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RESEARCH ON ZINC FORTIFIED POTATO STARCH AND ON ITS USE IN DESSERT PRODUCTION*

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Background. Modified potato starch is used as a thickener in foods or as a dessert component. Modification by oxidizing causes production of carboxyl radicals, which can bind elements in the coordination manner, inside starch granules. Zinc is one of the most essential microelements in the human body, and therefore the objective of our research was to determine the level of zinc adsorption from modified oxidized starch, to examine the changes in the starch's functional properties and the possibilities of using the starch for manufacturing dry mixes of milk desserts such as puddings.
Material and methods. The adsorption efficiency was examined with the Varian AAS atomic absorption spectrometer. The colour parameter was examined by Chroma Meter CR-300 Minolta and the viscosity of 3.3% of starch gels by Brabender viscosimeter. The organoleptic tested was determined in pudding prepared with fortified starch.
Results. Result of microelement adsorption it ranges from 49% to 84%, depending on concentration of salt used for adsorption. The colour of preparations with zinc did not show significant differences, while their viscosity was variable and higher from the viscosity of marketed pudding starch. Results were analysed and the recipe for zinc fortified pudding was prepared.
Conclusions. The best organoleptic properties were described for the dessert for which one portion contains approx. 7.5 mg of zinc, which is 50% RDA for an adult person.

Key words: modified starch, oxidized starch, food fortification, zinc, pudding – milk dessert

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INTRODUCTION

Fortification is a process of foodstuff enrichment with a mineral component or a vitamin of choice. The history of fortification commenced in 1923, when Switzerland was first to introduce iodized table salt. In 1940, fortification of flour with calcium, iron, niacin and thiamin was started in the United Kingdom. In the Philippines, rice has been enriched with vitamin B1 since 1946 [Gawęcki and Hryniewiecki 2000]. Fortification of drinking water with fluorine has been performed since 1967 in Poland [Składniki... 2002]. In 1980, Asian countries commenced a program of rice fortification with iron in which coated premix of ferrous sulfate is used and added to rice during the industrial rice hulling. In 1990, in the USA and Europe fortification with iron was extended from flour also onto cereals and dairy products [Reilly 1996, Watzke 1998], while in 1998 the USA started to fortify flour with folic acid as well. In China, on the other hand, ferrous compounds are used for fortification of soya souse, which is consumed on a large scale [Vankatesh Mannar i Sankar 2004].

Three types of fortification can be distinguished, depending on the purpose of this process. The food enhancement can be used in order to prevent extensive deficiencies of nutrients (intervention fortification), to balance a foodstuff's nutritious profile, e.g. in replacement products (improvement fortification) or to compensate the losses resulting from the food processing (compensative fortification) [Gawęcki and Hryniewiecki 2000]. Enrichment substance used in the fortification process are synthetic compounds, isolates or concentrates obtained from natural sources. They should be chemically stable, cost-effective and ensure good bio-availability. However, while they should not cause the undesired changes of the colour, flavour or smell of the fortified product [Gawęcki and Hryniewiecki 2000]. In Poland, the process of food enrichment is governed by Regulation (EC) No. 1925/2006 of the European Parliament and of the Council of 20 December 2006 on the addition of vitamins and minerals and of certain other substances to foods. As the diet supplementation with the use of tablets is a good solution for adults, but it is significantly more difficult and not always so efficient in children, introduction of a foodstuff that is enriched with a specific ingredient into the diet will make it easier to prevent illnesses and nutrient deficiencies, e.g. in children.

Earlier research on the possibility of using modified starches as carriers of food fortifiers has given positive results. An increase of adsorption of microelements on starch was proved proportional to an increase of concentration of ions in the solution, as well as more equal distribution of copper and iron ions in a product was confirmed when an adequate dose of the microelement was used. In the adsorbed starch, coordination bonds and not chemical bonds were found in the starch-microelement complexes, which results in an easier release of an element during enzymatic degradation of starch and thus in an increased assimilability of that element [Śmigielska et al. 2005].

