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NEW RS PREPARATIONS – PHYSICOCHEMICAL PROPERTIES AND STRUCTURE

Abstract

New RS preparations were obtained by physical modification of potato, tapioca, maize and wheat starches and they contained respectively 30.84%; 18.34%; 25.48% and 26.34% RS determined according to the Champ method. Starch samples were investigated using the Brabender rheological method, X-ray diffractometry and light and scanning electron microscopy.

It was found that all RS preparations showed lower gelatinisation temperature as compared to native ones. The light microscopy study however proved that RS preparations are more difficult to disperse in water than native starches. It was observed that the dispersion process depends on the amylose content in starch. The scanning electron microscopy study showed that the forms of preparations were similar to those of pregelatinised starches (drum dried or extruded). The X-ray diffraction studies showed that all preparations obtained from both tuber and cereal starches showed a B-type X-ray diffraction pattern characteristic of native tuber starches.

Introduction

Resistant starch (RS) is a physiologically important indigestible starch fraction. It is not digested in the small intestine, but may be fermented by micro-organisms in the large intestine. RS cannot be properly defined chemically due to the fact that the resistance of starch to digestive enzymes is related to hydrolysis conditions (nature of the enzymes, ratio starch/enzyme, characteristic of the hydrolysis, etc.) [1]. There are four types of resistant starch: physically inaccessible, locked in plant cell walls; native resistant starch (represented by native potato, banana and high amylose starch); retrograded or crystalline non-granular starch; and specific, chemically modified or re-polymerised starches. Retrograded starch is the most common RS in the diet and, from the technological point of view, is the most important type resistant starch because it forms as a result of food processing [2]. It is generally believed that this resistant starch

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fraction consists mainly of retrograded amylose and shows a B-type crystalline structure [3-9]. On the other hand, it is found that RS formed at the temperature of 100°C shows an A-type X-ray diffraction pattern. B-type starch is formed at a significantly lower temperature (0–68°C) [10]. It is also possible to obtain enzyme-resistant starch by retrogradation of amylopectin, but the crystallisation of amylopectin is a slow process continuing over a period of several days or weeks [11]. The melting endotherm of amylopectin is observed at about 60°C, while for amylose crystallites at about 150°C. One of the most important issues in starch chemistry and technology is the correlation between starch structure and its functionality. The aim of our work was to determine the structure and physicochemical properties of new RS preparation invented by a research team from Starch and Potato Products Research Laboratory and the Institute of Animal Reproduction and Food Research of Polish Academy of Sciences.

Materials and methods

Resistant starch preparations were obtained by solubilisation of native starches and water and their isolation from the solution without any non-solvents or complexing agents. The procedure is described in detail in the Polish patent specification [12].

The course of gelatinisation was followed with a Brabender viscograph procedure under the following conditions: measuring cartridge 700 cmg; heating/cooling rate 1.5°C/min; thermostating 30 min.

The starch samples to be examined by light microscopy were prepared by the smear method according to Kaczyńska et al., [13]. Starch suspensions were heated at the initial gelatinization temperature (as measured according to Brabender), and at 90°C. A drop of starch paste was smeared over a microscope glass, cooled, stained with iodine and observed in a Olympus BX60 light microscope.

The starch samples to be examined by scanning electron microscopy were prepared according to Fornal [14] and observed with a Jeol JSM 5200 microscope.

X-ray diffractometry was performed with a TUR 62 (Carl Zeiss, Germany) X-ray diffractometer under the following conditions: X-ray tube CuK α (Ni filter); voltage 30 kV; current 15 mA; scanning from $\Theta = 2^\circ$ to 18° .

