



Analysis of molecular structure of starch citrate obtained by a well-established method[☆]



Małgorzata Kapelko-Żeberska^{a,*}, Krzysztof Buksa^c, Antoni Szumny^b, Tomasz Zięba^a,
Artur Gryszkin^a

^a Department of Food Storage and Technology, Wrocław University of Environmental and Life Sciences, Chelmońskiego 37/41, 51-630 Wrocław, Poland

^b Department of Chemistry, Wrocław University of Environmental and Life Sciences, C. K. Norwida 25, 50-375 Wrocław, Poland

^c Department of Carbohydrates Technology, University of Agriculture in Krakow, Balicka 122, 30-149 Krakow, Poland

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ABSTRACT

Nuclear magnetic resonance spectroscopy (NMR) and high-performance size exclusion chromatography (HPSEC) were applied to investigate the molecular structure of starch citrate produced under various conditions. Native potato starch and retrograded starch (produced by freezing and defrosting of native potato starch in the concentration of 10 g of starch per 100 g of solution) were roasted at 100 °C with citric acid applied at doses of 10 or 20 g per 100 g starch. The NMR analyses of the produced starch citrates demonstrated that retrograded starch was characterized by greater susceptibility to esterification than the native starch, and that only starch esters were produced upon esterification conducted under the applied experimental conditions. The molecular mass (M_w) distribution profiles of diesters and products after basic de-esterification as well as the molecular mass balance enabled concluding that intermolecular crosslinking occurred between dextrans (produced during acidic hydrolysis) that were linking with each other or were attaching to high-molecular amylopectin. The study excluded explicitly the formation of crosslinks between high-molecular fractions of starch.

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1. Introduction

Starch citrate is an ester of two compounds of natural origin. Citric acid occurs in many organisms because it is an intermediate compound in the Krebs's cycle. It is produced on the industrial scale mainly via citrate fermentation and is used as a food additive (E330) as an acidity modifier and antioxidant. Starch – which is a natural renewable biopolymer – serves the function of a storage substance of many plants and is produced on the industrial scale from, e.g., cereals or potato. The applicability of starch in the native form is little. Its properties may, however, be changed through enzymatic, physical or chemical modifications. The modified preparation may then be applied in the food industry as well as in

other industry branches as, e.g. component of textile dressings or drilling fluids.

Esterification of starch with citric acid decreases its solubility in water (Olsson, Hedenqvist, Johansson, & Järnström, 2013; Ma, Jian, Chang, & Yu, 2008) and susceptibility to enzymatic hydrolysis (Xie & Liu, 2004) along with an increasing degree of substitution. Considering the practical application of starch citrates, two main concerns are addressed in scientific studies, the results of which may found in worldwide literature. The first concern is the use of this modified preparation in biodegradable plastics (Olivato, Grossmann, Yamashita, Eiras, & Pessa, 2012; Kahar, Ismail, & Othman, 2012). The hydrophilic character of native starch curbs wider application of this biopolymer because plastics produced with its addition change their properties in contact with water (Figiel, Zięba, & Leszczyński, 2004). The use of sodium citrate allows eliminating this drawback of plastics (Olsson et al., 2013). The second research trend addresses both the production of the so-called resistant starch (i.e. not digested in the alimentary tract of man) which plays a health-promoting role in the body (Shin et al., 2009) as well as determination of the possibilities of its application in food production (Wepner et al., 1999). The low-substituted

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* Corresponding author.

E-mail address: malgorzata.kapelko@wnoz.up.wroc.pl (M. Kapelko-Żeberska).

starch citrate, which will often be resistant to amylolysis and will not lose its hydrophilic properties, may become a carrier of bioactive or therapeutic substances.

Citric acid possesses three hydroxyl groups. Therefore, its reaction with starch may result in the formation of both starch monoesters and starches crosslinked with acidic residues (Fig. 1). Properties of the resultant modified preparation are determined by the mode of linking, by the degree of substitution with citric acid residues and by the type of starch applied (Ostrio et al., 2014; Tharanathan, 2005; Xie & Liu, 2004). In a work by Menzel et al. (2013), a titration method was developed for the quantitative determination of mono and diesters of starch with citric acid. Scientific literature lacks, however, works on the esterification of retrograded starch with citric acid and on the molecular structure of starch citrates determined with the technique of nuclear magnetic resonance (NMR) and high-performance size exclusion chromatography (HPSEC).

The aim of this study was to determine – using high-performance NMR and HPSEC – the molecular structure of starch citrate produced under various conditions from native and retrograded potato starch as well as to determine the effect of the type of raw material applied and reagent dose on selected properties of the resultant modified preparation.

2. Materials and methods

2.1. Materials

The initial material included Superior Standard potato starch produced by PEPEES Łomża and citric material purchased at POCH SA Gliwice, Poland.

