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Effect of Heat-Moisture Treatment on Structural Characteristics and Physico-chemical Properties of Corn Starch-Hydrocolloid: A review

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ABSTRACT

The use of modified starch, especially from cereal sources in food products, is still very limited in Indonesia. Corn has a fairly high carbohydrate content so it is very potential to modify starch, such as using the heat moisture treatment (HMT) method. The HMT method is a physical modification method of starch, which will be able to produce starch with a moisture content of less than 35%. Several studies have stated that physical modification using HMT and/or can be combined with pectin, gum arabic, xanthan gum and guar gum can improve the physical characteristics of the resulting product. This review aims to determine the physical characteristics of corn starch treated with HMT modification with and without a combination of treatments using Arabic gum, xanthan gum, and guar gum. The results showed that the HMT treatment (100°C, 16 hours, 25%) had the lowest swelling power and solubility values compared to other samples. The HMT-Pectin treatment had a low syneresis value, as the impact it has good freeze- thaw stability compared with the others. Meanwhile, corn starch-modified by HMT with gum (gum arabic, xanthan gum, and guar gum) significantly did not change the type of crystallinity of starch.

Keywords: Corn starch, heat moisture treatment, hydrocolloid

Introduction

Corn contains high carbohydrates, which is about 72-73%, and the starch content consists of 25-30% amylose and 70-75% amylopectin (Chung, 2000). These two components play an active role in the sensory characteristics of food, especially in texture and taste, so that it is closely related to its amylografi properties. However, in its application, pure corn starch still has many weaknesses that will reduce its effectiveness and functionality of starch.

Starch is the main source of carbohydrates or the most abundant polysaccharides in plants. Amylose and amylopectin are two components of starch granule macromolecules (Be Miller, 2007). Starch in the food industry can provide functional properties, modify food texture, consistency, and so on. Not only is the starch capacity important for the texture of a particular product, but also the type of starch used greatly affects the final product yield.

Hydrocolloids, as general functional macromolecules, are often used in the food industry. Mixing the combination of starch with hydrocolloids can modify its functional characteristics, such as paste properties, viscoelasticity, encapsulation, thickening, and thermal properties (Heyman et al., 2014; Mahmood et al., 2017; Ptaszek et al., 2009).

Heat-moisture treatment (HMT) is a physical modification in which the starch has a low water content of less than 35% water (% w/w) which is then heated above the glass transition temperature and below the gelatinization temperature for a certain period (Shaikh et al al., 2020). HMT was carried out to improve the functional characteristics of natural starch so that good functional properties were produced.

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Starch characterization can be improved through starch modification and this has been done with research on physical modification, chemical modification, and enzymes (Sun et al., 2014; Palavecino et al., 2019; Anggreini et al., 2018). Modification of starch needs to be done to reduce the basic properties of natural starch which are less favorable such as the tendency of retrogradation, synergism, and low paste stability.

It has been reported that HMT can significantly affect the morphology, structure, and functional properties of starch (Zavareze et al., 2011; Zavareze et al., 2010). Many biopolymers have been shown to have the potential to modify starch with certain functional properties, such as in the study of gum arabic and guar gum which are very helpful for increasing the stability of starch gels through interactions with starch molecules (Zhou et al., 2020). Pectin, as a natural hydrocolloid, shows excellent water absorption capacity (Zhang, Liao & Qi, 2020; Zhang et al., 2020). In addition, HMT treatment can increase the interaction between starch and a series of natural hydrocolloids such as sodium alginate (Shang et al., 2017), gum arabic, xanthan gum, and guar gum (Zhou et al., 2020).

This review aims to summarize the effect of physical modification of starch using moisture heat treatment with the addition of hydrocolloids on the physicochemical characteristics and functionality of the resulting product.

HMT (Heat Moisture Treatment)/ Moist Heat Method

Heat moisture treatment (HMT) is a physical modification of starch in which starch granules with a low moisture content below 35% are then heat treated for some time and at a relatively high temperature (90–120 oC), that is, above the glass transition temperature but at a lower temperature and below initial gelatinization temperature of starch (Sui et al., 2015). The effects of HMT on starch include an increase in the initial gelatinization temperature, changes in X-ray diffraction patterns, granule morphology, thermal properties, swelling power, solubility, and enzyme digestibility (Shang et al., 2017).

