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Physicochemical properties of heat-moisture treated, stearic acid complexed starch: The effect of complexation time and temperature

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ABSTRACT

Starch modification has been extensively studied to alter its physicochemical properties based on human needs. Lowering the digestion rate of starch is one of the interests in food science research, since when it is nutritionally improved, it can reduce the risk of human chronic diseases. In this study, heat-moisture treatment (HMT) followed by inclusion complexation with stearic acid at various temperatures and times was applied to improve the functional properties of starch. Thermal analysis suggested the formation of type I and type II complexes after complexation at 90 °C, indicated by a endothermal peak at 107 and 122 °C, respectively, while native starch after complexation only resulted in type I complexes. The formation of crystalline complexes was also confirmed by XRD showing peaks at $2\theta = 13.1°$ and 20.1°. Furthermore, the modified starch displayed a higher pasting temperature, considerably less swelling and significantly lower viscosity behavior. This implied that the starch granules were thermally and mechanically more stable. The granular appearance of the modified starch was confirmed with light microscopy that presented more intact granules and less ruptured granules, even after heating to 90 °C. This study offers a way to upgrade the nutritional properties of starch.

1. Introduction

Starch has a broad function, not only as a food ingredient but also as a raw material for many non-food products. Modifying starch, leads to different physicochemical properties and therefore also influences the nutritional value. Starch can also be tailor-made to investigate the relation among starch molecules and study its properties [1–3]. One of the focuses on starch modification is slowly digestible and resistant starch instead of rapidly digestible starch. Enzymatic [4], chemical [5] and physical modifications [6] could be performed to alter the properties of starch. Physical modification is relatively cheap, easy and an environmentally friendly way to transform the structural and functional properties of starch. One of the physical modifications commonly used is a HMT. During HMT, the starch granules are heated at high temperature (above the glass transition temperature but below the gelatinization temperature) and at a low moisture content (<35% of water, *w*/w) [6–8]. HMT successfully altered the physicochemical properties of starch without destroying the whole granular structure of the starch and the HMT modified starch displayed an improved resistance toward enzymatic degradation compared to native starch [9–12]. HMT also increased the relative reactivity of amylose in starch [13].

Amylose is the second largest constituent in starch. It is a long linear glycopolymer composed of glucose monomers linked together *via* α[1→4]-glycosidic bonds [14]. The molecular weight range of amylose is approximately 1×10^5–1×10^6 and the degree of polymerization (DP) is around 1000–10,000 glucose units [14–16]. When starch is heated at gelatinization temperature in an excess amount of water, the crystalline regions of starch melts and the amylose leaches out from the granules [17]. In a hydrodynamic process, the amylose can form an extended shape, however, in the presence of small ligand molecules, amylose tends to wind up to form a left-handed single helix structure with intramolecular hydrogen bonding mostly between O_2—O_3 and O_2/O_3—O_3 in the outer part of the helix and the hydrophobic cavity in the inner part of the helix [18]. In the presence of small hydrophobic ligand molecules such as lipids and fatty acids, inclusion complexes will be formed between the hydrophobic ligand molecules which are included into the hydrophobic cavity of the amylose, the so-called V-type helical structure [19]. The long-chain hydrophobic molecule is located inside the amylose helix while the hydrophilic functional group of the ligand is located outside the helix [20–22]. The hydrophobic interaction is the main force of the inclusion complex formation. Amylose is not only able to include small hydrophobic molecules but also supramolecules, such as polymers [23–28]. Amylose-polymer inclusion complexes have been successfully prepared either by direct mixing or by "vine-twinning polymerization" [29–32]. The V-helical complexes may consist of 6, 7 and 8 glucose units per helix

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turn, and are the so-called V_6, V_7, and V_8-type amylose complexes, respectively. Formation of the V-type complexes depends on the physicochemical properties of the ligand structure, such as the bulkier the ligand structure, the more glucose units are required in a one turn helix [30,33].

In native potato starch, the gelatinization starts at 66 °C, and further heating causes the melting of the crystalline amylopectin part and leaching of the amylose, hence some starch fragments can be observed [9,34]. Putseys et al. reported that lipids coated the surface of the granules to slow down water ingression and repressed the amylose leaching [35]. Another paper investigated the physicochemical properties of maize starch-galactomannan (several species including guar, tara and locus) complexes with HMT and reported similar phenomena for HMT starch-guar and HMT starch-locus complexes at different galactomannan concentrations, while HMT starch-tara showed the increase of the swelling power with the increase of the galactomannan concentration [7]. The V-type amylose inclusion complexes are less easy to be degraded by enzymes (slowly digestible) and some parts were not digested but fermented in the large intestine (resistant starch) [33,36,37].

There are some factors affecting the formation of amylose-guest complexes, including the effect of the amylose chain length [22,38], enzymatic pre-modification, such as debranching of starch [39], the ligand structure [17,40,41], the temperature, time and pH [42–45]. Very often the value of enthalpy change (ΔH) on the melting of amylose-guest complexes during a DSC measurement is used to estimate the relative amount of complexed crystallites formed [46]. The ΔH is described as the energy required to disaggregate and dissociate the helical complexes for the type I polymorph, and to melt the semi-crystalline type II complexes [44]. Type I polymorph formed due to rapid nucleation of the complexes, while type II polymorph is caused by slow nucleation at high reaction temperature [38,44]. The amylose inclusion complexes are supposed to be formed around the temperature of the gelatinization of starch [34,43]. However, this might be different in the case of heat-moisture treated starch.

Starch modification to improve its physicochemical properties and resistance against enzymatic digestion has been widely investigated for inclusion complexes with fatty acids. However, these complex formations can be enhanced by other pre-treatments prior to complexation, such as heat-moisture treatment [47,48]. We found that the onset of the melting temperature (T_{onset}) of amylose-linoleic acid complexes was around 80 °C and the peak temperature (T_{peak}) was 100 °C [9]. This means that, if the application temperature of heating is at around the boiling temperature of water-based food products, the amylose-linoleic acid complexes have been mostly melted. Hence, in this study, we used stearic acid as ligand molecules which is saturated and has a higher melting point in order to enhance the complex formation. The melting temperature of the formed complexes increased and therefore also the stability of the complexes. The effects of temperature and time on the complex formation were investigated.

