



## Research Paper

# Comparative study of the effect of starches from five different sources on the rheological properties of gluten-free model doughs



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## ABSTRACT

We investigated the effect of wheat (WS), corn (CS), tapioca (TS), sweet potato (SS) and potato (PS) starches on the rheological properties of starch–hydroxypropylmethylcellulose (HPMC) model doughs. Significant differences were found among model doughs made with different starches in terms of water absorption, development time, and strength. The PS-HPMC dough presented higher maximum creep compliance, followed successively by SS-, TS-, CS-, and WS-HPMC doughs, and the same order was found for the degree of dependence of  $G'$  on frequency sweep, suggesting that the resistance to deformation depends on network structure stability. More water distributed between hydration sites of HPMC and starch surface, leading to more hydrogen bonds and the formation of stable network. In conclusion, the rheological properties of model doughs are largely due to variation in structural and physicochemical properties of different starches, as well as varying interactions between different starches and HPMC.

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## 1. Introduction

Celiac disease is related to the inflammation of the small intestine, and leads to intestinal mucosa damage and malabsorption of several important nutrients such as iron, folic acid, calcium, and fat-soluble vitamins (Kelly, Feighery, Gallagher, & Weir, 1990). Reports from recent epidemiological studies have shown that the prevalence of celiac disease has been significantly underestimated in a number of countries, including China (Gallagher, Gormley, & Arendt, 2004; Yuan, Jiang, Hu, Gao, & Chen, 2015). Gluten has been identified as the responsible pathogenic factor in celiac disease (Sivaramakrishnan, Senge, & Chattopadhyay, 2004; Ronda, Gómez, Caballero, Oliete, & Blanco, 2009), and for the patients with celiac

disease, the only effective treatment is a strictly gluten-free diet (Witczak, Juszcak, Ziobro, & Korus, 2016). Therefore, the development of gluten-free products that are suitable for people suffering from celiac disease is highly important.

Starch and hydrocolloids are major ingredients in gluten-free diets (Shi & Bemiller, 2002). Hydrocolloids can be used as a substitute for gluten, and have been widely studied in gluten-free doughs (Mancebo, Picón, & Gómez, 2015). Hydroxypropylmethylcellulose (HPMC) was found to be one of the best improver for gluten-free products (Hager & Arendt, 2013). Much research has focused on the development of the gluten-free diet (Demirkesen et al., 2014; Hager & Arendt, 2013; Moreira, Chenlo, & Torres, 2013; Mancebo, Picón et al., 2015; Mariotti, Pagani, & Lucisano, 2013). Apart from hydrocolloids, starches, which are another major ingredient (ranged from 60% to 90%) in the gluten-free diet, also play an important role in the gluten-free diet (Witczak et al., 2016). For instance, wheat, corn and tapioca starches could make gluten-free bread with great volume

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and overall acceptability including crumb texture, cell structure and color (Mancebo, Merino, Martínez, & Gómez, 2015; López, Pereira, & Junqueira, 2004). Sweet potato starch is widely used to produce gluten-free noodle with preferable firmness and rehydration characteristic when compared with other starches (Collado & Corke, 1997). Potato starch is often used in gluten-free pasta, and its addition could increase the overall quality (including appearance, color, odor, and hardness) of gluten-free pasta made from corn, rice, and sorghum flours (Ferreira et al., 2016). However, compared to hydrocolloids, the importance of starch in the gluten-free diet is still undervalued (Witczak et al., 2016).

Dough is a viscoelastic material with a high degree of elasticity, as well as considerable plasticity and viscosity (Schofield & Blair, 1933). The rheological properties of doughs are extremely important because they can influence the mechanical and technological properties of doughs, including extensibility, molding and shaping capacities, mixing behavior, gas-holding capacity, steaming and baking performance, and the quality of the products (Van Bockstaele, de Leyn, Eeckhout, & Dewettinck, 2011; Dobraszczyk & Morgenstern, 2003; Lazaridou, Duta, Papageorgiou, Belc, & Biliaderis, 2007). In recent years, many studies have focused on the rheological properties of gluten-free doughs. However, most of the tested doughs were made with whole flours (e.g., rice flour, corn flour, etc.) containing a variety of ingredients, making it difficult to find the role of starch on the rheological properties (Aprodu, Alexandra Badiu, & Banu, 2016; Mancebo, Picón et al., 2015; Pongjaruvat, Methacanon, Seetapan, Fuongfuchat, & Gamonpilas, 2014; Witczak et al., 2016).

Therefore, in order to exclude the interference of other ingredients, starches from five different sources (wheat, corn, tapioca, sweet potato, and potato) were used, respectively, to make starch-HPMC model doughs, and the rheological properties of the model doughs were investigated. In addition, the moisture distributions of the starch-HPMC model doughs were analyzed to further explore the mechanism of how the starches with different structures influence the rheological properties and starch-HPMC interactions in gluten-free doughs. This study could provide theoretical support for the manufacture of gluten-free products.

## 2. Materials and methods

### 2.1. Materials

The starches from five different botanical sources (wheat starch, WS; corn starch, CS; tapioca starch, TS; sweet potato starch, SS; and potato starch, PS) were purchased from a local market in Beijing. HPMC was obtained from Henan Zhongxin Chemical Co., Ltd. (Zhengzhou, Henan, China). The molecular weight of HPMC is 166,700 kDa, and its degrees of methoxyl and hydroxypropyl substitution are 27.2% and 6.8%, respectively. All other chemical reagents were of analytical grade, and were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd (Beijing, China).

### 2.2. Proximate composition and amylose/amylopectin ratio of starches

The starches from the five different sources were re-suspended in distilled water and centrifuged (5000g, 20 °C, 20 min) at least three times, and dried in a hot air dryer (DGG-9240B; Senxin Instruments, Shanghai, China) at 45 °C for 24 h. The dried starch was finely ground using a high-speed universal hand mill (FW100; Tianjin TaiSiTe Instrument Co. Ltd., Tianjin, China) and then sieved with a 100- $\mu$ m screen to obtain starches of uniform particle size.

The proximate composition of the starch was determined according to the following methods: The moisture content of the

samples was determined by drying them in triplicate in an oven at 105 °C overnight until the weight remained constant (AOAC 925.09). The crude protein content was determined by the manual Kjeldahl method, and the total nitrogen was converted to the protein content by using a factor of 6.25. Crude fat was determined by the Soxhlet extraction method (AOAC 960.36). The ash content was determined by carbonizing the sample in a muffle furnace for 8 h at 550 °C (AOAC, 923.03). The starch content was determined by using a Total Starch Assay Kit according to the manufacturer's instructions (Megazyme, Wicklow, Ireland). The amylose/amylopectin ratio of the starch was determined using an Amylose/Amylopectin Assay Kit according to the manufacturer's instructions (Megazyme, Wicklow, Ireland).

### 2.3. Dough preparation

Based on the results of our previous study, 2.0% HPMC was added to the starch (WS, CS, TS, SS and PS) to prepare the gluten-free model doughs. An appropriate amount of water (according to the water absorption results obtained from the Mixolab apparatus; see Section 2.4.) was added, and the dough was mixed for 15 min.

The starch-HPMC doughs were packaged using a fresh-keeping film and allowed to rest for 25 min before further analysis.

### 2.4. Thermomechanical properties of the model doughs

The mixing and pasting behaviors of the starch-HPMC doughs were studied using a Mixolab apparatus (Chopin Technologies, Villeneuve-la-Garenne, France), which determines the rheological properties of dough during the process of mixing at a constant temperature as well as during periods of constant heating and cooling (Hadnađev, Dokić, Hadnađev, Pojić, & Torbica, 2014). Measurements were performed using the Mixolab "Chopin + 90" protocol (ICC 173, ICC Standards, 2008). The following settings were used in the test: 30 °C for 8 min, heating at a rate of 4 °C/min to 90 °C; at this point, there was an 8-min holding period at 90 °C, followed by cooling at 4 °C/min until the mixture reached 50 °C, and then 6 min of holding at 50 °C. The stirring speed during the entire test was 73 rpm. The process was repeated twice for each sample.

The parameters from the Mixolab recorded curve included the maximum dough consistency at the initial mixing stage,  $C_1$  (in Newton meter, Nm); minimum torque or the minimum value of torque produced by the dough passage subjected to mechanical and thermal constraints,  $C_2$  (Nm); peak torque or the maximum torque during the heating stage,  $C_3$  (Nm); the minimum torque during the heating period ( $C_4$ , Nm) and the torque obtained after cooling at 50 °C ( $C_5$ , Nm) (Kahraman et al., 2008).

