CRediT author statement:

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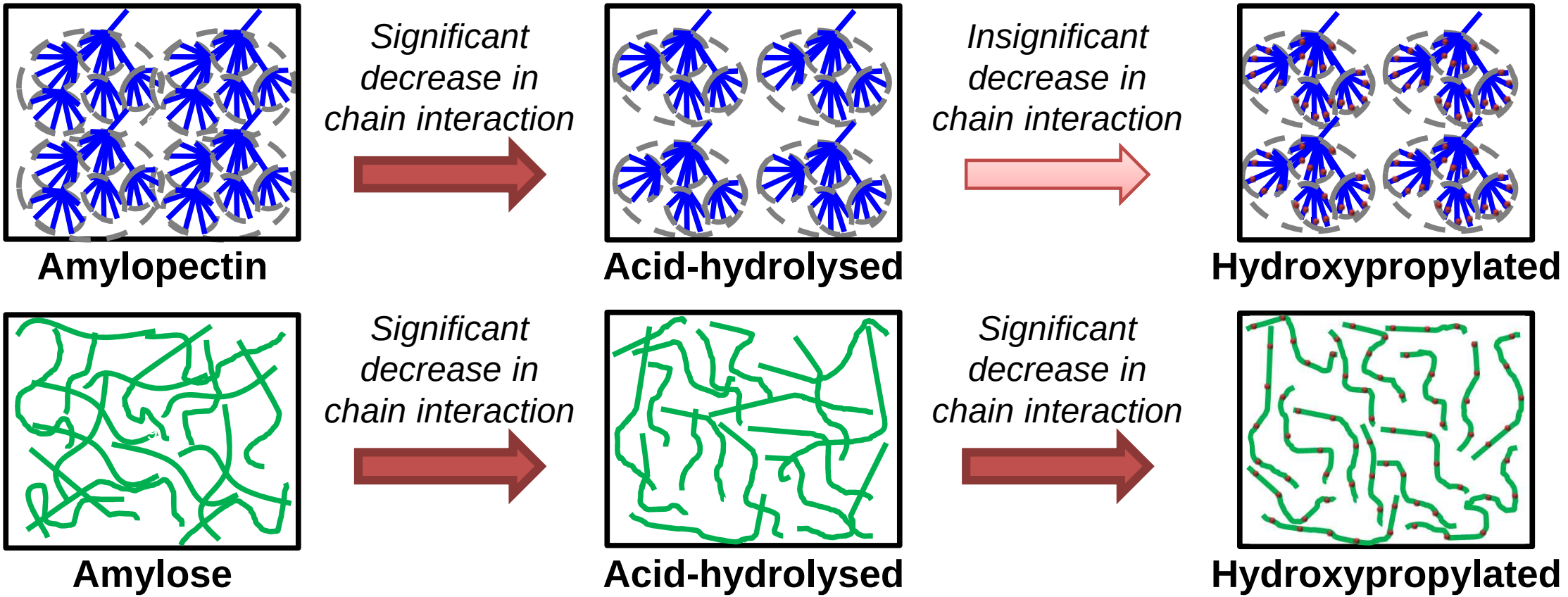

Comparison of the structure and properties of hydroxypropylated acid-hydrolysed maize starches with different amylose/amylopectin contents

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Abstract

Dually modified regular maize starch (RMS) and high-amylose maize starch (HAMS) were successfully prepared by first acid hydrolysis and subsequently hydroxypropylation. The effects of hydrolysis time (0–24 h) and propylene oxide (PO) content (10–30%) on the structure and physicochemical properties were investigated. The molar substitution (MS) of HAMS samples (up to 0.163) was generally higher than that of RMS samples (up to 0.149), suggesting the higher reactivity of amylose for hydroxypropylation. Besides, PO content had a greater influence on MS whereas the effect of acid hydrolysis time was minor. For both starches, the dual modifications did not cause apparent changes to the granule morphology but reduced gelatinisation temperatures and enthalpy; and a higher PO content led to higher relative crystallinity. These results suggest that hydroxypropylation occurred mainly on the surface of HAMS granules and had little influence on the compact granular structure, whereas this reaction impacted the internal structure of RMS much more. The rheological study shows the introduced hydroxypropyl bulky groups weakened the entanglements between amylose chains or amylopectin chains with long branches. Thus, this work provides insights into the rational design of modified starch products containing different amylose/amylopectin contents with tailored properties.

Keywords: maize starch; hydroxypropylation; acid hydrolysis; rheological properties; intrinsic viscosity; gelatinization

1 Introduction

Starch is a type of natural biomacromolecule formed by the photosynthesis of plants. It is an abundant, cheap, biodegradable, and environmentally friendly resource and has great potential in a diversity of applications such as food ingredients, pharmaceutical materials, and biodegradable plastics (Yang et al., 2016). However, native starch has some drawbacks such as its insolubility in water and easy retrogradation. Therefore, starch usually needs to be modified for specific and enhanced applications (Liu, Ramsden, & Corke, 1999; Kaur, Singh, & Singh, 2004; Chun & Yoo, 2007; Lawal, 2011; Lee & Yoo, 2011).

Hydroxypropyl starch (HPS) is a popular modified starch product that has been widely used in industry since the first patent about it published in 1968 (Toshio, 1968). Hydroxypropylation introduces hydrophilic bulky groups to the starch backbone, which increases its solubility, paste clarity, cohesiveness, freeze-thaw stability, and enzymatic digestibility (Lawal, 2011; Lee & Yoo, 2011). Due to the enhanced properties, HPS has found important applications in food (Miyazaki, Van Hung, Maeda, & Morita, 2006), biodegradable films (Woggum, Sirivongpaisal, & Wittaya, 2015b), and pharmaceutical capsules (Zhang et al., 2013).

However, for HPS, it is challenging to achieve high molar substitution (MS) and the reaction is usually limited on the granule surface (Fouladi & Mohammadi Nafchi, 2014). To improve the reactivity, Fouladi & Mohammadi (Fouladi & Mohammadi Nafchi, 2014) have attempted a dual modification method with a combination of acid hydrolysis and hydroxypropylation, which showed synergistic effects on the functional properties (e.g. solubility) of sago starch. Li et al. (Li et al., 2018) reported the superior gelling and gel properties of acid-hydrolysed and hydroxypropylated potato starch.

The overall reactivity can be determined by not only the granule architecture (whether there are channels in the granule) but also the reactivity of starch chains within the granule (Bemiller, 1997; Kaur, Ariffin, Bhat, & Karim, 2012). Traditionally, depending on the chain structure, there are two types of starch biomacromolecule identified, namely amylose and amylopectin (Chen, Yu, Chen, & Li, 2006; Chen et al., 2009). Amylose is in the form of mainly long, linear chains with limited branches, which tend to entangle with each other, while amylopectin has large amounts of highly-branched, short chains with limited capability for entanglement (Liu, Yu, Xie, & Chen, 2006; Liu et al., 2011). The molecular weight of amylose (10^5–10^6) is much lower than that of amylopectin (10^7–10^9) (Pérez, Baldwin, & Gallant, 2009).