Results and discussion

Our resistant starch preparations like many others presented in patent descriptions were not pure indigestible starch fractions, but a mixture of digestible and indigestible ones [15-20]. The variation in the indigestible fraction content (table 1) depended on the nature of starch, mainly on amylose and lipids content. It is generally accepted that the resistant starch formation is based on amylose retrogradation, therefore amylose content could be the most important factor influencing this process [3-9]. It is also

reported that endogenous lipids substantially decrease the yield of RS – due to the amylose-lipids complexes formation [23]. The highest value of indigestible fraction (table 1) was found in the RS preparation obtained from potato starch – a variety characterised by a high amylose content but a low lipids content.

Table 1

Indigestible fraction content in RS preparations

Origin of starch	Resistant starch content in RS preparation, %	Amylose content in native starch [21-23], %	Lipids content in native starch [22], %
Potato	30.84	20-24	0.05
Tapioca	18.34	17	0.1
Maize	25.48	24-28	0.7
Wheat	26.34	22-28	0.8

X-ray diffraction studies (fig. 1 and 2) showed that all preparations obtained from both tuber and cereal starches showed a B-type X-ray diffraction pattern characteristic of native tuber starches which is generally compatible with data reported by other authors [3-9]. Brabender viscosity curves (fig. 3-6) showed that potato and tapioca RS preparations kept high swelling characteristics, whereas maize and wheat changed the type of swelling characteristics to higher than the native ones. High type of swelling characteristics and B-type crystallinity is typical of tuber starches. These data suggest that the presence of B-type of crystallinity is a necessary condition of starch indigestibility.

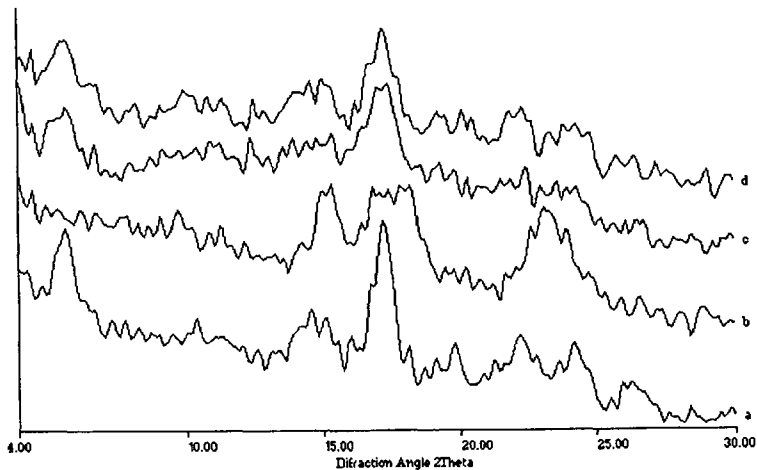


Fig. 1. X-ray diffraction patterns of: a – native potato starch; b – native tapioca starch; c – RS preparation obtained from potato starch; d – RS preparation obtained from tapioca starch.

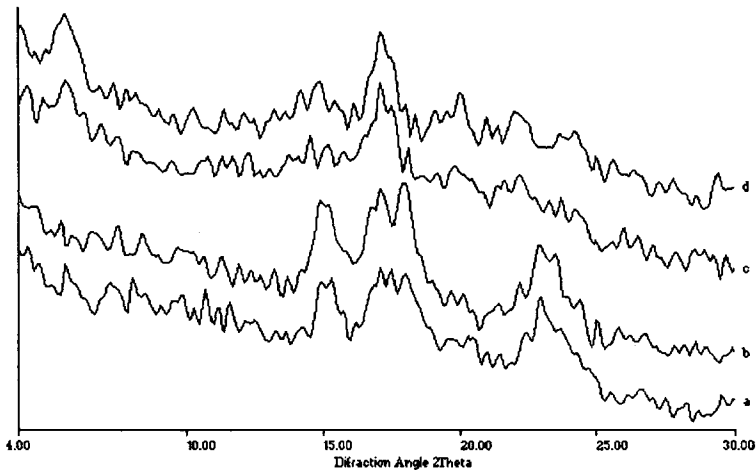


Fig. 2. X-ray diffraction patterns of: a – native wheat starch; b – native maize starch; c – RS preparation obtained from wheat starch; d – RS preparation obtained from maize starch;

