Impact of single and dual modifications on physicochemical properties of *japonica* and *indica* rice starches

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**A B S T R A C T**

The *japonica* (JR) and *indica* (IR) rice starches were modified by acetylation, hydroxypropylation, cross-linking, and dual modification (cross-linked acetylation and cross-linked hydroxypropylation) and the effects of single and dual chemical modifications of JR and WR on the physicochemical properties were investigated. The JR had a greater substitution degree of acetyl or hydroxypropyl groups than IR. The dual-modified JR showed a broader gelatinization temperature range than the corresponding single-modified starches, but narrower in IR. The dual-modified JR and IR showed higher pasting temperature and lower breakdown than their corresponding single-modified starches. The dual modification with JR and IR induced significant increase in gel hardness as compared to the corresponding unmodified and single-modified starches. The dual-modified JR had a greater hardness, gumminess, and chewiness than the dual-modified IR. The different impact of single and dual modification with JR and IR on the physicochemical properties could be due to the differences in the location and distribution of substituent groups on the starch molecules.

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1. Introduction

Rice is a global staple food and is consumed principally as a whole grain. Starch, which is the major component of rice, mainly determines the acceptability of a rice cultivar in terms of its physicochemical properties and cooking characteristics (Sasaki et al., 2009). Although the utilization of rice starch is much less than the other cereal starches from corn and wheat, rice starch has several advantages, including hypoallergenicity, bland flavor, small granules, white color, greater acid resistance, spreadability, and relatively good freeze-thaw stability (Wani et al., 2013). These unique characteristics of rice starch make it ideal for various food applications. Rice starch, like other starches, consists of two polysaccharides, amylose and amylopectin (Hizukuri, 1996). Amylose is an essentially linear molecules of \(\alpha-(1\rightarrow4)-O\)-glucopyranosyl units with a few branches, whereas amylopectin has a high molecular weight and highly branched structures consisting of \(\alpha-(1\rightarrow4)-O\)-glucopyranosyl units with 5–6% non-randomly distributed \(\alpha-(1\rightarrow6)-O\)-glucopyranosyl units (Hizukuri, 1996). These two polymers are organized into a semi-crystalline structure. Rice can be divided into two sub-species, *indica* and *japonica*. Amylose content of *indica* rice starches is generally higher than that of *japonica* rice starches (Takeda, Hizukuri, & Juliano, 1987; Chung, Liu, Lee, & Wei, 2011).

Non-chemically modified starches have been used as food ingredients such as thickening, gelling, stabilizing, and binding agents in the food industry to improve the physical properties. However, non-chemically modified starches do not meet the industrial requirements because of its instability under shear and acidic conditions, retrogradation tendency, and high syneresis (Liu, Ramsden, & Corke, 1999). To overcome the inherent deficiencies of non-chemically modified starches, starch can be structurally modified by various chemical means with acetylation, hydroxypropylation, cross-linking and dual-modification (Liu et al., 1999; Das, Singh, Singh, & Riar, 2010). Starch modification involves alteration of the physicochemical characteristics of starches and can be used to tailor them to specific food applications (Eliasson & Gudmundsson, 1996). Several previous studies have investigated the physicochemical properties of chemically modified starches from different plant starch sources such as corn, tapioca, wheat,
waxy corn, waxy barley and rice, with a range of modifications including substitution, oxidation and cross-linking, and varied reaction conditions including temperature, pH and concentration of catalyst salts (Lim & Seib, 1993; Wattanachant, Muhammad, Hashim, & Rahman, 2003; Das et al., 2010). However, a comparison of the effectiveness of various chemical modifications in different rice cultivars (japonica vs. indica) has not been fully investigated. The objective of this study was to investigate the effects of several single and dual mode chemical modifications (acylation, hydroxypropylation, cross-linking and dual modification) with different rice starchy from *japonica* and *indica* on physicochemical properties.

### 2. Materials and methods

#### 2.1. Materials

The *japonica* and *indica* rices were obtained from the National Institute of Crop Science (Suwon, Korea) and General Food Products Co. (Nakhorratchasima, Thailand), respectively.

#### 2.2. Starch isolation

Rice starches were isolated from the rice cultivars according to the alkaline steeping method described by Lim, Lee, Shin, and Lim (1999).

#### 2.3. Amylose and protein contents

The amylase contents of the isolated rice starches were measured using high performance size-exclusion chromatography (HPSEC). The HPSEC system consisted of a pump (P2000, Spectra System, San Jose, CA), an injector (Rhodyne 7072, Cotati, CA), the SEC column (Superdex 75HR, Amersham Pharmacia Biotech, Uppsala, Sweden) and a refractive index detector (Shodex RI-71, Tokyo, Japan). The protein contents of the rice starches were measured using a Kjeldahl system (Kjeltec 1026, Tector, Hoganas, Sweden).

