

Physicochemical properties and conformations of water-soluble peach gums via different preparation methods

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ARTICLE INFO

Article history:

Received 8 December 2017

Received in revised form

7 March 2018

Accepted 28 March 2018

Available online 29 March 2018

Keywords:

Peach gums

Physicochemical properties

Chain conformation

Emulsion stability

Whey protein isolate

ABSTRACT

Physicochemical properties and conformations of WEPG (water extracted peach gum), AEPG2.0 (alkali extracted peach gum, 2 M NaOH) and HPPG8 (H₂O₂ extracted peach gum, 8 h), prepared from the gum of *Prunus persica* Batsch, were investigated. The yields of WEPG, AEPG2.0 and HPPG8 were 77.25%, 82.60% and 83.34%, respectively. All of the three peach gums were arabinogalactan-type polysaccharides with similar chemical composition. Conformational analysis revealed that WEPG, AEPG2.0 and HPPG8 were macromolecules with compacted coil structures and their molecular weights of 1.34×10^7 g/mol, 1.64×10^7 g/mol and 5.17×10^6 g/mol, respectively. Rheological test showed that WEPG, AEPG2.0 and HPPG8 exhibited non-Newtonian behavior, and their apparent viscosities followed the order of AEPG2.0 > WEPG > HPPG8. Results also indicated that all of the three peach gums significantly ($P < 0.05$) enhanced the stability of whey protein isolate oil-water emulsions, and AEPG2.0 was the optimal gum extract showing no phase separation over 5 weeks, suggesting it could be used as an effective stabilizer in food emulsions and beverage industry.

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1. Introduction

Peach gum is secreted from the branches and trunk of peach trees (*Prunus persica*, family Rosaceae), when they are subjected to infection, insect attack, mechanical and chemical injury, and other environmental stresses (Bouaziz, Koubaa, Ghorbel, & Chaabouni, 2016). Peach trees are cultivated throughout most regions of China, such as Anhui, Guizhou and Zhejiang provinces, making peach gum a very abundant resource. The reported yield of peach gum is more than 10 billion tons annually in China (Zhou, Huang, He, Zhang, & Li, 2014). However, a large amount of peach gum in China is not fully utilized making it a huge waste stream presenting both ecological and economic challenges. As an important byproduct of peach trees, it would be beneficial to improve the utilization of peach gum.

The monosaccharide composition of peach gum is arabinose, galactose, xylose, mannose and uronic acid. Among these saccharides, arabinose and galactose are present at the highest levels, however, the proportions in each polysaccharide varies (Qian, Cui, Wang, Wang, & Zhou, 2011; Simas et al., 2008; Simas-Tosin et al., 2009, 2010). Peach gum possesses a high molecular weight ($>10^6$ Da) and a highly branched molecular structure and is composed of (1 → 3)-linked β-D-Galp units in the main-chain and arabinogalactan in the side chains (Simas et al., 2008; Simas-Tosin et al., 2009).

In ancient times, peach gum was utilized as a traditional Chinese medicine for the treatment of stranguria due to hematuria, urolithic stranguria, dysentery, diarrhea and concretions (Wang, Xie, Zhong, & Du, 2008). Recently, additional functions of peach gum have been identified, including antioxidant activity, antibacterial activity (Yao, Cao, & Wu, 2013), improvement of spermatogenesis in KKAY mice (Qian, Wang, Song, & Chen, 2017), and treatment of diabetes (Wang et al., 2017). Peach gum shows interesting rheological behavior and functional properties, such as excellent adsorption performance,

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facile availability, favorable compatibility and intriguing functionality, and can be utilized as an anionic polyelectrolyte (Huang & Zhou, 2014) or an environmental cleaner (Zhou et al., 2014), making it worthy of further investigation. Compared with gum arabic, peach gum has a better emulsion capacity and stability (Qian et al., 2011; Simas-Tosin et al., 2010), giving it potential use in the food industry as a replacement or partial replacement for gum arabic.

Peach gum, collected from the branches and trunk of peach trees, is called raw peach gum. Usually, raw peach gum is a crystalline-like material, which is very hard and translucent with brown yellow color. At ambient temperatures, raw peach gum has a high molecular weight and poor solubility, seriously restricting its industrial application. It is reported that many methods have been applied in extracting polysaccharides from plant, mushroom, animal tissues, etc., such as water extraction, acid extraction, alkaline extraction, enzymatic extraction, ultrasonic extraction, supercritical fluid extraction, microwave extraction and combined extraction of multiple technologies (Nie & Xie, 2011; Zhang et al., 2017; Zhu et al., 2016). In achieving these goals it was necessary to develop an approach to decrease the molecular weight of raw peach gum using water extraction, alkaline extraction or H₂O₂ extraction (Qian et al., 2011; Simas-Tosin et al., 2010; Yao, Cao, Pan, & Wu, 2013), which are the main methods adopted to extract the peach gum, to obtain a gum with improved solubility and viscosity properties. However, the impact, of different preparation methods on the physicochemical and functional properties of peach gum, has not been previously reported.

In the present study, peach gum as a natural biopolymer resources with high utilization value, a comprehensively comparison of the physicochemical properties and conformation of peach gums, prepared by different preparation methods was necessary. The properties examined included chemical composition, color parameters, molecular weight, intrinsic viscosity, chain conformation, rheological properties and emulsion stability. The objective of this study is to investigate different preparation methods to improve the physicochemical properties and morphology of peach gums contributing to their fuller utilization.

2. Material and methods

2.1. Materials

Peach gum exudates from the trunk and branches of white peach (*Prunus persica* Batsch.) tree were collected at the Yuandong countryside peach farm (Jinhua, Zhejiang Province, China). Peach gum was ground into powder (80 mesh). Soybean oil was purchased from a local grocery in Zhejiang (China). Whey protein isolate (WPI 9400) was obtained from Hilmar Ingredients (Hilmar, CA, USA). Gum arabic (derived from acacia tree) was purchased from Sigma-Aldrich (CAS: 90000-01-5, USA). All other chemicals were analytical grade.

2.2. Preparation of water-soluble peach gums

Three kinds of extraction methods, hot water extraction, alkaline extraction and H₂O₂ extraction were applied to prepare water-soluble peach gums to investigate the effect of different extraction methods on the physicochemical properties of water-soluble peach gums.