Starch modifications are carried out in order to eliminate certain defects of natural starches and to produce starch with better functional, texture-creative and organoleptic properties [Lewandowicz and Mączyński 1990]. One of the modification methods includes the oxidation process using sodium hypochlorite. The increased number of carboxyl groups facilitates creation of starch-element complexes, increases the amount of adsorbed ions and starch becomes a good carrier [Śmigielska et al. 2005]. Oxidized starch in the foodstuff industry is used mainly in the production of ready-made desserts, e.g. puddings.

Zinc is one of the necessary microelements in the human organism, as it is present in approximately 200 enzymes participating in various vital processes. Zinc can work in the enzymes as a co-factor, catalyst or stabilizer, or it can be the enzyme component. The best known zinc-dependent enzymes include the alkaline phosphatase, carbonic anhydrase and alcohol dehydrogenases that catalyzes transformation of vitamin A into its active form – retinol in the eye's retina, which adopts the sight apparatus for seeing in the dark [Składniki... 2002]. Zinc deficiency causes taste and smell disturbances [Konopka et al. 2003] as well as psoriasis-like skin changes, dermatitis and hair loss. It is an essential component of DNA and RNA polymerases, which are enzymes responsible for the genetic material replication and transcription [Fernandez-Madrid 1973]. It is also needed for heme synthesis and insulin crystallization as well as ACTH, gonadotropin and growth hormone production [Ziemlański 2001]. Zinc participates in production of prostaglandins that regulate blood pressure, heart beat, skin secretion functions and cholesterol level in blood. It has also an impact on maintaining balance of other trace elements such as manganese, magnesium, selenium and copper. Zinc's favourable impact on the organism covers general improvement of metabolism and bone mineralization, acceleration of wound healing – particularly skin losses, mental agility enhancement and immunological functions correction [Ibs and Rink 2003]. Absorption from the digestive tract is regulated hormonally and depends on the demand. Daily consumption of zinc for children at the age of 2-8 years should reach the lever of 8.3 mg. Youngsters should consume approx. 14 mg, adult men 12-15 mg and adult women 10-12 mg of zinc daily. However, the demand of pregnant and breast-feeding women is greater and it is recommended to supply 16-21 mg Zn/day [Ziemlański 2001]. In case of low zinc supply in a pregnant woman's food such consequences are possible as: inhibited fetus development resulting from brain underdevelopment, as due to zinc deficiency the brain produces a reduced number of neurons [Obserleas and Prasad 1974]. Therefore zinc is an element which is really needed in the human body. In the event of insufficient zinc supply in the regular diet, its level could be enhanced by consuming fortified foods and thus preventive or healing approach could be applied to help combat numerous illnesses.

The objective of our research was to determine the level of zinc adsorption from modified oxidized starch, to examine the changes in the starch's functional properties, and finally to produce and evaluate organoleptically a milk dessert, which was the zinc carrier. It is anticipated that one portion of the dessert would contain minimum 50% RDA of zinc for an adult.

MATERIAL AND METHODS

Starch from Wielkopolskie Przedsiębiorstwo Przemysłu Ziemniaczanego S.A. in Luboń with the trade name of "Skrobia Budyniowa" (meaning "Pudding Starch") was the input material, while the Superior Standard natural potato starch was used as the reference material for the colour determination. Microelement sorption was made from a water solution of zinc sulfate (VI) in the suspended granulated starch below the gel formation temperature (50°C), while the product isolation was performed through the vacuum filtration. Four doses of the microelement were used: 0.5; 1; 1.5; 2 mg per 1 gram of starch. Thus prepared preparations of fortified starch were subject to the quantitive analytical and rheological examination.

In order to determine the content of the adsorbed zinc ion on the starch, samples were mineralized using the wet method, in the concentrated nitric acid, in the MARS5 microwave oven by CEM. The level of the zinc adsorption was analysed using the Varian 800 atop absorption spectrometer, using the flame method, with the wave length of 213.865 nm in three repetitions. The obtained results of the zinc content examination, expressed in mg/dm^3, were analysed using the average parameter estimation with the t--Student test and standard deviation re-estimation with the X square test.

