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STRUCTURAL CHANGES OF TUBER STARCHES BY MICROWAVE IRRADIATION

Abstract

Time-temperature profiles of model starch water-systems, containing 0–35 % of water were studied, under microwave irradiation and effect of this treatment on physico-chemical properties of starch were recognized. Brabender rheological method, light microscopy, scanning electron microscopy and X-ray diffractometry were involved. Microwave irradiated starch containing more than 20 % of water underwent isothermal structural transformation. Consequently gelatinisation temperature rose and starch partially lost its solubility in water. The most dramatic change took place in case of potato starch. Its crystal structure changed from B into the A type. Tapioca starch changed to a lesser extent. Both tapioca and potato starch with less than 20 % of water solely lost their humidity on short irradiation then dextrinized.

Introduction

Microwaves deliver the nonionizing energy that causes a rise in temperature within a penetrated medium as a result of rapid electromagnetic field changes at high frequency. The design of microwave process involves not only thermal properties of foods, which are relative intensive to temperature differences, but also a number of interrelated electrical properties which vary extensively with the processing frequency and with product time-temperature profiles. At microwave frequencies, the most basic of these electrical properties – the dielectric constant and loss factor – are largely determined by product moisture and salt content [1]. Therefore, dry food components such as unmodified starch granules are thought to be electrically inert [2]. The most of experiments on starch – microwave irradiation interaction concern systems containing considerable amount of water [2–4]. Rashed Khan et al. hydrolyzed starch in water by heating with microwave energy at high temperatures and pressures inside the glass

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tubes. They obtained brown caramel-like starch hydrolysates containing oligosaccharides ranging from G_1 to G_8 [3]. Gordon and Davies examined in detail some physico-chemical properties of starch water – systems. They found that the distribution of variously swollen granules and the range in degree of swelling within the samples depend on the heating method. However, there are no structures unique to gels prepared, either by microwave irradiarion, or by convection heating [4]. Dielectric constants of modified and unmodified starches – water systems remained constant during heating, while dielectric loss factors and absorptivities decreased slightly during heating except during starch thermal transition times as measured by DSC [2]. There are also found dielectric properties of wheat starch powder containing 12.1 % of water (dielectric constant of 2.23 and dielectric loss factor of 0.23). Irradiation of air dried maize, potato and cassava starches leads to obtainment of dextrines [5]. The viscosity of its gels dramatically changes (decreases by one to three orders of magnitude), temperature of gelation slightly decreases and the colour becomes progressively yellow and brown. Reaction of starches with formaldehyde as well as with acetylene carried out by microwave irradiation gave products with enhanced viscosity [5].

Chemical modification reactions in solid state usually are carried out in rotating roasters. The design of this processes needs first of all detail knowledge about temperature and humidity of reaction mixture. The application of microwave ovens instead of rotating roasters seems to be attractive, but needs knowledge how microwave processing affects starch. The main purpose of the paper was to determine time-temperature profiles of model starch water-systems under microwave irradiation and the influence of microwave irradiation on physico-chemical properties investigated starches.

Materials and Methods

Commercial potato and tapioka starches were air-dried or humidified to obtain samples with required moisture values. 200 g starch samples were irradiated in 600 ml glass beakers covered (A-method) or not (B-method) with a special foil suitable for microwave ovens. DeLonghi microwave oven (Italy), 800W microwave output power and 2450 MHz microwave frequency were used to perform irradiation process. The power in experiments was set on minimum level (about 10 % output power). The temperature of starch layer was measured periodically with a mercury termometer after removing the beaker from the oven.

A gelatinisation course of starch samples was determined by a Brabender viscograph under the following conditions:

- measuring cartridge 700 cmg
- heating/cooling rate 1,5°C/min

- thermostating 30 min.

X-ray diffractometry was conducted by a X-ray diffractometer type TUR 62 Carl Zeiss Germany under the following conditions: X-ray tube CuKα (Ni filter); voltage 30 kV; current 15 mA; scanning from $\Theta = 2^{\circ}$ to 18°.