2.2.1. Water extraction

Peach gum powder (5 g) was soaked in 500 mL distilled water at room temperature for 24 h. It was next extracted using a magnetic stirrer at 500 r/min and maintained at 90 °C for 2 h. The sample solution was, then, centrifuged at 4000 r/min for 20 min. The

supernatant was collected and the insoluble gum was added, and was extracted a second and third time into 500 mL distilled water for under the same conditions. The combined supernatants were concentrated and precipitated by adding 4 vol of ethanol. The precipitate was re-dissolved in H₂O and freeze-dried to obtain a water-soluble peach gum fraction called WEPG.

2.2.2. Alkaline extraction

Peach gum powder (5 g) was soaked in 500 mL distilled water at room temperature for 24 h. NaOH was added to form solutions of 0.1 M, 0.5 M, 1 M, 1.5 M, 2.0 M, 2.5 M, 3.0 M and 4.0 M alkali (0.1–4.0, respectively). The peach gum suspensions were extracted using magnetic stirrer (500 r/min) at 60 °C for 2 h. After neutralization with HCl, the extracts were transferred to a dialysis bags (8–14 KDa) and dialyzed against distilled water for 3 days. Desalted sample solutions were centrifuged at 4000 r/min for 20 min. The supernatants were concentrated and 4 vol of ethanol were added to afford a precipitate. The precipitated gums were re-dissolved in H₂O and freeze-dried to give water-soluble peach gum called AEPG0.1–4.0, respectively.

2.2.3. H₂O₂ extraction

Peach gum powder (5 g) was soaked in 500 mL distilled water at room temperature for 24 h. The pH of peach gum suspensions were adjusted with NaOH to pH 10 and 5% H₂O₂ (v/v) was added. The peach gum suspension was immediately stirred (500 r/min) at room temperature for 2 h, 4 h, 6 h, 8 h and 10 h (2–10, respectively). The peroxide in the resulting solutions were quenched with 0.6% NaHSO₃ (w/v) and then dialysis for 24 h. After centrifuging at 4000 r/min for 20 min, the supernatants were concentrated and 4 vol of ethanol were added to afford a precipitate. The precipitates were dissolved in H₂O, and freeze-dried to give water-soluble peach gum HPPG2-10.

2.2.4. Purity identification

The purity of each peach gum was identified by SEC chromatography (SB-806 and SB-804 HQ column, 7.8 mm × 300 mm) on a SEC-MALLS-RI-VISC system (according to Section 2.6). Protein content was assayed by scanning ultraviolet spectrum over a range of 250–350 nm (UV-2550, SHIMADZU, Japan).

2.3. Color measurement

The color of peach gums, prepared using different extraction methods, was evaluated using a Hunter lab colorimeter (ColorFlex EZ, HunterLab Inc., Osaka, USA). The colorimeter was calibrated using a standard white plate prior to measurement. Color measurement was conducted by placing the peach gum solution (10 mg/mL) in the transparent test cup in colorimeter using distilled water as a standard. All measurements were performed in triplicate. The total color difference (ΔE), whiteness (WI) and yellowness (YI) indexes of sample solutions were calculated according to the following equations (1)–(3), respectively (Bolin & Huxsoll, 1991).

$$\Delta E = \sqrt{(L^* - L)^2 + (a^* - a)^2 + (b^* - b)^2} \quad (1)$$

$$WI = 100 - \sqrt{(100 - L)^2 + a^2 + b^2} \quad (2)$$

$$YI = \frac{142.86b}{L} \quad (3)$$

where L^* , a^* , and b^* are the color parameter values of the standard

and L , a , and b are the color parameter values of the sample.

2.4. Monosaccharide composition

Monosaccharide compositions of peach gums were prepared by pre-column derivatization with 1-phenyl-3-methyl-5-pyrazolone (PMP) and identified by RP-HPLC (Zhang et al., 2013) with modification. Briefly, 3 mg of peach gum was dissolved in 1 mL of 2 mol/L TFA in a sealed tube, and hydrolyzed for 8 h at 121 °C. After being completely hydrolyzed, the excess trifluoroacetic acid (TFA) was dried under nitrogen at 70 °C by adding 200 μ L methanol three times. The hydrolysate was then dissolved in 1 mL of distilled water for further derivatization. Standard monosaccharide mixture (450 μ L of 2 mM) or the peach gum hydrolyzate were added to 450 μ L of 0.3 M NaOH and 450 μ L of 0.5 M PMP in methanol and heated at 70 °C for 30 min. After cooling to room temperature the hydrolyzates were neutralized with 0.3 M HCl and the resulting solutions were extracted twice, each time with a same volume of chloroform. The aqueous layer was recovered and filtered through a 0.45 μ m filter membrane prior to HPLC analysis.

Analysis of 10 μ L of the PMP-labeled monosaccharides in the filtered aqueous layer was performed on a Waters 2695 HPLC system (Waters, US) equipped with a PDA 2996 detector (Waters, US). The analytical column used was a Zorbax Eclipse XDB-C18 column (4.6 mm \times 250 mm, 5 μ m, Agilent, USA). Elution was carried out at a flow rate of 1.0 mL/min at 25 °C, which consisted of 0.05 M sodium phosphate (KH₂PO₄-NaOH, pH 6.8) with (A) 15% and (B) 40% acetonitrile, applying a linear gradient as follow: 0 \rightarrow 10 min \rightarrow 30 min \rightarrow 35 min \rightarrow 40 min, corresponding to buffer B 0 \rightarrow 15% \rightarrow 25% \rightarrow 25% \rightarrow 0. The wavelength of UV detection used was 250 nm.

2.5. Fourier-transform infrared (FT-IR) spectroscopy

Structural information of peach gums was obtained using a Fourier-transform infrared spectrophotometer (Nexus IS10 FTIR, Thermo Nicolet, USA). Peach gum (2 mg) was pressed into 40 mg KBr pellet. The Fourier transform-infrared spectra were recorded in the range of 4000 to 400 cm^{-1} and processed using Thermo Nicolet software.

