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Effect of hydrothermal modifications on properties and digestibility of grass pea starch

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ABSTRACT

This study aimed to investigate functional and thermal properties and digestibility of grass pea starch, and provide information on the effect of hydrothermal modifications - annealing (ANN) and heat-moisture treatment (HMT) on the physico-chemical characteristics of the starch and digestibility, especially after processing (cooking, storage after cooking and freezing). After heat treatment, especially after cooking and storage at a temperature of −18 °C, the total content of slowly digestible starch and resistant starch in grass pea starch was high, which may indicate its great tendency for retrogradation. The HMT and ANN modifications of grass pea starch caused changes in its crystalline structure and increased integrity of its granules, which in turn resulted in a lower swelling power and amylose leaching, however this effect was more pronounced upon HMT which contributed to starch polymorphic type transformation from C to A. Despite greater resistance of granules of modified starches to swelling during cooking their suspensions, after cooking these starches were characterized by a higher predicted glycemic index than the non-modified ones. A similar content of resistant starch determined in modified and non-modified gelatinized starches stored at lowered temperatures indicates that starch modifications, HMT in particular, cause no changes in its susceptibility to retrogradation.

1. Introduction

The increased incidence of type II diabetes observed worldwide, has contributed to a growing interest in seeds of pulses. The major part of starch in legume seeds is represented by slowly digestible starch (SDS), owing to which these seeds have a low glycemic index. In addition, part of starch escapes digestion and is not absorbed in the small intestine; this is the so-called resistant starch (RS), classified as a dietary fiber fraction, which exerts a beneficial effect on human body [1–3]. The slow and incomplete digestion of starch in seeds is caused by the presence of intact tissue structures coating starch granules, by a high amylose content (25–65%), a high content of highly viscous soluble fractions of dietary fiber, presence of digestibility-impairing compounds like amylase inhibitors, and also by C type of starch crystallinity [4].

A special interest is aroused in scientific research by the feasibility of using starch isolated from legume seeds in food products. Starch with a low glycemic index (IG) could be used in functional foods and in products intended for particular nutritional uses, especially for consumers whose diets – due to allergy or metabolic diseases – are mainly based on starch isolated from wheat or rice which has a high GI value [5]. This is a highly unbeneficial circumstance because celiac disease is very often accompanied by type I diabetes [6]. Investigations presented in literature indicate that once starch is isolated from legume seeds its digestibility usually increases, but still largely dependents on seed species [1, 7, 8]. In addition, functional properties of legume starch often limit is applicability in the food industry. Enzymatic, chemical and physical modifications are used to improve the functional properties of starch. Since the use of chemically-modified starches raises some anxiety among consumers, a growing interest is observed in the physical methods of starch modification. These methods include hydrothermal modifications that are divided into: annealing (ANN) – heating starch in the excess of water (>60%) or at the intermediate water content (40–55%), as well as heat-moisture treatment (HMT) – heating starch at a low water content (<35%) [9]. The ANN modification is conducted at temperatures lower by ca. 3–4% from the initial gelatinization temperature (T_o) [9, 10] or at temperatures lower by 10–15 °C than T_o [11], or at a fixed temperature independent of the thermal properties of starch and usually fitting within the range from 40 to 60 °C [12]. In turn, the HMT modification is performed at temperatures of 84–130 °C or even higher [11]. Regardless the conditions applied, HMT and

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ANN induces changes in the physicochemical properties of starch without disrupting the starch granule [13].

HMT modifies properties of starch because it facilitates interactions between starch chains in the amorphous and crystalline regions and/or break down of starch crystallites. The extent of these changes depends on conditions of the HMT modification (moisture content, temperature, duration), botanical origin of starch, as well as amylose (AM) to amylopectin (AMP) ratio and their structure [13, 14]. Changes in starch structure after HMT evoke a decrease in starch granule swelling and an increase in pasting temperature [11, 15, 16]. They are typical of the starch cross-linking process and thus HMT starch may be an alternative to the chemically-modified starches [17]. In addition, the HMT is listed among the methods which increase the content of SDS and/or RS [13]. However, most studies on HTM starch digestibility refer to non-gelatinized starches and report various effects: SDS content increase and RS content decrease [18–20], only RS content increase [11, 21] and SDS and RS levels increase [15, 22] compared to the native starch. The few studies available have demonstrated higher contents of SDS and RS in HMT gelatinized starch than in the non-modified starch [11, 23].

ANN modification also causes changes in the structure of starch: reorganization of the granular structure an increase in granular stability, an increase in crystallinity and an increase in the interactions between starch chains in the amorphous and crystalline regions of the granules [11, 24, 25]. The changes of starch structure lead to a decrease in swelling power and amylose leaching and to a decrease in the gelatinization temperature range [26]. ANN influences also starch digestibility. Most investigations conducted with non-gelatinized ANN starch demonstrated an increase in its digestibility after modification [11, 12, 18], but some works report its digestibility to decrease [15]. Studies addressing digestibility of ANN gelatinized starch are sparse and demonstrated its lower digestibility compared to the gelatinized native starch [11, 16].

