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REVIEW

Pressure moisture treatment and hydro-thermal treatment of starch

Hui-Yun Kim[1] · **Moo-Yeol Baik**[1]

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Abstract Starch is often subjected to denaturation treatment to improve its useful properties and eliminate its shortcomings. Various methods have been developed to produce modified starches with different properties and for a variety of uses. Because physically modified starch can be produced without chemical substances or biological agents, the modification method is very simple and inexpensive, and the resulting material can be used as clean label starch. Among these physical modification technologies, heat moisture treatment (HMT) is a universally valid technology, but little is known about pressure moisture treatment (PMT)-related technology. Physical modification of starch using PMT results in new functions and value-added characteristics required by industry, and PMT has the potential to produce starch with new functions. In this paper, PMT-related technologies for physically modified starch, the difference between PMT and the hydro-thermal treatment, and clean label starch manufacturing using HMT and PMT were investigated.

Keywords Clean label starch · Pressure moisture treatment · Heat moisture treatment · Physically modified starch

Introduction

Starch is a naturally occurring, biodegradable, inexpensive, renewable and abundantly available polysaccharide polymer. Starch is now widely used in the food, chemical, medical and biological industries. To satisfy the functional characteristics required in various industries, starch needs to have different characteristics from those of native starch. Therefore, the denaturation of starch has infinite possibilities in applications such as food materials, cosmetic materials, and pharmaceutical materials, which represent a large market for new functions and added value (Kaur et al., 2012).

Commercial use of native starch is limited by various problems such as insolubility in water and the formation of unstable paste and gel due to syneresis caused by aging. Chemically modifying these starches both reduces aging and gelation of paste and improves the transparency and gloss of the paste, the paste and gel texture as well as film formation and adhesion (Jacobs et al., 1998). However, the recent trend in the food market involves finding a way to physically improve the properties of native starch without chemical elements (Ortega-Ojeda and Eliasson, 2001).

Physical denaturation of starch is a technique that is environmentally friendly and safe compared to chemical denaturation (Lawal and Adebowale, 2005). Physical denaturation techniques are popular because they do not involve chemical treatments that can be harmful to humans. Physical denaturation of starch can change its solubility and granule size. Hydro-thermal treatment is generally used the most for physical denaturation, and recent studies related to high hydrostatic pressure (HHP) treatment are being conducted.

Hydro-thermal treatment includes heat moisture treatment (HMT) and annealing (ANN). The common feature

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✉ Moo-Yeol Baik
mooyeol@khu.ac.kr; mikoel@khu.ac.kr

[1] Department of Food Science and Biotechnology, Institute of Life Science and Resources, Kyung Hee University, Yongin 17104, South Korea

of the two methods is that they are treated at a temperature higher than the glass transition temperature (Tg) of starch and lower than the amylopectin double helical melting temperature (Tm) or gelatinization temperature. Also, these methods cause rearrangement of starch molecules in a state where gelatinization does not occur. It is known that the moisture content in HMT is limited to 35% (w.b) or less (Anderson and Guraya, 2006; Collado and Corke, 1999; Gunaratne and Hoover, 2002; Jacobs et al., 1998; Tester and Debon, 2000), and ANN occurs at 50–60% (w.b) moisture content with high moisture content. Treatment at 40–50% (wet basis) moisture content is referred to as intermediate moisture content treatment (Tester and Debon, 2000).

On the other hand, HHP is a technology that changes the characteristics of food while minimizing the sensory effects and nutrition of the food. According to Pascal's principle, HHP is transferred instantaneously to the center (rather than slowly like heat) so that the non-covalent bond can be changed while minimizing the effect on the covalent bond. When HHP is added to a biopolymer, it reduces the space between molecules and promotes the reaction between chains, and it provides properties suitable for food processing (Cheon et al., 1997; Muhr and Blanshard, 1982; Stute et al., 1996).

When starch suspension (30%, w/w) is treated with HHP, high pressure destroys the internal structure of starch with a driving force, allowing water molecules to permeate and hydrate the inside of starch (Stolt et al., 2000). This is called pressure induced gelatinized starch. Pressure induced gelatinized starch is fully gelatinized, but unlike heat induced gelatinized starch, granules are not destroyed (Song et al., 2015).

Studies have reported that partial gelatinization of HMT occurs when the moisture content is 30–35% (Gunaratne and Hoover, 2002; Liu et al., 2019). It is not possible to determine whether the altered properties after HMT treatment are due to molecular rearrangement or partial gelatinization. While we were contemplating a method that would cause only molecular structure rearrangement without partial gelatinization, we considered the possibility of a new method of transforming starch without changing covalent bonds by treating starch (less than 30%, wb) with HHP. This method was named pressure moisture treatment (PMT).

In this paper, we explain the principle of physical denaturation treatment of starch, and the discussion focuses on the characteristics of the modified starch prepared by each method. As a result, heat and HHP give motility to the water molecules present inside the starch, which will help us understand the process of physically denaturing starch and the possibility of their mutual substitution. In addition, the physicochemical properties of various starches treated with hydro-thermal treatment and HHP were analyzed and compared to confirm the possibility of a new physically modified starch manufacturing method called PMT.

