Carbohydrate Polymers 90 (2012) 667–674

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Thermal behavior and gelling interactions of *Mesona Blumes* gum and rice starch mixture[☆]

Tao Feng[a,∗], Ran Ye[b], Haining Zhuang[c], Zhongxiang Fang[d], Hanqing Chen[e]

[a] *State Key Laboratory of Dairy Biotechnology, Bright Dairy & Food Co. Ltd., No.1518 West Jiangchang Road, Shanghai 200436, China*
[b] *Department of Food Science and Technology Department, University of Tennessee, 2605 River Drive, Knoxville, TN 37996-4539, USA*
[c] *Whistler Center for Carbohydrate Research, Purdue University, 745 Agricultural Mall Drive, West Lafayette, IN 47907, USA*
[d] *School of Agriculture and Food Science, The University of Queensland, St Lucia, Brisbane QLD 4072, Australia*
[e] *School of Biotechnology and Food Engineering, Hefei University of Technology, No. 193 Tunxi Road, Hefei, Anhui 230009, China*

ARTICLE INFO

Article history:
Received 7 January 2012
Received in revised form 22 May 2012
Accepted 25 May 2012
Available online 2 June 2012

Keywords:
Gelling interaction
Mesona Blumes gum
Rice starch
Rheological behavior
Hydrogen bond generation
Hydrogen bond breaking
Hyperchem 8.0

ABSTRACT

In this research, thermal behavior and gelling interactions of *Mesona Blumes* gum (MBG)/rice starch mixture were extensively investigated. MBG/rice starch gel displayed significant endothermal and exothermal properties at different MBG concentrations, indicating essential interactions between MBG and rice starch. In addition, the gelling interaction between MBG and rice starch was studied by using hydrogen-bond forming agents (1,4-butanediol, ethane-1,2-diol, glycerol) and hydrogen-bond breaking agents (urea, tetramethyl urea, ethanol, methanol) on rheological spectra. The results indicated that the hydrogen bond between MBG, rice starch and water might be the major force of maintaining the complete structure of the mixed gel. Their hypothetic interactions have been schemed in computer using hyperchem 8.0.

1. Introduction

Liangfen cao (*Mesona Blumes*), an annual herbal plant with a unique aroma grown in China and other countries of Southeast Asia, such as Indonesia, Vietnam and Burma, has been widely utilized in biomedical field due to its remedial effectiveness for heatstroke, hypertension, diabetes and muscle or joint pain (Lai, Chou, & Chao, 2001). Conventionally, this plant is treated as an herbal tea or as a functional food ingredient used in the production of jam-type dessert (a mixed gel with non-waxy type starch) in China (Lai et al., 2001). Liangfen cao contains an ionic polysaccharide gum and a neutral polysaccharide, named *Mesona Blumes* gum (MBG), which exhibits the capability of forming a lower viscous solution with a pronounced shear-thinning characteristic, compared with other commercial gums (Feng, Gu, & Jin, 2007). MBG can be isolated into a neutral polysaccharide and an acidic polysaccharide (Feng, Gu, & Jin, 2008a), the latter possessing an α-(1→4)-galacturonan backbone with some α-1,2-rhamnose residues. The branches of arabinogalactan, arabinan, galactan and xylan were attached to the backbone via O-4 of rhamnose residues. In addition, some rhamnose residues on the backbone terminated with α-L-arabinose and some O-6 in galacturonic acid residues were acetylated or methyl esterified (Feng, Gu, & Jin, 2008b).

Many studies have focused on the interaction of MBG with non-waxy starch (Lai & Liao, 2002a, 2002b; Lai & Lin, 2004; Lai, Liu, & Lin, 2003). Previously, we examined the effect of MBG on the formation of two types of cereal starch (wheat and rice) gels (Feng, Gu, Jin, & Zhuang, 2010b). The results suggested that flow curves of MBG-starches exhibited pseudoplastic behavior at shear rates between 0.01 and 10 s^{-1}, following the Power Law rheological model. Also, small amplitude oscillation test revealed that typical strong gels were generated in the frequency between 0.1 and 10 Hz. MBG-wheat starch and/or MBG–rice starch gel possessed typical viscoelastic properties (Feng, Gu, Jin, & Zhuang, 2010a). To further understand the properties of MBG-starch gels, the rheological properties of rice starch–MBG mixtures were extensively studied by our group (Feng et al., 2010a). Rice starch–MBG mixtures with different concentrations of MBG at 25 °C exhibited a high shear-thinning behavior with high Herschel–Bulkley yield stress values (σ_0). Concurrently, the mixture of rice starch with 0.1–0.5% MBG displayed the rheological behavior similar to those of solid-like gels (Feng et al., 2010b).

[☆] Supported by the Open Project Program of State Key Laboratory of Dairy Biotechnology, Bright Dairy & Food Co. Ltd. (No. SKLDB2011-007).

[∗] Corresponding author. Tel.: +86 21 60873669; fax: +86 21 60873669.
E-mail address: fengtao@sit.edu.cn (T. Feng).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.05.094

Furthermore, some researchers also investigated the mechanism between starch and non-starch polysaccharide interactions. Ahmad and Williams (2001) studied the effect of galactomannan on thermal and rheological properties of sago starch, indicating that the freeze–thaw stability of starch gels was improved significantly in the presence of galactomannans. Since the galactomannans assumedly inhibited the aggregation process through acting as a physical barrier to prevent amylose/amylopectin self-association or by associating with amylose aggregated chains, it reduced syneresis of starch gels after freezing and thawing by alleviating the expulsion of water. Lai and Chao (2000) supposed a schematic figure to indicate the structure of the mixed gel between a wheat starch and MBG. In their work, a large amount of the amylose was leached out of the starch granules and rearranged themselves for formation of a coupled network with MBG. In addition, the results illustrated that the existence of cations in the mixed system could increase the number of junction zones and decrease the rotational freedom of parallel links (Lai & Chao, 2000).

Thus, the main purpose of this work was to elucidate the thermal behavior of MBG and rice starch and gelling interaction mechanism between them by using hydrogen-bond forming agents (1,4-butanediol, ethane-1,2-diol, glycerol) and hydrogen-bond breaking agents (urea, tetramethyl urea, ethanol, methanol) on rheological spectra.