2.6. Molecular weight, intrinsic viscosity and conformation

Molecular information of peach gums, including weight-average molecular weight (M_w), number-average molecular weight (M_n), the radius of gyration ($R_{g,z}$), polydispersity (M_w/M_n) and chain conformation in solution were performed by a size exclusion chromatography equipped with a multi-angle laser light scattering system with refractive index detector (SEC-MALLS-RI, Wyatt Technology, USA). SEC columns (SB-806 HQ and SB-804 HQ column, 7.8 \times 300 mm, Shodex, Japan), protected by a OHPak SB-G guard column (Shodex, Japan), and SEC was performed at 25 °C. Hydrodynamic radius ($R_{h,z}$) and intrinsic viscosity ($[\eta]$) were obtained using a viscometer (ViscoStar™ III, Wyatt Technology, USA), connected to and the SEC-MALLS-RI system. The value of dn/dc (specific refractive index increment) was estimated at 0.138 mL/g. Sodium chloride solution, 0.2 M NaCl containing 0.02% NaN₃ (pH 7.0), was used as mobile phase, at a flow rate of 0.5 mL/min. Eluent was filtered (0.22 μ m filter membranes, Millipore) and degassed. Sample was dissolved directly in mobile phase (3 mg/mL), and filtered through 0.22 μ m filter membranes (Millipore). The injection volume was 50 μ L and running for 100 min. Data acquisition and calculations were performed by the ASTRA software, version 7.1.2 (Wyatt Technology).

2.7. Rheological test

The rheological properties of peach gums, prepared by different extraction methods, were determined at 25 °C with a HAAKE RheoStress 6000 rheometer (Thermo, USA) using a cone-plate (C60/1, Thermo Fisher Scientific, USA). A shear rate range of from 0.1 to 100 s^{-1} , with a 0.052 mm gap, was used to evaluate the flow behavior of peach gum solution at a concentration of 5% (w/v). Frequency sweep test was performed at 25 °C with a HAAKE RheoStress 6000 rheometer (Thermo, USA) using a parallel-plate (P60, Thermo Fisher Scientific, USA) with 1 mm gap. Prior to frequency sweep tests, the linear viscoelastic range was determined by strain sweep from 0.01% to 1000% at a constant frequency of 1 Hz. A strain of 5% (within linear viscoelastic range) was applied to peach gum solutions. The dynamic frequency sweep tests were conducted at 25 °C in the frequency range from 0.1 to 10 Hz at 5% strain to monitor the changing of storage modulus (G') and loss modulus (G'') of the samples. Rheological data acquisition and fitting were both conducted using RheoWin Job Manager and RheoWin Data Manager, respectively.

2.8. Effects of peach gums on the emulsion stability of whey protein isolate

2.8.1. Emulsion preparation

Whey protein isolate (WPI) at 2% (w/v) and peach gum and gum arabic (GA) stock solutions at 10% (w/v) were prepared in distilled water by dissolving under gentle stirring at room temperature for 24 h to ensure complete dissolution. Sample solutions were prepared by adding equal volume of distilled water or gum solutions to 2% (w/v) WPI with sufficient mixing. Sodium azide was used as antimicrobial agent in emulsion at a concentration of 0.02% (w/v). All the gum solutions were mixed with 50% (v/v) soybean oil (Qian et al., 2011) and homogenized using a FSH-2A homogenizer (Jiangyiyiqi, China) for 2 min at 17000 rpm. The final composition of the emulsions consisted of 5% (w/v) gum, 1% (w/v) WPI and 25% (v/v) soybean oil with the final pH of 6.85.

2.8.2. Centrifuge stability and storage stability

Centrifuge and storage stability measurements were conducted according to the method described previously (Naji-Tabasi & Razavi, 2016). The emulsions were centrifuged at 2000 g for 10 min (ZONKIA, China) immediately after preparation. The emulsion stability (ES) was calculated as:

$$ES = \frac{V_e}{V_t} \times 100 \quad (4)$$

where V_e is the emulsion volume, V_t is the total volume. All samples were prepared in duplicate.

For emulsion storage stability measurements, each emulsion was transferred into a test tube fitted with a cap, and stored at room temperature for 5 weeks. ES was calculated after storage according to Eq (4). All samples were prepared and tested in duplicate.

2.9. Statistical analysis

The data were expressed as the mean \pm standard deviation (SD) with three replicates per sample. Statistical analysis involved use of the statistical analysis system software package (SPSS Statistics 17.0). The experimental data was evaluated by one-way analysis of variance (ANOVA) for a completely random design to determine the least significant difference at the level of $P < 0.05$.

3. Results and discussion

3.1. Preparation and purity of water-soluble peach gums

The yields of water-soluble peach gums, prepared by various methods, are showed in Fig. 1A. The yield of water extracted peach gum (WEPG) was 77.25%. The yields of alkaline extracted peach gum exhibited a tendency to first rise and then decline, and the highest yield was 82.60%, when it was extracted with 2.0 M NaOH (AEPG2.0). With extension of treatment time, the yields of H₂O₂ extracted peach gum showed a tendency similar to the alkaline extracted peach gum, showing the highest yield of peach gum was about 83.34% (HPPG8, extracted by H₂O₂ for 8 h). However, extraction with more than 2.0 M NaOH or extraction with H₂O₂ for 10 h afforded a reduced yield of peach gum, which might be associated with gum degradation caused by excessive alkali or H₂O₂. WEPG, AEPG2.0 and HPPG8 gave the highest yields under the different extraction methods and were used to study differences in physicochemical properties. Curves of WEPG, AEPG2.0 and HPPG8 all showed a single symmetrical peak (Fig. S1 A–C) by SEC chromatography suggesting each were homogeneous polysaccharide preparation of good purity and without protein components (Fig. S1 D–F).

