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## Modification of Sorghum bicolor (L) Moench Starch: Review of HMT (Heat Moisture Treatment), Autoclaving Cooling, and Annealing Methods

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### Abstract

The use of sorghum in Indonesia is still not optimal even though it ranks as the third most cultivated cereal category. Its carbohydrate content, especially starch, is high enough to provide a large enough potential for sorghum to be developed and applied to food products. Starch is used for improving the final product characteristics such as texture, flavor, and functionality. Several physical modification methods have been investigated to improve the final product characteristics of sorghum. The physical modification method of starch has advantages over chemical or enzyme methods, it is easy to apply, safe, and faster. This review aims to summarize the physical modification of sorghum starch using heat moisture treatment, autoclaving cooling, and annealing methods for the characteristics or functionality produced. Heat moisture treatment (HMT) and Annealing have affected the swelling power and solubility significantly while Autoclaving Cooling increases the amylose content and significantly reduces the digestibility of the starch.

**Keywords:** sorghum, modification, heat moisture treatment, autoclaving cooling, annealing

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### INTRODUCTION

Sorghum is a cereal with a high starch content  $\pm$  70% (Singh et al., 2011). Sorghum is a plant that grows in the tropics and belongs to the Poaceae family, which usually grows in Africa, Asia, and Latin America (Anglani, 1998). The largest sorghum-producing country in the world is the United States, which is then followed by India, Nigeria, Africa, and Mexico (Vijayakumar and Santhi, 2013). In Indonesia, sorghum ranks third after rice and maize, however, its utilization was still not optimal. Starch is the main component stored in cereal grains. Sorghum is a source of carbohydrates with a content of approximately 60-80%, so it has the potential to be applied to the food industry (Zhang et al., 2003; Cousidine and Cousidine, 1982). Ariyanti (2016) said the nutritional content of sorghum seeds is carbohydrates by 84.16%, fat 0.35%, and protein 3.58%.

Starch is usually widely applied to various kinds of food products, both as raw materials and as food additives. Starch is a food additive that can act as a thickener, thickening, gelling agent, and water absorbent. However, the characteristic of starch depends on the content of the resistance starch itself. Starch with low content of resistant starch affect its characteristics.

The characteristics of starch can be improved by modifying starch, and this has been done by several studies such as physical, modification chemical and enzymes (Sun et al., 2014; Palavecino et al., 2019; Anggreini et al., 2018), however, the physical method has advantages including easy to apply, safer and faster. Modifying starch methods can also rise resistant starch so that it can be applied to food products (Shaikh et al., 2020).

This review aims to summarize the physical modification of sorghum starch using heat moisture treatment, autoclaving cooling, and annealing methods for the resulting characteristics or functionality.

#### HMT (HEAT MOISTURE TREATMENT) / MOIST HEAT METHOD

Modification of starch using the heat moisture treatment (HMT) method is a physical modification that is generally used to improve the functional characteristics of natural starch so that it can give good results when applied to food products. The starch used in this method has a limited water content of less than 35% water (% w/w), which is then given a heating process above the glass transition temperature and below the gelatinization temperature for a certain period (Shaikh et al., 2020). Research showed that modified sorghum starch with a moisture content of 20-25% and a temperature range of 55-95 °C, using a convection oven for 10 hours, led to a decrease in swelling power and solubility (%) (Sun et al., 2014). The same result stated that forage can reduce swelling power and solubility in white sorghum starch with KA 18-27% heated in an oven temperature of 110 °C (Olayinka et al., 2008). This decrease was probably caused by the formation of back starch molecules and can cause the formation of a double helix of amylopectin, causing the starch structure to become more rigid (Lawal and Adebowale, 2005). This phenomenon then causes solubility and swelling power unload. This statement is also reinforced, that the decrease in solubility and swelling power in barley starch is due to an increase in crystallinity, decreased hydration ability, increased intermolecular bonds, and amylose-lipid complexes are formed. The formation of amylose-lipid complexes may also contribute to reducing the solubility and swelling power of forage starch (Waduge et al., 2006).