Next the humidity and 3.3% viscosity of gels made of fortified starches only were determined using Brabender viscograph coupled with a computer and with the following measurement conditions applied: measurement can: 0.07 Nm; heating in the range of 25-92.5°C with 1.5° per min; hold the step and keep at the temperature of 92.5°C for 20 min; cooling in the range of 92.5-25°C with 1.5° per min.

Differences were also determined in the starch's colour before and after zinc adsorption using the absolute colour measurement in the CIE Yxy and L*a*b* systems by means of Chroma Meter CR-300 by Minolta.

In order to examine functional properties of the enriched pudding starch a number of milk desserts – puddings were produced, where in the recipes fortified and non-fortified starch was included. The desserts were examined for their organoleptic properties and for the curd's compliance with standard PN-A-74706. They were compared with desserts prepared from mixes available on the market. The pudding curd obtained from the non-fortified pudding starch was the reference model. The amount of starch needed for the dessert was calculated using the formula given in standard PN-A-74723:

$$N = (35.2 \cdot 100) / 100 - W$$

where: N – excessive weight volume, g
W – humidity of the given fortified pudding starch, %.

The exemplary course of action when preparing pudding from pudding starch fortified with zinc was as follows: 19.4 g of clean (non-fortified) pudding starch and 19.4 g of zinc fortified pudding starch, in which the zinc content was 0.76 mg Zn per 1 g of starch, were measured and put into a 200 ml beaker. This way one portion of the obtained pudding mix contained 50% RDA of zinc for an adult. 100 ml cold milk and 20 g white sugar were added to the obtained mix of non-fortified and fortified pudding starch. In a separate container 400 ml milk was boiled. At the milk heating point the suspended starch was poured into the milk. The suspension was heated for 30 seconds starting from the moment when first air bubbles occurred on the pudding surface. After this time the product was poured into two porcelain evaporating dishes wetted with cold water and left for four hours to cool. After that time a team of experts examined the pudding desserts.

RESULTS AND DISCUSSION

When analysing the impact of zinc ion concentration on the level of adsorption on the pudding starch, it was observed that an increase of doses of zinc ions in the series 0.5 → 1.0 → 1.5 → 2.0 mg per 1 g starch causes an increase in the amount of zinc adsorbed from approximately 0.43 mg per 1 g starch to 0.91 mg per 1 g starch. Similar dependencies occurred in case of copper ions adsorption [Śmigielska et al. 2006], which can be explained with the chemical similarity of the two elements. Results for the process efficiency expressed in % as a relation of the amount of zinc ions adsorbed to its amount introduced into the system illustrates that with a low ion content in the solution the efficiency is close to 84%, while as the ion concentration in the solution is increased, the efficiency drops to 45%. This proves that in the economical terms application of the dose of 0.5 mg Zn per 1 g starch is most efficient due to very little losses of zinc salt solution during the adsorption process. Below we present a diagram illustrating the degree of the Zn^{2+} ion adsorption depending on the dose used in the reaction (Fig. 1) and results of the statistical analysis (Table 1).