Starch samples subjected to examinations in a light microscope were prepared by a smear method. The starch suspensions were heated at temperatures corresponding to initial gelatinization temperature measured by a Brabender method and at 95°C. Drop of the starch paste was smeared on the microscope glass and after cooling smears were coloured by iodine according to Kaczyńska et al., [6] and observed in a Nicon FX light microscope. Starch samples examined in a scanning electron microscope were prepared according to Kaczyńska et al., [6] also Fornal [7] and observed in Jeol JSM 5200 microscope.

Results and Discussion

On the base of determined time- temperature profiles (pictures not shown) a strong correlation between water content in starch samples and time-temperature profiles character was found. Samples containing small amounts of water show quick and almost linear temperature rise. Higher water content in starch samples causes less vertical slope of the curves. This phenomenon is probably related to high water specific heat value. For starch samples containing over about 20 % of water one can observe plateau. Plateau interval length rises when water content in starch samples increases. This observation points to some kind of isothermal transformation which takes place in starch samples. More precise observation of changes between time temperaure profiles (pictures not shown) of samples irradiatied in covered and uncovered beakers shows that plateau interval lengths are higher for irradiated samples covered with foil. This observation points to critical role of water in isothermal transformation course mentioned.

If above hypothesis presented were true, starch samples irradiated with different water content should have different physico-chemical properties. In general a strong relationship between water content in irradiated starch samples and their Brabender curves course (pictures not shown) can be observed. Dry starch samples show high viscosity decrease after microwave irradiation, meanwhile the gelatinization temperature remains constant. Higher water content in starch samples up to 20 % causes less viscosity decrease. Starch samples containing approx. 20 % water show after microwave irradiation almost the same Brabender curves course in comparision to native starch. The situation is quite different for starch humid samples in the range from 20 % to 35 %. Higher water content causes viscosity decrease and the rise of the gelatinisation temperature value. More precise observation of changes between Brabender

curves course (pictures not shown) of samples irradiatied in covered and uncovered beakers shows that gelatinisation temperature rise is higher for irradiated samples covered with foil. This observation points to strict correlation between plateau interval length in time temperature profiles and gelatinisation temperature value of starch samples. That also leads to conclusion that above mentioned isothermal transformation which takes place in microwave irradiated starch samples causes changes in gelatinisation temperature and consequently perhaps in other physico-chemical properties. Intensities of Brabender curves course changes are higher for potato in comparision with tapioka starch. It is presented in the figure 1. The most important conclusion resulting from this figure is change in the Brabender curves character. Native potato starch reveals the course typical for tuber starches meanwhile the irradiated one (humidity of 35 %) is typical for cereal starches.

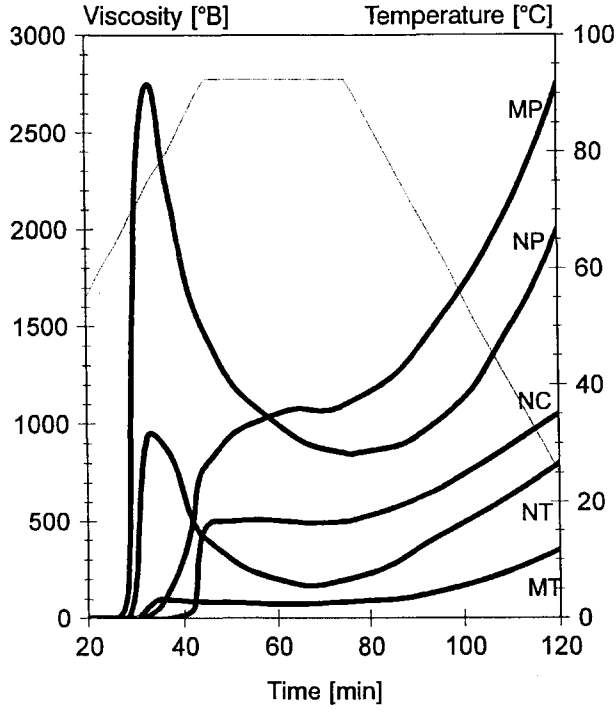

Fig. 1. Amylograph pasting curves for 8 % suspensions on native and microwave irradiated starch samples MP, potato starch microwave irradiated at 35% of humidity NP, native potato starch NC, native corn starch NT, native tapioca starch MT, tapioca starch microwave irradiated at 35 % of humidity.

