Determination of Rapid Visco Analyser Parameters in Rice by Near-Infrared Spectroscopy

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ABSTRACT

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The objective of these studies was to find alternative Rapid Visco Analyser (RVA) viscoelastic parameters that are predictable by near-infrared spectroscopy (NIRS). Currently, RVA instruments are widely used in assessing cooking and processing characteristics in rice. The ability to predict RVA parameters by NIRS would be useful in rapidly determining rice pasting qualities, but NIRS does not correlate with the traditional parameters (peak viscosity, final viscosity, breakdown, consistency, and setback). Alternative RVA parameters were sought by collecting RVA and NIRS data for a total of 86 short, medium, and long grain rice cultivars. The amylose contents were 0.41–24.90% (w/w) and protein concentrations were 8.47–11.35% (w/w). Partial least squares (PLS) regression models generated for the entire NIR spectrum against the RVA curve showed viscosity at 212–228 sec (80°C ± 1) varied linearly with NIR spectra (1,100 to –2,500 nm). Regression coefficient values were R = 0.961 for 212 sec and R = 0.903 for 228 sec. The PLS correlation coefficient for the prediction of amylose at 212–228 sec decreases along with the NIRS correlation to the same time frame. An opposite trend was observed for the correlation with protein at 212–228 sec. This comparison suggests the importance of amylose and protein in water absorption during this time frame.

Rice properties such as texture, processing strength, and pasting are determined using a Rapid Visco Analyser (RVA) that measures viscosity changes during a set temperature ramping profile. RVA parameters (peak viscosity, final viscosity, setback, consistency, and breakdown) are determined from maximum and minimum viscosity values and are used as a measure of cooking and processing characteristics in cereal grains. However, problems have been encountered with the application of these parameters to rice quality.

The use of near-infrared spectroscopy (NIRS) to determine RVA parameters in rice would be rapid and nondestructive. NIRS has been ineffective in predicting RVA parameters (Delwiche et al 1996). The use of RVA measurements for determining sensory qualities would be advantageous. However, Champagne et al (1999) demonstrated that RVA parameters are weakly correlated to rice textural attributes. These limitations may be linked to the properties measured by the current RVA parameters.

The standard RVA parameters are related to viscosity intensities. Another important property in RVA curves is gelling rates. Several factors including the amylopectin-to-amylose ratio and temperature affect the rate of gelling (German et al 1992). These rates dictate the time and temperature that peak viscosities occur. Hence, the traditional RVA parameters that relate to the viscosity intensities also relate to gelling rates. The contribution of gelling rates to RVA parameters is often unreported, therefore these considerations are not included in calibrations. Shortcomings in the use of standard RVA parameters in rice may be, in part, linked to the absence of gelling rate information.

Using set experimental conditions for RVA measurements, the viscosity intensity at a constant time and temperature reflects differences due to gelling rates, unlike the traditional RVA parameters. If NIRS correlates with these data points, calibrations may be developed and pasting rate information may be obtained noninvasively. The objective of the present work was to determine constant time-temperature RVA data points that correlate with NIRS. The correlation of potential RVA parameters to standard RVA parameters, the pasting process, amylose, and protein composition was investigated.

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MATERIALS AND METHODS

Rice samples (86 long, medium, and short grain) were obtained from USDA-ARS laboratories in Beaumont, TX, and New Orleans, LA. Amylose contents of samples was 0.41–24.90%. Protein content was 4.89–11.35%. Both values were determined and discussed in previous studies (Barton et al 1998). A milling protocol appropriate for yielding rice with whiteness values of ≈40 ± 2 was used (Champagne et al 1999). The samples were shelled (model SB, Satake) and then immediately milled. Regular (light) milling was accomplished using a laboratory one-pass mill (pearler, model SKD, Satake) (Barton et al 2000). The first pass had a 50-g weight in the 5th position; the second pass had a 50-g weight in the 3rd position. Milling was for 1 min at 1,250 rpm using a fine mesh abrasive wheel. Brokens were removed from samples before grinding. Samples of ground flour were obtained with a Satake cyclone mill that was heated and equipped with a vibrating trough to permit a steady and uniform supply of rice to the mill. The apparent amylose content (AAC) was determined by the method of Juliano (1971). Protein (N × 5.95) was determined by the combustion method (AOAC 1990). Moisture was determined by the AOAC air-oven procedure before measurement.

