



Influence of physico-chemical modification of waxy corn starch on changes in its structure



Marzena Włodarczyk-Stasiak ^{a,*}, Artur Mazurek ^a, Jerzy Jamroz ^a, Mieczysław Hajnos ^b, Zofia Sokołowska ^b

^a Department of Analysis and Evaluation of Food Quality, University of Life Sciences in Lublin, Faculty of Food Science and Biotechnology, Skromna Street 8, 20-704, Lublin, Poland

^b Institute of Agrophysics, Polish Academy of Sciences, Doświadczalna Street 4, 20-290, Lublin, Poland

ARTICLE INFO

Article history:

Received 11 November 2016

Received in revised form

6 March 2017

Accepted 3 April 2017

Available online 6 April 2017

Keywords:

Degree of cross-linking

Structure of waxy corn starch

Water vapour sorption

Nitrogen adsorption

Mercury porosimetry

ABSTRACT

The paper presents a study on structure changes of waxy corn starches after physicochemical modification. The hydrothermal treatment (physical modifications) allowed to obtain pre-gelatinised starch (Merigel) or untreated starch of cook-up type (Resistamyl). Different degrees of cross-linking (low, medium and high) and medium level of substitution were the results of chemical modification of starch. The changes in the structure of modified starch were analysed with the use of the methods of low temperature nitrogen adsorption/desorption and of water vapour sorption. The BET equation was used to determine monolayer capacity (a_m) from isotherms of water vapour desorption, while the BJH equation was used to determine the surface area (S_{BJH}), volume (V_{BJH}) and mean diameter of pores (D_{BJH}). Starches of the pre-gelatinisation type were characterised by $S_{BET}N_2$ values in the range of 0.18–0.45 m²/g, and starches of the cook-up type - 0.13–0.66 m²/g. Higher values of S_{BJH} were noted for the cook-up starches (S_{BJH} : 0.23–0.60 m²/g) in reference to the starches of the pre-gelatinisation type (S_{BJH} : 0.12–0.32 m²/g). The medium degree of cross-linking of pre-gelatinisation type starches caused a lowering of the value of their monolayer capacity ($a_{m\ ads}$, $a_{m\ des}$), while for the cook-up type starches an increase of that value was observed, determined with adsorption and desorption water vapour isotherms. Porosity of the modified starch was determined with the use of mercury porosimetry. A decrease of porosity was noted for starch of the cook-up type (porosity 38.3–52.3%), compared to native waxy corn starch (59.3%). Starches of the pre-gelatinisation type (Merigel) were characterised by an increase of the value in question with increase in the degree of cross-linking: low ML (53.5%) < medium MM (59.2%) < high MH (65.7%). Starches of pre-gelatinisation type were characterised by pore volume (V_{MP}) values in the range of 0.83–1.34 cm³/g, while starches of cook-up type had V_{MP} values in the range of 0.57–0.79 cm³/g.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The structure and the physicochemical properties of native starches of various botanical cultivars are fairly well researched and documented. There is constant ongoing research on the acquisition of starches with properties that will be new, universal, and expected by the food industry. The shaping of specific physicochemical properties of starch is conducted through physical, chemical and enzymatic modification, and through compound modification.

Modified starches are used in the food industry as food additives

that allow the acquisition of desirable texture and functional properties. They are valuable additives to such products as sausages and pastes, or to ready meals (soups, sauces). The drastic production and storage conditions enforce the use of modified starches with high temperature stability. Chemically modified starches are also commonly used as filler for water- and milk-based fruit desserts and in infant food (Rutenberg & Solarek, 1984).

Starches with strongly diversified functional properties, relative to the native material, are obtained primarily through chemical modification. Esterification, etherification, oxidation or the insertion of various functional groups into starch molecule are the main directions of modification (Czerwinska, 2011; Singh, Kaur, & McCarthy, 2007; Zdybel, 2006).

Factors that differentiate the run of chemical modification

* Corresponding author.

E-mail address: marzena.stasiak@up.lublin.pl (M. Włodarczyk-Stasiak).

Nomenclature

| | |
|-----------------------|--|
| $a_{m \text{ ads}}$ | monolayer value, calculated of water vapour adsorption isotherm (mg H ₂ O/1 g d.m.) |
| $a_{m \text{ des}}$ | monolayer value, calculated of desorption isotherm (mg H ₂ O/1 g d.m.) |
| S_{BET} | specific surface area, calculated from of BET equation (m ² /g) |
| V_{BJH} | volume mesopores, calculated from of BJH equation (cm ³ /g) × 10 ⁻³ |
| S_{BJH} | cumulative surface of pores, calculated from of BJH equation (m ² /g) |
| mean D_{BJH} | average diameter of mesopores, calculated from of BJH equation (nm) |
| V_t | całkowita objętość porów wyznaczona na podstawie jednego punktu izotermy dla $p/p_0 = 0,99$, calculated from of BET equation (m ³ /g) × 10 ⁻³ |
| V_{MP} | volume pores, calculated of mercury porosimetry (cm ³ /g) |
| S_{MP} | specific surface area, calculated of mercury porosimetry (m ² /g) |
| mean D_{MP} | average diameter of mesopores, calculated of mercury porosimetry (nm) |

include such process conditions as the concentration of reagents, time of reaction, pH value and the presence of a catalyst, kind and degree of substitution, and the botanical origin of the modified starch (Hirsch & Kokini, 2002; Kavitha & BeMiller, 1998; Rutenberg & Solarek, 1984; Steeneken & Woortman, 1995).