HMT Method is also able to increase the curing temperature of sorghum starch (Sun et al., 2014), and this can be attributed to an increase in crystallinity due to modification. The increase in crystallinity makes it difficult for amylose to leach so that it has an impact on decreasing the swelling capacity. Modification of heat moisture can increase and decrease the crystallinity of starch this is influenced by the moisture content of the material and the process temperature (Syamsir et al., 2012). This is linear with the results of Sun et al. (2014), that the crystallinity of sorghum starch modified with HMT with 20% moisture content was 33.42%, meanwhile, sorghum starch with 25% moisture content had a crystallinity of 29.62%. The lower yield of sorghum starch with 25% moisture content indicated that the starch was partially gelatinized (Vermeyleen et al., 2006) stated that giving too high a temperature or moisture content could reduce crystallinity.

Modification of starch using the HMT method also affects the structure of the starch granules produced. The results of the Scanning electron micrographs (SEM) test from Sun et al. (2014) showed that sorghum starch-modified using HMT had a damaged starch granule shape compared to sorghum starch and unmodified sorghum flour. The surface shape of starch granules in unmodified flour and sorghum starch is smoother and has a more regular shape. Sun et al. (2014) stated that the damage to starch granules could be seen from the formation of holes on the surface of the HMT

sorghum starch samples with moisture 25% and 20%, with the holes in the sorghum starch HMT moisture 25% larger. From these results, we can see that the amount of moisture in starch modification using the HMT method has a role in the shape of the liver granules, where the higher the moisture content, the greater the damage formed. The formation of holes on the surface of the sorghum starch granules as an effect of HMT modification may be due to the re-formation of starch granules and the occurrence of damage to the central tissue. This is also reinforced by Lee et al., (2012), that surface damage of starch granules is caused by partial swelling and damage to starch granules due to excess water molecules. In addition, according to Zhang et al. (2010). Furthermore, HMT can lead to the formation of more compact starch granules. The results of the SEM analysis of sorghum starch with HMT modifications can be seen in Figure 1.

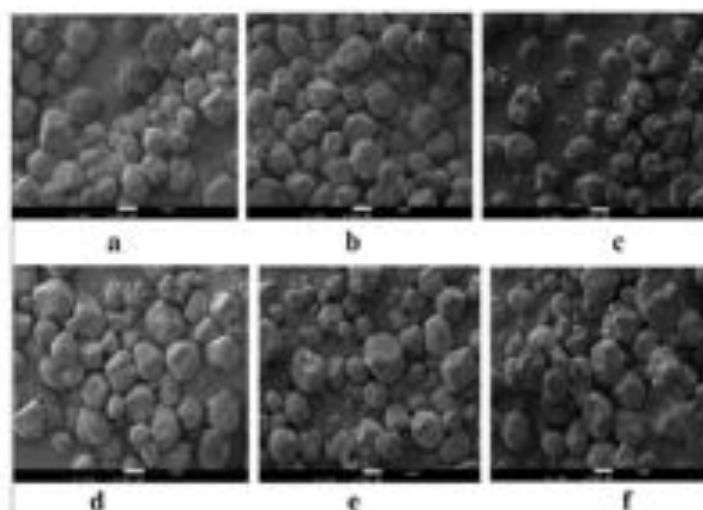


Figure 1. SEM results of HMT modified and unmodified sorghum flour and starch. a) sorghum starch; b) 20% moisture content HMT sorghum starch; c) 25% moisture content HMT sorghum starch; d) sorghum flour; e) 20% content moisture HMT sorghum flour; f) 25% moisture content HMT sorghum flour (Sun et al., 2014)

The results of swelling power and water absorption capacity of red sorghum's HMT modified starch showed that modified red sorghum starch with HMT using temperatures of 30°C, 65°C, and 90°C significantly ( $p < 0.001$ ) rise (Vijayakumar et al., 2013). This increase in water absorption capacity is probably due to the pressure and the high amount of amylose produced by the HMT, thereby improving the hydration and gelatinization ability (Premavally et al., 2005; Vijayakumar et al., 2013).