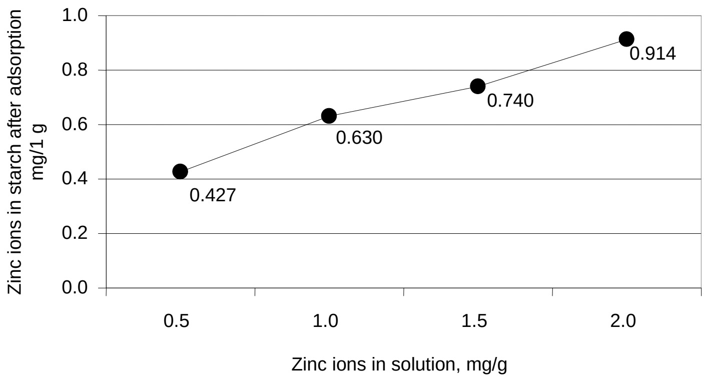

Fig. 1. Average content of zinc ions in pudding starch after adsorption

Colour parameters of starch with zinc ion additions (Table 2) were insignificantly different from parameters of pudding starch without any addition of such ions, and have not been much different from the colour of natural potato starch, which is the white reference for this kind of products. Zinc sulfate salt did not change the colour of starch (as it was the case with copper sulfate, which coloured the starch blue, and with iron sulfate – yellowish) [Śmigielska et al. 2006]. In order to illustrate the colour differences

Table 1. Results of statistical analysis of the zinc ions adsorption process, at the trust factor of 95%

Dose of Zn/1 g of starch mg/g	Average content of zinc mg/g	Estimated deviation σ test X^2	Estimation of average m-test parameter
0.5	0.42731	0.0069 < σ < 0.0186	0.42025 < m < 0.43438
1.0	0.63047	0.0017 < σ < 0.0046	0.62873 < m < 0.63220
1.5	0.73993	0.0023 < σ < 0.0062	0.73757 < m < 0.74230
2.0	0.91370	0.0069 < σ < 0.0185	0.90333 < m < 0.91740

Table 2. Colour parameters in modified starch without fortification and with zinc fortification in systems Yxy and L*a*b*

Modified starch	Colour parameters in systems Yxy			Colour parameters in systems L*a*b*		
	Y	x	y	L	a	b
Potatoes starch Superior Standard no fortification	84.49	0.3124	0.3217	93.66	–1.54	+2.44
Pudding starch no fortification	84.42	0.3135	0.3221	93.63	–1.2	+2.76
Pudding starch with zinc fortification Zn 0.5 mg/g starch	84.86	0.3119	0.3207	93.82	–1.31	+1.97
Pudding starch with zinc fortification Zn 1 mg/1 g starch	84.53	0.3118	0.3207	93.67	–1.35	+1.95
Pudding starch with zinc fortification Zn 1.5 mg/g starch	84.93	0.3117	0.3207	93.85	–1.42	+1.92
Pudding starch with zinc fortification Zn 2 mg/g starch	83.65	0.3134	0.3223	93.29	–1.38	+2.81

between zinc fortified starch and white reference the overall evaluation of colour difference was made in the L*a*b* system according to the following formula:

$$\Delta E = \sqrt{}\,(\Delta L)^2 + (\Delta a)^2\,(\Delta b)^2$$

The colour difference test as specified in the L*a*b* system between the starches fortified with zinc in various mass relations and the non-fortified pudding starch indicated a colour difference only in case of preparation of adsorption with 2 mg Zn per 1 g starch and it was at the level of 1.2, while for the doses of 0.5, 1.0 and 1.5 mg Zn per 1 g starch, the difference was approx. 0.4.

Viscosity of pudding gels prepared entirely from the zinc fortified starch was marked using the Brabender viscograph (Fig. 2). These tests proved a significant impact of zinc ions on the final viscosity of the fortified starch. For the doses of 0.5, 1.0 and 1.5 mg Zn per 1 g starch, the viscosity was higher than for non-enriched pudding starch and reached the range of 690-900 BU. Whereas the dose of 2 mg Zn per 1 g starch caused a dramatic decrease in the gel's viscosity throughout the measurement, and in the final phase it reached the level of merely 120 BU.

