The Journal of Agricultural Sciences - Sri Lanka
Vol. 18, No 1, January 2023. Pp 154-171
http://doi.org/10.4038/jas.v18i1.10105

Physicochemical, Rheological and Moisture Adsorption Characteristics of Two Basmati Rice (*Oryza sativa* L.) Varieties Differing in Amylose Content

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Received:20th May 2022 / Accepted: 25th October 2022

ABSTRACT

Purpose: *The purpose of this study was to determine the physicochemical, viscosity and moisture sorption properties of high-amylose (At-306) and low-amylose (At-405) basmati varieties.*

Research Method: *The viscometer method was used to measure the apparent viscosity of the flour samples at 65 and 75°C. Moisture adsorption isotherms were determined by the gravimetric method at 28, 35 and 45°C.*

Findings: *The bulk-density, grain-hardness, gelatinization temperature, protein and amylose contents of the At-306 and At-405 varieties were in the range of 794-780 kg m^{-3}, 55.5-49.7 N, 70.34-66.14 °C and 8.80-8.00% and 26.70-15.37%, respectively. At-405 samples showed significantly higher viscosity (8-13.5 Pa s) at 65°C and lower viscosity (1.4-5.3 Pa s) at 75°C but the opposite trend was observed for the At-306. The flow behavior index, varied with temperature between 0.55-0.54 and 0.75-45, respectively, for At-306 and At-405. At-306 showed a higher equilibrium moisture content (EMC) value compared to At-405 when a_w>0.70. The GAB isothermal model best described the experimental EMC data (R^2_{adj}>0.98 and MRD<3.8). At-306 has a higher specific surface area (≈115.5 m^2 g^{-1} d.b) and higher monolayer moisture content (≈3.3 g/100 g) than At-405. The effective pore size of At-306 and At-405 varied between 1.04-12.82 and 0.73-9.18 nm, respectively. The isosteric-heat of adsorption was significantly higher for At-405 than At-306.*

Research Limitations: *Further studies with medium amylose basmati are needed to confirm the applicability of these findings.*

Originality/ Value: *This result provides some information of the physicochemical, rheological and storability characteristics of low and high basmati flours for the food industry application.*

Keywords: *Amylose, Basmati, Isotherm, Physicochemical, Pore sizes, Viscosity*

INTRODUCTION

Basmati is a special type of rice (*Oryza sativa* L.) that has high consumer acceptance because of its pleasant aroma and acceptable quality attributes such as slender grain, excellent cooking properties and lengthwise elongation during cooking (Kaur *et al*. 2011; Calingacion *et al*. 2014; Verma *et al*. 2015). Basmati rice is characterized by the presence of high concentration of an aroma compound known as 2-acetyl-1-pyrroline and other volatile compounds such as hydrocarbons, acids, alcohols, aldehydes, ketones, esters are also responsible for aroma development in basmati (Calingacion *et al*. 2014). Some basmati types have been recognized because of their superior

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nutritional qualities such as low glycemic index and high antioxidant properties compared to other rice varieties (Chung *et al*. 2011; Gunaratne *et al*. 2020).

Although Sri Lanka has developed many high-yielding rice varieties including very few basmati types, about 99% of them can be classified as high or intermediate amylose rice but only few can be classified as a low-amylose basmati rice variety (Hettiarachchi *et al.* 2016; Sinthu *et al.* 2021; Rebeira *et al.* 2022). It is well-known fact that physicochemical, cooking, sensory and functional properties vary with the amylose content of rice (Chung *et al*. 2011; Calingacion *et al*. 2014; Verma *et al*. 2015; Kemashalini *et al.* 2018). On the other hand, the amylose/amylopectin ratio, the length of the amylose chain and their crystalline nature greatly influence the physicochemical and functional properties of rice starch, such as pasting properties, gelatinization, and retrogradation (Zhou *et al*. 2002; Noda *et al*. 2003; Cornejo-Ramírez *et al*. 2018; Kemashalini *et al.* 2018; Tong *et al*. 2019). High-amylose rice grains increase their volume and become flaky during cooking, but harden when cooling. Rice varieties with high-amylose content are more prone to solid loss during cooking as increased starch leaches out from the starch granules (Ojha *et al*. 2018; Tong *et al*. 2019). Low-amylose basmati is preferred for consumption due to its aromatic, soft, and sticky texture after cooking. Therefore, cooking, eating and flour properties of rice flours can be improved by blending a low-amylose rice cultivar with some high-amylose cultivars (Zhou *et al*. 2002; Noda *et al*. 2003; Ojha *et al*. 2018) which may provide a desirable paste characteristic for special food applications. Although the low-amylose rice flour has many potential applications in the bakery and confectionery industries, the rheological characteristics of rice flour determine its application as a raw material for the food industry.

Poor postharvest practices can cause discoloration of rice kernels during storage due to respiration, moisture adsorption or fungal invasion which finally results in mycotoxin production (Tong *et al*. 2019). These changes are directly affecting the grain moisture content, temperature and relative humidity (RH) of the storage environment (Iguaz and Vírseda, 2007; Hafeel *et al*. 2008; Bonner and Kenney, 2013). If the surrounding RH is not carefully controlled during storage, the hygroscopic nature of the paddy may lead to substantial moisture adsorption. Therefore, understanding the moisture sorption characteristics is essential for designing the drying process and extending the shelf-life of stored rice (Sun, 1999; Haque *et al*. 2007; Tong *et al*. 2019). In that context, equilibrium moisture content (EMC) is a useful parameter to determine the moisture loss or gain under certain conditions of environmental temperature and RH. The relationship between water activity (a_w) and EMC of a product is described by the moisture sorption isotherms. Each food commodity has a unique set of isotherms which is a powerful tool for predicting and extending the shelf-life of a product. A large number of mathematical models are available for the characterization of the moisture sorption behavior in foods and to predict the EMC of stored rice kernels at the given storage or package environmental conditions (Sun, 1999; Quirijns *et al*. 2005; Haque *et al*. 2007; Yanniotis and Blahovec, 2009; Takagi *et al*. 2017). The net isosteric heat of sorption (q_s) is defined as the difference between the total heat of sorption of water by solid food material, and the heat of vaporization of pure water. When q_s exceeds the heat of vaporization, it is considered as an indication of bound water in food (Mousa *et al*. 2014). Therefore, q_s is useful for estimating energy requirements for dehydration processes.

