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Physicochemical properties of heat-moisture treated, sodium stearate complexed starch: The effect of sodium stearate concentration

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ABSTRACT

Amylose-sodium stearate (SS) complexes (2, 5 and 8%) in heat-moisture treated potato starch (HPS) were evaluated for their physicochemical properties. Based on the DSC thermograms, the amylose - SS complexes were successfully formed with high thermal stability, indicated by a melt temperature (T_{peak}) of ≥ 112 °C for type I and ≥125 °C for type II complexes. Addition of 2% SS resulted in a single endothermal peak of the complexes, while 5 and 8% led to the formation of type I and II complexes with much higher enthalpy (ΔH) values. The XRD curve confirmed that the complexes were successfully formed. The pasting temperature increased from 66 °C for native to 91 °C for HPS145 complexed starch with 5% SS. Furthermore, the swelling power could be largely decreased, and the granular structure preserved. In addition, the inclusion complexation with SS on (HPS) succesfully improved the cook stabiliy.

1. Introduction

Starch is a macromolecule composed of glucose units as monomers, arranged in two polymeric forms, amylopectin and amylose (Jenkins et al., 1993; Tester et al., 2004). Starch is a widely used raw material for many applications, either for food or non-food products. In term of food products, starch satisfies special requirements such as vegan-friendly, halal, non-allergenic, and non-fat (Sweedman et al., 2013). Various types of modification have extensively altered the physicochemical properties of starch. Amylose – inclusion complexes are one of the preferable starch modifications, which can be prepared using diverse types of hydrophobic guest molecules such as iodine (Bluhm & Zugenmaier, 1981), alcohols (Nishiyama et al., 2010), lipids and fatty acids (Ahmadi-Abhari, Woortman, Hamer, et al., 2013; Cao et al., 2015). Fatty acids are commonly used guest molecules to form complexes with amylose in starch, whether or not combined with another starch modification process. Some researchers have investigated the effect of the chain length of fatty acids (Cao et al., 2015; Kawai et al., 2017), the saturation/unsaturation effect (Annor et al., 2015; Karkalas et al., 1995; Seo et al., 2015; Tufvesson et al., 2003), the functional group and the molecular shape (Kong et al., 2019), and the concentration of the fatty acids on the complex formation (Cheng et al., 2019; Tang & Copeland, 2007).

In terms of food-related applications, amylose inclusion complexes have successfully improved the nutritional value of starch and lowered its digestibility to give healthier food products (Putseys et al., 2010). For example, starch-lipid complexes are considered to be responsible for slowly digestible and resistant starch towards enzymatic digestion, resulting in less reducing sugars (Ahmadi-Abhari, Woortman, Oudhuis, et al., 2013). These inclusion complexes inhibited the formation of starch retrogradation and hardening processes for instance in bread (Lee et al., 2020). Retrograded starch has also been considered slower digestible, but the texture and taste are less favored by consumers. These effects are associated with the physicochemical property changes of complexed starch with ligand molecules, involving decreased swelling power, reduced solubility, and a higher gelatinization temperature (Eliasson et al., 1981).

Our previous study demonstrated the complex formation between amylose and stearic acid in initially heat-moisture treated starch (Yassaroh, Woortman, et al., 2021). Heat-moisture treatment prior to stearic acid addition successfully improved the complex formation with linoleic acid and stearic acid (Yassaroh et al., 2019; Yassaroh, Woortman, et al., 2021). However, the complex formation was still limited due to the weak solubility of fatty acids in water. The use of the salt form of fatty

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acids can be a choice to improve the complex formation since it is more water-soluble (Byars, Fanta, Kenar, Felker, 2012b; Fanta et al., 2010; Finkenstadt et al., 2016; Hay et al., 2019). Fanta et al. (2010) and Byars, Fanta, Kenar, Felker (2012b) investigated amylose-sodium palmitate complexes at different pH prepared by steam jet cooking and suggested a practical application of the complexes as a dispersant for lipids in food, water-based lubricant, and cosmetics. Finkenstadt et al. (2016) studied amylose-sodium stearate complexes with and without the addition of poly(vinyl alcohol) for the application of starch-based foamed packaging materials. Besides, Hay et al. (2019) found that the amylose inclusion complexes formed from high amylose corn starch-fatty acid salts were water-soluble and successfully utilized them as an emulsifier with superior surface-active emulsifying ability and a long-term storage stability.

Here we describe the preparation of amylose inclusion complexes with sodium stearate instead of stearic acid in heat-moisture treated starch. The use of sodium stearate allowed us to improve the complex formation since it is water-soluble. The sodium stearate was initially solubilized in water at 72 °C before complexation with starch. Potato starch was first pre-heated at its original moisture content (13.4%) in a pressure vessel (Yassaroh et al., 2019). The complexation with sodium stearate was conducted with heat-moisture treated starch in an excess amount of water. The complex formation was confirmed by thermal analysis using a Differential Scanning Calorimeter (DSC) and crystallinity observation using X-Ray Diffraction (XRD). This study also evaluates the effect of sodium stearate concentrations on the changes in starch physicochemical properties. To investigate this, gelatinization behavior and swelling ability of starch complexes with different concentrations of sodium stearate were analyzed. Different concentrations of sodium stearate resulted in different gelatinization properties, which suggests broad possible end-use applications of the products.

