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Effect of mineral elements on physicochemical properties of oxidised starches and generation of free radicals

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ABSTRACT

The objective of this study was to determine the effect of enrichment of oxidised starches with mineral compounds on their physicochemical properties and capability for free radical generation. Potato and spelt wheat starches were oxidised with sodium hypochlorite and, afterwards, modified with ions of potassium, magnesium and iron. The modified starches were analysed for: content of mineral elements, colour parameters ($L^*a^*b^*$), water binding capacity solubility in water at temperature of 50 and 80 °C, and susceptibility to enzymatic hydrolysis with α-amylase. In addition, thermodynamic characteristics of gelatinisation was determined by differential scanning calorimetry (DSC), and the number and character of thermally generated free radicals was assayed using electron paramagnetic resonance (EPR). Based on the results achieved, it was concluded that the quantity of incorporated minerals and changes in the assayed physicochemical parameters depended not only on the botanical type of starch but also on the type of the incorporated mineral element.

1. Introduction

Mineral elements constitute a group of chemical compounds indispensable for proper body functioning. In a human's body, they serve building functions, control metabolic processes, ionic balance and cell pressure, and sustain neuromuscular excitability. Owing to a lack of appropriate enzymatic systems, the minerals are not synthesised in a human body and have to be provided with food (Frossard, Bucher, Machler, Mozafar, & Hurrell, 2000; Soetan, Olaiya, & Oyewole, 2010). Nowadays, due to the contemporary lifestyle, demands for micro- and macroelements supplied with food products are observed to increase. Hence, producers are in the constant search for food components that would not only increase the sensory values of food, but would additionally be good carriers of deficit substances to the human body, including mineral elements (Śmigielska & Lewandowicz, 2007).

Starch is one of the natural and renewable raw materials abundant in nature. Owing to its specific structure, it easily interacts with different chemical substances, which results in the formation of modified starches with desirable physicochemical properties. For this reason, native and modified starches are one of the most multifunctional raw materials applied in the food industry (Tharanathan, 2005). One of the chemical methods of starch modification is its oxidation, which results in the formation of carbonyl and carboxyl groups. Their presence in oxidised starch enables better binding of metal ions (Kweon, Choi, Kim, & Lim, 2001; Śmigielska, Lewandowicz, Goslar, & Hoffman, 2005). Thereby, it is feasible to apply oxidised starch as a carrier of micro- and macroelements in a human diet, thus preventing metabolic diseases that result from the intake of excessively processed foods or from ill-balanced diets (Śmigielska & Le Thanh-Blicharz, 2010; Śmigielska, Lewandowicz, & Walkowski, 2005). This affords great opportunities for food producers and facilitates the production of foods enriched with mineral elements deficient to human. Owing to their physicochemical properties, the oxidised starches are integral constituents of creams, puddings, whipped cream, powder cake mixtures, sprinkles and coatings (Wurzburg, 1987).

Nevertheless, the presence of mineral elements incorporated to oxidised starches affects not only an increase in its nutritive value but also its physicochemical properties. Hence, the objective of this study was to determine the impact of mineral elements on physicochemical properties of oxidised starches and their capability for free radicals generation.

2. Materials and methods

2.1. Materials

The starch used for the study was potato starch produced by PPS Pepees S.A. (Łomża, Poland) and spelt starch isolated with the

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laboratory method from ECCO type 700 spelt wheat flour (Młyn Gospodarczy, Poland).

Oxidation was carried out following a procedure described by Forsell, Hamunen, Autio, Suorti, and Poutanen (1995). The modification was conducted in a 40% water suspension of starch, using NaClO (POCh, Poland) in amounts equivalent to 10 g Cl per kg of starch. The solution with pH = 10 was stirred for 50 min at temperature 20 ± 0.5 °C, neutralised to pH = 7, stirred and washed. Then, the starch samples were pulverised, dried and sieved.

The starches were modified by reactions with potassium, magnesium and iron ions. Potassium, magnesium and iron were incorporated into starch according to the following procedure. 100 g of starch were mixed with 250 cm^3 of water for 5 min and then the resulting dispersion was filtered through a filter funnel. The starch was mixed for 5 min with 200 cm^3 of the mixture of 1% (w/w) KCl and 0.05 M KOH in the volume ratio of 1:1 and of pH 12 or with 200 cm^3 of the mixture of 1% (w/w) $MgCl_2$ and saturated solution of $Mg(OH)_2$ in the volume ratio of 1:1 and of pH 8.5, or 1% (w/w) $FeSO_4$ respectively, for potassium, magnesium and iron. The resultant product was filtrated through a filter funnel and again 200 cm^3 of the mixture of potassium or magnesium salts and hydroxides or iron salt were added to the retentate, and then the sample was mixed for 5 min and filtrated. This action was repeated once again. The resultant starch preparation was rinsed with distilled water until chloride ions were absent, for modification with iron until sulphur ions were absent. Then, the starch samples were pulverised, dried and sieved.