The research of starch in the last two decades has further revealed the difference between high-amylose starch (HAS) and regular starch. Firstly, HAS contains not only amylose and amylopectin, but also intermediate components, which is branched amylose chains or amylopectin chains with long branches, functioning similarly as amylose (Jane et al., 1999; Vilaplana, Hasjim, & Gilbert, 2012; Li, Gidley, & Dhital, 2019). Moreover, HAS presents a compact granule structure with the absence of channels, which expresses the exo-corrosion pattern during the acid hydrolysis, in contrast to the endo-corrosion pattern for waxy starch (Chen et al., 2006; Liu et al., 2006; Chen et al., 2009; Xie et al., 2009; Wang et al., 2010; Li et al., 2011; Liu et al., 2011; Zou et al., 2012; Zhang et al., 2014; Xie et al., 2015; Qiao et al., 2016; Chen, Xie, Zhao, Qiao, & Liu, 2017a; Liu et al., 2017).

Therefore, it is interesting to compare the chemical reactivity between HAS and regular starch for dual chemical modifications (acid hydrolysis and hydroxypropylation) and to investigate the influence of such modification on the structure (morphology and crystalline structure) and

physicochemical properties (thermal and rheological properties) of these two starches, which has formed the intention of this study. We particularly compared the effects of the starch chain structure (highly-branched or linear) and the introduced hydroxypropyl groups on the rheological properties of the modified starch solutions, which is scientifically and practically interesting.

2 Materials and methods

2.1 Materials

A regular maize starch (RMS) and a high-amylose maize starch (Gelose 80, about 80% amylose content, as determined by the manufacturer) (HAMS) were purchased from National Starch Pty Ltd. (Lane Cove, NSW, Australia). All chemicals used for the starch modification were of analytical grade. Double-distilled water was used in all the experiments.

2.2 Dual modifications of starch

For acid hydrolysis, a starch slurry of 40% (w/v) concentration was prepared by adding 40 g of starch (dry weight) into 100 g of 0.14 mol/L HCl solution. The slurry was incubated for different times (6 h, 12 h, 18 h, and 24 h) in an oscillating incubator at 40 □ oscillated at 200 rpm. After that, the pH of the starch slurries was adjusted to 5.5 with 5% (w/v) NaOH solution with continuous stirring. The slurries were centrifuged (TDL-5-A, Shanghai Anting Scientific Instrument Factory, China) at 5000 rpm for 10 min to remove the supernatant. The sediments were washed with distilled water and then centrifuged at 5000 rpm for 10 min; and this procedure was performed three times. The obtained starch was oven-dried overnight at 40 □.

For hydroxypropylation, the hydrolysed starch slurries (20%, w/v) in flasks were added with 10% anhydrous sodium sulphate with constant stirring. The resultant slurries were kept to be stirred and

heated at 40 □ in a water bath for 10 min. After the pH of the slurries was adjusted to 10.5 with 5% (w/v) NaOH solution, certain amounts (10%, 20%, and 30%, based on the weight of starch dry basis) of propylene oxide (PO) were added. The flasks were capped and the slurries were stirred at 40 □ for 24 h. Afterwards, the pH of the slurries was adjusted to 5.5 with 10% (w/v) HCl solution. The slurries were centrifuged at 5000 rpm for 10 min to remove the supernatant. The sediments were washed with distilled water and then centrifuged at 5000 rpm for 10 min; and this procedure was performed three times. The starch was dried overnight in an oven at 40 □.

All the dually modified starches were coded in the form of, for example, RMS-A6-P20 or HAMS-A12-P10, where "RMS" or "HAMS" indicates the type of starch, A6 reflects the acid hydrolysis time (6 h), and P20 means the added amount of PO (20%).

2.3 Characterisation

2.3.1 Intrinsic viscosity

For the determination of intrinsic viscosity ([η]), RMS and HAMS samples were dispersed in 1.0M KOH solutions. The solutions were stirred in a boiling water bath for 10 min, and then cooled to room temperature (RT) and left overnight. Then, the solutions were centrifuged under 3000 r/min for 6 min, and the final concentrations of the solutions were 2.6–6.0 mg/mL. [η] was measured by an Ubbelohde dilution capillary viscometer (size 37, Shanghai Shenyi Glass Instrument Factory, China), which was immersed in a water bath maintained at 30.0±0.1 °C. The efflux time of solvent and solutions were measured in triplicate and averaged. Then, [η] can be calculated using the following equation:

$$[\eta] = \lim_{c\to 0} \frac{t-t_0}{c\times t_0} \quad (1)$$

where t is the efflux time of the starch solution (s), t_0 is the efflux time of the KOH solution (s), and c represents the concentration of the starch solution (g/mL).

2.3.2 Molar substitution (MS)

The molar substitution (MS) for hydroxypropylation was determined using the method proposed by Jones & Riddick (Jones & Riddick, 1957). This method involves the hydrolysis of the hydroxypropyl group to propylene glycol, which is then dehydrated to propionaldehyde and acryl alcohol. The products are reacted with ninhydrin to form a purple colour. The absorbance of this purple solution was measured using a UV-visible spectrophotometer (UV-3802, Unico (Shanghai) Instrument Co., Ltd., China) at λ = 590 nm with 1cm cuvettes to determine the concentration of propylene glycol based on a standard curve that had been pre-established. The measured content (g) of propylene glycol (W_{PG}) in 100 g of dually modified starch is converted into hydroxypropyl equivalent using the following equation:

$$MS = \frac{2.84W_{PG}}{100\text{-}W_{PG}} \quad (2)$$

2.3.3 Scanning electron microscopy (SEM)

The morphology of the starch granules was examined using a Philips XL30 FEG ESEM facility (Koninklijke Philips N.V., Amsterdam, Netherlands). Before the examination, the samples were coated with gold-palladium in a vacuum evaporator for 120 s. The samples were observed at a low acceleration voltage of 15 kV.

2.3.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns of the starch samples were detected using a Rigaku Ultima IV operating at 40 kV and 40 mA under Cu Kα radiation. The data were collected from 4° to 40° 2θ at a scanning speed of 2°/min. Relative crystallinity (X_c) was estimated using the MDI Jade 6.0 software

144 by deconvolution and fitting of crystalline peaks and the amorphous halo based on the XRD curves
145 between 4° and 40° 2θ. Then, X_c was calculated by the following equation:

146 $$X_c(\%) = \frac{A_c}{A_c + A_a} \times 100\% \quad (3)$$

147 where A_c and A_a are the integrated areas of all crystalline peaks and the amorphous halo,
148 respectively.

149 **2.3.3 Differential scanning calorimetry (DSC)**

150 The starch gelatinization behaviour was analysed using a PerkinElmer DSC 4000 facility
151 (PerkinElmer, Inc., Waltham, MA, USA). 3.5 mg (dry basis) of starch was weighed into a 40μL
152 aluminium pan and then distilled water was added to achieve a starch suspension containing 70% as
153 water. The samples were hermetically sealed and allowed to stand for 1 h at RT before DSC
154 measurements. Starch samples were heated at 5 °C/min from 20 to 130 °C under nitrogen.