2. Materials and methods

2.1. Materials

Native potato starch (NPS) with 13.4% moisture content, sodium stearate (SS) or stearic acid sodium salt with purity ≥ 99% (GC) and the amount of sodium (Na) is 6.6–7.7%, and calcium chloride dihydrate (A. C. S. reagent ≥ 99%, $CaCl_2.2H_2O$), monosodium phosphate monohydrate (A. C. S. reagent with purity ≥ 98%, NaH_2PO_4 x H_2O), and sodium phosphate dibasic (A. C. S. reagent with purity ≥ 99%, Na_2HPO_4) were all purchased from Sigma-Aldrich Chemical Company. Sodium chloride (A. C. S. reagent ≥ 99%, NaCl) was obtained from Merck Company (Germany). All chemicals were of analytical grade or better.

2.2. Preparation of heat-moisture treated potato starch (HPS)

The preparation procedure of heat-moisture treated potato starch was conducted according to literature. (Yassaroh et al., 2019). Native potato starch was heated till 125 °C and 145 °C in a homemade pressure vessel and then immediately cooled down to room temperature. Afterwards, the samples were stored and labeled HPS125 and HPS145, respectively.

2.3. Thermal analysis

The preparation of potato starch-SS complexes was conducted in a Rapid Visco Analyzer RVA-4 Newport Scientific (NSW, Australia). Initially, SS at various concentrations, 2, 5, and 8% (based on the dm content of 9% starch) was dissolved in simulated tap water of 10°dH (0.2621 g/L $CaCl_2{\cdot}2H_2O$ in distilled water) for 15 min at 72 °C. Starch with a concentration of 9% (w/w) was weighed and added to the SS solution. The complexation was carried out at 72 °C and 160 rpm for 30 min in the RVA. Afterwards, the complexed samples were freeze-dried in a freeze-dryer (CHRIST ALPHA 2–4 LO plus). The freeze-dried starch samples were weighted at a concentration of 20% (w/w based on total weight) and then mixed with water. The samples were equilibrated at room temperature for 1 h before thermal analysis. The thermal properties were analyzed using a Perkin Elmer Pyris 1 Differential Scanning Calorimeter (DSC). An amount of 55 μL from the starch suspensions was pipetted into hermetically sealed stainless-steel pans. A heating scan was performed from 20 °C to 140 °C at 10 °C/min and then cooled from 140 °C to 20 °C at the same rate. All samples were measured at least in duplicate. The thermal properties were analyzed using DSC Pyris series, Perkin Elmer Version 8 software.

2.4. Crystallinity of starch

The crystallinity of the native and modified potato starches was determined in an x-ray diffractometer (XRD) (D8 Advance, Bruker, Germany) with a wavelength of 1.5418 Å. The scanning of all samples was performed using a 40 kV voltage and 40 mA current from the radiation of Cu-Kα with time intervals of 0.02° per 1 s. The freeze-dried starch samples were compactly packed in a sample holder. The XRD measurements were performed from 2θ of 5–50° with an interval of 0.02° at 1 s per step.

2.5. Pasting temperature and gelatinization behavior

The viscosity behavior was monitored using an RVA. The viscosity measurement of the potato starch - SS complexes was prepared by mixing 9% (w/w in total weight 28 g) of starch with various SS concentrations (2, 5, 8% w/w based on the weight of starch) in water. The mixtures were equilibrated at room temperature for 15 min. The RVA measurement was started at 50 °C for 1 min, afterwards, heated to 95 °C at 6 °C/min and held at 95 °C for 5 min. Next, the samples were cooled to 50 °C at the same rate and held at 50 °C for 2 min. The speed of the rotation was 960 rpm for the first 10 s and 160 rpm for the rest of the experiment.

2.6. Swelling power

The swelling power measurement was conducted using a method explained in a previous study (Ahmadi-Abhari, Woortman, Hamer, et al., 2013; Yassaroh et al., 2019). Initially, 2, 5, and 8% (based on the dry matter of starch) of SS was dissolved in phosphate buffer (17 g, 0.0025M, containing 0.0075 M sodium chloride, pH 6.9). After that, a certain weight of starch was added to the screw cap pyrex tubes and heated at various temperatures 72 °C, 80 °C and 90 °C for 45 min while rotating in a ventilation oven. After cooling to room temperature, the tubes were centrifuged at 1000 rpm for 15 min in a Labofuge 400R. The height of the supernatant was measured and the swelling power was calculated. All samples were measured in duplicate.

2.7. Starch granular structure

The gelatinized starch granule structures were observed using a Nikon light microscope (Nikon, Eclipse 600, Japan). The freeze-dried starch samples, which were previously heated in the RVA at 72 °C and 95 °C at the same shear speed, were diluted in 10°dH to obtain a 1% suspension. The starch suspensions were observed under a light microscope with a 10× resolution objective lens. The images were captured using a Nikon camera (Nikon, COOLPIX 4500, MDC Lens, Japan).

2.8. Statistical analysis

The samples were analyzed in duplicate. SPSS®statistics program ver. 26 (IBM, New York, NY, USA) was used to perform statistical analysis, including the means, deviation standard and significant difference. Bonferroni's multiple-range test in one-way analysis of variance (ANOVA) was conducted to identify significant differences ($p < 0.05$).