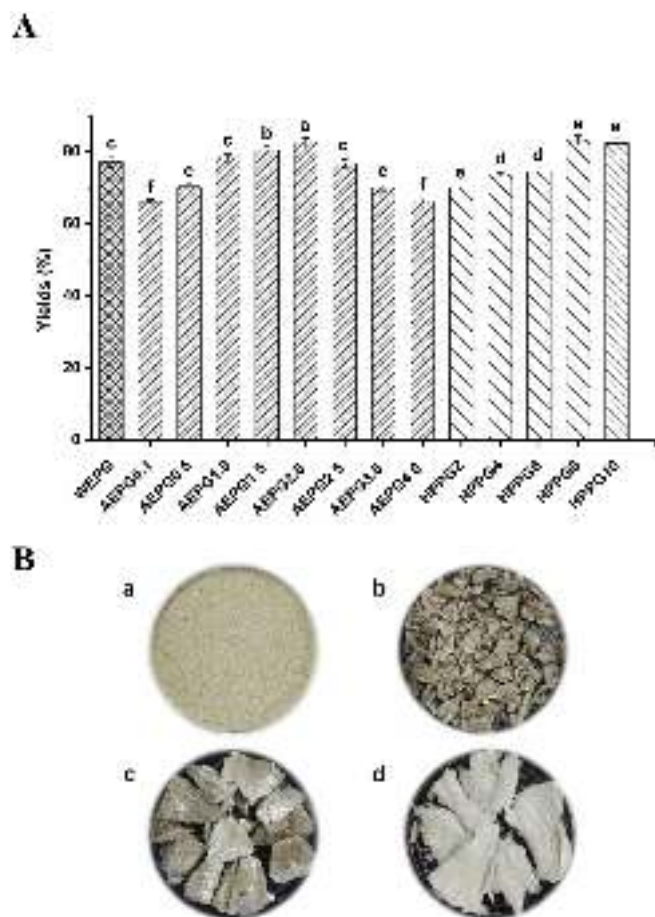


Fig. 1. (A) The yields of water-soluble peach gums extracted via different methods. WEPG: peach gum extracted by water; AEPG2.0: peach gum extracted by 2.0 M NaOH; HPPG8: peach gum extracted by H₂O₂ for 8 h. (B) Appearance of peach gums. (a) Raw peach gum powder, (b) WEPG, (c) AEPG2.0 and (d) HPPG8. Data are mean \pm standard deviation (SD) (n = 3). Letters indicate differences ($P < 0.05$) among samples.

3.2. Color measurement

The color parameters of the peach gum solutions are presented in Table S1. HPPG8 solution had the highest *L*, lowest values of *a* and *b* compared to WEPG and AEPG 2.0. Color functions such as ΔE , WI and YI indicate the degree of total color difference from the standard white plate ($L^* = 75.08 \pm 0.15$, $a^* = -1.17 \pm 0.03$, $b^* = 0.72 \pm 0.03$), the degree of whiteness and the degree of yellowness, respectively. HPPG8 possessed the optimal values of ΔE , WI and YI better than WEPG and AEPG 2.0 (Table S1), suggesting that HPPG8 could provide with better appearance ($P < 0.05$). These results were also in accordance with direct visual observations (Fig. 1B).

3.3. Monosaccharide composition

Results showed that WEPG, AEPG2.0 and HPPG8 had similar monosaccharide compositions, which consisted of mannose, rhamnose, glucuronic acid, glucose, galactose, xylose and arabinose in various proportions (Table 1). The compositions obtained were very similar to other gum exudates secreted from Rosaceae plants, such as nectarine gum (*Prunus persica* var. *nucipersica* Schneid.) (Simas-Tosin et al., 2009), peach gum (*Prunus persica* Batsch.) (Qian et al., 2011; Simas et al., 2008), and almond gum (*Prunus amygdalus* Batsch.) (Bouaziz et al., 2015). Galactose and arabinose were the predominant monosaccharide components without significant content differences in WEPG, AEPG2.0 and HPPG8, suggesting that they were arabinogalactan-type polysaccharides.

3.4. Analysis of infrared (FT-IR) spectroscopy

The FT-IR spectra of WEPG, AEPG2.0 and HPPG8 are presented in Fig. 2. The typical major broad bands around 3388–3397 cm^{-1} were assigned to stretching vibration of OH, and the peaks at 2926–2930 cm^{-1} were assigned to C–H stretching vibration. The peaks 1638–1634 cm^{-1} and 1423–1419 cm^{-1} were assigned to symmetrical and asymmetrical stretching vibration of the carboxyl groups (COO^-) (Zhang, Zhang, Liu, Ding, & Ye, 2015). There was no band at 1745 cm^{-1} , which could be attributed to carbonyl ester (C = O) groups (Alba, Laws, & Kontogiorgos, 2015), indicating the absence of methyl-esterified glucuronic acids in WEPG, AEPG2.0 and HPPG8.

In the fingerprint region of 1200–800 cm^{-1} , the peaks at 1159–1151 cm^{-1} were assigned to the vibrations of C–O–C glycosidic bonds (Chen et al., 2015). The peaks at 1084–1072 cm^{-1} are characteristic of β -galactan, while the peaks at 1040–1036 cm^{-1} are characteristic for arabinans (Kacurakova, Capek, Sasinkova, Wellner, & Ebringerova, 2000), indicating the presence of arabinogalactan type of polysaccharide. Moreover, the absorptions at 845–833 cm^{-1} and 901–897 cm^{-1} suggest the presence of both α - and β -configurations of aldopyranoses (Kacurakova et al., 2000). The bands around 778–776 and 710 cm^{-1} indicate the presence of furan ring (Shan et al., 2015).

3.5. Molecular properties of peach gums

Number-average molecular weight (*M_n*), weight-average molecular weight (*M_w*), Z-average molecular weight (*M_z*), root mean square radius (*R_g*), polydispersity (*M_w/M_n*) and chain conformation (rod-like chain, random coils or sphere) are important structural properties of polysaccharides. Molecular weight data in Table 2 show that WEPG, AEPG2.0 and HPPG8 vary considerably in molecular weight ($P < 0.05$), at 1.34×10^7 g/mol, 1.64×10^7 g/mol and 5.17×10^6 g/mol, respectively. The molecular weights of other Rosaceae gums, including nectarine gum (*Prunus persica* var.

Table 1
Monosaccharide compositions of peach gums with different extraction methods ^a.

Samples	Monosaccharide (mole %)						
	Mannose	Rhamnose	Glucuronic acid	Glucose	Galactose	Xylose	Arabinose
WEPG	3.14 ± 0.07 ^b	0.76 ± 0.04 ^a	3.24 ± 0.09 ^a	1.04 ± 0.05 ^b	34.35 ± 0.50 ^a	7.32 ± 0.20 ^a	50.15 ± 0.74 ^a
AEPG2.0	3.08 ± 0.06 ^b	0.73 ± 0.03 ^{ab}	3.08 ± 0.06 ^a	1.54 ± 0.10 ^a	34.95 ± 0.80 ^a	7.20 ± 0.10 ^a	49.41 ± 1.50 ^a
HPPG8	3.69 ± 0.10 ^a	0.65 ± 0.03 ^b	3.13 ± 0.17 ^a	1.46 ± 0.15 ^a	35.03 ± 0.60 ^a	6.25 ± 0.25 ^b	49.80 ± 1.00 ^a

^a Values are mean ± SD (n = 3). Different superscript letters within rows indicate differences ($P < 0.05$) among samples.