The functional groups inserted in the course of chemical modification react with hydroxyl groups of starch, forming permanent bonds. They can also affect the mutual interactions of starch chains that do not directly participate in the bonds, e.g. as a result of changes in hydrophilicity or hydrophobicity. The lateral links between starch chains, formed in the course of cross-linking, may contribute to a change in the porosity of the newly-formed structure. Porosity is of enormous importance in the run of many physical and chemical processes, such as solubility or reactivity. The techniques most frequently used for the estimation of the porosity of a material are sorption techniques (water vapour sorption, low-temperature nitrogen sorption) or mercury porosimetry. Those techniques, apart from the purely analytical aspect, are frequently chosen due to the possibility of acquisition of additional information important for the food industry. The factors that differentiate the methods include differences in the sorption mechanism and in the range of pores into which adsorbate molecules can penetrate. The diversity of mechanisms of the methods allows to acquire deeper knowledge of changes in the structure of starch resulting from the complex physicochemical modification. The diversity of the analytical methods characterises the material studied in the following aspects:

- chemical – the mechanism of sorption, possibility of determination of process parameters (monolayer capacity, specific surface area, volume of mesopores and mean pore diameter)
- applicability of the methods for the characterisation of modified starch and for the identification of changes in its structure
- technological – applicability of the methods for the determination of quality features of e.g. extrudates
- design and oriented modification of parameters of the physicochemical modification of starch.

The method accepted as a standard and recommended by IUPAC is low-temperature nitrogen adsorption/desorption, in which the calculated values of specific surface area are close to the actual (Brunauer, Emmett, & Teller, 1938). As an apolar adsorbate, nitrogen allows the determination of internal surface area and porosity in the range of meso- and macro-pores. Nitrogen molecule has small dimensions and spherical shape, displays hexagonal packing in liquid state and relatively weak interaction with functional groups on adsorbent surface (Ciembroniewicz, Klinik, Korta, Nodzeński, & Rewilak, 1977). Measurement data of low-temperature nitrogen sorption are processed with the use of the BET theory and also the BJH equation which permits the determination of pore surface area (S_{BJH}), mean pore diameter (D_{BJH}) and pore volume (V_{BJH}). (Barrett, Joyner, & Halenda, 1951).

Due to the permanent presence of water (in various states of concentration) and to its interaction with the food product (dehydration, rehydration, dissolution), analysis of water vapour sorption is the most useful of the methods under discussion. Analysis of the shapes of sorption isotherms can be used for the study of the structure of the adsorbent and for the estimation of its sorption properties. It is also helpful in the thermodynamic characterisation of adsorption and desorption, in the design of technological processes and in the selection of factors affecting the stability of products (Lewicki, 1997; Świtka & Krasowski, 1990). Monolayer capacity (a_m), determined in the range of $0 < a_w < 0.35$, is a factor characterising the sensitivity of a product to unfavourable quality changes such as clogging, hardening, loss of flavour or the appearance of foreign flavours and tastes, and growth of microorganisms (Acker, 1962; Świtka & Krasowski, 1990).

Mercury porosimetry is a fairly popular method of analysis of the structure and porosity of materials. The technique is based on the measurement of the volume of mercury, intruded under pressure into an analysed material, that fills the voids and pores from the range of macro- and meso-pores. The advantage of the method is that the material under study does not undergo deformation under the effect of mercury intrusion, which might lead to the destruction of the original structure or “open up” pores that were not accessible before. Mercury porosimetry is used for the determination of porosity of materials (solid and granular) (Hajnos & Świeboda, 2004). Measurement of porosity permits the identification of structures occurring on the surface and within a solid body, comprising the absolute (total) and the relative (open) porosity (Bartell & Ruch, 1959; Chibowski, 1992). Mercury porosimetry is one of very few methods that permit the determination of absolute porosity, i.e. the share of closed pores in the structure of a material. Pores of this kind affect the density of the material, its mechanical strength and thermal conductivity (Hajnos & Świeboda, 2004; Lowell & Shields, 1991). Mercury porosimetry was applied by Jamroz, Hajnos, and Sokołowska (1996) for the study of microstructure of potato starch extrudates, and by Fornal et al. (2012) for the analysis of the structure of chemically modified potato starch.

There are few literature reports on the analysis of changes to starch at the structural level as a result of chemical modification. Many researches analyse only the effect of insertion of a reagent molecule on the textural and functional properties, leaving out the changes and reorganisation in the structure of starch granule that take place during the modification.

As a result of physical modification consisting in pre-gelatinisation, starch of the Merigel type was obtained, while starch of the Resistamyl type (cook-up) was not subjected to any preliminary hydrothermal treatment. Chemical modification of Merigel and Resistamyl starches consisted in cross-linking (low, medium, high) and medium level of substitution. The objective of the study was the estimation of changes, at the structural level, in

Download English Version:

<https://daneshyari.com/en/article/4983867>

Download Persian Version:

<https://daneshyari.com/article/4983867>

[Daneshyari.com](https://daneshyari.com)