An analytical NIR spectrometer (Foss-NIRSystems model 6500, Silver Spring, MD) was used for reflectance measurements on duplicate rice flour samples. Whole grain ground flour (≈3.0 g) was scanned in a 5-cm diameter sample holder in the spinning cup module over a wavelength range of 400–2,500 nm. Partial least squares (PLS) calculations were performed using Unscrambler (v. 7.6, Camo ASA, Oslo, Norway).

RVA measurements were made with a Newport Scientific Super 3 type RVA (Foss North America, Inc., Eden Prairie, MN). Rice samples were run in duplicate by adding 25 mL of distilled water directly into a metal RVA canister to which 3.00 ± 0.01 g of rice flour was added. Standard RVA experimental conditions were used. The temperature was raised from 50 to 95°C ± 1°C in 0 to 5 min. A temperature of 95 ± 1°C was maintained for 2 min and cooled to 50°C over 7 to 12.5 min. Each experiment was initiated by a 10 sec, 960 rpm mixing period, followed by a 160 rpm paddle speed for the remainder of data collection.

RESULTS AND DISCUSSION

NIRS Correlation to Standard RVA Parameters

Rice samples with various compositions of protein and amylose were selected for this study. Large differences in viscosities, curve shapes, and peak times are evidence of the compositional diversity of these samples (Fig. 1). Although amylose seems to be centrally important in the gelling process, other components in rice can play a role. Combinations of starch structure, rice content, protein structure, and other properties may lead to differences in both viscosity intensities and gelatinization rates. As a result, there may be difficulties in spectroscopically predicting rheological properties by the current RVA parameters.

Studies by Delwiche et al (1996) showed that RVA parameter predictions by NIRS could not replace direct measurements. We performed PLS calculations for the prediction of RVA parameters by NIRS using 86 rice samples. Based on correlation coefficients, the potential to predict RVA parameters by NIRS seems limited (Table I). Regression coefficient values were $R = 0.856$ for final viscosity (or end), $R = 0.854$ for peak viscosity, and $R = 0.903$ for setback.

Limitations in predicting RVA parameters may be linked to the lack of information in calibrations. First, calibrations should represent all the forms of variation expected in unknown samples. There are many variations that can affect the pasting process and viscograms including rice composition, molecular structure, particle size, shear, gelling rates, and others. Many of these variables are controllable, except composition, molecular structure, and gelling rates. The composition of rice is mainly amylose and protein (Chrastil 1990), which governs rheology. Protein and fat are crucial for the glass transition and melting point in rice (Singh et al 2000). The phospholipid content was inversely proportional to the rate of retrogradation of starch (Lin and Czuchajowska 1998). In these studies, amylose has the widest concentration variation (0.41–24.90%); the protein content was 8.47–11.35%. The lack of rices that encompass a wide range of composition limits the development of useful calibrations.

Additional limitations in predicting RVA parameters may be linked to the lack of gelling rate information in calibrations. The common RVA parameters are dependent on gelling rates. That is, these parameters are observed at different times during the RVA experiment depending on the rice type. Although gelling rate information is available in viscograms, it is often not reported with the corresponding RVA parameters. As a result, this information is not incorporated in calibration models for the prediction RVA. For this reason, a simple viscosity measurement that reflects differences in gelling rates and is predictable by NIRS would be ideal for use in PLS calibrations.

NIRS Correlation to New RVA Parameters

One approach to solving problems associated with the standard RVA parameter prediction by NIRS was to find data points in RVA curves at a constant time-temperature that correlate with NIR spectra. Hence, the measured viscosity reflects differences in gelling rates and the extent of rice pasting with time. A PLS regression of NIR spectrum (1,100–2,500 nm) versus RVA (0–752 sec) was performed and showed that the highest correlation to NIRS was at 212–228 ($r = 0.961$–0.903) (Table I). The data points before 212 and beyond 228 displayed lower correlations to the NIR spectrum; for instance, at 208 $r = 0.959$, which drops significantly below this point. For all 86 samples in this study, the 212–228 region lies between the initial pasting time and peak viscosity. In this time frame in the RVA curve, the rice containing the highest amylose (24.90%) has ≈4% of its peak viscosity intensity, while the low-amylose rice (0.41%) is at 97% of the peak viscosity. This time frame is significant because of water absorption and rapid granular swelling. Differences in water