155 **2.3.4 Rheological analyses**

156 Starch pastes (5%, w/v) were prepared by dispersing the starch samples (dry basis) in $ZnCl_2$
157 aqueous solutions (42 wt.% concentration in distilled water), which were heated at 50 °C in a water
158 bath for 20 min and then cooled down to RT. The capability of this $ZnCl_2$ aqueous solution to
159 completely dissolve starch (even HAMS) have been demonstrated before (Lin et al., 2016; Chen et
160 al., 2017b; Liu, Li, Shang, & Xie, 2019). The rheological properties of starch pastes were tested
161 using an MCR502 rheometer (Anton Paar GmbH, Austria) with a 60-mm-diameter cone-plate
162 geometry and a Peltier temperature control system. The distance between the plates was set at 1 mm.
163 The steady-state viscosity (η) was recorded in a shear-rate ($\dot{\gamma}$) range of 0–500 s^{-1} at a fixed
164 temperature of 25 °C. At least duplicate tests were performed for each sample. The rheological data
165 was fitted based on the power-law model in the following equation:

$$\eta = K\dot{\gamma}^{n-1} \quad (4)$$

where η is the flow viscosity (Pa s) of the starch solution, $\dot{\gamma}$ is the shear rate (s^{-1}), *K* is the consistency (Pa s), and *n* is the power-law index.

2.3.7 Statistical Analysis

All the experiments were performed at least in triplicate and experimental data were analysed using analysis of variance (ANOVA) and expressed as mean value ± standard deviation. The significant differences were determined using Duncan's HSD test ($p < 0.05$) with the SPSS 22.0 statistical software (SPSS Inc., Chicago, IL, USA).

3 Results and discussions

3.1 Intrinsic viscosity of acid hydrolysed RMS and HAMS

Intrinsic viscosity ([η]) is an important parameter reflecting the molecular size or mass of a polymer in a given solvent at a certain temperature. Thus, it can be used to evaluate the influence of hydrolysis time on starch (Trinh & Dang, 2019; Li et al., 2020). **Fig. 1** shows that both native RMS and HAMS have higher [η] than their modified counterparts and prolonged time of hydrolysis led to reduced [η]. Besides, RMS samples had higher [η] values than HAMS samples, which could be attributed to the higher content of amylopectin in RMS. The molecular mass of amylopectin (10^8 Dalton) is much higher than that of amylose (10^6 Dalton) (Li et al., 2019).

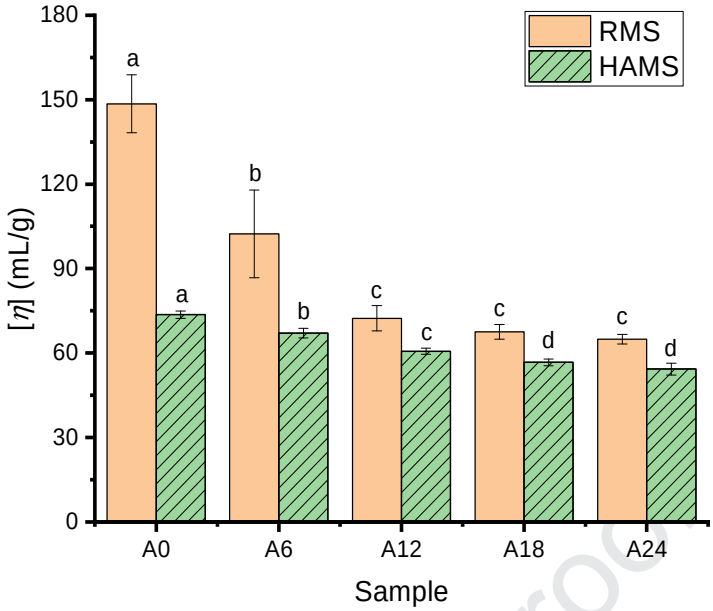


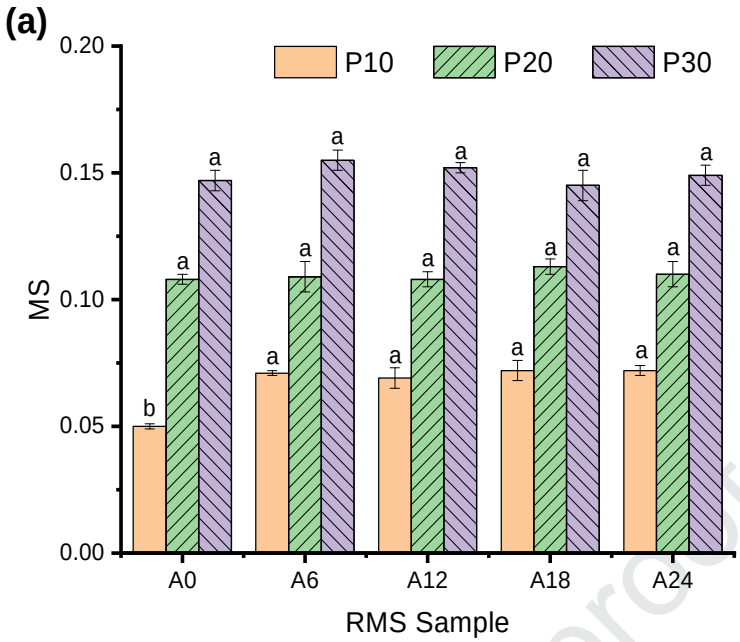
Fig. 1. Intrinsic viscosity ([η]) of RMS and HAMS samples. The different letters indicate significant differences ($p \leq 0.05$).

For RMS, [η] changed rapidly during the early period of acid hydrolysis (especially the first 6 h) whereas the changes are small with further prolonged time. Similar kinetics has been reported previously (Kim, Lee, Kim, Lim, & Lim, 2012; Wang & Copeland, 2015), which can be explained by the first, fast hydrolysis of amorphous regions in starch granules while the crystallites are resistant to hydrolysis. Moreover, after 12 h of hydrolysis, there was no obvious change for [η] ($p \leq 0.05$), indicating a stable state had been achieved during acid hydrolysis (Chen et al., 2017a). For HAMS, the acid hydrolysis resulted in more gradual and much smaller changes in [η], indicating HAMS granules are more resistant to acid hydrolysis than RMS, which has been noted before (Nakazawa & Wang, 2003; Wang & Copeland, 2015). While the small pores in the periphery of the RMS granule could allow easy access of H^+ ions to the hilum, the HAMS granule has a compact periphery without pores, which could hinder the penetration of H^+ ions and thus, the acid hydrolysis (Chen et al., 2009;

Chen et al., 2011; Yang et al., 2016). Besides, Jayakody et al. (Jayakody & Hoover, 2002; Jane, 2006) suggested that, in B-type starches, strong interaction exists between double helices, which are formed in crystallites to a larger extent by intertwining with linear amylose chains, whereas for A-type starches, the double helices in crystallites are constituted mainly by the intertwining of the outer branches of amylopectin and their interaction is relatively weak. This may also explain the greater resistance of HAMS, which is a B-type starch, against the acid hydrolysis. Besides, after 18 hours, the hydrolysed HAS also reached a stable stage ($p \leq 0.05$).