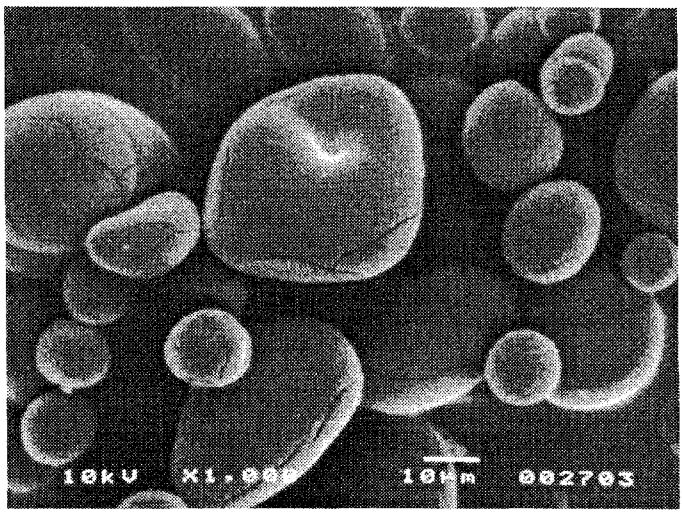

Fig. 2. Scanning Electron Micrograph dry potato starch after microwave irradiation.

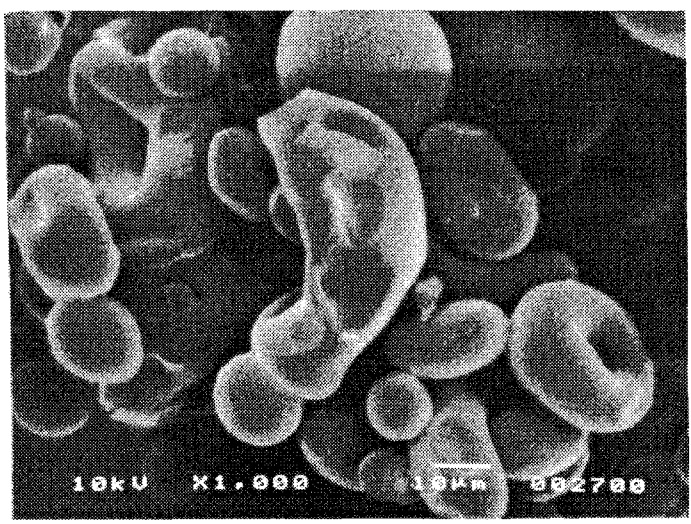

Fig. 3. Scanning Electron Micrograph of potato starch microwave irradiated at 35 % of humidity.

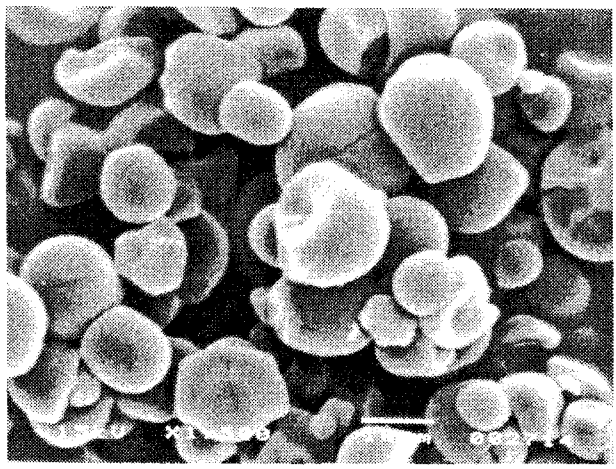

Fig. 4. Scanning Electron Micrograph of dry tapioca starch after microwave irradiation.

