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Short communication

Selected properties of acetylated adipate of retrograded starch☆

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ABSTRACT

Native potato starch (NS) and retrograded starch (R – obtained via freezing and defrosting of a starch paste) were used to prepare starch acetates: NS-A and R-A, and then acetylated distarch adipates: NS-ADA and R-ADA. The chemically-modified preparations produced from retrograded starch (R-A; R-ADA) were characterized by a higher degree of esterification compared to the modified preparations produced under the same conditions from native potato starch (NS-A; NS-ADA). Starch resistance to amylolysis was observed to increase (to 30–40 g/100 g) as a result of starch retrogradation and acetylation. Starch cross-linking had a significant impact on the increased viscosity of the paste in the entire course of pasting characteristics and on the increased values of rheological coefficients determined from the equations describing flow curves. The produced preparation of acetylated retrograded starch cross-linked with adipic acid (R-ADA) may be deemed an RS3/4 preparation to be used as a food thickening agent.

1. Introduction

Starch, which is a storage substance of many plants, is produced on the industrial scale mainly from maize, rice, potato, tapioca and wheat. The applicability of starch in the native form is low, but hydrolysates and modified preparations produced from it are widely used in practice (Zięba, 2009). One of the newest modified starch preparations used as a health-promoting food additive is resistant starch that occurs in various forms: RS1 – starch inaccessible to digestive enzymes, present in undigested plant cells; RS2 – non-pasted starch of selected plants (e.g. potato); RS3 – retrograded starch (Englyst, Kingman, & Cummings, 1992), RS4 – chemically- or physically-modified starch (Haralampu, 2000); and RS3/RS4 – retrograded chemically-modified starch (Zięba, Szumny, & Kapelko, 2011a). The name of the last type of starch was proposed after investigations of acetylated starch produced from retrograded potato starch (Kapelko, Zięba, Golachowski, & Gryszkin, 2012a; Kapelko, Zięba, & Michalski, 2012b; Zięba, Kapelko, & Gryszkin, 2007; Zięba, Juszczak & Gryszkin, 2011; Zięba et al., 2011a; Zięba, Szumny, & Kapelko, 2011b; Zięba, Kapelko, & Szumny, 2013). This type of starch is characterized by significant resistance to the action of amylases (ca. 40%) and – unlike preparations of RS3 starch available on the market – is capable of re-forming viscous pastes (Kapelko et al., 2012a; Zięba et al., 2011). The modification which has a positive impact on the rheological properties of prepared pastes is the cross-linking of starch with residues of adipic or phosphoric acid (Singh, Kaur, & McCarthy, 2007). The application of such modification to produce RS3/RS4 starch may increase the resistance and viscosity of pastes.

The aim of the present study was to produce acetylated adipate of retrograded starch via multi-stage modification of potato starch and to determine the effect of the applied modifications on selected properties of the resultant preparations.

2. Methodology

2.1. Materials

The initial experimental material included Superior Standard potato starch produced by PPZ Niechlów in 2010. Starch was modified with analytically pure acetic acid anhydride and analytically pure adipic acid, both purchased at POCH SA Gliwice, Poland.

2.2. Production of preparations

Starch preparations were produced according to the scheme presented in Fig. 1 (symbols used throughout the manuscript were provided in brackets in the Figure). Pastes were produced from native potato starch in the concentration of 10 g of starch per 100 g of solution, frozen at a temperature of −20 °C for 3 days and defrosted at a temperature of 20 °C for 2 days. The precipitated starch with a spongy structure was rinsed with distilled water, dried in an air dryer at a temperature of 30 °C for 24 h, ground and

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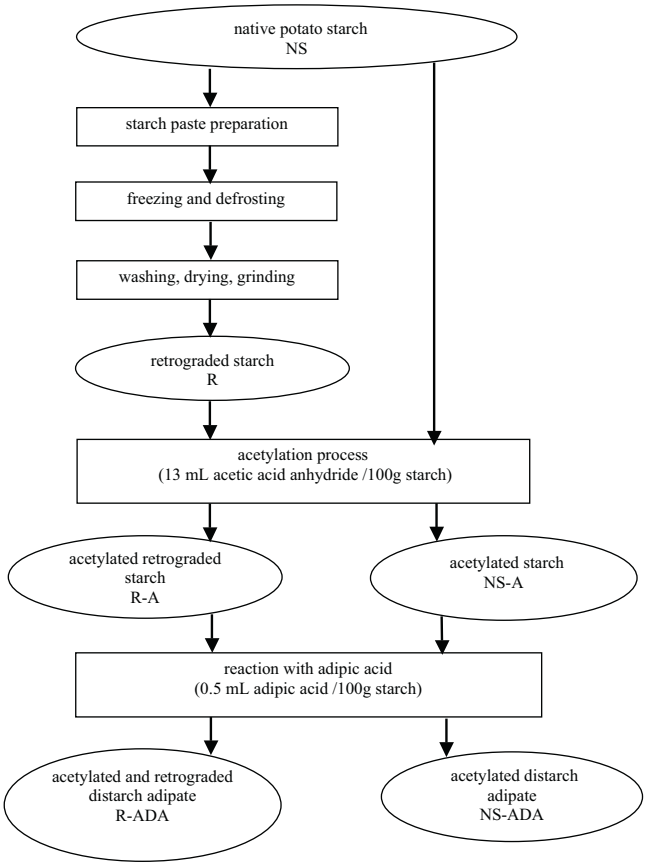

Fig. 1. Scheme of acetylated adipate production of retrograded or native starch.

sieved through a screen with a mesh diameter of 400 μm (Kapelko et al., 2012a).