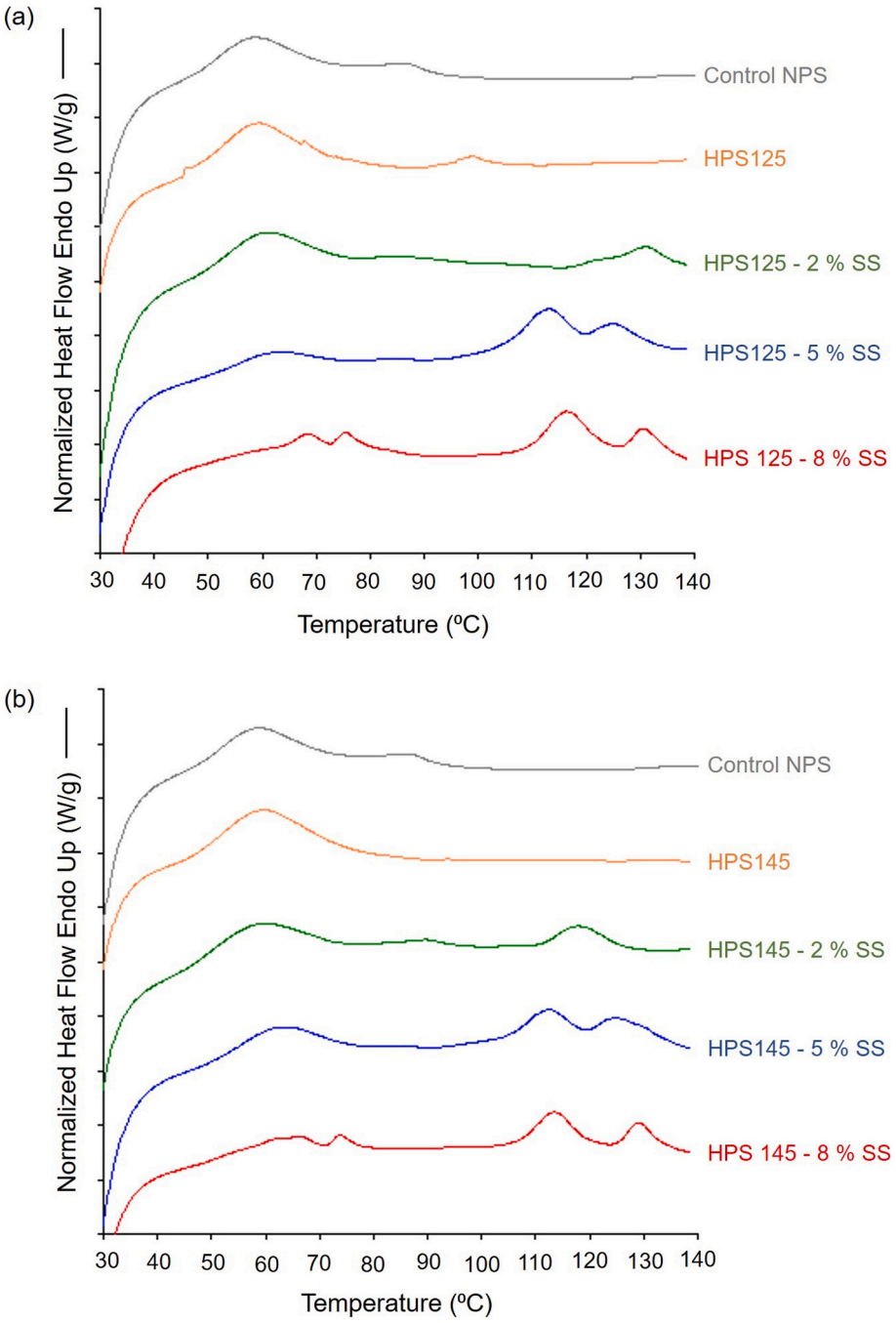

Fig. 1. DSC heating scan of 20% (a) HPS125 - SS and (b) HPS145 - SS after complexation at 72 °C for 30 min in 10°dH.

Graphing was dealt with OriginPro 9.0 (OriginLab Co., Northamptaon, MA, USA).

3. Results and discussion

Amylose inclusion complexes were prepared with sodium stearate as guest molecule. Sodium stearate was first solubilized in water at 72 °C before complexation and potato starch was pre-heated to 125 and 145 °C, respectively, at low moisture (13.4% moisture content) in a pressure vessel (Yassaroh et al., 2019). After that, the sodium stearate was mixed with heat-moisture treated starch in an excess amount of water to allow complexation. Different concentrations of sodium stearate were applied to study the complex formation and the effect on the physicochemical properties of starch. The complex formation and the changes on physicochemical properties are described below.

3.1. Thermal properties and complex formation

In this study, the thermal stability of amylose - SS complexes in heat-moisture treated starch was analyzed by DSC. The thermograms are presented in Fig. 1 and the values are shown in Table 1. The DSC thermograms of the starch samples showed a first endothermal peak between 45 and 70 °C, which is referred to the retrogradation of starch. The addition of SS reduced the starch retrogradation and resulted in a second and a third endothermal peak, that are referred to the amylose - SS complexes (Fig. 1 and Table 1). When 8% SS is added, the peaks between 65 and 80 °C correspond to free SS which is present in excess. This result is in agreement with a previous study (Ahmadi-Abhari,

Table 1
Thermal analysis data (heating scan) of 20% potato starch suspensions in 10°dH with various concentrations SS.

