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Physico-chemical, thermal and rheological properties of starches isolated from newly released rice cultivars grown in Indian temperate climates

Ali Abas Wani^{a,b,c,*}, Preeti Singh^{b,c,*}, Manzoor Ahmad Shah^a, Idrees Ahmed Wani^d, Alexander Götz^b, Michael Schott^b, Christian Zacherl^b

^a Department of Food Technology, Islamic University of Science & Technology, Awantipora, Jammu & Kashmir 190 221, India

^b Fraunhofer Institute for Process Engineering & Packaging IVV, 85354 Freising, Germany

^c Chair of Food Packaging Technology, Technical University of Munich, 85350 Freising-Weihenstephan, Germany

^d Department of Food Science & Technology, The University of Kashmir, Hazratbal, Srinagar, Jammu & Kashmir, India

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ABSTRACT

Starches isolated from three newly released rice cultivars were tested for different physico-chemical, thermal and rheological properties. The starch granule had either polygonal or irregular shapes with small particle size mainly falling in the range of 1–10 µm. SR-1 had more polygonal shapes than SKUAST-5 and SKUAST-27. SR-1 starch also showed significantly high ($p \le 0.05$) amount of amylose (28.6 g/100 g starch) which possibly was responsible for high swelling power (25.9 g/100 g starch), solubility (26.4 g/ 100 g starch) and syneresis (35.2 g/100 g starch). Thermal properties (T_0 ; T_p ; T_c) and enthalpy of gelatinization (ΔH_{gel}) also exhibited significant ($p \le 0.05$) differences thereby affecting the stability of crystalline structures among the rice starches. SKUAST-5 starch showed the lowest value for T_0 (58.5 °C) but exhibited highest value of ΔH_{gel} (18.5 J/g). SR-1 starch exhibited slightly higher degree of retrogradation (83.1 g/100 g starch) than SKUAST-5 (80.2 g/100 g starch) and SKUAST-27 (79.6 g/100 g starch). The flow behavior indicated differences in shear thinning behavior and hysteresis area. All samples showed high structural recovery indicating their suitable use in high shear processing. SKUAST-27 exhibited high value (42.4 g/100 g starch) of rapidly digestible starch (RDS) than SR-1 (39.8 g/100 g starch).

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1. Introduction

Rice (*Oryza sativa*) is the major cereal crop cultivated in the world and constitutes a staple food for several countries including India, China, Thailand, Philippines etc. In 2010, the total world rice production was estimated as 696324394 tons; India being one of the major producers has a major contribution of about 129349631 tons (FAOSTAT, 2012). Diversity in climatic conditions, genetic makeup and consumer preferences have led to natural and trans genetic evolution of about 2000 thousand rice cultivars (Deepa, Singh, & Naidu, 2008; Wani et al., 2012). Diversity in rice cultivars largely affects their physical properties, composition, cooking properties and aromatic compounds (Wani et al., 2012). Starch, being the major constituent, mainly determines the acceptability of

the rice cultivar in terms of physico-chemical properties and cooking characteristics. Rice starch has several advantages over other starches e.g. hypo-allergenicity, bland flavor, small granules, white color, greater acid resistance, spreadable and relatively good freeze thaw stability of gels (Wani et al., 2012). Additionally it offers several technological advantages as well as a wide range of amylose: amylopectin ratios (Lawal et al., 2011; Mitchell, 2009). These unique attributes together with large diversity makes rice as one of the best starch sources for industry (Vandeputte & Delcour, 2004). Evolution of rice cultivars has impact on physico-chemical properties of different rice starches as reported by several researchers (Ahmed, Ramaswamy, Ayad & Ali, 2008; Lawal et al., 2011; Wang, Xie, Xiong, Du, & Liao, 2012). Rice cultivar heterogeneity is exploited to produce starches with different technofunctionalities to meet the demand for novel starches in food, cosmetic and pharmaceutical applications.

Rice starch granules are the smallest known to exist in cereal grains, having a size in the range of $2-8 \mu m$ (Vandeputte & Delcour, 2004; Wang et al., 2012). The granules have a smooth surface but

^{*} Corresponding authors. Chair of Food Packaging Technology, Technical University of Munich, 85350 Freising-Weihenstephan, Germany. Tel.: +49 8161 491 194; fax: +49 8161 491 444.

E-mail addresses: ali.abbas.wani@gmail.com, waniabas@gmail.com (A.A. Wani), preeti_ndri@rediffmail.com (P. Singh).

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angular, irregular and polygonal shapes. The complexity of starch biosynthesis results in natural variability in amylose and amylopectin molecules, which is reflected in diversity of granule morphology. Starch properties depend on the physical and chemical characteristics such as mean granule size, granule size distribution, amylose/amylopectin ratio and mineral content (Madsen & Christensen, 1996). The role of amylose and amylopectin in the gelatinization and pasting properties of rice starch has been widely studied (Li, Shoemaker, Ma, Kim, & Zhong, 2008).

