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CHANGE IN THE GRANULE POROSITY ON MODIFICATION OF STARCH

Abstract

Potato, wheat, maize and oat starches were modified by physical, chemical and enzymatic treatment. The obtained preparations were characterized in terms of specific surface area, volume of mesopores and their average diameter with ASAP 2000 apparatus, by method of low-temperature adsorption of nitrogen. Changes in the properties of starch granules due to the applied modifications were observed. It was proved, that enzymatic modification had the highest influence on porosity. Among the α-amylase modified preparations, the highest increase of porosity occurred in oat and wheat starch, lower in maize and the lowest in potato starch. The above results were confirmed by granules morphology analysis performed by means of scanning microscopy.

Introduction

Native starches have limited application in technological processes. To obtain required properties starch is being modified. The most frequently used are physical, chemical and enzymatic methods of starch modification [Fornal, 1985; Wurzburg, 1988; Muzimbaranda, Tomasik, 1994; Słomińska, 1997]. Starch susceptibility to modifying agents depends on botanical origin of parent plant, size and structure of starch granules, amylose/amylopectin ratio and phosphoric acid content in starch granule [Swinkels, 1985; Lewandowicz, 1990; Soral-Śmietana, 1995]. Apart from carbohydrate substance an integral part of starch is water and the interaction starch granule – water is decisive for starch modification process [Bączkowicz, Tomasik, 1989]

Cereal starches differ from potato starch, among other things, in water binding capacity and rheological properties. They also contain more lipid-protein substances, which partly occur on the granules' surface and partly form stable complexes with amylose helices [Morrison, 1981; Soral-Śmietana, 1995]. Starch reactivity is also influenced by starch granule structure, thus one of the important factors determining

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starch susceptibility to modification is the specific surface area of granules and their porosity.

Cereal small granules differ from potato starch in larger specific surface area and volume of mesopores, while their average diameters of mesopores are similar [Fannon et al., 1992; Baldwin et al., 1994; Achremowicz et al., 1997]. Starch granules porosity has an impact on physico-chemical properties of starch and is widely investigated [Hellman and Melvin, 1950; Marousis and Saravacos, 1990; Fannon et al., 1992, 1993; Karathanos and Saravacos, 1993]. Various methods are used to measure starch granules porosity, among them: scanning microscopy [Fannon et al., 1992], confocal microscopy and atomic force microscope [Baldwin et al., 1994, 1997], mercuric porosimetry [Karathanos and Saravacos, 1993], helium stereopicnometry [Marousis and Saravacos, 1990], water sorption measurements [Aguerre et al., 1989], and methods based on physical adsorption from gas phase [Xano and Nogai, 1989, Achremowicz et al., 1997] or liquid phase [Fortuna et al., 1996]. The obtained porosity values vary due to starch source but also depend on the applied measurement method.

The aim of this paper was to find what is the influence of physical, chemical and enzymatic modification on the porosity of starch granules.

Material and methods

The following starches were used:
- potato starch 'Superior' produced by Potato Processing Company Pila,
- commercial wheat starch of German origin,
- commercial maize starch of German origin,
- commercial oat starch of Finnish origin

All the above starches were modified by physical, chemical and enzymatic treatment.

I. Physical modification was performed in 3 different ways:
  1. by convectional heating in 130°C for 2 hours
  2. by convectional heating in 200°C for 2 hours
  3. by irradiating with microwaves for 14 min., in microwave oven Moulinex FM A945GS (850 W, 2450 MHz)

II. Chemical modification was performed in water dispersion (pH = 9), using sodium trimetaphosphate as a modifying agent [Lim, Seib, 1993].

III. Enzymatic modification (mild hydrolysis with α-amylase) was performed using bacterial α-amylase preparation Maxamyl (20 µl/1g d.s. starch) after incubation in 40°C

In native as well as in modified starches specific surface area S_{BET} [Branauer et al., 1938], volume of mesopores and their medium diameter were determined. Specific surface area of the preparations and porosity were measured with multifunctional automatic apparatus ASAP 2000 (Micrometrics, Noxcross, Georgia USA), by means of absorption of highly purified nitrogen at liquid nitrogen temperature. Before the determination the probes were dried in vacuum at 35°C to remove excessive moisture. Then the preparations were additionally desorbed in degassing station working in automatic mode, utilizing washing with pure helium and vacuum treatment. The state of surface degassing was checked and for further experiments completely desorbed probes were used.