Sample	Sodium stearate (%)	Starch (1st heating)			Amylose – SS complexes (1st heating)					
					Type I			Type II		
		Onset (°C)	Peak (°C)	ΔH (J/g)	Onset (°C)	Peak (°C)	ΔH (J/g)	Onset (°C)	Peak (°C)	ΔH (J/g)
NPS	0	45.4	57.5	10.7 (0.14)						
HPS125	0	45.8	59.2	10.4 (0.14)						
HPS125 - SS	2	45.7	60.1	8.1 (1.06)	121.9	130.7	2.2[a] (0.14)			
	5	45.3	59.2	4.0 (0.42)	104.0	113.6	5.4[b] (0.14)	120.7	125.0	2.3[a] (0.14)
	8	*	*	*	108.9	116.2	5.5[b] (0.07)	127.0	130.5	2.3[a] (0.00)
HPS145	0	45.5	59.5	10.4 (0.21)						
HPS145 - SS	2	45.6	60.2	7.8 (0.85)	110.5	117.8	2.4[a] (0.28)			
	5	45.9	61.9	4.2 (0.14)	103.5	112.3	5.5[b] (0.28)	120.2	125.0	2.6[a] (0.07)
	8	*	*	*	106.0	113.5	6.0[b] (0.14)	125.3	129.2	2.5[a] (0.07)

The values in the parentheses represent deviation standards (n = 2).
*Not determined.
Means with different superscripts in the same column were significantly different ($p < 0.05$).

Table 2
Thermal analysis data (cooling scan) of 20% potato starch suspensions in 10°dH with various concentrations SS.

Sample	Sodium stearate (%)	Amylose – SA complexes (1st cooling)		
		Onset (°C)	Peak (°C)	ΔH (J/g)
HPS125 - SS	2	80.5	74.9	−0.7[a] (0.28)
	5	100.0	96.6	−7.6[b] (0.21)
	8	102.6	100.6	−8.2[b] (0.21)
HPS145 - SS	2	80.6	75.2	−1.5[a] (0.07)
	5	100.4	97.3	−7.5[b] (0.14)
	8	102.4	100.3	−8.2[b] (0.14)

The values in the parentheses represent deviation standards (n = 2).
Means with different superscripts in the same column were significantly different ($p < 0.05$).

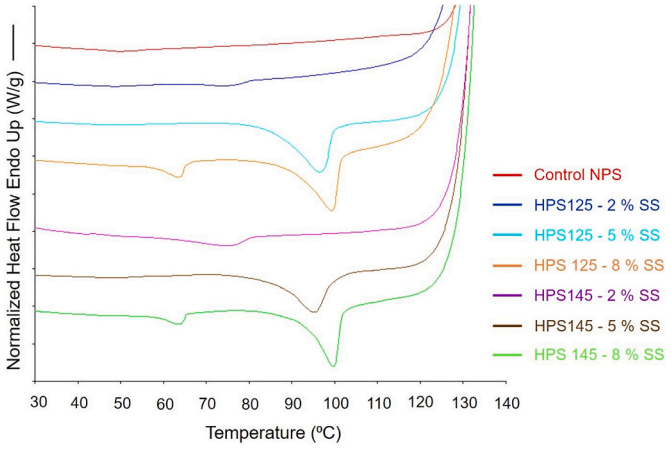

Fig. 2. DSC cooling scan of 20% HPS125 - SS and HPS145 - SS after complexation at 72 °C for 30 min in 10°dH.

Woortman, Hamer, et al., 2013). The presence of the second and third transition endothermal peaks confirmed the existence of amylose - SS complexes in the samples. All complexes dissociated (T_{onset}) at temperatures > 103 °C. This can be an advantage for cooking-related applications in a water-based system which proved that the complexes remained largely stable even till heating to the boiling temperature of water. The use of a charged fatty acid salt resulted in non-retrograding amylose complexes (Byars, Fanta, Kenar, Felker, 2012a; Fanta et al., 2010; Hay et al., 2019). Based on the nutritional point of view, the formation of these V-type amylose complexes made the starch slower digestible and the amylose-complexes largely resistant towards enzymatic digestion in the human intestine (Ahmadi-Abhari, Woortman, Oudhuis, et al., 2013; Yassaroh, Nurhaini, et al., 2021). In the bakery point of view, the V-amylose complexes could hinder the hardening of bread and make the texture more favorable compared to retrograded starch (Lee et al., 2020).