In this study, the starch-stearic acid complexation was also prepared in phosphate buffer, instead of simulated tap water. Phosphates are essential nutrients, which are naturally available in raw food materials, such as in potato starch, in the human body, and can also be added as food additives for human diet. Food-grade phosphates additives function as buffers, dispersants, nutrients, flavors, acidulants, bases, sequestrants, precipitants, cryoprotectants, free-flow (anticaking) and ion-exchange agents [49,50]. In cereal and grain food products, food-grade phosphates are used to chemically leaven battered and breaded foods, cakes, doughnuts, muffins, pancakes, biscuits, crackers, waffles, and cookies. Dietary intake of phosphate is required for human health, not only to give functional properties in those food products; there is an Acceptable Daily Intake (ADI) required and recommended for the consumption [51,52]. Since stearic acid has a low solubility at low pH, the stearic acid dissolution and complexation with starch was also performed in phosphate buffer to maintain neutral pH.

Combining HMT and complexation is a promising way to modify both amylopectin and amylose [53]. There were some studies about the dual effect of HMT and complex formation with lipid or protein on the physicochemical properties of starch [47,48,54]. There were only a few studies combining HMT and inclusion complexes with stearic acid [53,55]. Mapengo et al. [53] and Mapengo and Emmambux [55] used maize meal to be modified in their project. In our project, potato starch was employed since it is a clean starch, contains a low amount of damaged starch and it does not contain natural lipid [56]. However, the application of native potato starch is limited for particular applications either in food or non-food products due to non-optimal condition and it requires some modifications to obtain desired properties for specific purposes. HMT followed by stearic acid complexation has a potential effect to substitute chemically modified starches and being more favorable for food application.

2. Materials and methods

2.1. Materials

Native potato starch (NPS) with 13.4% moisture content, stearic acid (SA) with reagent grade 95% (melting point 67–72 °C), casein sodium salt (CSS) from bovine milk with sodium content ≤3%, Lugol (iodine/potassium iodide solution for microscopy), 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 heat-moisture treated starch was prepared according to the previously reported procedure [9] by heating the NPS (13.4% moisture) till 125 °C and 145 °C in a pressure vessel, which afterwards was cooled down to room temperature. The products were stored in a closed vessel and named HPS125 and HPS145, respectively.

2.3. Thermal properties and complex formation

Thermal analysis on the samples was conducted using a Perkin Elmer Pyris 1 DSC (Differential Scanning Calorimetry) to study the complex formation of starch. Initially, an oil in water (o/w) emulsion was prepared by mixing 10% (w/w based on dry matter of starch) casein sodium salt and 5% (w/w based on dry matter of starch) stearic acid in simulated tap water (10°dH) (by dissolving 0.2621 g/L $CaCl_2 \cdot 2H_2O$ in distilled water) and heated at 80 °C while stirring to obtain a nicely dispersed emulsion. The emulsion was, while continuous stirring, cooled to room temperature, where after 20% of starch (against total weight) was added. The starch suspension was rotated at 50 rpm in a sealed bottle at room temperature for 1 h. For the DSC measurements 50 μL of the starch suspensions were pipetted into stainless steel DSC pans. The DSC pans were initially held at 72, 80 and 90 °C for 5, 30 and 120 min in the DSC to allow complexation, and then cooled down to 20 °C. 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 in duplicate. The thermal properties were analyzed using DSC software (Pyris series, Perkin Elmer Version 8).

To improve the solubility of stearic acid and its complex formation with starch, phosphate buffer (17 g, 0.0025 M, containing 0.0075 M sodium chloride, pH 6.9) was employed. The samples were prepared in sealed bottles and rotated for 120 min at different temperatures (72, 80, and 90 °C) in a ventilation oven to allow complexation in phosphate buffer. Afterwards, the samples were washed with pre-warmed phosphate buffer at 80 °C to remove free stearic acid and then centrifuged

at 2000 rpm for 15 min at 25 °C in a Labofuge 400R. The washing process was performed three times. The thermal properties of the samples were analyzed by DSC using the same heating-cooling scan profile.

2.4. Crystallinity of starch

The crystallinity of starch was observed in an X-ray diffractometer (XRD) (D8 Advance, Bruker, Germany) using CuKα radiation with a voltage of 40 kV and the current of 40 mA at a wavelength of 1.5418 Å. The complexation of 9% (w/w against total weight) starch in 5% stearic acid (w/w based on dry matter of starch) and 10% CSS (w/w based on dry matter of starch) was initially prepared in a ventilation oven at 72, 80 and 90 °C while rotating for 30 min. The samples were then freeze-dried in a freeze-dryer (CHRIST ALPHA 2–4 LO plus) for XRD measurements. The freeze-dried starch samples were compactly packed in a sample holder. The x-ray 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

A Rapid Visco Analyzer RVA-4 Newport Scientific (NSW, Australia) was employed to analyze the viscosity behavior of the starch suspensions. Stearic acid and CSS with 5% and 10% concentrations respectively (w/w based on dry matter of starch) were dispersed in simulated tap water at 80 °C until well-dispersed stearic acid was obtained and then cooled to ambient temperature. Starch with 9% concentration (w/w based on the total weight 28 g) was added to the solution in the RVA cup and let it equilibrate for 15 min. The RVA measurement was started by equilibration 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 sample was 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. The viscosity measurement was also prepared in phosphate buffer. In this case the stearic acid and CSS were solubilized in phosphate buffer instead of simulated tap water. Starch with 9% concentration (w/w based on the total weight 28 g) was added to the solution in the RVA cup and equilibrated for 15 min. The RVA measurement was performed using the same profile as mentioned before.

2.6. Swelling power

The swelling power measurement was conducted using the previously reported method with some modifications [9,34]. A previously determined amount of starch, 5% of stearic acid and 10% of CSS based on the dry matter of starch were mixed in phosphate buffer and heated at various temperatures 72 °C, 80 °C and 90 °C for 45 min while rotating in a ventilation oven. Afterwards, the mixture was centrifuged at 1000 rpm for 15 min in a Labofuge 400R. The height of the supernatant was measured and the swelling power was calculated based on the volume of precipitated starch. All samples were measured in duplicate.