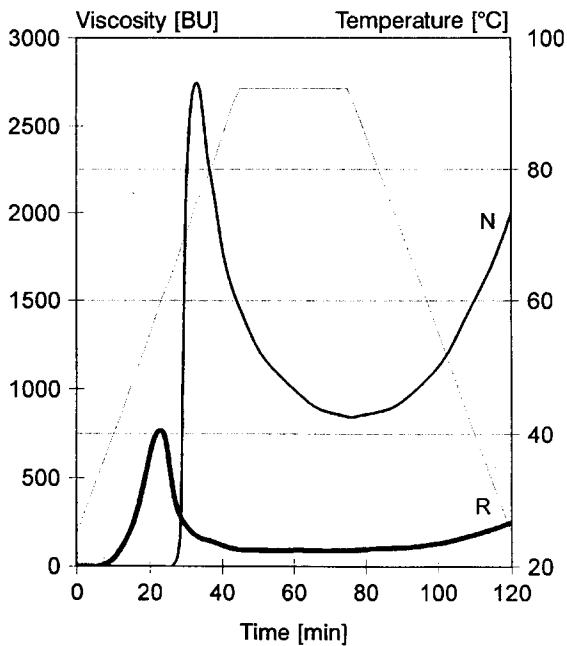


Fig. 3. Brabender viscosity curves for 8% solutions of RS preparation obtained from potato starch as compared to native one: R – resistant starch preparation; N – native starch.

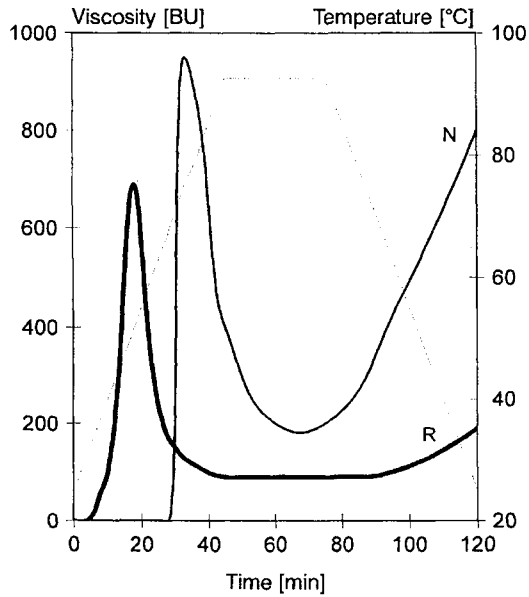


Fig. 4. Brabender viscosity curves for 8% solutions of RS preparation obtained from tapioca starch as compared to native one: R – resistant starch preparation; N – native starch.

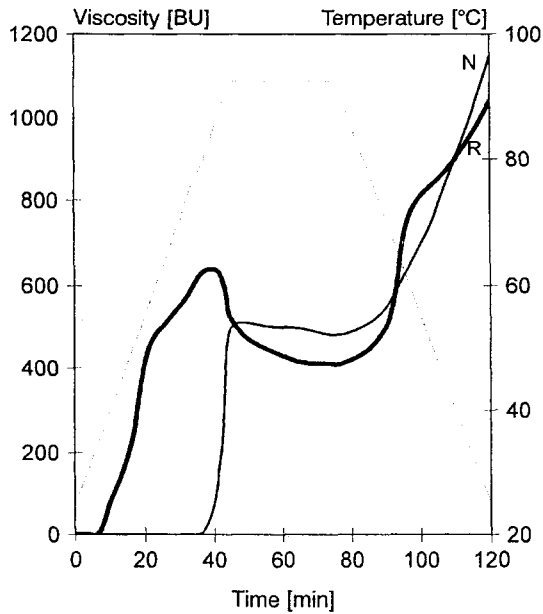


Fig. 5. Brabender viscosity curves for 8% solutions of RS preparation obtained from wheat starch as compared to native one: R – resistant starch preparation; N – native starch.