Production of rice-based foods such as bread, noodles, biscuits, cakes and other oriental food products is expected to increase the consumption of rice and as well as gluten-free food products. Basmati rice flour has greater potential to use in many rice-based foods products than other non-basmati varieties due to its unique taste and aroma. Although many studies have been conducted to identify the relationship between rice varieties and their functional properties, limited amounts of research have been conducted to determine the relationship between amylose content, rheological properties and stored EMC of basmati varieties. Such information is very important for applications of basmati for rice-based food processing. However, low-amylose basmati rice has been used to a limited extent as a flour source in the food industry compared to high-amylose basmati rice. Therefore, the objectives of this study were to measure the physicochemical, rheological and experimental moisture adsorption characteristics of low-amylose and high-amylose basmati varieties at 28, 35 and 45°C, to evaluate the performance using sorption isothermal models.

MATERIALS AND METHODS

Recently harvested (February/2020) high-amylose (>25%) At-306 and low-amylose (12-20%) At-405 basmati rice varieties were obtained from the Department of Agriculture, Sri Lanka. Prior to the study, paddy samples were sun-dried to a moisture content of 13 ± 0.7% (d.b) without exposure to high temperatures. The moisture contents of the paddy samples were determined by the microwave drying method at a 550 W described by Nirmaan *et al*. (2020).

Determination of Physical Properties of Rice

Randomly selected 20 undamaged paddy grains were taken in triplicate from each variety. The length (L), thickness (T_i) and width (W) of the dehusked brown rice kernels were measured using a micrometer. The size and shape of the rice grains were measured and classified according to the method described by Calingacion *et al*. (2014). Considering a prolate spheroid shape for a brown rice kernel, the equivalent diameter (D_p) was calculated using Eq. (1). The grain volume (*V*), geometric mean diameter (B) and surface area (S) of brown rice kernels were calculated using Eqs. (2) and (3) (Varnamkhassti *et al*. 2008).

$$D_P = \left[L\frac{(W+Ti)^2}{4}\right]^{\frac{1}{3}} \tag{1}$$

$$V = 0.25\left[\left(\frac{\pi}{6}\right)L(W+Ti)^2\right] \tag{2}$$

$$S = \frac{\pi \times B \times L^2}{(2L-B)} \tag{3}$$

Where;

$$B = \sqrt{W \times Ti}$$

To determine the bulk paddy weight, 100 dehusked paddy samples were selected randomly from each variety and weighed separately (AACC, 2000). The average sample weight of 100 dehusked paddy kernels was obtained from five replicates. A sample of weighed dehusked paddy kernels was filled into a graduated measuring cylinder and the occupied volume was recorded to determine the bulk density (kg m^{-3}).

Grain Hardness and Gelatinization Temperature

About twenty-five, paddy grains were first manually dehusked and 20 undamaged brown rice grains were selected by using a grain scope (TX 200-KETT, Japan). The hardness of the selected rice kernels was measured using a grain hardness tester (Stake No.174886, Japan). Force at the first rupture (N) of the rice kernel to nearly half was considered as the yield point. The gelatinization temperature (GT) was measured using the alkali spreading values of kernels (AACC, 2000). Ten milled kernels were arranged in a glass Peri dish with adequate space and the kernels were soaked in 10 ml of 1.7% (w/v) potassium hydroxide (KOH) for 23 h at 30°C. A seven-point scale was used to rank the degree of alkali spreading (X) from low to high. Approximate GT values were calculated using the following Eq. (4) (AACC, 2000).

$$GT = 74.54 - (1.4 \times X) \tag{4}$$

Determination of Proximate Composition and Amylose Content

Crude protein, crude fat, crude fiber and crude ash content of the two basmati varieties were analyzed following the AACC (2000) approved method. The dehusked paddy samples were cooked and then oven-dried at 65°C for 3.5 h before analysis. The dried rice samples were powdered using a grinder and subjected to proximate analysis. Crude protein and crude fat contents were evaluated using micro-kjeldhal and soxhlet extraction methods respectively. The ash content was determined by incinerating the sample at 550°C in a muffle furnace. Apparent amylose content was determined using the iodine-binding method (AACC, 2000). A flour sample of 0.1 g was heated in a water-bath by adding 95% ethanol and sodium hydroxide (1 M). One milliliter of acetic acid (1 M) and 2 ml of iodine solution were added to the flour solution. The absorbance of the starch solution was measured at 620 nm using a UV-visible spectrometer (Shimadzu, UV-1601, Japan). The amylose content of the samples was determined based on a standard curve prepared using a known amount of potato amylose.

Determination of Rheological Properties

Raw rice samples of At-306 and At-405 were first milled using a laboratory de-husker and rice polisher (Model K-1, NgekSeng-Huat, Thailand). Milled rice samples were ground into flour using a pin mill (Alpine, Augsburg, Germany). The coaxial viscometer method was used to measure the viscosity of heated flour slurry samples. A rice flour sample of 7.4 g (d.b) was mixed with 92.6 ml of distilled water to prepare 8% (wt/wt) flour slurry in a 100 ml beaker. The flour suspension was heated in a water bath (Memmert-WNB 14, Germany) to 65 ± 0.5 °C or 75 ± 0.5 °C while continuous stirring and held for 2 min, then cooled to room temperature (28 ± 0.5°C). The paste was transferred to the coaxial viscometer (Brookfield Model-DVE, USA) to determine the shear properties. The data were collected for steady shear behavior (shear rate vs. shear stress) of the paste within 5 min under four ramped Shear rate (γ) ranging from 0.1 s^{-1} to 1 s^{-1}. Measurements were repeated at least 3 times with fresh samples. During the test, the temperature of the flour slurry samples and the water bath were recorded using T-type thermocouples and a data logger (TC 08-PicoTech, UK). The recorded data were fitted to the two-parameter power-law model (Ostwald de Waele relationship) to define the distinction in rheological properties (apparent viscosity η) of samples under steady shear, as shown by Eq. (5) (Bender *et al*. 2017; Mohamed *et al*. 2021). Flow behavior index (n) and consistency coefficient of K (mPa s^n) were obtained from the fitted model.

$$\eta = K\,\gamma^{n-1} \tag{5}$$

Moisture Sorption Isotherms

The adsorption isotherms were determined by the gravimetric method described by Prasantha and Amunogoda (2012). Approximately 20 g of milled rice samples packed in nylon bags were placed in air-tight glass jars which contained saturated solutions of different salts which provided a_w in the range of 0.25-0.92 (Wexler, 1999; Haque *et al*. 2007). Seven glass jars of each paddy variety were placed into temperature-adjusted incubators to obtain a constant equilibrium relative humidity (ERH) at 28 ± 0.5°C, 35 ± 0.5°C and 45 ± 0.5°C. Sample weights were taken every 5 days' intervals until nearly constant weight (±0.1 mg) was achieved after 24 days. The initial moisture content (m) and EMC (g/100 g d.b) were obtained by drying the samples in an air oven at 130 °C temperature for 2 hours (AACC, 2000). The sample a_w was measured using a water activity meter (Rotronic Hygrolab-3, Switzerland). Three parameters, the modified Henderson model (Eq. (6)), modified Halsey model (Eq. (7)) and five parameters, Guggenheim-Anderson-deBoer model (Eq. (8)) were used to analyze the adsorption isotherms (Quirijns *et al*. 2005; Prasantha and Amunogoda, 2012; Bonner and Kenney, 2013).

