

Physicochemical Properties of Pre-gelatinized Wheat Starch Produced by a Twin Drum Drier

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ABSTRACT

Wheat starch is the most common type of starch in Iran as well as many other parts of the world with enormous applications in food and non-food products. To improve its physicochemical properties or create new functionalities, starch can be modified by changing its molecular structure. Amongst different methods for starch modification, physical methods have received more attention recently. Pre-gelatinization of starch is a physical method to modify the properties of native starch. The main aim of this research was to study the physicochemical properties of pre-gelatinized wheat starch produced using a small scale industrial twin drum drier. The results indicated that drum drying destroyed native starch granules, degraded molecular structure and reduced the degree of crystallinity of starch. Pre-gelatinized starch (PGS) showed cold water viscosity at 25 °C, while native wheat starch was not able to increase the viscosity under this condition. It also increased water absorption and swelling of the starch compared to its native counterpart. Pre-gelatinized wheat starch can be used as a thickening agent in instant food products to eliminate heating stage in their production or in manufacturing of the products sensitive to high temperature.

Keywords: Wheat starch, Pre-gelatinized wheat starch, Physical modification, Physicochemical properties.

INTRODUCTION

Starch is an abundant biopolymer that is commercially extracted from many botanic sources such as potato, maize, wheat, and rice (Thomas and Atwell, 1999; Tester et al., 2004). Native starch has numerous applications in food and other industries. As a food component, it may act as water absorbent, thickening, gelling and dusting agents and also as a nutrient since it can provide up to 80% of the calories consumed by human every day (Eliasson, 2004). However, limitations such as low shear and thermal resistance, thermal decomposition, and high tendency towards retrogradation limit its applications in modern food

industry (Meister, 2000). Starch modification, which involves the alteration of the physicochemical properties of native starch to improve its functional characteristics, can be used to adapt starch to specific applications. Starch modification is generally achieved through chemical, physical, enzymatic, and genetic methods or a combination of them (Singh et al., 2006). Amongst them, physical methods have received more attention since they are chemical free and fairly easier than the other methods.

Pre-gelatinized starch (PGS) is a common type of physically modified starch with wide applications, especially in food industry. PGS, also referred to as "pre-gel" or "instant

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starch", is generally produced by drum drier, spray drier, and, less commonly, by extruder (Anastasiades et al., 2002; Kalogianni et al., 2002; Mounsey and O'Riordan, 2008). Depending on the method, condition and source of starch, the produced PGS has different properties (Mercier 1987; Kalogianni et al., 2002). Amongst the different methods available for production of pre-gel starch, drum drying is the most economical and the easiest method available compared to the other methods (Thomas and Atwell, 1999).

Drum-drying results in specific physicochemical modifications of starch granules and is performed in two consecutive stages: gelatinization and drying. In a double or twin drum dryer, gelatinization takes place inside the "pool" of material formed between the upper halves of two horizontal drums. The actual drying starts only after the gelatinized material leaves the pool through the clearance between the drums and forms a thin film upon the surface of the drums (Gavrielidou et al., 2002).

The process of gelatinization causes substantial changes in both chemical and physical nature of granular starch due to the rearrangement of intra- and inter-molecular hydrogen bonding between water and starch molecules resulting in the collapse or disruption of molecular orders within the starch granules. This causes irreversible changes in the starch properties including loss of organized structure of starch, granule swelling, loss of birefringence and crystallinity (Cooke and Gidley, 1992; Anastasiades et al., 2002).

Previous studies examined the characteristics of pre-gelatinized starches using single drum dryers as regards industrial applications. For instance, the effects of the throughput rate and moisture content of the end product on the performance of a single drum dryer were studied by Colonna et al. (1984) and Kozempel et al. (1986). Recently, many studies focus on production of pre-gelatinized starch using twin drum dryers.