2.2. Production of retrograded starch preparation

Retrograded starch was produced according to methodology provided by the authors in their earlier works (Kapelko, Zięba, Golachowski, & Grysztyn, 2012). To this end, native potato starch was used to prepare a 5-kg portion of paste with the concentration of 10 g of starch per 100 g of the solution. For complete pasting of starch, the paste was left in a water bath (Memmert, Germany) at 94 °C for 6 h, afterward cooled, frozen for 3 day at –20 °C and defrosted for 2 day at 20 °C. The precipitated starch with a spongy structure was rinsed with distilled water, dried in an air dryer (Memmert, Germany) at 35 °C for 24 h, ground and sieved through a screen with mesh size of 400 μm.

2.3. Production of starch preparations esterified with citric acid

The crosslinking of starch with citric acid was conducted according to the methodology described by Klaushofer, Berghofer, and Steyrer (1978), by changing reagent dose and roasting temperature. Native starch (NS) or retrograded starch (R) were esterified with citric acid using two doses of the reagent (Fig. 2). Appropriate doses of the acid (10 or 20 g per 100 g of starch dry matter) were dissolved in water, then solution's pH was adjusted to 3.5 using a 10 mol/L NaOH solution. Native or retrograded starch was thoroughly mixed with the citric acid solution. Moisturized starch was conditioned for 12 h at a room temperature, then dried in an air dryer (Memmert, Germany) at 50 °C for 12 h. The dried material was roasted at 100 °C for 3 h. In order to remove the unbound citric acid, the roasted samples were rinsed three times with ethyl alcohol (at the alcohol: preparation ratio of 5:1), each time decanting the solution from above the precipitate. The eluted

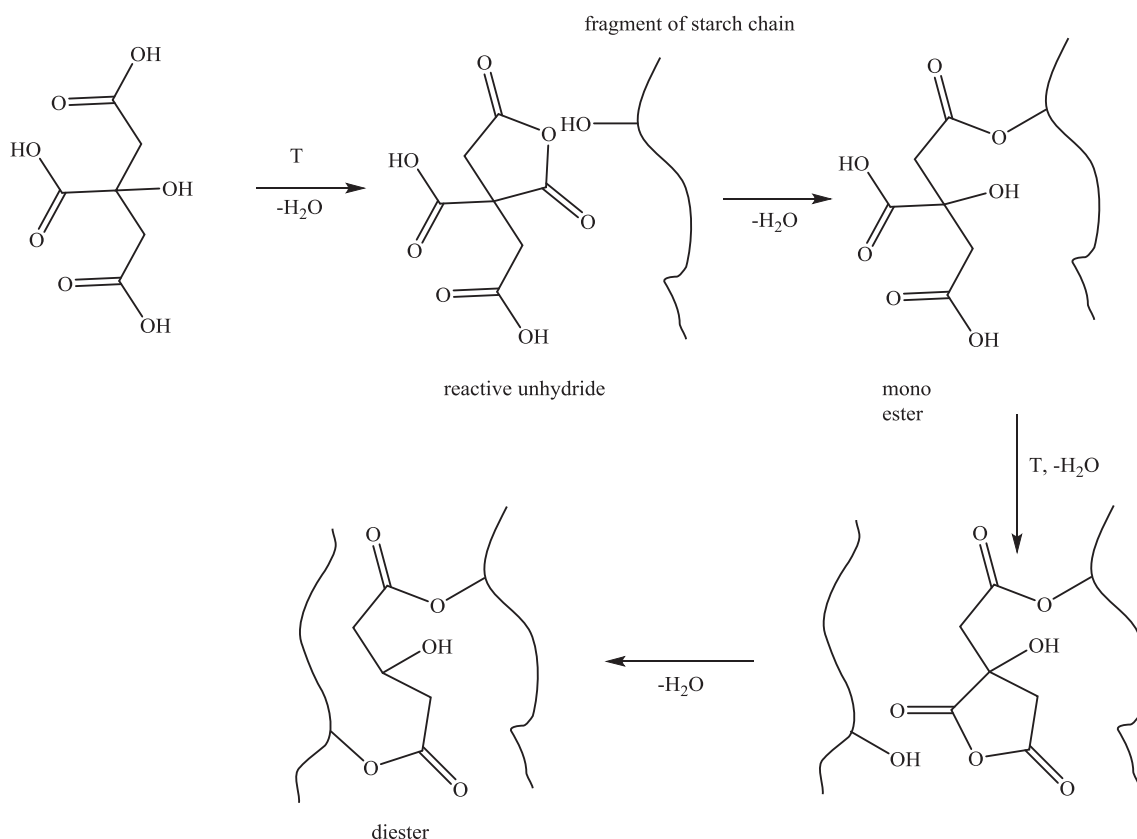


Fig. 1. Mechanism of starch esterification by citric acid.

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