#### 2.4. Preparation of single and dual-modified rice starches

The rice starch slurry was prepared by dispersing the JR and IR (500 g, db) in distilled water (750 mL). For acetylation, acetic anhydride (5% of solid) was added dropwise to the slurry with simultaneously stirring at room temperature while maintaining the pH within 7.8–8.2 using 4% NaOH. The reaction was allowed to proceed for an additional 5 min after the completion of acetic anhydride addition. For hydroxypropylation, propylene oxide (5% of solid) was added to a starch slurry that has been adjusted to pH 11.5 using 1 N NaOH and stirred in a water bath at 45 °C for 24 h. Cross-linked starches were prepared by adding phosphorous oxychloride (0.02%) to a starch slurry with pH 11.5 using 1 N NaOH and stirred in a water bath at 45 °C for 2 h. For dual modification, the rice starch was first cross-linked using phosphorous oxychloride (0.02%) and then reacted with acetic anhydride (5%) or propylene oxide (5%). After the reactions, all starch slurries were neutralized with 1 N HCl, washed with five volumes of distilled water, and dried at 40 °C in a convection oven for ~12 h to a moisture content of 10–12%.

Acetyl, hydroxypropyl, and phosphorous contents of modified starches were determined and the degree of substitution (DS) was calculated by using the methods reported by Wurzburg (1964), Johnson (1969), and Smith and Caruso (1964), respectively.

#### 2.5. Thermal properties

The thermal properties of the single- and dual-modified rice starches were measured using a differential scanning calorimeter (DSC6100, Seiko Instruments, Chiba, Japan). The starch (3 mg, db) was weighted into a 15 μL aluminum pan (Seiko Instruments, Chiba, Japan) with 6 μL of distilled water. The pan was then sealed and equilibrated at room temperature for 12 h and then heated from 10 to 130 °C at a heating rate of 5 °C/min. An empty pan was used as a reference.

#### 2.6. Pasting properties

The pasting properties of the single- and dual-modified rice starches were analyzed using Rapid Visco-Analyzer (RVA-3D, Newport Scientific, Warriewood, Australia). Starch suspensions (7% w/w db, 30 g of total weight) were equilibrated at 50 °C for 1 min, heated to 95 °C at 13 °C/min, held at 95 °C for 3 min, cooled to 50 °C at 13 °C/min, and held at 50 °C for 4 min.

#### 2.7. Swelling power and solubility

The swelling power and solubility of the starches were measured according to the methods reported by Schoch (1964). A starch suspension (0.5 g of starch in 30 mL of water) in a centrifuge tube with a cap was heated at 95 °C for 30 min with continuous shaking (200 rpm). The heated sample was cooled rapidly to room temperature and then centrifuged at 3500 rpm for 20 min. The swelling power was determined by measuring the sedimented paste weight and the solubility with respect to the solid content of the supernatant.

#### 2.8. Gel properties

To prepare gels, starch suspensions (10% w/w db) were heated from 25 to 95 °C at 13 °C/min, held at 95 °C for 10 min and then cooled to 50 °C at 13 °C/min using Rapid Visco-Analyzer. The hot starch paste was transferred into a cylindrical plastic container (50 mm diameter, 0.9 mm height) and stored at 4 °C for 48 h. The texture of the starch gels was determined using a texture analyzer (TA-XT2, Stable Microsystems, Surrey, UK). The gel was compressed using a cylindrical plunger (20 mm diameter) to a depth of 4 mm at a speed of 1.0 mm/s.

#### 2.9. Statistical analysis

The data reported were the means of triplicate measurements. Statistical analyses with Duncan’s multiple test (P < 0.05) were carried out using SPSS V. 8.2 software (SPSS Institute Inc., Cary, NC).

### 3. Results and discussion

#### 3.1. Chemical composition and substitution characteristics

The amylase contents of JR determined using size exclusion chromatography (SEC) was lower than that of IR (Table 1). Similar results with higher the amylase content in *indica* rice starch (IR) than *japonica* rice starch (JR) had been reported (Takeda et al., 1987; Chung et al., 2011). The protein contents, which indicate the purity of the isolated starches, were below 1% in JR and IR (Table 1).

The amounts of substituted groups and DS in acetylated and hydroxypropylated starches were greater in JR than IR (Table 1). These results indicate that JR was more easily substituted than IR. Biladeris (1982) suggested that substitution occurs preferentially in the amorphous domains of amylopectin molecules. Chen, Schols, and Voragen (2004) also claimed that substitution took place in
amorphous regions of amylose and amylopectin but most substituent groups were located in the amylopectin. Consequently, the relatively large amount of amylopectin in JR could be caused its relatively higher degree of substitution in the amorphous regions of amylopectin. In contrast, the phosphorous contents and DS of the cross-linked starches were not significantly different between JR and IR (Table 1).