Accordingly, the process condition and properties of the final product were studied. For instance, the effects of the processing conditions such as feed concentration, drum speed, and temperature on the properties of pre-gelatinized maize starch produced by a twin drum drier were studied by Kalogianni et al. (2002); Anastasiades et al. (2002); and Gavrielidou et al. (2002). Furthermore, the impacts of moisture content on the physicochemical properties of pre-gelatinized banana and other starches were studied by Fechner et al. (2005). These starches were produced using twin drum drier. Moreover, the crystallinity and rheological properties of pre-gelatinized rice starches produced by twin drum drier were investigated by Nakorn et al. (2009).

Generally, twin drum drying has less mechanical shear and can produce thinner films compared to single drum drier. The pre-gelatinized starch produced by twin drum drier has slightly higher viscosity and less grainy structure compared to its counterpart produced by single drum drier (Mercier 1987; Thomas and Atwell, 1999).

From the literature, it can be concluded that the physicochemical characteristics of PGS are affected by many factors including the methods, conditions and the source of starch used for production of PGS. Additionally, choosing the right type of modified starch is of great importance, since it has a significant effect on the quality of final products. Therefore, for characterization of the final product, all crucial parameters including source of starch, the method, and conditions of the process should be considered.

In Iran, as well as many parts of the world, wheat starch is the most available type of starch that may be modified using different methods. Accordingly, the main aim of this research was to characterize the physicochemical properties of pre-gelatinized wheat starch produced by a small scale twin drum drier.

The results of this study could be useful in predicting the final quality of the products made with pre-gelatinized wheat starch.

Moreover, understanding the properties of PGS can introduce new applications for this product in food and non-food applications.

MATERIALS AND METHODS

Pure wheat starch was purchased from Fars-Glucosin Co. Shiraz, Iran. Other chemicals were of analytical grade and were obtained from Merck, Germany. Pure amylose from potato and pure amylopectin from maize were obtained from ICN Biomedicals, Inc., USA.

Determination of amylose content of the sample

The amylose content of wheat starch was determined by iodine method (Blazek and Copeland, 2008). The principle of this method is based on the blue color developed by addition of iodine reagent to a solution containing starch under standard conditions. The quantity of amylose was determined from a standard curve developed using amylose and amylopectin blends. To determine amylose content using this method, wheat starch was first defatted using diethyl ether as a solvent.

Production of pre-gelatinized wheat starch

Wheat starch was first dispersed in cold water (10% w/w, starch in water), then, it was dried using a twin drum drier (Model Benton Harbor, USA) at drum speed of 5 rpm, steam pressure of 5 bar, clearance between the drums of 0.4 mm and the surface temperature was 158 °C. The dried starch sheet with moisture content of 7.3% ± 0.2 (dry weight basis) was milled using a laboratory mill and then sieved to obtain a powder with particle size of 150-250 µm. The PGS was packed in polyethylene bags and stored at room temperature for further experiments.

Microscopic structure of starch

To study the microscopic structure of the starch samples, scanning electron microscope (SEM) (Model 5526, Mark Cambridge, UK) was used. To prepare the samples, a tiny amount of each sample was sputter coated with gold/palladium. Finally, the samples were transferred to the microscope where they were observed at 20 kV.

Intrinsic viscosity

Intrinsic viscosity is an indication of molecular structure in terms of size, shape, and molecular weight of macromolecules fully solubilized in dilute solutions (Harding, 1997). To determine the intrinsic viscosity of the pre-gelatinized samples, solutions of 6 mg/ml starch in 1M KOH were prepared according to Anastasiades et al. (2002). Similar method was also used to solubilize native wheat starch. Since starch should be fully solubilized in the solvent before being used in this experiment, the solubility of the samples in 1M KOH was checked by light transmission method according to Lawal, et al. (2005). Therefore, light transmittance of the solutions was measured at 640 nm against the blank (1M KOH).