Heat-moisture treatment (HMT)

HMT is a hydro-thermal treatment at 90–120 °C for 15 min–16 h at a limited moisture content of 35% or less (Liu et al., 2019). HMT is treated at high temperature with limited moisture content to give starch molecular mobility via heat energy. Changes in starch structure and properties by HMT vary depending on the starch source. For example, root and tuber starches are more sensitive to HMT than cereal and pulse starches (Gunaratne and Hoover, 2002; Hoover and Vasanthan, 1994; Jacobs and Delcour, 1998; Mathobo et al., 2020). HMT results in several changes to the starch, decreasing solubility, swelling power, amylose leaching and viscosity, but it tends to increase the paste temperature (Pinto et al., 2012; Sui et al., 2011; Zia et al., 2017). When starch was treated with HMT, the degree of change in the crystalline and amorphous areas was different (Hoover and Manuel, 1996). In addition, it was confirmed that the amorphous area of the starch granule showed the greatest change in various types of starch (cereal, tuber, and pulse) (Hoover and Vasanthan, 1994; Jacobs et al., 1998; Vermeylen et al., 2006). Moisture content, temperature, starch source, and treatment time affect the changes caused by HMT. Among these conditions, the most extensively studied conditions are moisture content and temperature (Ambigaipalan et al., 2014; Vermeylen et al., 2006). Table 1 summarizes the various HMT treatment conditions reported so far.

Annealing (ANN)

ANN is a physical modification method that causes changes by heating starch suspended in excess water. The moisture content of starch granule ANN treatment is higher than that of HMT, and it is classified into two categories: (1) high moisture content (less than 60%, w.b) and (2) medium moisture content (40–50%, w.b). Various conditions exist for the ANN method of starch extracted from various botanical sources, and the ANN treatment conditions are summarized in Table 2.

The purpose of ANN is to heat the material near the Tg, which improves molecular mobility when the starch is in a non-gelatinized state. In addition, it has the advantage of increasing the crystallinity of starch and weakening structural relaxation, and it provides theoretical evidence for the improvement of starch properties by enhancing thermal stability and mechanical properties (Lv et al., 2015). ANN

Table 1 Heat-moisture treatment conditions for various starches

Starch	Moisture content (%, w.b)	Time (h)	Temperature (°C)	References
Borlotti bean	22	16	100	Güzel and Sayar (2010)
Cassava	18–24	3–16	110	Abraham (1993)
	30	10	100	Gunaratne and Hoover (2002)
Canna	18–25	16	100	Watcharatewinkul et al. (2009)
	20–30	5–30 min	110	Zhang et al. (2009)
Chickpea	22	16	100	Güzel and Sayar (2010)
Chestnut	25–28	3	110	Singh et al. (2009)
Corn	30	2	100–120	Chung et al. (2009)
	20	15–60 min	120	Pukkahuta et al. (2008)
	13.5	–	120–130	Miyazaki and Morita (2005)
	15–27	16	110	Kweon et al. (2000)
	18–27	16	100	Franco et al. (1995)
Finger millet	20–30	16	100	Adebowale et al. (2005)
Ginger	27	16	100	Vieira and Sarmento (2008)
Lentil	30	2	120	Chung et al. (2009)
	10–30	16	100	Hoover and Vasanthan (1994)
Pea	30	2	120	Chung et al. (2009)
Peruvian carrot	27	16	100	Vieira and Sarmento (2008)
Potato	24	16	100	Varatharajan et al. (2010)
	17–26	24	90–130	Vermeylen et al. (2006)
	30	10	100	Gunaratne and Hoover (2002)
	10–30	16	100	Hoover and Vasanthan (1994)
Sago	20	1	100–120	Pukkahuta and Varavinit (2007)
Sweet potato	27	16	100	Vieira and Sarmento (2008)
	25	4–16	110	Collado and Corke (1999)
Wheat and yam	10–30	16	100	Hoover and Vasanthan (1994)
White sorghum	18–27	16	110	Olayinka et al. (2008)

is known to enhance the interactions of amylopectin long chains by rearranging amylose molecules. Therefore, ANN decreases solubility, which means that amylose limits leaching of the granules. This rearranges the molecules in the starch granule and further liberates the amorphous area as the Tg increases (Hoover and Vasanthan, 1994; Morrisin et al., 1993). Meanwhile, the enhanced amylopectin interactions improved the uniformity and stability of the crystalline structure.

The main purpose of ANN is to use a plasticizer such as water or glycerol to lower the glass transition temperature (Tg), increase the mobility of starch molecules at a temperature lower than the gelatinization temperature, and prevent gelatinization at the same time.

The amorphous region is static and glassy before water absorption, and the hydration of the amorphous area increases after ANN treatment (Waigh et al., 2000). This phenomenon causes vibrational movement in the starch molecule chain in the amorphous and crystalline regions (Tester and Debon, 2000). As the ANN process continues, the number of incomplete crystals decreases, and the crystal structure becomes more perfect due to rearrangement of the remaining crystalline structures (Jayakody and Hoover, 2008).