The thermal properties of amylose - SS complexes are dependent on the SS concentration. Remarkably, in HPS125 with addition of 2% SS, the complexes melted at a higher temperature (T_{peak} = 130.7 °C) than in HPS145 (T_{peak} = 117.8 °C), while only a single endothermal peak of the complexes was formed in both samples. This indicated different polymorphic forms of the V-type amylose complexes. At concentrations of 5 and 8% SS, there was a mixture of two endothermal peaks of the V-type amylose complexes formed for both HPS125 and HPS145 starches (Fig. 1a and b). At a concentration of 5% SS, the type I complexes melted at around T_{peak} = 113 °C and the type II complexes melted at around T_{peak} = 125 °C. At addition of 8% SS, the type II complexes even melted at a higher temperature (T_{peak} = 130 °C). These results implied that the amylose - SS complexes were associated in a more ordered crystalline structure when the SS concentration increased. Amylose - guest complexes often have varying degrees of organization and order, performing different endothermal peaks, melting temperatures, and enthalpy values on the DSC thermogram (Karkalas et al., 1995). Type I complexes are formed due to rapid nucleation and are randomly distributed in the starch granules, while the type II complexes are formed due to slow

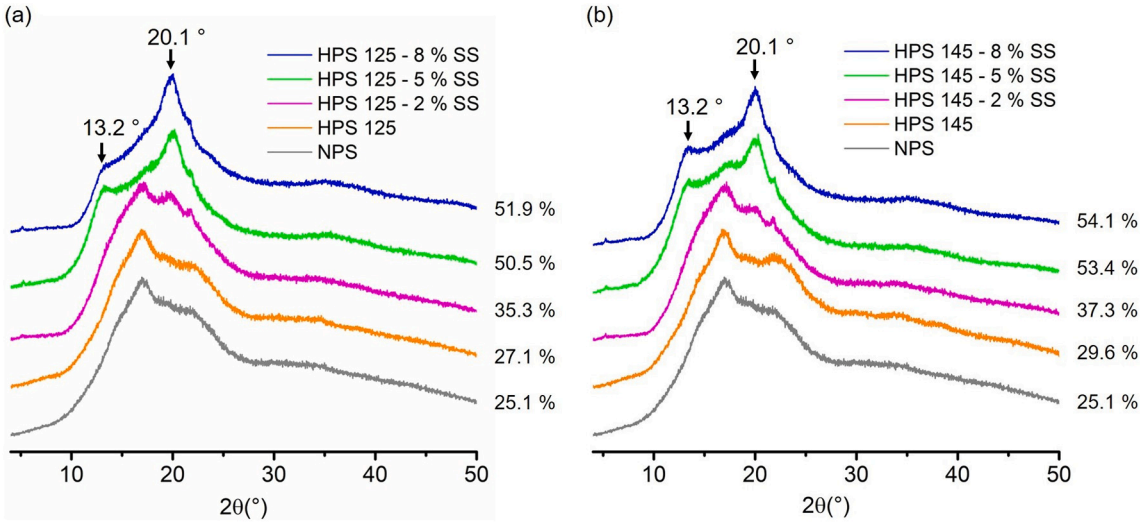

Fig. 3. Crystal pattern of freeze-dried HPS125 and HPS145 after complexation with SS at various concentrations for 30 min at 72 °C.

Table 3
Pasting temperature of 9% NPS, HPS125, and HPS145 without and with addition of SS in 10°dH.

Sample	Pasting temperature (°C)	Peak		Breakdown (cP)	Final viscosity (cP)
		Viscosity (cP)	Time (s)		
NPS	66.0	6989	344	4456	3374
HPS 125	66.8	2983	548	549	3761
HPS 125–2% SS	66.0	4976	652	518	8848
HPS 125–5% SS	66.4	5218	656	724	6542
HPS 125–8% SS	67.2	6909	540	233	8248
HPS 145	72.8	*	*	*	2857
HPS 145–2% SS	86.3	*	*	*	1853
HPS 145–5% SS	91.0	1632	888	*	400
HPS 145–8% SS	90.5	2436	912	*	480

*Not determined.

nucleation and organized in a well-defined structure (Karkalas et al., 1995).

The enthalpy of the complexes describes the quantity of the crystalline complexes that are formed. Based on Table 1 and Fig. 1, increase of the SS concentration from 2% to 8% increased the melting enthalpy of the complexes. At a concentration of 2% SS, the amylose was not completely complexed due to the limited numbers of SS, resulting in a significant lower enthalpy of the complexes compared to 5% SS. The increased SS concentration to 8% gave only a slight increase on the enthalpy of the complexes. Thus, it is suggested that 5% was close to the maximum SS complex formation concentration. This result is in agreement with (Lee et al., 2020) who utilized stearic acid as ligand molecules at different concentrations and found that 5% of stearic acid resulted in the highest enthalpy value due to the saturating starch-stearic acid concentration ratio. Compared to stearic acid complexation prepared in our previous study (Yassaroh, Woortman, et al., 2021), the amylose – sodium stearate complexes are thermally more stable. This can be explained due to the fact that the onset of the melting endotherm (T_{onset}) of amylose – 5% sodium stearate complexes was 103 °C, which is higher than the amylose – 5% stearic acid complexes which melted at 90 °C. Furthermore, the amylose – sodium stearate complexes formed type I and type II complexes after complexation at 72 °C, while the amylose – stearic acid complexes formed only type I complexes after complexation at that temperature and required complexation at 90 °C to form type I and type II complexes. This is explained by better solubilization of sodium stearate in water, which leads to better complexation compared to stearic acid. During cooling, the melted amylose-sodium stearate complexes will recrystallize. This recrystallization also confirms the existence of the complexes. As shown in Table 2, starches containing 2% sodium stearate start to recrystallize at 80 °C, while starches containing 5 and 8% of sodium stearate recrystallized at 100 and 102 °C. At 8% sodium stearate, a peak appeared at 65 °C which is referred to the recrystallization of uncomplexed free sodium stearate (Fig. 2).

