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CALCIUM OCTENYL SUCCINATE STARCH - PREPARATION AND SELECTED PHYSICOCHEMICAL PROPERTIES

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Abstract: Potato starch was esterified with octenyl succinic anhydride (OSA) and enriched with calcium ions (OSA+Ca). The aim of this study was to investigate the effect of calcium ions on the physicochemical properties of OSA starch. On the basis of the results it was stated that incorporation of calcium ions into starch granules increased water binding capacity and solubility in water. The colour parameters indicated that OSA and OSA+Ca starches were characterized by lower values of the parameter b* than blank sample. Starch incorporation in calcium ions resulted in increase of susceptibility to enzymatic hydrolysis using α-amylase and decrease susceptibility to retrogradation during 21 days of storage.

Keywords*:* octenyl succinate starches, enrichment, calcium, physicochemical properties

INTRODUCTION

Starch due to its specific chemical structure can easily reacted with various chemical substances. One of the methods of starch modification is 1-octenylsuccinylation. OSA-modified starch was reported to be an effective emulsifier due to the addition of dual functional hydrophilic and hydrophobic groups **(Bao et al,. 2003, Hui et al. 2009)**. Morover the presence of hydroxyl, as well as ortophosphoric groups in potato starch, allow the binding of metal ions into starch chains **(Pietrzyk et al., 2011)**. Therefore, there is a possibility to use OSA starch as a bifunctional preparation: emulsifier and carrier of minerals in food fortification. However introduction these new functional groups and minerals into starch affects its physicochemical properties. The aim of this work was to evaluate the effect of calcium ions on the physicochemical properties of OSA starch.

MATERIALS AND METHODS

The potato starch used for this study was bought from Przedsiębiorstwo Przemysłu Ziemniaczanego SA in Niechlow (Poland). High-purity OSA was purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). The other chemicals used in the study were of analytical grade.

OSA starch samples were prepared according to **Hui et al., (2009)** procedure. Potato starch (300 g, d.w) was suspended in distilled water with agitation to obtain 35% (w/w) starch concentration. The pH of the suspension was adjusted to 8.0 with a pH-meter by dropping 3% NaOH solution. OSA solution in concentration 3% (calculated on d.w of starch) five-fold diluted with absolute alcohol was adding slowly during 1 h. The reaction was continued for 3.5 h with sample agitation. After required time, the pH was adjusted to 6.5 with 3% HCl solution, the mixture was centrifuged, washed twice with distilled water and 70% aqueous alcohol. Then the solid was oven-dried at 45 ^{o}C for 24 h, then passed through mechanical sieve with a diameter of mesh 200 μm. To obtain a blank sample, the same process was carried out without addition of OSA to the starch solution.

The OSA starch was modified by reaction with the calcium ions. 100 g of starch was mixed with 250 cm^3 of distilled water for 5 min and then the resulting dispersion was strained through filter funnel. 200 cm^3 of mixture of 1% (w/w) $CaCl_2$ and saturated solution of

$Ca(OH)_2$ in the ratio of 1:1 and of pH=8.5 was added to the starch and whole was stirring for 5 min. The resulting product was strained through filter funnel and 200 cm^3 of the mixture $CaCl_2$ and $Ca(OH)_2$ was added to the retentate and the sample was stirring for 5 min. The action was repeated one more time. The starch was rinsed with distilled water until chloride ions were absent (using 0.1 M $AgNO_3$ solution), and then it was filtered, air dried and sieved.

Starch preparations were conducted the following analyses:

1. determination of the degree of substitution. The degree of substitution (DS) is the average number of hydroxyl groups substituted per glucose unit. The DS of OSA starch was determined by titration (Hui et al., 2009). An OSA starch sample (5 g, d.w.) was accurately weighed and dispersed by stirring for 30 min in 25 ml of 2.5 M HCl isopropyl alcohol solution. 100 ml of 90% (v/v) aqueous isopropyl alcohol solution were added and the slurry was stirred for an additional 10 min. The suspension was filtered through a glass filter and the residue was washed with 90% isopropyl alcohol solution until no Cl^- could be detected any longer. The starch was re-dispersed in 300 ml of distilled water, and then the dispersion was cooked in a boiling water-bath for 20 min. The starch solution was titrated with 0.1 M standard NaOH solution, using phenolphthalein as an indicator. Simultaneously native starch was also titrated as a blank sample. The DS was calculated by the following equation:

$$DS = \frac{0.162 \cdot (A \cdot M)/W}{1 - [0.210 \cdot (A \cdot M)/W]}$$

where A is the titration volume of NaOH solution (ml), M is the molarity of NaOH solution, and W is the dry weight (g) of the starch.

