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Application of High Hydrostatic Pressure in Modifying Functional Properties of Starches: A Review

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Abstract: Starch, after cellulose is the second abundant compound in nature. Natural structure of starches generally restricts their functions in industry and particularly in food industry. Various chemical, physical and enzymatic methods have been used for starch modification. In this paper, the characteristics of starch and its changes during high hydrostatic pressure (HHP) processing are discussed. In general, HHP restricts the swelling power of starch granules, so their viscosity is lower in comparison with the samples processed by heating. On the other hand, it provides the possibility of starch gelatinization at room temperature or even below 0°C. A number of starches when pressurized at concentrations higher than 15% produce paste with creamy texture which can be used in dietary foods instead of oil. Furthermore, HHP treatment prevents the harmful effect of starches in some tissues due to reduced size of starch granules. In addition, HHP treatment produces resistant starches, which are valuable in the treatment of diabetes and some cancers. In all, since the degree of similarity of changes is achievable in different situation, that it has great importance in food industry, because of the optimum pressure condition is determined, based on the main objectives alike deactivation of microorganisms and enzymes, transferring, mixing, pumping, maintaining quality, aroma, texture, etc.

Key words: HHP・Electrical conductivity・Swelling power・Gelatinization・Dietary food

INTRODUCTION

The potential of using HHP treatment in food preservation was introduced by Hite [1], when he processed milk at pressures about 680 MPa for 10 minutes to destroy much of the microorganisms. Bridgman (1914) showed that if egg processes with high pressures, albumin will clot [2]. After a long pause, researches on this technology resumed in 1980. In 1989, the Ministry of Agriculture, Forestry and Fishery of Japan established the association of study of application of high pressure technology in foods. Later in 1991, products such as fruit juices, jams, jellies and yogurt were introduced in department stores. In the past decade, utilization of HHP treatment in food processing was studied. High pressure technology involves using an uniform pressure throughout of a product. In food industry, pressures range from 400 to 900 MPa can be used, while in metal and ceramic industries pressures around 200 MPa are needed. There are different methods for producing high pressures such as direct compression, indirect compression and heating, which are applicable in cold, warm and hot modes. In food industry, the cold mode is more common. Among extensive issues regarding novel non-thermal technologies, high pressure application has the following advantages: first, high pressures only destroy the second and third structures of large molecules. Thus, molecules and cell membranes of microorganisms will be denatured and enzymes active status will be changed due to oxidation of thiol-groups and the main sources of food spoilage will be destroyed without using heating. Second, the primary structure that has covalent bonds, does not damage. This means that compounds such as vitamins, pigments and substances affecting flavour will remain intact. Foods also can be processed quickly and independent of their sizes and shapes by high pressures, that is an important feature in comparison with thermal processing. Therefore, any solid or liquid food packaging can be processed with high pressures. Finally, HHP treatment provides the possibility of producing some products with a higher nutritional value, more desirable sensory properties and a new texture [3].

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Starch, after cellulose is the second abundant compound found in nature. Starch molecules are homogeneous polymers of glucose units in linear and branched forms. Enzymatic reactions in plants join two molecules of glucose through glycoside bonds between carbons 1 and 4 and sometimes 1 and 6. Natural structure of starches limits their usage in industries, especially food industry. Corn, waxy maize and tapioca starches, for example, which easily swell, simply break and form a sticky and weak paste. However, when they are modified, their paste becomes resistant against adverse environmental conditions. Starch modification is carried out in order to achieve one or more of the following purposes: changing the properties of dough, increasing stability and endurance, increasing resistance against freezing, preventing gel formation, reducing synersyis, increasing or decreasing the viscosity, increasing or decreasing the water holding capacity, reducing the gelatinization temperature, decreasing or increasing retrogradation, increasing hydrophilic or hydrophobic properties [4-7]. Starch modification is done by various chemical [8, 9], physical [10-14], enzymatic, [15-18] and genetic/biotechnological [19, 20] methods. In these processes, the chemical structure of starch, especially some D-glucose pyranosyl units, are changed. The processes depend on factors, such as plant sources, modification method, molecular weight of starch and the ratio of amylose to amylopectin [21, 22].