The intrinsic viscosity was determined using a U-tube viscometer at 20 ± 0.1 °C according to Harding, (1997). Then, the relative, the reduced, and the intrinsic viscosities were determined using the Equations 1-3, respectively (Harding, 1997).

$$\eta_{rel} = \frac{\eta}{\eta_0} = \left(\frac{t}{t_0}\right) \cdot \left(\frac{\rho}{\rho_0}\right) \quad (1)$$

Where η_{rel} is relative viscosity, t and t_0 are the times required for the sample and solvent (KOH 1M) to pass through the U-tube, respectively. ρ and ρ_0 are the densities of sample and solvent, respectively.

Then, the reduced viscosity was determined according to Equation 2:



$$\eta_{red} = \frac{\eta_{rel} - 1}{C} \quad (2)$$

Where, η_{red} is the reduced viscosity and C is the concentration of the sample.

Later, intrinsic viscosity; η , was determined using Equation 3:

$$[\eta] = \lim_{c \rightarrow 0} \eta_{red} \quad (3)$$

Wide angle X-ray diffraction

To determine the crystalline diffraction pattern of the starches, nearly 2 g of each sample equilibrated at relative humidity of 75% were pressed into a sample holder. Diffractograms were recorded using an X-ray diffractometer (Model D8 Advance, Germany). The scattered X-ray radiation was recorded by a proportional moving detector over a 4-38° (2 θ) angular range with an angular velocity of 0.05°/min. The degree of starch crystallinity was determined using Equation 4. The area was calculated using the software developed and supplied by the instrument manufacturer (EVA, Version9.0). Degree of crystallinity(%)

$$= \left(\frac{\text{Area under the peaks}}{\text{Total curve area}} \right) \times 100 \quad (4)$$

Rapid Visco Analyzer (RVA) pattern

A Rapid Visco Analyser (Newport Scientific Pty. Ltd., Warriewood, Australia) equipped with the software ThermoLine for Windows was used to study the pasting properties and to measure the apparent viscosity of the native and modified samples as a function of temperature (Batey and Curtin, 1996; Bason and Booth, 1996).

An aliquot amount of each sample (4 g d.w.b.) was added to 25.0 g distilled water. The paddle blade was placed into the canister containing the sample and water and the canister was then inserted into the RVA. The stirring speed was 960 rpm for the first 10 seconds and 160 rpm for the rest of the experiment. To study the pasting profile of

the native and the PGS, samples were initially held at 25 °C for 2 min to study the cold-water viscosity; then, they were heated to 95 °C at a constant rate of 14 °C/min, and were held at that temperature for 3 min, then, cooled down to 25 °C at the same rate and were held at that temperature for 5 min.

Water solubility

The water solubility of the samples was determined according to Leach et al. (1959) with slight modification. Starch was dispersed in distilled water (3% w/w, starch in water) and heated up to 95 °C and held for 30 min. Then, it was centrifuged at 700g for 15 min. The supernatant, containing solubilized starch was collected, dried at 120 °C to constant weight, and the residue was weighed. Starch solubility was determined according to Equation 5 (Leach et al., 1959).

$$\text{Solubility (\%)} = \frac{\text{weight of dried supernatant}}{\text{dry weight of initial starch}} \times 100 \quad (5)$$

Water absorption

To determine water absorption, samples were prepared in the same way as described for determination of water solubility. However, after centrifugation, the supernatant was discarded and the pellet was weighed. The water absorption was then calculated using Equation 6 (Leach et al., 1959):

$$\text{Water absorption (\%)} = \frac{\text{weight of pellet} \times 100}{\text{dry weight of initial starch}} \quad (6)$$

Statistical analysis

The experiments were performed in a completely randomized design. All experiments were conducted in triplicates and the mean values and standard deviations were calculated. Analysis of variance (ANOVA) was performed and results were

separated using the Multiple Ranges Duncan's test ($\alpha < 0.05$), using statistical software of SPSS 13 (SPSS, New Jersey).

RESULTS AND DISCUSSION

The amylose content of wheat starch was 24.20%. This value is in the range of amylose content reported for wheat starch by Majzoubi (2004) and Blazek and Copeland (2008). It should be mentioned that amylose content of the starch samples depends on the source of starch, the method used for determination of amylose content, and the chemical composition of starch (Tester et al., 2004; Copeland et al., 2009).