3.2. Crystallinity of starch

The crystallinity of the starches was determined with XRD. NPS at room temperature exhibited a reflection peak at 5.5°, 15°, 17.1°, and 22–24° 2θ (Yassaroh et al., 2019). When the native starch was heated at 72 °C, only a sharp peak at 17.1° and a broad peak at 22° remained, while other peaks disappeared. This suggested the rupture of the crystalline region in NPS after heating to 72 °C due to the gelatinization process. However, the intensity peaks at 17.1° and 22° were higher and more visible for the HMT starches, particularly for HPS145. This confirmed that HMT improved the thermal stability of the starch, hence the gelatinization process could be partly hampered. The XRD analysis also confirmed that the amylose - SS complexes were successfully formed. The X-ray scattering patterns show reflection peaks at around 13.2° and 20.1° 2θ (Fig. 3), indicating the formation of amylose inclusion complexes containing six glucose units per helix turn, known as V_6-type amylose crystallite (Finkenstadt et al., 2016; Hay et al., 2019; Yassaroh et al., 2019). The V_6-type is an extremely tightly packed crystalline unit cell (Da Róz et al., 2012). For both HPS125 and HPS145 - SS complexes, the % crystallinity increased with increase of the SS concentration, confirming a more ordered crystalline area formed due to amylose - SS complex formation. These results are in agreement with the DSC results above. At a concentration of 2% SS, the reflection peak at 2θ 13.2° was not clearly observed and only a small peak appeared at 20.1° as compared to reflection peaks displayed in 5 and 8% of SS complexation. This implied that 2% SS was too low and only a few complexes were formed. A broad peak at 2θ 13.2° in case of addition of 5 and 8% SS

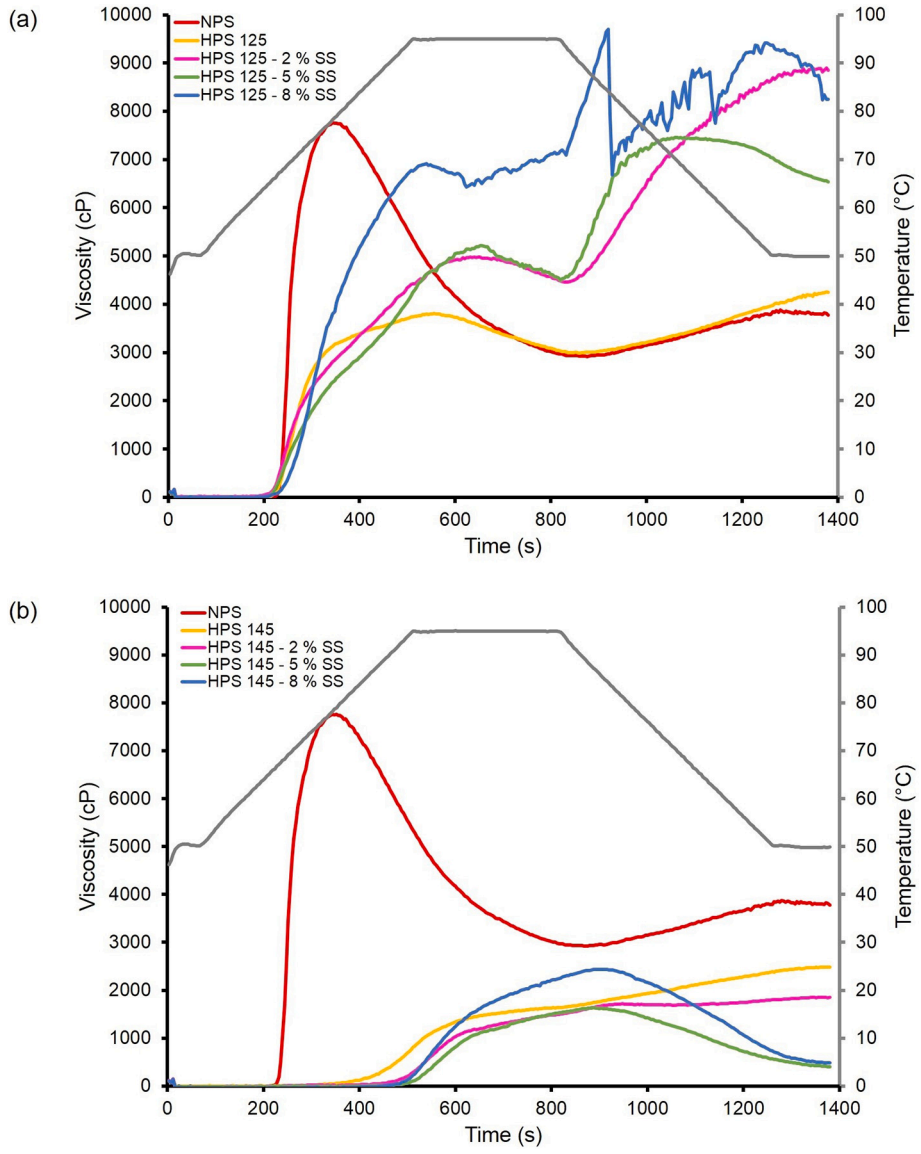

Fig. 4. RVA viscosity profiles of 9% (a) HPS125 - SS and (b) HPS145 - SS after complexation in 10°dH at 72 °C for 30 min.