3.2. Thermal properties

The thermal properties of the modified rice starches are presented in Table 2. The onset (T<sub>o</sub>), peak (T<sub>p</sub>), and conclusion (T<sub>c</sub>) gelatinization temperatures and gelatinization enthalpy (ΔH) varied significantly among the tested modification methods. JR had lower onset (T<sub>o</sub>) and peak (T<sub>p</sub>) temperatures and a wider gelatinization temperature range (T<sub>c</sub> – T<sub>o</sub>) than IR. Similar results were reported by Chung et al. (2011). Gelatinization enthalpy (ΔH) of JR was higher than that of JR although JR contained more amylopectin because amylopectin plays a major role in gelatinization enthalpy of starch (Sasaki et al., 2009). Gelatinization enthalpy indicates the loss of double helical order (Cooke & Gilley, 1992), which is related to the amylopectin molecular structure. The amylopectin of JR had a greater branch chain length than that of JR (Chung et al., 2011; Umemoto, Nakamura, Satoh, & Terashima, 1999), which could explain the much higher gelatinization enthalpy of IR in this study.

The gelatinization temperatures of the JR and IR significantly decreased after acetylation (JAC and IAC) and hydroxypropylation (JHP and IHP) (Table 2). The gelatinization temperatures are a measure of the perfection of starch crystallites (Tester & Morrison, 1990). The substitution with acetyl or hydroxypropyl groups weakens the hydrogen bonds between starch chains and facilitates water penetration and absorption into the starch granules, thereby increasing the initial rate of plasticization of the amorphous regions (Yook, Pek, & Park, 1993; Seow & Thevamalar, 1993). The internal plasticization through incorporation of substituent is associated with promoting gelatinization, resulting in lowering melting temperature (Seow & Thevamalar, 1993). Acetylation and hydroxypropylation of IR did not significantly affect the gelatinization enthalpy, whereas JAC and JHP showed lower gelatinization enthalpies than JR (Table 2). Perera, Hoover, and Martin (1997) suggested that the introduction of a hydroxypropyl group disrupts double helices because of the rotation of the flexible hydroxypropyl groups within the amorphous regions. The modified JR contained more acetyl and hydroxypropyl groups than those of IR (Table 1). Consequently, the disruption of the double helices in the crystalline regions by substitution had a significant effect on JR, but little effect on the IR because of the difference in the substitution degree.

Cross-linking of IR (ICL) did not significantly impact the gelatinization temperatures and enthalpy, whereas the cross-linked starch with JR (JCL) showed a slight increase in T<sub>o</sub>, T<sub>p</sub> and T<sub>c</sub> relative to JR (Table 2). This result indicates that the introduction of phosphate groups into starch tightens the molecular structure, resulting in gelatinization at a higher temperature (Chaturakonnda, Varavinit, & Chinchati, 2000).

Interestingly, the dual modification affected the gelatinization behaviors of JR and IR differently (Table 2). Acetylation (JCL) and hydroxypropylation (JCLHP) of cross-linked JR resulted in significantly higher T<sub>p</sub> and T<sub>c</sub> than those of the corresponding single-modified starches (JAC and JHP), whereas T<sub>c</sub> did not change significantly. In contrast, the ICLAC and ICLHP had significantly higher T<sub>p</sub> and T<sub>c</sub>, and similar T<sub>c</sub> to IAC and IHP, respectively. Thus, the dual modification of the JR and IR resulted in broader and narrower endotherms, respectively, than those of the corresponding single-modified starches (Table 1). The gelatinization enthalpy values of JCLAC and JCLHP were greater than those of IAC and JHP but similar to those of JR and JCL, whereas ICLAC and ICLHP showed significantly lower gelatinization enthalpy than IR and the single-modified starches (IAC, IHP, and ICL). The presence of cross-linking in the dual-modified starches increased the T<sub>o</sub> in JR but resulted in a marked increase in T<sub>c</sub> for the IR. These results were probably due to greater DS (Table 1) and shorter amylopectin branch chain length (Chung et al., 2011) of JR compared to those of IR. The greater amylopectin branch chain length and lower DS in IR could impart a stronger granule structure after cross-linking, resulting in delayed gelatinization and thus increased conclusion temperature of gelatinization.

3.3. Pasting properties

RVA viscosograms of the single- and dual-modified rice starches are presented in Fig. 1, and the analyzed pasting parameters are summarized in Table 3. JR and IR showed similar pasting patterns with low swelling, high pasting temperature, and great resistance to shear-thinning (Fig. 1). JR had a similar pasting temperature and peak viscosity as IR whereas final viscosity of IR was greater than that of JR (Table 1). During cooling of the starch paste, leached amylose molecules rapidly aggregate and this aggregation is responsible for the final viscosity (Jane et al., 1999). The greater final viscosity of IR could be attributed to its higher amylose content (Table 1).

