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Crystallinity and Rheological Properties of Pregelatinized Rice Starches Differing in Amylose Content

Three rice starches with different amylose contents (Glutinous: 1.4%, Jasmine: 15.0% and Chiang: 20.2%) were pregelatinized in a double drum dryer at 110, 117 and 123°C. Starch crystallinity was determined by X-ray diffractometry and Fourier transform infrared (FTIR) spectrometry. Rheological properties were assessed by a Rapid Visco Analyser (RVA) and rheometer. Pregelatinized starches obtained from Glutinous (PGS) and Jasmine rice (PJS) gave an RVA pasting profile with cold peak viscosity. At drum temperature 110°C, PGS and PJS showed X-ray patterns that were indicative of amorphous structures. However, pregelatinized Chiang rice starch (PCS) exhibited RVA hot peak viscosity and the presence of an amylose-lipid complex with remaining granule structure. The PCS had a lower water absorption index (WAI) and water solubility index (WSI) than PJS and PGS. After pregelatinization at increased drum temperature (117, 123°C), the PGS had a lower WAI, whereas PCS showed an opposite trend indicating lower degree of granule disruption. In addition, the cold peak viscosity of PGS and PJS decreased with increasing drum temperature. For all drum temperatures, the apparent viscosity at 25°C for PGS and PJS decreased with increasing shear rate, indicating shear-thinning behavior.

Keywords: Pregelatinization; Rice starch; Granular structure; Starch viscosity

1 Introduction

Native rice starches have unique properties. However, they lack the versatility to function adequately in the entire range of food applications. Therefore, starches are modified to improve their functional properties. Pregelatinization is one of the physical methods used for modification. Pregelatinization can be brought about by, e.g., drum drying, spray drying and extrusion. Of these, drum drying is a common industrial practice for pregelatinization [1]. Pregelatinized starches, also referred to as instant starch slurries, are those that have been simply precooked to give products that readily disperse in cold water to form moderately stable suspensions [2]. Such products have been mainly applied as thickener in many food products such as baby foods, instant soups and instant desserts.

Perez-Sira and Gonzalez-Parada [3] investigated the functional properties of cassava starch modified by two physical methods, extrusion-cooking and pregelatinization by drum dryer. Lai [4] studied the effects of hydrothermal treatment and heat treatment on the physicochemical properties of pregelatinized rice flour. The rheo-

logical and physical characterization of pregelatinized maize starch [5] and the performance of double drum dryer for producing pregelatinized maize starch [6] were noted. In addition, the properties of pregelatinized rice flour made by hot air or gun puffing were investigated by Lai and Cheng [7]. However, there is limited information on structure and rheological properties of pregelatinized rice starch differing in amylose content. Therefore, the objective of this study was to investigate the effect of amylose content on crystallinity and rheological properties of pregelatinized rice starches produced by a double drum drying.

2 Materials and Methods

2.1 Starch preparation

Two commercial rice starches, i.e. Glutinous rice (1.4% amylose) and Jasmine rice named Khao Dawk Mali 105 (15.0% amylose) were acquired from Bangkok Industrial Co., Ltd. Thailand. Chiang rice was obtained from the Rice Research Center, Phattalung, Thailand. The starch from the Chiang rice (20.2% amylose) was isolated by the alkaline method [8] in our laboratory. Soluble amylose was measured using the iodine binding procedure [9]. All starch samples were stored at 4°C until they were used.