2.7. Granular structure

Starch granules were observed using a Nikon light microscope (Nikon, Eclipse 600, Japan). The freeze-dried starch samples, which were previously processed in the RVA, were diluted in simulated tap water to obtain a 1% suspension. After shaking and several minutes of equilibration the starch suspensions were observed under bright-field illumination of the 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 or triplicate. SPSS®statistics program ver. 26 (IBM, New York, NY, USA) was used to perform statistical analysis, including means, standard deviation and significant difference. Bonferroni's multiple-range test in one-way analysis of variance (ANOVA) was conducted to identify significant differences ($p < 0.05$). Graphing was performed with OriginPro 9.0 (OriginLab Co., Northamptaon, MA, USA).

3. Results and discussion

The general starch modification process reported here involves two steps. The first step is the HMT on native potato starch, while the second step is the inclusion complexation. Unlike our previous study using linoleic acid as a guest molecule for inclusion complex formation, stearic acid was employed to investigate the improvement on the complex formation, since the melting temperature of stearic acid is higher. Prior to complexation of starch with stearic acid, emulsification of stearic acid in water was initially performed. Casein sodium salt is one of well-known emulsifier tested for fatty acids [57]. The emulsification of stearic acid with casein sodium salt in water was aimed to improve the solubility and dispersion of stearic acid in water, hence, facilitate the complexation with starch. In general, the procedure of starch modification by HMT followed by complexation is schematically outlined in Fig. 1. The differences in time and temperature of complexation were also examined in this project.

3.1. Thermal properties and complexes formation

DSC is a well-known and widely used technic to investigate the amylose-guest inclusion complex formation since the melting of the complex occurs at higher temperature than the starch itself. The DSC thermograms presented in Fig. 2 shows the influence of temperature (72, 80 and 90 °C) and time (5, 30, and 120 min) of complexation on the thermal behavior of the starch-stearic acid complexes. In Fig. 2a and b, the endotherm peak at the lowest temperature (60–78 °C) corresponded to the melting of the free stearic acid aggregates which were not complexed with starch as this peak does not appear in the measurements of the control native starch without stearic acid addition. DSC of only stearic acid and casein sodium salt (without starch) can be observed in Fig. S3. Complexation at 72 °C and 80 °C resulted in type I complexes, indicated by the endotherm onset (T_{onset}) at 91 °C and the endotherm peak (T_{peak}) at 107 °C. The complexation at 90 °C resulted in type I and type II complexes melted (T_{peak}) at 107 and 122 °C (Fig. 2a and Table 1). This result is in agreement with Kong et al. [40], who indicated the formation of type II amylose complexes-C10 and C16 alkyl chains after annealing at 90 °C which was not observed at 60 °C.

The heating process in HMT increased the starch chain mobility and disorganized the ordered structure of the crystalline region. This process increased the accessibility of amylose for inclusion complex formation with ligand molecules, such as stearic acid. Interestingly, in our study, the type II complexes were only formed in the heat-moisture treated starch after complexation with stearic acid, while only type I complexes were formed in native starch-stearic acid complexation (Table 1). This can be explained by the effect, that the HMT forces the formation of better organization of amylose-stearic acid complexes, particularly at elevated temperature of complexation. This resulted in a crystal structure with higher melting temperature of the heat-moisture treated, complexed starch. The HMT induced more and better organization of the complexes because due to the HMT particularly at 145 °C, the granules were partly gelatinized, hence the complex formation was easier. In case of lipid, including fatty acids, the complex formation is hard at temperatures below the gelatinization temperature of starch and the majority of the complexes occurs during the gelatinization process. Thus, the HMT is the first way to start the beginning of gelatinization. Furthermore, the HMT also increased the thermal stability of the starch granules due to the physical crosslinking among the starch chains. Hence, the complexation with stearic acid on starch could be prepared at

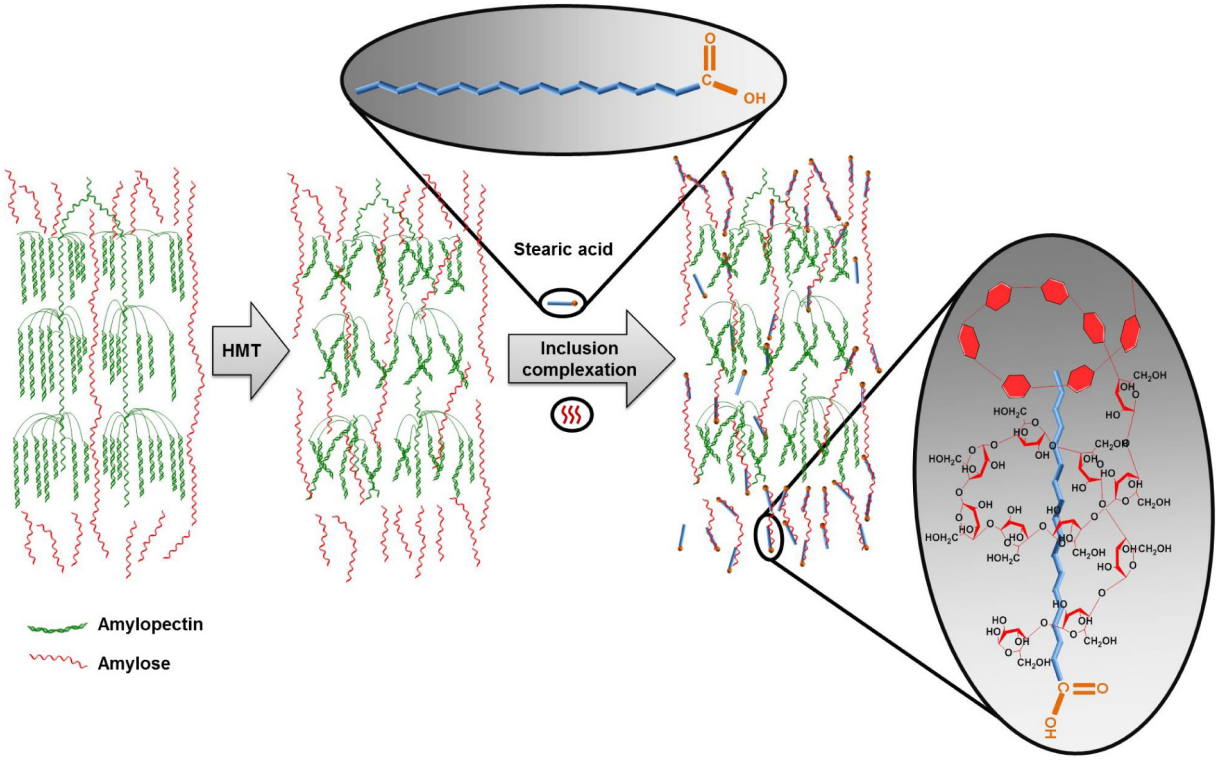

Fig. 1. Schematic representation of the procedure of HMT followed by inclusion complexation with stearic acid.