3.2 MS of modified RMS and HAMS

Fig. 2 shows the MS results of the native and modified starch samples. Among the P10 series of RMS samples, RMS-A6-P10 had an apparently higher MS value than RMS-A0-P10. Similar phenomena were observed in previous studies (Wang & Wang, 2001; Wang, Truong, & Wang, 2003; Zhang et al., 2017; Jiang et al., 2018). In this regard, acid hydrolysis could make more active hydroxyl groups in starch granules available for reaction with PO, leading to higher MS (Zhang et al., 2017; Jiang et al., 2018). Nevertheless, further acid hydrolysis (from A6 to A24) did not cause significant changes to MS ($p \leq 0.05$). This well corresponds to the [η] trend. On the other hand, when the PO content was high (for the P20 and P30 series), there was no significant variation in MS among the samples with or without acid hydrolysis (from A0 to A24) ($p \leq 0.05$). Given this, it is likely that when the PO content is high enough, PO can penetrate starch granules effectively for reaction with active hydroxyl groups. A similar phenomenon was reported for sago starch (Fouladi & Mohammadi Nafchi, 2014).



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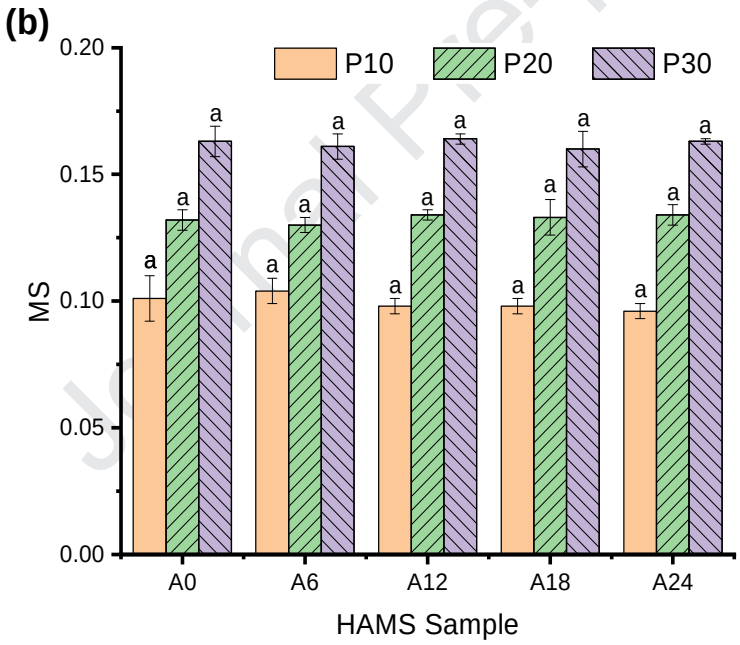

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222 **Fig. 2** Molar substitution (MS) of dually modified starches for RMS (a) and HAMS (b). The

223 different letters indicate significant differences ($p \leq 0.05$).

224

For HAMS samples, the MS was only affected by PO content but not apparently influenced by acid hydrolysis time ($p \leq 0.05$). This can be explained by the low susceptibility of HAMS granules to acid hydrolysis as shown by the [η] data.

Also, it is interesting to observe that the MS values of HAMS were generally higher than those of RMS irrespective of acid hydrolysis time. This may indicate the high reactivity of starch chains, especially amylose or intermediate components, which has lower molecular mass, in the HAMS granule. HAMS presents the exo-corrosion pattern during acid hydrolysis. As a result, under the alkaline condition (pH = 10.5) for hydroxypropylation, OH^- ions could weaken the hydrogen bonding between starch chains and assist PO penetration. Therefore, it is likely that PO penetration did not rely on the channels or pores on the granule surface, and the MS is predominately influenced by PO content. Similarly, for potato starch subjected to hydroxypropylation, amylose was found to be modified to a greater extent than amylopectin (Kavitha & BeMiller, 1998).

3.3 Morphology of modified RMS and HAMS

The morphologies of native RMS and HAMS have been widely reported before. Native RMS has spherical shapes with surface depressions and pores (Chen et al., 2006; Sujka & Jamroz, 2009; Chen et al., 2017a) and native HAMS granules appear to be smooth with elliptical or rounded shapes (Chen et al., 2006; Chen et al., 2017a). Compared with these native starches, **Fig. 3** shows that the dual modifications did not apparently vary the granule morphology including the shape and size for both RMS and HAMS. The starch granules were largely maintained under either the acid or alkaline treatment.