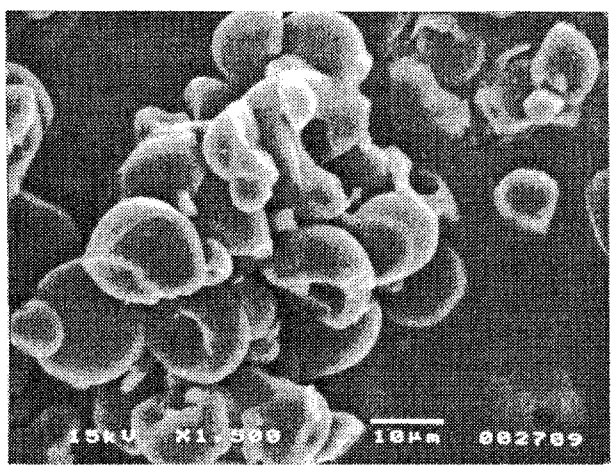

Fig. 5. Scanning Electron Micrograph of tapioca starch microwave irradiated at 35 % of humidity.

The light microscopy (photographs not presented) was used to examine other aspects of gelatinisation process. A typical image for initial gelatinisation period i.e. amylose efflux out of the starch granule is presented in the picture of native potato starch at the temperature of 68°C. At the temperature of 95°C native potato starch granules are almost solubled. The situation is different for microwaved starch. At the temperature of 68°C there are not any symptoms of gelatinisation process, when at the temperature of 90°C the image is the same like in the temperature 68°C for native starch. This facts reflect deep changes in the starch granule structure which cause some difficulties in the solubilisation process. In other words starch – starch intermo-

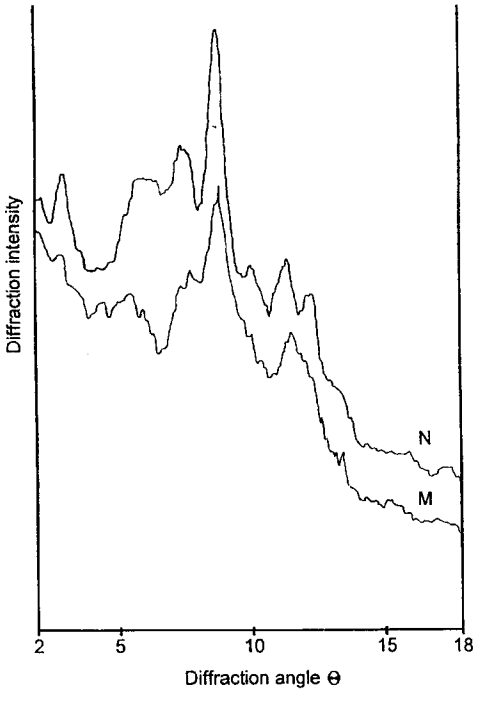

Fig. 6. X-ray diffraction patterns of potato starch samples N, native starch M, starch microwave irradiated at 35 % of humidity.