JAC and IAC had lower pasting temperatures than the corresponding native starches, whereas their breakdown, setback and final viscosity were substantially higher than those of the native starches (Table 3). The introduction of an acetyl group caused weakening of molecular structure by interrupting hydrogen bonds and helical structure, resulting in a decreased pasting temperature and increased breakdown. The greater setback and final viscosity indicate the greater re-association degree of molecules in JAC and IAC. Peak viscosity of JAC and IAC were marginally lower and slightly higher than those of their corresponding native starches, respectively (Table 3). Hydroxypropylation caused a substantial decrease in the pasting temperature and significant increases in the peak viscosity, breakdown, setback, and final viscosity. Loosening of the starch structure after hydroxypropylation could permit granules to swell to a greater extent and at lower temperature, resulting in a higher peak viscosity and lower pasting temperature (Gunaratne & Corke, 2007). Structurally weak granules could also explain the increased breakdown. The extent of the increase and decrease of the pasting parameters was greater after hydroxypropylation than after acetylation because of the
greater steric hindrance of the hydroxypropyl group, which results in much significant interruption of hydrogen bonding in the starch chain.

The pasting temperature of the JAC and JHP was higher than that of IAC and IHP, and the peak viscosity of IAC and IHP was greater than those of JAC and JHP, respectively (Table 3). However, the DS of acetylation and hydroxypropylation in JR was slightly greater than that in IR. Substitution occurs mainly in the amorphous regions of amylopectin molecules (Biliaderis, 1982). Kavitha and BeMiller (1998) suggested that both amylopectin and

**Table 2**

Thermal properties of single and dual-modified rice starches.a.

<table>
<thead>
<tr>
<th>Rice starch</th>
<th>$T_o$ (°C)</th>
<th>$T_p$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$T_c - T_o$ (°C)</th>
<th>$\Delta H$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JR</td>
<td>56.2 ± 0.4b</td>
<td>64.6 ± 0.2c</td>
<td>71.1 ± 0.1bc</td>
<td>14.9 ± 0.4d</td>
<td>13.4 ± 1.3b</td>
</tr>
<tr>
<td>JAC</td>
<td>54.7 ± 0.4e</td>
<td>61.4 ± 0.1f</td>
<td>69.0 ± 0.2e</td>
<td>14.4 ± 0.2e</td>
<td>9.8 ± 1.4e</td>
</tr>
<tr>
<td>JHP</td>
<td>51.8 ± 0.8g</td>
<td>60.2 ± 0.1h</td>
<td>68.3 ± 0.6gh</td>
<td>16.5 ± 0.9gh</td>
<td>12.1 ± 0.2h</td>
</tr>
<tr>
<td>JCL</td>
<td>55.7 ± 0.3b</td>
<td>65.1 ± 0.1i</td>
<td>72.8 ± 0.3i</td>
<td>17.1 ± 0.1s</td>
<td>13.6 ± 0.1i</td>
</tr>
<tr>
<td>JCLAC</td>
<td>56.3 ± 0.1h</td>
<td>62.9 ± 0.1d</td>
<td>68.9 ± 0.1de</td>
<td>12.5 ± 0.0d</td>
<td>13.9 ± 0.3h</td>
</tr>
<tr>
<td>JCLHP</td>
<td>55.8 ± 0.4h</td>
<td>61.9 ± 0.1e</td>
<td>67.9 ± 0.2e</td>
<td>12.1 ± 0.8d</td>
<td>12.8 ± 0.7h</td>
</tr>
<tr>
<td>IR</td>
<td>59.1 ± 0.1e</td>
<td>65.4 ± 0.1eh</td>
<td>71.2 ± 0.2eh</td>
<td>12.1 ± 0.1d</td>
<td>16.5 ± 0.8h</td>
</tr>
<tr>
<td>IAC</td>
<td>54.4 ± 0.2f</td>
<td>60.6 ± 0.1f</td>
<td>66.7 ± 0.1f</td>
<td>12.4 ± 0.3d</td>
<td>16.1 ± 1.2h</td>
</tr>
<tr>
<td>IHP</td>
<td>54.0 ± 0.0g</td>
<td>60.3 ± 0.3gh</td>
<td>66.9 ± 0.8gh</td>
<td>12.9 ± 1.1gh</td>
<td>15.4 ± 0.5h</td>
</tr>
<tr>
<td>ICL</td>
<td>59.2 ± 0.2a</td>
<td>65.5 ± 0.0a</td>
<td>71.4 ± 0.2a</td>
<td>12.2 ± 0.4d</td>
<td>16.5 ± 0.4h</td>
</tr>
<tr>
<td>ICLAC</td>
<td>54.1 ± 0.0f</td>
<td>63.0 ± 0.1f</td>
<td>70.3 ± 0.1f</td>
<td>16.2 ± 0.1f</td>
<td>12.6 ± 0.3h</td>
</tr>
<tr>
<td>ICLHP</td>
<td>54.2 ± 0.0g</td>
<td>61.4 ± 0.1g</td>
<td>68.8 ± 0.1g</td>
<td>14.5 ± 0.1g</td>
<td>9.8 ± 0.11h</td>
</tr>
</tbody>
</table>

