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Effects of amylose content, cooling rate and aging time on properties and characteristics of rice starch gels and puffed products

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ABSTRACT

This study aimed at investigating the effects of amylose content (AC) of 0.12–19.00% w/w on dry basis, cooling rate (1, 3, 5, and 9 °C/min), and aging time (24, 48, and 72 h) on structure, physical properties and sensory attributes of rice starch-based puffed products. They had an influence upon the crystalline type, and the relative crystallinity (RC). The thermal and physical properties of starch gels were also determined. Amorphism was found for starch gels with 0.12% AC. The polymorphisms (B and V) and differential scanning calorimetric endotherms were found for those with AC ≥4.00%. The RC, retrogradation enthalpy (ΔH_r) and gel hardness increased with AC and aging time. The cooling rate did not affect RC, but increased ΔH_r and gel hardness. The higher AC and aging time resulted in higher hardness, fracturability, crispiness and bulk density, but lower expansion ratio and less oiliness of the puffed products. The hardness, fracturability, crispiness and bulk density of puffed products were well correlated with the RC of starch gel.

1. Introduction

Starch-based snacks and ready-to-eat breakfast cereals continue to increase in sales worldwide. Starch-based snacks are commonly made in the form of puffed products. Puffed products are appreciated mainly for their lightness and crispness. These quality attributes are related to the air cell structure and degree of expansion. Puffing is a process used for expansion of food materials to give them a light, airy and crispy texture (Mariotti et al., 2006). The process of making starch-based puffed products included the gelatinization of starch, cooling, drying, and then explosive expansion (Chen and Yeh, 2001; Norton et al., 2011; Tongdang et al., 2008). After starch gelatinization, retrogradation of amylose and amylopectin occurred during the cooling and aging of the pastes (Mariotti et al., 2006; Perdon et al., 1999). The amylose-amylopectin ratio, which was commonly reported in terms of AC, has been known to be an important parameter affecting physical properties of starch pastes/gels and characteristics of puffed products (Chen and Yeh, 2001; Tongdang et al., 2008; Saeleaw and Schleining, 2010). Gelation occurred upon the cooling of gelatinized high amylose starch. Amylose was reported to retrograde within a day of aging and involves a crystallization process. This retrograded amylose was considered to be the crystal nuclei, which served as a site for crystal growth (Yu et al., 2009). A higher AC led to a faster starch retrogradation generating a higher ΔH_r and gel hardness (Vandeputte et al., 2003). B-type crystallites appeared during amylose retrogradation (Marsh and Blanshard, 1988). The aging temperature and water content affected the arrangement of the starch molecules in the crystal. For rice starch gel, the B-type appeared at 40 °C, while the more stable A-type appeared at 95 °C (Shamai et al., 2003). The presence of B-type occurred at >43% water content, whereas the A-type took place at <29% water content (Osella et al., 2005). Thus, it was concluded that the A-type formed in warm and dry conditions and the B-type formed in wet and cold conditions. The amylose-lipid complexes were formed after starch gelatinization. These amylose-lipid complexes gave the V-type which was reported to transform to B-type upon aging (Hibi et al., 1990). While amylose retrogradation and formation of amylose-lipid complexes occurred right after cooling, amylopectin retrogradation took more time (Fu et al., 2013). Therefore, RC, which indicated the quantity of crystalline structures, increased with aging time (Aguirre et al., 2011; Primo-Martin et al., 2007). Starch crystallization required diffusion and rearrangement of starch molecules, therefore it was cooling rate dependent. A lesser

Abbreviations: AC, amylose content; RC, relative crystallinity; DSC, differential scanning calorimeter; XRD, X-ray diffraction; ΔH_r, retrogradation enthalpy; ΔH, enthalpy; SEM, Scanning electron microscope.

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RC was expected for the faster cooling rate due to limited time for diffusion and reorganization of starch molecules (Nordmark and Ziegler, 2002).

Starch gelation created a network which later serves as the air cell wall of puffed products. During puffing, heat caused vaporization in food materials. Vaporization enlarged air cells and expanded the starch network. Breaking or cracking of the network upon vaporization should be avoided to obtain good quality attributes of products. This requires balancing between the strength of starch network and the pressure of the vapor. The parameter responsible for expansion/deformation of the network without breaking is its flexibility. It is hypothesized that crystallites formed during retrogradation are responsible for the strength and flexibility of the starch network, which consecutively affects the puffed products' characteristics and properties. Therefore, RC and ΔH_r are significant parameters that determine the physical properties (hardness, fracturability, bulk density and expansion ratio), air cell characteristics and the sensory attributes of the puffed products. The number of published studies is limited.

Therefore, this research aims at 1) identifying effects of AC, aging time and cooling rate on a) the crystalline type, RC, ΔH_r and the hardness of starch gel, b) the physical properties of puffed products and c) the sensory attributes of puffed products, and 2) establishing correlation between RC and the physical properties of puffed products.

2. Materials and methods

2.1. Starch isolations

Starch was isolated from either waxy rice (RD6, Royal Umbrella Brand, Ayutthaya, Thailand) or non-waxy rice (Soa-hi, Pin-Ngern Brand, Nonthaburi, Thailand) by wet milling (distilled water: rice = 5:1 in weight) with a stone mill (Sodhi and Singh, 2003). Alkaline steeping, at pH 8.5 adjusted with 0.1 M NaOH (Ajax Finechem, NZ), was used for protein removal. After neutralization with 1 M HCl (Ajax Finechem, NZ) and washing, starch suspension was filtered through a 100-mesh sieve, and then sedimented. The starch cake was dried at 50 ± 1 °C for 14 h in a hot air oven (HA−100S, Yeoheng Co., Ltd., Thailand), ground into powder with a blender (HR2001, Philips, Belgium), and then sieved through a 200-mesh screen. Waxy starch and non-waxy starch were separately packed in aluminum foil bags and stored at 4 ± 1 °C.