#### MODIFICATION OF HEATING AND COOLING (AUTOCLAVING COOLING) METHOD

In general, starch that is modified using the retrogradation method can be categorized as type 3 resistant starch. One of the ways to produce retrograded starch is by repeated cooling heating. The results of the research by Shaikh et al., (2020) showed that Johar sorghum starch was given a cooling heating treatment using the extrusion method with a temperature range of 100 °C-125 °C then continued with a storage temperature of 4 °C for 0.7 and 14 days, showed the results. that modification

of starch using this method can change the crystallinity type of starch. XRD (X-ray diffraction) results showed a change in crystallinity type from type A to B starch sorghum after heating and cold storage for 7 and 14 days. These changes are influenced by the length of the amylopectin chain, storage temperature, and moisture content. The results of the percent transmittance showed that the clarity of the sorghum starch paste has decreased along with the length of cold storage, this is due to the increasing re-formation of the amylose chain, which formation will be stronger and increase with the length of cold storage.

Meanwhile, the results of FTIR (analysis Fourier transform infrared and texture showed that the swelling power, solubility, springiness, and gumminess of Johar sorghum starch decreased significantly with the longer storage time using cold temperatures, and these results were inversely proportional to the crystallinity value which significantly increased with increasing cold storage time. The crystallinity results obtained by Shaikh et al. (2020) are linear with retrogradation results, which are indicated by the value of  $\Delta H_{\text{art}}$ /melting enthalpy which increases with the length of cold storage, this is due to the formation of crystalline structures at low temperatures. Mestres et al. (1988) stated, during the heating process by extrusion, the high shear treatment caused the breaking of the amylose and amylopectin bonds, which then when cold storage occurred the formation of a semi-crystalline structure consisting of crystalline amylopectin which binds to amylose. Karim et al. (2020) added that sorghum starch retrogradation is the rearrangement of hydrogen bonds with amylose and amylopectin, which results in a more crystalline structure and has an effect that is difficult to digest by digestive enzymes, and this understanding is also linear with the results of Shaikh et al. (2020), that the starch content of sorghum resistant starch with an autoclaving cooling temperature of 4 °C increases with the length of cold storage.

Setiarto et al. (2018) stated that white sorghum flour of the Numbu variety which was given autoclaving cooling treatment for 3 cycles, significantly ( $p < 0.05$ ) could increase the resistant starch content (18.86 % db) compared to control (4.85 % db), autoclaving cooling treatment 1 cycle (8.91% db) and 2 cycles (11.36 % db). This result is also linear with the value of Rapidly digestible starch which has decreased, from 52.84 % db (control) to 47.52 % db in autoclaving 1 cycle, 42.72% db in autoclaving 2 cycles, and 33.51% db in autoclaving cooling 3 cycles. In this study, 3 cycles of autoclaving cooling also affected the increase in amylose ( $p < 0.05$ ), which was 12.35 % db compared to 10.77% db control, 11.87 % db of autoclaving cooling 1 cycle, and 11.73 % db of 2- cycle autoclaving cooling. An increase in amylose can increase the crystallinity of white sorghum starch of the Numbu variety given autoclaving cooling treatment, this is due to the increase in starch crystallinity. Autoclaving cooling 3 cycles also significantly affected the decrease in digestibility tested in vitro compared to other treatments, namely 26.5% on 3 cycles of autoclaving cooling, 31.88% on 2 cycles of autoclaving cooling, 34.83% on 1 cycle of autoclaving cooling, and 37.78% of control. During the autoclaving cooling process, sorghum starch retrogradation occurs, namely the restructuring of hydrogen bonds with amylose and amylopectin molecules, which then causes the formation of starch structures that are more complex and difficult to digest by digestive enzymes. Shin et al. (2004) added that amylose in general causes more rapid retrogradation of starch than amylopectin.