2. Materials and methods

2.1. Proximate compositions of MBG and rice starch

Mesona Blumes samples (*Mesona Chinensis Benth* variety) were purchased from a market in Wuping County of Fujian Province, China. The *Mesona Chinensis Benth* leaves were stored at 25 °C. The procedure of gum extraction from *Mesona Chinesis Benth* leaves followed the protocol from our previous work, with a MBG yield of 29.4% (w/w) (Feng et al., 2007). As for proximate composition of MBG, 42.2% total sugar was determined by phenol-sulphuric acid method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956), which took D-glucose as the standard; 13.8% uronic acid was determined by meta-hydroxyl biphenyl method using L-(+)-D-galacturonic acid as the standard (Blumenkrantz & Asboe-Hansen, 1973); 9.74% crude protein, 30.9% ash and 2.98% crude fiber were determined by the respective AOAC method (2006) 960.52, 920.39C, 978.10. Rice starch was generously donated by Jiangsu Baobao Group (Zhangjiagang, Jiangsu, China) with 26.49% amylose. Its moisture content has been determined by AOAC (2006) method 934.01, the moisture content of rice starch is about 12.69%.

2.2. Thermal behavior studies of mixed gels of MBG and rice starch

Approximately 15 mg of the mixture of MBG, rice starch and distilled water were weighted in an aluminum pan. MBG concentration in the pan was 0, 0.1, 0.35, 0.5% (w/w, d.b.), respectively and rice starch concentration in the mixture was 6% (w/w, d.b.). After being sealed up, the aluminum sample pan was equilibrated at 30 ± 1 °C in a differential scanning calorimetry (DSC) furnace (TA Instruments, Shanghai, China) for 10 min, and increased to 120 ± 1 °C by 5 °C/min, and equilibrated at 120 ± 1 °C for 10 min, then decreased to 30 ± 1 °C by 5 ± 1 °C/min. An empty pan was used as control. The gel and sol temperature, gel and sol enthalpy were recorded and analyzed during the round of heating and cooling (Lai & Chao, 2000).

2.3. Studies of MBG/rice starch interaction

2.3.1. Sample preparation

0.5% (w/w) MBG and 6% (w/w) rice starch were weighted carefully and dispatched in dimethylsulfoxide (DMSO) completely. 30% (w/w), 50% (w/w) water or other solvents (50% (w/w) ethane-1,2-diol, 50% (w/w) 1,4-butanol, 50% (w/w) glycerol, 30% (w/w) methanol, 30% (w/w) ethanol, 50% (w/w) 5.56 mol/L urea in DMSO and 30% (w/w) 1,1,3,3-tetra methylurea (TMU) (Kim & Yoo, 2006; Pongsawatmanit, Temsiripong, Ikeda, & Nishinari, 2006; Rosalina & Bhattacharya, 2002)) were quantitatively introduced into the media consistently. Then, the mixture was heated to 95 °C in a magnetic heater with magnetic stirring at 200 rpm for 6 h. Subsequently, the temperature of the mixture was cooled to room temperature of 25 °C. During the cooling the mixture was also stirred.

2.3.2. Rheological experiments

All the samples suspension for rheological assay firstly had been degassed at 25 °C, and then these samples had been further poured in the rheometer plate.

Rheological experiments were conducted at 25 ± 0.1 °C by a stress-controlled rheometer (AR-1000, TA Instruments, DE, USA). The sample was introduced on the platform of the rheology, and the silicon oil was added gently around the plate for preventing the water loss of the sample. The parallel-plate system was used with 40 mm diameter and 1 mm gap between plates. Prior to test, the sample was equilibrated for 10 min.

The shear rate was set in the range of 0.01–100 s^{-1} in static shear rheology tests. Dynamic rheology tests were conducted in the linear viscoelastic range (LVR). For strain (1–100%) sweeping tests, angular frequency was set as 1.0 rad/s in order to determine the LVR of samples. The angular frequency (0.1–100 rad/s) sweeping was performed at the strain 1% in LVR (Jiménez-Avalos, Ramos-Ramírez, & Salazar-Montoya, 2005; Kim & Yoo, 2006).

2.3.3. Molecular dynamic (MD) simulation of MBG & rice starch interaction

Rice amylose fraction, MBG fragments and waters' interactions were simulated in a required periodic box (56 × 38 × 38 Å) by using MD module of HYPERCHEM8.0 software (Hypercube Inc., Waterloo, Canada). In brief, the proposed model of amylose fraction was formed by eighteen polymeric glucose units in a rather stiff left-handed helix and dissolved in the water (60%, w/w), the model of MBG fragments was composed of several neutral monosaccharide and galacturonic acid in a random coil configuration in the water (60%, w/w) (Fig. 3). By imposing a limitation on a gradient of 4.187×10^{-2} kJ/(mol Å), this model of the interaction was energetically optimized by using the AMBER force field. The obtained configuration was directly performed at a step size of 10^{-3} ps under 95 °C (368 K) for 2 ps. This optimized stable model was illustrated to analyze the possible interactions between rice amylose fraction and MBG fragments in the water (Tian et al., 2010).

2.4. Statistical methods

Two-way analysis of variance (ANOVA) was used to determine statistical inference on the data obtained at the MBG level of 0.5% (w/w) and significance level was set at 0.05 ($p < 0.05$). The Levene test was used to check the significance of variances. Multiple paired comparisons were used to determine which mean values differed from one another. The Bonferroni test was used where variances were presumed equal and the Tamhane T2 test was used where equality of variances could not be assumed (Herrero & Requena, 2006). All rheological experiments were conducted in triple trials, and the data were analyzed using SPSS11.0 (SPSS Inc., Chicago, IL, USA) and expressed as means ± standard error.

3. Results and discussion

3.1. *Thermal properties of mixed gels of MBG and rice starch*

Dynamic rheology or DSC (differential scanning calorimetry) is generally utilized to study interaction or gel–sol transitions of polysaccharide gum/starch mixed system by identifying the difference of enthalpy of samples under identical reaction conditions (Lai & Chao, 2000; Nishinari, 1997). Due to the ratio relationship between thermo energy and enthalpy, the phase transition energy of polymers could be calculated by the heat flow of maintaining the temperature equally. Since most of the gel–sol transitions of polysaccharide gum are related to endothermal or exothermal procedures, the gelling mechanism or phase transition can be investigated by heating or cooling procedures (McGrane, Mainwaring, Cornell, & Rix, 2004).