higher temperature and longer period of time which forces better organization of the complexes without destroying the whole granular structure due to the HMT. Our result is also supported by the fact that HMT increases the relative reactivity of amylose in starch granules toward substitution of the –OH group with diethylaminoethylchloride [13]. Furthermore, HMT prior to complexation increased the thermal stability of starch granules, hence, the complex formation could be prepared at elevated temperatures while preserving most of the granule structure. The starch granules were not easily ruptured even at 90 °C of complexation, thus, the stearic acid was able to form complexes in the more ordered type II structures. Fig. 2b and S1 show the effect of various complexation times at 90 °C. The longer reaction time permitted the type I crystals to be transformed into more stable and more ordered type II crystals, hence the formation of type II crystal became more obvious.

Table 1 shows the enthalpy change (ΔH) values of the V-type complexes. It was found that the longer the complexation time and the higher the temperature, the more complexes were formed, indicated by the higher enthalpy (ΔH) of the complexes (Table 1). By increasing the time at a complexation temperature of 90 °C, the melting enthalpy of the type I complexes decreased, while the melting enthalpy of the type II complexes increased. At longer time periods, the amylose and the ligands have more time to assemble in a better ordered organization and hence force the conversion of type I into type II amylose-stearic acid complexes. This finding is in agreement with previous reports [58,59]. When the type I complexes are heated, the helixes which are

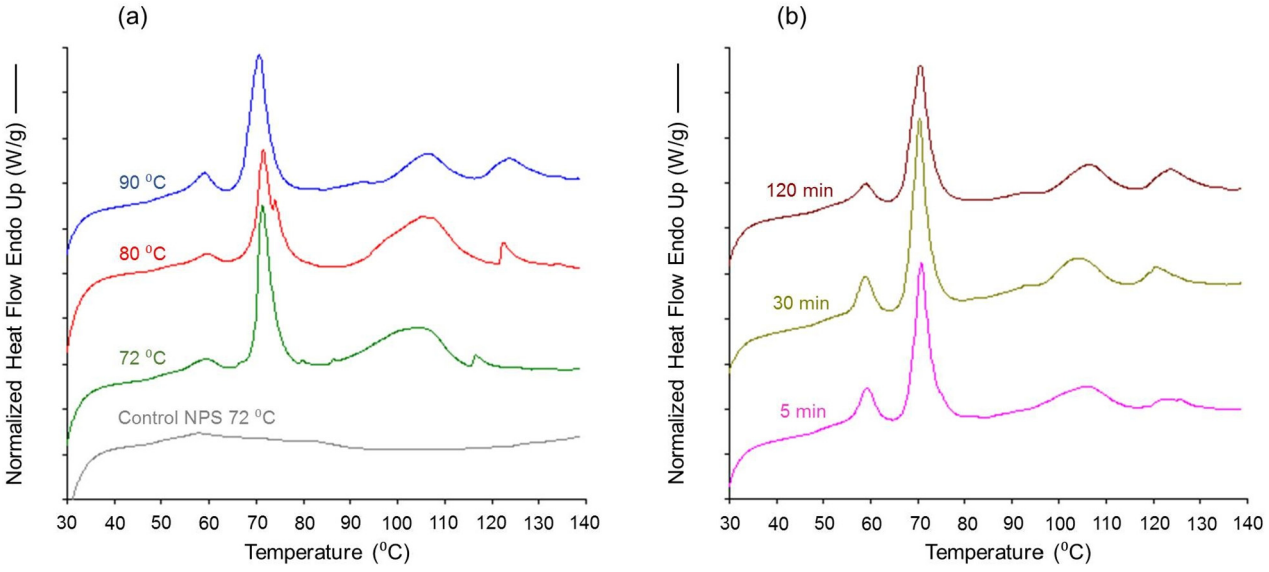

Fig. 2. DSC thermogram (heating mode) for HPS145-SA complexes after (a) 120 min complexation at various temperatures and (b) at 90 °C complexation at various times.

Table 1
Thermal analysis of 20% native and HMT potato starch suspensions in simulated tap water with stearic acid at various times and temperatures of complexation.

