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Effect of metal ions on physicochemical and rheological properties of octenyl succinate starches

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ABSTRACT

The objective of this study was to determine the effect of substituting octenyl succinate potato starches with magnesium, calcium and potassium ions on their physicochemical and rheological properties. Materials used for the study were potato starches esterified with using 30 mL/kg or 90 mL/kg of octenyl succinic anhydride (OSA) and afterwards substituted with metal ions. The effectiveness of the esterification process and contents of magnesium, calcium, and potassium were determined in the study. All starch samples were analysed for: molecular weight distribution, water binding capacity and solubility in water. Pasting properties, intrinsic viscosity and flow curves were studied as well. The results indicated that the apparent number-average (M_n) and weight-average (M_w) molecular weights as well as intrinsic viscosity of OSA starches decreased, with the greatest effect observed for the substitution with magnesium ions. The OSA starches substituted with potassium ions showed the highest solubility in water. In turn, the presence of magnesium ions in the starches esterified with 30 mL/kg of OSA resulted in a decrease in all viscosity values and also in values of shear stress within the shear rate range. Out of the starches esterified with 90 mL/kg of OSA such changes were observed upon substitution with calcium ions.

1. Introduction

Octenyl succinate starch (so-called OSA starch) is usually produced in the reaction of octenylsuccinic anhydride (n-OSA) with native starch in an alkaline aqueous solution (Hui, Qi-he, Ming-liang, Qiong, & Guo-qing, 2009). The modification extent of OSA starch used in food products is limited by legislation (Commission Regulation, 2012). Due to the presence of hydrophilic and hydrophobic groups, OSA starches are characterized by physicochemical properties significantly different from these of their non-modified counterparts. Starch octenyl succinate esters are widely used in many industries, particularly where surface active properties are desired. In the food industry, OSA starch is mainly applied as an emulsifier in salad dressings, creams, and beverages (Chaudhari, Pan, & Nitin, 2015; Chivero, Gohtani, Hidefumi, & Nakamura, 2016; Tesch, Gerhards, & Schubert, 2002; Yusoff & Murray, 2011).

In order improve the application properties of starch, some researchers have combined different methods of its modification and termed them as dual modifications. For example, Fouladi and Mohammadi Nafchi (2014) found that dual modification of sago starch by acid hydrolysis and propylene oxide hydroxypropylation has synergistic effect on the physicochemical properties of obtained starch. Dual modification of starch was also performed by Mehboob, Moshin Ali, Alam, and Hasnain (2015), who investigated the effect of succinylation, acid-thining and combination of both method on selected properties of white sorghum starch. Authors found, that succinylation improved cold storage stability and reduced the percent of retrogradation of acid-thinned starches. Dual modification of starch using combination of octenylsuccinylation and any other methods (e.g. substitution with mineral elements) is also a potential way to alter the physicochemical and functional properties of obtained starch derivatives (Królikowska,Fortuna, Grabarz, & Pająk, 2014). Čižová, Sroková, Sasinková, Maloviková, and Ebringerowa (2008) showed that octenyl succinates of carboxymethyl starch derivatives exhibited excellent emulsifying properties, which were comparable and even

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better than these of the commercial synthetic emulsifier. While, Ren et al. (2016) performed the crosslinking of a starch nanocrystals (SNCs) followed by their esterification using OSA. In this case, the dual modification led to a decrease in polarity and to an increase in hydrophobicity of SNCs.

Food processing has been demonstrated to contribute to a reduction in the content of vitamins and minerals in the finished product (Watzke, 1998). One of the new methods for dual modification of starch is its chemical modification and reaction with metal ions (Śmigielska & Le Thanh-Blicharz, 2010). The purpose of this modification is to enhance starch properties particularly in specific applications such as to improve its nutritive value. One of the elements essential for human nutrition is magnesium. It takes part in more than 300 biochemical processes in the human body and affects the proper functioning of the immune, nervous, and neuromuscular systems. Another essential element is calcium, which is a constituent of bones and teeth. It also assists in blood clotting, muscle contraction, and nerve transmission. An important dietary mineral is also potassium, which is the major cation of the intercellular fluid and ensures the acid-base balance, regulation of osmotic pressure, and conduction of nerve impulses (Soetan, Olaiya, & Oyewole, 2010).

Starch - especially in the modified form - is reported to be a good carrier of mineral elements (Kweon, Choi, Kim, & Lim, 2001; Rożnowski, Fortuna, Szuba, & Łabanowska, 2015). Nevertheless, metal ions introduced into a starch structure affect its functional properties. The influence of OSA starch substitution with metal ions on its properties has not been investigated yet, hence it requires a comprehensive view. The objective of this study was, therefore, to evaluate the effect of substituting octenyl succinate potato starches with magnesium, calcium and potassium ions on their physicochemical and rheological properties.