Additionally, the following parameters were calculated from the Mixolab recorded curve: the amount of water absorption required for the dough to produce a torque of  $1.10 \pm 0.07$  Nm for "Chopin+90",  $W_{abs}$  (%); dough development time for gluten-free doughs or the time required to form uniform network structure via hydrogen bonds and entanglements between starch and HPMC, DDT (min); dough strength against mixing or the difference between the maximum dough consistency at the initial mixing stage ( $C_1$ ) and the minimum value of torque produced by the dough passage subjected to mechanical and thermal constraints ( $C_2$ ),  $C_1 - C_2$  (Nm); and set-back or the difference between the torque obtained after cooling at 50 °C ( $C_5$ ) and the minimum torque during the heating period ( $C_4$ ),  $C_5 - C_4$  (Nm).

### 2.5. Dynamic rheological characterization of the model doughs

The dynamic rheological characteristics of the doughs were measured in triplicate using a controlled stress rheometer (Physica MCR301; Anton Paar, Graz, Austria) operated with parallel-plate

geometry, with a 25-mm diameter and a gap of 1 mm. After being mixed and resting for 25 min, each dough sample was placed between the plates, and the test was started after allowing the dough to rest for another 10 min. The rim of the dough sample was coated with silicone oil to prevent water evaporation during the test.

### 2.5.1. Dynamic strain sweep

The linear viscoelasticity region (LVR) of the model doughs was determined by dynamic strain sweep, which was performed over a strain range of 0.01–10% at an angular frequency of  $10\text{ s}^{-1}$  and  $25^\circ\text{C}$ . The strain sweep provided information relating to the relative strength of the junction zones formed within model doughs, as well as their relative resistances to flow. The relative strength of the junction zones formed within model doughs and their relative resistance to flow were assessed by the storage modulus ( $G'$ ) and loss modulus ( $G''$ ).

### 2.5.2. Dynamic frequency sweep

Frequency sweep tests were performed on the dough from  $0.1$  to  $100\text{ s}^{-1}$  at a strain of 0.1% and temperature of  $25^\circ\text{C}$  to determine  $G'$  and  $G''$  as functions of frequency. The degree of dependence of  $G'$  on the frequency sweep ( $z'$ ) and the inter- or intramolecular strength of interaction ( $K$ ) were obtained by fitting the frequency sweep data into the power law model:

$$G' = K'(\omega)^{z'}$$

where  $\omega$  is the angular frequency, and the values of  $z'$  and  $K'$  reflect the type and strength of molecular interactions of the dough, respectively.

### 2.5.3. Temperature sweep

A temperature sweep was performed from  $25$  to  $90^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$ . During the temperature sweep, the  $G'$  and  $G''$  of the mixtures were recorded at a constant frequency of  $1\text{ Hz}$  and strain of 0.05%. The complex shear modulus ( $|G^*|$ ) and the loss factor ( $\tan \delta$ ) were also recorded during the temperature sweep.

### 2.5.4. Creep and recovery measurements

Creep and recovery measurements were carried out as follows: The creep phase was recorded at a shear stress of  $250\text{ MPa}$ , which exceeds the LVR for  $300\text{ s}$ , followed by a recovery phase of  $300\text{ s}$  at a stress of  $0\text{ MPa}$ . Measurements were performed at  $25 \pm 0.1^\circ\text{C}$ . Creep and recovery curves were recorded and analyzed by RHEOPLUS/32 version 3.21 software to obtain the parameters, including the maximum creep compliance ( $J_{\text{max}}$ ), zero shear viscosity ( $\eta_0$ ), relative elastic part of the maximum creep compliance ( $J_e/J_{\text{max}}$ ), and the relative viscous part of the maximum creep compliance ( $J_v/J_{\text{max}}$ ). All rheological measurements were performed in triplicate.

### 2.6. Moisture distribution analysis of the model doughs

Proton relaxation studies were carried out using a low-resolution MesoMR spectrometer (Niumag, Shanghai, China) operating at a  $^1\text{H}$  resonance frequency of  $23\text{ MHz}$ . In this study, Carr–Purcell–Meiboom–Gill (CPMG) pulse sequences were employed to measure the spin–spin relaxation time,  $T_2$ . The typical pulse parameters were as follows: dwell time,  $17\text{ }\mu\text{s}$ ; echo time,  $400\text{ }\mu\text{s}$ ; recycle time,  $1500\text{ ms}$ ; echo count,  $5000$ ; and scan repetitions,  $4$ . Each measurement was performed in duplicate.

### 2.7. Statistical analysis

Statistical analysis was performed by means of one-way ANOVA followed by a Duncan multiple-comparison test with the SAS ver-

sion 9.2 software (SAS Institute Inc., Cary, NC, USA).  $P < 0.05$  was considered statistically significant. The results were expressed as mean  $\pm$  standard deviation (S.D.).

## 3. Results and discussion

### 3.1. Proximate composition and the amylose/amylopectin ratio of the starches

Table 1 shows the proximate composition and amylose/amylopectin ratio of the starches from the five different sources. The starch content of WS, CS, TS, SS and PS was 86.87%, 87.63%, 88.95%, 89.97%, and 86.0%, respectively.

WS and CS are cereal starches, and are classified as A-type starches, with the highest amylose content (26.40% and 28.49%, respectively), followed by PS (24.16%), which is a B-type starch. SS and TS exhibited the lowest amylose content (18.82% and 17.71%, respectively), and are classified as C-type starches.

### 3.2. Thermomechanical properties of the model doughs

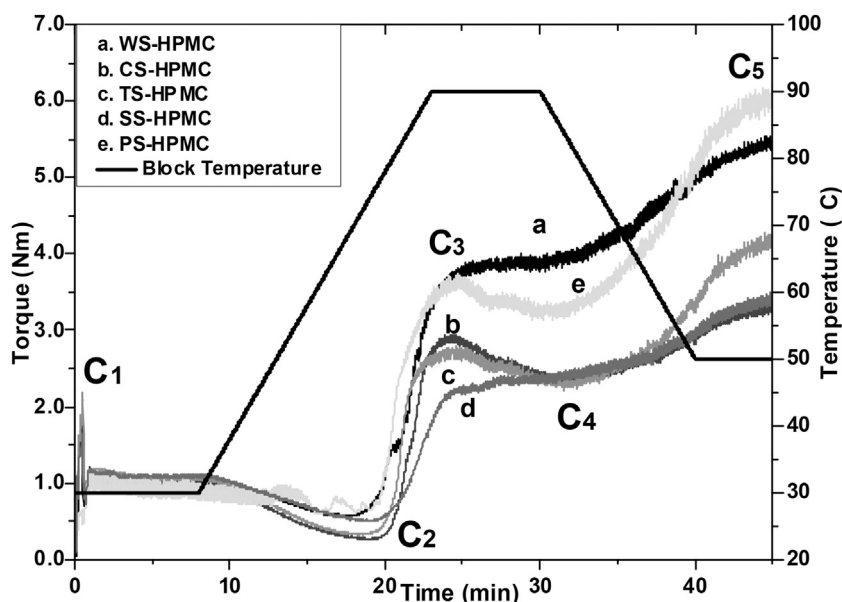
The Mixolab apparatus measures the torque that is produced by the passage of dough between two kneading arms in real time, thus allowing the study of physicochemical behavior. Thermomechanical graphs of the starch–HPMC model doughs are shown in Fig. 1, and the parameters derived from the thermomechanical graphs are summarized in Table 2.