Granules' morphology was characterized with scanning electron microscope (SEM) Jeal JSM 5200. The probes were prepared according to Fornal [1985].

Results and discussion

Particular native starches and products obtained by their modification had different specific surface area of granules (Tab. 1). Oat starch was characterized by the largest surface area and potato starch by the smallest. Also the volume of mesopores in oat starch was the biggest. Average mesopores diameters are close for all native starches. Results of Fannon et al. [1992, 1993] confirm differences in porosity between starches from different sources. Also the origin of the pores is different. Part of them appears during starch granules formation in plant tissue [Fornal, 1984], some when thermal or hydrothermal processes take place, while amylose migrates from the inside of granule to its surface [Baldwin et al., 1994], other are mechanical cracks and damages caused by grain processing [Niemann, Whistler, 1992]. Due to the performed modifications the properties changed. Preparations modified by physical treatment obtained from potato starch were distinguished by larger surface area and volume of mesopores as well as their smaller average diameter. In maize starch preparations there such a change was not observed. This proves that maize starch is more resistant towards the modifying agents (convectional heating, microwave irradiation). Stability of corn starch is probably due to the occurrence of lipids in surface and helical amylose complexes [Tomasik et al., 1996]. Hellman and Melwin [1950] in their research determined specific surface area of starch, by means of nitrogen absorption, to be 0.70 m^2/g for maize, 0.28 m^2/g for tapioca and 0.11 m^2/g for potato. According to Karathanos and Saravacos [1993] specific surface area of waxy corn was 0.39 when determined by low pressure mercuric porosimeter.

Estrification of the starches with ortophosphoric (V) acid also resulted in changes of granules porosity increasing surface area and volume of mesopores (except maize starch). Oat starch after chemical modification showed a little increase of surface area while volume and mean diameter of mesopores were highly enlarged.

Table 1

Porosity (pore characteristics) of initial and modified starch granules

Starch source	Specific surface area $[m^2/g]$	Volume of mesopores $[cm^3/g] \times 10^{-3}$	Average diameter of mesopores $[m] \times 10^{-10}$
POTATO: initial	0.24	0.35	57.2
convectional heating at 130°C	0.34	0.40	47.4
convectional heating at 200°C	0.35	0.37	42.7
microwave heating	0.51	0.57	44.7
chemical modification	0.40	0.55	54.0
enzymatic modification	0.62	1.36	87.7
WHEAT: initial	0.53	0.76	57.0
chemical modification	0.70	1.26	71.8
enzymatic modification	3.74	10.65	113.9
MAIZE: initial	0.69	1.10	64.2
convectional heating at 130°C	0.71	1.13	64.0
convectional heating at 200°C	0.77	1.24	64.4
microwave heating	0.68	1.11	65.3
chemical modification	0.65	1.07	66.1
enzymatic modification	3.12	7.67	98.3
OAT: initial	1.22	1.80	58.8
chemical modification	1.26	2.45	77.6
enzymatic modification	8.41	22.50	107.1

The greatest changes in porosity of starch granules were observed in enzymatically modified preparations. The highest surface area after α-amylase treatment was found for oat starch: 8.41 m^2/g, much lower for wheat and maize and the lowest for potato. A similar trend concerned volume and mean diameter of mesopores. When amylolytic enzymes act on native starches, porosity of its granules plays an important role. Starches with larger surface area could be easier attacked by amylolytic enzymes. Starch granules from roots and tubers are more resistant towards amylases then those from grains [Sugimoto et al., 1980; Słomińska, 1997]. Sugimoto [1980] showed that potato and banana starch granules are more resistant towards amylases then maize starch granules.