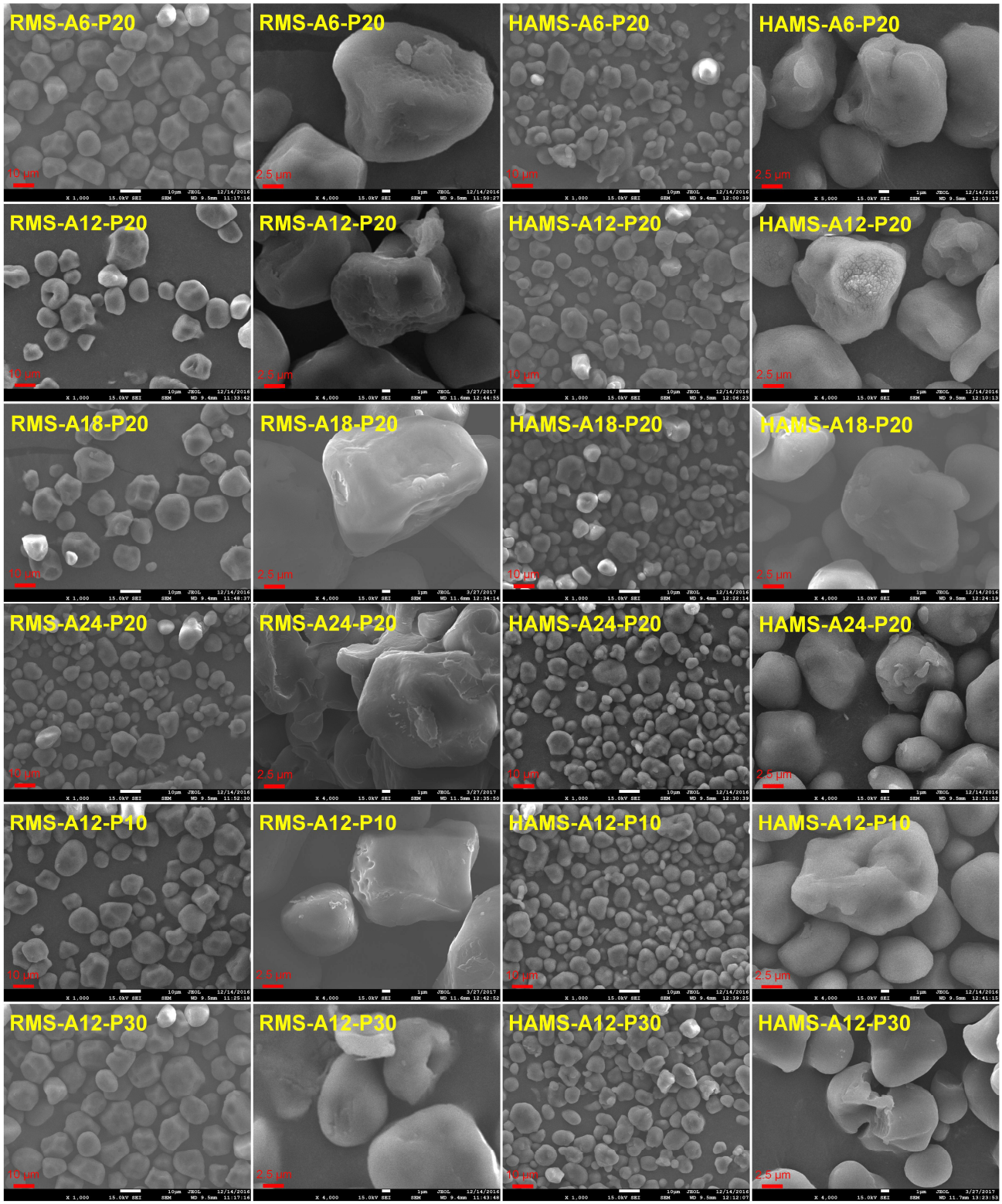
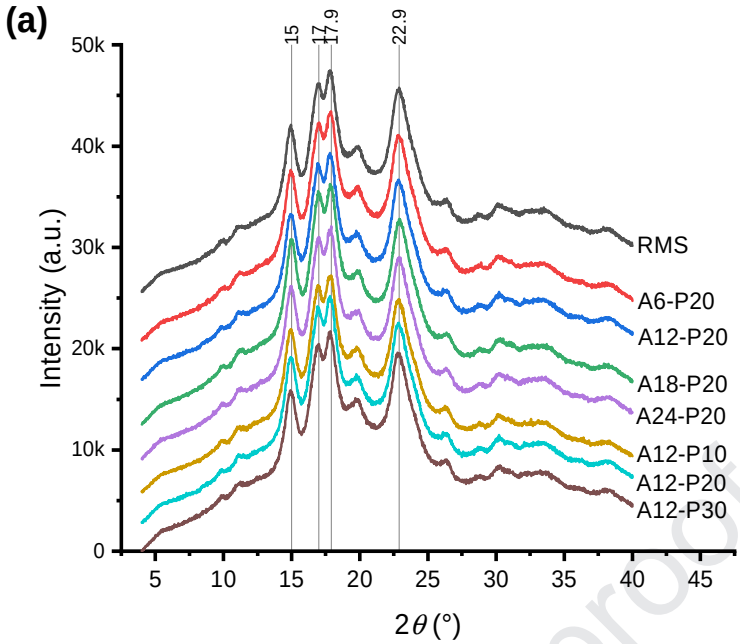


Fig. 3 SEM images of dually modified RMS and HAMS samples.

Fig. 3 shows the acid hydrolysis with prolonged time did not cause apparent variation to the granule morphology. In contrast, a higher content PO led to significant changes in the granule morphology, such as the appearance of deep grooves on the granules of RMS-A12-P30 and the fragmentation of granules for HAMS-A12-P30. These types of erosion should be attributed to the chemical treatment (Hazarika & Sit, 2016). Similar results have been observed in the study by Kaur et al. (Kaur et al., 2004), where potato starch granules treated with 10% PO showed the apparently altered granule structure with folding, depressions, fragmentation, and/or deep grooves. They proposed that hydroxypropylation mainly occurred in the less organised central region of the granule. Since both HAMS and potato starch have B-type crystallinity with no pores on the surface, hydroxypropylation is likely to have occurred in the depression regions of the granules.

3.4 Crystalline structure of modified RMS and HAMS

Fig. 4(a) and **(b)** show the XRD patterns for the native and modified starch samples. Native RMS shows the A-type XRD pattern with strong reflections at 2θ of 15.0°, 17.0°, 17.9°, and 22.9°, and native HAMS exhibits the B-type XRD pattern, which is inferred from four main reflections at 2θ of 5.6°, 17.0°, 19.7°, and 22.1° (Cheetham & Tao, 1998; Tan, Flanagan, Halley, Whittaker, & Gidley, 2007; Lopez-Rubio, Flanagan, Gilbert, & Gidley, 2008). For both RMS and HAMS, the dual modifications did not cause any significant changes to the XRD patterns. Similarly, a previous study (Jiang et al., 2018) showed no significant difference in the XRD pattern between native and acid-thinned starches, meaning the mild acid treatment could not apparently alter starch crystallites.



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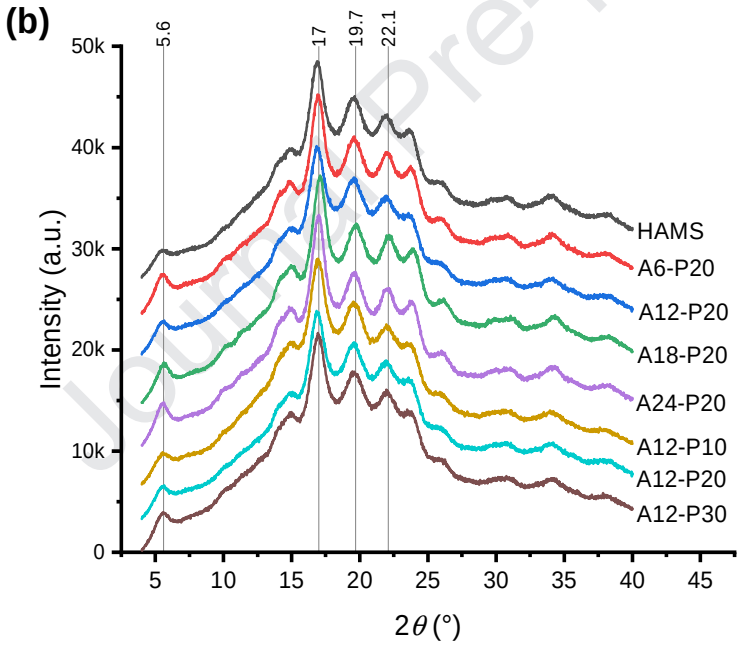

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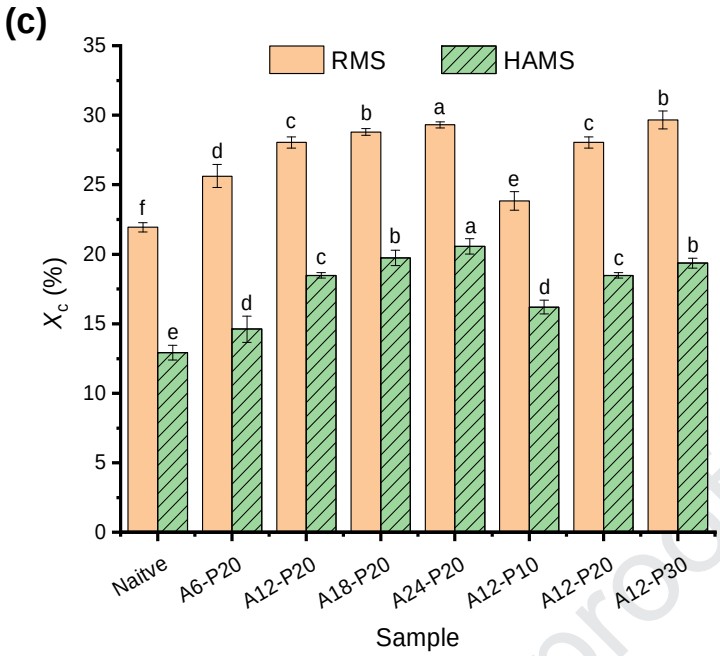

Fig. 4. (a) and (b) XRD patterns for naive and modified RMS and HAMS, respectively; (c) Relative crystallinity (X_c) of native and modified RMS and HAMS. The different letters indicate significant differences ($p \leq 0.05$).