High hydrostatic pressure (HHP)

The HHP treatment process is characterized by applying uniform pressure to the entire product. The food industry uses HHP in the range of 100–1000 MPa to process food materials (Zia et al., 2017). When HHP treatment is used for starch, it is treated with a high moisture content (70% or more, w.b). The high pressure of HHP causes the driving force to destroy the secondary and tertiary structures of starch and hydrate water molecules in the starch to induce molecular rearrangement. In general, HHP treatment limits the swelling power of starch granules, so the viscosity is

Table 2 Annealing conditions for various starches and references

Starch	Moisture content (%, w.b)	Time (h)	Temperature (°C)	References
Bambarra groundnut	50	24	50	Adebowale and Lawal (2002)
Barley	Excess	0.5–4	29–31	Kiseleva et al. (2004)
	Excess	72	50	Waduge et al. (2006)
Black bean	75	24	50	Hoover and Manuel (1996)
cassava	80	72–240	50	Gomes et al. (2005)
	80	24–192	50	Gomes et al. (2004)
	50	48	50–60	Serrano and Franco (2005)
Corn	Excess	72	30–50	Liu et al. (2009)
	Excess	24	10 and 15	Chung et al. (2009)
	Excess	72	25–65	Tester et al. (2000)
	90	72	20 and 50	Kohyama and Sasaki (2006)
Lentil	Excess	24	10 and 15	Chung et al. (2009)
Navy bean	Excess	24	50	Chung et al. (2010)
Pea	Excess	24	10 and 15	Chung et al. (2009)
	50	24	50	Jacobs et al. (1995)
Potato	50	24	50	Jacobs et al. (1995)
	90	72	20 and 50	Kohyama and Sasaki (2006)
	50	24	48 and 53	Jacobs et al. (1998)
Rice	75	16	45–55	Dias et al. (2010)
	75	8–24	45–55	Hormdok and Noomhorm (2007)
	50	24	55	Jacobs et al. (1995)
Sago	80	5	60	Wang et al. (1997)
Waxy maize	Excess	168	55	Qi et al. (2005)
Wheat	50	24	45	Jacobs et al. (1995)
	90	72	20 and 50	Kohyama and Sasaki (2006)
	50	24	48 and 53	Jacobs et al. (1998)
Yam bean	50	24	50	Adebowale et al. (2009)

lower than that of heat-treated starch (Nasehi and Javaheri, 2012). In addition, starch extracted from various botanical sources can be gelatinized through HHP treatment at room temperature or below 0 °C. Many researchers conducted various experiments on starch gelatinization through HHP treatment (Bauer et al., 2005; Błaszczak et al., 2007; Kawai et al., 2007; Oh et al., 2008; Vallons and Arendt, 2009). It has been reported that the properties of the modified starch paste and gel obtained by HHP treatment are different from those of the starch gelatinized by the heat treatment process (Stolt et al., 2000). When a suspension of waxy corn starch was prepared using a sufficient amount of water and was then HHP-treated at 650 MPa for 3 min, the birefringence (Maltese-cross) of the starch granule was lost. The starch granule was gelatinized, and the inside of the starch granule was reconstituted, becoming completely amorphous (Błaszczak et al., 2005a, 2005b). In contrast, the birefringence did not completely disappear when Hylon VII starch (amylose content of 70% or more) was treated with HHP at the same pressure of 650 MPa (Błaszczak et al., 2005a, 2005b). In the case of potato starch molecules treated at 600 MPa for 3 min, there was a slight change in the surface of the starch granules by the HHP treatment process, but the crystallinity of the starch granules was preserved (Błaszczak et al., 2005a, 2005b). When waxy corn starch was treated with HHP at 650 MPa for 9 min, sufficient destruction was induced in the crystalline and amorphous areas in the starch granules, confirming that the starch granules were completely gelatinized (Błaszczak et al., 2005a, 2005b). In addition, it was reported that starches extracted from other plants were also fully gelatinized in different HHP ranges (Stute et al., 1996). On the other hand, HHP-treated potato, barley, corn and wheat starch maintained granule shapes and showed limited swelling power (Stolt et al., 2000; Stute et al., 1996). HHP-treated starches are used as a substitute for lipids. Since starch granules are fine granules, they can provide the same or similar effects as lipids (Stolt et al., 2000; Tomasik, 2004). Table 3 summarizes the various HHP treatment conditions reported so far.

Morphology

HMT starch

HMT did not change the size or shape of potato, taro, cocoya, yam, cassava (Gunaratne and Hoover, 2002), corn (Hoover and Manuel, 1996), wheat (Hoover and Vasanthan, 1994), rice (Wang et al., 2007) or canna (Watcharatewinkul et al., 2009) starch granules. In addition, Zavareze and Dias (2011) studied the effect of HMT on the granules of rice starch with different amylose contents. The above authors reported that the HMT (35%, w.b) of high- and middle amylose rice starch granules slightly affected the shape and degree of agglomeration and made the granules more aggregated and the granule surface more irregular compared to native ones. The change in the shape of the granule surface of rice starch by HMT is probably due to HMT treatment with high moisture content. This is because this condition is more sensitive to partial gelatinization and morphological changes.

ANN starch

When ANN was applied to wheat, oat, lentil, potato and yam starch, there was no change in the starch granule form (Adebowale et al., 2005; Hoover and Vasanthan, 1994; Jacobs and Delcour, 1998; Jayakody et al., 2009; Stute, 1992). However, Kiseleva et al. (2005) confirmed that the form of high amylose and waxy wheat starch treated with ANN changed, and the degree of change was greater in waxy wheat starch. Dias et al. (2010) showed more pores than native high amylose rice starch granules on the surface of ANN treated high amylose rice starch granules. ANN slightly affected the shape of middle and low amylose rice starch and agglomerated more than native starch. Liu et al. (2009) showed that all corn starch samples treated with ANN at 30 °C showed thermal properties similar to native corn starch, indicating that the temperature was not high enough to affect the microstructure of the starch. However, when ANN was performed at 50 °C, the granule size increased in the corn starch samples with different amylose contents, and the average size increased as the amylopectin content increased. The cause of the increase in granule size is the influx of water through the amorphous area during ANN processing.

