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Milling of rice grains: Effects of starch/flour structures on gelatinization and pasting properties

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ABSTRACT

Starch gelatinization and flour pasting properties were determined and correlated with four different levels of starch structures in rice flour, i.e. flour particle size, degree of damaged starch granules, whole molecular size, and molecular branching structure. Onset starch-gelatinization temperatures were not significantly different among all flour samples, but peak and conclusion starch-gelatinization temperatures were significantly different and were strongly correlated with the flour particle size, indicating that rice flour with larger particle size has a greater barrier for heat transfer. There were slight differences in the enthalpy of starch gelatinization, which are likely associated with the disruption of crystalline structure in starch granules by the milling processes. Flours with volume-median diameter ≥56 μm did not show a defined peak viscosity in the RVA viscogram, possibly due to the presence of native protein and/or cell-wall structure stabilizing the swollen starch granules against the rupture caused by shear during heating. Furthermore, RVA final viscosity of flour was strongly correlated with the degree of damage to starch granules, suggesting the contribution of granular structure, possibly in swollen form. The results from this study allow the improvement in the manufacture and the selection criteria of rice flour with desirable gelatinization and pasting properties.

1. Introduction

Rice (*Oryza sativa* L.) is one of the most widely grown cereal crops for food. Rice heads are mostly consumed as cooked polished grains for staple food in many countries, whereas broken rice grains are commonly milled or ground into flour and used as an ingredient in baby foods, noodles, puddings, and many Asian cuisines. The largest component in rice grains is starch (>80%, dry weight basis), which is an important factor determining the quality of rice products. The structures of starch in rice grains can be simplified into six hierarchical levels (Dona, Pages, Gilbert, & Kuchel, 2010; Tran et al., 2011): individual linear branches of starch molecules (Level 1), macromolecular branched structure (Level 2), alternating crystalline and amorphous lamellae (Level 3), growth rings (Level 4), individual starch granules (Level 5), and a whole grain (Level 6). Although a whole rice grain contains not only starch granules, but also non-starch components, including lipids, proteins, and non-starch polysaccharides, it is included as one of the starch structural levels in the present study due to the fact that the interactions between starch and non-starch components, such as entrapment by cell-wall or protein matrices and starch–lipid complex, can affect the structures and properties of starch. Levels 1 and 2 are the molecular structure and comprise mainly two types of glucose polymers, namely highly branched amylopectin with a larger number of short branches and smaller amylose with few long branches. Furthermore, these six levels are not the only levels of starch structures in the grains. There are other levels, including superhelical (Oostergetel & van Bruggen, 1993) and blocklet structures (Gallant, Bouchet, & Baldwin, 1997), which are excluded here as they are not commonly studied and might complicate the discussion of the results from the present study.

Abbreviations: ANOVA, Analysis of variance; AUC, Area under the curve; CM10C2, Rice flour produced by two cycles of 10-min cryogenic milling; CM10C3, Rice flour produced by three cycles of 10-min cryogenic milling; CM10C4, Rice flour produced by four cycles of 10-min cryogenic milling; CM5C1, Rice flour produced by one cycle of 5-min cryogenic milling; CM5C2, Rice flour produced by two cycles of 5-min cryogenic milling; DP, Degree of polymerization; DSC, Differential scanning calorimetry/calorimeter; ΔH, Enthalpy of starch gelatinization; HM1000P1, Rice flour produced by one pass through a hammer mill with 1000-μm screen; HM1500P1, Rice flour produced by one pass through a hammer mill with 1500-μm screen; HM500P1, Rice flour produced by one pass through a hammer mill with 500-μm screen; HM500P2, Rice flour produced by two passes through a hammer mill with 500-μm screen; HM500P3, Rice flour produced by three passes through a hammer mill with 500-μm screen; $N_{de}(\bar{X})$, SEC number molecular size distribution of debranched starch; R, Correlation coefficient; $\bar{R}_h$, Average hydrodynamic radius; RVA, Rapid visco analyser; SEC, Size exclusion chromatography; T_c, Conclusion starch-gelatinization temperature; T_o, Onset starch-gelatinization temperature; T_p, Peak starch-gelatinization temperature; $\bar{X}$, Average DP.

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Milling or grinding to break cereal grains (Level 6 starch structure) into flour can cause damage to starch granules (Level 5 structure) (Dhital, Shrestha, & Gidley, 2010a; Hasjim, Srichuwong, Scott, & Jane, 2009; Tran et al., 2011), disruption of starch crystalline lamellae (Level 3 structure) (Dhital, Shrestha, Flanagan, Hasjim, & Gidley, 2011; Morrison, Tester, & Gidley, 1994), and degradation of starch molecules (Levels 1 and 2 structures) (Dhital et al., 2011; Morrison & Tester, 1994; Tran et al., 2011; Yin & Stark, 1988). It is well documented that grinding of isolated starch granules alters starch gelatinization and pasting properties. Gelatinization temperature, enthalpy of gelatinization, and RVA pasting viscosity decrease with the increase of grinding time (Chen, Lii, & Lu, 2003; Dhital et al., 2010a, 2011; Han, Campanella, Mix, & Hamaker, 2002; Morrison et al., 1994), which is associated with the damage to starch granules (Level 5 structure) and/or the disruption of starch crystalline lamellae (Level 3 structure). Grinding of isolated starch granules, although it allows the study of grinding effects on starch structures and properties without the interference from the non-starch components in cereal grains, is not a common practice in food industry and does not replicate the grinding of cereal grains, where the protein and cell-wall matrices in the grains may provide protection to starch granules against structural degradation during grinding, and the size of grains (mm) is much larger than the size of isolated starch granules (μm). Furthermore, the use of ground isolated starch granules neglects the effects of flour particle size (Level 6 starch structure) on starch gelatinization and pasting properties, which is important in understanding the cooking quality of flour. Hence, it is crucial to study the effects of grinding on starch gelatinization and pasting properties using flour because of the complexity in the starch structures in grains and flour compared with those of isolated starch granules.

