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The effect of amylose content and level of oxidation on the structural changes of acetylated corn starch and generation of free radicals

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ABSTRACT

This study was aimed at determining the effect of starch oxidation on its acetylation, structure of starch granules, and generation of free radicals. Corn and waxy corn starches were oxidised by NaClO applied in doses of 10, 20, and 30 g Cl/kg of starch, and then acetylated using acetic acid anhydride. The carboxyl, carbonyl, acetyl groups were determined in modified starches. Structural properties of starch granules were evaluated based on molecular weight distribution, gelatinisation, crystallinity, specific surface, intrinsic viscosity. EPR measurements were carried out to establish starch susceptibility to UV irradiation induced generation of free radicals. It was found that the number of carbon centered radicals was dependent on the kind of starch and its chemical modification. Study results allowed concluding that the applied modifications contributed to significant changes in starch granules that were determined not only by the amylose content of starch but also by the degree of its oxidation.

1. Introduction

Starch is one of the most important and renewable resources ubiquitous in nature. Owing to its specific structure, it easily enters into reactions with various chemical substances that result in the production of modified starch preparations with desirable physicochemical properties. For this reason, native and modified starches are one of the most multi-function raw materials applied in the food industry. Starch susceptibility to chemical modification results from its structure – it has free hydroxyl groups that may undergo, e.g., oxidation or esterification reactions. In the oxidation reaction of starch, its hydroxyl groups are oxidised to carbonyl and carboxyl groups. In turn, esterification consists in starch reaction with e.g., acetic, propionic or formic acids, as a result of which its hydroxyl groups are substituted with respective acid residues. Apart from starch oxidised with sodium chlorate(I) (E1404) and starch acetylated with an acetic anhydride (E1420), also starch that was modified simultaneously with two reagents may be applied in the food industry. This double modified starch was assigned the symbol E 1451 and named acetylated oxidised starch. Generally, oxidised starch, acetylated starch and acetylated oxidised starch exhibit low paste viscosity and high paste clarity as well as high solubility in water. Therefore, modified starches are used in food industry most of all as thickening, gelling or stabilising agents. Moreover, acetylated oxidised starch has more stable paste viscosity in an acidic environment and at high sugar concentration. For this reason, this double modified starch is often a component of children's confectionery products such as jelly candies (Abbas, Khalil, & Hussin, 2010; Masina et al., 2017; Singh, Kaur, & McCarthy, 2007; Vanier, Halal, Dias, & Zavareze, 2017).

Earlier works addressing acetylated oxidised starches (Ali & Hasnain, 2014; Khalil, Hashem, & Hebeish, 1995; Nur & Purwiyatno, 2010; Pietrzyk, Fortuna, & Wojtanowska, 2012; Pietrzyk, Juszczak, Fortuna, & Ciemniewska, 2014; Zamudio-Flores, Bautista-Baños, Salgado-Delgado, & Bello-Pérez, 2009; Zamudio-Flores, Gutierres-Meraz, & Bello-Pérez, 2011) present mainly results of analyses of the functional properties (swelling power, solubility in water, viscosity of pastes, susceptibility to degradation) of starches double modified in this way. However, changes in the physicochemical properties of chemically-modified starches are due to changes in the external and internal structure of starch granules. These changes are affected, most of all, by the newly-formed and/or introduced functional groups and processes of starch granule degradation elicited not only be the reagent but also by process conditions. In addition, the changes in granule structure of double-modified starches are influenced by the earlier process of starch oxidation and are likely to affect the successive modification process (e.g. acetylation), and thereby also the physical and chemical properties of starch made with the use of these reagents.

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Considering that little information is available in literature on the effect of oxidation-induced starch granule structure disorganisation on the acetylation process, the objective of this study was to determine the effect of amylose content and oxidation degree of starch on the structure of starch granules and generation of free radicals in acetylated oxidised starches.

2. Materials and methods

2.1. Materials

Corn starch (amylose content of 20%) and waxy corn starch (amylose content of 1%) produced by Roquette (Lestrem, France) were used in this study.

Oxidation was carried out following the procedure described by Forssell, Hamunen, Autio, Suorti, and Poutanen (1995). The modification was conducted in a 40% water solution of starch, using NaClO in amounts equivalent to 10, 20 and 30 g Cl per kg of starch (oxidation level I, II and III, respectively). The solution with pH = 10 was stirred for 50 min at room temperature, neutralised to pH = 7. After reaction, the modified starch was washed with distilled water, dried at a temp. of 20 °C for 48 h, pulverised, and passed through a sieve with 0.125 mesh.