The X_c values of the native and modified starches are plotted in **Fig. 4(c)**. Native RMS had X_c = 21.9 ± 0.3% and HAMS had X_c =12.9 ± 0.5%, similar to the data reported elsewhere (Chen et al., 2017a; Liu et al., 2019; Li et al., 2020). The modified RMS and HAMS samples followed similar trends of variation in X_c. For both starches, X_c increased with longer time of acid hydrolysis (from A0-P20 to A24-P20) and a higher PO content for hydroxypropylation. This variation can be explained that both hydrolysis and hydroxypropylation takes place in the amorphous regions (Wang & Wang, 2001; Jayakody & Hoover, 2002; Wang et al., 2003; Zhang et al., 2017), and the reduction in amorphous content means higher X_c for the total samples.

3.5 Gelatinisation of modified RMS and HAMS

Fig. 5 shows the DSC curves for the native and modified starch samples, with associated gelatinisation parameters shown in **Table 1**. For both RMS and HAMS, increasing PO content led to decreases in the gelatinisation onset and conclusion temperatures (T_o and T_c) as well as enthalpy change (ΔH). In this regard, the introduction of hydroxypropyl groups could reduce the hydrogen bonding between starch chains, destroy double helices, and make it easier for starch granules to undergo swelling and melting of crystallites, leading to reduced gelatinisation temperatures and enthalpy change (Seow & Thevamalar, 1993; Liu et al., 1999; Kaur et al., 2004; Chuenkamol, Puttanlek, Rungsardthong, & Uttapap, 2007; Gunaratne & Corke, 2007; Lawal, 2009, 2011; Lee & Yoo, 2011; Woggum, Sirivongpaisal, & Wittaya, 2015a). Moreover, for RMS, with a higher PO content, the difference in T_o and T_c between samples are obvious, but for HAMS, the difference is small between P10 and P20 samples and becomes obviously between P20 and P30 samples. This result can be attributed to the different reaction site of hydroxypropylation between HAMS and RMS.

Specifically, for HAMS, which presents the exo-corrosion pattern during acid hydrolysis, hydroxypropylation should occur mainly on the surface of granules but have little influence on the compact granular structure. As a result, the T_o and T_c values between P10 and P20 samples are similar to each other. The compact granular structure could only be weakened with a large number of hydroxypropyl groups introduced. On the other hand, for RMS, since it displays an endo-corrosion pattern during acid hydrolysis, hydroxypropylation strongly influenced its inner structure of granules, leading to apparent changes in T_o and T_c.

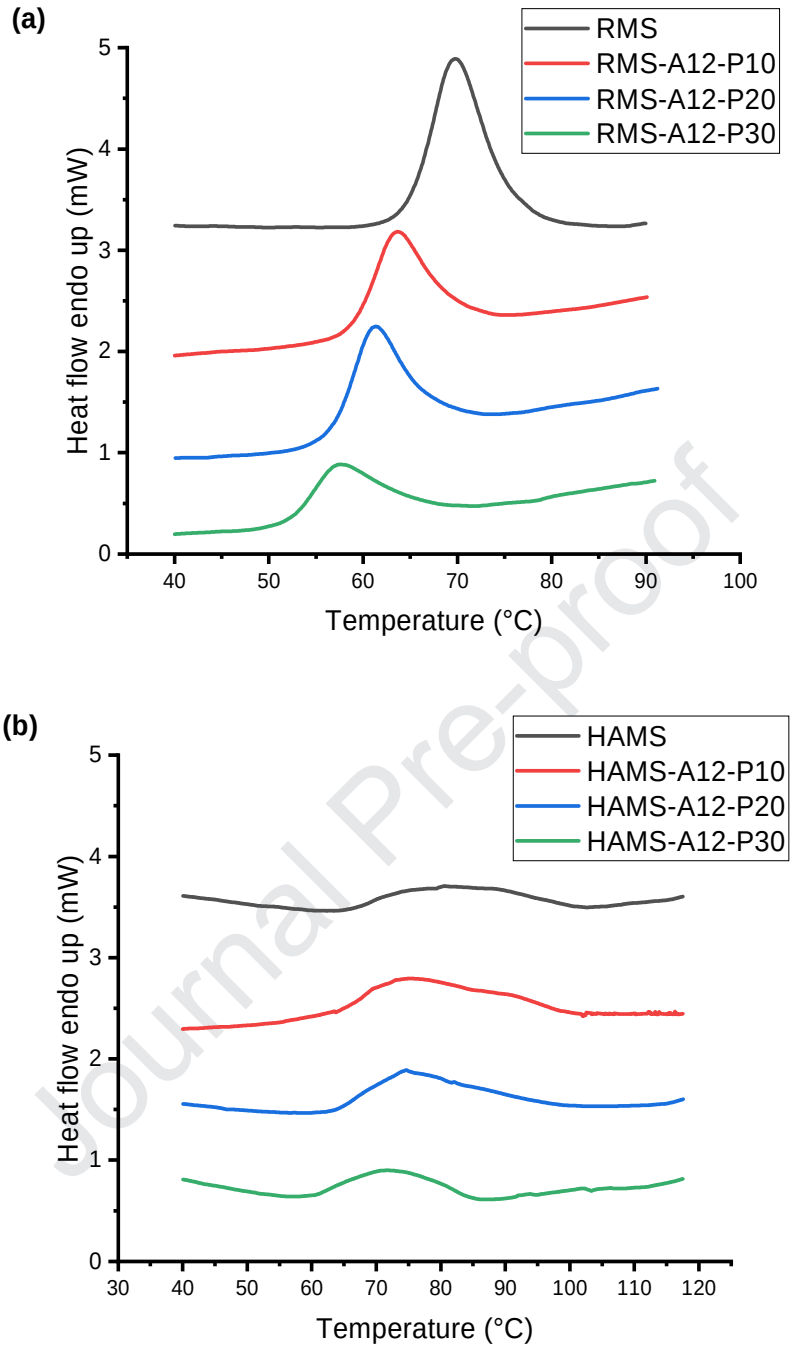

Fig. 5. DSC curves for native and modified RMS (a) and HAMS (b) samples.

Table 1. Onset temperature (T_o), conclusion temperature (T_c) and enthalpy change (ΔH) of gelatinisation measured by DSC for native and modified RMS and HAMS samples.