HHP starch

When proso millet starch was treated with HHP in the range of 150–600 MPa, starch granules maintained their shape at 150–300 MPa HHP, but the granules were damaged at pressures of 450 MPa and higher (Li et al., 2018). When starch was treated at 600 MPa, the starch granule structure was destroyed, and a gel-like structure formed. Hu et al. (2017) reported that waxy wheat starch granules were not damaged at 300 MPa but had wrinkles on the surface. In the 400 MPa treatment, some cracks due to melting were found, but the original shape was maintained. In starch granules treated at 500 MPa, noticeable damage was observed at the granule boundary. At 600 MPa, the granules were completely destroyed, and their shape disappeared. Also, Guo et al. (2015) confirmed a clear increase in granule size ($p < 0.05$) by HHP treatment.

Table 3 High hydrostatic pressure conditions for various starches and references

Starch	Moisture content (%, w.b)	Time (min)	Temperature (°C)	Pressure (MPa)	References
Buckwheat	Excess	20	25	300–600	Hu et al. (2017)
Chestnut	Excess	10	25–70	400–600	Ahmed and Al-Attar (2017)
Corn	75	25	25	550	Song et al. (2015)
Lentil	Excess	20	25	450	Ahmed et al. (2009)
Lotus seed	Excess	25	25	100–600	Guo et al. (2015)
Mung bean	Excess	25	25	120–600	Jiang et al. (2015a)
Pea	Excess	15	25	300–600	Leite et al. (2017)
Potato	Excess	2–3	20	600	Błaszczak et al. (2005b)
Quinoa	Excess	15	25	300–600	Li and Zhu (2018)
Rice	Excess	30	25	120–600	Jiang et al. (2015b)
Sorghum	Excess	10	20	300–600	Vallons and Arendt (2009)
Tapioca	Excess	20	25	600	Vittadini et al. (2008)

Crystallinity

HMT starch

Native wheat starch has an A-type crystalline structure. When wheat starch was treated with HMT, an amylose–lipid complex was formed and changed from A- to A + V type (Wang et al., 2016). High amylose maize starch had a B-type crystalline structure, and when it was treated with HMT, it was changed from B- to A + B type (some V-type) (Wang et al., 2016). Mung bean, pea, and lentil starches have a C-type crystalline structure. When HMT was treated with C-type structure starches, the crystal type did not change (Adebowale et al., 2009; Barua and Srivastav, 2017; Chung et al., 2010; Hoover et al., 2010). There is a common part among these three types of starch, which is that the relative crystallinity tends to decrease when the HMT treatment is performed with a moisture content of 30–35% (w.b). The decrease in relative crystallinity was proportional to the increase in moisture content and time during HMT treatment (Bet et al., 2018). On the other hand, the relative crystallinity of sweet potato, tapioca, green banana, and wheat starch treated with HMT was increased at a moisture content of 15–25% (w.b) (Chen et al., 2015; Zheng et al., 2016). When HMT treatment was performed, the structure of starch tends to become more stable. As a result, the interactions in the amylose-amylopectin chain became stronger, and the rearrangement of the crystalline region occurred during cooling. The movement of water molecules inside the starch may be the cause of the increase in relative crystallinity and change in shape.

ANN starch

When XRD was measured after ANN treatment on native starch, starch crystallinity changed regardless of the starch source. Similar to HMT, the interaction of amylose-amylose and amylose-amylopectin chains was strengthened, and the amorphous area, amylose structure, and amylose–lipid complex were affected (Lan et al., 2008; Yao et al., 2018). However, during ANN treatment, there was no decrease in relative crystallinity due to changes in moisture content and time, which was different from HMT (moisture content was 30% or more).

HHP starch

In general, A-type starch is most sensitive to HHP, B-type starch has high pressure resistance and is resistant to ultra-high pressure, and C-type starch behavior falls somewhere between A-type starch and B-type starch. Wheat starch, potato starch, and tapioca starch showed XRD patterns of A-type, B-type and C-type, respectively (Jayaprakasha et al., 2000). Wheat starch with an A-type XRD pattern was reported to be the most sensitive to HHP (Bauer and Knorr, 2005). The B-type pattern potato starch had the highest pressure resistance, and a phase change occurred in tapioca starch at a higher temperature and HHP than that of wheat starch, but below the phase change of potato starch (Pei-Ling et al., 2010). This is expected because the C-type crystalline structure of tapioca starch is a mixture of A-type and B-type crystals (Sarko and Wu, 1978). However, there are a few exceptions. Below 600 MPa, A-type taro starch has clear birefringence. That is, taro has a higher pressure resistance than other A-type starches, so there is no change in the crystalline area (Pei-Ling et al., 2010). In the case of B-type starch, only high amylose corn starch is partially destroyed (Błaszczak et al., 2005a, 2005b; Knorr et al., 2006).