JR, native japonica rice starch; IR, native indica rice starch; AC, acetylation; HP, hydroxypropylation; CL, cross-linking; CLAC, cross-linking followed by acetylation; CLHP, cross-linking followed by hydroxypropylation; $T_o$, onset temperature; $T_p$, peak temperature; $T_c$, conclusion temperature; $\Delta H$, gelatinization enthalpy.

a Values followed by the different superscripts in the same column are significantly different ($P<0.05$).

Fig. 1. Pasting visograms of single- and dual-modified rice starches.
amylose in the amorphous regions are non-uniformly substituted. Chen et al. (2004) claimed that substitution occurs in all amorphous regions containing amylose and amylpectin and only crystalline regions in the outer lamellae of small granules although the substitution could not take place throughout the crystalline regions of the whole granule due to the poor penetration ability of substituent in starch granules. The different impacts of substitution on the pasting parameter of JR and IR could be attributed to differences in the location and distribution of substituent groups on the amylose and amylpectin molecules.

JCL and ICL showed slightly increased peak viscosity and decreased pasting temperature than JR and IR, respectively (Table 3). The pasting properties of cross-linked starch depend significantly on the degree of cross-linking (Chatakanonda et al., 2000). Mild cross-linking results in higher peak viscosity than the native starches, while a higher degree of cross-linking results in lower viscosity and a higher pasting temperature. Our results imply that the rice starches were cross-linked to a lesser extent. JCL and ICL had relatively low breakdown and setback, indicating the increased pasting stability after cross-linking. The extent of increase in pasting parameters by cross-linking was comparable between JR and IR due to similar cross-linking degree as found in Table 1.

The cross-linked acetylated or hydroxypropylated starches (CLAC and CLHP) showed higher pasting temperature and lower breakdown than the corresponding AC and HP starches, respectively (Table 1). This result indicates that the tightening starch granule structure by the cross-linking causes the swelling of granule at higher temperature and the reduction of shear thinning. The dual-modified starches had higher final viscosity than the corresponding AC and HP starches, which indicates that the re-association degree of the dual-modified starches was greater. Interestingly, the cross-linked acetylated starch (JCLAC and ICLAC) had higher peak viscosity than JAC and IAC, whereas the cross-linked hydroxypropylated starch (JCLHP and ICLHP) had lower peak viscosity than the corresponding hydroxypropylated starches (JHP and IHP). This result implies that introduction of acetyl groups to mildly cross-linked starches could loosen the starch structure, which could permit granules to swell to a greater extent than in starches that were only acetylated. In contrast, hydroxypropylation of cross-linked starches stabilized the viscosity of the starch paste with restricted swelling as compared to that of hydroxypropylated starches.

When comparing JR and IR on dual modification, the dual-modified IR was greater peak and final viscosities but lower pasting temperature than the corresponding JR. This trend was similar with single modification by acetylation and hydroxypropylation from unmodified starches. This result indicates that the location and distribution of substituent groups may not be quite different either substitution from unmodified starches or substitution from cross-linked starch during dual modification.

3.4. Swelling power and solubility

The swelling power and solubility of the single- and dual-modified rice starches are presented in Table 4. The swelling power of IR was slightly higher than that of JR, which was consistent with peak viscosity result. The swelling ability at 95 °C reflects the magnitude of starch chain interactions within the gelatinized granules (Gunaratne & Corke, 2007) and the structural characteristics of amylose and amylpectin (Hooper & Ratnayake, 2002). The marginally higher swelling power of IR could be attributed to increased starch chain interactions because the higher amylose content (Table 1) and longer branch chains in amylpectin (Chung et al., 2011) would reduce swelling. The higher protein content of IR versus that of JR could also increase the swelling power because of the higher water binding capacity of proteins.

The swelling power of JAC and IAC was not significantly different with those of their native starches (Table 3). Similarly, the peak viscosity was only marginally affected by acetylation of JR and IR. Hydroxypropylation (JHP and IHP) increased the swelling power compared with their corresponding native starches, whereas the swelling power of JCL and ICL was significantly lower than that

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Table 3

Pasting properties of single and dual-modified rice starches.

