Octenyl succinylated starch is frequently used as emulsifier in creams, salad dressings and is used as clouding agent in drinks due to its well emulsifying action, pasting properties and slow digestibility (Altuna *et al.*, 2018, p.97-110). Using crosslinked starch as fat replacer not only has the same functionality as native starch, but also has greater emulsifying ability, lower digestibility and fewer calories (Chen *et al.*, 2018, p.283-321). With the incorporation of crosslinked waxy maize starch for partial substitution of wheat flour, the nonfried noodles exhibited a soft texture with bright and yellow appearance (Zhou *et al.*, 2015, p.1035-1043). Acetylated starch can meet the changing demands of food industry for its improvements in transparency, water absorption, precipitation and condensation (Lin *et al.*, 2017, 316-326). The acetylated starch also could be applied in high concentrations than native starch for its lower swelling power and solubility, providing higher concentrations of solids (Colussi *et al.*, 2015, p.1076-1082).

**Materials and Methods.** In the course of work, we used one sample of native starch and three samples of starches of various modifications: native potato starch – NS, cold swelling thickener - MS 1, gelling agent - MS 2, brewing thickener - MS 3.

X-ray structural studies were carried out using a DRON-3 diffractometer. From the obtained diffractograms, the degree of crystallinity was determined by the Mathews method. The drag-forming ability was determined organoleptically. A solution of starch samples was prepared and the condition of the formed jelly was analyzed: structure, consistency, color, transparency, and storage stability.

The degree of pasteurization of starch was determined by measuring the pasteurization time and pasteurization temperature.

Results and Discussion. Starch pasteurization is the process of starch transformation into a starch paste due to the swelling and partial dissolution of starch grains in water during heating due to the penetration of water into the hydrogen bonds between starch macromolecules. In food production, this indicator is important.

Starch polysaccharides are very labile, reactive compounds that actively interact with metal ions, acids, oxidants, and surfactants. This makes it possible to modify starch molecules - to change their ability to pasteurize. Some types of modification help to increase the solubility of starch in water, others limit swelling. The results of the study of the pasteurization process of starch pastes are presented in Table 1.

Table 1

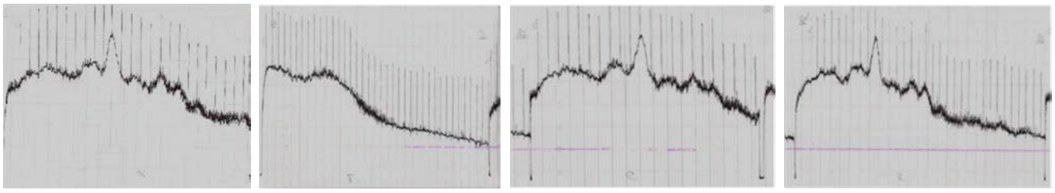
**Conditions of the pasteurization process of modified starches**

| Sample | Initial temperature of pasteurization, °C | Time of beginning of pasteurization, τ | Time of end of pasteurization, τ | Time during which pasteurization was formed, min |
|---|---|---|---|---|
| NS | 67-70 | 12.31 | 12.35 | 5 |
| MS – 1 | 15-18 | 12.22 | 12.23 | 1 |
| MS – 2 | 62-65 | 12.28 | 12.32 | 4 |
| MS – 3 | 61-65 | 12.41 | 12.46 | 5 |

As can be seen from the table, sample MS - 1 pasteurized the fastest. Pasteurization took the longest in samples NS and MS - 3. Sample MS - 3 has a pasteurization temperature similar to that of native potato starch. This is explained by the fact that the cross-linked types of starch are characterized by a low rate of swelling and pasteurization, which creates the effect of prolonged action. Split starches due to the effect on them of high temperatures during modification are already partially pasteurized, so they swell immediately when they are introduced into water. In addition, studies have shown that the process of modification of native starch leads to a slight decrease in the temperature of pasteurization.

Starch refers to compounds that look like spherocrystals under a microscope under polarized light. This property is explained by the fact that during the growth of starch grains, branched polysaccharide chains are oriented in the radial direction. This contributes to the formation of regions with an ordered structure characteristic of crystals, the nature of which has a significant impact on the properties of the starch polymer and depends on many factors of the nature of the polymer, the ratio of amylose and amylopectin, their molecular weight, the degree of branching, the length and conformation of external branches, as well as from the shape and size of the crystalline zones in the internal molecular lattice.

It is known that the assimilation of the product by the human body depends on the degree of crystallinity. Therefore, the ratio of crystalline and amorphous phases in the studied samples was determined using the X-ray method. The radiographs shown below showed that different modifications of starch have different crystallinity (Fig. 1).



1 2 3 4

**Figure 1 - Study of the crystallinity of modified starches: 1 – NS, 2- MS 1, 3 – MS 2, 4 – MS 3.**

Analysis of the nature of the diffractograms of potato starch shows that after modification, the relative degree of crystallinity generally changes due to the breaking of existing bonds, as well as the formation of new ones in the process of modification. For oxidized and cross-linked starches, the degree of crystallinity increases, for swelling starches, an amorphous structure is formed.

Since a decrease in the degree of crystallinity leads to a better attack of starch by enzymes, the human body better assimilates products that have undergone the destruction process, but the use of cross-linked and oxidized starches allows you to obtain pastes of the required structure.