Sample	T_o (°C)	T_c (°C)	ΔH (J/g)

RMS	59.73±0.36^{c}	84.94±0.06^{e}	13.17±0.33^{a}
RMS-A12-P10	54.99±0.06^{e}	76.32±0.30^{f}	10.11±0.28^{c}
RMS-A12-P20	51.86±0.18^{f}	75.94±0.17^{f}	11.08±0.34^{bc}
RMS-A12-P30	49.02±0.13^{g}	72.60±0.12^{g}	8.44±0.09^{d}
HAMS	64.16±0.06^{a}	102.75±0.06^{a}	11.89±0.39^{ab}
HAMS-A12-P10	63.56±0.42^{a}	101.10±0.23^{c}	12.45±0.31^{ab}
HAMS-A12-P20	62.55±0.12^{b}	101.86±0.13^{b}	11.18±0.31^{bc}
HAMS-A12-P30	58.26±0.18^{d}	86.96±0.24^{d}	8.63±0.92^{d}

Different letters in the same column indicate statistical significance ($p < 0.05$).

Since the ΔH is the enthalpy for the phase transition of crystallinity, it is interesting to see that a high PO content caused an increase in X_c but a decrease in ΔH. Gelatinisation reflects the loss of molecular order (helical structures) rather than that of crystallinity (Cooke & Gidley, 1992). The introduction of hydroxypropyl groups could weaken the hydrogen bonding in helical structures and thus, reduce the enthalpy change. Similarly, hydroxypropylated acid-hydrolysed sago starch also shows apparently reduced gelatinisation temperature and enthalpy change (Fouladi & Mohammadi Nafchi, 2014).

3.6 Rheological properties of modified RMS and HAMS

Since the T_c values for the modified HAMS samples are still higher than 100 °C, it is difficult to obtain their homogeneous gelatinised solutions in water. Thus, a $ZnCl_2$ aqueous solution of 42 wt.% concentration was used to dissolve the starch samples fully (Lin et al., 2016; Chen et al., 2017b; Liu et al., 2019) for studying the rheological properties of the modified starch solutions.

Fig. 5 shows the viscosity–shear rate curves for modified RMS and HAMS samples. All the samples displayed shear-thinning behaviour in the $\dot{\gamma}$ range in question (10–500 s^{-1}) and can be

considered as the pseudo-plastic fluids. Accordingly, the relationship between η and $\dot{\gamma}$ can be fitted using a power-law model (**Eq. (4)**) and the calculated parameters are listed in **Table 2**.

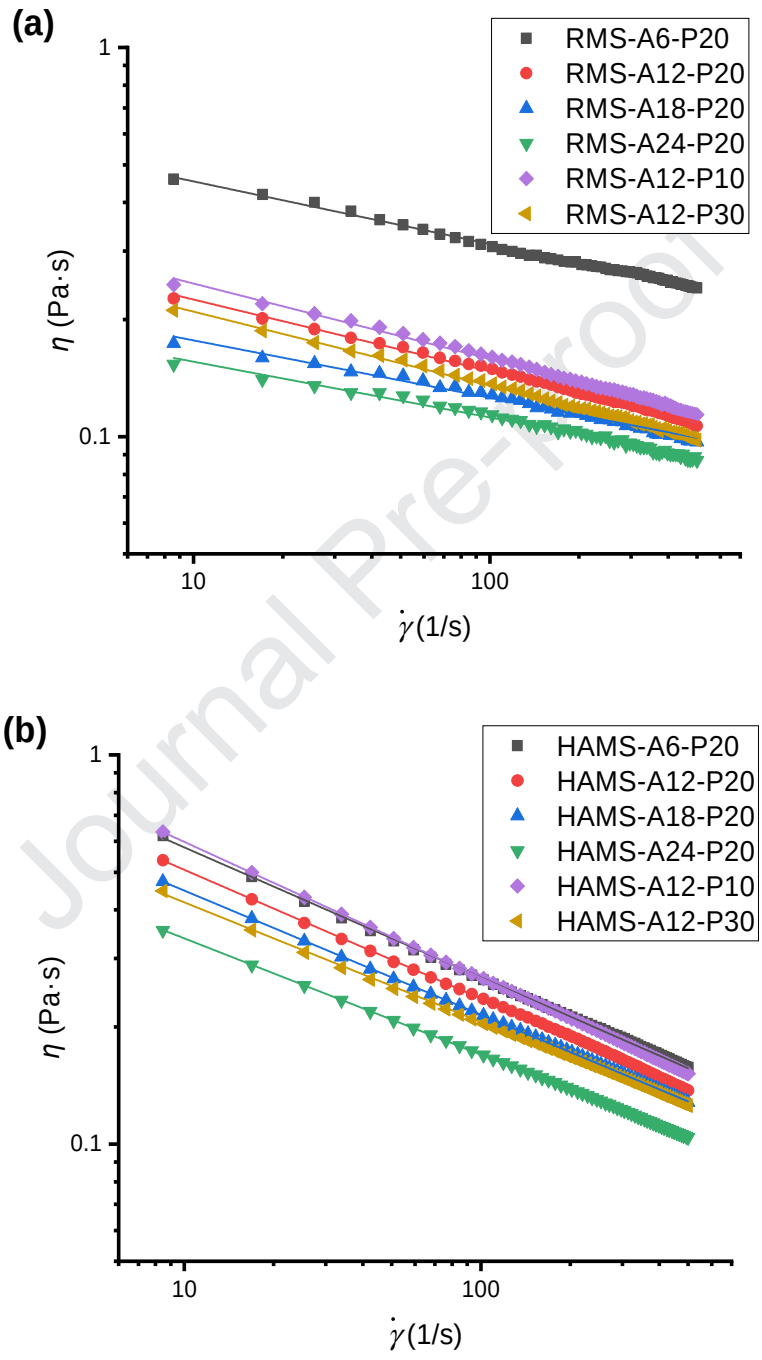

Fig. 6. Viscosity–shear rate curves for modified RMS and HAMS samples.

334 **Table 2.** Power-law parameters for modified RMS and HAMS samples.

Samples	*K* (Pa·s)	*n*
RMS-A6-P20	0.66 ± 0.01^{b}	0.83 ± 0.01^{def}
RMS-A12-P20	0.34 ± 0.01^{a}	0.82 ± 0.001^{bcdef}
RMS-A18-P20	0.23 ± 0.02^{a}	0.85 ± 0.01^{ef}
RMS-A24-P20	0.21 ± 0.01^{a}	0.86 ± 0.01^{f}
RMS-A12-P10	0.37 ± 0.03^{a}	0.81 ± 0.01^{bcdef}
RMS-A12-P30	0.31 ± 0.08^{a}	0.82 ± 0.03^{cdef}
HAMS-A6-P20	1.15 ± 0.14^{de}	0.70 ± 0.05^{ab}
HAMS-A12-P20	0.95 ± 0.19^{cd}	0.71 ± 0.06^{abc}
HAMS-A18-P20	0.81 ± 0.17^{bc}	0.73 ± 0.07^{abcd}
HAMS-A24-P20	0.60 ± 0.09^{b}	0.75 ± 0.07^{abcdef}
HAMS-A12-P10	1.25 ± 0.13^{e}	0.69 ± 0.06^{a}
HAMS-A12-P30	0.74 ± 0.15^{bc}	0.74 ± 0.05^{abcde}

335 Different letters in the same column indicate statistical significance ($p < 0.05$).

336

337 The modified HAMS samples had higher viscosities and lower *n* values than those of the
338 modified RMS samples, indicating greater shear-thinning behaviour and stronger chain interaction
339 for the former. The different rheological behaviours of the RMS and HAMS samples could be
340 attributed to the different conformations of amylose (or amylopectin with long branches) and
341 amylopectin in a solution. Specifically, the interaction between amylopectin chains can be limited by
342 the steric hindrance provided by the large amounts of short and highly-branched side chains which
343 are inflexible, whereas the interaction and entanglement between amylose (or amylopectin with long
344 branches) chains can be easier (**Fig. 6**) (Yu & Christie, 2005; Tajuddin, Xie, Nicholson, Liu, &
345 Halley, 2011).