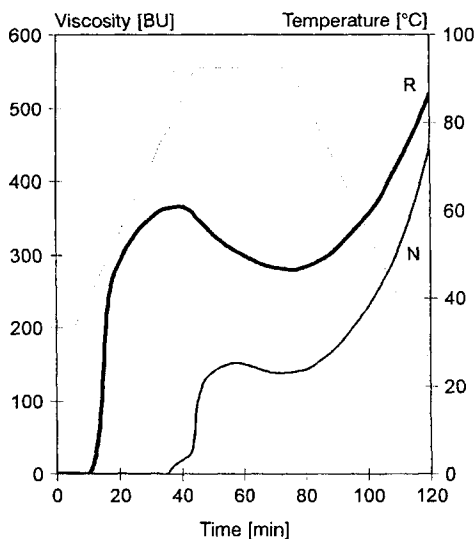


Fig. 6. Brabender viscosity curves for 8% solutions of RS preparation obtained from maize starch as compared to native one: R – resistant starch preparation; N – native starch.

Brabender viscosity curves (fig. 3-6) also showed that starch preparations revealed a lower gelatinisation temperature as compared to native ones. This was unexpected, because starch indigestibility is thought to be connected with their insolubility. However a verification of Brabender's data by light microscopy studies (photographs not presented) proved that RS preparations were more difficult to disperse in water than the native starches. At the temperature of gelatinisation it was impossible to observe any symptoms of solubilisation (for example amylose leakage from the starch granules) and the RS preparation remained unchanged. At a temperature of 90°C the majority of RS preparations showed brown-black coloured images, which indicated some hindrance in starch solubilisation (mainly amylose), and amylose iodine complexation processes. The only exception was the RS preparation obtained from tapioca starch which revealed a similar image as the native starch, which was correlated with low resistant starch and amylose contents. These observations proved that the gelatinisation of RS preparations was based on amylopectin hydration, whereas amylose fraction remained insoluble. Amylose formed very strong inter- and intramolecular starch-starch bonds, nonsusceptible to association with water molecules or to complexation with iodine atoms. These observations still did not provide an answer to the question about the correlation between starch structure and digestibility. It is believed that during gelatinisation the crystal regions of starch are disrupted. On the other hand, it is believed that the resistant starch fraction consists mainly of retrograded amylose and shows a B-type crystalline structure [3-9]. Our RS preparations underwent gelatinisa-

tion, thus their viscosity increased during heating, but up to 90°C they were only partially soluble. These phenomena can be explain in two ways:

- during heating amorphous amylopectin underwent association with water molecules, but amylose of B-type crystallinity remained insoluble, or
- during heating amylopectin of B-type crystallinity underwent association with water molecules, but amorphous amylose remained insoluble

The latter hypothesis is probably more difficult to accept, but probably it is true. It should be taken into consideration that authors reporting about B-type crystallinity of resistant starch do not claim that even pure RS fraction (isolated by enzyme procedure) reveals 100% crystallinity degree. Moreover, native potato starch granules of RS₂ type containing 66.5% RS [25] reveals average crystallinity degree of 28% [26], so the correlation is rather poor. Furthermore, there is also a type of RS₃ which reveals an A-type of X-ray diffraction pattern [11]. So, it is possible that the B-type of crystallinity is not a necessary condition of starch indigestibility. Probably the following two connected processes exist:

- formation of an indigestible starch fraction, and
- formation of a starch fraction of B-type crystallinity.