$$m=\left[\frac{\ln(1-a_w)^{\frac{1}{c}}}{-a(T+b)}\right] \tag{6}$$

$$m=\left[\frac{-\exp(a\times t+c)}{\ln(a_w)}\right]^{\frac{1}{c}} \tag{7}$$

$$m=\frac{m_0\times C\times K\times a_w}{[(1-K\times a_w)(1-K\times a_w+C\times K\times a_w)} \tag{8}$$

The coefficients m_o, C, and K are temperature-dependent parameters of the GAB model and can be expressed using Arrhenius-type Eqs. (9) -(11) (Prasantha and Amunogoda, 2012).

$$C=c_0\exp\left[\frac{g}{T}\right] \tag{9}$$

$$K=k_0\exp\left[\frac{i}{T}\right] \tag{10}$$

$$m_0=m_a\exp\left[\frac{e}{T}\right] \tag{11}$$

Whereas;

$g = h_m\text{-}h_n/R$ and $i = h_i\text{-}h_n/R$

On which, c_o and k_o are entropic accommodation factors, m_a is temperature dependence of monolayer (K), m_o is monolayer moisture content (g/100 g d.b), g is monolayer and multilayer water enthalpy difference (K), i is multilayer and free water enthalpy difference (K), e is temperature dependence constant of monolayer (K), T is absolute temperature (K) and R is universal gas constant (J mol^{-1} K^{-1}). According to the Arrhenius equations estimated enthalpy values h_m, h_n and h_i are consider as monolayer sorption enthalpy (J mol^{-1}), multilayer molar sorption enthalpy (J mol^{-1}) and molar sorption enthalpy of free water (J mol^{-1}), respectively.

Once the m_o content was known, the specific surface area of the active binding sites (ss) of dry matter (m^2 g^{-1} d.b) was determined using Eq. (12) (Prasantha and Amunogoda, 2012).

$$ss=3.53\times10^3\times\left[\frac{m_0}{100}\right] \tag{12}$$

Where the constant 3.53 m^2 g^{-1} = Avogadro number × surface area of a water molecule/molar weight of water.

The effective average pores radius or pore size (R_p) at any given moisture content of the rice samples was determined by the sum of critical pore radius (r_c) of capillary condensation and multilayer thickness (t) of the adsorbed moisture (Eq. (13)). The respective r_c and t were calculated (nm) by the Kelvin and Halsey equations respectively (Vel´azquez-Guti´errez *et al*. 2015).

$$R_p=\frac{-2\times\sigma\times V_m}{R\times T\times\ln(a_w)}\times10^9+0.354\left(\frac{-5}{\ln(a_w)}\right)^{\frac{1}{3}} \tag{13}$$

Whereas; σ is surface tension (N m^{-1}) and V_m is standard molar volume (m^3 mol^{-1})

Calculation of Net Isosteric Heat of Moisture Sorption

The net isosteric heats of moisture adsorption (q_s) values of two rice verities (J/mol) were calculated using the Clausius-Clapeyron Equation (Eq. (14)).

$$\frac{d(\ln aw)}{d\left(\frac{1}{T}\right)}=-\frac{q_s}{R} \tag{14}$$

The value of q_s is calculated from the slope of the linear regression line plotted between ln (a_w) and 1/T at constant moisture (Haque *et al*. 2007; Bonner and Kenney, 2013).

Statistical Analysis

All analytical samples were replicated 3-4 times. The experimental data were analyzed using one-way ANOVA and Tukey´s test used to determine the statistical significance at P ≤ 0.05 using the SAS 9.4 software (SAS Institute

Inc., NC, USA). The SAS-NLIN least-square estimation was used to fit the experimental data for three isothermal equations in the tested a_w range. Statistical parameters such as adjusted coefficient of determination (R^2_{adj}), residual sum of squares (RSS), standard error of estimate (*SEE*), and mean relative percentage deviation modulus (*MRD* %) values were used to evaluate the goodness-of-fit of the mathematical model to the experimental data (Sun, 1999; Prasantha and Amunogoda, 2012). The values of *MRD* (Eq. (15)) and *SEE* (Eq. (16)) are defined as;

$$MRD = \left(\frac{100}{n}\right)\sum_{i-1}^{n} \frac{[m_i - m_p]}{m_i} \tag{15}$$

$$SEE = \left[\sum_{i-1}^{n} \frac{(m_i - m_p)^2}{df}\right]^{\frac{1}{2}} \tag{16}$$

Where m_i is the observed moisture content at the ith experiment; m_p is the predicted moisture content at the ith experiment; *df* is the degrees of freedom, and *n* is the number of observations. Lower values of *MRD* and *SEE* indicate better goodness of fit (Sun, 1999).

RESULTS AND DISCUSSION

Physicochemical Properties

Measurement of physicochemical properties is an indirect method of estimating the eating quality of rice (Calingacion *et al*. 2014; Hettiarachchi *et al*. 2016). The Physicochemical characteristics of basmati At-306 and At-405 varieties are presented in Table 01. The amylose contents of At-306 and At-405 were 26.7 ± 1.2% and 15.4 ± 0.62%, respectively. Therefore, At-306 can be categorized as a high-amylose basmati variety and At-405 was considered as a low-amylose basmati variety. Generally low-amylose rice becomes stickier and does not expand in volume during cooking compared to high-amylose rice (Hettiarachchi *et al*. 2016; Kemashalini *et al*. 2018; Sinthu *et al*. 2021). Whereas, rice with intermediate or high-amylose content has a higher expansion volume and is non-sticky but becomes harder upon cooling after cooking (Garcia *et al*. 2011).