Microstructure of starch samples

Comparison of the micrographs obtained for native and PGS (Figure 1) revealed that pre-gelatinization of starch destroyed the granular structure of native starch. Instead, a sheet like structure was observed for PGS in which air bubbles were randomly distributed inside the continuous solid. This may indicate that all the starch granules underwent gelatinization during drying.

For native wheat starch, the typical A (large) and B (small) starch granules were visible. Similar observations were also reported by Anastasiades et al. (2002) for pre-gelatinized maize starch.

Intrinsic viscosity of starch samples

Intrinsic viscosity measurements are customarily used to grade the degree of granule breakdown and, in essence, the severity of the thermal treatment (Mercier, 1987). It is an indication of molecular characteristics of macromolecules in solution. For ideal solutions of monodisperse macromolecules, it is possible to determine the molecular weight, size and shape; however, since starch solutions are regarded as non-ideal and extremely polydisperse, determination of such values are not possible from intrinsic viscosity data. The only information that can be obtained is the relative values of molecular structure (Harding, 1997). Since the starch should be fully solubilized in a solvent before being used in the U-tube, the solubility of the samples was determined. The results showed that all the samples were fully solubilized since the transmission% of the samples was greater than 95%.

Determination of intrinsic viscosity of the samples (Table 1) showed that PGS had significantly lower intrinsic viscosity than the native starch. This may indicate that using drum drying could cause molecular degradation of starch molecules since the drums attain high temperatures that can intensify thermal processing (Vallous et al., 2002). Similar observation was also reported for pre-gelatinized wheat starch produced by a single drum drier (Colonna et al., 1984) and for pre-gelatinized maize starch produced by twin drum drier (Anastasiades

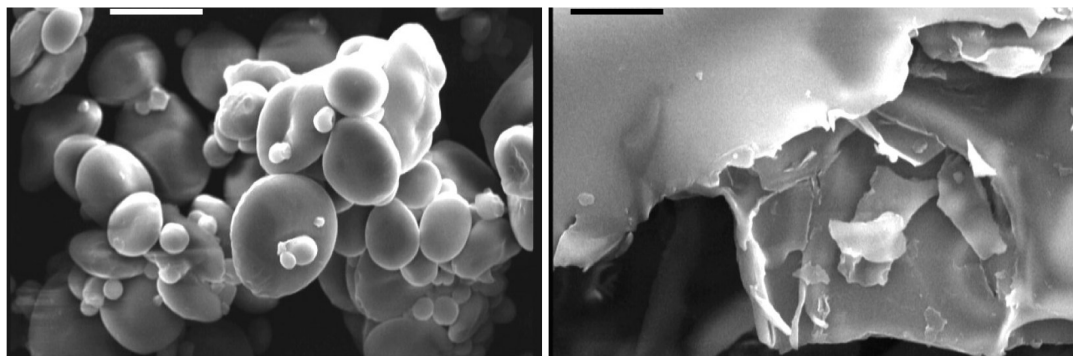


Figure 1. Scanning electron micrographs of native (left) and PGS (right) Bars on the micrographs represent 20 μm .

**Table 1.** Physicochemical characteristics of the native and the pre-gelatinized wheat starch^a.

Characteristics	Native starch	PGS
Amylose content (%)	24.20 ± 0.20	nd ¹
Intrinsic viscosity (ml/g)	186.32 ^a ± 10.00	169.38 ^b ± 5.00
Crystallinity (%)	40.08 ^a ± 0.50	2.22 ^b ± 0.37
Water solubility (%)	13.60 ^a ± 0.04	18.50 ^b ± 2.90
Water absorption (%)	8.13 ^a ± 0.12	19.40 ^b ± 0.73

^aValues are the average of triplicates ± 1SD. Different letters in each column show statistical difference between the samples ($\alpha < 0.05$).

et al., 2002). They indicated that in drum drying, the reduction of the intrinsic viscosity may indicate the degradation of the starch macromolecules. Such modifications may occur during the gelatinization stage in the pool or during the subsequent intense drying or both.