As can be seen in Fig. 1, the starch–HPMC dough presented one sharp peak at the very beginning of the kneading process. HPMC has excellent swelling capacity because of the presence of hydrophilic reactive functional groups such as hydroxypropyl (Wach, Mitomo, Yoshii, & Kume, 2002). The rapid water absorption of HPMC results in the swelling of the dough and increases the torque during the kneading of the dough (Lazaridou et al., 2007). In general, we found significant differences in the thermomechanical behavior of the gluten-free model doughs made with starches from different botanical sources (Fig. 1).  $C_3$  and  $C_5$  are the maximum torque of the dough during the heating stage and the torque obtained after cooling at  $50^\circ\text{C}$ , respectively. The WS- and PS-HPMC doughs showed significantly higher  $C_3$  and  $C_5$  than the other doughs, indicating higher strength and viscosity during the processes of starch gelatinization and retrogradation. Starch with high swelling power can result in high maximum viscosity of the dough (Tipples et al., 1980). Christianson (1982) proposed that the effect of hydrocolloids on the maximum viscosity is mainly caused by two phenomena: 1) their interaction with solubilized starch and 2) an increase of the effect of this interaction on the granules, which affects the breakdown of the granule and the amount of solubilized starch (especially the amylose in the starch). Bahnassey and Breene (1994) also found the presence of synergistic interactions between starch and hydrocolloids, which are dependent on the properties of the starch and the structure of the hydrocolloid. Therefore, during the gelatinization of the dough, not only the swelling power of the starch, but also the interactions between the starch and HPMC affect the maximum viscosity of the PS- and WS-HPMC doughs. The higher  $C_3$  value of the PS-HPMC dough could be attributed to the swelling power of PS, which was higher than that of the other four starches (Supplementary Table 1). Although the swelling power of WS was clearly lower than that of PS (Supplementary Table 1), the  $C_3$  value of the WS-HPMC dough was similar to that of the PS-HPMC dough, which indicates stronger interactions between WS and HPMC during starch gelatinization. Previous studies have shown that this is because it is easier for the amylose to dissolve out of the WS granule and interact with HPMC during the heating of the dough (Christianson, 1982; Jekle, Mühlberger, & Becker, 2016). Another

**Table 1**  
Proximate composition and amylose/amylopectin ratio of the starches from the five different sources (%).

Samples	Starch	Protein	Fat	Moisture	Ash	Amylose	Amylopectin
WS	86.87 ± 0.23 <sup>d</sup>	0.31 ± 0.01 <sup>b</sup>	0.74 ± 0.01 <sup>b</sup>	12.15 ± 0.01 <sup>b</sup>	0.15 ± 0.00 <sup>c</sup>	26.40 ± 3.75 <sup>a</sup>	73.60 ± 3.75 <sup>b</sup>
CS	87.63 ± 0.76 <sup>c</sup>	0.25 ± 0.00 <sup>c</sup>	0.62 ± 0.01 <sup>c</sup>	11.29 ± 0.07 <sup>c</sup>	0.10 ± 0.09 <sup>d</sup>	28.49 ± 2.15 <sup>a</sup>	71.51 ± 2.15 <sup>b</sup>
TS	88.95 ± 0.16 <sup>b</sup>	0.02 ± 0.00 <sup>f</sup>	0.14 ± 0.04 <sup>d</sup>	10.93 ± 0.05 <sup>d</sup>	0.10 ± 0.01 <sup>d</sup>	17.71 ± 4.87 <sup>c</sup>	82.29 ± 4.87 <sup>a</sup>
SS	89.97 ± 0.35 <sup>a</sup>	0.06 ± 0.00 <sup>d</sup>	0.13 ± 0.01 <sup>d</sup>	9.72 ± 0.04 <sup>e</sup>	0.11 ± 0.01 <sup>d</sup>	18.82 ± 2.05 <sup>c</sup>	81.18 ± 2.05 <sup>a</sup>
PS	86.80 ± 0.41 <sup>d</sup>	0.04 ± 0.01 <sup>e</sup>	0.12 ± 0.07 <sup>d</sup>	13.01 ± 0.02 <sup>a</sup>	0.40 ± 0.01 <sup>a</sup>	24.16 ± 1.16 <sup>b</sup>	75.84 ± 1.16 <sup>b</sup>

Values are the mean ± S.D. of three replicates. Data followed by the same letter in the same column are not significantly different ( $P > 0.05$ ). WS, wheat starch; CS, corn starch; TS, tapioca starch; SS, sweet potato starch; PS, potato starch.



**Fig. 1.** Thermomechanical graphs of the starch-HPMC model doughs. HPMC, hydroxypropylmethylcellulose; WS, wheat starch; CS, corn starch; TS, tapioca starch; SS, sweet potato starch; PS, potato starch. C<sub>1</sub> (Nm), the maximum dough consistency at the initial mixing stage; C<sub>2</sub> (Nm), minimum torque produced by dough passage subjected to mechanical and thermal constraint; C<sub>3</sub> (Nm), the maximum torque during the heating stage; C<sub>4</sub> (Nm), the minimum torque during the heating period; C<sub>5</sub> (Nm), the torque obtained after cooling at 50 °C.

**Table 2**  
Parameters derived from the Mixolab (thermomechanical graphs) and the rheometer (temperature sweep graphs) results.

Model doughs	W <sub>abs</sub> (%)	DDT (min)	C <sub>1</sub> (Nm)	C <sub>1</sub> -C <sub>2</sub> (Nm)	C <sub>5</sub> -C <sub>4</sub> (Nm)	T <sub>C2</sub> (°C)	T <sub>C3</sub> (°C)	T <sub>tanδmax</sub> (°C)	T <sub>1[G*]max</sub> (°C)
WS-HPMC	72.90 ± 0.60 <sup>a</sup>	1.12 ± 0.13 <sup>ab</sup>	1.16 ± 0.01 <sup>a</sup>	0.63 ± 0.05 <sup>bc</sup>	1.85 ± 0.08 <sup>c</sup>	55.6 ± 0.1 <sup>c</sup>	75.7 ± 0.5 <sup>c</sup>	65.1 ± 0.0 <sup>d</sup>	73.1 ± 0.0 <sup>e</sup>
CS-HPMC	71.70 ± 0.40 <sup>b</sup>	1.18 ± 0.09 <sup>ab</sup>	1.13 ± 0.03 <sup>a</sup>	0.59 ± 0.04 <sup>c</sup>	0.93 ± 0.04 <sup>e</sup>	55.5 ± 0.3 <sup>c</sup>	80.0 ± 0.1 <sup>b</sup>	72.1 ± 0.0 <sup>a</sup>	78.1 ± 0.0 <sup>b</sup>
TS-HPMC	70.50 ± 0.10 <sup>c</sup>	1.30 ± 0.11 <sup>ab</sup>	1.16 ± 0.00 <sup>a</sup>	0.83 ± 0.02 <sup>a</sup>	2.24 ± 0.16 <sup>b</sup>	57.4 ± 0.1 <sup>b</sup>	80.1 ± 0.1 <sup>b</sup>	69.2 ± 0.0 <sup>c</sup>	76.1 ± 0.0 <sup>c</sup>
SS-HPMC	68.00 ± 0.30 <sup>d</sup>	1.08 ± 0.03 <sup>b</sup>	1.16 ± 0.01 <sup>a</sup>	0.66 ± 0.02 <sup>b</sup>	1.15 ± 0.03 <sup>d</sup>	60.4 ± 0.5 <sup>a</sup>	86.0 ± 0.3 <sup>a</sup>	71.2 ± 0.0 <sup>b</sup>	83.1 ± 0.0 <sup>a</sup>
PS-HPMC	70.30 ± 0.20 <sup>c</sup>	1.33 ± 0.10 <sup>a</sup>	1.05 ± 0.02 <sup>b</sup>	0.39 ± 0.03 <sup>d</sup>	2.79 ± 0.10 <sup>a</sup>	60.2 ± 0.6 <sup>a</sup>	80.2 ± 0.0 <sup>b</sup>	71.2 ± 0.0 <sup>b</sup>	75.1 ± 0.0 <sup>d</sup>

Values are the mean ± S.D. of three replicates. Data followed by the same letter in the same column are not significantly different ( $P > 0.05$ ). HPMC, hydroxypropylmethylcellulose; WS, wheat starch; CS, corn starch; TS, tapioca starch; SS, sweet potato starch; PS, potato starch. W<sub>abs</sub> (%), water absorption for the dough to produce a torque of 1.1 ± 0.07 Nm; DDT (min), dough development time; C<sub>1</sub>-C<sub>2</sub> (Nm), dough strength; C<sub>5</sub>-C<sub>4</sub> (Nm), dough setback. T<sub>C2</sub>, the temperature at C<sub>2</sub> value; T<sub>C3</sub>, the temperature at C<sub>3</sub> value; T<sub>1[G\*]max</sub>, the temperature at the maximum |G\*| ([G\*] was derived from the temperature sweep graphs of the rheometer); T<sub>tanδmax</sub>, the temperature at the maximum tan δ (tan δ was derived from the temperature sweep graphs of the rheometer).

instrument, the Rapid Visco Analyser (RVA), is commonly used to determine the thermomechanical properties of dough (Zaidul, Norulaini, Omar, Yamauchi, & Noda, 2007). However, the RVA analyzes dough pasting properties under the condition of excess water, which results in different outcomes compared to the pasting properties of starch in the dough during the actual production of dough (Xie et al., 2009). The Mixolab apparatus can be used to measure the pasting properties of starch in doughs, as well as physical properties of the dough such as dough strength and stability (Kahraman et al., 2008).