Many studies have shown the effects of flour particle size (Level 6 starch structure) (Mahasukhonthachat, Sopade, & Gidley, 2010; Marshall, 1992), damaged starch granules (Level 5 structure) (Dhital et al., 2011, 2010a; Morrison et al., 1994), and molecular structure (Levels 1 and 2 structures) (Srichuwong, Sunarti, Mishima, Isono, & Hisamatsu, 2005a, 2005b; Vandeputte, Derycke, Geeroms, & Delcour, 2003) separately on starch gelatinization properties and starch or flour pasting properties. However, existing literatures to date have not addressed the starch structure – gelatinization/pasting property relationships at four different levels of starch structures in a single study. Furthermore, it is not well understood whether the effects of the flour particle size is (partially or completely) contributed by the damage to starch granules and/or the degradation of starch molecular structure. The objective of this study is to understand which level of starch structures is the dominant factor determining the starch gelatinization properties of rice flour and flour pasting properties. This will provide a better insight in the effects of flour particle size, damaged starch granules, and molecular degradation, as separate entities, on the properties of rice flour.

In a previous study (Tran et al., 2011), a series of rice flours were produced from rice grains using cryogenic milling and hammer milling. The resulting flours had different flour particle sizes, degrees of damaged starch granules, and degrees of molecular degradation as summarized in Table 1. The hammer-milling process resulted in a greater damage to starch granules (Level 5 structure) than the cryogenic-milling process when the grains were ground to a similar volume-median flour particle diameter (Level 6 structure). Starch molecular structure (Levels 1 and 2 structures) was little or not affected by the cryogenic-milling process, whereas the degradation of both amylopectin and amylose molecules was clearly observed in the hammer-milled flours as analyzed using size exclusion chromatography (SEC) (Supplementary Data Figure S1). The preferential cleavage of longer branch chains with degree of polymerization (DP) >10,000, such as those of amylose, during the grinding of rice grains, especially by the hammer-milling process, was shown using the method of Vilaplana and Gilbert (2010), which reduces the SEC number molecular size distribution of debranched starch (individual branches, Level 1 structure) to a single parameter. These rice flours were used in the present study to provide variations in starch structures at four different levels in order to achieve the aforementioned objective of the study.

2. Materials and methods

2.1. Materials

Polished long-grain rice grains were purchased from a local grocery store. The starch content of the rice grains was 83% (w/w, dry flour basis) as determined by Total Starch (AA/AMG) assay kit (Megazyme International Ltd., Co. Wicklow, Ireland). The amylose content was 15% (w/w, dry starch basis) as determined from the ratio of the area under the curve (AUC) of amylose branches to the total AUC of both amylose and amylopectin branches in the SEC weight molecular size distribution of enzymatically debranched starch (Supplementary Data Figure S1A). The grains were ground into flour using cryogenic or hammer milling as described by Tran et al. (2011). The cryogenic milling of rice grains was performed using a Freezer/Mill 6870 (SPEX CertiPrep, Metuchen, NJ, USA) at $10\,s^{-1}$ in liquid nitrogen bath in cycles of 5- and 10-min to total cryogenic milling times of 5, 10, 20, 30, and 40 min. The hammer milling of rice grains was performed by passing the rice grains through a hammer mill (Janke & Kunkel, IKA-Labortechnik, Staufen, Germany) with 500-, 1000-, or 1500-μm screen at ambient temperature. The temperature of the rice flour immediately after passing through the hammer mill with 500-μm screen was about 40–45 °C, which should minimize any heat damage by hammer milling on flour/starch structures. The cryogenic- and hammer-milling treatments are summarized in Table 1 along with the structural attributes of the resulting rice flours as determined in the previous study (Tran et al., 2011): volume-median diameter of flour particles (Level 6 starch structure) analyzed using a Mastersizer 2000 with Hydro MU (Malvern Instruments Ltd., Malvern, UK), damage to starch granules (Level 5 starch structure) analyzed using Starch Damage assay kit (Megazyme International Ltd.), average hydrodynamic radius ($\bar{R}_h$) of whole (fully branched) starch molecules (Level 2 starch structure) calculated from the SEC weight molecular size distribution, and slope of the SEC number molecular size distribution of longer (amylose) branches with DP between 5×10^3 and 20×10^3 determined by plotting the SEC number molecular size distribution of debranched starch (Level 1 starch structure) as ln (Nde(X)/X) against DP X. Higher slope represents fewer longer branches. The SEC weight molecular size distributions of whole (fully branched) starch and the SEC number molecular size distributions of debranched starch from all rice flour samples are shown in Supplementary Data figure S1B and C, respectively. The starch contents of all rice flour samples did not vary significantly (Tran et al., 2011), implying that the grain composition was not significantly affected by the cryogenic- and hammer-milling processes. Since commercial starch granules and laboratory-isolated starch granules inevitably contain some degree of damage (Dhital et al., 2010a; Hasjim et al., 2009), it is not possible to obtain undamaged starch control for comparison with the samples in the present study.

2.2. Isolation of starch granules from rice flour

Starch granules were isolated from rice flour by laboratory-scale wet milling following the method of Syahariza, Li, and Hasjim (2010). A screen with 53-μm openings was used to filter the flour