2. determination of calcium content using Atomic Absorption Spectrometer (Avanta Sigma, GBC, Australia) with acetylene-nitrous oxide flame according to Polish Standard PN-91R-04014. The starch was mineralized in mixture of nitric and sulphuric acids at temperature of 250°C (Wet Digester, Büchi, Switzerland).

3. water-binding capacity and solubility in water at 25, 50 and 80°C using Leach's method **(Richter et al., 1968).**

4. color parameters in the CIE L*a*b* system (measuring geometry d/8°, illuminant D65, 10° observer) using a spectrophotometer 5i (X-Rite, USA),

5. susceptibility to enzymatic hydrolysis of starch using α-amylase according to **Englyst et al., (1992).**

6. susceptibility to retrogradation during storage of 2% starch pastes by turbidimetric method of **Jacobson (1997).** The pastes of starch were stored at temperature of 8°C for 21 days. The measurements of turbidance were made on the 1st, 3rd, 5th, 7th, 10th, 14th, 21st day of storage.

The significance of differeces between the means were evaluated by a one-way analysis of variance and the Tukey test at significance level $\alpha = 0.05$.

RESULTS AND DISCUSSION

Potato starch modified with 3% level of OSA was subjected to DS analysis. DS value of OSA starch was 0.013±0.001%. Similar trend in reactivity of OSA with starches was observed by other authors (Bao et. al 2003, Hui et. al 2009). The rate and efficiency of the chemical modification process depends on the reagent type, botanical origin, the size and structure of starch granules (Huber and BeMiller 2001). Content of calcium in tested starches was presented in Table 1. OSA+Ca starch is characterized by the highest amount of calcium as compared to other starches, that proves that the modification process was effective.

Tab. 1 Calcium content of blank, OSA and OSA+Ca starches

Starch	**Calcium [mg/100g dw]**
Blank sample	68.28±4.08
OSA	59.53±1.56
OSA+Ca	84.71±3.10
LSD$_{(\alpha=0,05)}$	5.57

Solubility in water (SW) and water-binding capacity (WBC) of all starch preparations increased with increasing temperature of determination (Tab. 2). OSA+Ca starch was characterized by higher SW and WBC than other starches irrespective of temperature test. Special attention should be paid to the fact, that OSA+Ca starch at 25°C has a 14 times greater SW and 3 times better WBC than blank sample. The increase in SW may be due to weakening of intermolecular hydrogen bond due to introduction of OSA group (Perez et. al 1993).

Tab. 2 Solubility in water and water binding capacity blank, OSA and OSA+Ca starches

Starch	**Solubility in water [%]**			**Water-binding capacity [g/g s.s]**		
	25 ^{o}C	**50 ^{o}C**	**80 ^{o}C**	**25 ^{o}C**	**50 ^{o}C**	**80 ^{o}C**
Blank sample	0.37±0.11	2.66±0.20	7.00±0.18	1.43±0.01	6.89±0.06	13.56±0.33
OSA	1.62±0.06	5.30±0.06	9.90±0.60	2.23±0.01	7.30±0.11	18.31±0.75
OSA+Ca	4.99±0.37	8.55±0.58	19.51±0.81	3.93±0.11	11.73±0.15	28.62±1.61
LSD$_{(\alpha=0,05)}$	0.95	1.49	1.75	0.26	0.47	4.35

In Table 3. colour parameters in CIE L*a*b* system were presented. OSA starch was characterized by the highest lightness (L*) from the tested starches. There were no differences between the lightness of blank sample and OSA+Ca starch.

Tab. 3 Colour parameters in CIE L*a*b* system of blank, OSA and OSA+Ca starches

Starch	**Parameter**		
	L*	**a***	**b***
Blank sample	96.39±0.05	-0.26±0.02	2.04±0.04
OSA	96.69±0.07	-0.21±0.02	1.49±0.03
OSA+Ca	96.31±0.01	-0.24±0.02	1.23±0.02
LSD$_{(\alpha=0,05)}$	0.13	0.05	0.08

All the starch preparations did not differ in the a* value. However, there were significant differences between starches in the values of the parameter b*. OSA and OSA+Ca starches were characterized by lower values of the parameter b* than the natural starch. This indicates lower participation of yellow colour in octenyl succinate starches.