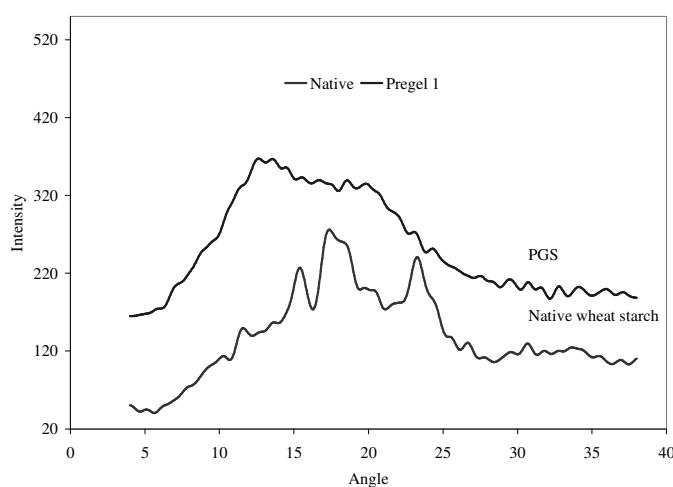
The crystalline structure

The x-ray diffraction pattern of PGS and native starch are presented in Figure 2. The typical A-pattern that is normally observed for native cereal starches can be observed for the native wheat starch. This is due to the present of a semi-crystalline structure of amylopectin inside the granules (Zobel, 1988). The degree of crystallinity of native wheat starch was 40.08%. (Table 1). Crystallinity values of 36% and 39% were reported for wheat starch by Morrison et

al.(1994) and Cooke and Gidley (1992), respectively. It has been documented that starches from different wheat cultivars have different level of crystallinities. For PGS, no clear crystalline structure can be observed. On the other hand, the A-pattern was devastated by the process. The degree of crystallinity of 2.22% for PGS is significantly much less than determined for the native starch.

Pasting properties

The pasting curve obtained from a RVA is a measure of the viscosity of starch or cereal suspension during the heating cycle, which reflects the molecular events occurring in the starch granules. Therefore, the integrity of starch granules and hydration properties resulting from the starch native properties, or from the inter- or intra-molecular interactions

**Figure 2.** X-ray diffraction patterns of native and PGS obtained by X-ray diffractometer.

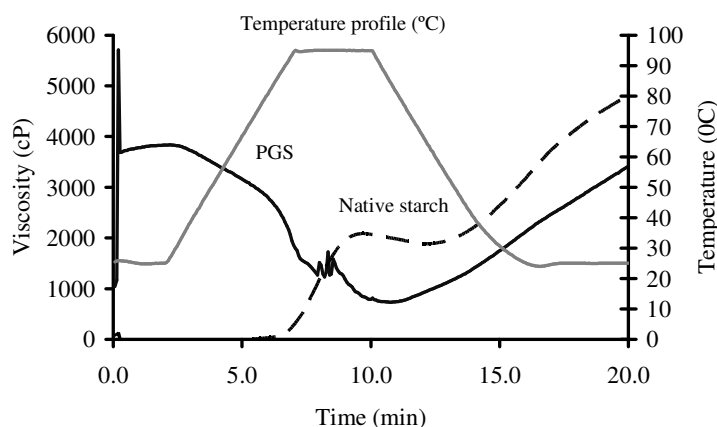


Figure 3. The RVA profiles of native and PG wheat starch.

during hydrothermal treatment, can be easily investigated by measuring the pasting curves before and after modification.

Figure 3 shows the RVA patterns of the PGS and the native starch. A cold water viscosity of 3833 centi Poise (cP) was observed for PGS at 25 °C, while no peak was seen for the native starch at this temperature. For the latter, a peak viscosity of 2011 cP was observed at 95 °C when the sample was held for 11 min. Nakorn et al. (2009) studied pasting properties of pre-gelatinized rice starch using RVA. They also found that a cold peak viscosity can be obtained for pre-gelatinized rice starch of high amylose content.