Acetylation was performed according to Mężyński (1972). 200 grams of starch (native or oxidised) were dispersed in 460 g of distilled water at room temperature. Then, 15 cm^3 of acetic anhydride was added drop-wise (1 cm^3/min) to the stirred starch suspension with pH kept between 8 and 9 by adding a 2% NaOH solution. When the whole amount of acetic anhydride was added, the suspension was further stirred for 15 min. Following this, the pH value of the slurry was adjusted to 5.2–5.6 using 10% hydrochloric acid solution. After reaction the modified starch was washed with distilled water, dried at a temperature of 20 °C for 48 h, pulverised, and passed through a sieve with 0.125 mesh.

2.2. Effectiveness of oxidation and acetylation processes

Assessment of the effectiveness of oxidation and acetylation was based on the increase in the contents of carboxyl groups (ISO 11214, 1996), carbonyl groups (Whistler, BeMiller, & Paschall, 1967), and acetyl groups (Wurzburg, 1964) in starch.

2.3. Molecular weight distribution

The molecular weight distribution of starches was determined by a gel permeation chromatography (GPC). The column OHpak SB-806 (Shodex, Japan) thermostated at a temperature of 25 °C and connected with an RI detector (Knauer, Germany) was used and a flow rate was set to 0.5 mL/min. The apparent number-average molecular weight and the apparent weight-average molecular weight of the starch were calculated relative to standard solutions of Pullulan Standard P-82 (Shodex, Japan). A 0.1 M sodium nitrate solution containing 0.02% sodium azide was used as an eluent.

2.4. Thermodynamic characteristics of gelatinisation by DSC

The thermodynamic characteristics of gelatinisation was 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.

2.5. Crystallinity

The content of the crystalline phase in the modified starches was determined with the use of an Empyrean X-ray diffractometer by PANalytical (Almelo, The Netherlands). Measurements were conducted using monochromatic radiation with a wavelength corresponding to an emission line $K_{\alpha 1}$ of copper, at an angle range of 5–70°, in a scale of 2θ with a measuring step of 0.008.2θ.

2.6. Specific surface area

The specific surface area was determined using a multipurpose automatic apparatus ASAP 2000 (Micrometricis, USA), by measuring the adsorption of high-purity nitrogen. The measurement involved determining the isotherm of nitrogen adsorption at the temperature of liquid nitrogen (77.3 K) and calculating the monolayer capacity with the adsorption isotherm equation of Branauer-Emmet-Teller (BET) (Branauer, Emmet, & Teller, 1938). Prior to measurements, the samples were dried under vacuum conditions at a temperature of 35 °C (± 1 °C) for 24 h, and next automatically desorbed at a degassing station and flushed with pure helium at a temperature of 22–24 °C for 3 h. Before measurements the samples were checked for the presence of gas at a measuring station.

2.7. Intrinsic viscosity

The viscometric measurements were made at a temperature of 25 °C. A weighed amount of 1 g of starch was dissolved during stirring in 0.5 M KOH over 24 h at room temperature, and then made up to 100 cm^3 with a 0.5 M KOH solution (Paterson, Mitchell, Hill, & Blanshard, 1996). The flow time of starch solutions was measured automatically by using an Ubbelode capillary viscometer (K = 0.009631 m^2/s^2) equipped with a ViscoClock system (Schott Instruments, Germany), over a concentration range 0.0006–0.02 g/cm^3. Intrinsic viscosity was determined from the relationship between specific viscosity and concentration, described by the Huggins equation:

$$\eta_{sp}/\ c = [\eta] + k'[\eta]^2 \cdot c$$

where: η_{sp} – specific viscosity, c – concentration [g/cm^3], [η] – intrinsic viscosity [cm^3/g], k' – Huggins constant.

2.8. EPR measurement

An X-band Bruker ELEXSYS 500 spectrometer (Karlsruhe, Germany) with 100 kHz field modulation was used to measure EPR spectra. The spectra of natural and chemically modified starches as well as those subjected to UV irradiation were recorded at 293 K with modulation amplitude of 0.1 mT and at microwave power of 3.0 mW. UV irradiation of the samples was performed in quartz tubes by 15 min in the cavity of the spectrometer using the UV Irradiation System ER 203 (100 W mercury lamp LSB610 Hg, Bruker BioSpin, Germany). A simulation procedure with the program SIM 32 (Spałek, Pietrzyk, & Sojka, 2005) allowed finding EPR parameters such as g-factor value, hyperfine splitting constant A, and peak-to-peak line width ΔB_{pp}. As a g factor standard 1,1-diphenyl-2-picrylhydrazyl (DPPH) was applied. Spectra of three samples of each starch were recorded two times. The accuracy of determination of EPR parameters was ± 0.0005 for g values and ± 0.1 mT for parameters A of radical signals.

2.9. Statistical analysis

The analysis were performed in triplicate, except for crystallinity measurement which was performed once. 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