<table>
<thead>
<tr>
<th>Rice starch</th>
<th>Pasting temperature (°C)</th>
<th>Peak viscosity (cp)</th>
<th>Breakdown (cp)</th>
<th>Setback (cp)</th>
<th>Final viscosity (cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JR</td>
<td>90.8 ± 0.4a</td>
<td>353 ± 13h</td>
<td>26 ± 1f</td>
<td>30 ± 1f</td>
<td>357 ± 1i</td>
</tr>
<tr>
<td>JAC</td>
<td>84.5 ± 0.3h</td>
<td>311 ± 1</td>
<td>91 ± 0</td>
<td>553 ± 5</td>
<td>773 ± 0</td>
</tr>
<tr>
<td>JHP</td>
<td>73.4 ± 0.8h</td>
<td>892 ± 64a</td>
<td>407 ± 32b</td>
<td>956 ± 39a</td>
<td>1498 ± 71b</td>
</tr>
<tr>
<td>JCL</td>
<td>77.5 ± 0.8f</td>
<td>487 ± 9d</td>
<td>58 ± 1f</td>
<td>37 ± 3j</td>
<td>466 ± 7h</td>
</tr>
<tr>
<td>JCLAC</td>
<td>86.0 ± 0.4b</td>
<td>515 ± 16e</td>
<td>8 ± 1</td>
<td>429 ± 15a</td>
<td>936 ± 30c</td>
</tr>
<tr>
<td>JCLHP</td>
<td>75.9 ± 0.0f</td>
<td>769 ± 6f</td>
<td>130 ± 5d</td>
<td>1000 ± 2b</td>
<td>1639 ± 3b</td>
</tr>
<tr>
<td>IR</td>
<td>91.3 ± 0.0</td>
<td>402 ± 2b</td>
<td>—</td>
<td>449 ± 3h</td>
<td>895 ± 2</td>
</tr>
<tr>
<td>IAC</td>
<td>82.5 ± 0.8d</td>
<td>436 ± 11e</td>
<td>132 ± 2d</td>
<td>591 ± 14f</td>
<td>1433 ± 50h</td>
</tr>
<tr>
<td>IHP</td>
<td>71.2 ± 0.8d</td>
<td>1134 ± 53a</td>
<td>579 ± 30d</td>
<td>878 ± 27g</td>
<td>1433 ± 50c</td>
</tr>
<tr>
<td>ICL</td>
<td>77.9 ± 0.4d</td>
<td>556 ± 2e</td>
<td>53 ± 1</td>
<td>33 ± 1f</td>
<td>536 ± 2</td>
</tr>
<tr>
<td>ICLAC</td>
<td>83.2 ± 0.1d</td>
<td>643 ± 1d</td>
<td>16 ± 1h</td>
<td>457 ± 0</td>
<td>1084 ± 2d</td>
</tr>
<tr>
<td>ICLHP</td>
<td>74.2 ± 0.4f</td>
<td>930 ± 5f</td>
<td>202 ± 6h</td>
<td>1126 ± 10b</td>
<td>1854 ± 9</td>
</tr>
</tbody>
</table>

JR, native japonica rice starch; IR, native indica rice starch; AC, acetylation; HP, hydroxypropylation; CL, cross-linking; CLAC, cross-linking followed by acetylation; CLHP, cross-linking followed by hydroxypropylation.

A Values followed by the different superscripts in the same column are significantly different (P < 0.05).

B Not detected.

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Table 4

Swelling power and solubility of single and dual-modified rice starches.

<table>
<thead>
<tr>
<th>Rice starch</th>
<th>Swelling power</th>
<th>Solubility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JR</td>
<td>32.2 ± 1.3f</td>
<td>19.0 ± 4.2f</td>
</tr>
<tr>
<td>JAC</td>
<td>30.8 ± 0.4f</td>
<td>18.0 ± 0.0f</td>
</tr>
<tr>
<td>JHP</td>
<td>36.3 ± 5.3d</td>
<td>22.0 ± 1.1b</td>
</tr>
<tr>
<td>JCL</td>
<td>13.3 ± 0.4f</td>
<td>13.0 ± 1.4d</td>
</tr>
<tr>
<td>JCLAC</td>
<td>12.7 ± 1.3d</td>
<td>14.4 ± 0.1d</td>
</tr>
<tr>
<td>JCLHP</td>
<td>16.6 ± 1.9d</td>
<td>18.0 ± 0.1f</td>
</tr>
<tr>
<td>IR</td>
<td>33.5 ± 1.3d</td>
<td>17.0 ± 4.2f</td>
</tr>
<tr>
<td>IAC</td>
<td>31.1 ± 0.2e</td>
<td>14.0 ± 0.0d</td>
</tr>
<tr>
<td>IHP</td>
<td>41.9 ± 2.4e</td>
<td>28.0 ± 2.8a</td>
</tr>
<tr>
<td>ICL</td>
<td>13.0 ± 0.3c</td>
<td>10.0 ± 2.8b</td>
</tr>
<tr>
<td>ICLAC</td>
<td>14.3 ± 1.8e</td>
<td>12.9 ± 0.8f</td>
</tr>
<tr>
<td>ICLHP</td>
<td>17.3 ± 0.0d</td>
<td>17.2 ± 0.4h</td>
</tr>
</tbody>
</table>

JR, native japonica rice starch; IR, native indica rice starch; AC, acetylation; HP, hydroxypropylation; CL, cross-linking; CLAC, cross-linking followed by acetylation; CLHP, cross-linking followed by hydroxypropylation.