Thermal properties

HMT starch

HMT affects To, Tp, Tc, and the gelatinization enthalpy (ΔH) of starch, and the effect varies according to moisture content, type of starch, and amylose content (Zavareze and Dias, 2011). These changes include potato, cassava, yam (Gunaratne and Hoover, 2002), corn (Chung et al., 2009; Hoover and Manuel, 1996; Maache-Rezzoug et al., 2008), pea, lentil (Chung et al., 2009) and canna starch (Watcharatewinkul et al., 2009). The changes in To, Tp, and Tc were attributed to the structural rearrangement of starch molecules due to enhanced interactions between the amylose-amylose chain and amylose–lipid complex (Hoover and Vasanthan, 1993).

Adebowale et al. (2009) found that the gelatinization process, including melting of the crystalline area and the double helix, is determined by the hydration and swelling of the amorphous area of the starch granule. When the amorphous area swells, stress is applied to the crystalline area, and the polymer chain is released from the starch crystalline surface (Zavareze and Dias, 2011). After HMT, the interaction of the amylose-amylose and amylose–lipid complexes reduced the mobility of the amorphous area. As a result, HMT-starch caused swelling and destruction of the crystalline area and requires a higher temperature to increase To, Tp and Tc (Zavareze and Dias, 2011). A decrease in ΔH promoted by HMT was also reported in potato, cassava (Gunaratne and Hoover, 2002), corn, pea, and lentil starch (Chung et al., 2009).

However, Hoover and Manuel (1996) found that the ΔH of corn starch treated with HMT at 100 °C did not decrease. Gunaratne and Hoover (2002) reported that the decrease in ΔH due to HMT was double helix melting in the crystalline and amorphous areas of the granule. Furthermore, Hormdok and Noomhorm (2007) argued that the decrease in ΔH after HMT treatment may be due in part to gelatinization of the less stable amylose and amylopectin molecules during heating.

ANN starch

Stute (1992) reported that the type of hydro-thermal treatment of the starch can be determined by the change in the DSC curve. In addition, it was emphasized that the narrow peaks generated after ANN treatment showed greater homogeneity during melting of the crystalline area and swelling and hydration of starch granules. The effect of ANN on the properties can be clearly seen using DSC, and the To, Tp, and Tc of the starch increase, ΔT (Tc–To) decreases, and ΔH increases. An increase in gelatinization temperature is associated with a decrease in swelling power when some granule structure is maintained (Tester and Debon, 2000). Adebowale et al. (2005) said that the increase in To, Tp, and Tc was due to the effect of recrystallization by strengthening the interaction between amylose-amylose and amylose-amylopectin chains along the starch chain. This interaction imparts thermal stability to the granule, inhibits swelling and gelatinization, and increases To, Tp, and Tc values. Waduge et al. (2006) studied the effect of ANN on barley starch and reported that treatment increased To, Tp and Tc and decreased the temperature range (Tc–To). They also suggested that these changes form a new double helix due to the integrity of the crystalline structure and enhanced amylose-amylose and amylose-amylopectin interactions.

HHP starch

Stolt et al. (2000) reported that enthalpy decreased as HHP increased using barley starch, and the degree of gelatinization increased for a given treatment time. Leite et al. (2017) reported that pea starch showed slight gelatinization (31%) when it reached 400 MPa, and that enthalpy decreased from 3.79 to 2.57 J/g ($p < 0.05$). In addition, full gelatinization was possible using a higher hydrostatic pressure (500–600 MPa), and no endothermic peak was detected in DSC measurements. Li et al. (2018) compared the enthalpy of peas treated with HHP for 30 min with native peas (6.2 J/g) and showed that it significantly decreased from 150 MPa (5.7 J/g) to 450 MPa (3.8 J/g), and no gelatinization peak was detected at 600 MPa. In the study results of lotus seeds, mung bean, and rice starch, the decrease in enthalpy was related to the energy required to break the intra-hydrogen helix bond in the crystalline area. Thus, the reduction in enthalpy means that less energy is required to break these bonds, as more crystallinity is disrupted with increasing HHP treatment (Guo et al., 2015; Li et al., 2012, 2011).

Some authors observed incomplete gelatinization in some starches. The gelatinization degree of corn starch treated at 600 MPa for 5 min was 57% (Li and Zhu, 2018), wheat treated at 600 MPa for 30 min was 79% (Hu et al., 2017), and night starch treated at 600 MPa for 10 min was 40% (Ahmed and Al-Attar, 2017). When buckwheat and sorghum were treated at 600 MPa for 20 min, the gelatinization rates were 62% and 53% (Liu et al., 2016a; 2016b), respectively. These results mean that starch can be completely gelatinized when the pressure, processing time, and temperature are higher.

Vallons and Arendt (2009) observed that the proportion of gelatinized starch granules for HHP and temperature treatment reached complete gelatinization at 600 MPa or 75 °C along a sigmoidal curve. Also, the proportion of damaged starch was highly correlated with gelatinization ($r2 = 0.9917$ and 0.9927 for HHP and temperature treatment, respectively). Some authors have confirmed that HHP treatment can significantly alter the gelatinization temperature. It is also reported that the decrease in gelatinization temperature and each gelatinization temperature range show a positive correlation with HHP (Liu et al., 2016a; 2016b). According to the above authors, the energy required for starch gelatinization decreases when ΔH decreases, and the gelatinization temperature decreases. On the other hand, the range of the gelatinization temperature indicates the stability of the crystalline area. The decrease in the gelatinization temperature range as the pressure of HHP increased indicates that the HHP treatment destroys the crystalline area of the starch and becomes more unstable.