As can be seen in Table 2, The W<sub>abs</sub> of starch-HPMC doughs ranged from 68.00% to 72.90%. Other researchers have determined the W<sub>abs</sub> of starch-gluten (gluten-containing) model doughs, which are lower than the W<sub>abs</sub> results found in the present

study (Petrofsky & Hosene, 1995). This suggests that more water is required to form uniform starch-HPMC (gluten-free) model doughs, which could be attributed to the large difference in both the mixing characteristics of gluten and HPMC as well as the interactions between starch and HPMC/gluten (Hadnadev et al., 2014). The higher W<sub>abs</sub> of the starch-HPMC model doughs could be attributed to the hydrophilic nature of the HPMC polymer (Lazaridou et al., 2007). In addition, for the starch-HPMC doughs, the starch granules adhere to one another in the presence of HPMC, with a change in their mobility, resulting in a changeable cell structure; thus, the system as a whole has more space to entrap more water compared with gluten-containing doughs (Sivaramakrishnan et al., 2004). According to Petrofsky and Hosene (1995), DDT of the starch-gluten model doughs is higher than that of starch-HPMC model doughs.

This could be attributed to the fact that the network structure in gluten-containing doughs mainly forms through disulfide bonds between different protein polymers, which need plenty of mixing time to develop (Singh & MacRitchie, 2001). In contrast, uniform starch–HPMC doughs form via hydrogen bonds resulting from the hydroxyl groups in the HPMC structure and the entanglements between starch and HPMC, which form more easily (Rosell, Collar, & Haros, 2007).

Parameters derived from the thermomechanical graphs of starch–HPMC model doughs were strongly influenced by the botanical source of the starch (Table 2). We observed that the TS– and PS–HPMC doughs presented higher DDT than the CS–, WS– and SS–HPMC doughs. This might have been ascribed to the textural properties of the PS (the peak viscosity and water-binding capacity are 2700 BU and 0.38 g H<sub>2</sub>O/g dry starch, respectively), which is stringy, cohesive, long-bodied, viscoelastic, and fluid; the characteristics of the TS (1000 BU and 0.34 g H<sub>2</sub>O/g dry starch) are similar to those of the PS, although the former is generally less stringy and less cohesive. However, the texture of the CS (the peak viscosity and water-binding capacity are 600 BU and 0.30 g H<sub>2</sub>O/g dry starch, respectively), WS (300 BU and 0.33 g H<sub>2</sub>O/g dry starch) and SS (480 BU and 0.32 g H<sub>2</sub>O/g dry starch) is short, soft, heavy-bodied and non-cohesive (Swinkels, 1985). When mixing with HPMC, more stringy and cohesive starches (PS and TS) take more time to form uniform doughs, while less stringy and cohesive starches (CS, WS and SS) take less time to form uniform doughs. The  $W_{abs}$  was highest for the WS–HPMC model dough (72.90%), followed successively by the CS–, TS–, PS– and SS–HPMC model doughs (71.70%, 70.50%, 70.30% and 68.00%, respectively). This indicates that the cereal starches (WS and CS) requires more water than the tuber and root starches (TS, PS and SS) to form uniform starch–HPMC doughs.  $C_1 - C_2$  is the difference between the maximum dough consistency at the initial mixing stage ( $C_1$ ) and the minimum value of torque produced by dough passage subjected to mechanical and thermal constraint ( $C_2$ ). The higher the  $C_1 - C_2$  values, the lower the dough strength against mixing (Rosell et al., 2007). Doughs made with SS and TS presented lower strength against mixing, followed by WS, CS and PS. Dough strength against mixing might closely be related to the amylose content in starch (Christianson, 1982). Amylose is dissolved out of starch granules in the presence of water during initial heating, and entangles or forms hydrogen bonds with the HPMC polymer, reducing the weakening effect of the dough resulted from the water swelling of the starch and HPMC. Thus, the lower amylose content of SS and TS (18.82% and 17.71%, respectively) resulted in lower dough strength against mixing. However, although the amylose content of PS was lower than that of WS and CS, the more stringy and cohesive textural properties of the PS made the PS–HPMC model dough more stable against mixing (Swinkels, 1985).  $C_5 - C_4$  is the difference between the torque produced after cooling and the torque after the period of heating, and reflects the setback of the dough. The higher the  $C_5 - C_4$  values, the faster the retrogradation rate. The dough made with CS presented the lowest  $C_5 - C_4$  values (0.93 Nm), followed successively by the SS–, WS–, TS–, and PS–HPMC doughs (1.15, 1.85, 2.24 and 2.79 Nm, respectively). Thus, the CS–HPMC had the slowest retrogradation rate, whereas the PS–HPMC doughs had the fastest retrogradation rate. These results could be attributed to the fact that the amylopectins in A-type starches (such as CS and WS) retrograde more slowly than those in B-type starches (such as PS) and C-type starches (such as TS) (Chung, Han, Yoo, Seib, & Lim, 2008). As an exception, model dough made with SS (C-type starch) exhibited a relative lower  $C_5 - C_4$  value compared to those of TS (C-type starch) and WS (A-type starch), attributing to the higher content of water-soluble sugars in SS, which delayed the retrogradation rate of the model dough (Galliard & Bowler, 1987).