Native starch (NS) and the produced preparation of retrograded starch (R) were acetylated with acetic acid anhydride under conditions provided by Kapelko et al. (2012a). The basic dose of acetic acid anhydride was adapted correspondingly to its quantity used in the acetylation process in the starch industry (13 mL/100 g starch).

The cross-linking of native starch and retrograded starch with adipic acid was conducted analogously to acetylation by instilling 1 mL of the cross-linking agent and hot-dissolving 20 g of adipic acid in 80 g of acetic anhydride.

The produced preparations of acetylated native starch (NS-A), acetylated native starch cross-linked with adipic acid (NS-ADA), acetylated retrograded starch (R-A), and acetylated retrograded starch cross-linked with adipic acid (R-ADA) were rinsed with distilled water, dried in an air dryer at a temperature of 30 °C for 24 h, ground and sieved through a screen with a mesh diameter of 400 μm.

2.3. Determination of the content of acetate groups

Ten grams of the preparations were poured into a conical flask, filled with 65 mL of distilled water, and neutralized by adding a few drops of 0.01 M NaOH in the presence of phenolphthalein until pale pink color was maintained for ca. 1 min. Next, 25 mL of 0.5 M NaOH was added and blended at ca. 25 °C for 35 min. The resultant mixture was titrated with 0.5 M HCl (Golachowski, 2003). The percentage of acetylation was calculated according to the method of Wurzburg (1964):

$$\text{percent of acetylation} = \frac{(25 - x) \cdot 0.043 \cdot 0.5 \cdot 100}{a} \left[\text{g}/100\text{g}\right]$$

where x – amount of 0.5 M HCl used for titration of a sample, and a – weight of starch (in conversion to dry weight).

2.4. Determination of the content of adipate groups

One gram of the cross-linked starch was weighed and transferred to a conical flask using 50 mL of distilled water. Then, 1 mL of an aqueous solution of glutaric acid was added to starch, the sample was mixed and 50 mL of 4 N NaOH was added. The sample was mixed for 5 min on a shaker. Afterwards, 20 mL of 12 N HCl were added and the flask was placed in a cold water batch. The cooled mixture was extracted three times with 100 mL of ethyl acetate in a separator into 250 mL. Each time, the upper layer was decanted to a conical flask containing 20 g of anhydrous potassium sulfate. The flask with the mixture was shaken for 10 min in a water bath with a shaker, and then the mixture was filtered. The filtrate was evaporated under vacuum at a temperature of 40 °C, under the pressure of 50 mmHg. Afterwards, 2 mL of pyridine and 1 mL BSTFA were added to dry residues, the mixture was mixed for homogenization and left for 1 h at a room temperature. Then, 2 mL were sampled to an ampoule and analyzed. Chromatographic assays were carried out on a PYE UNICAM series 104 gas chromatograph with an FID detector and a glass column (2.1 m in length and 1.83 mm in diameter). The mobile phase was 5% OV-17 on G DMCS AW chromosorb with 100/120 mesh granulation.

Parameters of separation:

Carrier gas – nitrogen; flow rate – 40 mL/min; detector temperature – 250 C; injector temperature – 240 C; column temperature – 140 C; injection volume – 0.1 μL; retention time: 2.8 min with glutaric acid, 4.5 min with adipic acid.

2.5. Determination of resistance to amyloglucosidase (Zięba et al., 2011a)

Under continuous stirring, starch suspensions were heated to the boiling temperature and then cooled to a temperature of 37 °C at which the samples were hydrolyzed with amyloglucosidase (Amigase by Genecor, Denmark). The concentration of the enzyme was adjusted so as to assure the complete saccharification of pasted native starch after 120 min of the process. The content of free glucose was determined with the use of a CECIL CE 2010 colorimeter (Cecil Instruments, England) at a wavelength of $\lambda = 500$ nm, using a Biosystem company (Spain) reagent for glucose concentration assay that contains glucose oxidase and peroxidase.

2.6. Determination of pasting characteristics with a Brabender viscograph (Zięba et al., 2013)

Pasting characteristics was determined with a Brabender viscograph (Germany), using a measuring vessel (700 cmg type). Briefly, 450 mL of a suspension containing 6 g of starch per 100 g of solution were was prepared in the viscograph vessel. The suspension was heated to a temperature of 40 °C under stirring at 75 rpm and kept at this temperature for 10 min. Afterwards, contents of the vessels were heated at the rate of 1.5 °C/min to a temperature of 94 °C, and kept at this temperature for 10 min. Then, the mixture was cooled to 30 °C at the rate of 1.5 °C/min and kept at this temperature for another 10 min.