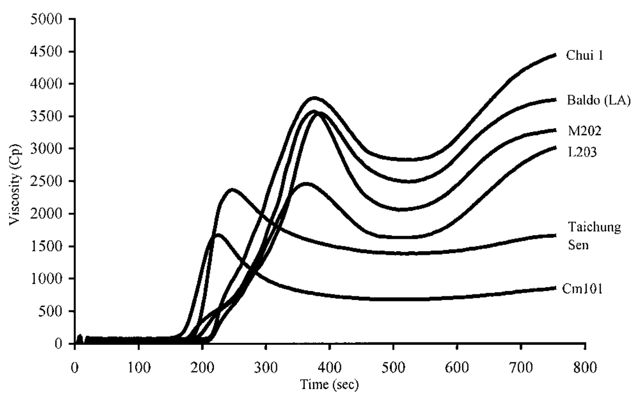

Fig. 1. Viscograms for various rice cultivars (12%, w/w) in water.

TABLE I
Correlation (*r*) Between RVA Parameters, Rice Composition, and NIR Spectra[a]

Parameter	NIR	Amylose	Protein
212 sec	0.961	0.798	0.019
216 sec	0.959	0.792	0.007
220 sec	0.927	0.772	0.031
224 sec	0.915	0.744	0.053
228 sec	0.903	0.715	0.072
Final viscosity	0.856	0.598	0.067
Consistency	0.867	0.730	0.022
Breakdown	0.656	0.433	0.101
Peak viscosity	0.854	0.021	0.039
Setback	0.903	0.842	0.053
Final viscosity	0.856	0.598	0.067
Trough	0.768	0.368	0.122

[a] $n = 86$ rice flour samples; r determined by partial least squares analysis. NIR region 1,100–2,500 nm.

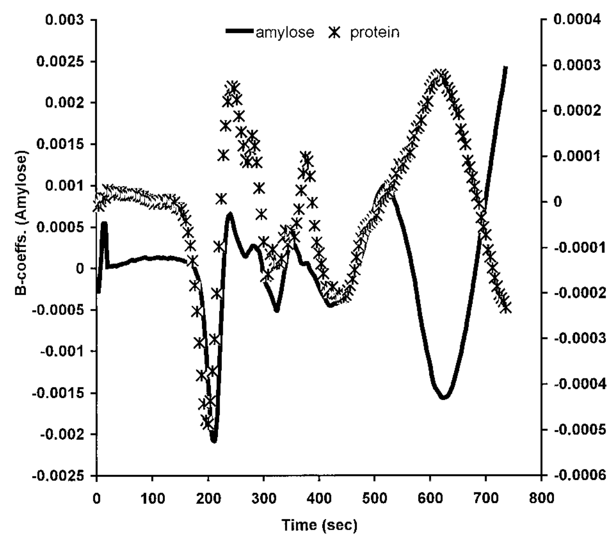

Fig. 2. Regression coefficients for RVA prediction of amylose (solid line) and protein (broken line).

TABLE II
Correlation (*r*) Between Time Parameters and Standard RVA Parameters[a]

Time (sec)	Breakdown	Consistency	Final Viscosity	Setback	Trough	Peak Viscosity
212	0.057	0.747	0.708	0.596	0.433	0.379
216	0.060	0.749	0.714	0.599	0.440	0.383
220	0.059	0.744	0.717	0.595	0.449	0.393
224	0.058	0.729	0.716	0.583	0.461	0.406
228	0.059	0.712	0.714	0.571	0.473	0.416

[a] n = 86 rice flour samples; r determined by partial least squares using NIR region (1,100–2,500 nm).

absorption, granule disruption, and the progression of gelatinization could be used to distinguish the relative potential of rice flours to form pastes. Because the gelatinization rate is inferred from the viscosity measurement, there is a possibility of determining the length of time needed to reach the peak viscosity. Hence, NIRS has the potential to predict kinetic and viscoelastic information in a single measurement. This region correlates significantly more strongly to NIR spectra than the traditional RVA parameters. One explanation may be the assertion that time-temperature are constants and the differences in gelling rates are considered for all samples. The viscosity at a constant time-temperature reflects the progression of the pasting process at that point, which differs for samples with various gelling rates. Viscosities used in calculating the traditional RVA parameters are measured at different times-temperatures, thus the gelling rate is unknown.