Samples	Temperature (°C)	Time (min)	Amylose – SA (1st heating)						Amylose – SA (1st cooling)		
			Onset (°C)	Peak (°C)	ΔH (J/g)	Onset (°C)	Peak (°C)	ΔH (J/g)	Onset (°C)	Peak (°C)	ΔH (J/g)
NPS - SA	72	5	91.3	108.3	2.8^{a} (0.21)				86.2	80.2	−2.8^{a} (0.07)
		30	90.6	107.9	3.5^{ab} (0.28)				85.0	80.5	−3.6^{ab} (0.14)
		120	91.4	108.8	4.1^{ab} (0.35)				86.4	81.3	−4.0^{ab} (0.21)
	80	5	93.3	109.1	3.6^{ab} (0.28)				86.7	82.1	−3.6^{ab} (0.21)
		30	92.9	109.3	4.2^{ab} (0.21)				87.0	81.1	−4.0^{ab} (0.07)
		120	92.6	108.3	4.7^{b} (0.21)				86.5	80.0	−4.1^{ab} (0.07)
	90	5	94.5	110.8	4.1^{ab} (0.14)				89.1	82.9	−3.7^{ab} (0.14)
		30	98.1	112.9	4.8^{b} (0.14)				90.9	85.6	−4.3^{ab} (0.07)
		120	98.7	109.0	5.1^{b} (0.07)				91.5	80.7	−4.9^{b} (0.14)
HPS 125 - SA	72	5	90.5	107.6	3.4^{ab} (0.85)				86.6	83.7	−3.0^{ab} (0.84)
		30	90.5	107.1	3.9^{ab} (0.49)				87.4	82.3	−3.6^{ab} (0.57)
		120	90.7	105.6	4.4^{b} (0.07)				85.5	80.7	−4.6^{ab} (0.07)
	80	5	90.1	106.9	4.3^{ab} (0.00)				85.9	82.0	−3.8^{ab} (1.13)
		30	90.8	108.1	4.1^{ab} (0.57)				87.4	82.3	−4.2^{ab} (1.06)
		120	91.1	104.1	4.6^{b} (0.49)				87.0	79.2	−4.0^{ab} (0.21)
	90	5	91.0	106.1	3.7^{ab} (0.14)	120.0	122.4	0.2^{a} (0.14)	84.2	78.7	−3.9^{ab} (0.21)
		30	92.6	107.3	3.8^{ab} (0.07)	118.6	122.5	0.6^{ab} (0.14)	86.0	80.7	−4.2^{ab} (0.35)
		120	97.2	108.0	3.8^{ab} (0.77)	119.3	124.5	1.5^{abc} (0.42)	86.3	80.4	−4.1^{ab} (0.57)
HPS 145 - SA	72	5	90.9	105.1	4.3^{ab} (0.42)				84.4	80.7	−4.2^{ab} (0.14)
		30	90.5	105.3	4.7^{b} (0.21)				84.5	79.4	−4.4^{ab} (0.21)
		120	90.9	105.1	4.9^{b} (0.07)				85.3	80.3	−4.9^{b} (0.21)
	80	5	91.0	105.1	3.6^{ab} (0.14)				84.3	80.7	−3.8^{ab} (0.14)
		30	91.9	106.6	4.3^{ab} (0.07)				86.3	81.4	−4.5^{ab} (0.14)
		120	91.4	105.3	4.9^{b} (0.21)				87.3	81.1	−4.9^{b} (0.14)
	90	5	93.1	105.6	4.0^{ab} (0.35)	119.2	122.8	0.9^{abc} (0.21)	84.9	81.0	−4.5^{ab} (0.21)
		30	96.2	106.4	4.2^{ab} (0.14)	117.7	121.0	1.4^{bc} (0.07)	83.5	79.5	−4.7^{b} (0.07)
		120	96.9	107.1	3.9^{ab} (0.49)	118.1	123.5	1.7^{c} (0.00)	85.5	79.5	−4.9^{b} (0.35)

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

disaggregated and dissociated into free amylose coils and lipids, rearranged into more ordered V-type II complexes [44].

In our previous study, starch-linoleic acid complexes had also been prepared on heat-moisture treated starch [9]. It is revealed that the starch-stearic acid complexes in this study have a higher thermal stability than starch-linoleic acid complexes. The endotherm peak of the amylose-stearic acid complexes is higher than the endotherm peak of amylose-linoleic acid complexes, however, the onset of the melting temperature of amylose-stearic acid complexes was also still below 100 °C (Table 1). The more stable amylose-stearic acid complexes are attributed to the fact that the stearic acid has a higher melting point than linoleic acid. Moreover, the cis-double bond in unsaturated fatty acids causes a bent or non-linear conformation, thus becomes more complicated to be included in the helix of amylose compared to linear saturated fatty acids, such as stearic acid. Our results are in agreement with other reports investigating the effect of saturated/unsaturated alkyl chains on the complex formation [42,44,46,60,61].

The solubility of stearic acid could largely be improved in phosphate buffer (pH 6.9). Therefore, in this part of the research, the complexation was also conducted in phosphate buffer; hence the excess of free stearic acid could be easily removed. Better solubility of stearic acid in phosphate buffer encouraged the formation of more amylose-stearic acid complexes and increased its stability, particularly after complexation at 90 °C. It is shown that the amylose-stearic acid complexes in phosphate buffer started to melt at ≥100 °C (see Figs. 3, S2 and Table 2). However, there was only one endotherm of the complexes at higher

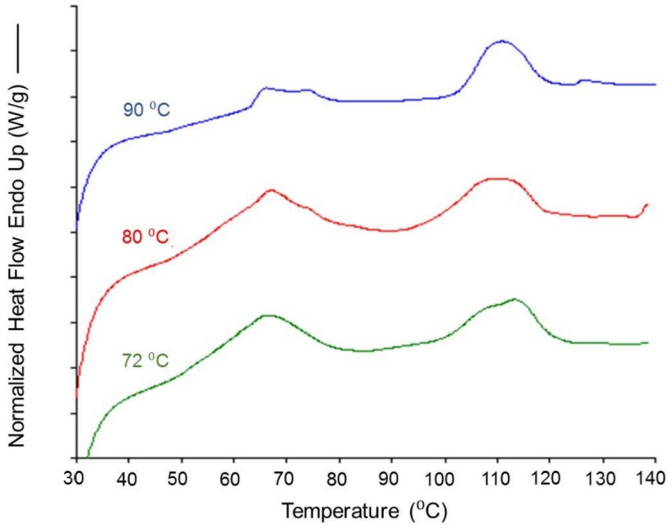

Fig. 3. DSC thermogram (heating mode) for HPS145-SA complexes after 120 min complexation in phosphate buffer.

temperature. Furthermore, the endotherm at low temperature (60–78 °C) which was referred to the free stearic acid largely disappeared after washing with phosphate buffer.

3.2. Crystallinity

Amylose forms left-handed single helixes with a hydrophobic cavity inside the helix which enables to wrap hydrophobic guest molecules and then crystallizes in a V-type structure. To confirm the formation of V-type amylose-stearic acid crystallites, XRD measurements were performed. Fig. 4 displays the XRD pattern of freeze-dried starch-stearic acid complexed samples. Compared to the amorphous uncomplexed HPS starch, the HPS-stearic acid complexes exhibited several additional reflection peaks. There is an obvious peak at $2\theta = 19.7–20.1°$ and a broader peak at 12.9–13.1° which were referred to the V_6-type amylose-guest complexes [9,16,27,62]. The appearance of these reflection peaks in XRD confirmed the DSC results above. The V_6 structure is corresponding to the formation of 6 glucose molecules per helical turn of the amylose. The additional peak at $2\theta = 24°$ confirmed the formation of retrograded B-type crystallite of the starch which was not visible in both non-complexed HPS125 and HPS145 [40]. The sharp peak at $2\theta = 21.8°$ was referred to as the free uncomplexed stearic acid aggregates [48,63]. The % crystallinity of the samples is shown in the right side of each graphs in Fig. 4 and Table S2. The % crystallinity of HPS-SA was calculated excluding the pure free stearic acid peak. The % crystallinity of HPS with addition SA was higher than HPS without SA for all temperatures condition. In the absence of SA, the crystallinity of starch decreased with the increasing of the heating temperatures, while in the presence of SA, the crystallinity increased with the increasing of the temperature. This was attributed to the formation of V-type complex crystallites on the starch contributing by peak formation at 19.7 –20.1°, hence the % crystallinity increased. At higher temperature of complexation, the more complexes formed, induced the increase in crystallinity. The % crystallinity of HPS145-SA was higher than HPS125-SA, indicating that the complexes amylose-stearic acid was better and more developed after HMT at 145 °C.