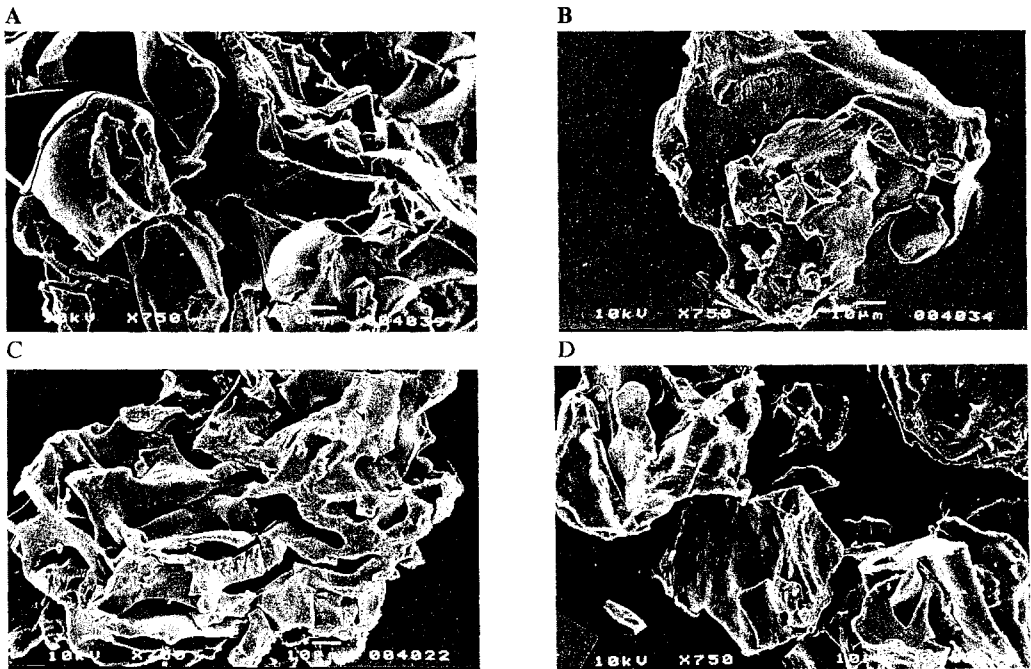


Fig.7. Scanning electron microphotographs of: A – RS preparation obtained from potato starch; B – RS preparation obtained from tapioca starch; C – RS preparation obtained from wheat starch; D – RS preparation obtained from maize starch;

Pictures of RS preparations obtained using scanning electron microscopy did not reveal any significant differences in their structure (fig. 7). Starch granules changed their granular shape into shapeless corrugated particles which final shape and size depended on final grinding procedure. All RS preparations revealed similarity in form to pregelatinised or extruded starches. The particles of RS preparations were thicker than those of extruded starch however [27].

The research was supported by grant no. 5 P06 G 008 10 from the State Committee for Scientific Research (KBN)

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NOWE SKROBIE ODPORNE – WŁAŚCIWOŚCI FIZYKOCHEMICZNE I STRUKTURA

Streszczenie

Nowe skrobie odporne otrzymano przez fizykochemiczną modyfikację skrobi ziemniaczanej, tapiokowej, kukurydzianej i pszennej. Nowe preparaty zawierały odpowiednio 30,84%; 18,34%; 25,48% i 26,34% skrobi odpornej według oznaczeń metodą Champa. Zbadano reologiczne właściwości tych próbek metodą Brabendera, i ich budowę metodą rentgenografii proszkowej i elektronowym mikroskopem skanningowym.

Stwierdzono, że wszystkie preparaty skrobi odpornej miały niższą temperaturę kleikowania w porównaniu ze skrobiami natywnymi. Mikroskopia wykazała, że preparaty skrobi odpornej dyspergowwały w wodzie trudniej od skrobi natywnej, dyspersja zależała od zawartości amylosy w danym preparacie. Mikroskopia elektronowa pokazała, że skrobie odporne przypominały swą budową skrobie wstępnie skleikowaną (suszoną w bębnach lub ekstrudowaną). Badania rentgenowskie wykazały, że wszystkie preparaty uzyskane ze skrobi roślin bulwiastych i zbożowych należały do krystalograficznego typu B charakterystycznego dla skrobi z roślin bulwiastych. ☒