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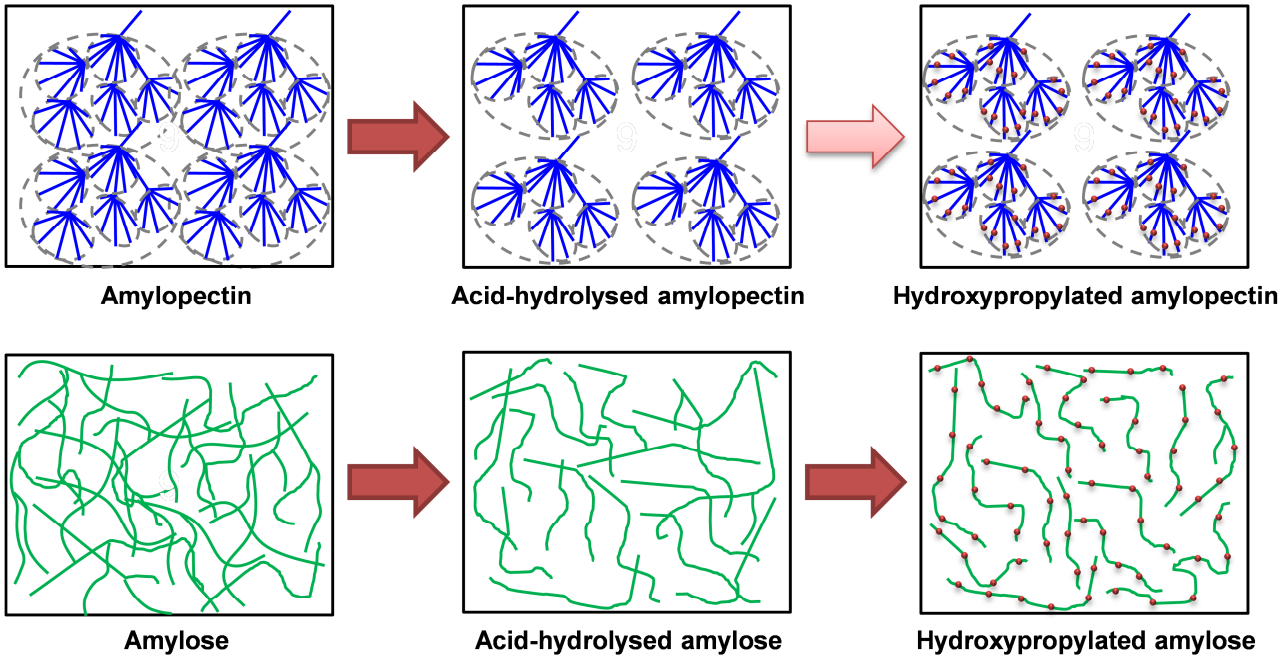

Fig. 6. Schematic representation of chain conformations of amylose (or amylopectin with long branches) and amylopectin in a dissolved state. Arrows of dark red colour indicate a significant change in chain interaction whereas arrows of light red colour mean the change in chain interaction is insignificant.

It can be seen from **Table 2** that for both RMS and HAMS, acid hydrolysis and hydroxypropylation did not cause significant changes to *n* and thus, to the shear thinning behaviour. However, for both starches, *K* apparently decreased with longer time of acid hydrolysis, meaning a reduced extent of chain interaction. For HAMS, hydroxypropylation also significantly decreased *K* whereas this effect was not apparent for RMS. In this regard, we propose that the introduction of hydroxypropyl groups onto the amylose (or amylopectin with long branches) chains can effectively decrease the chain interaction and entanglement and thus, the solution viscosity. However, the introduction of hydroxypropyl groups onto the amylopectin chains have a limited effect to reduce the chain interaction and entanglement as these have already been largely constrained by the steric

hindrance provided by the inflexible short branches. These different effects of the dual modifications on the chain interaction and entanglement of RMS and HAMS are schematically shown in **Fig. 6**.

4 Conclusion

In this work, we have revealed the different effect of a dual modification method (i.e. first acid hydrolysis and subsequently hydroxypropylation) on the structure and properties of RMS and HAMS. Firstly, for both starches, PO content had a greater influence on MS whereas the effect of acid hydrolysis time was minor. In this regard, the alkaline treatment could swell starch granules and facilitate the chemical reaction. Secondly, the MS values of HAMS were generally higher than those of RMS irrespective of acid hydrolysis time. This indicates the high reactivity of amylose or intermediate components, which has a lower molecular mass in HAMS. In addition, from the results of gelatinisation temperatures (T_o and T_c) and enthalpy change (ΔH), it can be deduced that, for HAMS, with the exo-corrosion pattern during acid hydrolysis, hydroxypropylation occurred mainly on the granule surface but had little influence on the compact granular structure. Moreover, the rheological results indicate that hydroxypropylation had very different effects on starch chains due to their conformation in the solution. For amylose chains or amylopectin chains with long branches, the introduced hydroxypropyl groups weakened the chain interaction and entanglement. Therefore, the shear-thinning behaviour for these types of chains was much greater than amylopectin chains with short branches.

The new understandings obtained from this work could provide insights into the rational design of modified starch products containing different amylose/amylopectin contents with tailored properties.

Acknowledgements

This research was funded by the China Postdoctoral Science Foundation (grant No. 2017M612679), the Sailing Scheme of Guangdong Province (grant No. 2017YT05H077), the Guangxi Key Laboratory for Polysaccharide Materials and Modification, Guangxi University for Nationalities (grant No. GXPSMM18ZD-02), and the Natural Science Foundation of Guangdong Province (project No. 2018A0303130048). F. Xie acknowledges support from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 798225.

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Highlights:

- ✓ Regular and high-amylose maize starches (RMS and HAMS) were dually modified
- ✓ HAMS had higher hydroxypropyl molar substitution (MS) than RMS
- ✓ Acid hydrolysis weakly affected MS and but strongly impacted rheological properties
- ✓ Hydroxypropylation largely decreased the solution viscosity for HAMS
- ✓ The effect of hydroxypropylation on the solution viscosity of RMS was insignificant

The authors declare that there is no conflict of interest regarding the publication of this article.