3.3. Pasting temperature and gelatinization behavior

To measure the gelatinization behavior of starch suspensions against controlled shear, commonly a Rapid Visco Analyzer (RVA) is used. During a heating and cooling process in the RVA, the gelatinization phenomena, pasting, and retrogradation could be determined. The gelatinization process involves the pasting (the starch begins to absorb water) and viscosity phenomenon. Starch gelatinization is an irreversible process in which crystalline parts are melting and then the starch granules are disrupted [56].

In this study, HMT largely increased the pasting temperature and lowered the peak viscosity of the starch (Fig. 5a, b, and Table S1). This phenomenon could be attributed to the enhancement of the interaction among amylose-amylose, amylose-amylopectin, and amylopectin-amylopectin chains due to higher chain mobility during HMT [6,9]. A further reduction in peak viscosity and further increase in pasting temperature was obtained for heat-moisture treated, stearic acid complexed starch (Fig. 5a) and apparently resulting in non-gelling paste. This finding is similar to the report from Mapengo et al. [53] on maize meal. The reduction in peak viscosity is an indication of a lower water-binding capacity and reduced swelling power of the starch which makes it more difficult to be disintegrated. The complexation with ligand molecules repressed the leaching of amylose and hindered the water uptake, hence the pasting temperature increased [9,34]. The pasting temperature of the starch largely increased when the process was performed in phosphate buffer (with and without NaCl) instead of simulated tap water (Figs. 5b and S4). This could be attributed to the formation of more stable amylose-stearic acid complexes due to better solubility of stearic acid in phosphate buffer. The development of these inclusion complexes hindered the water susceptibility to the starch granules. This modification process successfully improved the

Table 2
Thermal analysis of 20% HMT potato starch suspensions after 120 min complexation with stearic acid in phosphate buffer.

Samples	Temperature (°C)	Amylose – SA (1st heating)						Amylose – SA (1st cooling)		
		Onset (°C)	Peak (°C)	ΔH (J/g)	Onset (°C)	Peak (°C)	ΔH (J/g)	Onset (°C)	Peak (°C)	ΔH (J/g)
HPS 125 - SA	72	101.7	110.4	3.2^{a} (0.00)				95.0	92.8	-4.5^{a} (0.42)
	80	99.9	109.1	4.1^{b} (0.07)				94.7	92.8	-4.2^{a} (0.14)
	90	106.8	116.4	4.1^{b} (0.07)				95.1	92.6	-4.5^{a} (0.42)
HPS 145 - SA	72	100.6	113.4	3.6^{ab} (0.35)				100.3	93.1	-4.6^{a} (0.14)
	80	100.1	108.8	4.2^{b} (0.07)				100.0	92.4	-4.7^{a} (0.14)
	90	102.8	110.8	3.8^{ab} (0.00)	121.9	126.5	0.6 (0.07)	100.1	92.4	-5.0^{a} (0.07)

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

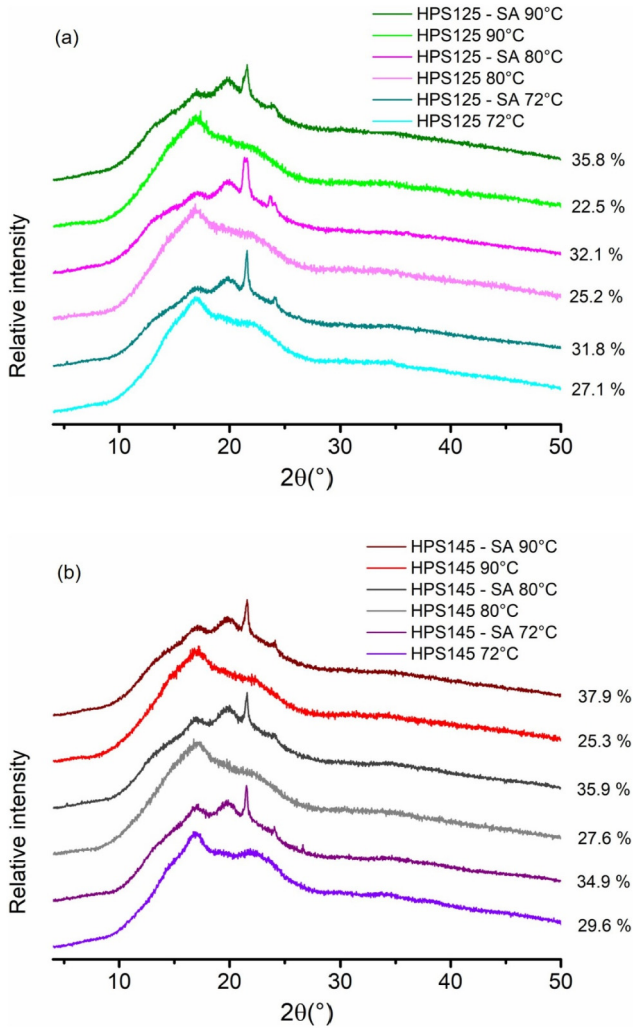

Fig. 4. Crystal pattern of (a) HPS125 and (b) HPS145 before and after complexation with stearic acid at 72, 80 and 90 °C for 30 min.