These results showed that two varieties belong to long and slender grain type. Rice kernel size and shape dimensions are important technical data for rice milling and cooking. The grain shape of the basmati rice was classified as slender but considered as a very long-grain variety when the ratio of length/width >4, suggesting that these are superfine basmati varieties with extra-long slender grains (Kaur *et al*. 2011; Verma *et al*. 2015). Grain volume, equivalent diameter and the surface area did not show significant variation ($p > 0.05$) but were slightly higher in the At-405 variety compared to the At-306. The equivalent diameter of At-306 and At-405 kernels varied from 2.40 ± 0.07 mm to 2.48 ± 0.18 mm respectively. There were no significant differences ($p < 0.05$) between other physical parameters such as length, width, 100-grain weight and grain hardness. The bulk density of high-amylose At-306 (794 ± 2.0 kg m^{-3}) exhibited a significantly higher bulk density ($p < 0.05$) than the low-amylose At-405 (780 ± 3.5 kg m^{-3}) basmati variety. The bulk density results may help to understand the appropriate processing and storage conditions of basmati because the size, shape, and hardness of both basmati grains were similar, thus indicating quality and better processing of grains into flours irrespective of their amylose contents.

Alkali spreading value (ASV) has been widely used to evaluate the approximate GT of rice kernels as an indirect method. The ASV reflects the endosperm compactness of starch granules (SG) and approximate GT value (Kaur *et al*. 2011). According to the ASV (3 for At-306 and 6 for At-405), the high-amylose At-306 basmati has a relatively higher GT (70.34°C) than the low-amylose At-405 basmati (66.14°C). This suggests that the starch of the tested At-306 and At-405 varieties belong to the intermediate and low gelatinization classes, respectively (Sinthu *et al*. 2021). Previous studies have shown that the peak GT of low-amylose, intermediate-amylose and high-amylose basmati vary in the range of 64-69^{o}C, 74.2^{o}C and 74-78^{o}C, respectively (Wickramasinghe and Noda, 2008; Ahmed *et al*. 2008; Gunaratne *et al*. 2020). Cornejo-Ramírez *et al*. (2018) reported that GT increased with high-amylose content and was negatively correlated with the amount of amylopectin short chains and also positively correlated with amylopectin long chains. Chung *et al*. (2011) reported that high-amylose basmati contained a comparatively higher amount of average chain length of amylopectin molecules than low-amylose basmati. This may be the obvious reason that the low-amylose At-405 was easily gelatinized and required less heat energy for gelatinization than high-amylose basmati (Kemashalini *et al*. 2018).

Although the moisture, crude fat, crude fiber and ash contents did not show significant differences ($p > 0.05$) between the two basmati varieties, a significantly higher ($p < 0.05$) crude protein content was observed in At-306 (8.80 ± 0.28%) compared to the At-405 (8.00 ± 0.41%) basmati. According to Hu *et al*. (2021), protein content positively correlated with grain hardness but negatively correlated with palatability and stickiness. In fact, grain hardness did not show a significant difference ($p > 0.05$) between varieties, high-amylose At-306 showed 10.5% higher grain hardness than At-405. A previous study has reported comparable grain hardness values similar to this study but observed significantly higher hardness values of the stored At-306 than the stored At-405 basmati (Hafeel *et al*. 2008). Chung *et al*. (2011) found that the arrangement of SG in the protein matrix may significantly affect the grain hardness. This indicates that protein content may positively correlate with the grain hardness. The amylose content of the SG is an important for determining the eating and cooking qualities of rice. Hence, low-amylose and low-protein content may contribute to a higher cooking quality than high-amylose basmati rice (Hu *et al*. 2021). Generally, high protein rice absorbs water at a slower rate during cooking and retards the gelatinization process (Kaur *et al*. 2011).

Table 01: Physicochemical characteristic of two basmati rice varieties

Grain characters	Basmati rice variety (mean ± SD)	
	Variety At-306	Variety At-405
Moisture content (% d.b)	13.41±0.5^{a*}	13.62±0.7^{a*}
Pericarp color	white	white
Length (mm)	6.56 ± 0.25^{a}	6.65 ± 0.32^{a}
Grain size	long	long
Width (mm)	1.60 ± 0.16^{a}	1.57 ± 0.17^{a}
Length/Width ratio	4.25 ± 0.24^{a}	4.27 ± 0.48^{a}
Grain shape	slender	slender
Volume (mm^{3})	7.20 ± 0.60^{a}	7.81 ±1.80^{a}
Equivalent diameter (mm)	2.40±0.07^{a}	2.48±0.18^{a}
Surface area (mm^{2})	16.70±0.91^{a}	17.50 ±1.12^{a}
100 grain weight (g)	1.99 ± 0.01^{a}	1.96 ± 0.01^{a}
Bulk density (kg m^{-3})	794 ± 2.0^{a}	780 ± 3.5^{b}
Grain hardness (N)	55.5 ± 4.43^{a}	49.7±3.14^{a}
Gelatinization temperature (^{o}C)	70.34	66.14
Crude protein (%)	8.80 ± 0.28^{a}	8.00 ± 0.41^{b}
Crude fat (%)	1.60 ± 0.60^{a}	1.51 ± 0.54^{a}
Crude fiber (%)	0.11 ± 0.01^{a}	0.10 ± 0.02^{a}
Ash (%)	1.52 ± 0.74^{a}	1.71 ± 0.61^{a}
Amylose content (%)	26.72 ± 1.2^{a}	15.37 ± 0.62^{b}

**Mean ± SD values with the same superscript letter within a row are not significantly different (P > 0.05)*

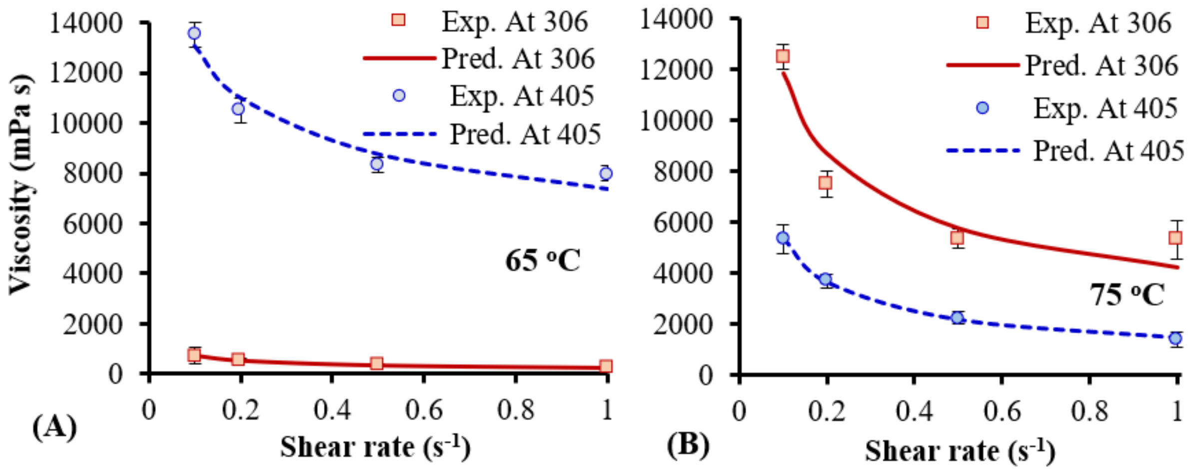

Figure 01: **Experimental (Exp.; mean±SE) and predicted (Pred.) apparent viscosity (mPa s) behavior of basmati rice flour obtained from two basmati rice varieties At-306 and At-405 at the heating temperature of 65°C (A) and 75°C (B).**

Rheological Properties

Understanding the effect of temperature on the rheological behavior of low and high amylose basmati flour is essential to identify the appropriate food industry application because ranges of temperatures are applied during food processing or storage. The viscous fluid flow behavior pattern of basmati flour paste is proportional to the rotational speed of the coaxial viscometer spindle (Figure 01).