### 3.3. Dynamic rheological characterization of the model doughs

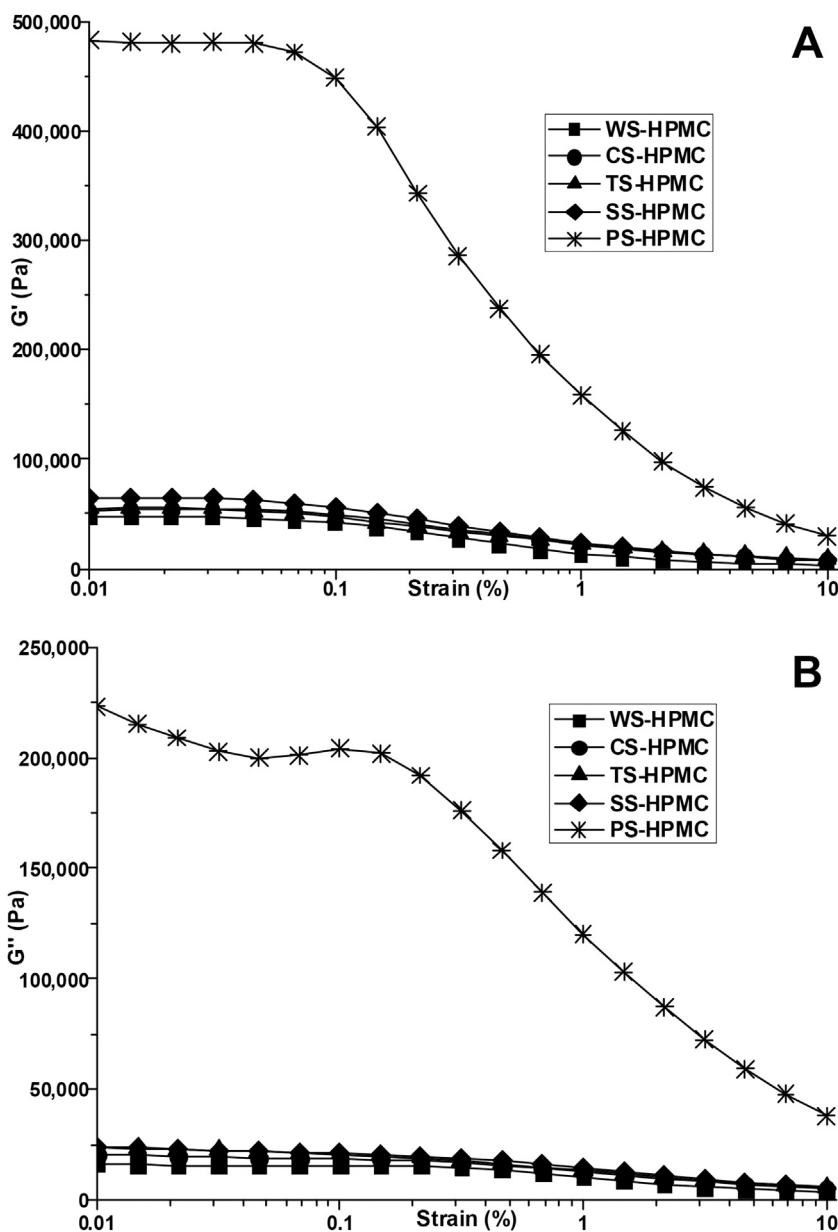
#### 3.3.1. Dynamic strain sweep

The effect of the starches source on the rheological properties of the model doughs was determined by the viscoelastic changes. The LVRs for the starch–HPMC model doughs, as established by the strain sweep experiments, are shown in Fig. 2. In general, the LVRs were limited up to a strain of 0.05% for the starch–HPMC model doughs; the drop in the elastic modulus,  $G'$ , started to occur at 0.05% strain and increased at above 0.05%, indicating the structural breakdown of the starch–HPMC model doughs beyond this deformation level. Previously studies have shown that wheat flour–water doughs exhibit LVRs at a strain level of 0.1–0.25% (Phan-Thien and Safari-Ardi, 1998; Phan-Thien, Safari-Ardi, & Morales-Patiño, 1997). The starch–HPMC model doughs exhibited lower LVRs limits, which could be attributed to the fact that the wheat flour dough generally consisted of a strong and stable gluten network, whereas the starch–HPMC model doughs generally comprised a weak and fragile polysaccharide network. The abovementioned results imply that gluten-free doughs are more prone to shear-thinning and that it is more difficult for them to hold their shape than gluten-containing dough, which is the major technological challenge for the production of gluten-free products (Lazaridou et al., 2007). The doughs made with CS presented the highest LVRs limits (0.123% for CS–HPMC doughs), followed by the WS–, SS–, TS– and PS–HPMC doughs (0.104%, 0.106%, 0.104% and 0.077%, respectively, see Supplementary Table 2). This suggests that different structural and physicochemical properties of the starches cause discrepancies in the viscoelastic properties of the HPMC matrix, which might be mainly because the embedded starch granules could affected the stability of the HPMC network's structure in the model doughs. The PS–HPMC dough showed a significantly higher  $G'$  in the LVR; however, the  $G'$  sharply decreased when the strain value was higher than 0.077% (Supplementary Table 2). The results indicate that, in the PS–HPMC dough, PS and HPMC formed stronger microstructural interactions in the relatively low strain range, but that the stability of this network decreased quickly at higher strain values in comparison with the other starch–HPMC doughs.

#### 3.3.2. Dynamic frequency sweep

In a frequency sweep, frequency ( $\omega$ ) varies while the strain remains constant. Frequency sweep experiments performed in the LVR do not disturb or destroy the inherent structure of the dough, and are of great value for studying the influence and action of starch in starch–HPMC dough systems because dynamic mechanical parameters are highly sensitive to the properties of the starch (Weipert, 1990).

Supplementary Fig. 1 shows the plot of  $G'$  and  $G''$  as functions of  $\omega$ . For all the dough formulations in this study, the frequency sweep experiments showed that the elastic/storage modulus ( $G'$ ) was greater than the viscous/loss modulus ( $G''$ ) over the whole frequency range, and both moduli slightly increased with increasing frequency, which suggests a solid elastic-like behavior in the model doughs. Bonds between the particles in a sample may be made and broken over the observation time, either spontaneously or from applied forces. Bond-breaking and bond-making lead to structural changes that affect rheological properties (Renard, van de Velde, & Visschers, 2006). Entanglement networks are usually characterized by  $G' \sim \omega^2$  and  $G'' \sim \omega^1$  at low frequency and a crossover between  $G'$  and  $G''$  at high frequency; further, covalent linkage is frequency independent, whereas physical linkage is slightly frequency dependent (Doucet, Gauthier, & Foegeding, 2001; Kavanagh & Ross-Murphy, 1998). The dependence of  $G'$  on frequency can be determined from the logarithmic plot of  $G' = K'(\omega)^{z'}$  ( $\log G' = z' \log \omega + K$ ) as proposed by Egelandsdal, Fretheim, and Harbitz (1986).



**Fig. 2.** Dynamic strain sweep data for starch-HPMC model doughs. (A) Storage modulus ( $G'$ ) versus strain (%); (B) Loss modulus ( $G''$ ) versus strain (%). HPMC, hydroxypropylmethylcellulose; WS, wheat starch; CS, corn starch; TS, tapioca starch; SS, sweet potato starch; PS, potato starch.

The  $z'$  values show the degree of dependence of  $G'$  on frequency, which can reflect the type of molecular interactions in the doughs. In the logarithmic plot,  $z' = 0$  suggests a covalent linkage with a stable network structure, whereas  $z' > 0$  suggests a physical linkage with a less stable network structure. The  $K'$  values show the strength of the doughs, with a higher  $K$  value ( $K = \log K'$ ) indicating higher strength of the dough (Kim & Yoo, 2009). The goodness of fit was evaluated by means of the corresponding coefficients of determination ( $R^2$ ).

Table 3 shows the  $z'$  and  $K$  in the equation of  $\log G' = z' \log \omega + K$ . The slopes ( $z'$ ) from the logarithmic plot of  $G'$  versus the logarithm of  $\omega$  show that all the model doughs in this study had  $G'$  values that were dependent on  $\omega$  ( $R^2 > 0.99$ ). The  $z'$  values ranged from 0.160 to 0.236 for the starch-HPMC model doughs, signifying physical linkage with low stability in the network structure (Moreira et al., 2013). The role of hydrocolloids in the rheological properties of gluten-free dough may be related to the molecular structure and chain conformation of the polysaccharides, which determine the

physical intermolecular associations (crosslinks or entanglements) of the polymeric chains (Lazaridou et al., 2007). Starches from the different botanical sources affected the  $z'$  and  $K$  values differently. The WS-HPMC dough exhibited the highest  $z'$  (0.236) and the lowest  $K$  (4.450), indicating a less stable dough network structure and lower strength of the dough matrix compared to other doughs. This might be explained by Sipes (1993) et al., who found that surface lipid films of WS decreased the interactions between WS and HPMC. It is worth noting that heating could destroy these surface lipid films, and change the interactions between WS and HPMC as discussed in Section 3.2 (strong interactions between WS and HPMC during heating). The PS-HPMC dough showed the lowest  $z'$  (0.160) but the highest  $K$  (5.562), implying a more stable network structure and higher strength of the dough matrix compared to other doughs. The big difference between the rheological properties ( $z'$  and  $K$  values) of the PS-HPMC model dough could be attributed to the stronger water-binding capacity caused by the high phosphorus content in PS, which result in tighter adhesion of the hydrated

**Table 3**

The  $z'$ ,  $K$  and  $R^2$  values of the starch-HPMC model doughs obtained by fitting the frequency sweep data into power law model and the parameters obtained from the creep-recovery curves of starch-gluten model doughs.

Model doughs	$z'$	$K$	$R^2$	Creep phase		Recovery phase	
				$J_{\max} \times 10^5$ (1/Pa)	$\eta_0 \times 10^{-6}$ (Pa s)	$J_e/J_{\max}$ (%)	$J_v/J_{\max}$ (%)
WS-HPMC	0.236 ± 0.003 <sup>a</sup>	4.450 ± 0.009 <sup>d</sup>	0.999 ± 0.000	67.83 ± 2.10 <sup>a</sup>	7.10 ± 0.02 <sup>d</sup>	31.79 ± 1.37 <sup>c</sup>	68.21 ± 2.34 <sup>c</sup>
CS-HPMC	0.208 ± 0.002 <sup>b</sup>	4.628 ± 0.017 <sup>c</sup>	0.998 ± 0.000	37.21 ± 1.21 <sup>b</sup>	13.94 ± 0.91 <sup>b</sup>	24.38 ± 1.79 <sup>ab</sup>	75.62 ± 1.53 <sup>b</sup>
TS-HPMC	0.230 ± 0.005 <sup>a</sup>	4.442 ± 0.021 <sup>d</sup>	0.999 ± 0.000	38.03 ± 1.28 <sup>b</sup>	12.55 ± 1.04 <sup>b</sup>	25.70 ± 1.22 <sup>a</sup>	74.30 ± 2.07 <sup>b</sup>
SS-HPMC	0.189 ± 0.007 <sup>c</sup>	4.662 ± 0.024 <sup>b</sup>	0.999 ± 0.000	21.34 ± 1.05 <sup>c</sup>	22.22 ± 1.05 <sup>a</sup>	23.69 ± 0.91 <sup>b</sup>	76.31 ± 1.95 <sup>b</sup>
PS-HPMC	0.160 ± 0.004 <sup>d</sup>	5.562 ± 0.031 <sup>a</sup>	0.999 ± 0.000	7.31 ± 0.64 <sup>d</sup>	7.38 ± 0.24 <sup>c</sup>	19.33 ± 0.79 <sup>c</sup>	80.67 ± 2.06 <sup>a</sup>

Values are the mean ± S.D. of three replicates. Data followed by the same letter in the same column are not significantly different ( $P > 0.05$ ). HPMC, hydroxypropylmethylcellulose; WS, wheat starch; CS, corn starch; TS, tapioca starch; SS, sweet potato starch; PS, potato starch.  $z'$ , the degree of dependence of  $G'$  on frequency sweep;  $K$ , the strength of molecular interactions;  $R^2$ , the corresponding coefficients of determination;  $J_{\max}$ , the maximum creep compliance;  $\eta_0$ , the zero shear viscosity,  $J_e/J_{\max}$ , the relative elastic part of maximum creep compliance;  $J_v/J_{\max}$ , the relative viscous part of maximum creep compliance.