Solubility and swelling power

HMT starch

As a result of the effect of HMT, a decrease in the swelling power of potato, cassava (Gunaratne and Hoover, 2002), rice (Hormdok and Noomhorm, 2007), sorghum (Olayinka et al., 2008) and corn starch (Chung et al., 2009) was reported. The decrease in swelling power is due to an increase in crystallinity, a decrease in hydration (Waduge et al., 2006), an increase in interaction between amylose and amylopectin chains, strengthening of the intramolecular complex (Jacobs et al., 1995), formation of an amylose–lipid complex (Waduge et al., 2006), and a change in the crystalline area arrangement of the starch (Hoover and Vasanthan, 1994).

Starch solubility occurs due to leaching of amylose, which separates and diffuses from the granule during swelling. This leaching represents a transition from order to disorder within the starch granules that occurs when starch is heated with water (Tester and Morrison, 1990). The solubility of HMT-starches decreased (Adebowale and Lawal, 2002; Olayinka et al., 2008), and the decrease in solubility was improved by increasing the moisture content (Olayinka et al., 2008).

The reduction in swelling power and solubility following HMT has been attributed to the internal rearrangement of the starch granules, which causes further interactions between the starch functional groups (Hoover and Manuel, 1996), the formation of more ordered double helical amylopectin side-chain clusters and the formation of amylose–lipid complexes within the granules (Olayinka et al., 2008; Tester and Morrison, 1990).

ANN starch

ANN generally reduces the swelling power of starch. This decrease is strongly influenced by the degree of crystalline perfection and the interactions between the amylose-amylose and amylose-amylopectin interactions. The crystalline perfection with the amylose chain reduces the hydration of the amorphous area of the starch, resulting in decreased granule swelling. Hoover and Vasanthan (1994) observed reduced granule swelling during ANN in potato starch. In addition, ANN reduces the swelling power of barley (Waduge et al., 2006), fermented cassava (Gomes et al., 2005), bambarra groundnut (Adebowale and Lawal, 2002), and wheat starch (Lan, et al., 2008). Swelling power is affected by the structure of amylopectin (Sasaki and Matsuki, 1998), the content of amylose, and the strength of the interaction between amylose-amylose and amylopectin-amylopectin chains (Tester and Debon, 2000). The reason for the decreases in swelling power and solubility was due to recrystallization (Gomes et al., 2005).

The decrease in solubility of the ANN-starch is because the binding between amylose and amylopectin or between amylopectin molecules is strengthened, thereby inhibiting amylose leaching from granules (Gomes et al., 2005). Waduge et al. (2006) showed that the swelling power of ANN-barley starch was lower than that of native barley starch. Many authors reported that the degree of solubility decrease depends on the amylose content of barley starch and follows the order of normal > waxy > high amylose. The decrease in the swelling power of waxy starch during ANN is due to the perfection of starch crystallites.

This is because the perfection of starch crystallites reduces hydration of the amorphous area (Zavareze and Dias, 2011; Waduge et al., 2006). In contrast, in the ANN of normal and high amylose starch, the interaction between perfection of starch crystallites and amylose-amylose chains may be the cause of the decrease in swelling power (Iuga and Mironeasa, 2020; Zavareze and Dias, 2011).

HHP starch

According to Ahmed et al. (2018), the solubility and swelling power of quinoa starch treated with 300–600 MPa pressure increased at 25–70 °C. HHP treatment increased the amount of damaged starch, which in turn strengthened the moisture-retaining ability of the starch granules and naturally increased the swelling power. The increase in solubility at 70 °C is due to enhanced leaching of water-soluble substances after HHP treatment. Ahmed et al. (2016) reported that the swelling power (at 25 °C) of lentil starch treated with 600 MPa significantly increased ($p < 0.05$). However, solubility decreased with pressure and was lowest at 600 MPa. Guo et al. (2015) showed that lotus seed starch had higher swelling and solubility in the 55–75 °C range than native starch. However, the value decreased with increasing pressure at 85–95 °C. These results were confirmed by Li et al. (2012), who reported similar results. Swelling and solubility increased at 50–90 °C, whereas different trends were observed as the temperature increased at 600 MPa. HHP-treated starch showed higher swelling and solubility at lower temperature (50–60 °C) than native starch, and lower swelling and solubility at higher temperature (70–80 °C). Li et al. (2011) reported that mung bean starch treated at a 120–600 MPa pressure was reduced in swelling and solubility at 90 °C when compared with native mung bean starch. Li et al. (2018) explained that temperature-dependent increases in swelling and solubility may be associated with granule damage. Dispersing the starch in excess water and heating it breaks the hydrogen bonds between amylose and amylopectin. Once the internal structure of the granule is destroyed, –OH in the starch formed a free bond with water molecules, so swelling and solubility increased with temperature. Also, amylose–lipid crystals formed at low temperatures, limiting swelling. Above 85 °C, crystals melt, while swelling and solubility increase. The increase in swelling and solubility at higher pressures and at lower temperatures may be due to amylose aggregation under pressure that disrupts the lipid-starch boundary (Liu et al., 2016a; 2016b; 2016c). The decreased swelling and solubility values at higher temperatures may be due to amylose molecular rearrangement. Li et al. (2012) reported that swelling is mainly caused by amylopectin. Starch granules are often intact or partially destroyed after HHP treatment, thus limiting amylose solubilization. This may be due to stabilization of amylopectin by the remaining amylose, which prevents some crystal structures from melting.