Since the control of microorganisms and enzymes, is the most important factor in the shelf life increasing of foods, most of researches have been done on the effects of HHP treatment on microorganisms, enzymes and proteins. In other words, information about other aspects especially the effect of HHP treatment on starch is limited. On the other hand, series of studies that have been done in this regard have fundamental differences in terms of starch type, the amount of used pressure, time and processing characteristics [23]. The purpose of this paper is to review the main and acceptable changes in the following characteristics of starches during high pressure processing.

Gelatinization: When granules are heated in the presence of water, hydrogen bonds of amorphous regions which are weaker, break and absorb water and swell up several times. But the structure of granules is preserved by strong bonds of crystalline section, till it breaks and completely disrupts. During this process, amylose releases in the water and the viscosity of suspension increases. Gelatinization of starch is detectable using dual optical dispersion, enthalpy, electron microscopy and electrical conductivity. The most common way to identify the distribution of starch granules is by light microscopy. Therefore, at the temperature that dual optical dispersion decreases, gelatinization starts and when 98%of the granules lose this characteristic, gelatinization ends [24]. The identification of optical dispersion of gelatinized granules from non-gelatinized granules, especially those left intact and unswollen, after HHP treatment is difficult. Katopo, *et al*. investigated the effect of 690 MPa pressure for 5 minutes on gelatinization properties of starch suspensions in (1:1) and (2:1) ratios of water to starch. The results showed that suspension of rice and corn starch in the (1:1) ratio produces a fragile gel. Gel texture was softer with the increase of water content. The suspension of waxy maize starch in the (1:1) ratio turned into a stiff gel, but in the (2:1) ratio a viscous gel produced. Tapioca starch showed a similar behavior like waxy corn starch, but with less viscosity. Potato starch in the ratio of (1:1) produced a fragile cake, which had a lot of free water. The texture of the cake with 2-fold increase in the water content became softer. In conclusion, by increasing water content, gelatinization amount of starches increased, but potato starch was slightly gelatinous. Appearance suspension in high amylose starches did not change [23].

Stolt *et al*. showed that starch gelatinization by high pressure depends on the amount of pressure and process time. They investigated suspensions with 10% and 25% barley starch within 75 minutes processing with 400, 450 and 500 MPa. The results showed that structural changes at low pressures occured more slowly and at 400 MPa pressure during 75 minutes, gelatinization was incomplete. While all changes occured at 550 MPa pressure at the beginning and increasing the process time did not cause further changes. On the other hand, the granules structure remained intact after 50 minutes processing, but the birefringence completely went away in the early moments. The same results were shown for tapioca starch [26]. The effect of high pressure processing on starches showed that the birefringence of granules was completely destroyed at pressures over 400 MPa. Also, wheat starch produced a gel at room temperature with a pressure of 300 MPa, but in the same conditions, potato starch required pressures around 600 MPa [27]. The wheat and tapioca starches gelatinization amount increased with rising pressure up to 530 MPa. Since these starches tolerate pressures about 200 MPa due to their increased volume, the gelatinization temperature in the range of 150 to 250 MPa increased and then decreased [26]. Wheat starch gelatinization starts in the pressure of 100 MPa and at 440 MPa ends, while tapioca starch gelatinization happens at 400 MPa and at 600 MPa pressure finishes [26, 28, 29].

Investigating several studies since 1980 about the effect of HHP treatment on starch gelatinization showed that gelatinization temperature increases with rising pressure up to 200 MPa. But at higher pressures, gelatinization temperature decreases, so starches, which are processed at very high pressures can be gelatinized at room temperature. Since in most researches, pressures less than 600 MPa have been used, a temperature about 50°C is necessary for the occurrence of complete gelatinization [28].

Treatment of waxy maize starch with a high pressure (650 MPa for 9 min), resulted in the complete gelatinization, but when amylose is added to starch, the degree of gelatinization was decreased. Also, the effect of high pressure on the formation of the three-dimensional gel network was observed for all studied systems [30].