Resistant starch is a component of starch that passes gastric acid by hydrolysis and cannot be digested by digestive enzymes ( $\alpha$ -amylase), which later ferment in the colon

into **Short Chain Fatty Acids (SCFA)** and produce organic acids (Sagulan et al., 2005; Sajilata et al., 2006; Shaikh et al., 2020). Resistant starch has the same physiological effects as dietary fiber, including the effect of lowering blood glucose, colon health, which can provide a longer effect of fullness, making it suitable for weight control, and colon health. Resistant starch has several health roles, including reducing the risk of colon cancer and diabetes (Shaikh et al., 2020).

In general, resistant starch can be divided into 5 types, namely physically protected starch (type 1), non-gelatinized granules (type 2), retrograded starch (type 3), chemically modified starch (type 4), and amylose complex starch-lipids (type 5) (Birt et al., 2013).

#### ANNEALING METHOD

The starch modification using the annealing method is done by heating the starch with a large quantity of water for a certain time. The water content in the starch suspension is between 40% to more than 60% (w/w) (Ardhiyanti et al., 2017). The heating temperature in this method is the same as the HMT method, which is above the glass transition temperature and below the gelatinization temperature. The results of Ogundiran and Afolabi (2018) showed a significant change in the physical properties of sorghum after annealing. In this study, the sorghum starch suspension was heated at 50°C for 24 hours. Modified starch showed a decrease in solubility and swelling power compared to unmodified starch. These results are linear with the research of Adebowale (2005) about the effect of the annealing method on red sorghum starch modified by heating 50°C for 24 hours. The decrease in solubility and swelling power with starch in the annealing process occurs due to changes in the molecular arrangement of the starch granules. Changes in the amorphous structure of amylose to form a helix cause an increase in amylose chain interactions and changes in the interaction of crystalline structures with the matrix amorphous during the annealing process. High water content in the starch suspension and hot temperatures during the annealing process causes the starch granules to swell but is limited and irreversible. According to Rahayu (2020), the amylose structure is degraded into a shorter polymer during the modification process using the annealing method which causes water to bind more easily, causing more amylose components to be degraded and increasing the solubility of starch. The effect of pH and swelling power in Adebowale (2005) showed that modified starch by annealing method can be applied well to foods with high acidity (pH 2).

The modification by annealing could decrease the peak viscosity in sorghum starch, through viscosity, breakdown viscosity, and final viscosity (Table 1) and was correlated with its swelling power (Singh et al., 2011). The decrease in the peak viscosity was caused by hydrogen bonding in the chain of annealed starch (Ariyantoro et al., 2018). Annealing modified starch has a lower breakdown viscosity than native starch (Singh et al., 2011; Ali and Hasnain, 2016). This is due to a decrease in amylose content and granular swelling (Singh et al., 2011). The annealed starch has lower setback viscosity than native starch due to several factors such as granule size, length of the amylose chain, and amylose leaching (Singh et al., 2011).

The pasting characteristic is shown in Table 2. native sorghum starch and annealing sorghum starch did not have significantly different in terms of pasting characteristics, possibly because the annealing process could not enhance the perfection of sorghum starch crystallites (Singh et al., 2011). A different result from Ali and Hasnain's (2016) study is that high pasting temperature in annealing sorghum

starches indicates improvement in granular stability of white sorghum starch on annealing. The improvement of granular stability results in the greater energy required for the structural disintegration of annealed starch granules, thus increasing the pasting temperature. The increased interaction between amylose-amylose chains and amylose-amylopectin on annealing causes increased resistance to the breakdown of annealing starches granules.

Table 1. Characteristics of sorghum starch modification by annealing method

Parameters	Annealing conditions (Temperature, Heating time, Water:starch ratio)			
	Singh et al. (2011)		Ali & Hasnain (2016)	
	Native	50°C, 24h, 4:1	Native	55°C, 72h, 3:1
Swelling power (g/g)	12.2	8.2	11.8	10.6
Solubility (g/100 g)	ns	ns	1.5	1.4
Pv	3213	2706	2770	2420
Tv	2302	2185	4260	2302
Bv	911	511	935	760
Fv	3390	2929	ns	ns
Sv	1088	744	2895	760
PT	79.3	79.5	73.4	75.4
XRD Pattern type	A type	A type	A type	A type

Native (no modification), ns: data not provided, Pv: Peak viscosity (mPas), Tv: Through viscosity (mPas), Bv: breakdown viscosity (mPas), Fv: final viscosity (mPas), Sv: setback viscosity (mPas), PT: Pasting temperature (°C).