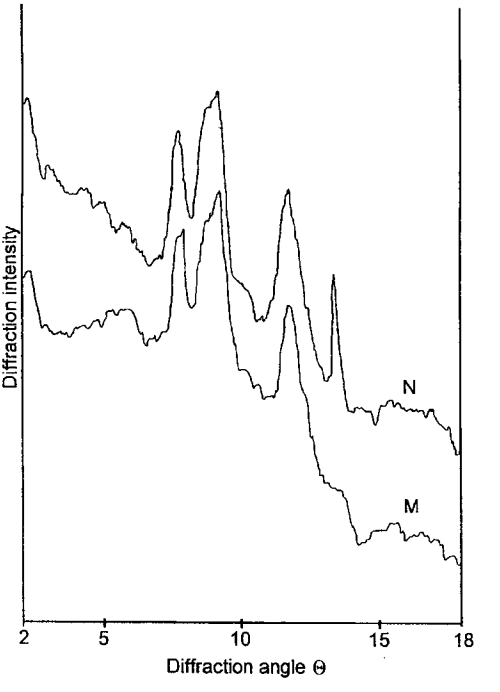

Fig. 7. X-ray diffraction patterns of tapioca starch samples N, native starch M, starch microwave irradiated at 35 % of humidity.

lecular interactions are stronger in microwave modified starch than in the native one. Tapioca starch shows lower structural changes reflected by light microscopy (photographs not shown). At the temperature of 68°C microwave modified tapioca starch shows low but appreciable amylose efflux out of the starch granule. At the temperature of 73°C the image is almost the same like at the temperature 68°C for native starch. Such radical changes in gelatinisation mechanism suggests essential alteration in the starch structure. SEM pictures of microwaved starches are shown in the figures 2–5. Predominant phenomenon in the case of dry starch samples is formation of superfacial cracks, what can be caused also by electrone beam. More interesting in our opinion are starch granules which collapse at the centre. Starch samples irradiated by high humidity show granules deformation first of all as a result of collapse at the centre. The results are similar to obtained by Kawabata et. al. for heat/moisture treated starches [8]. Heat/moisture treatment was described in detail first by Sair and later by Lorenz and Kulp et.al. It causes similar consequences [9–15]. Heat moisture treatment changes the physical properties of starches. The largest change takes place in the

root starches. The treatment changes sorption properties with corresponding changes in gelatinisation temperature, transluency, and pasting characteristics; in the case of potato starch, the B X-ray diffraction pattern is changed to the A pattern. Classical heat/moisture treatment is effected by heating in a pressure cooker at 100 % relative humidity; i.e. heating at 95°C for time periods from 2 to 18 hr., or by heating at temperatures 100–110°C for periods ranging up to 18 hr. In our microwave irradiation experiments the temperature of isothermal transformation is in the range of 80–90°C, and the time ranging up to 2.5 hr., so the conditions were milder. X-ray diffractometry investigations were carried out to check if by microwave irradiation takes place heat/moisture treatment. Figures 6–7 present X-ray diffraction patterns of microwave irradiated wet starch samples. The comparison of X-ray diffraction patterns of native and modified potato starches shows that there are changes from type B to type A. For tapioca starch which exhibits intermediate type of X-ray diffraction pattern, it is difficult to determine exactly it's type after microwave irradiation, but distinct differences between diffraction properties of native and microwaved ones were found.

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WYWOŁANE PROMIENIOWANIEM MIKROFALOWYM ZMIANY STRUKTURALNE W SKROBI Z ROŚLIN BULWIASTYCH

Streszczenie

Badano wpływ czasu i temperatury na właściwości fizykochemiczne modelowych układów skrobia – woda (0 do 35 % wody) ogrzewanych mikrofalami. W tym celu posłużono się wiskozymetrem Brabendera, mikroskopem, elektronowym mikroskopem skanningowym i rentgenografią proszkową. Skrobia zawierająca ponad 20 % wilgoci podczas ogrzewania mikrofalowego ulegała strukturalnym przemianom izotermalnym. W następstwie wzrastała temperatura kleikowania i malała rozpuszczalność w wodzie. Najwidoczniejsze zmiany zachodziły w skrobi ziemniaczanej. Jej struktura krystalograficzna zmieniała się z typu B na typ A. W mniejszym stopniu zmieniała się skrobia tapiokowa. Zarówno skrobia ziemniaczana jak i tapiokowa z zawartością wilgoci poniżej 20 % przy krótkotrwałym ogrzewaniu jedynie traciły wilgoć, a potem dekstrynizowały.