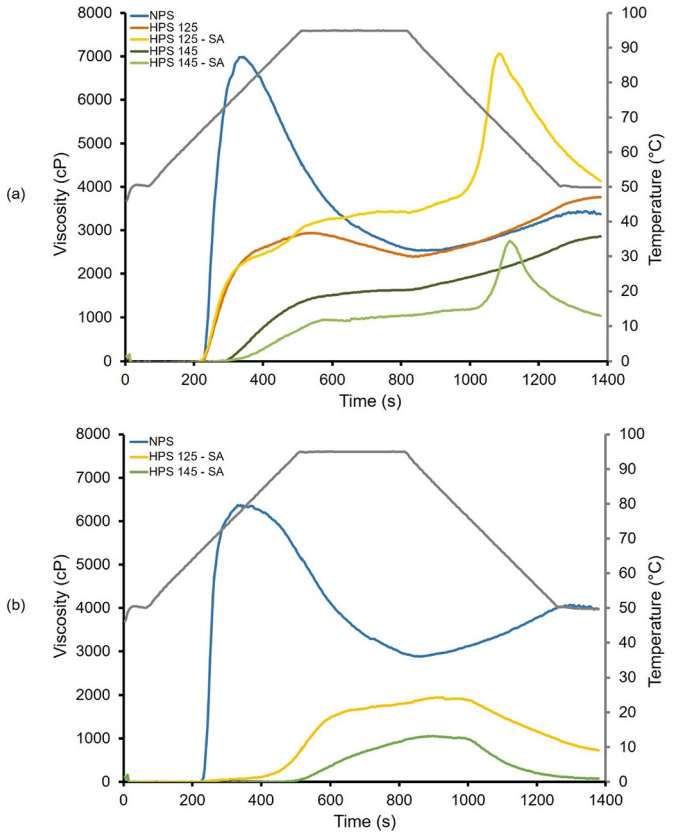

Fig. 5. RVA viscosity profiles of 9% NPS, HPS125, and HPS145 without and with addition of stearic acid (a) in simulated tap water and for NPS without and HPS 125 and HPS 145 with stearic acid (b) in phosphate buffer containing NaCl.

stability of starch granules toward the heating and stirring process. In starch paste systems that were mixed with stearic acid as complexing ligand (HPS125-SA and HPS145-SA), peaks during the cooling process were observed at a 68 °C and 65 °C (respectively) in the RVA (Fig. 5a). This peak might be attributed to the complex formation between some leached amylose and excess free stearic acid in the solution [64,65]. Wang et al. [65] found the same high peak during cooling in complexes of starch-linoleic acid which suggested that the peak is mostly caused by the formation of amylose-fatty acid complexes rather than fatty acid recrystallization since linoleic acid does not solidify at 50 °C. The addition of stearic acid hinders the formation of a double helical conformation (retrogradation) because the V-type amylose-ligand complexes form single helical structures, which are favorable conformations [66].

The effect of various temperatures of incubation for 30 min is shown in Fig. 6. It is clearly observed that the viscosity increase could be largely suppressed as compared to the direct scanning without pre-incubation (Figs. 5a and 6). A major effect was observed when the heating is limited until 85 °C. The viscosity at the end of the RVA profile remained the same as at the beginning (Figs. 6 and S5). The interaction between amylose and guest molecules lowered the water solubility of the amylose, hence delayed the pasting process and increased the pasting temperature of the starch [67]. It is expected that a lower water-binding ability leads to less access for the enzyme to hydrolyze the starch. In HPS125-SA, HPS145, and HPS145-SA, the peak viscosity and the breakdown could not be determined (Fig. 5a). The absence of breakdown is correlated to less ruptured starch granules. The reduced and absence of breakdown viscosity is caused by the increased in cross-linking interaction among polymer chains during HMT process. These results in viscosity behavior is similar to the findings of Mapengo et al. that measured the effect of both HMT and stearic acid complexation on pasting properties and gelatinization of maize meal [53].

3.4. Swelling power

The gelatinization process of starch also involves the swelling of the granules. Upon heating to the gelatinization temperature in excess of

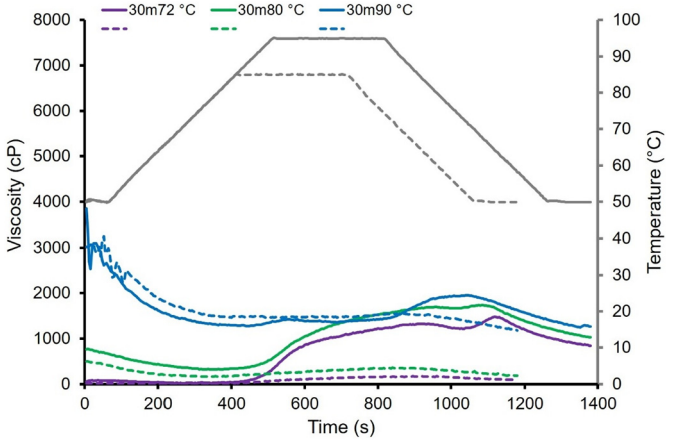

Fig. 6. RVA viscosity profiles of 9% HPS145 - stearic acid complexes after 30 min complexation at different temperatures in 10°dH: heating profile till 95 °C and 85 °C.

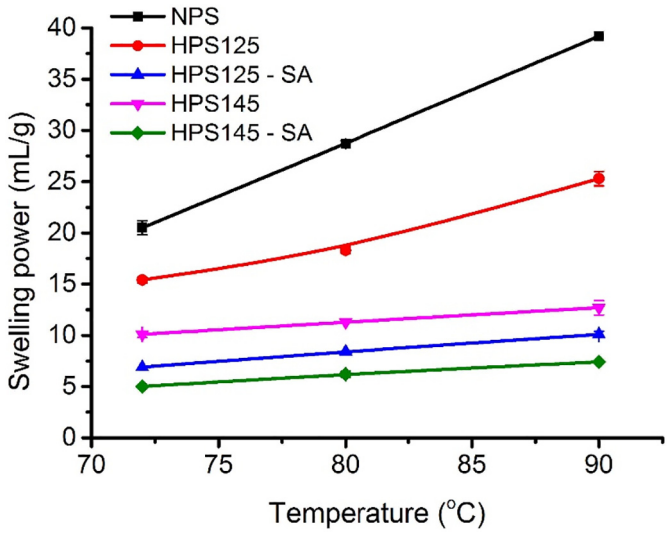

Fig. 7. Swelling power of NPS, and HPS125, HPS145 before and after complexation with stearic acid in phosphate buffer.

water, starch granules swell up several times of their original size. Fig. 7 shows the swelling properties of NPS, HPS, and HPS-SA complexes at various temperatures. In general, all starches showed an increase in swelling power at an increased temperature. Native potato starch clearly showed the largest slope and the highest degree of swelling (Fig. 7). When the starch granules are heated at high temperature, the granules swell into maximum size (peak viscosity) before they are broken down [15]. The HMT clearly reduced the swelling power, which was further reduced after complexation with stearic acid (Fig. 5). The reduction in swelling power of HPS was attributed to the crystallite stabilization, interaction among amylose and amylopectin chains, and also changes in the polymorphic forms B → A + B [68]. Furthermore, the complexation between amylose and stearic acid might have stabilized the amylose against leaching, hence, the starch granules were less swollen due to the fact that less water could migrate into the granules. This confirmed the viscosity measurement mentioned in Section 3.3.