A Values followed by the different superscripts in the same column are significantly different (P < 0.05).
of JR and IR, respectively. Hydroxypropyl group could facilitates the penetration of water molecules into the granules by weakening hydrogen bond between starch chains, whereas cross-linking induced a strengthened starch structure, which limited water absorption (Yook et al., 1993; Hung & Morita, 2005). The swelling power of IHP was higher than that of JHP (Table 3), which was in consistent with their peak viscosity result.

The swelling power of CLAC and ICLAC was not significantly different from that of corresponding JCL and ICL, respectively, but was substantially lower than that of JAC and IAC, respectively (Table 4). Hydroxypropylation of cross-linked starch induced a slight increase in swelling power. This result indicates that the swelling power of the dual-modified starches was mainly affected by cross-linking. The swelling power of dual-modified JR was not significantly different from that of the corresponding IR.

The amount of soluble solids in JR was marginally higher than that in IR. Acetylation of JR and IR resulted in a slight decrease in solubility. However, a significant increase in the solubility was observed after hydroxypropylation. It has been suggested that the main component that leaks from the granules is amylose (Mondala & Bayas, 2004). The weakening of the interactions between the starch chains caused by hydroxypropylation could facilitate amylose leaching from the starch granules. The solubility of IHP was greater than that of HP, probably due to the lower DS in HP. Shi and BeMiller (2002) claimed that the leaching of the substituted amylose decreased as the degree of modification of the starch granules increased. As expected, cross-linking substantially decreased the solubility. The solubility of the dual-modified starches was significantly lower than that of the substituted starches and greater than that of the cross-linked starches for both JR and IR. However, the solubility of dual-modified JR and IR was not significantly different (Table 4).

### 3.5. Gel properties

The gel properties of the single- and dual-modified rice starches are presented in Table 5. The hardness, springiness, cohesiveness, gumminess, and chewiness of JR were higher than those of IR. The gel structure after gelatinization is an ordered structure caused by the reassociation of starch chains. Both linear amylose and branched amylopectin participate in the gelled structure. The initial gel firmness of starch is mainly attributed to the short-term reassociation of amylose chains, while amylopectin has a longer reassociation time causing a reversible rigid and crystalline state of the starch gels (Thomas & Atwell, 1997). The greater firmness of the gel in JR could be attributed to the long-term aggregation of its greater amount of amylopectin molecules.

The chemical modification had a remarkable effect on the gel textures (Table 5). Acetylation (JAC and IAC) increased the gel hardness compared to the corresponding native starches and the IAC showed a greater extent of increase than JAC. Similarly, an increase in the gel hardness of acetylated rice starches was reported by Raina, Singh, Bawa, and Saxena (2006). They explained that acetylation enabled the starch to remain hydrated and increased its stability during low temperature storage. The modified starches obtained from different plant sources retrograde to various degrees and those with relatively higher amylose contents have shown greater change in gel strength (Thomas & Atwell, 1997). The greater increase in hardness of IAC as compared to JAC could be due to the higher amount of amylose in IR, which resulted in the rapid formation of a gelled structure upon cooling. Acetylation of JR (JAC) resulted in decreased gumminess and chewiness, while that of IR (IAC) increased them. This difference could be attributed to the different changes in the cohesiveness, which reflects the intermolecular forces in the gel matrix and underwent a greater decrease in JAC. Hydroxypropylation decreased the gel hardness of both rice starches and the magnitude of the decrease was greater in IHP than JHP (Table 5). Hydroxypropylation loosened the starch structure, which permitted more granules to breakdown and embedded more weak swollen starch granules in the gel matrix, resulting in a weaker starch gel. Gunaratne and Corke (2007) claimed that the substituted hydroxypropyl groups on the amylose chain might prevent amylose aggregation and interrupt the formation of a junction zone by amylopectin. Consequently, the greater amount of amylose in IR induced a higher degree of substitution in the amylose chain of the starch, leading to a greater decrease in gel hardness. In this study, the gel properties of the cross-linked rice starches were not measurable under the test conditions.

The dual-modified starches had higher gel hardness than the acetylated and hydroxypropylated starches (Table 5). Cross-linking of the rice starch induced a substantial reduction in amylose and amylopectin leaching (Table 4), which resulted in a decreased amylose concentration in the gel network and formation of a weaker gel network. However, introduction of acetyl or hydroxypropyl groups into the cross-linked starches increased the amylose leaching and thus more leached swollen starch molecules in the gel matrix led to the formation of more junction zones. The presence of rigid granules from cross-linking in the continuous gel matrix effectively increased the gel hardness of dual-modified starches, but was not effective in cross-linked starch. JCLAC and JCLHP had greater hardness, gumminess and chewiness than ICLAC and ICLHP, respectively. This result could be attributed to difference in the location and distribution of substituent groups on the amylose and amylopectin molecules.