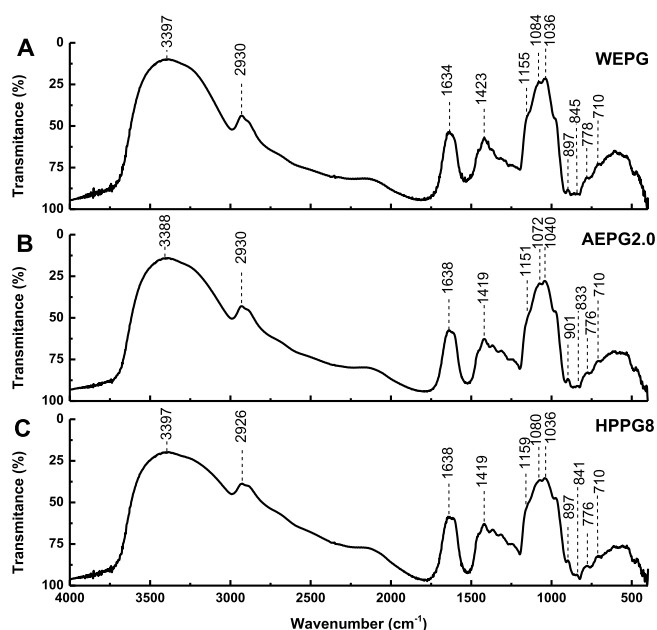


Fig. 2. FT-IR spectra of peach gums. (A) WEPG, (B) AEPG2.0 and (C) HPPG8.

Table 2
Molecular and conformation parameters of peach gums with different extraction methods ^a.

Parameters	Samples		
	WEPG	AEPG2.0	HPPG8
M_n (g/mol)	$6.10 \pm 1.78 \times 10^{6b}$	$7.47 \pm 1.80 \times 10^{6a}$	$2.18 \pm 0.61 \times 10^{6c}$
M_p (g/mol)	$8.37 \pm 1.28 \times 10^{6b}$	$1.18 \pm 1.66 \times 10^{7a}$	$3.24 \pm 0.88 \times 10^{6c}$
M_w (g/mol)	$1.34 \pm 3.18 \times 10^{7b}$	$1.64 \pm 3.48 \times 10^{7a}$	$5.17 \pm 1.70 \times 10^{6c}$
M_w/M_n	2.20 ± 0.10^{ab}	2.12 ± 0.15^b	2.37 ± 0.07^a
$R_{g,z}$ (nm)	193.8 ± 1.00^b	215.8 ± 1.00^a	114.3 ± 0.90^c
$R_{h,z}$ (nm)	112.80 ± 1.43^b	126.00 ± 1.66^a	82.05 ± 0.93^c
$[\eta]$ (dL/g)	3.58 ± 0.18^a	3.75 ± 0.09^a	2.95 ± 0.16^b
ν	0.48 ± 0.01^a	0.46 ± 0.01^a	0.48 ± 0.01^a
α	0.34 ± 0.004^b	0.37 ± 0.001^b	0.50 ± 0.003^a

^a Values are mean ± SD (n = 3). Different superscript letters within rows indicate differences ($P < 0.05$) among samples.

nucipersica Schneid.) 3.93×10^6 g/mol (Simas-Tosin et al., 2009), peach gums (*Prunus persica* Batsch.) 4.60×10^6 g/mol and 5.61×10^6 g/mol (Qian et al., 2011; Simas et al., 2008), almond gum (*Prunus amygdalus* Batsch.) 9.93×10^4 g/mol (Bouaziz et al., 2015) and zedo gum (*Amygdalus scoparia*) 4.74×10^6 g/mol (Fadavi, Mohammadifar, Zargarran, Mortazavian, & Komeili, 2014) have been reported.

Polysaccharides are generally heterogeneous and polydisperse having a range of molecular weights. The polydispersity coefficient (M_w/M_n) of WEPG, AEPG2.0 and HPPG8 were 2.20, 2.12 and 2.37, respectively (Table 2). Revealing that all the gums prepared were polydisperse polymers with a wide molecular weight distribution.

HPPG8 showed the greatest polydispersity ($P < 0.05$), which might be attributable to its degradation by hydrogen peroxide during the extraction process, resulting in a large number of chain fragments having different molecular weights.

3.6. Conformation of peach gums

Macromolecular polysaccharides are long chain molecule and can often curl into coils in the absence of external forces. Differences in the composition, structure and chain length, of these macromolecular polysaccharides can result in varying degrees of coiling, and represent unique properties and a major factor in determining the morphology of these macromolecules.

The root mean square radius ($R_{g,z}$) refers to the mass distribution of molecular barycenter and can be applied to characterize the size of molecular chain. For ideally flexible macromolecules, the molar mass is proportional to its $R_{g,z}$. The values of $R_{g,z}$ of WEPG, AEPG2.0 and HPPG8 were 193.8 nm, 215.8 nm and 114.3 nm, respectively (Table 2). HPPG8 gave the smallest particle size, corresponding to the lowest M_w . Moreover, for macromolecules with $R_{g,z} > 10$ nm, the relationship between $R_{g,z}$ and M_w ($R_{g,z} = kM_w^\nu$) provides conformation information. The slopes (ν) of $\log R_{g,z}$ vs. $\log M_w$ were 0.33, 0.5–0.6 and 1, reflecting molecular shapes of a sphere, random coil, and rigid rod, respectively (Burchard, 1999). The slope (ν) values for WEPG, AEPG2.0 and HPPG8 are 0.48, 0.46 and 0.48, respectively (Fig. 3), indicating that in solution WEPG, AEPG2.0 and HPPG8 are highly-branched macromolecules, with relatively compact conformations close to that of a random coil.

3.7. $[\eta]$ and conformation of peach gums

R_h and $[\eta]$ are important factors in investigating the chain conformations of WEPG, AEPG2.0 and HPPG8 in 0.2 M NaCl solutions. The sizes of $R_{h,z}$ of WEPG, AEPG2.0 and HPPG8 are markedly different ($P < 0.05$), 112.8 nm, 126.0 nm and 82.1 nm, respectively, which is proportional to their $[\eta]$ values, 3.58 dL/g, 3.75 dL/g and 2.95 dL/g, respectively (Table 2). These results differ from the $[\eta]$ values of previous studies: aqueous extracts (AE) of peach gum at 1.95 dL/g (Simas-Tosin et al., 2010) and alkaline extractable fractions, AE01 at 21.18 dL/g and AE05 at 21.76 dL/g (Qian et al., 2011). The Mark-Houwink-Sakurada equation ($[\eta] = KM^\alpha$) was used to evaluate the relationship between intrinsic viscosity ($[\eta]$) and molecular weight (M_w) (Robinson, Rossmurphy, & Morris, 1982). A characteristic constant, α , with values of 0, 0–0.3, 0.5–0.8, 1 and 1.8–2 indicate a polymer is in a sphere, compacted coil, flexible chain, semi-flexible chains and rod-like rigid chain, respectively (Burchard, 1999; J.; Wang & Zhang, 2009). The Mark-Houwink-Sakurada equations of WEPG, AEPG2.0 and HPPG8 were established in Fig. 3 as $[\eta] = 1.23M_w^{0.34}$ (mL/g), $[\eta] = 7.45 \times 10^{-1}M_w^{0.37}$ (mL/g), $[\eta] = 9.70 \times 10^{-2}M_w^{0.50}$ (mL/g), respectively. The exponent (α) of WEPG and AEPG2.0 were 0.34 and 0.37, reflecting that they behaved as compacted coils in 0.2 M NaCl solution due to their high molecular weight and branched structures. The exponent (α) of HPPG8 was 0.50, indicated it was a loosely compacted coil close to a