This indicates that the η of the basmati flour-gel exponentially decreases with the increasing shear rate. The high-amylose At-306 showed the lowest apparent viscosity values at 65°C (Figure 01A) but the viscosity increased substantially at 75°C treatment (Figure 01B). Exactly the opposite characteristic of viscosity behavior was shown by the low-amylose At-405 basmati flour-gel at the similar temperature treatments. The viscosity of starch depends on the amylose content and the distribution of starch chain-length in the SG. When starch is heated in excess water, the SG first swells and then gradually discharges the amylose and small amylopectin molecules from the SG. In high-amylose starch, SG has very low swelling-power due to high amylose-lipid complex and low-amylopectin content. Thus high-amylose starch showed lower viscosity even at high temperatures. In contrast to that, rice flour with higher amylopectin (low-amylose) is exhibited high swelling-power and higher viscosity even at lower temperatures (Cornejo-Ramírez *et al.* 2018). This could be the reason that low and high basmati flour-gel showed significantly opposite behavior of viscosity.

This flow behavior index (n) of the power-law model (Eq. (5)) reflects the rheological fluid flow behavior of basmati flour-gels. All parameters of the power-law model were best-fitted ($R^2_{adj} > 0.80$) to the apparent viscosity data (Table 02). Rice flour-gel showed typical shear-thinning or pseudoplastic behavior as indicated by the flow behavior index $0<n<1$ value. Pseudoplastic behavior denotes a decrease in viscosity at a higher shear rate during shear thinning, where lower n values indicate higher pseudoplasticity of starches. Basmati flour-gel showed a decreased n with increasing temperature 65-75°C. The n value of At-405 flour-gel varied significantly from 0.75 to 0.45 with increasing temperature from 65°C to 75°C respectively, whereas in high-amylose At-306 the n value did not significantly change (0.56-0.54) with temperature. This was mainly caused by the faster disruption of the amylose-amylopectin network due to the applied shear forces (Zhou *et al.* 2002; Noda *et al.* 2003; Garcia *et al.* 2011). This behavior can also be explained by the intertwined amylose chains formed straight chains, causing a reduction in chain entanglement due to applied shear forces and temperature (Mohamed *et al*. 2021). The consistency coefficient (K) was lower at 65 °C but a comparatively higher value at 75°C for high-amylose basmati (Table 02). In contrast to that a significantly higher K value showed at 65°C pasting temperature of low-amylose basmati. Therefore, the results of this study showed that differences in amylose content and pasting temperature are directly related to the flow behavior of basmati rice flour. The difference in K between the two-basmati flour-gels may be related to the SG size, shape, water absorption characteristics, granule matrix and amylose content. Nikolić *et al*. (2021) also indicated that amylose content influenced viscosity by large, however, variations in pasting properties can also be attributed to the differences in the other components such as the protein and fiber contents.

According to previous studies, At-405 basmati reported the lowest value of visco-amylograph pasting properties compared to the high-amylose rice varieties such as At-306 (Wickramasinghe and Noda, 2008; Kemashalini *et al*. 2018; Gunaratne *et al*. 2020). Noda *et al*. (2003) reported a comparatively lower pasting temperature of low-amylose rice than high-amylose rice. This study also showed distinctly lower viscosity of At-405 than At-306 basmati at 75°C heating which indicates that low-amylose basmati has a good potential to be used as an alternative flour mixture for confectionery products. This indicates that not only the size and swelling degree of the rice SG but also the amylose content of the rice varieties plays an important role in the rheological properties of rice flour (Takagi *et al*. 2017; Cornejo-Ramírez *et al*. 2018).

Table 02: The Power-law model parameters describe the rheological properties of two basmati rice varieties

Rice variety	Model parameters at 65°C			Model parameters at 75°C		
	K (mPa s^n)	n	R^2_{adj}	K (mPa s^n)	n	R^2_{adj}
At-306	260.14	0.555	0.98	4133.75	0.542	0.81
At-405	7391.60	0.751	0.85	1500.18	0.447	0.99

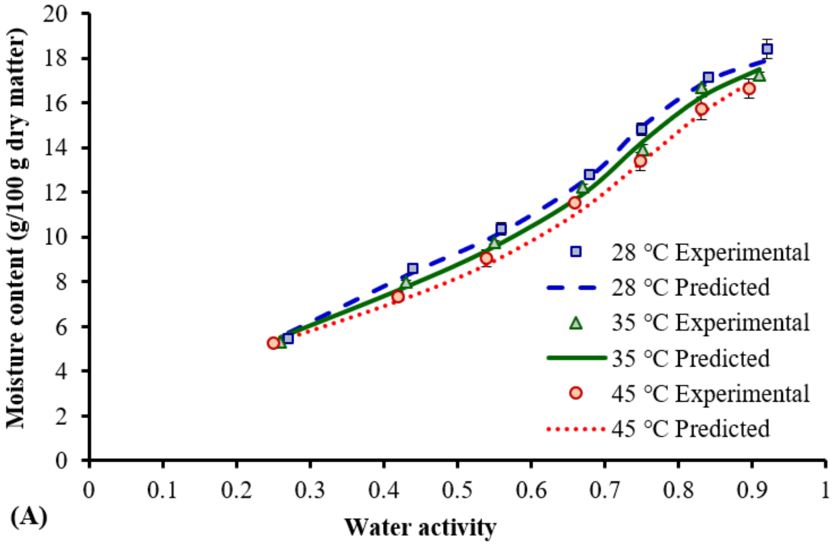

Figure 02: Experimental (mean±SE) and predicted equilibrium moisture adsorption isotherms of (A) basmati variety At-306 at 28°C, 35°C and 45°C storage temperatures.