### Table 5

| Textural properties of single and dual-modified rice starches.
<table>
<thead>
<tr>
<th>Rice starch</th>
<th>Hardness (g)</th>
<th>Springiness</th>
<th>Cohesiveness</th>
<th>Gumminess (g)</th>
<th>Chewiness (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JR</td>
<td>133.1 ± 5.1(^m)</td>
<td>0.88 ± 0.01(^a)</td>
<td>0.79 ± 0.04(^d)</td>
<td>104.9 ± 6.9(^d)</td>
<td>92.6 ± 6.7(^d)</td>
</tr>
<tr>
<td>JAC</td>
<td>144.8 ± 9.6(^b)</td>
<td>0.80 ± 0.03(^ab)</td>
<td>0.58 ± 0.07(^d)</td>
<td>84.1 ± 10.8(^a)</td>
<td>67.3 ± 10.1(^d)</td>
</tr>
<tr>
<td>JHP</td>
<td>111.5 ± 8.5(^d)</td>
<td>0.79 ± 0.04(^a)</td>
<td>0.58 ± 0.02(^d)</td>
<td>64.1 ± 3.3(^a)</td>
<td>50.9 ± 4.0(^a)</td>
</tr>
<tr>
<td>JCL</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>JCLAC</td>
<td>235.3 ± 6.6(^a)</td>
<td>0.85 ± 0.03(^b)</td>
<td>0.66 ± 0.02(^d)</td>
<td>155.7 ± 4.0(^a)</td>
<td>131.7 ± 8.8(^d)</td>
</tr>
<tr>
<td>JCLHP</td>
<td>189.6 ± 5.2(^d)</td>
<td>0.82 ± 0.03(^b)</td>
<td>0.72 ± 0.01(^b)</td>
<td>136.3 ± 4.0(^a)</td>
<td>111.8 ± 6.5(^d)</td>
</tr>
<tr>
<td>IR</td>
<td>107.1 ± 7.0(^b)</td>
<td>0.80 ± 0.10(^b)</td>
<td>0.64 ± 0.06(^d)</td>
<td>68.6 ± 1.7(^a)</td>
<td>54.9 ± 1.1(^d)</td>
</tr>
<tr>
<td>IAC</td>
<td>175.2 ± 13.1(^c)</td>
<td>0.85 ± 0.03(^b)</td>
<td>0.58 ± 0.06(^b)</td>
<td>101.7 ± 8.4(^c)</td>
<td>86.2 ± 7.8(^b)</td>
</tr>
<tr>
<td>IHP</td>
<td>73.8 ± 3.7(^e)</td>
<td>0.79 ± 0.03(^b)</td>
<td>0.67 ± 0.00(^d)</td>
<td>49.3 ± 2.6(^d)</td>
<td>38.7 ± 25.0(^d)</td>
</tr>
<tr>
<td>ICL</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ICLAC</td>
<td>190.0 ± 5.1(^a)</td>
<td>0.73 ± 0.03(^b)</td>
<td>0.62 ± 0.03(^d)</td>
<td>117.8 ± 3.8(^c)</td>
<td>86.3 ± 4.0(^a)</td>
</tr>
<tr>
<td>ICLHP</td>
<td>132.4 ± 13.9(^a)</td>
<td>0.80 ± 0.01(^d)</td>
<td>0.66 ± 0.01(^c)</td>
<td>87.7 ± 2.7(^d)</td>
<td>69.9 ± 3.0(^d)</td>
</tr>
</tbody>
</table>

JR, native japonica rice starch; IR, native indica rice starch; AC, acetylation; HP, hydroxypropylation; CL, cross-linking; CLAC, cross-linking followed by acetylation; CLHP, cross-linking followed by hydroxypropylation.

\(^a\) Values followed by the different superscripts in the same column are significantly different (P < 0.05).

\(^b\) Not measurable.
4. Conclusions

The chemical modification with acetylation, hydroxypropylation, and cross-linking significantly affected the physicochemical properties of rice starches. Dual-modification, acetylation and hydroxypropylation of cross-linked rice starches, provided desirable changes in the functional properties with increased gelatinization temperature, gel hardness, and gel chewiness and decreased breakdown, swelling, and solubility, which could enable a wide range of applications. The extent of change in the functional properties after the dual modification of japonica and indica rice starches was different possibly due to the differences in the amylopectin content, molecular structure of amylopectin, granular swelling, degree of substitution, and location of substituent groups.

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References