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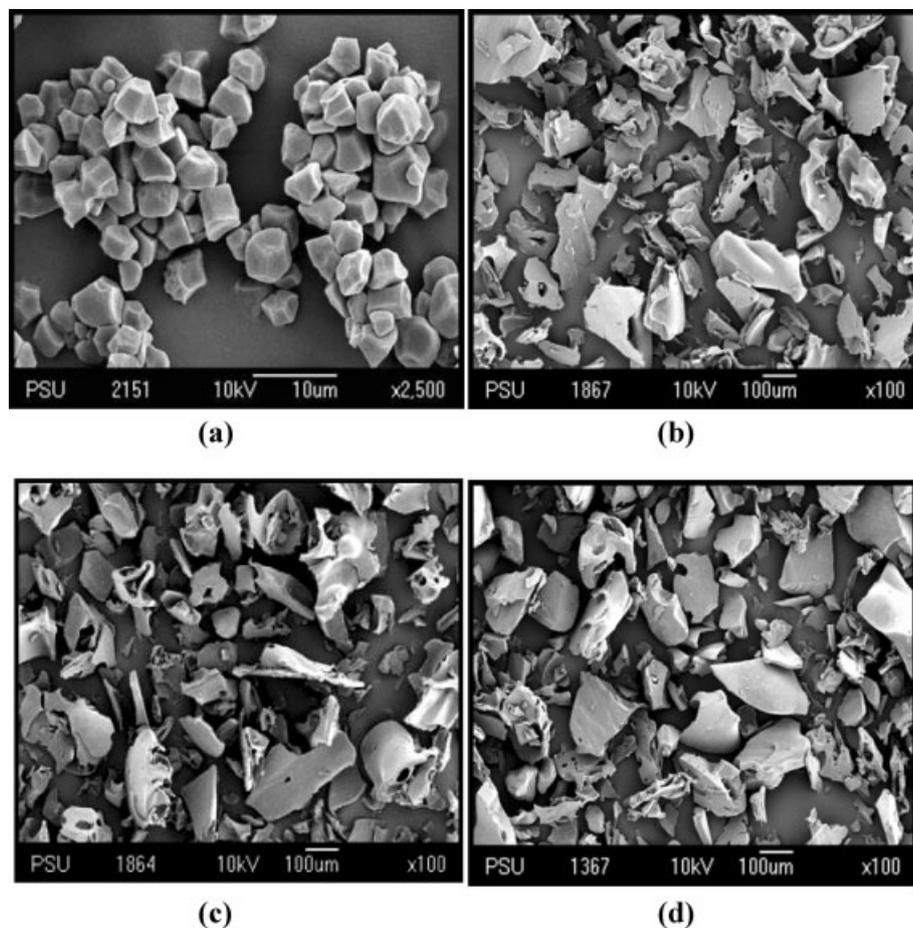


Fig. 1. Scanning electron micrographs ($\times 2500$) of native (a) and ($\times 100$) of pregelatinized Glutinous (b), Jasmine (c) and Chiang (d) rice starches.

2.2 Pregelatinization of rice starches

Three rice starches (Glutinous, Jasmine and Chiang) of 35% solid content were pregelatinized by a double drum dryer (30 cm diameter and 37 cm length) at a surface temperature of 110, 117 and 123°C, and a rotation speed of 4 rpm and gap width at 0.2 mm. The products obtained were milled to a particle size of 250 μm and stored in hermetic bags at 4°C for further analysis.

2.3 Structure characterization

2.3.1 X-ray diffraction

X-ray diffractograms of native and pregelatinized rice starches were obtained with an X-ray diffractometer (X'Pert. MPD, Phillips, Eindhoven, Netherland). Rice starch powders were tightly packed into the sample holder. The diffraction data were collected over an angular range from 4 to 30° (2 θ). The X-ray patterns were visually compared with the peak characteristics of a theoretical diffractogram given by Zobel [10].

2.3.2 Short-range molecular order

Infrared spectra were recorded to obtain information on the initial short-range order within the starch granule. Native or pregelatinized rice starches were put on the attenuated total reflectance sample cell of an Equinox 55 spectrometer (Bruker, Rheinfelden, Germany). Absorbance spectra were recorded at an incidence beam angle of 45°. The spectra obtained at a resolution of 4 cm^{-1} were averaged from 32 scans, recorded against an empty cell as background, and subtracted from the spectrum of water.