Probably this proves that small doses of zinc have a crosslinking effect on starch chains. Zinc cation is bivalent (has two protons in excess), and therefore can attract two atoms of oxygen from various starch chains that have free electron pairs. The maximum viscosity of starch fortified with 0.42 mg Zn per 1 g starch is 470 BU at 91.3°C. The maximum viscosity of starch fortified with 0.63 mg Zn per 1 g starch is 436 BU at 92.5°C. In case of starches fortified with 0.73 mg Zn per 1 g starch and with 0.91 mg Zn per 1 g starch the maximum viscosity is 371 and 59 BU respectively at the temperatures of 91.3°C and 83.5°C respectively. Systematic growth of zinc doses results in a drop of the starch viscosity. The most similar rheological properties – as compared to a non-fortified pudding starch – were observed for a starch fortified with 1.5 mg of zinc (0.74 mg Zn per 1 g of starch). Additions of greater and greater amounts of zinc

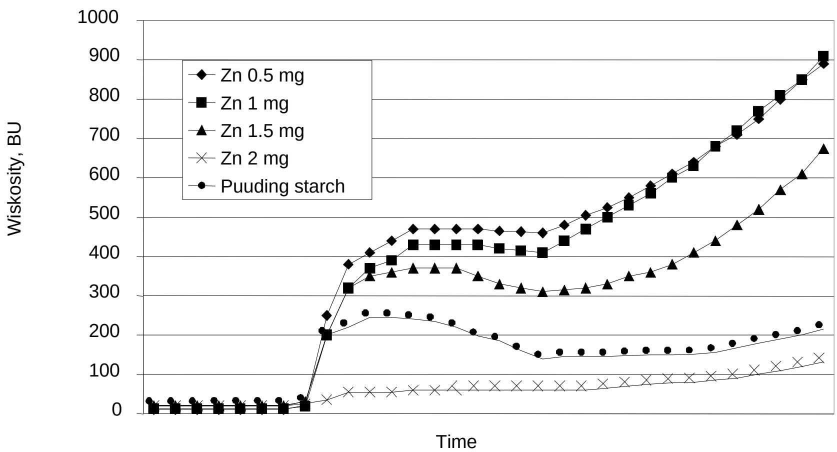

Fig. 2. Course of gel forming of 3.3% gel of pudding starch fortified with zinc ions in Brabender Apparatus

inhibit the gel forming process, which is probably caused by a significant association of starch components, i.e. amylose and amylopectin. It was observed also that an addition of the smallest amounts of zinc (0.5, 1.0 and 1.5 mg Zn per 1 g starch) does not cause any significant shifts of the gel forming process starting temperature. Only the addition of 2.0 mg Zn per 1 g starch caused a quite significant increase of the gel forming temperature (by 2.6°C) in reference to the non-fortified starch, which starts the gel forming process at 64°C.

These results decided on the selection of the best fortified starch used for preparing milk desserts – puddings. The starch was selected with the 0.74 mg Zn per 1 g starch content, for which the gel forming course was similar to the one for the non-fortified pudding starch. For organoleptic tests three desserts were prepared with various doses of pudding starch and fortified starch as well as a pudding from a store. Results are presented in Table 3.

Based on Table 3 the positive organoleptic evaluation was given to pudding no. 1, in which equal quantities of fortified and non-fortified starches were mixed, and 50% of the daily zinc demand of an adult was contained in one portion of the dessert (7.5 mg Zn). This very pudding was characterised by a very good and delicate taste, which was typical for this type of desserts. It had a slightly buttery consistency, but due to this consistency it gave the sensation of melting in the mouth. After four hours, its cross--section was uneven and slightly damaged, but after a few more hours of cooling, it was already smooth and went off the knife easily. Its consistency was the same as in case of pudding prepared from a mix bought in a store. It had no flavour and colour additives, which however had no negative impact on its taste and smell evaluation. The pudding containing more enriched starch and more zinc ions had its consistency changed, was more rubbery and had a perceptible metallic after-taste. These properties disqualified it in the organoleptic test.