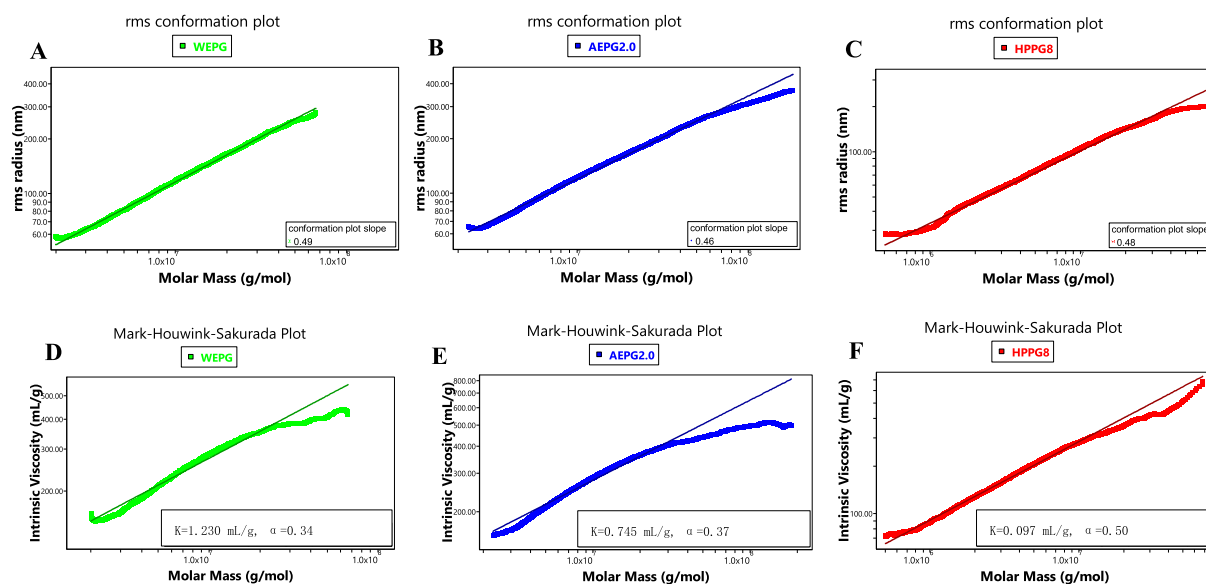


Fig. 3. Conformation plots of WEPG, AEPG2.0 and HPPG8 in 0.2 M aqueous NaCl solution at 25 °C. A, B and C were plots of WEPG, AEPG2.0 and HPPG8 from the relationship between R_g and M_w . D, E and F were Mark-Houwink-Sakurada plots of WEPG, AEPG2.0 and HPPG8 from the relationship between $[\eta]$ and M_w .

random coil.

The M_w of HPPG8 (5.17×10^6 g/mol) was about one-third of that of AEPG2.0 (1.64×10^7 g/mol), but the intrinsic viscosity of HPPG8 (2.94 dL/g) did not proportionally correspond to the intrinsic viscosity of AEPG2.0 (3.75 dL/g). Differences in their chain conformation might be responsible for these differences. HPPG8 is a random coil in 0.2 M NaCl solution and easily forms a network structure. Therefore, the interaction between HPPG8 molecules is greater than the interactions between the spherical chains of AEPG2.0 molecules, resulting in the marked increase in the intrinsic viscosity of HPPG8. The findings are consistent with the results described above.

3.8. Rheological properties

3.8.1. Flow behavior of peach gums

The flow behavior profiles of the three peach gums all display non-Newtonian shear-thinning behavior as illustrated in Fig. 4A (Vriesmann, Silveira, & Petkowicz, 2009). WEPG, AEPG2.0 and HPPG8 have the characteristics of a pseudoplastic fluid, in general agreement with previous literature (Qian et al., 2011; Simas-Tosin et al., 2010). There are chain entanglements between macromolecular chains, including physical entanglements and entanglements nodes generated by the interactions between molecular chains. Increasing shear rate and reducing entanglements nodes lead to a significant decrease in apparent viscosity, thus, resulting in shear thinning. The orientations of the molecular chains are another reason for the shear-thinning of peach gum solutions. Generally, the viscosity of flexible chain polymers decreases with the increase of shear rate, which is more obvious than the viscosity changes of rigid chain polymers. WEPG, AEPG2.0 and HPPG8 are flexible chains and possess shear-thinning behavior. Their apparent viscosity is positively correlated with their molecular weight. Thus, the order of apparent viscosities for the three peach gums at 5% (w/v) were AEPG2.0 > WEPG > HPPG8.

The power law and Cross model (Table 3) were adopted to fit the Cross relaxation time (τ)-shear rate ($\dot{\gamma}$) profiles and viscosity-shear rate profiles to provide a reasonable representation of the shear-thinning fluid (Gratao, Silveira, & Telis-Romero, 2007; Nwokocho & Williams, 2014). The m and n values refer to the consistency

index and flow index in the power law (Ostwald-de Waele) model: $\tau = m\dot{\gamma}^n$. Their values for different peach gums at 5% (w/v) and are presented in Table 3. The rate index (n) is a measure of the degree of dependence of viscosity on shear rate in the shear-thinning region for polysaccharide solution. These results also indicate that both m and n values of HPPG8 are significantly ($P < 0.05$) different from those of other samples, and HPPG8 possesses lower viscosity and better fluidity. Cross model parameters further showed that zero shear viscosity (η_0) of HPPG8 (0.27 Pa s) at 5% (w/v) is much lower ($P < 0.05$) than that of the other two peach gums at the same concentration. These results were also in agreement with their intrinsic viscosity and apparent viscosity.