Oh *et al*. exposed different types of starches in the pressures up to 600 MPa and then classified them into three groups: waxy starches, which could fully gelatinize at sufficiently high pressures (> 400 MPa); normal starches, which partially gelatinized under high pressure and pressure-resistant starches, such as potato starch that were not affected by high pressure treatment. They suggested that differences in the behaviour of these starches could be due to the differences in their physico-chemical properties [31].

Starch gelatinization in skim milk could be occurred at a higher pressure than in water due to the presence of soluble milk minerals and lactose. However, milk proteins did not affect the gelatinization degree. It was resulted from direct interactions between milk components and starch molecules, which may also contribute to retarded gelatinization [32]. Also, it confirmed that gels with regardless of structures and different levels of gelatinization can be obtained depending on the amount of pH and osmolarity [29].

Vallons and Arendt showed that pressures (300-600 MPa) like temperatures (60-75°C) led to the gelatinization of sorghum starch [33]. However, previous studied showed that gelatinization by pressure was significantly different from gelatinization by temperature in wheat [34] and barley [25]. Therefore, sorghum starch was classified into the group of starches, which are characterized by extensive swelling behavior and pasting properties similar to those obtained by heat gelatinization [35].

High pressure technology of flour produced paste with consistency lower than the heat processing. Therefore, the effect of high pressure on the starch gelatinization may be inhibited by gluten. It is established that 600 MPa pressure is sufficient to complete gelatinization of starch, but higher pressures or combination of pressure and temperature are needed to cause strong changes in the structure of gluten. However, flour could not be considered a simple blend of starch and gluten [33].

Retrogradation: Retrogradation in common starches such as rice starch was accelerated by HHP treatment, while in waxy starches, such as rice and maize starches it occured slightly after gelatinization and when they were freezed and then thawed, retrogradation did not happen. Studying differential scanning calorimetry diagrams of retrograded starch has shown that during and immediately after HHP treatment rapid retrogradation occurs [23, 35-38]. However, conflicting reports in this regard have been reported. For example, Stolt *et al*. showed that retrogradation in barley starch did not happen and the first peak appeared after one day storage at 40°C and during storage, it daily growed [22]. They also showed that the extent of retrogradation in starches gelatinized by heat was higher than those gelatinized at 600 MPa pressures [34, 39]. Because amylose did not leak from starch granules, retrogradation occures within them. Since retrogradation depends on botanical sources of starches, temperature and starch concentrations, it is important to explore the impact of high pressure processing on retrogradation characteristics of different starches. Although retrogradation is a typical quality loss of starchy foods, it is of interest to use this technology for producing resistant starch [40].

Crystal Structure: Literature review has shown that some starches are resistant to pressure and are not affected by HHP treatment due to their differences in the structure of external region of starch granules or crystalline properties [23, 31, 35, 38]. Starch granules of potato have a very compact layer that seems to be more resistant than the inner part of the granule and does not change by HHP treatment [41]. Vallons and Arendt showed that pressures up to 600 MPa was not sufficient to disintegrate the granular structure in some starches [42].

Using X-ray diffraction, starches can be classified as A-type (normal rice, waxy rice, normal corn and waxy corn starches), B-type (potato starch) and C-type (tapioca).

B-type starches are known to be more resistant to pressure than A- or C-type starches due to their higher water content. There are 36 molecules of water in this type and 8 molecules in others [23, 35, 43]. Also, crystalline structure of B-type has a lower compressibility than A-type [38]. However, these types of starches are inseparable at pressures above 600 MPa. The difference between A and B-type crystals is due to the form of amylopectin arrangement. Therefore, the flexibility of amylopectin branches can create new pores in the starch structure that hold water in themselves. Gelatinization temperature decreases by changing A-type crystals to B-type, because B-type crystals are viscous and swell at lower temperature, around 40°C [21].

Katupo *et al*. showed that starches of A-type convert to B pattern, after applying pressure. X-ray diffraction pattern of waxy corn starch indicated that the A-type did not exist, but in the suspension of common rice and corn starches, weak signs of B-type were shown [23]. It is also shown that in tapioca B-type crystals were formed. X-ray diffraction depends on moisture content, so when corn and rice starches are processed in hexan for 60 min at 500 MPa pressure instead of water, any changes will not be seen. In other words, no changes in the crystalline structure occur without water [38].