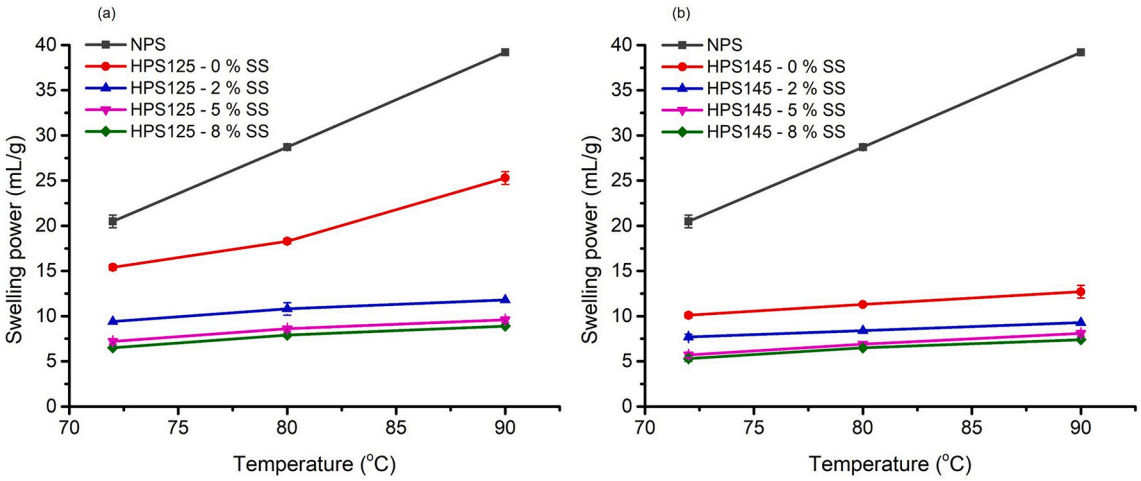

Fig. 5. Swelling power of (a) HPS125 - SS and (b) HPS145 - SS at various concentration of SS in phosphate buffer.

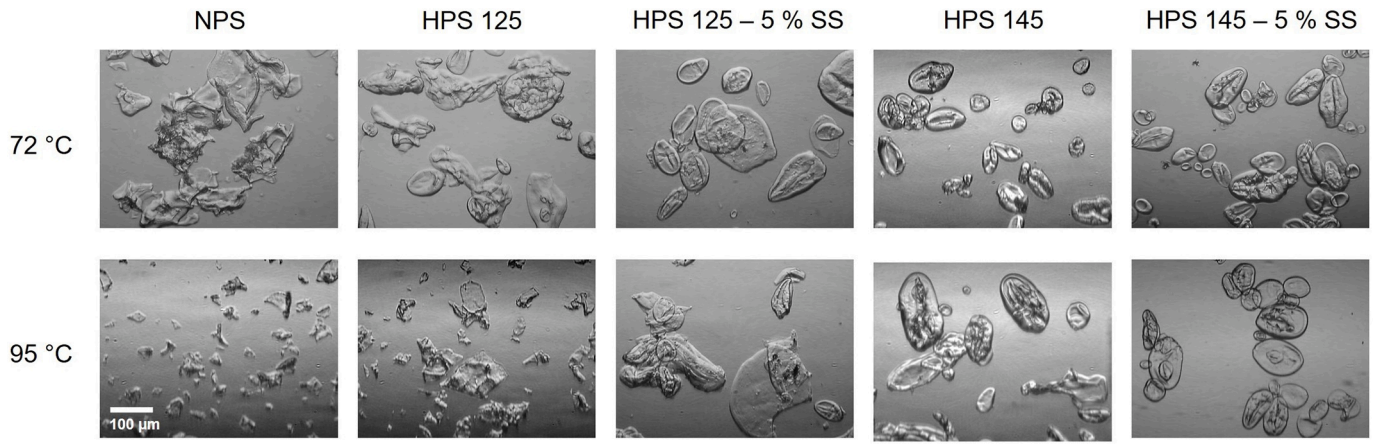

Fig. 6. Light microscopy images of NPS, HPS 125, and HPS 145 with and without SS in 10°dH after heating till 72 and 95 °C.

implied the formation of smaller amylose-SS complex crystallites, while a sharp peak at 20.1° indicated larger crystallites (Finkenstadt et al., 2016).