As shown in Table 1, typical endothermal and exothermal enthalpies corresponding to strong gel network occurred in all MBG/rice starch mixed systems. It was also noted that different concentrations of MBG on the gel–sol transition of the mixed system resulted in different thermal characteristics. Compared with other mixed systems in this study, rice starch with 0.5% (w/w) MBG displayed the highest endothermal enthalpy (4.458 J/g) and (0.832 J/g), respectively, during heating and cooling procedure. Table 1 shows gelling peak temperatures and enthalpies with the presence of different concentrations of MBG. It is well known that endothermal peak occurs when the system experiences order–disorder state transitions, for instance, the loss of crystalline zone and the transition from gel to sol or starch gelatinization etc. (Lai & Chao, 2000). Therefore, it is concluded that the strong or weak gel network could be associated with polymers' exothermal or endothermal enthalpy.

The phenomenon of thermal reversible gel–sol transition is usually demonstrated by zipper model (Lai & Chao, 2000). In this model, the gel of polysaccharide gum could be hypothesized as the two parallel molecules combining a zip closing, while the sol could be treated as a zip opening (Tarrega & Costell, 2007). The combination of single strand in zipper model was linked by hydrogen bonds (Tarrega & Costell, 2007). Noticeably, the transition of gel–sol of MBG/rice starch mixed system also fitted this zipper model perfectly. As the temperature decreased to gelling temperature, the molecular active energy of mixed system and free degree of rotating also decreased. Hence, MBG and rice starch interacted with each other, causing the large number of the elastic active chains to entangle into a gelling network. For example, the increase of the number of zips led to the closing of zips, further resulting in the formation of the gelling network structure. When the temperature increased to sol temperature, the molecular active energy rose up and free degree was enhanced significantly, which triggered the opening of the molecular zips between MBG and rice starch, further leading to the occurrence of the sol phenomenon.

3.2. *Gelling interaction of mixed gels of MBG and rice starch*

3.2.1. *Effect of hydrogen bond generating agents on the gel of MBG/rice starch*

Fig. 1 shows the viscosity curves of 0.5% (w/w) MBG and 6% (w/w) rice starch with different polyols. As depicted in Fig. 1, the typical curves of these mixture systems all exhibited pseudo-plastic rheological behavior with different pseudo-plastic indices. The curve of the sample with water or 1,4-butanediol revealed typical pseudo-plastic behavior with shear rate increment, which has

Table 1
DSC parameters of rice starch/MBG mixed system.

Starch	MBG% (w/w)	Endothermal parameters				Exothermal parameters			
		Onset T (°C)	Peak T (°C)	End T (°C)	ΔH (J/g)	Onset T (°C)	Peak T (°C)	End T (°C)	ΔH (J/g)
Rice starch	0	66.609 ± 0.013^{a*}	70.100 ± 0.031^{a}	75.754 ± 0.024^{ab}	2.234 ± 0.042^{a}	90.007 ± 0.024^{a}	87.675 ± 0.019^{b}	85.514 ± 0.053^{b}	−0.382 ± 0.087^{a}
	0.1	66.391 ± 0.003^{a}	69.595 ± 0.015^{b}	74.205 ± 0.036^{b}	3.590 ± 0.071^{b}	94.830 ± 0.069^{bc}	91.008 ± 0.027^{c}	88.838 ± 0.061^{bc}	−0.452 ± 0.032^{b}
	0.35	66.104 ± 0.023^{ab}	69.564 ± 0.043^{bc}	75.949 ± 0.027^{a}	3.902 ± 0.063^{c}	82.515 ± 0.071^{c}	77.519 ± 0.031^{a}	72.866 ± 0.028^{a}	−0.642 ± 0.051^{c}
	0.5	61.230 ± 0.033^{b}	63.842 ± 0.065^{c}	67.207 ± 0.046^{c}	4.458 ± 0.006^{d}	94.627 ± 0.057^{b}	92.400 ± 0.072^{d}	88.941 ± 0.091^{c}	−0.832 ± 0.063^{d}

[*] Different letters (a–d) in the same column mean the variance is significant between each other ($p < 0.05$).

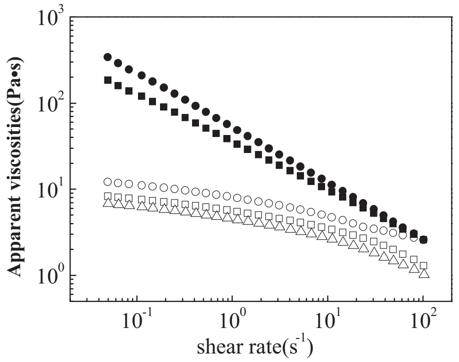

Fig. 1. Apparent viscosity vs. shear rate curves of 6% (w/w) rice starch/0.5% (w/w) MBG mixed system with different hydrogen-bond forming agents pasted in DMSO. (●) Water (50%, w/w), (○) glycerol (50%, w/w), (■) 1,4-butanediol (50%, w/w), (□) ethane-1,2-diol (50%, w/w), and (△) DMSO (100%, w/w).

0.12 ± 0.02 and 0.27 ± 0.04 flow behavior index (n) respectively, and the apparent viscosity was 336.3, 181.1 Pa s, respectively at a shear rate of $0.05\,s^{-1}$. For the samples with glycerol, ethane-1,2-diol and pure DMSO, the curves also displayed pseudo-plastic behavior with shear rate increment, which has 0.82 ± 0.02, 0.86 ± 0.05 and 0.91 ± 0.03 flow behavior index (n) respectively, and the apparent viscosity was 12.01, 8.18, 6.817 Pa s at a shear rate of $0.05\,s^{-1}$. As is well-known, when flow behavior index $n < 1$, it can be used to indicate the pseudo-plastic extent of fluid behaviors. The less flow behavior index n, the stronger flow pseudo-plasticity. Thus, it was concluded that the pseudo-plasticity order from strong to weak of 0.5% (w/w) MBG and 6% (w/w) rice starch with different polyols should be water, 1,4-butanediol, glycerol, ethane-1,2-diol and pure DMSO.