2.2. Effectiveness of the oxidation process, potassium (K), magnesium (Mg) and iron (Fe) content

Oxidised starches were examined for: the carboxyl group content according to the Standard method ISO 11214 (1996), carbonyl group content according to Whistler, BeMiller, and Paschall (1967), and potassium (K), magnesium (Mg) and copper (Cu) contents by Atomic Absorption Spectroscopy using an Avanta Sigma spectrometer (GBC, Australia) with an air-acetylene burner, measured at λ = 324 nm. Prior to measurement, starch was mineralised in a mixture of nitric acid and sulphuric acid at a temperature of 250 °C, using a Wet Digester B-440 (Büchi, Switzerland).

2.3. Colour parameters

Colour parameters of the samples before and after heating (at temperature 150 °C 30 min, and 210 °C 30 min) were determined in the CIE $L^*a^*b^*$ system (measuring geometry d/8°, illuminant D65, observer 10°) using a Colour i5 spectrophotometer (X-Rite, USA). Total colour difference (ΔE) between oxidised and oxidised and modified with metals starches was calculated according to the equation:

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

2.4. Water-binding capacity and solubility in water

Water-binding capacity and water solubility at temperatures of 50 and 80 °C were determined by the modified method of Leach (Richter, Augustat, & Schierbaum, 1968). A 1.25% (w/v) starch suspension was heated during 30 min at temperatures 50 and 80 °C and after this, the starch paste produced was recovered by mild centrifugation (2500 × g, ×15 min). Water binding capacity was calculated on dry mass of starch and solubility was based on soluble starch.

2.5. Susceptibility to enzymatic hydrolysis

The susceptibility to enzymatic hydrolysis was determined using α-amylase type VI-B, from porcine pancreas, activity 28 u/mg solid (Sigma–Aldrich, USA) following the method by Hung and Morita (2005) with own modification. To 40 mg of starch were added 38 cm^3 of water and 2 cm^3 solution (10 mg of α-amylase in 10 cm^3 0.05 M NaCl) of enzyme. The enzymatic hydrolysis of starch was maide at temperature 37 °C. Maltose content after hydrolysis was measured based on a colour reaction with 3,5-dinitrosalicylic acid after 20, 40, 60, 80, 100, and 120 min using a spectrophotometer. The extent of starch hydrolysis was presented as the percentage content of maltose in starch.

2.6. Thermodynamic characteristics of gelatinisation by DSC

The thermodynamic characteristics of gelatinisation were determined by using a differential scanning calorimeter DSC 204F1 (Phoenix Netsch, Germany). A starch–water (1:3) mixture was added to aluminium calorimetric cells, and left to stand for 24 h. Then, the samples were heated at temperatures in the range of 20–100 °C at a rate of 10 °C/min. An empty identical calorimetric cell was used as a reference. The temperatures at onset (T_o), peak (T_p), and end (T_e) of transition, and the enthalpy of transition related to the weight of starch (ΔH, J/g d.m.) were read from the thermograms.

2.7. EPR measurements

Samples of starch (about 20 mg) were placed in the quartz EPR tubes and heated in an oven upon air for 30 min at 423 K, followed by 30 min at 483 K. Before recording the EPR spectra, the tubes with the samples were cooled to a room temperature and closed with a paraffin membrane. Samples of starch enriched with iron ions were also studied without thermal treatment. EPR measurements were carried out on an X-band Bruker ELEXSYS 500 spectrometer (Karlsruhe, Germany) with 100 kHz field modulation. The spectra were recorded at 293 K with modulation amplitude of 0.5 mT and 0.1 mT before and after thermal treatment of the samples. They were registered at microwave powers: 10.0 and 3.0 mW. The 1,1-diphenyl-2-picrylhydrazyl (DPPH) was used as a g factor standard and as a reference sample (with the number of spin equal to 1.07×10^{15}/g) for the estimation of radicals number in the samples. The maximum error of the quantitative measurements was 0.05×10^{15} spin/g.

EPR parameters such as g-factor value, hyperfine splitting constant A and peak-to-peak line width ΔB_{pp} were found by a simulation procedure, using the program SIM 32 (Spałek, Pietrzyk, & Sojka, 2005). The accuracy of determination of EPR parameters was ±0.0005 for g values and ±0.1 mT for parameters A of radical signals, whereas g factor of iron species was estimated with the accuracy of 0.02.

2.8. Statistical analysis

The significance of differences between the values of the parameters was assessed by using the one-way analysis of variance and the Tukey test at a significance level $\alpha = 0.05$.

3. Results and discussion

3.1. Effectiveness of the oxidation process, potassium (K), magnesium (Mg) and iron (Fe) contents

After oxidation, starches contained respectively, 0.035 ± 0.002% (potato starch) and 0.012 ± 0.001% (spelt starch) of carboxyl groups