2. Materials and methods

2.1. Materials

The starch used in the study was native potato starch “Superior Standard” purchased from PEEPES S.A. (Lomza, Poland). High-purity octenyl succinic acid anhydride (n-OSA) was supplied from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA).

The OSA starch samples were prepared according to Hui et al. (2009) procedure. The esterification was conducted in a 350 g/kg water starch water suspension. The pH of the suspension was adjusted and maintained at 8.5 by addition of 30 g/L NaOH solution. Then, the octenyl succinic anhydride solution in concentrations of 30 mL/kg or 90 ml/kg (calculated per d.w. of starch) was added by dropping to the starch suspension for 1 h and agitation was continued for 3.5 h at 35 °C ± 2. Then pH value was adjusted to 6.5 with a 30 mL/kg HCl solution. The resulted mixture was centrifuged, rinsed twice with water and twice with 700 mL/L ethanol solution, each time the residue was centrifuged. Afterwards, the starch samples were dried, milled and sieved. To obtain a blank sample (called as non-esterified starch), the same process was carried out without any addition of OSA to the starch solution.

The OSA starches with a different degree of substitution were substituted with metal ions: magnesium, calcium and potassium according to Królikowska, Fortuna, Pietrzyk, and Gryszkin (2017) procedure. A suspension of 100 g of OSA starch in 250 mL of water after mixing for 5 min was filtered through a filter funnel. Afterwards, 200 mL of the solution of the particular metal salt was added to the starch and mixed for 5 min. The mixtures of 10 g/L $MgCl_2$ and a saturated solution of $Mg(OH)_2$ in the volumetric ratio of 1:1, 10 g/L $CaCl_2$ and a saturated solution of $Ca(OH)_2$ in the volumetric ratio of 1:1 or 10 g/L KCl and 0.05 mol/L KOH in the volume ratio of 1:1, respectively, for magnesium, calcium or potassium were used. The obtained product was strained through a filter funnel. After filtration, again 200 mL of the above-mentioned mixtures of magnesium, calcium or potassium salts and hydroxides were added to the retentates and the samples were stirred for 5 min again. The action was repeated one more time. The starch was rinsed with distilled water until chloride ions were absent and then it was filtered, air dried and sieved.

2.2. Methods

2.2.1. Effectiveness of the esterification process, contents of magnesium (Mg), calcium (Ca) and potassium (K)

The OSA starches were examined for the degree of substitution (DS). The DS of OSA starches was determined with the titration method (Hui et al., 2009) and calculated using the following equation (1):

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

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

The introduction of carbonyl and carboxyl groups into starch chain was confirmed by FTIR–ATR spectra of the non-esterified and OSA modified starches recorded in the range of 4000-700 cm^{-1} at 4 cm^{-1} resolution using a MATTSON 3000 FT-IR (Madison, Wisconsin, USA) spectrophotometer equipped with a 30SPEC 30 Degree Reflectance adapter fitted with the MIRacle ATR accessory (PIKE Technologies Inc., Madison, Wisconsin, USA).

The OSA starches substituted with metal ions were also examined for magnesium, calcium and potassium contents. Starch was mineralised in a mixture of nitric acid (650 g/kg) and sulphuric acid (950 g/kg) in a volumetric ratio of 1:1 for 150 min at a temperature of 250 °C (Wet Digester, Büchi, Flawil, Switzerland). The quantitative analysis was performed by atomic absorption spectrometry (Avanta Sigma, Braeside, Victoria, Australia) in acetylene/air flame.

2.2.2. Molecular weight distribution

The molecular weight distribution of starches was determined with a gel permeation chromatography (GPC). The column OHpak SB-806 and OHpak SB - 805 (Shodex, Tokyo, Japan) thermostated at a temperature of 25 °C and connected with an RI detector (Knauer, Berlin, Germany) was used and a flow rate was set to 0.5 mL min^{-1}. The apparent number-average (M_n) and the apparent weight-average (M_w) molecular weights of starch were calculated related to standard solutions of Pullulan Standard P-82 (Shodex). A 0.1 mol/L sodium nitrate solution containing 0.2 g/kg sodium azide was used as an eluent.

2.2.3. Water binding capacity and solubility in water

Water binding capacity and solubility in water at temperatures of 55 and 75 °C were determined with the modified method of Leach, McCowen, and Schoch (1959). Distilled water (70 mL) was added to 1 g of starch (based on d.w.) in a weighed centrifuge tube. Starch suspension was heated with constant stirring during 30 min at temperatures of 55 or 75 °C. Afterwards distilled water was added to the mixture to make the total volume up to 80 mL. The suspension was centrifuged at 1500 g for 15 min. To determine the solubility in water, 20 mL of supernatant was taken to pre-weighed weighing vessel, then evaporated, and dried at 130 °C to the constant weight. Solubility in water was calculated using the following equation (2):