Yamada et. al. [1995] in the scanning microscopy experiments on porosity of maize starch after amylase action, found that the enzyme mainly attacks amorphous regions.

Figs. 1-4 present photos from scanning electron microscopy of modified starches preparations. Granules morphology confirms the greatest changes occurring in probes treated with α-amylase.

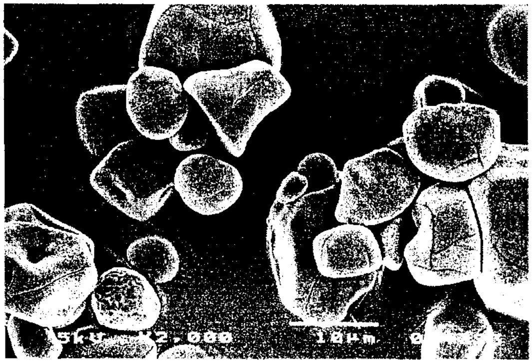

Fig. 1. Maize starch after convectional heating at 200°C.

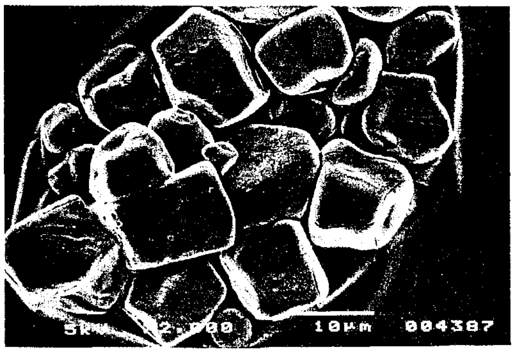

Fig. 2. Maize starch after microwave heating.

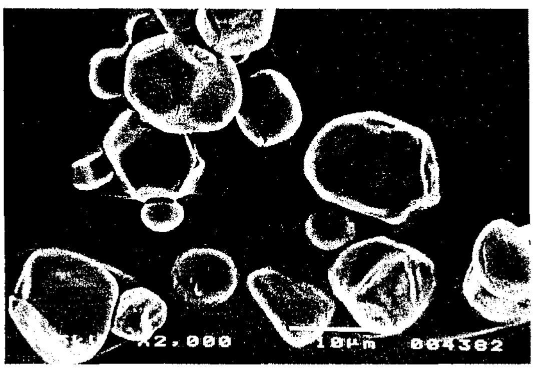

Fig. 3. Maize starch after chemical modification.

Fig. 4. Maize starch after enzymatic modification.

Conclusions

1. Modification of starch granules with the applied physical treatments causes different changes of starch properties, depending on its origin (enlargement of surface area and volume of mesopores and decrease of their average diameter in potato starch granules).
2. Chemical modification also caused porosity changes, increasing surface area of granules and volume of mesopores (except maize starch).
3. The greatest changes in porosity were obtained after enzymatic modification. The highest increase of specific surface area among the enzymatically modified preparations was found for oat starch, much lower for wheat and corn starches, and the lowest for potato starch.
4. Morphology analysis of starch granules confirmed the above results.

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WPŁYW MODYFIKACJI SKROBI NA POROWATOŚĆ JEJ ZIARN

S t r e s z c z e n i e

Skrobie ziemniaczaną, pszenną, kukurydzianą i owsianą poddano modyfikacji fizycznej, chemicznej i enzymatycznej. Uzyskane preparaty przebadano odnośnie powierzchni właściwej, objętości mezoporów i średniej ich średnicy za pomocą aparatu ASAP 2000, przy zastosowaniu metody niskotemperaturowej adsorpcji azotu. W wyniku zastosowanych modyfikacji stwierdzono zmiany badanych właściwości ziarn skrobiowych. Wykazano, że największe zmiany w porowatości spowodowała modyfikacja α-amylazą. Wśród preparatów modyfikowanych enzymatycznie największym wzrostem porowatości odznaczała się skrobia owsiana i pszenna, mniejszym kukurydziana, a najmniejszym ziemniaczana. Powyższe wyniki potwierdziła analiza morfologii ziarn wykonana za pomocą mikroskopii skaningowej.