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Structure-function relationship between galactomannans and their effects on freeze-thaw stability, retrogradation, and texture of corn starch gels during cold storage

Fan Xie[a,1], Chunmei Yuan[b,1], Hui Zhang[a], Yan Wu[c], Lianzhong Ai[a,*]

[a] Shanghai Engineering Research Center of Food Microbiology, School of Health Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China

[b] Yunnan Maodouli Group Food Co., Ltd., Yuxi 653100, China

[c] Department of Food Science & Technology, School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

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ABSTRACT

In this study, structural characteristics of Fenugreek (FG), Guar (GG), Locust bean (LBG), and Tara gums (TG) and their influence on physicochemical properties of corn starch (CS) gels were investigated. Results showed that FG presented a rigid rod structure, and GG, LBG, and TG showed an extended structure. The Mannose/Galactose (Man/Gal) ratio of FG, GG, LBG, and TG was 1.37, 1.96, 2.99, and 3.46, respectively. The molecular weight (M_w) of FG, GG, LBG, and TG was 0.89×10^6, 2.71×10^6, 3.61×10^6, and 2.77×10^6 Da, respectively. The structure–function relationship indicated that galactomannans with a high Man/Gal ratio and extended structure presented a higher apparent viscosity, formed gel more easily, and could limit retrogradation and improve freeze–thaw stability and textural profile of CS gels. Consequently, the results could be beneficial for the application of galactomannans in starch-based foods to improve their sensory characteristics and storage quality.

1. Introduction

In recent years, starch-based foods have become increasingly popular worldwide, including glue pudding and other starch foods. Pregelatinized starch in starch-based foods undergoes retrogradation, in which starch molecules rearrange. After retrogradation, the foods become firmer and the digestion rate is limited (Pongsawatmanit, Chantaro, & Nishinari, 2013). When starch-based foods are stored at −20 °C, freeze–thaw may induce dehydration, condensation, hardening, and sponging of starch gels. Currently, certain polysaccharides have been used to prevent the retrogradation and improve the freeze–thaw stability of starch gels.

Galactomannan is a polysaccharide that contains a mannose backbone and galactose side groups. Galactomannans are composed of (1 → 4)-β-D-mannopyranose backbone with varying amounts of single D-galactose substituents linked to the backbone by (1 → 6)-α-glycosidic bonds. There are several kinds of galactomannans used in food industry, such as Fenugreek gum (FG), Guar gum (GG), Locust bean gum (LBG), and Tara gums (TG). The ratio of galactose to mannose of these galactomannans was 1:1, 1:2, 1:2.5–3, and 1:3.5–4, respectively (Pawar & Lalitha, 2014). The ratio of galactose to mannose also determines certain properties of galactomannans such as water solubility, thickening ability, and synergistic interactions (Pawar & Lalitha, 2014). GG, LBG, and TG can be used as stabilizers in dairy products, frozen desserts, and ice cream to improve the appearance and textural profiles since they can bind free water and prevent ice crystal proliferation (Maity, Saxena, & Raju, 2018).

The use of galactomannans has been reported to improve freeze–thaw stability and prevent retrogradation of starch gels. Nawab, Alam, Haq, and Hasnain (2016) found GG could effectively reduce syneresis of mango kernel starch and improve gel firmness. Arocas, Sanz, and Fiszman (2009) found LBG reduced structural changes of native starch gel during freeze–thaw thus improving its stability. Moreover, monosaccharide composition, molecular weight, conformation, and rheological properties of galactomannans directly affect their physicochemical properties. However, the relationship between structural characteristics of galactomannans and their effect on freeze–thaw stability, retrogradation, and texture of starch gels is not yet clearly understood (Kim, Lee,

* Corresponding author at: University of Shanghai for Science and Technology, 516 Jungong Road, Shanghai 200093, China.
E-mail address: ailianzhong1@126.com (L. Ai).

[1] These authors contributed equally to this work.

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& Yoo, 2006).

Therefore, this study aimed to investigate the effects of structure and conformation of galactomannan from different sources (FG, GG, LBG, and TG) on the freeze–thaw stability, retrogradation, and textural properties of corn starch (CS) gels during cold storage. Also, structure–function relationship between galactomannans and their effects on the properties of CS gels was explored. The results may be useful for the improvement of the sensory characteristics and storage quality of starch-based food products.