3.8.2. Viscoelastic behavior of peach gums

The frequency sweeps of 5% (w/v) peach gum solutions are illustrated in Fig. 4B. The viscoelastic behavior of all peach gum solutions exhibits a typical macromolecule behavior. At low angular frequency range, all peach gum solutions exhibit loss modulus (G'') dominance, while, at high angular frequency, they exhibit storage modulus (G') dominance. The crossover points for WEPG, AEPG2.0 and HPPG8 were at frequency of 6.83 rad/s, 7.86 rad/s and 51.25 rad/s, respectively. An entanglement network system showing G'' and G' curves intersecting at the middle of the frequency range, indicate a clear tendency for more solid-like behavior at higher frequencies (Ross-Murphy, 1994). Therefore, the G' and G'' moduli of AEPG2.0 are larger than those of WEPG and HPPG8, and are proportional to their molecular weight, indicating that more molecular chain entanglement has occurred, leading to increased viscoelastic properties (Wang & Lu, 2014). Because peach gum solutions are able to move slowly even under low shear forces and glide along each other, these entanglements likely result from mechanical interactions, rather than from chemical or physical-chemical bonds.

3.9. Effect of peach gums on emulsion stability of WPI

After preparation, the final composition of the emulsions consisted of 5% (w/v) gum, 1% (w/v) WPI and 25% (v/v) soybean oil with the final pH of 6.85. The emulsion centrifuge stability (ES) (Fig. 5A) of WPI was 60.13%, and the ES of WPI-GA, WPI-AEPG2, WPI-WEPG

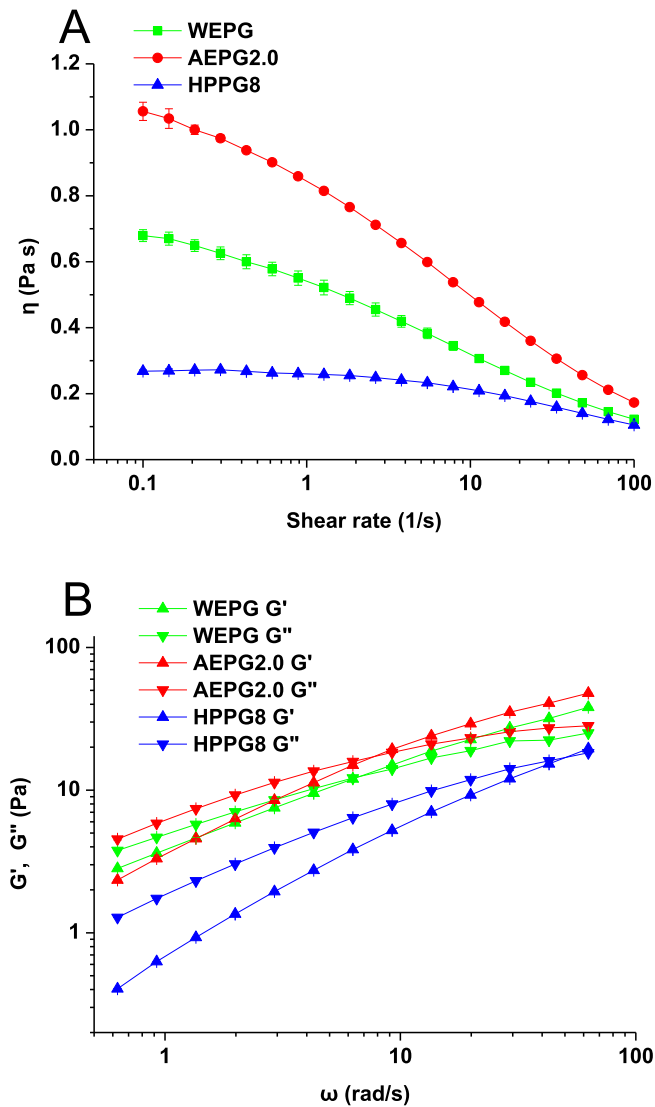


Fig. 4. Rheological properties of WEPG, AEPG2.0 and HPPG8. (A) Shear rate profiles of peach gums at 5% (w/v), (B) Frequency sweep tests of peach gums at 5% (w/v).

and WPI-HPPG8 were 61.67%, 95.42%, 80.91% and 66.67%, respectively. All of the three peach gums (5% w/v) significantly ($P < 0.05$) enhanced the ES of WPI, and the AEPG2 displayed the best ES. The various ES of gum-protein complexes might be mainly attributable to the viscosity of the emulsion solutions. AEPG2 (5% w/v) had higher viscosity than WEPG (5% w/v) and HPPG8 (5% w/v) (Fig. 4A), and these viscosities directly depend on their molecular weights (Table 2). The higher viscosity of peach gums in emulsions result from the enhanced interaction between WPI and AEPG2, which increases the emulsion stability of WPI.

Table 3

Power law parameters and Cross model parameters for peach gum solutions 5% (w/w) in deionized water^a.

Samples	Power law ($\tau = m\dot{\gamma}^n$)			Cross			
	m (Pa s)	n	R^2	η_0 (Pa s)	$\dot{\gamma}_\beta$	n	R^2
WEPG	0.78 ± 0.02^b	0.60 ± 0.01^{ab}	0.99	0.77 ± 0.05^b	6.55 ± 0.15^b	0.51 ± 0.01^b	0.99
AEPG2.0	1.30 ± 0.10^a	0.57 ± 0.02^b	0.99	1.18 ± 0.20^a	7.92 ± 0.10^b	0.51 ± 0.01^b	0.99
HPPG8	0.44 ± 0.03^c	0.70 ± 0.08^a	0.99	0.27 ± 0.08^c	42.85 ± 1.53^a	0.81 ± 0.10^a	0.99

^a Values are mean \pm SD ($n = 3$). Different superscript letters within rows indicate differences ($P < 0.05$) among samples.