2.4 Water absorption index (WAI) and water solubility index (WSI)

Native and pregelatinized rice starches (300 mg) and 10 mL of distilled water were added to centrifuge tubes, and then incubated in a shaking incubator at 30°C and 174 rpm for 30 min. Tubes were centrifuged at 2500 rpm for 15 min. The supernatant was dried at 105°C overnight. The weight of the solid residue was recorded, and then the

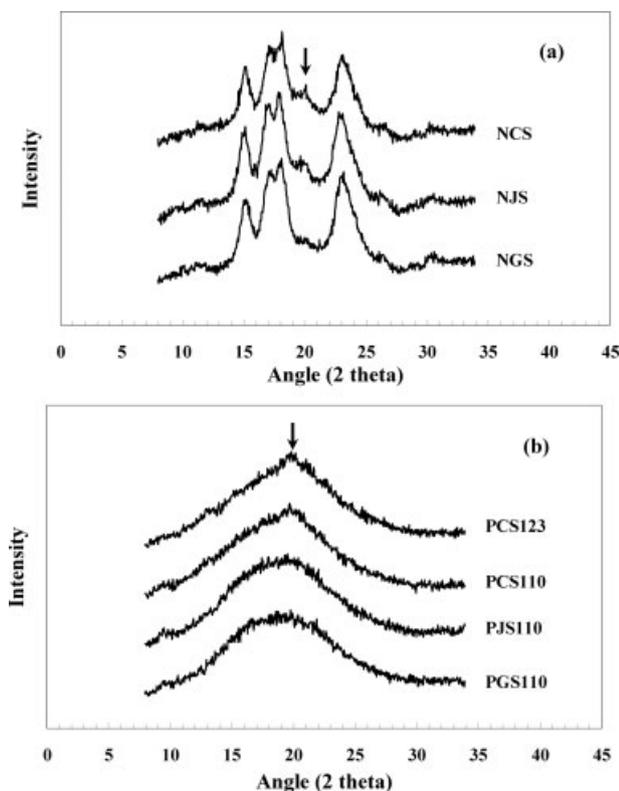


Fig. 2. X-ray diffractogram of (a) native Glutinous (NGS), Jasmine (NJS) and Chiang (NCS) rice starches and (b) pregelatinized Glutinous (PGS), Jasmine (PJS) and Chiang (PCS) rice starches using drum temperature at 110°C and 123°C. The arrow indicates the peak at 20° (2θ).

water absorption and water solubility indices were calculated by Equations 1 and 2 [11].

$$\text{WAI} = R/W \quad (1)$$

$$\text{WSI} (\%) = (S/W) \times 100 \quad (2)$$

where R = weight of residue (g)

W = dry weight of starch (g)

S = weight of soluble starch (g)

2.5 Rheological Properties

2.5.1 Pasting properties

The pasting characteristics of native and pregelatinized rice starches were determined in a Rapid Visco Analyser (Newport Scientefic, Warriewood, NSW, Australia). In principle, native and pregelatinized rice starch suspensions of 12% (dry weight) were prepared in an RVA can. The RVA was set as follows: holding the sample at 25°C for 2 min, ramping up to 95°C at 14°C/min, holding for