Grass pea (*Lathyrus sativus* L.) is mostly cultivated for stock-feed and only partly for human consumption. Its seeds are a potential source of starch, since they contain about 48% of starch [27]. Studies addressing grass pea starch demonstrate some of its physicochemical and rheological properties to differ from properties of other legume starches due to, among other things, high amylose content [28]. Scarce studies have addressed digestibility of grass pea starch, but only in the non-gelatinized state. Digestibility analyses of non-gelatinized starch are of low usability because starch-containing foods are subjected to hydrothermal treatment before consumption, which affects starch digestibility. Moreover, based on available literature, it can be concluded that the influence of the hydrothermal modification on properties of grass pea starches was not examined in contrary to other legume starches or cereal and potato starches.

Considering the above, the objective of this study was to characterize grass pea starch and provide information on the effect of hydrothermal modifications - annealing (ANN) and heat-moisture treatment (HMT) on the physico-chemical characteristics of the starch and its structure and digestibility, especially after heat treatment (cooking, storage after cooking and freezing).

2. Materials and methods

2.1. Materials

The experimental material were seeds of grass pea (*Lathyrus sativus*) var. Derek and var. Krab, originating from the Plant Breeding and Seed Production Centre "Spójnia" in Nochów, Poland. Seeds were ground without dehulling in a laboratory mill (IKA M20), sieved through a screen with a mesh diameter of 125 μm.

2.1.1. Starch isolation

Grass pea starch was isolated with 0.1% NaOH as described by Piecyk et al. [8]. The residue was air dried, milled and passed through a sieve with 90 μm openings.

2.1.2. Hydrothermal modification

Annealing. Starch was annealed by dispersing native starch samples (20 g, db) in water (1:3 starch to water). The samples in closed containers were incubated at 10 °C below the onset temperature (T_o) of gelatinization for 24 h in a water bath. Samples were centrifuged (3000*g*) and supernatant was decanted. The annealed starches were air dried at room temperature and then passed through a through a sieve with 90 μm openings.

Heat-moisture treatment. Starch samples (20 g, db) were weighed into glass containers. The moisture content was adjusted by adding water to obtain starch samples with moisture contents of 20% w/w. The starch samples were mixed thoroughly during the addition of water. The containers were sealed, kept for 24 h at ambient temperature, and then placed in a oven at 120 °C for 2 h. Afterwards the containers were opened, and the starch samples were air dried.

2.2. Chemical composition of starch

Moisture content was determined by gravimetry heating (130 °C for 2 h), using 5 g of sample. Ash and protein content were determined in accordance with AOAC method [29]. Starch lipids were determined by the procedure of Vasanthan & Hoover [30]. A total starch assay kit (Megazyme International, Ireland) was used to determine the total starch (TS) content. Apparent amylose content was determined using the method of Williams, Kuzina, and Hlynka [31].

2.3. Scanning Electron Microscopy (SEM)

Morphology of native starch was examined at a magnification of 2000× using a Scanning Electron Microscope (Hitachi S-4200, Japan).

2.4. Differential scanning calorimetry (DSC)

Gelatinization temperatures were measured and recorded on a differential scanning calorimeter (DSC, TA Instruments Q 200) equipped with a thermal analysis data station. Sample were prepared according with procedure described by Piecyk et al. [8]. The samples were heated from 20 °C up to 110 °C with the heating rate of 10 °C per minute. The onset (T_o), peak (T_p), conclusion (T_c) temperatures and the gelatinization enthalpy (ΔH) were estimated directly from the instrument software.

2.5. X-ray diffraction (XRD) characterization

X-ray diffractograms were obtained with an X-ray diffractometer (D8 Discover, Bruker Co.) under operating conditions as follows: the X-ray generator was run at 40 kV and 40 mA, and the scanning range of 3–30° 2θ and scan speed of 1.0°/min. Sample were prepared according with procedure described by Piecyk et al. [8].

2.6. Physicochemical properties

2.6.1. Swelling power and amylose leaching

The swelling power and amylose leaching of starch was determined as described by Leach et al. [32], with modifications of Piecyk et al. [8].

2.6.2. Turbidity of starch paste

Turbidity was determined using the method described by Perera & Hoover [33]. A 2% aqueous suspension of starch was heated in a water bath at 97 °C for 1 h. The pastes were cooled for 1 h at 30 °C and then stored for 24 h at 4 °C in a refrigerator (to increase the nucleation). Later samples were stored for 14 days at 40 °C. The development of turbidity at specific time intervals was estimated by measuring the absorbance at 640 nm against a water blank in spectrophotometer (UV-1601, Shimadzu).

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