In Figure 1 susceptibility to enzymatic hydrolysis of the tested starches was presented. Starch enrichment in calcium ions resulted in increase of this tendency. OSA starch was the most resistant to enzyme action and the values of susceptibility to enzymatic hydrolysis were almost the same during the experiment time. Han and BeMiller (2007) reports that modifications such as 1-octenylsuccinylation reduce the extent of enzyme-catalyzed hydrolysis (digestibility or biodegradability) what is in accordance with the results presented in this paper.

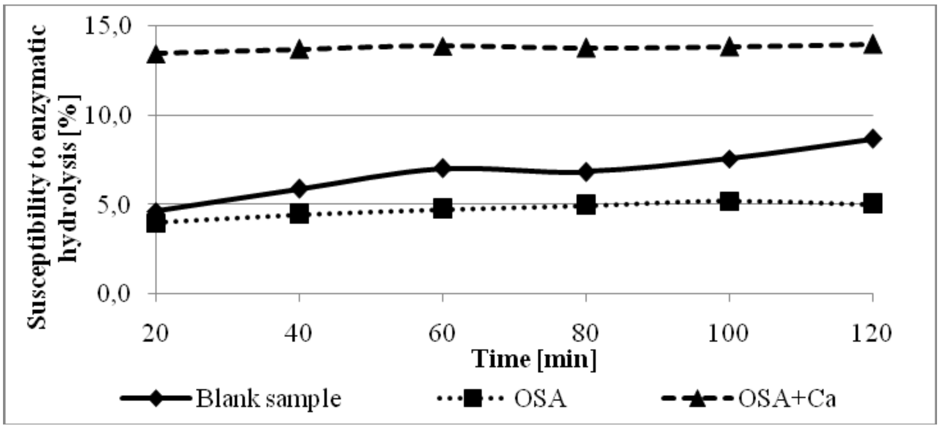

Fig. 1 Susceptibility to enzymatic hydrolysis of blank, OSA and OSA+Ca starches

In Figure 2 susceptibility to retrogradation of tested starches was presented. It is known from literature data that chemical modification can alter susceptibility to starch retrogradation (Karim et al., 2000, Pietrzyk et al., 2011).

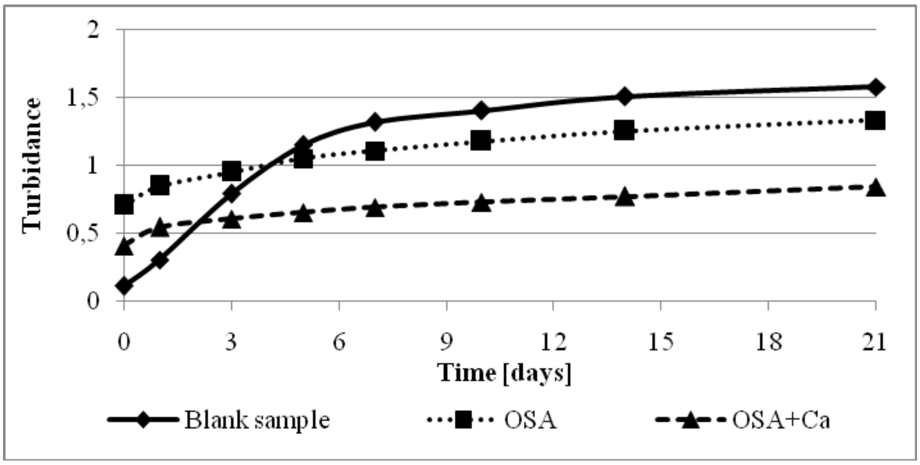

Fig. 2 Susceptibility to retrogradation during storage of blank, OSA and OSA+Ca starches

Modified starches analyzed in this paper exhibited lower susceptibility to retrogradation than natural potato starch. These results indicated that introduction of new substituents (octenyl groups and calcium ions) to starch structure hindered reassociation of amylose chains and their precipitation from aqueous solution (Pietrzyk et al., 2011).

CONCLUSIONS

1. On the basis of the results it was stated that incorporation of calcium ions into starch granules increased water binding capacity and solubility in water.

2. The colour parameters indicated that OSA and OSA+Ca starches were characterized by lower values of the parameter b* than blank sample.

3. Enrichment in calcium ions resulted in increase of susceptibility to enzymatic hydrolysis using α-amylase and decrease susceptibility to retrogradation during 21 days of storage.

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