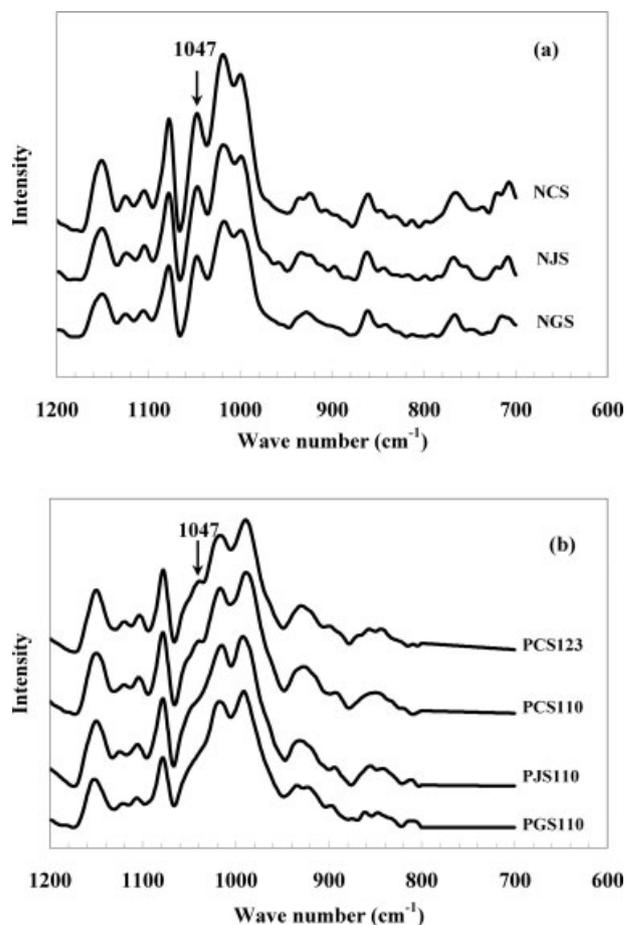


Fig. 3. Deconvoluted ATR spectra of (a) native Glutinous (NGS), Jasmine (NJS) and Chiang (NCS) rice starches and (b) pregelatinized Glutinous (PGS), Jasmine (PJS) and Chiang (PCS) rice starches using drum temperature at 110°C and 123°C. The arrow indicates the IR-absorbance band at 1047 cm⁻¹.

3 min, cooling to 25°C, again at 14°C/min, and holding at this temperature for a further 5 min. The RVA analysis program measured cold peak viscosity (highest viscosity in 0–2.33 min) and hot peak viscosity (highest viscosity during ramp to 95°C) [12].

2.5.2 Flow behavior

Pregelatinized rice starches of 4% (dry weight) were stirred at 25°C until a clear solution was obtained. The flow behavior of all samples was determined at 25°C using a rotational rheometer (Rheo Stress RS75, Haake, Karlsruhe, Germany) equipped with coaxial cylinder geometry (Z41). Each sample was submitted to a shear rate from 10 to 1000 s⁻¹.