2.2. Starch mixture preparation

The rice starch mixtures were prepared by mixing waxy starch and non-waxy starch at weight ratios of 100:0, 75:25, 50:50, 25:75, and 0:100. The AC of the prepared rice starch samples that had been isolated from waxy rice and non-waxy rice and their mixture (at weight ratio of 50:50) was determined by the amperometric titration method (Larson et al., 1953). The AC was found to be 0.12% $w/w_{dry\ starch}$ for waxy rice starch and 19.00% $w/w_{dry\ starch}$ for non-waxy rice starch. The AC for their mixtures was found to be 4.00, 9.00, and 14.00% $w/w_{dry\ starch}$ for weight ratios of waxy starch to non-waxy starch of 75:25, 50:50, and 25:75, respectively. These starch mixtures were separately packed in aluminum foil bags and stored at 4 ± 1 °C.

2.3. Starch pellet preparation

Starch (30 g dry weight) was dispersed in water (28 g). This dispersion was poured in hot water at 95 ± 2 °C to obtain a total suspension weight of 100 g. The 100 g starch suspension was cooked at 110 ± 1 °C for 20 min in the closed system (1 L capacity) equipped with a hand mixer (BUO-153263, Buono, Germany) with continuous stirring at speed level 5. The moisture content of the starch paste was determined. The starch paste was spread onto wax paper (Pankraft paper, Daiso, Japan) to obtain a thin slab (17.8 × 28.0 × 0.2 cm). The temperature of the starch paste was determined to be 40 ± 3 °C after spreading. The spread pastes were cooled from 40 ± 3 °C–4 °C in the cooling box. This cooling box (35.5 × 30.5 × 29.5 cm) was made of polystyrene foam having a 2.3 cm thickness, containing 6 blocks of dry ice (block size and weight were 20.0 × 15.0 × 2.5 cm and 1.17 ± 0.02 kg) and equipped with an electric fan (9 V direct current power supply, Suksapanpanit Scientific Apparatus and Instruments, Bangkok, Thailand). The fan can be operated at three speeds of 49 ± 0.33, 40 ± 0.33, and 30 ± 0.33 Hz as measured by the frequency counter (Leybold Didactic GMBH, Germany). For varying cooling rates, the fan was operated at these speeds for 3, 6, and 9 min, respectively. The control sample was kept in an incubator (MIR-153, Sanyo, Japan) at 4 °C for 42 min. During cooling, the temperature and time was recorded by a data logger (AI2100, Wisco, Thailand). The sample temperature at 4 points was measured by calibrated resistance temperature detector (RTD) sensors (SK JB-T, Sang Chai Meter Co., Ltd., Thailand) until the temperature went down to 4 °C. A total of four sensors were placed in the middle of the slab along its length with equal separation. The cooling rates were found to be 1, 3, 5, and 9 °C/min, respectively. After cooling to 4 °C, the starch gel was wrapped in plastic film and kept in a plastic box enclosing/containing silica gel and aged at 4 ± 1 °C in an incubator for 24, 48, and 72 h. The sample was cut into squares measuring 2 × 2 cm and then dried in a hot air oven (FD 240, Binder, Germany) at 40 °C for 10 h. The moisture content of all prepared pellets was found to be 15% w/w on a dry basis.

2.4. Puffing

For each batch, 6 g dried starch pellets were puffed by deep frying in 500 g palm oil (Morrakot, Morrakot Industries Co., Ltd., Thailand). The oil was heated on a hot plate (IH-EOV-40B-4, Alfa Kitch, Alfa One Trading Co., Ltd., Korea) that turned to the highest setting. The oil temperature was monitored and recorded using a calibrated thermocouple (Type K, SK PCR-1, Sang Chai Meter Co., Ltd., Thailand) and data logger (AI2100, Wisco, Thailand). The pellets were dropped in oil when it reached 210 °C, and they were fried for 50 s. The recorded temperature during frying was found to be 210 ± 1 °C.

2.5. X-ray diffraction (XRD) pattern

The gel was freeze-dried (at −50 °C, 50 × 10^{-3} mbar for 12 h). The dried pellets were kept in a vacuum desiccator at 25 ± 0.7 °C for 2 weeks. For controlling humidity, saturated sodium chloride solution was placed in a desiccator. The XRD pattern and RC were determined as described in Primo-Martín et al. (2007). The X-ray diffractometer (D5005, Siemens AXS, Germany) was equipped with a copper tube operating at 40 kV and 40 mA and producing monochromatic copper K_α with 0.154 nm wavelength. The data was collected from 5° to 45° 2θ at 0.02° intervals with a rate of 0.04°/s. The RC was determined using a peak-fitting software (Origin-version 8.0, Microcal Inc., USA).

2.6. Thermal properties

Thermal properties were determined using a differential scanning calorimeter, DSC (DSC 8000, Perkin−Elmer, Norwalk, VA, USA) as described by Perdon et al. (1999). The sealed sample and empty reference pans (stainless steel) were heated in DSC from 20 to