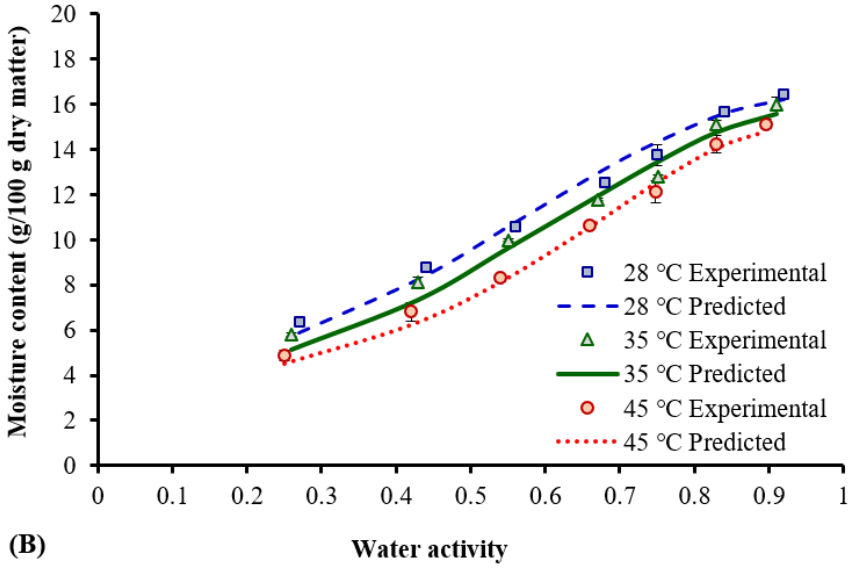

Figure 02: **Experimental (mean±SE) and predicted equilibrium moisture adsorption isotherms of (B) basmati variety At-405 at 28°C, 35°C and 45°C storage temperatures.**

Moisture Sorption Isotherms

The relationship between a_w and EMC of At-306 and At-405 basmati varieties at three different temperatures (28°C, 35°C and 45°C) are presented in Figures 02A and 02B, respectively.

The moisture adsorption relationship of the At-306 and At-405 basmati varieties showed a typical type II sigmoidal shape similar to the previous isothermal studies (Sun, 1999; Mousa *et al*. 2014). The effect of temperature on moisture adsorption behavior showed that the EMC of the two rice varieties decreased as the storage temperature increased from 28°C to 45°C. However, this behavior did not show a noticeable difference among the adsorption isotherms of the high-amylose At-306 variety. Compared to the At-405, high-amylose At-306 adsorbed a significantly higher amount of moisture in the condensation region of the EMC curves when a_w >0.70. Rice varieties vary according to their protein and amylose contents, which may lead to differences in the EMC in relation to storage temperature (Mousa *et al*. 2014). Cornejo-Ramírez *et al*. (2018) noted that high-amylose starch is composed of larger molecular size of amylose and long chains of amylopectin molecules which could absorb more water than low-amylose starch.

The six-parameter GAB model, three-parameter MHEE model and MHAE model were analyzed for the goodness of fit for the experimental sorption data of two basmati rice varieties. The estimated model constants and statistical parameters are summarized in Table 03. The R^2_{adj}, *SEE* and MRD (%) modulus values were used to select the most appropriate model for the adsorption isotherm. All mathematical models showed a higher coefficient of determination R^2_{adj} >0.95 for both varieties. For the GAB, MHEE and MHAE models, the corresponding *SEE* values of At-306 were 0.39, 0.75 and 0.80 respectively. The *SEE* values of At-405 were 0.50 for the GAB model, 0.57 for the MHEE model and 0.68 for the MHAE model. Thus, the lowest values of the SEE variables were given by the GAB model and it showed the best fit to the experimental data than the other two models (Prasantha and Amunogoda, 2012). According to the MRD% values, all 3 models were in good agreement with the experimental data of moisture adsorption of two basmati varieties. If the MRD value is < 10%, the most suitable model/s adequately explains the goodness-of-fit to the experimental data (Iguaz and Vírseda, 2007; Prasantha and Amunogoda, 2012). The GAB and MHEE models yielded the lowest MRD values compared to the MHAE model. According to Yanniotis and Blahovec (2009), the GAB model has been recommended as a theoretical equation to estimate the EMC within the wider range of a_w (0.11- 0.93) compared to the other isothermal models.

A number of studies have shown that the GAB model can successfully fit many sorption data of several foods including rice (Quirijns *et al*. 2005; Iguaz and Vírseda, 2007; Bonner and Kenney, 2013; Vel´azquez-Guti´errez *et al*. 2015). However, previous studies have reported that the Henderson model (Sun, 1999; Samapundo *et al*. 2007) is a good predictor for the moisture sorption characteristics of rice and other starch-based materials. Although the MHEE model showed some accuracy in predicting the EMC data, the results showed that the experimental EMC data of two basmati samples have been most accurately predicted by the GAB model. The GAB model describes sigmoidal-type isotherms when $0<K<1$ and $C>0$ (Yanniotis and Blahovec, 2009). The values of *K* indicate the interactions between water molecules and the rice starch in the multilayer. The parameter *K* increased from 0.70 to 0.72 when parameter *C* decreased from 16.3 to 16.0, respectively, with increasing temperature from 28°C to 45°C of high-amylose basmati. However, the parameters *K* (= 0.85) and *C* (= 1.26) did not change significantly of the low-amylose basmati, irrespective of temperature changes from 28°C to 45°C. When K=>1 indicates that there is a significant amount of moisture adsorbed into multilayer than a monolayer region (Quirijns *et al*. 2005). The parameter *C* of the GAB is more related to the heat of moisture adsorption by the rice starch. The larger *C* parameter indicated the stronger water–starch interaction in the monolayer adsorption of the At-306 than the At-405. Results of this study observed the comparatively larger enthalpy differences between the monolayer and multilayer moisture adsorption of At-306 basmati (*g* =14.5 K) than At-405 (*g* = 2.9 K) basmati.