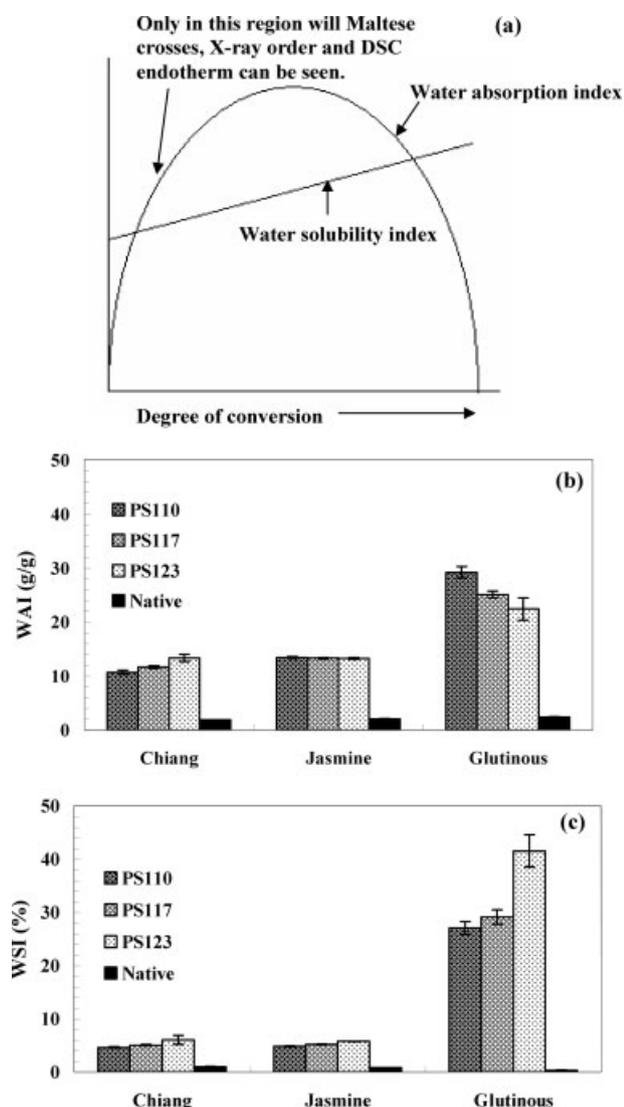


Fig. 4. (a) Typical relationships between parameters used to estimate the amount of starch conversion (modified from [17]), (b) water absorption index (WAI) and (c) water solubility index (WSI) of native and pregelatinized Glutinous, Jasmine and Chiang rice starches using drum temperatures of 110°C (PS110), 117°C (PS117) and 123°C (PS117).

3 Results and Discussions

3.1 Starch crystallinity

The rice starches granules appeared to be disintegrated and holes were formed after pregelatinization as observed in the scanning electron micrographs (Fig. 1). The higher degree of disintegration of the granular and macromolecular structure of pregelatinized Glutinous rice starch (PGS) and pregelatinized Jasmine rice starch

(PJS) (Figs. 1b and 1c) was due to the increased release of soluble components during thermal treatment [13]. This was confirmed by the completely amorphous X-ray diffractograms of PGS and PJS indicating a complete loss of the granular order (Fig. 2). However, the granular structure of high-amylose Chiang rice starch was less destroyed. The appearance of a peak at 20° (2θ) in the X-ray diffractogram indicated the formation of a V-type crystalline amylose-lipid complexes structure in the pregelatinized Chiang rice starch (PCS). Fourier transform infrared (FT-IR) spectroscopy was applied to examine the crystallinity change in the short-range order structure in the C-C and C-O stretching range at 1300–800 cm⁻¹ [14]. The IR-absorbance band at 1047 cm⁻¹, which is sensitive to the amount of crystalline starch present, was found for all native rice starches as indicated by the arrow (Fig. 3a). This IR band still appeared as a small peak for PCS indicating less severe granule disruption. However, the IR band at 1047 cm⁻¹ disappeared for PGS and PJS (Fig. 3b).

3.2 Water absorption index and water solubility index

The water absorption index (WAI) and water solubility index (WSI) of native and pregelatinized rice starches are shown in Fig. 4. The WAI and WSI give the mass of water taken up by dry starch and the amount of soluble components that have leached out from the granules [15]. The lower WAI and WSI of native rice starches imply a greater degree of associative forces in granules. The higher WAI and WSI values of pregelatinized rice starches can be attributed to the macromolecular disorganization and the degradation of starch during thermal treatment [16]. PGS had a higher WAI and WSI than PJS and PCS (Fig. 4). The increase in amylose content of the rice starches caused a decreased destruction of the granule structure and hence a decrease in the WAI and WSI. Increased drum temperatures resulted in increased rupture of the granular structure and hence a decrease in the WAI was noted for PGS (Fig. 4b). This was accompanied by an increase in the soluble component (WSI) released from the ruptured granule (Fig. 4c). Based on the schematic representation of starch conversion measures (Fig. 4a) [17], PGS was located on the right-hand side of the WAI curve showing that the starch granules were significantly solubilized and they lost their granule integrity, whereas PCS was located on the left-hand side of the WAI curve showing that PCS was less severely disrupted. PJS was located in the middle zone of the WAI curve, showing that its starch granules were less degraded products than those of PGS, but more than those of PCS.