Based on Table 1. HMT treatment caused a decrease in swelling power and solubility. This decrease was probably due to the formation of starch swelling and weakened starch structural stability due to the decomposition of the double helix during HMT (Varatharajan et al., 2011). This phenomenon then led to solubility and swelling loading capacity. This statement was also strengthened, that the decrease in solubility and swellability in barley starch was caused by an increase in crystallinity, a decrease in hydration ability, an increase in intermolecular bonds, and the formation of amylose-lipid complexes. The formation of amylose-lipid complexes can also contribute to reducing the solubility and swellability of forage starches (Waduge et al., 2006).

The comparison of starch pastes properties according to Table 1. Shows that the higher the water content used, the lower the peak viscosity, breakdown viscosity, and setback viscosity. The high temperature and the length of time for HMT modification have a close effect on the characteristics of starch because it will further disrupt the hydrogen bonds between molecules in the starch granules (Vermeylen et al., 2006). Hoover and Ratnayake (2010) found that the physicochemical bonding of starch was also influenced by the water content level and the botanical source of starch. During the heating process, there is a change in the amorphous region during hydrothermal treatment due to an increase in the degree of regularity rather than an increase in the degree of crystallinity, which leads to higher rigidity of the starch granular structure in the amorphous region which will disrupt the crystal structure of the starch granules (Jacobs & Delcour, 1998).

Based on Table 1. X-ray patterns of native starch and HMT showed a strong pattern of double-centered diffraction peaks at 2θ = 15.1, 17.2, 18.1, and 23.2° which is known as the "Type A" diffraction pattern. Increasing the water content or heating time increased the peak intensity of the HMT starch but, did not change the diffraction pattern inherent in the original starch. Research from Hoover and Ratnayake (2002) found that the X-ray diffraction pattern in type B could be converted into "type A" starch through the HMT method, while the type A cereal type remained unchanged even after HMT treatment was given.

Table 1.Characteristics of corn starch modification by HMT method

Parameters	HMT Conditions (Temperature, Heating time, Moisture content) Z.Sui et al. (2015)			
	Native	100 °C, 16h, 20%	100 °C, 16h, 25%	100 °C, 16h, 30%
Swelling power (g/g)	7,7	6,6	5,9	6,0
Solubility (%)	2,6	1,1	1,7	2,6
Pv	220	194	143	88
Bv	130	38	15	1,9
Fv	266	256	176	101
Sv	137	100	48	15
XRD pattern type	A type	A type	A type	A type

Native (no modification), Pv: Peak viscosity (mPas), Bv: breakdown viscosity (mPas), Fv: final viscosity (mPas), Sv: setback viscosity (mPas)

The HMT treatment and the high water content used were able to reduce the swelling power value of starch, so it can be seen in table 1. that the temperature, length of time, and the level of water content affect the decrease in the swelling power value. The decrease in the value of swelling power occurs due to changes in the structure of starch crystallites as well as interactions between starch components on the amorphous side of the granules during treatment, where the transformation of amorphous amylose into a helical shape causes increased interactions between amylose chains (Adebowale et al., 2015). In addition, the HMT process will cause the starch granule molecules to become denser so that it is more difficult to experience swelling.

The solubility value of HMT starch is lower than that of pure starch. This happens because the length of time and high temperature affects the decrease in the solubility value. Water imbibition occurs during HMT modification causing a rearrangement of amylose and amylopectin molecules in starch granules which has an impact on changes in the physicochemical properties of starch, changes in starch structure which will cause loss of free hydroxyl groups which makes solubility decrease (Sennayake, et al., 2013)

Freeze-thaw stability is the ability of starch to resist unwanted physical changes that may occur during freezing and thawing. In the study of Zhang et al., (2021) it was found that the HMT treatment was able to reduce the syneresis percentage value of pure corn starch by 45.9% to 36.2%. The high syneresis value indicates that pure corn starch has low freeze-thaw stability. The freeze thaw stability of starch is influenced by the interaction of amylose and amylopectin during the HMT process (Pinto et al. 2015).

Figure 1. shows a micrograph of starch samples observed under normal and polarized lamps. As shown, the N-S granules are seen to have highly sensitive shapes with different sizes and clear birefringence under polarized light. Compared to HM-S grains, it did not show any noticeable change in appearance, although some of them were broken or had no visible birefringence in the middle. This is following by previous reports that physical treatment did not damage the integrity of starch granules (Gunaratne et al., 2002; Zavareze et al., 2011), whereas it could lead to a less regular molecular orientation, which most likely could be attributed to the mobility of the amylopectin chains (Chung et al., 2009).