Table 03: The best-fitted coefficients of adsorption isotherms and statistical parameters of mean relative percentage deviation modulus (MRD %), the adjusted regression coefficient of determination (R^2_{adj}), standard error of estimate (SEE) and residual sum of squares (RSS) for three different isotherm-models of high-amylose At-306 and low-amylose At-405 basmati varieties

Equation coefficients§	Isotherm models of basmati					
	Variety At-306			Variety At-405		
	GAB	MHEE	MHAE	GAB	MHEE	MHAE
a		50.1	0.9		40.13	0.4
b		1.2	12.12		0.6	5.04
c		0.8	50.2		0.501	70.43
m_a	3.2			2.43		
e	6.5			2.5		
c_o	15.5			1.25		
g	14.5			2.9		
k_o	0.72			0.82		
i	-5			9.70		
MRD (%)						
28°C	2.60	4.30	7.30	2.01	1.52	4.42
35°C	2.70	3.60	6.00	3.80	3.60	6.88
45°C	2.30	6.50	7.17	3.56	4.40	6.60
R^2_{adj}	0.98	0.98	0.96	0.99	0.98	0.97
SEE	0.39	0.75	0.80	0.50	0.57	0.68
RSS	1.86	9.00	9.66	4.45	2.11	6.86

§Units are given in the nomenclature section; GBA = Guggenheim-Anderson-deBoer Model; MHEE = Modified Henderson model; MHAE = Modified Halsey model

Monolayer Moisture Content

The m_o content of two basmati varieties at three different temperatures was estimated using the GAB model (Table 04). The m_o is the minimum moisture content that covers the active hydrophilic binding site of the starchy and provides the necessary information to predict the maximum storage period with the minimum quality loss. According to the calculated values, m_o slightly decreased with an increase in temperature. For the storage temperature between 28-45 °C, the m_o of At-306 and At-405 were within the range of 3.30-3.26% and 2.45-2.43%, respectively. Basmati variety At-306 showed nearly 26% higher m_o values compared to the At-405. This phenomenon can further be explained by the *ss* values of two basmati samples which were calculated by the m_o values using equation 12 (Table 04). Basmati variety At-306 has a significantly higher *ss* values (115.8-115.1 $m^2 g^{-1}$ d.b) compared to the *ss* values of At-405 (86.5-86.1 $m^2 g^{-1}$ d.b). Corresponding higher *ss* values were recorded in the At-306 basmati may relate to its higher amylose and protein contents. These results demonstrated that when temperature increases, the ability to obtain *ss* for the hydrophilic bonding of m_o decreases and the energy to form hydrogen bonds with the starchy polymer also decreases (Bonner and Kenney, 2013; Vel´azquez-Guti´errez *et al.* 2015).

Similar to the *ss* values, depending on the EMC and temperature, the R_p values of high-amylose At-306 basmati and low-amylose At-405 basmati varied between 1.04 - 12.82 nm and 0.73 - 9.18 nm respectively (Figure 03).

Table 04: Estimated monolayer moisture, specific surface area of dry matter, monolayer moisture content and equilibrium moisture content corresponding to 75% relative humidity of two basmati rice variety At-306 and At-405 at different storage temperatures

Temperature	Monolayer moisture content (g/100 g d.b)		*ss* active binding site ($m^2 g^{-1}$ d.b)		EMC at 75% RH (g/100 g d.b)	
	At-306	At-405	At-306	At-405	At-306	At-405
28°C	3.30±0.20*	2.45±0.10	115.78	86.49	15.96±0.2	14.95±0.5
35°C	3.27±0.11	2.45±0.05	115.43	86.48	15.37±0.2	14.13±0.3
45°C	3.26±0.20	2.43±0.15	115.08	86.13	14.88±0.1	13.45±0.2

** Values are presented as mean ± SD.*

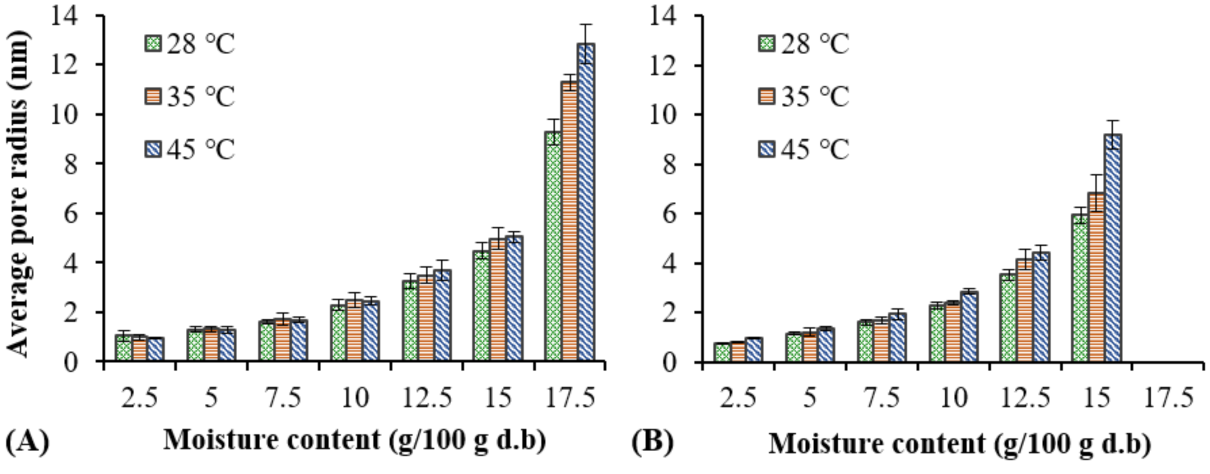

Figure 03: **Average pore radius, R_p (nm) of two basmati varieties At-306 (A) and At-405 (B) at 28°C, 35°C and 45°C storage temperatures and equilibrium moisture content (g/100 g d.b).**

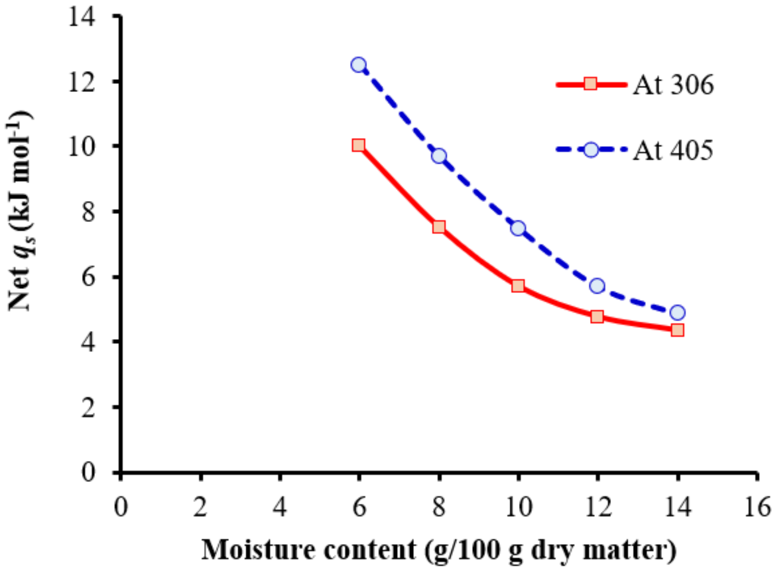

Figure 04: **Net isosteric heat of adsorption (q_s) of two basmati rice varieties At-306 and At-405.**