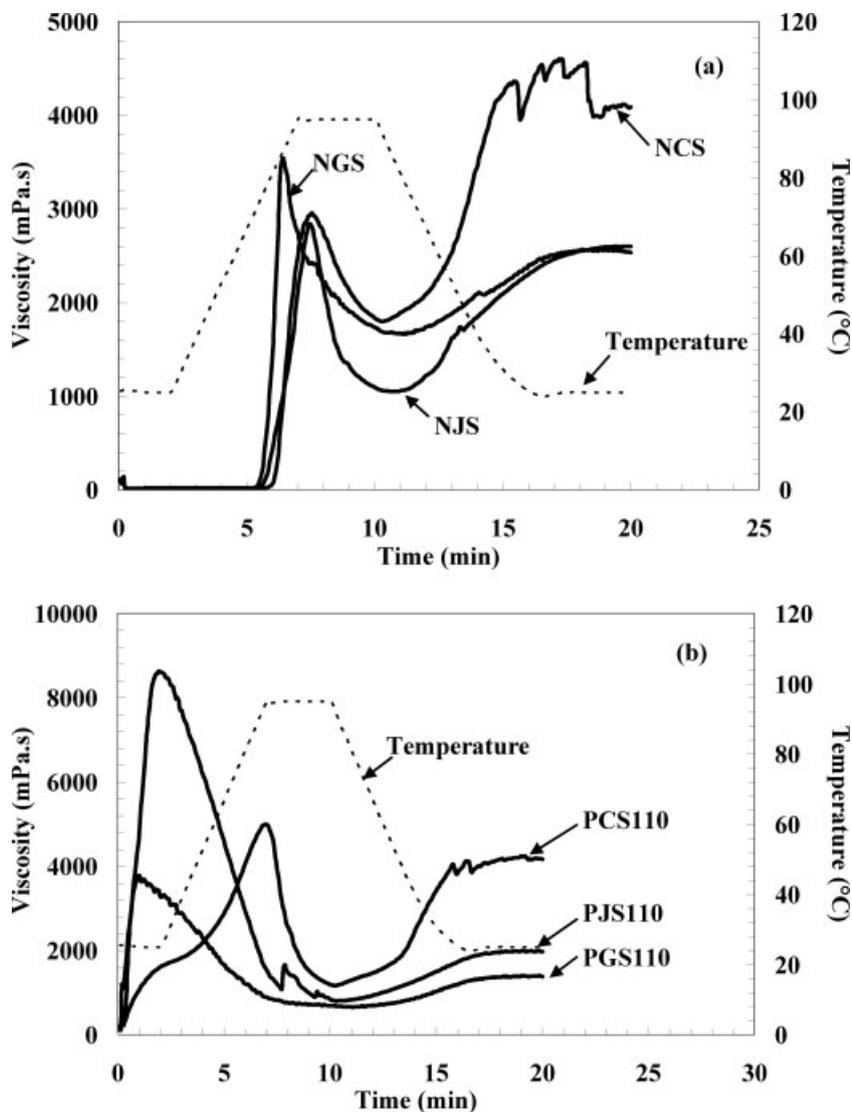


Fig. 5. RVA profiles of (a) native Glutinous (NGS), Jasmine (NJS) and Chiang (NCS) rice starches; and (b) pregelatinized Glutinous (PGS), Jasmine (PJS) and Chiang (PCS) rice starches using drum a temperature of 110°C.

3.3 Pasting properties

The pasting properties of the native and pregelatinized rice starches are shown in Fig. 5. The RVA was used to provide viscosity characteristics of the pregelatinized starch and can be used in combination with the WAI and WSI [17]. All native rice starches show an RVA hot peak viscosity, and the highest viscosity during ramping to 95°C (Fig. 5a), indicating the presence of remnants in the starch granules. This RVA hot peak viscosity was still observed for the PCS. However, a higher RVA hot peak viscosity was found for PCS than for native Chiang starch. For PGS and PJS, a cold peak viscosity (highest viscosity in 0–2.33 min) was observed (Fig. 5b). This is an indication of the severe disruption of the native rice starch granules during the heating process. This was also confirmed by the X-ray diffractograms (Fig. 2b) and FTIR spectra

(Fig. 3b) which showed complete amorphousness for PGS and PJS, indicating the complete loss of the granule order. The RVA cold peak viscosity of PGS was lower than that of PJS, indicating that in the rice starch with lower amylose content the granule structure was more disintegrated with a higher breakdown of the starch macromolecules. At higher drum temperatures, PGS and PJS had the lower RVA cold peak viscosity (Fig. 6a and 6b). This implied that the thermal stress on the granule structure due to the higher drum temperature resulted in a more severe disruption of the starch structure, hence a decrease in the RVA cold peak viscosity. The RVA cold peak viscosity was also an indication of the cold swelling behavior of pregelatinized starch, showing a similar trend to WAI indicating the severe process conditions at high temperature. The RVA hot peak viscosity was still shown for the PCS processed at high temperature (Fig. 6c).