RVA Correlation to Amylose and Protein Content

To define new RVA data points (212–228 sec), PLS correlation between 212–228 data and rice composition was determined. The correlation of amylose to the 212–228 region is stronger than with traditional parameters, except for setback (Table I). The decrease in the correlation coefficient over time from 212 to 228 seems to show that as starch granule disruption occurs, the influence of amylose changes. This drop in correlation corresponds to a decrease in NIRS correlation to the 212–228 region, which may indicate the influence of amylose on spectra. Although correlation to protein is low during this same time frame, the correlation coefficient increases with time >212 sec. Both amylose and protein correlations with 212–228 viscosities may be useful in obtaining essential information about the pasting process. The extremely low correlation of the 212–228 data points to protein using PLS may suggest that other components, possibly complexes, influence this portion of the curve. For instance, phospholipids complex with amylose and the long branch chains of amylopectin resulting in limited granular swelling (Jane et al 1996). Possibly, protein could be involved with such complexes. An additional explanation for low correlation of protein using PLS linear routines is that nonlinear relationships exist.

As noted in literature (Juliano et al 1964), amylographs have a positive correlation with amylose content. Regression coefficients from a PLS model display correlations between amylose and the entire RVA curve as a predictor ($r = 0.941$) (Fig. 2). Inspection of regression coefficients shows that the influence in the prediction of amylose from RVA curves lies in the 200 and 600 regions, where the samples in this study undergo water absorption and retrogradation, respectively. This suggests the importance of amylose content in these processes. In regions where RVA does not seem to be a good predictor of amylose content, factors other than the amylose may affect pasting. These factors could include particle size, amylose-to-amylopectin ratio, protein, and amylose complexation, and other factors. In these studies, the particle size was controlled (Barton et al 2000). In this study, the amylose and protein components in rice were determined for the rice flours, but the concentration of other components was unknown.

The correlation of the entire RVA curve with protein is poor ($r = 0.568$). But this poor correlation may not be an indicator of the importance of the overall protein content on rheological properties. Hamaker et al (1990) found that protein structure and type could be mutually important to pasting. As with amylose, protein content seems to be related to events at 200 and 600 sec. However, the regression coefficients for the protein and RVA PLS model show positive correlations later in the pasting process (Fig. 2). This may be evidence that concurrent but opposing viscoelastic properties are being expressed by protein and amylose during retrogradation. Possibly, protein and amylose containing complexes are being disrupted due to the breakup of starch granules. Due to the low correlation ($r^2 = 0.568$, calibration) of protein with RVA, our argument is only qualitative.

Correlation Between New and Standard RVA Parameters

The correlations between new and standard parameters are low, but with clear distinctions between the levels of correlation (Table II). The strongest relationships were for consistency (final viscosity and trough) and the 212–228 time frame followed by final viscosity, setback (final viscosity – peak viscosity), trough, peak viscosity, and breakdown (peak viscosity – trough). Consistency is used to gauge the texture of starch pastes. Correlation of consistency to 212–228 the 212–228 time frame may be evidence that the initial water absorption is related to texture. Final viscosity, the second highest correlating parameter and mathematically related to consistency, measures the viscosity of a cool paste generated at 50°C. Setback, trough, peak viscosity, and breakdown exhibit much lower correlations to data points at 212–228 sec. This may suggest that these parameters are weakly related to pasting that occurs before peak viscosity (212–228 range). An additional explanation for the low correlation of breakdown and setback with the new parameters is that they are mathematically related to peak viscosity. The interrelationships between RVA parameters may also be linked to shortcomings in NIRS predictability.

CONCLUSIONS

The initial studies show a correlation of NIR spectra to the 212–228 sec RVA data points. This region is a measure of the disruption of starch granules and water absorption, which is related to rice composition. This region is unique in that single data points can be used to provide the relative viscosities of different rices as a function of gelatinization rates. In terms of processing and cooking qualities, the potential of rice to bind water, gelatinize, and form a paste are essential for product quality. In addition, water binding in rice determines the storage conditions needed to preserve quality.

Choosing single data points to compare rheological properties allows gelling rates to be incorporated as constituents in NIRS calibrations. Further analyses with larger numbers of select samples in the 1–12% amylose content range and a wider range of protein contents will make it possible to develop better calibrations and define and validate the usefulness of the 212–228 sec data region of RVA curves.

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