HPMC around the surface of the PS granules (Zaidul, Yamauchi, Kim, Hashimoto, & Noda, 2007).

### 3.3.3. Temperature sweep

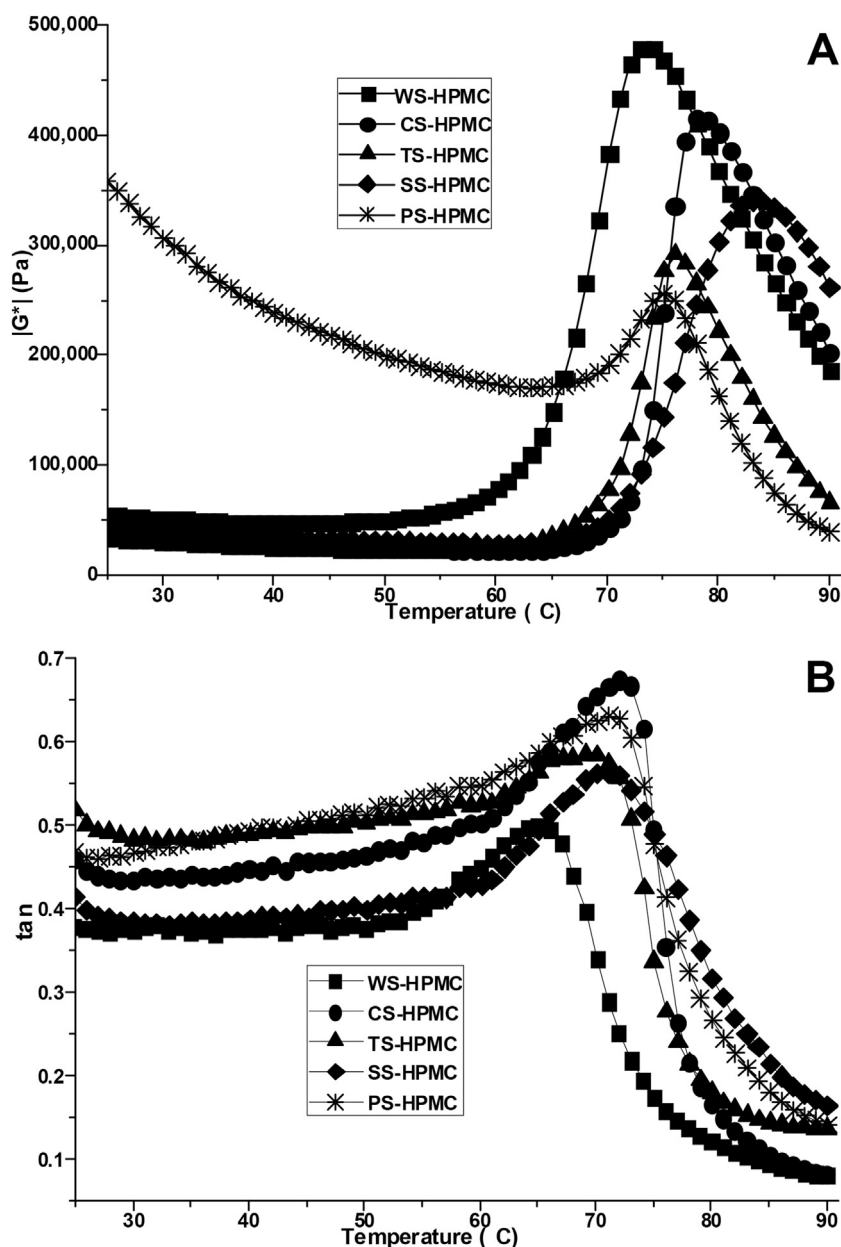
The starch gelatinization process in the starch-HPMC model doughs can be easily monitored by the course of the dynamic modulus.  $|G^*|$  is the absolute value of the vector between  $G'$  and  $G''$  measured by the oscillation test, and is a combination parameter that describes the intensity of the sample. A higher  $|G^*|$  indicates a firm dough (or a dough with high intensity).  $\tan \delta$  is a parameter that describes the relationship between  $G'$  and  $G''$ . A higher  $\tan \delta$  indicates dough with high viscosity. For  $\tan \delta < 1$ ,  $G'$  is greater than  $G''$ , which indicates a predominance of elastic over viscous properties in the model dough.

Fig. 3 shows the plot of the complex shear modulus  $|G^*|$  and the loss factor  $\tan \delta$  as functions of temperature. The increase of  $|G^*|$  during heating has been reported as being proportional to the starch content of the dough, which indicates that the physicochemical changes in heated dough are essentially due to changes in the starch fraction of the dough (Angioloni and Dalla Rosa, 2005). During the initial stage of heating (from 25 to 60 °C),  $|G^*|$  decreased slowly because of the water swelling of the starch and HPMC, which caused an increase of the dough volume and an initial softening of the doughs (Rosell et al., 2007). During this phase, the high  $|G^*|$  in the PS-HPMC dough (indicating higher dough intensity) decreased quickly compared with that in the other model doughs, which could be attributed to the larger PS granules and the relatively loose internal structure of PS (Martínez & Gómez, 2017).  $|G^*|$  clearly increased with increasing temperature (from 60 to 90 °C), and this represents the onset of starch gelatinization.  $|G^*|$  peaked ( $|G^*|_{\max}$ ) and then decreased significantly during the rest of the temperature increase from 60 to 90 °C. The higher  $|G^*|_{\max}$  of the model doughs made with WS and CS compared to that of the other doughs indicates higher maximum intensity and the maximal structural hardening, which could prevent dough cracking caused by oven-spring in the early stage of heating (Jekle et al., 2016). In the case of the WS-HPMC and CS-HPMC model doughs, the higher  $|G^*|_{\max}$  could be ascribed to the higher  $W_{\text{abs}}$  (as shown in Table 2) and amylose content (as shown in Table 1) of WS and CS. Amylose leached from the WS and CS granules, forming sufficient network structure with HPMC in the presence of enough water. With increasing temperature,  $\tan \delta$  increased, peaked ( $\tan \delta_{\max}$ ), and then decreased. Although CS-HPMC model dough could prevent dough cracking (presented higher  $|G^*|_{\max}$ ), a large viscosity drop (a substantial decrease of  $\tan \delta$ ), which suggests that the CS-HPMC dough becomes fragile more easily in the later stage of heating than the other doughs, resulting in a relatively loose structure in the final product; conversely, the performance of the SS- and WS-HPMC doughs clearly differed from that of the CS-HPMC dough (Rojas, Rosell, & de Barber, 1999; Olkku & Rha, 1978).