Under the same condition, the PGS had its lowest viscosity of 738 cP. The native starch had higher final viscosity (4810 cP) than the PGS (3406 cP).

The results indicate that the PGS had the ability to increase the viscosity at temperatures below gelatinization temperature of native starch. At high temperatures, however, the native starch was able to increase the viscosity. Moreover, if PGS is heated and then cooled down, it produces lower final viscosity than native starch.

Determination of water solubility and absorption indices

Table 1 shows that PGS starch had significantly higher water solubility and

absorption indices compared to the native starch. This can be attributed to the destruction of starch granules, reduction of the degree of crystallinity, and degradation of starch molecules during pre-gelatinization (as confirmed previously in this study by electron microscopy, crystallinity, and intrinsic viscosity results). Apparently, the porous structure of PGS can readily absorb more water compared to the native starch. Slaughter et al. (2001) also reported higher water solubility and swelling for fully gelatinized wheat, maize, and rice starches. Higher solubility and water absorption values were also reported for pre-gelatinized banana starch by Waliszewski et al. (2003).

CONCLUSION

Drum drying imparts a number of morphological and textural characteristics to the modified starches, reflecting the intensity of the treatment. In this study, PGS produced using drum drier had the following properties: it had no granular structure, low crystalline structure, high cold water viscosity, and high water solubility and absorption. The results support the notion that the integrity of starch granules has a great contribution to the rheology of starch paste.

PGS produced under different conditions and starch concentration may have different



porosity and, consequently, slightly different rheological properties that should be considered before application.

Based on these properties, PGS can be used mainly as a thickening and gelling agent in refrigerated and instant foods or heat sensitive products such as cold desserts, salad dressing, cake and bakery mixes, and baby foods. PGS is able to viscofy the solutions or mixes in which it is being used without any heat treatment (Karaoglu et al., 2001; Fechner et al., 2005).

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خواص فیزیکی و شیمیایی نشاسته گندم پیش ژلاتینه شده تولید شده به روش خشک کن دو غلطکی

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چکیده

نشاسته گندم متداولترین نشاسته تولیدی در ایران و بسیاری از کشورهای جهان می باشد که کاربردهای بسیاری در صنایع غذایی و غیر غذایی دارد. به منظور بهبود خواص فیزیکی و شیمیایی و یا ایجاد خواص عملکردی جدید، می توان با ایجاد تغییراتی در ساختار نشاسته آنرا اصلاح نمود. از میان روشهای متعدد موجود جهت اصلاح نشاسته، روشهای فیزیکی اخیرا مورد توجه بسیار قرار گرفته اند. تولید نشاسته پیش ژلاتینه شده یکی از روشهای فیزیکی برای اصلاح نشاسته طبیعی می باشد. هدف اصلی از انجام این تحقیق مطالعه خواص فیزیکی و شیمیایی نشاسته گندم پیش ژلاتینه شده است که به کمک یک خشک کن دو



غلطکی در سطح آزمایشگاهی تولید شد. نتایج این تحقیق نشان داد که استفاده از خشک کن دو غلطکی برای تهیه نشاسته پیش ژلاتینه شده باعث تخریب ساختار گرانولی، تجزیه مولکولهای نشاسته و کاهش درجه کریستالی نشاسته گردید. نشاسته پیش ژلاتینه شده دارای ویسکوزیته آب سرد (در دمای 25°C) بود، در حالی که نشاسته طبیعی قادر به ایجاد ویسکوزیته در این شرایط نبود. نشاسته اصلاح شده همچنین دارای قدرت جذب آب و تورم بیشتری نسبت به نشاسته طبیعی بود. با توجه به این خصوصیات، نشاسته پیش ژلاتینه شده قابلیت استفاده شدن به عنوان تغلیظ کننده در غذاهای آماده مصرف و یا محصولات حساس به حرارت به منظور حذف یا کاهش حرارت دهی را دارد.