Swelling Power: HHP treatment reduces swelling power of starch. This effect has been proven by comparing starches, which gelatinized by temperature and pressure. However, this effect is different on various starches, for example the diameter of corn starch granules slightly increases, while waxy corn and tapioca starches swell more and showes similar behavior as thermal gelatinization. Vallons and Arendt also did not observe differences in swelling power of sorghum starch, which gelatinized by pressure or temperature. During applying pressure, amylose joins to lipids and develops into spiral complex structures that are called V crystals. These complexes then connect to amylopectin and prevent starch swelling, especially amylopectin [42]. The waxy corn starch shows a different behavior in the same conditions, because there is a little amylose in it, thus V crystals do not form [38]. It has also been proven that increasing the amount of amylose in the mixtures of waxy maize starch decreases the swelling index and reduces the mobility of free and bound water molecules in gels [30]. After processing with high pressures, starches can be divided into two groups based on their swelling power. The first group has a high swelling power similar to starches that gelatinized by heat and the second group has a small swelling power and produces two kinds of soft and rigid gels. However, soft gel formation according to the characteristics of starch granules under pressure is expectable. Based on low swelling, rapid retrogradation and no amylose leakage from granules of some starches, there is a question that how a stiff gel can be produced from these starches [23].

Enzymatic Properties: Incomplete gelatinization like retrogradation reduces the effect of enzymes on starch. Therefore, amyloglucosidase has a little effect on starches, which are slightly and incompletely gelatinized by HHP treatment. The birefringence fully goes away at 450 MPa, but starch does not degrade completely by enzymes like thermal gelatinization. This phenomenon is probably due to fast retrogradation, which is the act of applied high pressures [44].

Regina *et al*. processed wheat and barley flours with pressures from 100 to 800 MPa for 10 or 20 minutes and showed that changes in total soluble carbohydrates and reducing sugars at 100 to 300 MPa pressures were similar to the control samples. The amount of these compounds rapidly increased by raising pressures up to 600 MPa. Therfore, due to degradation of starch, the quantity of maltose increased and enzymes could easily degrade them. On the other hand, at 700 to 800 MPa pressures, the amount of these compounds was less or similar to the control samples. Also the amounts of reducing sugars were less than the total soluble carbohydrates [27].

Electrical Conductivity: Bauer and Konrr investigated electrical conductivity changes in 5% suspension of tapioca and wheat starches after applying up to 530 MPa pressure. They showed that by increasing pressure, electrical conductivity increased due to the release of ions. Also the release of ions and gelatinization in both starch suspensions simultaneously started and ended. In other words, good correlation existed between these two parameters, so the degree of gelatinization would be determined using electrical conductivity [26]. Conductance measurements may also have the potential to accurately quantify the extent of gelatinization [45].

CONCLUSION

It has been shown that HHP treatment is effective on physicochemical properties of starch polymers. It restricts the swelling power of starch granules, so their viscosity is lower compared with the samples, which processed by temperatures. In other words, transferring, mixing and pumping of these starches are possible even at concentrations of 25 to 30%. And regarding the starch gelatinization, it can be carried out by HHP treatment at room temperature or even below zero. Also some starches at concentrations higher than 15% when processed with this technology, could produce paste with creamy texture that can replace oil in diet foods, such as mayonnaise, confectionary products, desserts, dairy products,. Furthermore, HHP treatment reduces water holding capacity of starches and plant fibers by decreasing their sizes, preventing the harmful role of them in some tissues. In addition, HHP treatment produces resistant starches, which have a similar role as soluble fibers and are beneficial to human health. So the use of these materials for controlling diabetes and some cancers is recommended. Application of high pressure technologies increases the digestibility of amylose that improves baking characteristics. In conclusion, since the degree of similarity of changes is achievable in different situations, that has a great importance in food industry, because of the optimum pressure condition is determined, based on the main objectives.

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