According to the IUPAC, these pore sizes can be classified as micropores (<2 nm) and mesopores (2-50 nm). The pore size increased as EMC and temperature increased in both basmati samples. This study shows that, depending on the amylose content, the pore size distribution of the two basmati varieties differs significantly ($p < 0.05$) with the moisture adsorption. High-amylose At-306 consists of largest mesopores sizes in the range of 9.26-12.83 nm (28-45°C and a_w = 0.88-0.92) compared to the low-amylose basmati at the saturated EMC of 17.5 g/100 g (d.b). However, the largest pore size of low-amylose At-405 basmati was observed at the saturated EMC of 15.0 g/100 g (d.b) and was in the range of 5.9-9.18 nm size (28-45°C and a_w = 0.81-0.89). Results of moisture adsorption isotherms also indicated that the high-amylose basmati absorbed more moisture into the mesopores when a_w >0.80 (Figure 02A). Ito *et al.* (1988) found a similar pore radius of two Japanese rice varieties but high-amylose *Yamadanishiki* was comprised of comparatively larger pore volume than the low-amylose *Japonica* variety. Takagi *et al.* (2017) suggested that the specific surface area of the pores structure may be affected due to the composition of the rice starch than the size and shape of the SG. Results of this study indicated that the larger surface area of moisture sorption of high-amylose rice starch may exist due to the existence of an intrinsic microporous structure and the size of pores structure. This may relate to the structural differences between the amylose and amylopectin molecules in the basmati SG. Table 04 also gives the EMC for 75% RH which is the average RH of the local environment, for product a_w in the range of 0.7-0.8. Basmati variety At-306 has higher EMC at 75% RH than variety At-405. Therefore, the high-amylose At-306 variety has a comparatively high moisture adsorption capacity and is less storable than the low-amylose At-405 basmati.

Isosteric Heat of Sorption

The q_s of adsorption for varieties At-306 and At-405 were plotted against moisture content and it was estimated based on the GAB model (Figure 04).

Similar to the previous findings, the result of this study also showed that the heat of adsorption of both basmati varieties was continuously decreased with increasing moisture content (Samapundo *et al.* 2007; Prasantha and Amunogoda, 2012; Bonner and Kenney, 2013; Mousa *et al.* 2014). The negative relationship between the moisture content and the q_s is due to the fact that the sorption is most likely to take place on the exposed *ss* of the food. According to the Clausius-Clapeyron Equation (14), estimated q_s was higher in the At-405 basmati compared to the At-306. The corresponding q_s of At-306 and At-405 varieties at the moisture content between 6-14 g/100 g (d.b) were in the range of 10.1-4.4 kJ mol^{-1} and 12.5-4.9 kJ mol^{-1} respectively. The corresponding q_s of adsorption of the At-306 and At-405 basmati at EMC of 10 g/100 g (d.b.) were 5.7 kJ mol^{-1} and 7.5 kJ mol^{-1} respectively. Haque *et al*. (2007) and Iguaz and Vírseda, (2007) reported that the q_s of paddy at same EMC (10 g/100 g) was 9.980 kJ mol^{-1} and 9.230 kJ mol^{-1}, respectively. These results showed marginally smaller q_s values than what were reported in previous findings for different rice varieties (Haque *et al*. 2007). As moisture increases, high-amylose starch of the At-306 basmati may tend to swell and build up a higher amount of moisture in the condensation region of the EMC curves resulting in low q_s at the high-moisture region. Bonner and Kenney (2013) noted that higher moisture adsorption may reduce the available hydrophilic binding and *ss* sites of the structure of the kernel. Once the hydrophilic sites are not available anymore, binding takes place with the lesser active site providing lower q_s values (Quirijns *et al*. 2005). The very high q_s at low moisture content was an indication of strong water–starch interactions in the rice kernels. The correlation between the moisture content and the q_s is depending on the available *ss* and R_p of rice kernel for moisture adsorption. At low moisture content, moisture may have strongly adsorbed into *ss* of nano-sized capillaries of the At-405 kernel structure than At-306 basmati. Basmati At-405 showed significantly higher ($p < 0.05$) R_p values at 10-15 g/100 g (d.b) moisture content than At-306 (Figure 03) basmati. This indicates that the stronger binding energies are associated with the monolayer and multilayer adsorption of water to the At-405 basmati SG structure than At-306. Although basmati At-405 has low-amylose content, it may contain a higher amount of highly branched short chain amylopectin structure (Chung *et al*. 2011). Amylopectin molecules may have a higher affinity to retain multilayer moisture than amylose (Takagi *et al*. 2017) but amylose molecules may have a higher affinity to binding with m_o within the kernel structure.

CONCLUSIONS

Basmati variety At-306 comprises 73% higher amylose content than At-405. Grain bulk density was higher in low-amylose At-405 compared to the high-amylose At-306 variety. Crude protein and amylose contents were significantly higher in At-306. According to the gelatinized temperature, high-amylose At-306 and low-amylose At-405 varieties belonged to high-intermediate and low gelatinization temperature groups, respectively. Low-amylose At-405 showed high apparent viscosity at a lower temperature than the high-amylose basmati variety. Flour samples of basmati showed shear-thinning or a typical pseudoplastic fluid behavior. The moisture adsorption isotherm curves of the two basmati showed the characteristics of type II isotherms and the moisture sorption behavior of the two basmati was best described by the GAB model. The differences in moisture adsorption behavior of the two varieties may be due to differences in their physicochemical properties such as amylose and protein contents. The large sorption surface area of high-amylose rice starch may exist due to the existence of a high intrinsic microporous structure and the size of pores structure. Isosteric heat of sorption decreased with the increase of moisture content and the value of q_s is higher in the low-amylose At-405 variety compared to the high-amylose At-306 variety. The results of this study showed that low-amylose aromatic basmati flour can be used in various forms of food applications due to its unique characteristic flow behavior and has high storability of milled rice due to its low moisture adsorption capacity compared to high amylose basmati. Therefore, these experimental results would provide some useful information for the bakery industry to use low and high amylose aromatic basmati flour for the development of gluten-free food products.

Conflicts of Interest

The authors declare that they have no competing interests.

Author Contribution

AGA Bandara: Laboratory studies; Statistical analysis; Original writing. BDR Prasantha: Methodology; Supervision; Writing- review; Editing. K Kemashalini: Investigation; Formal analysis; Writing. KAKL Chandrasiri: Methodology; Analysis.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the Department of Food Science and Technology, University of Peradeniya, Sri Lanka.

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