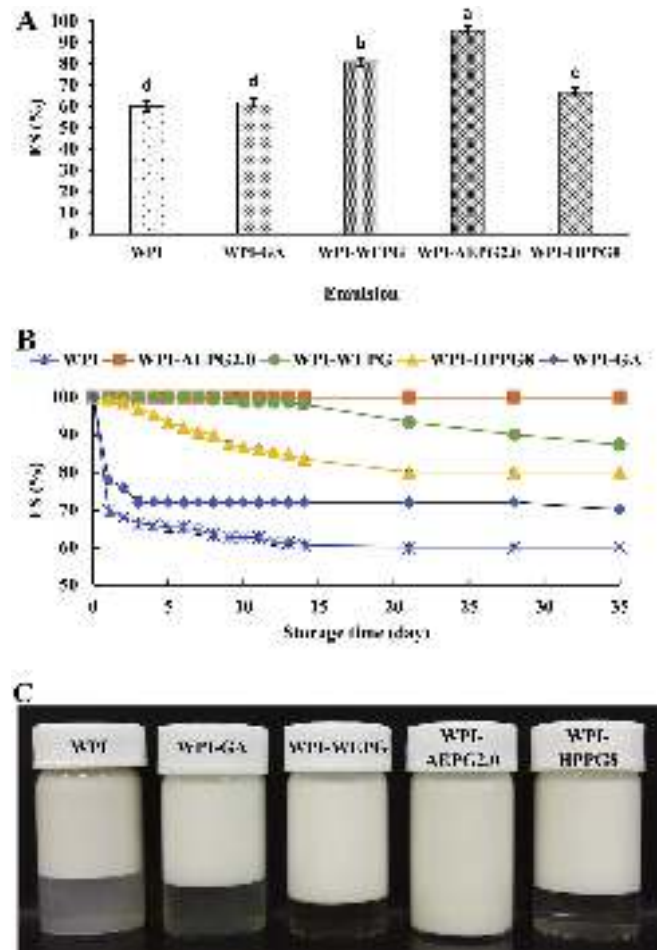


Fig. 5. Effects of peach gums on the stability of whey protein isolate (WPI) stabilized oil-water emulsions. (A) Centrifuge stability of WPI emulsions stabilized with peach gums, (B) Storage stability of WPI emulsions stabilized with peach gums at 25 °C in 5 weeks, (C) Appearance of WPI emulsions stabilized with peach gums and gum Arabic after storage for 5 weeks at 25 °C. Data are mean \pm standard deviation (SD) ($n = 3$). Letters indicate differences ($P < 0.05$) among samples.

The effects of peach gums on the emulsion storage stability of WPI were studied over a 5-week period to further understand the behavior of emulsions (Fig. 5B). All of emulsions were composed of 5% (w/v) gum, 1% (w/v) WPI and 25% (v/v) soybean oil with pH of 6.85 in the final composition. The emulsion storage stability over 5 weeks result in the order WPI-AEPG2>WPI-WEPG>WPI-HPPG8>WPI-GA>WPI. The emulsion containing only WPI exhibited a rapid phase separation within 24 h, and a slow phase separation in 2 weeks, and then tended to be stable thereafter. The emulsion with WPI-GA exhibited a rapid phase separation in 3 days, and then tended to be stable. The emulsion with WPI-HPPG8 revealed a slow phase separation within 3 weeks. The WPI-WEPG emulsion was stable for a week, showed only a slight phase

separation within the second week, and then a linear change in phase separation from the third week. The emulsion with WPI-AEPG2 was most stable and no phase separation was observed over 5 weeks. Emulsions with gum-protein complexes were more stable than the emulsion containing only WPI, consistent with the results of centrifuge stability. These results indicate that peach gums could significantly ($P < 0.05$) enhance the emulsion stability of WPI.

Whey protein isolate is a nutritional ingredient and a surface-active protein. It can adsorb on the surface of oil droplets and prevent the droplets from aggregating (Sun, Gunasekaran, & Richards, 2007). Therefore, WPI has been widely applied in the formation and stabilization of food emulsions. Previous studies reported that several gums, including gum arabic (Klein, Aserin, Svitov, & Garti, 2010), pure gum (Li, Li, Shen, Niu, & Fu, 2016), xanthan gum/enzyme-modified guar gum mixtures (Chityala, Khouryeh, Williams, & Conte, 2016), had the ability to further enhance the stability of WPI stabilized oil-water emulsions. The main factors contributing to the stabilizing action of polysaccharides in these emulsions are viscosity enhancement or gelation, which can precipitate/adsorb onto oil droplets and sterically stabilize dispersed particles or droplets in the emulsions against flocculation and coalescence (Dickinson, 2003). According to our observation, the ability of peach gums to enhance the stability of WPI stabilized oil-water emulsion directly depended on their molecular weight. The higher molecular weight of peach gum resulted in the higher viscosity of emulsion and greater emulsion stability. In addition, all of the three peach gums have compacted coil structure, which may easily form a secondary protective layer adsorbing on the WPI droplets surface (Salminen & Weiss, 2014). Thus, with their higher viscosity and more compact coil structures, peach gums were able to improve the emulsion stability of WPI.

4. Conclusion

The yields of WEPG, AEPG2.0 and HPPG8 were 77.3%, 82.6% and 83.3%, when prepared by hot water extraction, alkaline extraction and H_2O_2 extraction, respectively. Color measurements showed that the WI of three peach gum solutions were $HPPG8 > AEPG2.0 > WEPG$. These gums had similar chemical compositions, consisting of mannose (3.08–3.69%), rhamnose (0.65–0.76%), glucuronic acid (3.08–3.24%), glucose (1.04–1.54%), galactose (34.35–35.03%), xylose (6.25–7.32%) and arabinose (49.41–50.15%). The molecular weights of WEPG, AEPG2.0 and HPPG8 were 1.34×10^7 g/mol, 1.64×10^7 g/mol and 5.17×10^6 g/mol, respectively, and were proportional to their $[\eta]$ values, 3.58 dL/g, 3.75 dL/g and 2.94 dL/g, respectively. These gums behaved as compact coils in 0.2 M NaCl solution.

WEPG, AEPG2.0 and HPPG8 at 5% (w/v) exhibit Non-Newtonian shear-thinning behavior, and the apparent viscosities of three peach gums followed the order $AEPG2.0 > WEPG > HPPG8$. The frequency sweeps of 5% (w/v) peach gums solutions exhibit typical macromolecular behavior with the viscous modulus (G'') dominating the elastic modulus (G') at the low angular frequency range, followed by the domination of elastic modulus at higher angular frequency. Emulsion stability results indicate that all of the three peach gums significantly ($P < 0.05$) enhance the emulsion stability of WPI. The emulsion with WPI-AEPG2 was more stable than those with WPI-WEPG, WPI-HPPG8 and WPI-AG, which are directly dependent on their molecular weight and viscosity. These results provide fundamental and useful data for further studies and for utilization of peach gum. Peach gum has good rheological properties and emulsion stability, and has great potential for the application in food industry.

Acknowledgments

This research was supported by the Key Research and Development Project of Zhejiang Province, China (2015C02036) and Public Welfare Project of Zhejiang Province, China (2015C32088).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.foodhyd.2018.03.049>.

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