3.3. Pasting temperature and gelatinization behavior

The complexation and gelatinization measurements were prepared in 10°dH instead of distilled water to mimic the real application in daily cooking processes either at home or in the industry. Furthermore, the presence of ions in 10°dH has a positive effect on suppressing the viscosity increase of potato starch (Nutting, 1951). Table 3 shows that the pasting temperature of NPS and HPS125 (without or with the addition of SS) had more or less a similar pasting temperature of around 66 °C. There was only a slight increase in pasting temperature on HPS125 with an addition of 8% of SS (Fig. 4a and Table 3). The pasting temperature increased expressively after a heat-moisture pretreatment at 145 °C, and further increased with the addition of SS to form complexes with starch (Table 3 and Fig. 4b). The highest pasting temperature (91 °C) was obtained in HPS145 with the addition of 5% SS. The increase in pasting temperature is attributed to the formation of physical crosslinking among the starch chain during the HMT. Furthermore, the formation of amylose - SS complexes suppressed the leaching of amylose from the starch granules and then hampered the water absorption, hence the pasting temperature was shifted to a higher temperature (Ahmadi-Abhari, Woortman, Hamer, et al., 2013; Varatharajan et al., 2010; Yassaroh et al., 2019).

The peak viscosities of all modified starch samples were lower than the native starch. The heat-moisture treatment prior to complexation successfully depressed the peak viscosity of the starch due to the formation of physical cross-linking among the starch molecules. The addition of 2, 5, and 8% SS in HPS125 increased the final viscosity of the starch (Fig. 4a) which is probably attributed to the formation of complexes between leached amylose and SS in the solution (Tang & Copeland, 2007; Wang et al., 2016; Yassaroh, Woortman, et al., 2021). On the contrary, the final viscosity was reduced with the addition of SS in HPS145 (Fig. 4b). This implied that a higher heat-moisture treatment temperature (145 °C) increased the complex formation with SS inside the starch granules, hence the leaching of amylose could be more hindered. This led to a lower final viscosity in the RVA measurement for HPS145 - SS complexes. Based on the RVA measurement results, the lowest viscosity increase was obtained in at 145 °C heat-moisture treated potato starch with the addition of 5% SS.

3.4. Swelling power

Swelling is a part of the gelatinization process, whereby starch granules can swell up too many times of the original size upon heating in an excess amount of water. The heat-moisture treatment clearly reduced the swelling ability of the starch granules compared to native starch. The swelling was further diminished by the addition of SS compared to native starch (Fig. 5a and b). The higher the concentration of SS, the lower the swelling ability of the starch granules. The reduced swelling power of starch in the presence of SS can be attributed to the formation of amylose - SS complexes which prevented the leaching of amylose and reduced the water uptake. The lower swelling power of HPS145 - SS compared to HPS125 - SS could be attributed to the formation of more stable complexes between amylose and SS since HPS145 is more reactive towards complexation (Yassaroh et al., 2019; Yassaroh, Woortman, et al., 2021). Furthermore, the physical crosslinking formed in the heat-moisture treated starch at higher temperature treatment also strengthened the granular structure towards swelling and rupture upon heating in an excess amount of water in the RVA (Yassaroh et al., 2019). Moreover, a higher temperature during the heat-moisture treatment possibly reduced the water-holding capacity of starch granules more, hence less water could be associated with the hydroxyl groups in the starch molecules.

3.5. Granular structure

The granular appearance of the starch granules after heating to 72 and 95 °C was observed under a light microscope. It is observed that NPS granules were largely gelatinized at 72 °C and ruptured at 95 °C (Fig. 6). This appearance is more or less similar to HPS125. For HPS145, the starch granules remained largely intact even after heating to 95 °C (Fig. 6). This is attributed to the formation of physical crosslinking among starch molecules on the HPS, and this effect is more pronounced at higher HPS temperature (Yassaroh et al., 2019). The presence of SS to form amylose - SS complexes hindered the leaching of amylose and inhibited starch swelling, thus improved the starch granules stability. Furthermore, 72 and 95 °C are below the melting temperature of the complexes as shown in the DSC thermogram, hence, the starch granules were less swollen. Furthermore, the presence of hydrophobic ligand molecules might partly have covered the surface of the starch granules, limiting water absorption, hence hinder the starch granules from swelling (Eliasson et al., 1981).

4. Conclusions

Potato starch was modified via a processing method using low-cost food grade ingredients by first performing a heat moisture treatment, followed by amylose-inclusion complexation with sodium stearate (SS). This resulted in food-grade cook resistant products, due to a melt temperature (T_{onset}) of the complexes at $\geq$ 103 °C. Complexes containing 5% of SS are close to the maximum concentration for the complex

formation. Tuning the heat moisture temperature and the concentration of SS, the system can provide a wide range of possible applications, for example as a filler, an emulsifier, or as thermally stable thickener. For example, $\geq$ 5% of SS resulted in a largely decreased swelling power, less retrogradation and a mostly remained shape of the starch granules, while the use of 2% SS in HPS125 showed a very high RVA end-viscosity compared to native starch. The cook resistant heat-moisture treated SS complexed starches seem promising candidates for slow and resistant starch-based food products and can also be used as a replacement of chemically cross-linked starch, being safer and more favorable for food application products.

CRediT authorship contribution statement

Yassaroh Yassaroh: Conceptualization, Methodology, Formal analysis, Investigation, Funding acquisition, Writing – original draft. **Feni F. Nurhaini:** Formal analysis, Investigation, Writing - review & editing. **Albert J.J. Woortman:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – review & editing. **Katja Loos:** Conceptualization, Supervision, Resources, Funding acquisition, Writing – review & editing.

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