Furthermore, MBG/rice starch mixtures treated with ethane-1,2-diol, glycerol and pure DMSO, respectively, possessed a relatively lower viscosity at the shear rate below $0.1\,s^{-1}$. However, samples revealed a rheological behavior behaving like a weak pseudo-plastic flow with the increase of shear rate ($>0.1\,s^{-1}$). Compared with the system treated by ethane-1,2-diol or pure DMSO, the viscosity of the system with glycerol was much higher, since glycerol itself is a viscous low shear thinning fluid (its viscosity is about 1 Pa s).

Although the dependence of shear rate on the viscosity of the MBG/rice starch mixed system in each solvent at a lower shear rate ($0.05\,s^{-1}$) was distinctly different, the apparent viscosity of all samples were fallen into in the range of 1–10 Pa s at the higher shear rate ($\sim 100\,s^{-1}$), indicating that the spatial network structure of gels in different polyols, water and DMSO were not strong. It would lead to the fragmentation of gel under the certain mechanical shear force. In terms of these results, MBG/rice starch gels were considered to be physical gels and the hydrogen bond between chains in these gels might be the main force for the gel formation (Shi & BeMiller, 2002).

The strain sweeps and mechanical spectrums of MBG/rice starch with diol or triol in DMSO solvent are described in Fig. 2. In pure DMSO solvent, MBG/rice starch generated a weak gel by the interaction between the hydrogen bonds of hydroxyl group in starch or/and MBG molecules. In 50% (w/w) water solution, the elastic modulus of gel has been increased by one order of magnitude, resulting in 10-fold differences between elastic modulus G' (G' has no relationship with the enhancement of frequency, which showed a typical strong gel (Mortimer, Ryan, & Stanford, 2001)). It indicates that the gel structure between starch, MBG and water molecules could be maintained by hydrogen bonds. Furthermore, water molecules might serve as a bridge between the gelatinized rice starch and MBG molecules. A proposed schematic demonstration of the structure is shown in Fig. 3.

Strong gels exhibit the characteristics of true gels where they manifest behaviors typical of viscoelastic solids and, above a critical deformation value; they rupture rather than flow under small deformation conditions. On the other hand, impositions of large or continuously increasing deformation of weak gels lead to rapid breakdown of their networks into smaller clusters. These systems can flow homogenously with flow properties typical of dispersed systems. At low strains (in the linear viscoelastic region (LVR)), these systems exhibited gel-like mechanical spectrum (G' is almost independent of frequency and G'' increases with frequency) where $\tan\delta$ increased with the increase of frequency (Domenico & Bruno de Cindio, 2001). MBG/rice starch gels generated in 50% of diol (w/w) DMSO solution, and its gel strength enhanced with the increase of the number of carbons in polyols. Actually, the effect is probably related with distance between the hydroxyl groups and not exactly with the number of carbons in polyols. For the mechanical spectrum of MBG/rice starch gel formed in 50% (w/w) ethane-1,2-diol of DMSO solution, elastic modulus G' was always equal to viscous modulus G'' in the range of most frequencies. Of note, the modulus was highly correlated with frequency, representing that the interaction inside the gel was rather weak (Vriesmann, Silveira, & Petkowicz, 2010). However, a stronger MBG/rice starch gel was achieved in 1,4-butanediol DMSO solution (1:1, w/w) since G' was higher than G'' but not much higher. The gel strength of MBG/rice starch gel in 1,4-butanediol of DMSO solution with 4 carbons was equivalent to that of MBG/rice starch gel which formed in water, illustrating that linkage types of these gels were identical although the configurations of hydrogen bond linkage between chains are different.

Strain sweeps in Fig. 2 reflect more details on microstructures of these gels. The shift of the crossover point of G' and G'' of the sample toward the lower strain was attributed to the increasing number of carbons, i.e. the gel brittleness would also increase with the enhancement of the gel strength. In the glycerol in DMSO solution (1:1, w/w), G' and G'' of strain sweeps of the MBG/rice starch gel were integrated in the entire range of the frequency, showing the occurrence of a rather low extent of spacial network (Fig. 2). The similarity of the changing trend of G' and G'' with frequency between glycerol in DMSO solution (1:1, w/w) and ethane-1,2-diol in DMSO solution (1:1, w/w) represented that the linkage of the glycerol mainly by 1,2-OH during the interaction with starch molecules or MBG molecules was identical with the hydrogen bond of ethane-1,2-diol in Fig. 3. There are some reasons contributing to this result. Firstly, $-CH_2-OH$ was not able to link with other starch molecules or MBG molecules by hydrogen bond due to the steric hindrance effect; secondly, the intramolecular hydrogen bonds were formed within the single starch or MBG molecule at the hydroxyl group in glycerol. In contrast, the formation of the intermolecular hydrogen bonds between starch and/or MBG molecules did not occur due to the weak gel strength of the gel in glycerol/DMSO solution (Silva, Oliverita, & Rao, 1998). These results represented that water molecule offered an advantage over ethane-1,2-diol on the gel structure formation of MBG/rice starch, indicating that the generation ability of the intermolecular hydrogen bond of water molecule might be superior to that of ethane-1,2-diol. However, the generation ability of the intramolecular hydrogen bond of ethane-1,2-diol might be even stronger than that of water (Hizukuri & Takeda, 1978).

3.2.2. Effect of hydrogen-bond breaking agents on the gel structure of MBG/rice starch

It is well known that urea and TMU are hydrogen bond breaking agents (Li, Vasanthan, & Bressler, 2011). In addition, some small molecular weight alcohols such as methanol and ethanol are