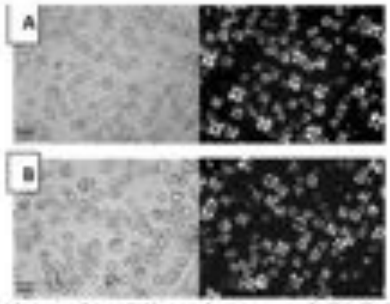

Figure 1. Microscopy images of starch samples; a) Normal corn starch (N-S); b) 30% moisture content starch (HM-S) (Zhang et al., 2021)

SEM micrographs of starch samples are shown in Fig. 2. Granules N–S has a shape that still looks round in some granules and is intact. While HMT-S looks irregular granule shape and the surface is uneven with many small indentations or pores. The research from Fadimu, et al. (2018) stated that the HMT moisture content of 20-30 percent caused the surface of the modified sweet potato starch granules to change to become rougher. According Tan et al. (2017) also added that the higher the water content of HMT used (15–35 percent) in the modification process caused more indentations to form on the starch surface due to the weakened structure of the tissue in the starch granules.

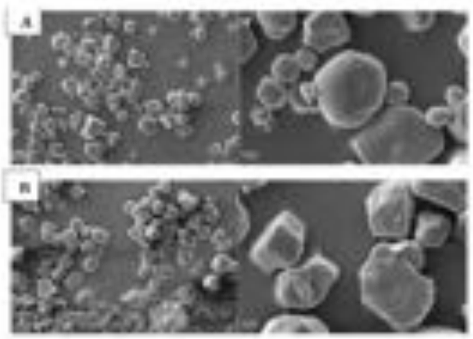

Figure 2. Scanning electron micrographs of native and HMT modified starch. a) native corn starch (N-S); b) 30% Moisture content (HMT-S) (Zhang et al., 2021)

Effect of HMT-Hydrocolloid modification on physicochemical properties of corn starch

Forage treatment has been applied as a safe, safe, efficient, and low damage rate physical modification technology in the food industry. For example, in a study (Zhou et al., 2020) xanthan gum, gum arabic, and guar gum are very helpful for increasing the stability of starch gels through interactions with starch molecules. HMT can significantly affect the morphology, structure, and functional properties of starch. In addition, HMT can enhance the interaction between starch and natural hydrocolloids. For example, pectin, as a natural hydrocolloid, exhibits excellent water absorption capacity (Zhang, Liao & Qi, 2020; Zhang et al., 2020), which is an advantage to help starch achieve a range of functional properties. For example, it was reported that the right amount of pectin (1–5%) can significantly reduce the syneresis of starch gels and influence their viscoelastic behavior (Dangi et al., 2020).

Properties of starch paste are presented in Table 2. There is a significant decrease in the breakdown value of the HMT-P samples. This happened due to the reduction of leached amylose (Rafiq et al., 2016). HMT treatment increased the interaction of the amylose-lipid and amylopectin-amylose complexes and thereby slowing the leaching of amylose molecules from the paste and increasing the resistance of starch granules under heat and mechanical shear (Kong et al., 2015). Meanwhile, the presence of pectin can increase strong physical interactions, and strengthen the resistance of starch granules which will reduce the level of damage to a lower level. The HMT-P sample displays the lowest breakdown and setback values. A lower breakdown viscosity indicates higher stability, and a lower setback value indicates a smaller tendency for retrogradation (Kong et al., 2015). Thus, our results show that HM-P/S paste has the highest stability.

Table 2. Characteristics of corn starch modification by HMT-hydrocolloid method

Parameters	HMT- Hydrocolloid modified starch Conditions (Temperature, Heating time, Moisture content) Y. Zhang et al. (2021)	
	Native	HMT-P (105 °C, 4h,30%)
Pv	205	141
Bv	20	1
Fv	266	146
Sv	64	29
PT (°C)	71,4	69,5

Native (no modification), Pv: Peak viscosity (mPas), Bv: breakdown viscosity (mPas), Fv: final viscosity (mPas), Sv: setback viscosity (mPas)

In Figure 3. the micrograph results of the HMT-P modified corn starch samples were significantly different where the structural surface of the starch granules was damaged and the birefringence decreased. Weak birefringence indicates a loss of radial orientation of the starch molecular chains and perhaps even a slight breakdown of the crystal structure within the granules. Then a repulsion occurs which results in a shift in the starch chain, and may even damage the compact granular structure of starch (Bharti et al., 2019). Moreover, the induced pectin might also partially contribute to the phenomenon because, under alkaline conditions, an elimination reaction occurs and causes the molecular weight of the pectin to decrease (Einhorn-Stoll et al., 2019). As a result, smaller pectin molecules penetrate more easily into slightly swollen granules and starch chains become tangled and structural changes occur.