Another of the most important characteristics of starch, which determines the specifics of their use, is gelatinizing ability. The formation of starch jelly occurs during the cooling of starch pastes of a sufficiently high concentration, as a result of the arrangement of the structure. The properties of dragees and their strength depend on the type of starch, the duration and temperature of cooking the paste, the intensity of mixing, the presence of impurities, cooling conditions, etc. Due to the formation of gels, branched amylopectin molecules complicate the process of ordering the structure, and linear amylose molecules tend to quickly associate and form micelles with an ordered structure.

To conduct the research, 50 $cm^3$ of distilled water and 40 ml of hot water were added to 10 g of starch in a flask. Solutions of each starch sample were pasteurized in a boiling water bath and poured into molds. After 24 hours, an organoleptic evaluation of the obtained jelly was carried out, the results of which are shown in Table 2.

The study of the organoleptic indicators of the formed jelly showed that the modification of starch leads to changes in its properties. Sample MS - 2 is able to form concentrated pastes of reduced viscosity and increased transparency. Valuable properties of pastes of this starch are high stability during storage, mixing and cooling. Such starch is produced for refrigeration (ice cream production), confectionery and bakery industry. Swellable starches include those types of starch that can swell in cold water (MC 1). The basis of obtaining such types of starch are physical transformations that lead to the destruction of starch molecules, partial or complete destruction of the structure of starch grains. Swelling potato starch is included in the recipes of dry ice cream mixes. It can also be with methylcellulose, thanks to

Table 2

**Organoleptic evaluation of gelatins of modified starches**

| Sample | Organoleptic assessment |
|---|---|
| NS | Forms a viscous thick paste of light gray color. Opaque. It delaminates during storage. |
| MS – 1 | Forms a highly viscous paste. Transparent. Does not form jelly (necessary special conditions of leaving in cold water to prevent the formation of lumps). |
| MS – 2 | Liquid transparent paste with minor film formations. They do not form dragles. It delaminates during storage. Has low viscosity at high concentrations. |
| MS - 3 | A thick homogeneous paste of light gray color. Short-blooded, relatively transparent, smooth. Does not form sludge. |

which the whippedness of the ice cream increases and the average diameter of air bubbles decreases. Cross-linked types of starch (MC 3) are characterized by a reduced rate of swelling and pasteurization, which creates the effect of prolonged action. Pastes of cross-linked types of starch are more viscous, resistant to external factors - high temperature, prolonged heating, low pH value, mechanical stress. Cross-linked starches are widely used in the production of sauces, pastes, and dairy products.

**Conclusion.** Nowadays, modification of starch is developing in the direction of multi-type, multi-compound and serialization, and modified starch can be applied in more fields in the future. The use of chemically modified starch is becoming more and more widely due to its unique properties. The study of modified starch is still a hot research field and has a very broad application prospect. Therefore, we should continuously deepen our understanding of modified starch, determine its performance properties and utility, and apply it in more suitable fields.

Starch modification allows you to change the properties of native starch. Modified starches differ from ordinary starches by the increased final viscosity of pastes, their greater stability to mechanical actions and the acidity of the environment, as well as to high and low temperatures. The spectrum of use of modified starches is quite wide. They are used to thicken canned meat, as a stabilizer of low-fat dietary mayonnaise, fat creams, sauces, jelly, quick-frozen foods, to improve the quality of bread, cookies, and waffles. Therefore, the study of the properties of modified starches is a necessary prerequisite for their use to ensure the creation of physiologically safe food products in conditions of increased environmentalization of production.

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***Властивості та застосування модифікованих крохмалів у харчових виробництвах***

*Крохмаль є найпоширенішою органічною сполукою в природі після целюлози. Властивості нативного крохмалю не завжди відповідають вимогам для його застосування у виробництві різноманітних харчових продуктів. Функціональні обмеження нативного крохмалю можна подолати шляхом модифікації крохмалю шляхом застосування різних фізичних, хімічних і ферментативних методів для надання йому нових властивостей та розширення сфери для використання. У цій статті розглянуто деякі поширені методи модифікації, такі як етерифікація,* *зшивання крохмалю, а також подвійна модифікація з використанням фізичних та хімічних методів або хімічних та ферментативних. У статті також висвітлено застосування модифікованих крохмалів в харчовій промисловості.*

*Аналіз літературних та інтернет-джерел показав, що серед добавок, які використовуються в харчовій промисловості, модифіковані крохмалі посідають особливе місце, а їх використання в сучасних харчових технологіях як структуроутворюючих добавок дозволяє створювати широкий асортимент продукції. Поряд з великою кількістю різних видів модифікованих крохмалів досліджень у напрямку вивчення їх властивостей і встановлення змін, які відбуваються в молекулі крохмалю при обробленні досить мало. Тому вивчення властивостей модифікованих крохмалів різної модифікації дозволить надати рекомендації для їх використання та встановити їх вплив на організм людини при їх споживанні у складі харчових продуктів.*

*Досліджено їхню драглеутворювальну здатність за органолептичними показниками сформованих драглів та процес клейстеризації модифікованих крохмалів.*

*Встановлено вплив різних видів модифікації на кристалічність модифікованого крохмалю та його властивості.*

*Аналіз характеру дифрактограм картопляного крохмалю показує, що після модифікації відносний ступінь кристалічності в основному змінюється за рахунок розриву існуючих зв'язків, а також утворення нових у процесі модифікації. Оскільки зниження ступеня кристалічності призводить до кращої атакованості крохмалю ферментами, організм людини краще засвоює продукти, що пройшли процес деструкції, але використання зшитого і окисленого крохмалю дозволяє отримувати пасти потрібної структури.*

***Ключові слова:*** *модифіковані крохмалі, хімічна модифікація, застосування, драглеутворююча здатність, органолептичні показники, процес клейстеризації.*