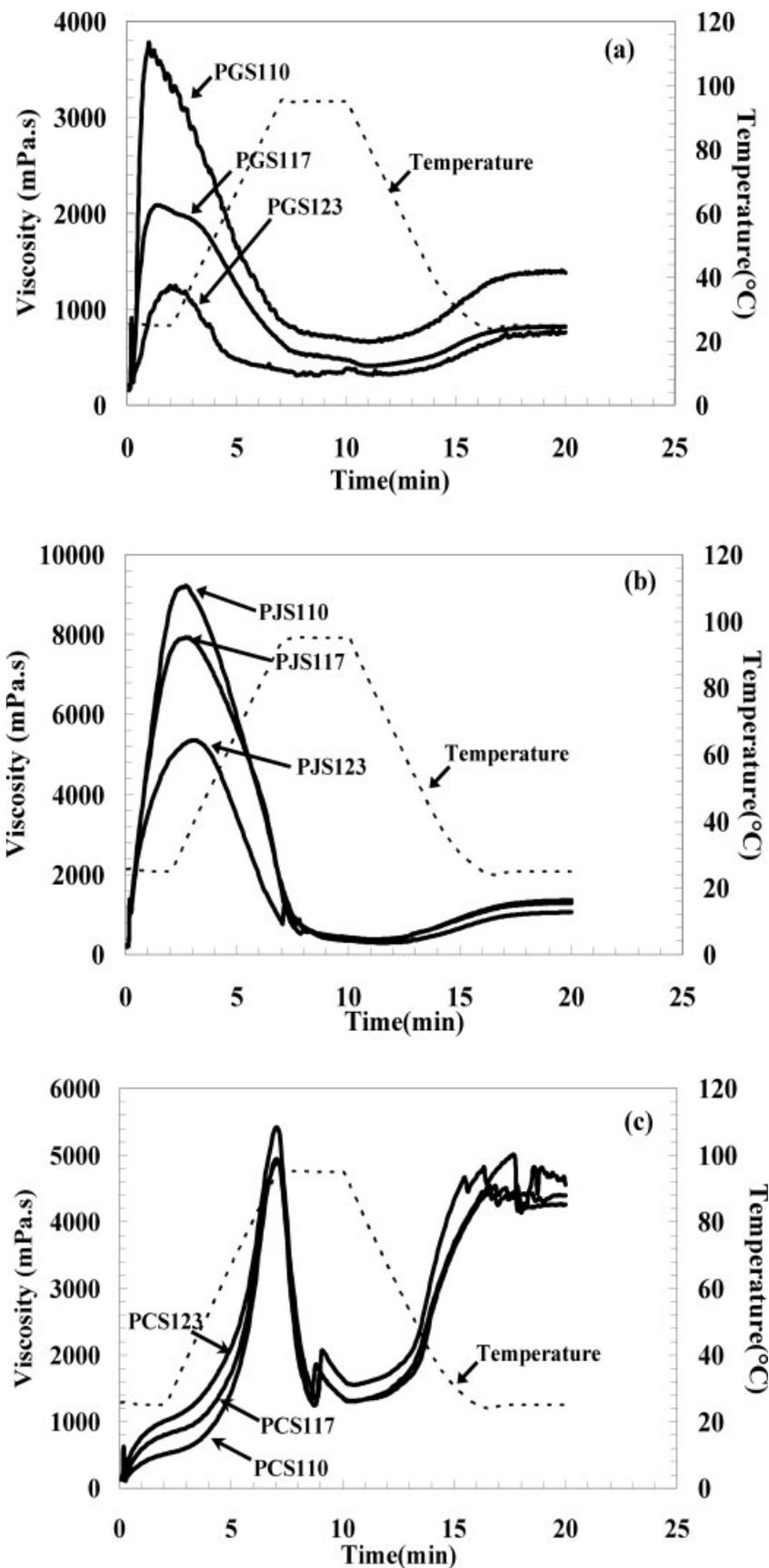


Fig. 6. RVA profile of (a) pregelatinized Glutinous rice starch (PGS), (b) pregelatinized Jasmine rice starch (PJS) and (c) pregelatinized Chiang rice starch (PCS) using drum temperature at 110°C, 117°C and 123°C.

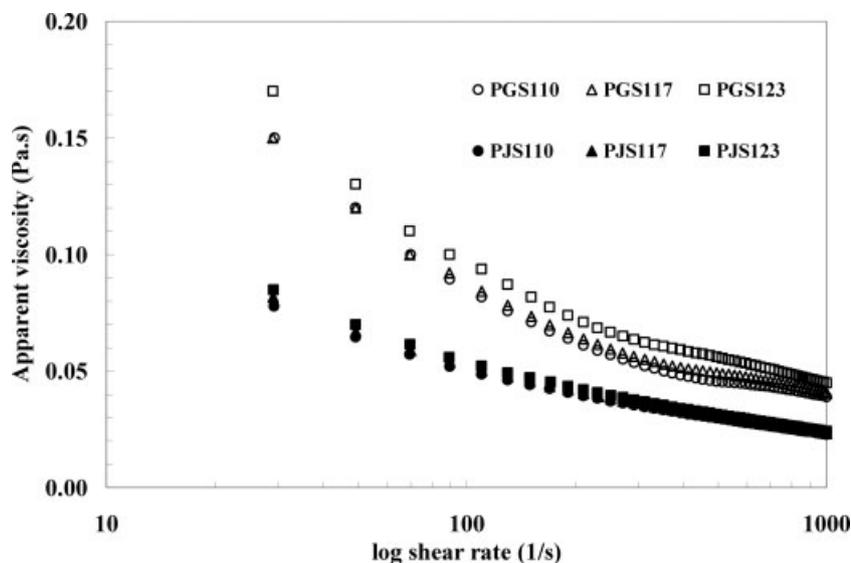


Fig. 7. Apparent viscosity of pregelatinized Glutinous rice starches (PGS) and pregelatinized Jasmine (PJS) rice starch using drum temperatures of 110°C, 117°C and 123°C.

3.4 Flow behavior

The flow behavior at 25°C of starch pastes from PGS and PJS followed the power law equation ($R^2 = 0.99$, $p < 0.05$). Both PGS and PJS exhibited shear-thinning behavior (Fig. 7), the apparent viscosity decreased with increasing shear rate. The apparent viscosity of PJS was lower than that of PGS, indicating that the granules of rice starch with lower amylose content were more strongly disrupted, exhibited higher swelling and developed more apparent viscosity than rice starch with higher amylose content. However, the viscosity at 25°C for PCS could not be developed due to less disruption of starch granules. The increase in drum temperature resulted in a slight increase in apparent viscosity for both PGS and PJS.

4 Conclusions

Pregelatinized starches obtained from low-amylose rice (Glutinous) and medium-amylose rice (Jasmine) showed RVA cold peak viscosity and an amorphous structure, whereas pregelatinized starch from high amylose rice (Chiang) showed RVA hot peak viscosity and an amylose-lipid complex structure. The explanation for this is that the granular structure of rice starch with lower amylose content was more disrupted by pregelatinization than that of rice starch with higher amylose content. Both PGS and PJS exhibit shear-thinning behavior at low temperature (25°C). Increasing drum temperature resulted in decreased cold peak viscosity for the PGS and PJS. However, apparent viscosity was only slightly affected by increased drum temperature. The PGS is preferred for thickening application, but only when it is cross-linked.

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