Table 3. Recipes of desserts with an addition of zinc fortified starch and their organoleptic evaluation

Sample no	Pudding recipe	Zinc content mg	Portion	Percentage of RDA in 1 portion	Organoleptic evaluation	
					consistency	taste
1	19.4 g pudding starch + 19.4 g starch with Zn + 30 g sugar + 500 ml milk (2% fat)	14.74	2	50	after 4 hours: buttery, sticky cross-section uneven, damaged, rough after 12 hours: it goes off the knife easily, its consistency is exemplary	lack of any strange after-tastes, taste typical for puddings, delicate, melts in the mouth lack of any strange after-tastes, taste typical for puddings, delicate
2	38.8 g starch with Zn + 30 g sugar + 500 ml milk (2% fat)	29.49	2	100	after 4 hours: buttery, sticky, cross-section uneven, damaged after 12 hours: cross--section is even, it goes off the knife easily its consistency is exemplary	strange, explicitly metallic after-taste, which remains in the mouth for a long time although the pudding melts in the mouth, the strange, metallic after-taste remain in the mouth
3	30 g pudding starch + 30 g starch with Zn + 30 g sugar + 500 ml milk (2% fat)	22.80	2	75	after 4 hours: rubbery, jello-like, untypical for puddings, its cross-section is smooth and shiny, its surface is smooth and shiny after 12 hours – without any changes	without and strange after-tastes, it does not melt in the mouth easily, it is more jello-like without any changes

CONCLUSIONS

The objective of this research was to develop a foodstuff fortified with zinc ions. It was proven that:

1. Pudding starch is a good adsorbent of zinc ions. The best efficiency of the process is reached with small concentrations of ions in the solution for adsorption.
2. Colour of the fortified starch preparations does not diverge greatly from the white reference. The course of the gelling process in case of starch enriched with zinc ions is different from the one for the non-fortified pudding starch.
3. Viscosity of fortified starch decreased with a growth of zinc content. The most similar course of gel formation – as compared to pudding starch from a store – was observed for a starch fortified with 1.5 mg of zinc per 1 g of starch.

4. The appropriately composed recipe of the pudding powder gave a positive effect. The pudding in which one portion contained approx. 7.5 mg zinc (50% RDA) received a positive organoleptic evaluation and can be recommended as a zinc enriched foodstuff.

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BADANIE NAD SKROBIĄ ZIEMNIACZANĄ FORTYFIKOWANĄ CYNKIEM I WYKORZYSTANIEM JEJ W PRODUKCJI DESERÓW

Wprowadzenie. Skrobia ziemniaczana modyfikowana jest wykorzystywana jako substancja zagęszczająca w produktach spożywczych lub jako komponent deserów. Modyfikacja przez utlenianie powoduje wytworzenie wewnątrz granulek skrobiowych reszt karboksylowych, które mogą wiązać pierwiastki koordynacyjnie. Cynk jest jednym z niezbędnych mikroelementów w organizmie człowieka. Celem badań było określenie poziomu adsorpcji cynku na skrobi modyfikowanej utlenionej i zbadanie zmian jej właści-

wości funkcjonalnych oraz możliwości zastosowania do produkcji suchych mieszanek deserów mlecznych typu budyń.
Materiał i metody. Zbadano efektywność adsorpcji z użyciem spektroskopii AAS (met. płomieniowa). Barwę powstałych preparatów badano kolorymetrem Chroma Meter CR-300 firmy Minolta, a do sprawdzenia przebiegu krzywej kleikowania 3,3% kleików skrobiowych używano wiskozymetru Brabendera.
Wyniki. Efektywność adsorpcji wahała się od 49 do 84% w zależności od stężenia soli użytej do adsorpcji. Barwa preparatów z cynkiem nie wykazała istotnych różnic, natomiast lepkość była zmienna i większa od lepkości skrobi budyniowej niewzbogaconej. Wyniki przeanalizowano i stworzono recepturę budyniu fortyfikowanego cynkiem.
Wnioski. Produkt o najlepszych walorach smakowych i organoleptycznych uzyskano dzięki dodatkowi skrobi fortyfikowanej w ilości będącej nośnikiem w jednej porcji 50% dawki dziennej cynku dla organizmu ludzkiego.

Słowa kluczowe: skrobia modyfikowana, skrobia utleniona, fortyfikacja spożywcza, cynk, budyń – deser mleczny

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