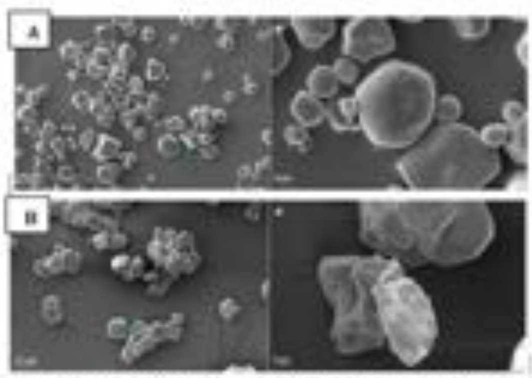

Figure 3. Scanning electron micrographs of a) Native Starch (N-S), b) Moisture Content 30% HMT-Pectin (HMT-P)(Zhang et al., 2021)

As shown in Figure 4. HMT modification resulted in a smooth starch surface, with indentations on the corn starch surface. Mixing the modification with Gum Arabic caused limited aggregation with the effect becoming more pronounced as the proportion of the compound was higher (Fig. 4. HMT-CA 100). While the appearance of Xanthan Gum (Fig. 4. HMT-CX 100) shows that the starch surface is not evenly distributed and looks rough on the surface with a fairly large starch granule size. Guar gum has a more even and finer granular appearance on the surface (Fig. 4. HMT-C6-100).

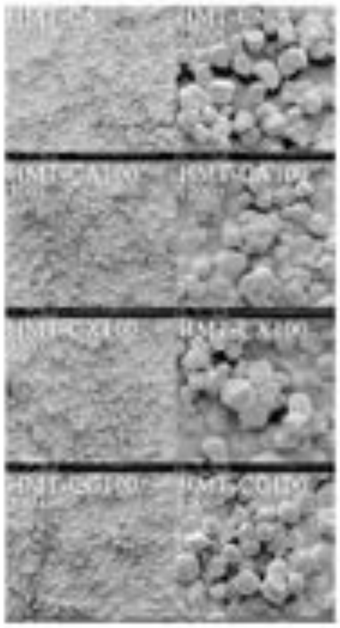

Figure 4. Scanning electron micrographs of a) Native starch (HMT-CS); b) HMT-Gum arab (HMT-CA 100); c) HMT-Xanthan Gum (HMT-CX100); d)HMT-Guar gum (HMT-CG100)

Zhou's research (2020) shows that the combination treatment of HMT modification on the hydrocolloid types of guar gum, xanthan gum, and gum arabic has the same type A crystal form in all samples, this proves that the crystal form is not affected by the HMT modification. The HMT-induced decrease in crystallinity could be attributed to the effect of high temperature and high water content disrupting the crystal structure so that the condition of the double helix in the partially broken crystallization region rearranges to a new structure, resulting in a decrease in relative crystallinity (Wang et al., 2017). The added hydrocolloid also plays a role in the interaction with the starch chain directly, thereby inhibiting the reformation of the double helix structure and thereby weakening the crystallization region.

Zhang et al. (2021) it was found that the HMT-hydrocolloid (pectin) treatment was able to reduce the syneresis value of pure corn starch by 45.9% to 6.3%. The addition of pectin decreases the percentage of syneresis but, increases the stability significantly of pure starch. The water adsorption capacity of the added pectin can prevent water from forming ice crystals, thereby reducing syneresis. There was an increase in the freeze-thaw due to a gradual decrease in gel syneresis, which phenomenon was attributed to the inhibition of water release from the gel, which was caused by an increase in amylose-amylopectin, amylose-pectin, and amylopectin-pectin interactions during the freeze-thaw cycle (Liu et al., 2019).

Conclusion

Physical modification of corn starch using the HMT- hydrocolloids can affect the functional characteristics of starch such as swelling power, solubility, paste clarity, starch crystallinity, morphology, and properties of starch paste. However, the determination of the method of HMT-hydrocolloids needs to be reconsidered through existing research results to achieve the desired functional characteristics of starch.

Technology related to the modification of HMT-hydrocolloids in the application of the food industry needs to be developed because it can increase usability. Thus, further research or testing is needed to examine the interaction relationship between the two factors.

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