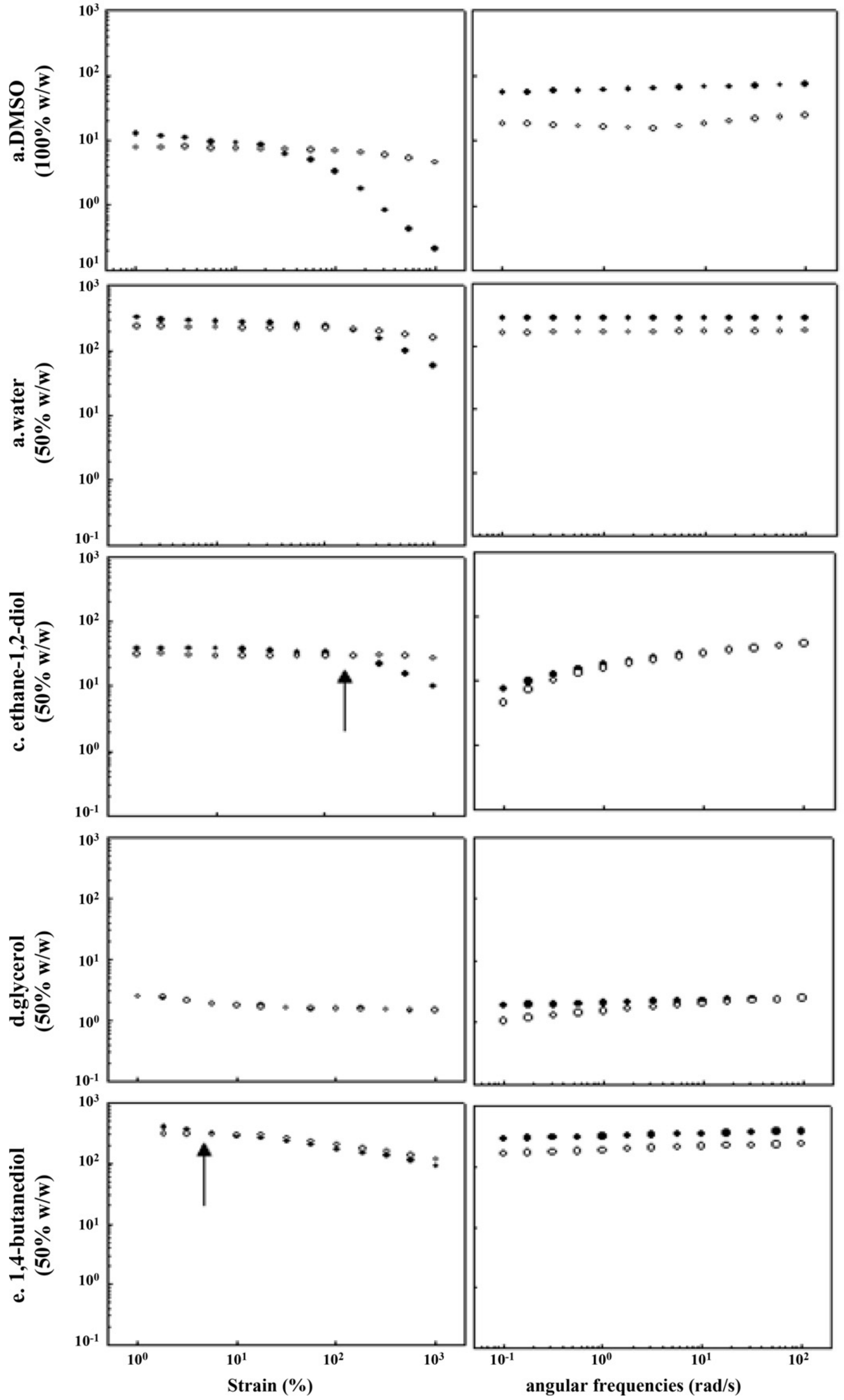

Fig. 2. Strain sweeps at 1.0 rad/s and mechanical spectra at 1% strain of 6% (w/w) rice starch/0.5% (w/w) MBG mixed system with different hydrogen-bond forming agents. (●) G' (Pa) and (○) G'' (Pa). The arrow represented when diol carbon chain length increased, G'/G'' crossover point shifted to low strain, thus made the gel brittleness increase.

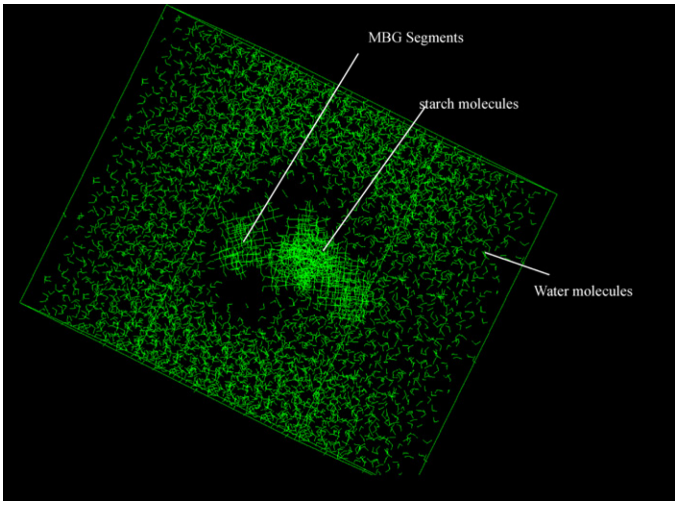

Fig. 3. Representation of hydrogen-bond network between starch, MBG and water, where dash line represents hydrogen-bond formed.

also commonly used as hydrogen bond breaking agent (Hizukuri & Takeda, 1978). Therefore, for this research, urea, TMU, ethanol and methanol in DMSO solution were selected for examination the effect of hydrogen breaking agents on the 0.5% (w/w) MBG and 6% (w/w) rice starch gel structure (in Fig. 4). Furthermore, moisture content during the trials was critically maintained at 30% (w/w) since gel structures could be easily broken down by hydrogen bond breaking agents (Telis, Telis-Romero, & Gabas, 2005).

The apparent viscosity of MBG/rice starch with 5.56 mol/L urea in DMSO solution decreased significantly ($p < 0.05$), with a value (1 Pa s) almost equivalent to that of the gel in 100% DMSO at 100 s^{-1}. Although the apparent viscosity of MBG/rice starch treated with the mixture of TMU/DMSO (3:7, w/w) solution also decreased somehow, it was less significant than that of the gel treated by urea, because their apparent viscosities were different from each other about one order of magnitude at 0.05–5 s^{-1} (in Fig. 4). Both rice starch and MBG molecules could easily be precipitated by high-concentration alcohol solutions. To prevent precipitation, a lower concentration of alcohol (30%, w/w) was introduced to the DMSO solution. In addition, the shear rheological behavior of gels in DMSO solution with alcohols was similar to Newtonian fluid, with the apparent viscosity about 0.1 Pa s (in Fig. 4). The result indicated that the apparent viscosity of gel in DMSO solution treated by 30% (w/w) ethanol was slightly higher than that of gel treated by methanol, which was consistent with the result in the literature (Rao, Delaney, & Skinner, 1995).