The X-ray diffraction of native sorghum starch showed an "A type" with peaks at  $2\theta = 15.1, 17.2, 18.1, \text{ and } 23.2^\circ$  (Ahmed et al., 2016). Generally, cereal starch has an "A-type" X-ray pattern. Annealing sorghum starch and sorghum native starch did not have significantly different in X-ray patterns. The crystallite orientations of the annealed starch remain unaffected as the XRD pattern remains unchanged (Singh et al., 2011). Wang et al (2014) also reported that native cereal starches and annealed cereal starches have A-type crystallinity. Consistent with the previous studies that there were no changes in the type of crystallinity pattern of annealed corn starch (Ariyantoro et al., 2018), annealed maize starch (Rocha et al., 2012), and annealed wheat starch (Wang et al., 2017).

Annealing increased the enthalpy of gelatinization ( $\Delta H$ ) of sorghum starch due to the double helices interaction of adjacent amylopectin chains in the crystalline region resulting in a stable structure (Singh et al., 2011). According to Ariyantoro et al. (2018), there are increased values of  $T_o$  (onset temperature),  $T_p$  (peak temperature),  $T_c$  (conclusion temperature) in annealed sorghum starch because of the perfection of the pre-existing crystallites. Zavareze et al., (2011) reported that a reduction in swelling power causes an increase in gelatinization temperature provided that some granular structure was maintained. This is reflected in a higher temperature for the onset of swelling and reduced swelling volume.

Adebowale et al., (2005) reported that an increase in  $T_o$ ,  $T_p$ , and  $T_c$  reflects the melting of crystallites that are formed as a result of interactions between amylose-amylose and amylose-amylopectin in the annealed starch chains. These interactions suppress the swelling of the granules leading to higher gelatinization temperature and higher  $T_o$ ,  $T_p$ , and  $T_c$  values. The scanning electron micrographs (SEM) of native

sorghum starch (Figure 2a) and Annealing sorghum starch (Figure 2b) showed a mixture of large (polygonal) and spherical) and small (mostly spherical) starch granules under 1000x magnification. The diameter of native starch granules varied between 11-21  $\mu\text{m}$  for large-sized granules and 5-7  $\mu\text{m}$  for small. Annealing did not significantly change the size and shape of starch granules (Ali and Hasnain, 2016).

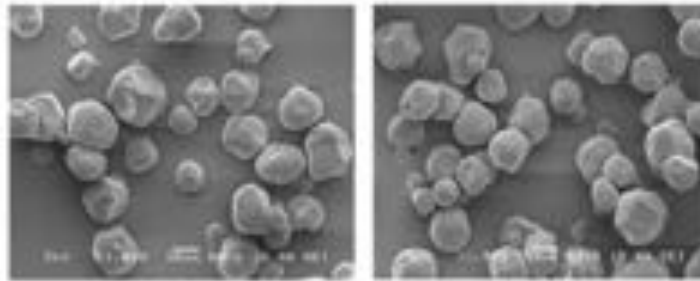


Figure 2: Scanning electron micrographs of native and annealed white sorghum starches. a) native sorghum starch 1000x; b) Annealing sorghum starch 1000x (Ali and Hasnain, 2016)

## CONCLUSION

Physically modified starch using HMT, cooling, and annealing method have affected the functional characteristics of sorghum flour or starch, such as reduced swelling power, solubility, clarity pasta, springiness, and gumminess; the increase in resistant starch, and the crystallinity of the melting enthalpy, so that the choice of physical modification method needs to consider the resulting starch characteristics.

The sorghum starch industry is needs expansion, and modification processes to increase its versatility. Applications of starch modifications (physical or chemical) can increase the use of sorghum starches. It is necessary to select the best modification method for sorghum starch according to the application requirements, market trends, availability, structural characteristics, and cost.

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