According to Jekle et al. (2016),  $\tan \delta_{\max}$  can be used as a tool to identify the start of gelatinization, indicating the lowest structural stability of the starch-HPMC dough, whereas  $|G^*|_{\max}$  can be used as a tool to identify the peak gelatinization, indicating the maximal structural hardening of the doughs. The  $|G^*|_{\max}$  and  $\tan \delta_{\max}$  at different temperatures ( $T_{|G^*|_{\max}}$  and  $T_{\tan \delta_{\max}}$ ) are shown in Table 2. The model doughs made with SS showed the highest value of  $T_{|G^*|_{\max}}$ , suggesting the highest temperature to reach the maximal structural hardening ( $|G^*|_{\max}$ ). This could be attributed to the higher content of water-soluble sugars in SS, including sucrose, glucose, and fructose, which increases the gelatinization temperature of the dough (Kohyama & Nishinari, 2002). In the same way, chemical composition, the amylose/amylopectin ratio, and factors related to the microstructural characteristics of the starch granules should be considered to explain these phenomena (Galliard & Bowler, 1987). The gelatinization temperature of model doughs can also be obtained using the Mixolab apparatus by evaluating the dough temperature when  $C_2$  and  $C_3$  are achieved. Table 2 shows the temperature when the torque reaches  $C_2$  and  $C_3$  ( $T_{C_2}$  and  $T_{C_3}$ ).  $T_{C_2}$  and  $T_{C_3}$  reflect the onset and peak gelatinization of starch in model doughs, respectively. It is worth noting that Mixolab systematically gave different  $T_{C_2}$  and  $T_{C_3}$  values relative to the measurements taken by temperature sweep using a rheometer ( $T_{C_2}$  and  $T_{C_3}$  correspond to  $T_{\tan \delta_{\max}}$  and  $T_{|G^*|_{\max}}$ , respectively). Although the dough experienced the same temperature rise process (30 °C–90 °C) in the determination of the Mixolab apparatus and the rheometer, however, the rheometer records the small deformation rheological properties of the model doughs, which stay within the LVR limits of the model doughs, whereas the Mixolab apparatus records the large deformation rheological properties of the model doughs, which exceed the LVR limits of the model doughs (Tronsmo et al., 2003). The Mixolab apparatus provides the measurement of the viscosity and strength changes of the dough, which is the macroscopic properties of the dough. In comparison to the Mixolab apparatus, the rheometer provides the measurement of the microstructure changes of the dough (including the gelatinization of the starch and the varying interactions between starch and HPMC). Although the results obtained from the Mixolab apparatus confirmed the varying interactions between different starch and HPMC during heating as discussed in Section 3.2, the clear difference in the results obtained from the rheometer and the Mixolab apparatus indicated that the microstructure changes of the model doughs could not be fully reflected by the variation of the macroscopic properties of the dough.

### 3.3.4. Creep and recovery measurements

Creep and recovery measurements were also made on the model doughs. A stress of 250 MPa, which exceeds the LVR limits, was applied in all the measurements for 300 s, and is sufficient for the sample to reach steady-state flow as determined by the instrument software. The creep-recovery curves of starch-HPMC doughs



**Fig. 3.** Effect of heating ( $5^\circ\text{C}/\text{min}$ ) on (A) complex shear modulus ( $|G^*|$ ) and (B) loss factor ( $\tan \delta$ ) for starch-HPMC model doughs. HPMC, hydroxypropylmethylcellulose; WS, wheat starch; CS, corn starch; TS, tapioca starch; SS, sweet potato starch; PS, potato starch.

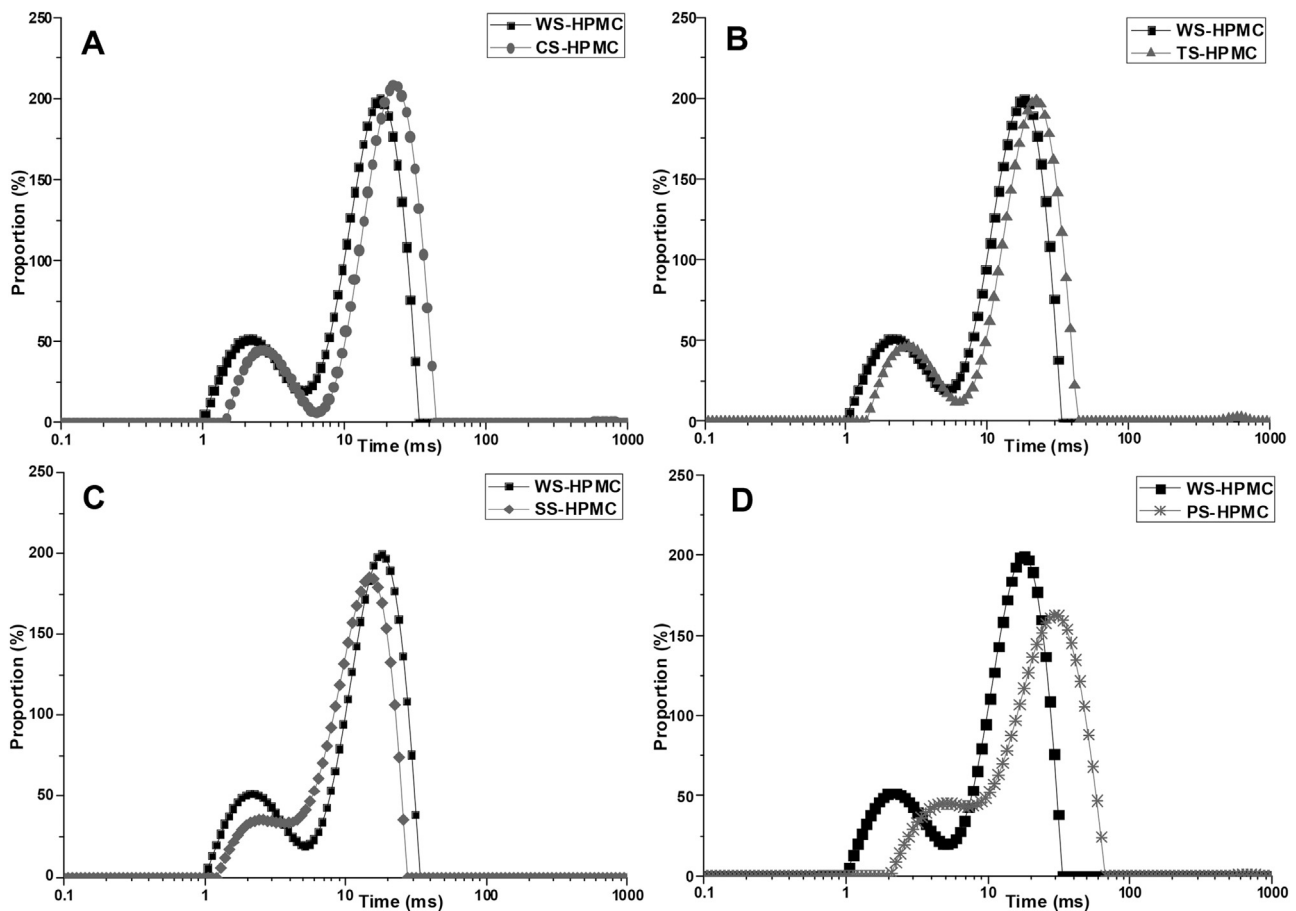
exhibited a typical viscoelastic behavior combining both viscous fluid and elastic components (Sivaramkrishnan et al., 2004).

The creep-recovery curves of the starch-HPMC model doughs are shown in Supplementary Fig. 2. The parameters obtained from the creep-recovery curves are presented in Table 3. The maximum creep strain ( $J_{\max}$ ) can be used to describe dough rigidity, and a previous study found that strong dough, such as bread flour dough, has greater resistance to deformation than softer doughs, such as pastry flour dough (Wang & Sun, 2002). The PS-HPMC model dough exhibited the highest deformation resistance ( $J_{\max}$  of  $7.31 \times 10^{-5}$  1/Pa), followed successively by the SS-, TS-, and CS-HPMC model doughs ( $J_{\max}$  of  $21.3 \times 10^{-5}$ ,  $38.03 \times 10^{-5}$  and  $38.21 \times 10^{-5}$  1/Pa, respectively). The WS-HPMC dough showed the lowest resistance ( $J_{\max}$  of  $67.83 \times 10^{-5}$  1/Pa) among all the gluten-free model doughs in this study. The starch in the model doughs acted as a rigid filler that helped to form the polysaccharide (HPMC) network (Hadnadev et al., 2014). The hydrocolloids form a barrier around the starch

granules for the hydration and flowability of the starch granules. In the presence of HPMC, the starch granules adhere to one another, and their mobility depends on the surface, shape, and size of the starch, as well as the varying interactions between starch and HPMC (Jekle et al., 2016; Lazaridou et al., 2007). In this study, we observed that the lower the  $z'$  value (which signifies higher stability of the network structure as discussed in Section 3.3.2), the higher the  $J_{\max}$  value. This suggests that although many factors play a role in the deference of the resistance to deformation of the model doughs made with starches of different botanical origins, the resistance to deformation mainly depends on the stability of the network structure.