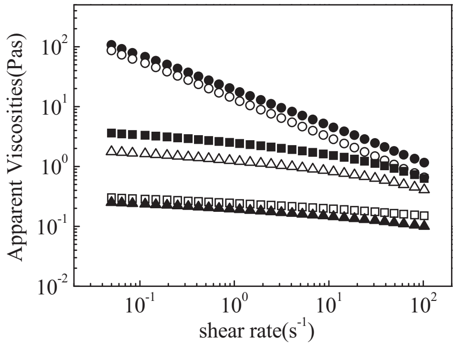

Fig. 4. Apparent viscosities vs. shear rate curves of 10% (w/w) rice starch/MBG mixed system with different hydrogen-bond breaking agents pasted in DMSO. (●) Water (30%, w/w), (○) TMU (30%, w/w), (■) 5.56 mol/L urea (50%, w/w), (△) DMSO (100%, w/w), (□) ethanol (30%, w/w), and (▲) methanol (30%, w/w).

The strain sweep and frequency sweep spectrums of the gels in the mixture of 0.5% (w/w) MBG and 6% (w/w) rice starch in DMSO solution with hydrogen bond breaking agents were shown in Fig. 5. For all treatments, the viscous modulus of the gel in DMSO solution treated by urea was higher than the elastic modulus in strain sweep and frequency sweep. Furthermore, both modules were highly correlated with the frequency. These results suggested that the mixture in DMSO solution treated by urea exhibited a rheological behavior of a viscous fluid (Nishinari, 1997), reflecting that urea is a very effective agent for breaking the gel structure.

However, the structure of the gel in DMSO solution treated by TMU (30%, w/w) was well maintained, based on the data of strain sweep and frequency sweep. Compared with the gel in water, the crossover point of G' and G'' of the gel in DMSO solution treated by TMU shifted toward the lower strain points. The values of both moduli of this gel were in agreement with those of the gel formed in water. These results are consistent with those reported by Cheetham and Tao (1998). It was concluded that urea failed to break down the intramolecular hydrogen bond of starch molecule, but it was able to break down the intermolecular hydrogen bonds. Conversely, TMU was capable of breaking down the intramolecular hydrogen bonds utilized to maintain the tight helical conformation of starch in DMSO solution. However, TMU failed to decomposed the intermolecular hydrogen bond used for the formation of the starch gel structure (Bakker & Petersen, 2011).

The data of strain sweep and frequency sweep (Fig. 5) in this work demonstrated that methanol and ethanol could remarkably reduce the mixed gel structure of MBG/rice starch, compared with the gel in 30% (w/w) water. For the sample treated by methanol, the values of G'' were in agreement with those of G' in the entire frequency range. In addition, the results indicated the gel solution with low viscosity maintained a weak gel structure after the usage of methanol due to the damage of the hydrogen bond linkage of the gel structure. However, the sample treated by ethanol was unable to form a gel structure since rheological behavior showed a viscous fluid ($G'' > G'$). It was assumed that alcohols with single hydroxyl group decomposed the mixed gel structure of MBG/rice starch through being linked with the hydroxyl group of starch or MBG molecules. More specially, due to only one hydroxyl group in each alcohol molecule, it was unable to link with the hydroxyl group of another starch molecule by hydrogen bond interaction after linking with the hydroxyl group of starch or MBG molecules. Furthermore, starch molecules would precipitate when employing of the alcohol with sufficiently high concentration (Brouillet, Baylac, Cartilier, & Bataille, 2010). Fig. 5 states ethanol provides an advantage over methanol on the inhibition of the hydrogen bond between starch and MBG molecules, causing more elastic modulus reduction for the mixed gel, due to its more steric hindrance and larger size of spacial structure than both of methanol. Moreover, Fig. 4 depicts the complex of MBG/rice starch/ethanol, exhibiting a slightly higher apparent viscosity than the complex of MBG/rice starch/methanol due to the higher molecular weight of the complex of MBG/rice starch/ethanol.

The hydrogen bonding is a key feature of the interactions of the molecules for understanding the structure of the dry amorphous starch. Hence, the water content has direct impact on the interactions of the starch chain with the surrounding molecules (intermolecular structure), as well as on the conformation of the chain itself (intramolecular structure). As described in the literature, amylose in DMSO owned a tight, rigid helical conformation maintained by intramolecular hydrogen bonding (Trommsdorff & Tomka, 1995). Also, DMSO molecules is helpful for the stabilization of intramolecular hydrogen bonding (Trommsdorff & Tomka, 1995). As suggested by our work, the intramolecular hydrogen bonds were replaced by intermolecular water bonds with the