Digestibility

HMT starch

Wang et al. (2016) reported that HMT-starch digested slowly when compared to the hydrolysis by enzymes with native high amylose corn starch after HMT treatment of high amylose corn starch. The structural rearrangement of starch may cause resistance to enzyme hydrolysis. After HMT, the crystallite perfection of the starch increased, and a denser starch matrix and packed amorphous starch molecules were produced. This phenomenon affects starch availability and enzyme hydrolyzes starch (Ashwar et al., 2016; Martens et al., 2018; Wang et al., 2016). When corn starch is treated with HMT (M.C 20%), slowly digestible starch (SDS) increases from 6.2 to 12.9%, and resistant starch (RS) increases from 2.1 to 4.2%. The increase in RS and SDS depends on the moisture content of the starch sample during HMT treatment (Wang et al., 2016). Silva et al. (2017) studied the rice starch granule behavior after HMT at various moisture contents and reported that the SDS and RS contents were high after HMT treatment due to the enhanced interactions between the rice starch granule components. In the rice starch treated with HMT, the SDS and RS content increased, and the RDS content decreased. Sharma et al. (2015) observed HMT in millet starch of various moisture contents, and Barua and Srivastav (2017) observed the same trend in mung bean starch. The change was greatly affected by the moisture content. As a result, the RS content increased after HMT according to the moisture content. The change in the moisture content affected hydrogen bonding, causing the amylose to form a stable double helix structure, resulting in resistance to the enzyme (Babu and Mohan, 2019; Li and Gao, 2010).

Meanwhile, the digestibility of starch is related to granule size, swelling power (SP), thermal and pasting properties (Ashwar et al., 2016; Silva et al., 2017). A lower SP and a higher ΔH result in greater interactions between the crystalline areas and an increase in RS (Silva et al., 2017). The glycemic index varies depending on the amylose-amylopectin ratio, and HMT rice flour was larger than that of native rice. High amylose rice showed a lower glycemic index than low amylose rice because it had lower reactivity to enzymes than low amylose rice (Ruiiz et al., 2018). Kim et al. (2017) reported an increase in RS and a decrease in RDS when rice flour was treated with HMT, and the SDS did not change significantly. HMT treatment made it more difficult to decompose using an enzyme due to the interactions between starch, protein and lipid, which inhibits degradation by enzymes (Chen et al., 2015; Roman and Martinez, 2019; Ye et al., 2018). Piecyk et al. (2018) reported that the digestibility of pea starch was affected by plant variety and HMT. An increase in the RS content of tapioca starch was also reported after HMT (Liu et al., 2016a; 2016b; 2016c). HMT showed a strong link between starch chains leading to higher RS content. Many changes occur during HMT. Some amorphous areas are converted to crystalline areas, and A-type starch becomes A + B type in the crystalline region, and there are stronger interactions in the amylose-amylopectin chain. Crystalline regions are more resistant to enzyme action than the amorphous area, which is why RS content is increased (Butterworth et al., 2011; Dupuis et al., 2014; Sharma et al., 2015; Sui and Kong, 2018).

However, an increase in enzyme hydrolysis (EH) of potato, yam, cassava, taro and new cocoyam starch was also reported after HMT treatment (Gunaratne and Hoover, 2002). These results seem to be influenced by the starch source and amylose-amylopectin ratio. That is, the first step in digestion is absorption of α-amylase from the starch granule surface. After HMT, some crystal cleavage occurred near the granule surface, leading to better enzyme penetration (Piecyk et al., 2018; Zavareze and Dias, 2011). As a result, new cocoya and cassava starch showed higher EH (67.3% and 69.5%, respectively) compared to other samples (taro 45.4%, potato 38.8%, and yam 17.2%) due to destruction of the crystalline area near the granule surface during HMT. α-amylase enters the starch granule more easily. Therefore, the increase in EH is due to the interactions between melted double helixes and amylose chains (Alcázar-Alay and Meireles, 2015; Gunaratne and Hoover, 2002).

ANN starch

ANN-wheat, sago and rice starch are more easily hydrolyzed by α-amylase than native starch (Dias et al., 2010; Jayakody and Hoover, 2008; Wang et al., 1997). These results are inconsistent with the findings of wheat, lentil and potato starch, but small starch granules (oats) were reported to be more readily hydrolyzed after ANN (Hoover and Vasanthan, 1994). The increase in hydrolysis by increasing the porosity of granules is the effect of ANN (O'Brien and Wang, 2008). After ANN treatment, the interaction between amylose-amylose and amylose-amylopectin was strengthened and enzyme-induced hydrolysis was decreased (Hoover and Vasanthan, 1994; Hoover and Zhou, 2003). ANN induces changes in the amorphous area of the granule to facilitate enzymatic activity. ANN increased the pores of the surface of starch granules (Nakazawa and Wang, 2003) and the sensitivity of wheat starch to fungal and bacterial enzymes (Jayakody and Hoover, 2008). Meanwhile, the degree of hydrolysis differs depending on the type of starch and the enzyme in the porous structure (O'Brien and Wang, 2008). Enzymatic hydrolysis of ANN treated waxy and high amylose corn starch was increased because ANN promotes the formation of pores or cracks on the surface of granules and facilitates the penetration of α-amylase to change the degree of hydrolysis (Wang et al., 1997). On the other hand, ANN rearranges the amorphous and crystalline lamella of the granule, but makes the enzyme more accessible to the amorphous area, resulting in increase in relative crystallinity but more sensitive to α-amylase than native starch (Serrano and Franco, 2005).