Starch sources with desirable physico-chemical properties (syneresis, turbidity, freeze thaw stability) are continuously explored by the scientists in hopes that chemical modifications can be avoided (Correja, Nunes, & Beirao-da-Costa, 2012). Therefore, the characterization of different starches is of great importance to select the starch for product specific end use. Rice starch is also used in some food products due to its desirable rheological properties. To understand the rheological properties, Rapid visco analyser and stress controlled rheometer are commonly used to study the pasting properties, flow behavior and dynamic rheological properties (Lin, Xiao, Zhao, Li, & Yu, 2009; Wani et al., 2012). These properties are reported to be affected by amylose, lipid contents and by branch chain length distribution of amylopectin. The rheological properties of starch pastes or gels may be investigated as flow behavior, viscoelasticity, mechanical spectra, creep, and gel strength (Ahmed et al., 2008; Lawal et al., 2011). The most frequently measured flow behavior index of rice starch dispersions in steady flow can be carried out during gelatinization or on a gelatinized paste. Power law and Herschell-Bulkely models are frequently used to describe the flow behavior of rice starches. These models give information on the flow behavior index (n) and the consistency coefficient (*K*) and yield stress (τ_0) of starch suspensions. The values of *n*, *K*, and τ_0 are dependent on starch type, starch concentration, and temperature. The gelatinized starch pastes preheated to temperatures of about 90 °C are reported to exhibit shear-thinning (pseudoplastic) behavior with values of *n* considerably less than 1.0. Lawal et al. (2011) reported the shear thinning behavior of 5 different rice starches from West Africa.

The objectives of the present work were to study the physicochemical, thermal, rheological properties of the starch for newly released rice cultivars.

2. Material & methods

2.1. Materials

Three newly released rice cultivars grown in Indian temperate climates were harvested in October 2010 and were procured form the Regional Rice Research Station, Sher-e-Kashmir University of Agricultural Sciences and Technology, Shalimar, Srinagar, J&K, India. All the reagents used in the study were obtained from Sigma–Aldrich, St. Louis, USA.

2.2. Starch isolation

The paddy grains were dehusked using a McGill sample sheller (Rapisco, Brookshire, TX, USA) followed by 5% polishing with Mc Gill mill No. 2 polisher (Rapisco, Brookshire, TX, USA). The polished rice was milled in a laboratory mill (LM120, Perten Instruments, Hägersten, Sweden). The starch was extracted following the alkali extraction method of Lawal et al., 2011.

2.3. Physico-chemical properties

2.3.1. Chemical composition

Ash, crude fiber, crude protein, and fat were determined according to the methods of AACC (2001). The moisture content

was determined with a moisture analyzer (MA 100, Sartorius AG, Gottingen Germany). Apparent amylose content was determined according to the method of Hoover and Ratnayake (2002).

2.3.2. Morphological properties

Starch granule size distribution was determined with a laser diffraction particle size analyzer (Malvern S Mastersizer, Malvern Instruments Limited, UK). Dry starch sample (0.1 g, dry weight basis) was mixed with 200 ml of HPLC-grade water, and the suspension was agitated at a slow speed using a magnetic stirrer for 1 h at 20 °C. The starch suspension was then filled into the small volume sample dispersion unit of the Mastersizer to obtain an obscuration level of around 20%. Refractive indices of 1.530 and 1.330 were used for the starch and liquid phases, respectively, while the starch granule absorption was 0.1 (Nayouf, Loisel, & Doublier, 2003).

For scanning electron microscopy, the dry starch granules were placed on an adhesive tape attached to a circular aluminum specimen stub and then coated vertically with gold. The samples were examined at 5 kV using a scanning electron microscope (ABT-55 ISI Abt, Akashi Beam Technology Corporation, Tokyo Japan).

2.3.3. Swelling power (g/100 g H_2O) and solubility (g/100 ml H_2O)

Swelling power and solubility of starch suspension was determined according to the methods of Wang et al. (2010).

2.3.4. Syneresis

Syneresis was determined by slight modifications to the methods of Lan et al. (2010). Starch dispersions (6.0 g/100 ml H₂O) were heated in a Rapid Visco Analyser at 95 °C for 30 min with constant stirring at 75 rpm. The paste was allowed to cool at room temperature; the water loss was weighed and added back to the sample. The samples were stored for 24 h at -22 °C and then equilibrated at 30 °C in a water bath. Syneresis was measured as water release (g/100 g starch) after centrifugation (3000 rpm; 20 min).

2.4. Thermal properties

Thermal properties of rice starches in the presence of water (1:3) were measured using a differential scanning calorimeter (DSC Q2000, TA Instruments, New Castle, DE USA). Starch (3.5 mg, db) was weighed into an aluminum pan (Tzero hermetic pan and lid, TA Instruments, New Castle, DE USA) and mixed with 2.05 mg H₂O to equilibrated to moisture. The sample pan was sealed, equilibrated at room temperature for 6 h and then heated from 20 to 120 °C at a heating rate of 10 °C/min. The samples were placed in a refrigerator at 5 °C for 5 days and the measurements were repeated for retrogradation studies. The instrument was calibrated with Indium and Zinc, while an empty sealed pan was used as a reference.

2.5. Pasting properties

The pasting properties were determined with a rapid visco analyser (RVA 4500, Perten Instruments, Kungens, Sweden). Starch, 3.5 g dry basis was weighed into an aluminum canister and then mixed with 25 g H₂O. The starch pasting was completed in a 13 min programmed cycle. The cycle started with the starch stirring (950 rpm, 10 sec) at 50 °C for 1 min. This was followed by heating the suspension from 50 to 95 °C at 6 °C/min and then held at 95 °C for 1.5 min, cooled to 50 °C and held for 2 min. The values of pasting temperature, peak viscosity, hot paste and cool viscosity were recorded and reported as average of three samples.

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