3.5. Granular structure

The appearances of the starch granules shape were examined after heating at different temperatures with a light microscope. It was clearly observed that the NPS lost its granular structure when exposed to 72 °C, and further ruptured at 90 °C (Fig. 6). The granular structure remained largely intact after the HMT, and even more after complexation with stearic acid (Figs. 8 and S6). The HPS-SA maintained the oval granular-like structure, was less swollen even after heating to 90 °C. The major effect was visible on the HPS145-SA granules. In HPS145-SA, the intact small granules were still observable at 72 °C, and even after heating at higher temperatures (Fig. 8). This could be explained by the higher pasting temperature and better thermal stability of the HPS-SA granules compared to NPS, hence less water absorption to the granules. In addition, the ligands might form a protective coating around the granules, hence less water uptake and a lower degree of granular disruption [69].

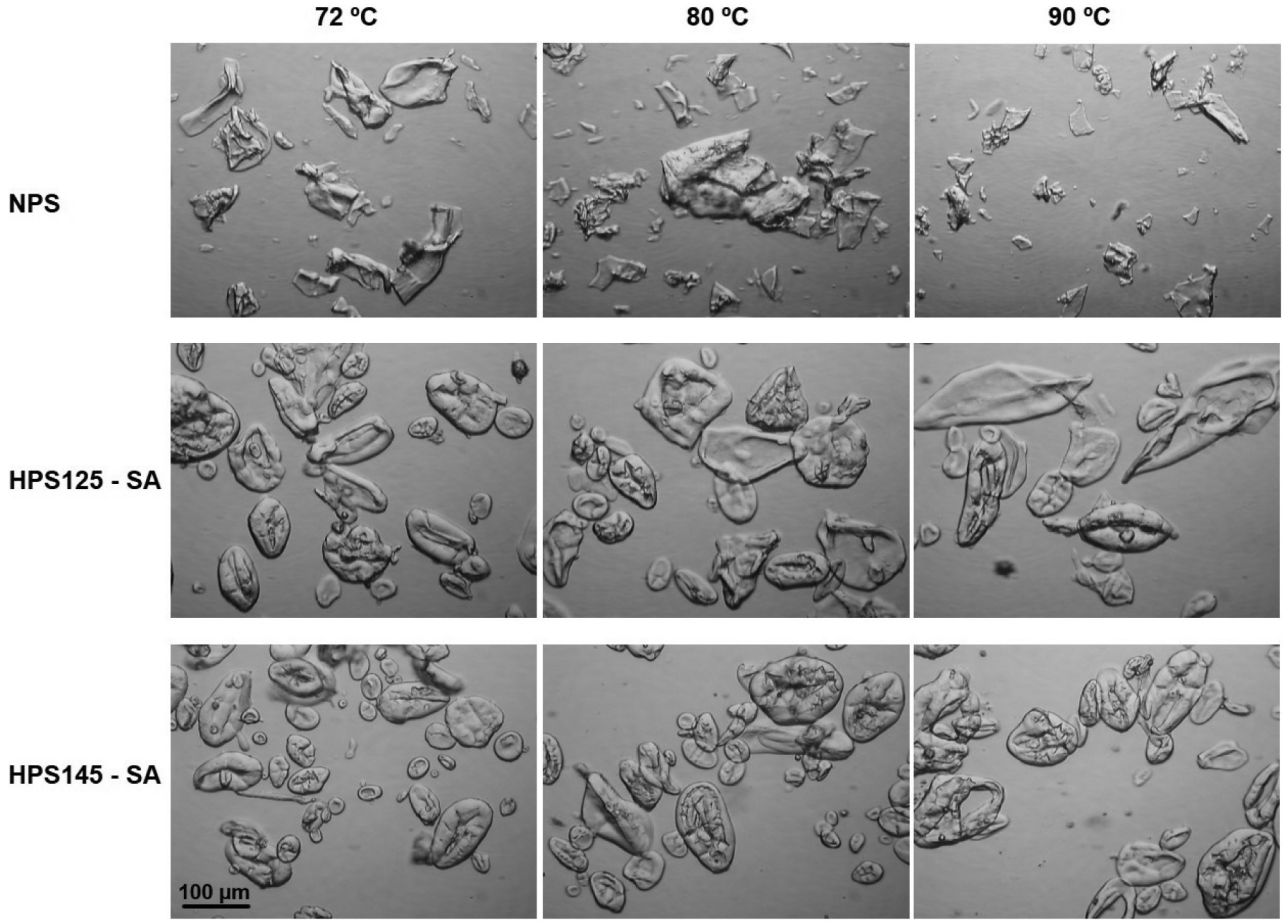

Fig. 8. Light microscopy (bright field) images of NPS, HPS 125-SA and HPS 145-SA after heating at different temperatures.

4. Conclusion

HMT followed by complexation with stearic acid clearly improved the heat and shear stability of potato starch in water system. HMT facilitates the formation of more stable amylose-stearic acid complexes, particularly at 90 °C of complexation in phosphate buffer without destroying the whole granules structure. The use of food-grade phosphate buffer can be a promising alternative to tap water for starchy food production, as it gives better functional properties, however, the amount of phosphate consumed everyday should follow the advice of the European Food Safety Authority (EFSA). The amylose-stearic acid complexes in the treated starch mostly remained intact even if the application heating temperature is around the boiling temperature of water-based food products since the complexes mostly melted above 100 °C. In addition, the heat-moisture treated, stearic acid complexes of starch successfully exhibited better thermal and mechanical stability as compared to native starch, confirmed by significantly lower swelling and gelling ability of the modified starch. This improved physicochemical properties of starch modified by HMT followed by stearic acid complexation is a promising alternative to substitute chemically cross-linked and modified starch. The *in vitro* digestibility study toward enzymatic degradation of the modified starch will be investigated in the near future.

CRediT authorship contribution statement

Yassaroh Yassaroh: Conceptualization, Methodology, Formal analysis, Investigation, Funding acquisition, Writing - Original Draft

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijbiomac.2021.01.124.

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