Chung et al. (2009) investigated the effect of ANN on the digestibility of corn, pea and lentil starch and reported that ANN increased RDS and decreased SDS levels in all native granule starches. O'Brien and Wang (2008) explained that the increase in RDS levels in ANN was due to the formation of a porous structure, allowing hydrolytic enzymes to more readily access the interior of the granule. Chung et al. (2009) found an increase in RDS and a decrease in SDS in a study using corn starch ANN at 50 °C. ANN was used to increase the RS content while maintaining the granule structure (Brumovsky and Thompson, 2001). There was no change in molecular structure due to the gelatinization process because the temperature conditions do not exceed the gelatinization temperature during ANN treatment. Therefore, ANN strengthens the connection between amylose and amylopectin molecules by making starch granules more organized and stable. Brumovsky and Thompson (2001) studied the effect of ANN on high amylose corn starch and reported that RS content increased compared to native starch. Chung et al. (2010) found that the RS content of ANN pea, lentil and dark blue soybean starch decreased compared to native starch, and the crystal integrity and amylose-amylose and amylose-amylopectin interactions theoretically increased RS content. However, the increased porosity on the granule surface due to ANN may negate the effect of crystalline integrity and starch chain interactions on enzyme hydrolysis. These authors studied the effect of double modifications (ANN–HMT and HMT–ANN) in a gelatinized sample, resulting in a further increase in RS content. Pomeranz (1992) and Kutoš et al. (2003) reported that RS content is associated with gelatinization and aging. However, the change in the RS content formed by ANN was not related to gelatinization and aging because the ANN-starch was not gelatinized. Therefore, changes in RS content are related to structural changes such as rearrangement of starch molecules by ANN and changes in starch crystallinity.

HHP starch

Hu et al. (2017) studied the in vitro digestibility of waxy starch and reported that the content of hydrolyzable starch increased while RS decreased as the treatment pressure increased from 300 to 600 MPa. Deng et al. (2014) obtained similar results in the rice starch study, and although no significant difference was detected in the starch fraction between the starch treated at 200 MPa for 30 min and the control, the digestible starch content increased, and the RS content decreased. Native starch had the highest hydrolysis, and the hydrolysis rate increased as the pressure increased from 150 to 600 MPa during pressure treatment. HHP starch (600 MPa) showed the lowest RDS content (24.1% and 58.1%, respectively) and the highest RS content (54.2% and 36.6%, respectively) compared to native starch (Liu et al., 2016a; 2016b; 2016c). A change in the starch structure was observed due to interactions between amylose and amylopectin chains, and the enzyme had low sensitivity to modified starch. Thus, hydrolysis was reduced, and the starch fraction content changed. Studies on starch digestibility are associated with glycemic index and prevention of non-insulin dependent diabetes mellitus (Liu et al., 2016a; 2016b; 2016c). Therefore, starch modified by HHP has the potential to prevent chronic diseases and maintain health. RS may protect from colon cancer, maintain cholesterol levels, lower the glycemic index, and reduce insulin response. The increase in RS content indicates that the interaction between amylose and amylopectin chains is strengthened. Several factors can affect the enzyme sensitivity of starch, including amylose content and starch crystal structure. Amylose content and crystallinity of the pressurized starch was superior to that of the native starch, resulting in a lower hydrolysis rate. However, it was observed that the content of digestible starch slowly increased due to pressure treatment, which may occur due to the formation of an intact structure of starch granules or a small amount of amylose–lipid complex. Interestingly, these authors reported that pressure-treated starch had a different polymorphism (B-type) than native starch (A-type). Therefore, HHP is a good physical modification technology to obtain starch with increased health benefits. Colussi et al. (2018) evaluated the effect of HHP treatment with starch aging on potato starch during in vitro digestion in the stomach and small intestine. The authors reported a significant decrease of 10–15% in the hydrolysis of starch modified with 6/10 cycles at 400 MPa with aging with respect to native and HHP starch. Similar results were observed for deformation after 3 cycles at 600 MPa, but with lower hydrolysis values. Also, the behaviors of starch transformed using 6 cycles at 600 MPa and 6 cycles at 400 MPa were similar. These data suggest that HHP treatment promoted RS and SDS formation for buckwheat and sorghum starch.

The physical modification method is an eco-friendly technology that imparts functional properties to starch to be used in various foods. These techniques are affected by several factors such as the origin and composition of starch, the ratio of amylose and amylopectin, temperature, and moisture content. Hydro-thermal treatment includes HMT and ANN, both of which are representative physical modification methods using thermal energy that change various physicochemical properties of starch without causing gelatinization. High hydrostatic pressure (HHP) is a technology for gelatinizing starch using pressure energy. It is a great feature to change the starch with minimal influence. As a result, both heat and HHP were applied as mechanisms for denaturing starch by stimulating water molecules inside the starch, suggesting the possibility of PMT technology that changes low-moisture starch by high pressure treatment. This review paper suggests that high hydrostatic pressure treatment under low moisture has the potential to change the internal structure of starch like HMT.

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Declarations

Conflict of interest None of the authors have conflicts of interest to disclose.

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