Creep-recovery experiments may provide some insight into dough macrostructure. For example, the zero shear viscosity ( $\eta_0$ ) gave the flowability of the model doughs at the end of applied stress (250 MPa). As seen in Table 3, the SS-HPMC dough exhibited the highest  $\eta_0$ , followed successively by the CS-, TS-, PS-,





**Fig. 4.** The continuous distribution of spin–spin relaxation time of WS–, CS– (A), TS– (B), SS (C) and PS–HPMC (D) model doughs. The continuous distribution of spin–spin relaxation time of WS–HPMC model dough was shown in every graph (A, B, C and D) as a control. HPMC, hydroxypropylmethylcellulose; WS, wheat starch; CS, corn starch; TS, tapioca starch; SS, sweet potato starch; PS, potato starch.

and WS–HPMC doughs. This suggests that it may be difficult to maintain the shape of gluten-free doughs made with SS and CS, whereas it may be easier for the WS– and PS–HPMC doughs to hold their shape. The higher the relative elastic part of maximum creep compliance ( $J_e/J_{max}$ ), the higher the recovery capacity of the dough (Wang & Sun, 2002). WS–HPMC dough exhibited the highest  $J_e/J_{max}$ , followed successively by the TS–, CS–, SS– and PS–HPMC doughs, indicating the decreasing order of the recovery capacity was WS–, TS–, CS–, SS– and PS–HPMC doughs. In addition, higher viscosity ( $J_v/J_{max}$ ) means better stability to trap gas (Weipert, 1990). The starch–HPMC dough made with PS exhibited the highest  $J_v/J_{max}$ , indicating better stability against the rupture of the dough film between gas cells, followed successively by the SS–, CS–, TS–, and WS–HPMC model doughs. The relatively higher  $J_v/J_{max}$  value of the PS–HPMC model dough could be ascribed to the fact that PS polymers, with their high content of phosphorus, dissolve more easily in water during dough preparation, thus increasing dough stickiness (Hadnađev et al., 2014).

#### 3.4. Moisture distribution analysis of the model doughs

The moisture distributions of the starch–HPMC model doughs were analyzed to further explore the mechanism of how the different starches influence the rheological properties of gluten-free doughs. Low-resolution  $^1\text{H}$  NMR has been used to measure  $T_2$  relaxation times in starch–HPMC model doughs. Two spin–spin relaxation time constants, the first relaxation time ( $T_{21}$ ) and the second relaxation time ( $T_{22}$ ), have been identified from the NMR

spectrum using the CPMG sequences. The existence of these time constants indicates that there are one or two fractions of water with different relaxation rates (Chen, Long, Ruan, & Labuza, 1997).

Fig. 4 shows the continuous distribution of the spin–spin relaxation time of the starch–HPMC doughs. Table 4 shows the spin–spin relaxation time ( $T_{21}$ ,  $T_{22}$ ) and the amplitudes of the two components ( $A_{21}$ ,  $A_{22}$ ).  $T_{21}$  ranged from 2.10 to 5.17 ms, whereas  $T_{22}$  ranged from 12.75 to 29.33 ms, corresponding to the different moisture distribution.

Many authors have studied the  $T_2$  distributions in starch–water mixtures (Chatakanonda et al., 2003; Choi & Kerr, 2003; Tananuwong & Reid, 2004; Tang, Brun, & Hills, 2001; Tang, Godward, & Hills, 2000) and gluten-containing doughs (Bosmans et al., 2012; Bushuk & Winkler, 1957; Willhoft, 1971). A previous study showed that two distinct regions of  $T_2$  distributions,  $T_{21}$  and  $T_{22}$  are usually observed in doughs, and these range from 2 to 5 ms and from 10 to 100 ms, respectively (Bosmans et al., 2012). It is generally recognized that starch and gluten have different water-binding capacities. However, the location and mobility behavior of water during dough preparation are still controversial. Bushuk and Winkler (1957) reported that more water binds to starch than to gluten, because of the higher water sorption capacity of starch. In contrast, Willhoft (1971) suggested that there is more water associated with gluten than with starch in doughs.

In the present study, we also observed two distinct regions of  $T_2$  distributions at  $T_{21}$  (2–5 ms) and  $T_{22}$  (10–100 ms) in the starch–HPMC model doughs, and starch and HPMC were the main components influencing the mobility of water in the model doughs.

**Table 4**  
The spin–spin relaxation time ( $T_{21}$ ,  $T_{22}$ ) and the amplitudes of the two components ( $A_{21}$ ,  $A_{22}$ ) of starch–HPMC model doughs.

Model doughs	$T_{21}$ (ms)	$T_{22}$ (ms)	$A_{21}$ (%)	$A_{22}$ (%)
WS–HPMC	2.17 ± 0.11 <sup>d</sup>	18.04 ± 0.00 <sup>c</sup>	21.80 ± 0.15 <sup>a</sup>	78.20 ± 0.14 <sup>e</sup>
CS–HPMC	2.67 ± 0.13 <sup>b</sup>	22.22 ± 0.00 <sup>b</sup>	18.29 ± 0.00 <sup>c</sup>	81.71 ± 0.03 <sup>c</sup>
TS–HPMC	2.77 ± 0.00 <sup>b</sup>	22.22 ± 0.00 <sup>b</sup>	18.35 ± 0.05 <sup>b</sup>	81.65 ± 0.09 <sup>d</sup>
SS–HPMC	2.50 ± 0.12 <sup>c</sup>	14.65 ± 0.00 <sup>d</sup>	13.34 ± 0.32 <sup>d</sup>	86.66 ± 0.32 <sup>a</sup>
PS–HPMC	5.17 ± 0.00 <sup>a</sup>	29.33 ± 0.00 <sup>a</sup>	14.95 ± 0.02 <sup>e</sup>	85.05 ± 0.03 <sup>b</sup>

Values are the mean ± S.D. of three replicates. Data followed by the same letter in the same column are not significantly different ( $P > 0.05$ ). HPMC, hydroxypropylmethylcellulose; WS, wheat starch; CS, corn starch; TS, tapioca starch; SS, sweet potato starch; PS, potato starch.  $T_{21}$ , the first relaxation time of  $T_2$ ;  $T_{22}$ , the second relaxation time of  $T_2$ ;  $A_{21}$  and  $A_{22}$  are the amplitudes of  $T_{21}$  and  $T_{22}$ , respectively.

However, because the HPMC content was constant, low-resolution  $^1\text{H}$  NMR results could reflect the effect of different starches on the water distribution of the gluten-free doughs. According to several researchers,  $T_{21}$  corresponds to water tightly bound to starch, whereas  $T_{22}$  corresponds to water hydration sites in the HPMC and on the starch surface (Esselink, van Aalst, Maliepaard, & van Duynhoven, 2003; Lu & Seetharaman, 2013). As can be seen in Table 4, the WS–HPMC model dough showed significantly lower  $T_{21}$  but higher  $A_{21}$  than the model doughs made with the other starches, implying tighter interaction between WS and water and the highest content of bonded water among the different starches. The PS model dough showed the highest  $T_{22}$  among the different doughs, suggesting higher mobility of water in this dough than in the other model doughs. Although  $T_{22}$  of the SS–HPMC model dough was the lowest among the different doughs, it also had the highest  $A_{22}$ , which indicates higher free water content.

Water distribution and the structure of gluten-free doughs are correlated. For the starch–HPMC model doughs, a higher  $A_{22}$  indicated more water distributed between the hydration sites of the HPMC and starch surface, leading to the formation of more hydrogen bonds. For gluten-free model doughs, more hydrogen bonds correspond to higher structural stability. Therefore, the highly stable network structure and higher viscosity of the PS–HPMC and SS–HPMC model doughs compared to the other doughs (as discussed in Sections 3.3.2. and 3.3.4.) could be attributed to the presence of more hydrogen bonds between the starch and HPMC.

#### 4. Conclusion

The botanical source of starches has an active role in determining the rheological properties of gluten-free dough. WS addition made the gluten-free model dough softer, but decreased the network stability. Model doughs made with CS showed the slowest retrogradation rate, but became fragile easier during heating. SS addition resulted in the shortest DDT, the lowest dough strength against mixing and the highest gelatinization temperature. PS addition increased the deformation resistance, viscosity, and retrogradation rate of the dough. According to the abovementioned findings, starches from different botanical sources contribute differently to the rheological properties of doughs. These differences are not only due to the different native properties of the starches, but also due to the varying interactions between starch and HPMC. Therefore, starches from different botanical sources should be chosen to improve the rheological properties of doughs according to the end product requirements. Furthermore, starch modification methods (e.g. high hydrostatic pressure, ultrasonic, etc.) should be considered to improve the rheological properties of doughs.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbpol.2017.08.025>.

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