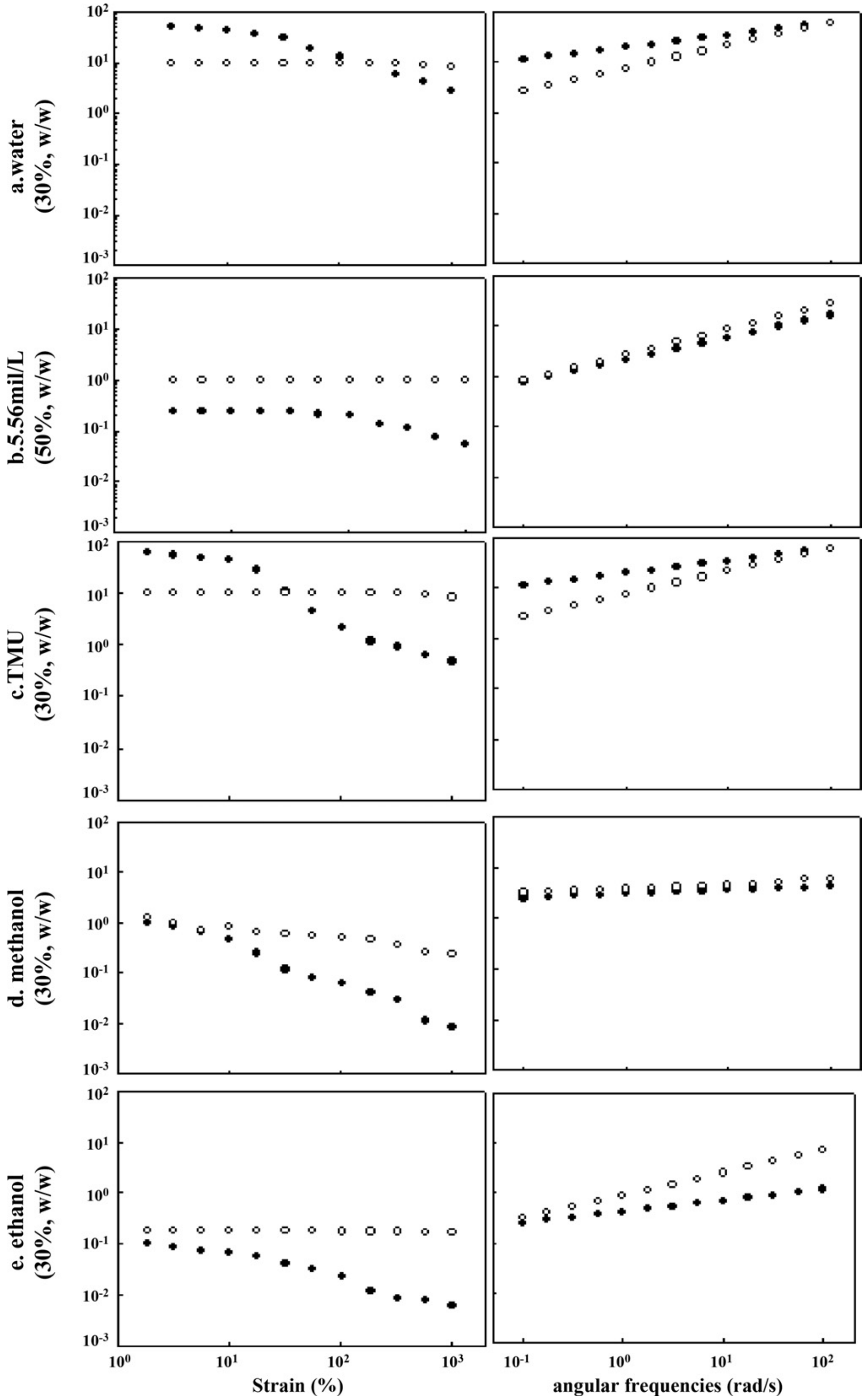

Fig. 5. Strain sweeps at 1.0 rad/s and mechanical spectra at 1% strain of 10% (w/w) rice starch/MBG mixed system with different hydrogen-bond breaking agents. (●) G' (Pa) and (○) G'' (Pa).

addition of water. In addition, water content was a critical factor for the interaction between amylose molecules, and elastic gels with amylose and MBG. Thus, gels were produced by the interaction between adjacent amylose, and MBG molecules through hydrogen bonds of intermolecular water molecules.

It was found that amylose and MBG were able to form strong, elastic gels by the addition of various polyols in the absence of water. In addition, polyols, such as 1,4-butanediol, were capable of forming an intermolecular hydrogen bonded network between amylose and MBG molecules, similar to that formed by water.

Furthermore, amylose and MBG gel strength could be significantly reduced by the existence of the intermolecular hydrogen bond-breaking agent, for instance, urea. This reduction was not so apparent when introducing the intramolecular bond-breaking agent, for example, TMU.

4. Conclusions

In this study, it was concluded that the interactions of MBG and rice starch during heating procedure were correlated with MBG concentrations. In rice starch-rich environment, the increase of MBG concentration resulted in the increase of the amounts of zippers of MBG–rice starch molecules complex. The higher the enthalpy, the stronger the gelling network structure formed by aggregation. The DSC studies showed that MBG and rice starch gels could be classified into typical thermal-irreversible gels. Their endothermal enthalpy and exothermal enthalpy were highly dependent on MBG concentration of the gel. In addition, water played a substantial role in hydrogen bonding during rice starch gelatinization and interaction with MBG. An intermolecular hydrogen bonded network of starch and MBG molecules was formed in the presence of water-rich environment and in the absence of polyols such as ethane-1,2-diol or 1,4-butanediol. It was assumed that MBG-starch gels were synthesized by the interaction between adjacent rice starch amylose and MBG molecules through hydrogen bonded intermolecular water molecules. Furthermore, the hydrogen breaking agents such as urea, methanol and ethanol have a significant effect on reducing the gel strength except TMU. The results clearly demonstrated that hydrogen bonding is significant for the formation of a rice starch–MBG gel and the mechanism of rice starch–MBG gelling was primarily via hydrogen-bond interactions in rice starch and MBG systems, initiating rice starch–MBG gel formation followed by a phase separation through crystalline aggregation.

References

Ahmad, F. B., & Williams, P. A. (2001). Effect of galactomannans on the thermal and rheological properties of sago starch. *Journal of Agricultural and Food Chemistry*, *49*, 1578–1586.

AOAC. (2006). *Official methods of analysis of the AOAC international* (18th ed.). Gaithersburg, MD: Association of Official Analytical Chemists., pp. 25–28.

Bakker, H. J., & Petersen, C. (2011). Hydrophobic Molecules slow down the hydrogen-bond dynamics of water. *Journal of Physics and Chemistry A*, *115*(10), 1821–1829.

Blumenkrantz, N., & Asboe-Hansen, G. (1973). New method for quantitative determination of uronic acids. *Analytical Biochemistry*, *54*(2), 484–489.

Brouillet, F., Baylac, G., Cartilier, L., & Bataille, B. (2010). High-amylose sodium carboxymethyl starch matrices for oral, sustained drug release: Development of a spray-drying manufacturing process. *Drug Development and Industrial Pharmacy*, *36*(7), 795–805.

Cheetham, N. W. H., & Tao, L. P. (1998). Amylose conformational transitions in binary DMSO/water mixtures. *Carbohydrate Polymers*, *35*(3–4), 287–295.

Da Silva, J. A. L., Oliverita, J. C., & Rao, M. A. (1998). Rheological properties of heated cross-linked waxy maize starch dispersions. *International Journal of Food Properties*, *1*, 23–24.

Domenico, G., & Bruno de Cindio, P. D. (2001). A weak gel model for foods. *Rheologica Acta*, *40*, 120–127.

Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., & Smith, F. (1956). Colorimetric method for determination of sugars and related substances. *Analytical Chemistry*, *28*(3), 350–356.

Feng, T., Gu, Z. B., & Jin, Z. Y. (2007). The chemical composition and some rheological properties of *Mesona Blumes* gum. *Food Science and Technology International*, *19*, 50–59.

Feng, T., Gu, Z. B., & Jin, Z. Y. (2008a). Structural studies of an acidic polysaccharide of *Mesona Blumes* gum. *Journal of the Science of Food and Agriculture*, *88*, 24–34.

Feng, T., Gu, Z. B., & Jin, Z. Y. (2008b). Isolation and characterization of an acidic polysaccharide from *Mesona Blumes* gum. *Carbohydrate Polymers*, *71*, 159–169.

Feng, T., Gu, Z. B., Jin, Z. Y., & Zhuang, H. N. (2010a). Rheological properties of rice starch–*Mesona Blumes* gum mixtures. *Journal of Texture Studies*, *41*, 685–702.

Feng, T., Gu, Z. B., Jin, Z. Y., & Zhuang, H. N. (2010b). Rheological properties of cereal starch gels and *Mesona Blumes* gum mixtures. *Starch/Stärke*, *62*, 480–488.

Herrero, A. M., & Requena, T. (2006). The effect of supplementing goats milk with whey protein concentrate on textural properties of set-type yogurt. *International Journal of Food Science and Technology*, *41*, 87–92.

Hizukuri, S., & Takeda, C. (1978). Studies on the gelatinization of starches, part 2. Effect of Lower alcohols on the gelatinization of cereal starches. *Starch/Stärke*, *30*(7), 228–233.

Jiménez-Avalos, H. A., Ramos-Ramírez, E. G., & Salazar-Montoya, J. A. (2005). Viscoelastic characterization of gum arabic and maize starch mixture using the Maxwell model. *Carbohydrate Polymers*, *62*, 11–18.

Kim, C., & Yoo, B. (2006). Rheological properties of rice starch–xanthan gum mixtures. *Journal of Food Engineering*, *75*, 120–128.

Lai, L. S., Chou, S. T., & Chao, W. W. (2001). Studies on the antioxidative activities of hsian-tsao (Mesona procumbens Hemsl) leaf gum. *Journal of Agricultural and Food Chemistry*, *49*, 963–968.

Lai, L. S., & Chao, S. J. (2000). A DSC study on the gel–sol transition of starch and hsian-tsao leaf gum mixed system. *Journal of Agricultural and Food Chemistry*, *48*, 3267–3274.

Lai, L. S., & Liao, C. L. (2002a). Dynamic rheology of structural development in starch/decolourised hsian-tsao leaf gum composite systems. *Journal of the Science of Food and Agriculture*, *82*(10), 1200–1207.

Lai, L. S., & Liao, C. L. (2002b). Steady and dynamic shear rheological properties of starch and decolorized hsian-tsao leaf gum composite systems. *Cereal Chemistry*, *79*(1), 58–63.

Lai, L. S., & Lin, P. H. (2004). Application of decolorized hsian-tsao leaf gum to low-fat salad dressing model emulsions: A rheological study. *Journal of the Science of Food and Agriculture*, *84*, 1307–1314.

Lai, L. S., Liu, Y. L., & Lin, P. H. (2003). Rheological/textural properties of starch and crude hsian-tsao leaf gum mixed systems. *Journal of the Science of Food and Agriculture*, *83*(10), 1051–1058.

Li, J. H., Vasanthan, T., & Bressler, D. C. (2011). Improved cold starch hydrolysis with urea addition and heat treatment at subgelatinization temperature. *Carbohydrate Polymers*, *87*(2), 1649–1656.

McGrane, S. J., Mainwaring, D. E., Cornell, H. J., & Rix, C. J. (2004). The role of hydrogen bonding in amylose gelation. *Starch/Stärke*, *56*, 122–131.

Mortimer, S., Ryan, A. J., & Stanford, J. L. (2001). Rheological behavior and gel-point determination for a model Lewis acid-initiated chain growth epoxy resin. *Macromolecules*, *34*, 2973–2980.

Nishinari, K. (1997). Rheological and DSC study of sol–gel transition in aqueous dispersions of industrially important polymers and colloids. *Colloid & Polymer Science*, *275*, 1093–1168.

Pongsawatmanit, R., Temsiripong, T., Ikeda, S., & Nishinari, K. (2006). Influence of tamarind seed xyloglucan on rheological properties and thermal stability of tapioca starch. *Journal of Food Engineering*, *77*, 41–50.

Rao, V. N. M., Delaney, R. A. M., & Skinner, G. E. (1995). Rheological properties of solid foods. In A. S. M. Rao, & S. H. Rizvi (Eds.), *Engineering Properties of Foods* (pp. 152–168). New York: Marcel Dekker.

Rosalina, I., & Bhattacharya, M. (2002). Dynamic rheological measurements and analysis of starch gels. *Carbohydrate Polymers*, *48*, 191–202.

Shi, X. H., & BeMiller, J. N. (2002). Effects of food gums on viscosities of starch suspensions during pasting. *Carbohydrate Polymers*, *50*, 7–18.

Tarrega, A., & Costell, E. (2007). Colour and consistency of semi-solid dairy desserts: Instrumental and sensory measurements. *Journal of Food Engineering*, *78*, 655–661.

Telis, V. R. N., Telis-Romero, J., & Gabas, A. L. (2005). Solids rheology for dehydrated food and biological materials. *Dry Technology*, *23*, 759–780.

Tian, Y. Q., Li, Y., Xu, X. M., Jin, Z. Y., Jiao, A. Q., Wang, J. P., et al. (2010). A novel size-exculsion high performance liquid chromatography (SE-HPLC) method for measuring degree of amylose retrogradation in rice starch. *Food Chemistry*, *118*(2), 445–448.

Trommsdorff, U., & Tomka, I. (1995). Structure of amorphous starch. 2. Molecular interactions with water. *Macromolecules*, *28*, 6138–6150.

Vriesmann, L. C., Silveira, J. L. M., & Petkowicz, C. L. D. O. (2010). Rheological behavior of a pectic fraction from the pulp of cupuassu (*Theobroma grandiflorum*). *Carbohydrate Polymers*, *79*, 312–317.