2. Materials and methods

2.1. Materials and reagents

The FG, GG, LBG, and TG were purchased from Shanghai Yuanye Bio-Technology Co., ltd. Corn starch (CS) (amylose content 28 %, w/w) was provided by Ingredion, Inc. (Shanghai, China). Before analyzing, alcohol (90 %, v/v) was used to purify the galactomannans and the precipitate was collected and freeze-dried under vacuum at −60 °C for 48 h (FreeZone 6, Labconco Corporation, Kansas City, MO, USA).

2.2. Structural characteristics

2.2.1. HPSEC-MALLS analysis

A high-performance liquid chromatography (Agilent 1260 Infinity II HPLC) system including a multi-angle laser light scattering detector (MALLS, DAWN HELEOS-II), a refractive index (Optilab *T*-Rex, RI) detector, and a differential pressure viscometer (ViscoStar III, DP) (Wyatt Technology, Santa Barbara, CA, USA) was used to analyze molecular weights and conformational characteristics of the galactomannans. Galactomannan was dissolved in mobile phase (50 mM $NaNO_3$) with a concentration of 1.0 mg/mL. The flow rate was 0.6 mL/min and the column temperature was 40 °C. The DN/DC value was 0.145 mL/g.

2.2.2. Monosaccharide compositions

The galactomannans were dissolved in 3 M TFA at a concentration of 1.0 mg/mL, hydrolyzed at 120 °C for 3 h, and dried with nitrogen. Afterward, 5 mL of deionized water was added to dissolve the dried samples and diluted 10 times with deionized water. Then the solution was centrifuged at 12, 000 rpm for 5 min, and the supernatant was collected and passed through a 0.22 μm membrane for analysis (Zhang, Zhang, Liu, Ding, & Ye, 2015). Monosaccharide composition analysis was conducted using a high-performance anion-exchange chromatography system (HPAEC-PAD, Dionex ICS-5000, USA).

2.2.3. Atomic force microscopy

The galactomannans were dissolved in deionized water and diluted to a concentration of 1.0 μg/mL. A 5 μL of the solution was placed on a freshly cleaved mica and dried to form a thin film. The apparent morphology of the galactomannans was analyzed using a Dimension FastScan Bio AFM (Bruker, Germany) with a Si_3N_4 probe. The scan speed was set at 1.0 Hz (Xie, Zhang, Lan, Gong, Wu, & Wang, 2018).

2.3. Rheological properties of galactomannans solution

Viscosity of the galactomannans solution (1.0 % w/w) was determined in the shear rate range of 0.1 to 100 s^{-1}. Viscoelastic properties (storage modulus, G′ and loss modulus, G″) were determined in the range of 0.1 to 100 rad/s (1.0 Hz). These measurements were conducted using a rotary rheometer with a parallel plate geometry (40 mm) at 25 °C (Discovery, HR-3, TA instrument Inc., USA).

2.4. Freeze-thaw stability

After gelatinization, corn starch-galactomannans mixtures (10:1, w/w) were stored at −20 °C for 24 h, and then the samples were unfrozen at a 40 °C water bath for 4 h, this was called one freeze–thaw cycle. After 3 and 5 freeze–thaw cycles, respectively, the samples were centrifuged at 3000*g* for 5 min. Syneresis of the samples was calculated using equation (1):

$$\text{Syneresis} = \frac{W_0 - W_P}{W_0} \times 100\% \tag{1}$$

where W_0 was the weight of gelatinized pastes and W_p was the weight of precipitate, respectively (Ma, Zhu, & Wang, 2019).

2.5. Retrogradation analysis

After corn starch-galactomannans mixtures (10:1, w/w) were gelatinized and stored at 4 °C for 30 days, the starch gels were freeze-dried, smashed into powder, and passed through a 100 μm sieve. Approximately 10 mg of the powder was weighed in an aluminum pan and mixed with 20 mg of distilled water. The pan was heated from 30 to 90 °C at a rate of 5 °C/min using a differential scanning calorimetry (DSC) (DSC-214, NETZSCH, Germany). The enthalpy (ΔH) and transition temperatures were collected.

2.6. Textural profile analysis (TPA)

The gelatinized pastes were stored at 4 °C for 1 day and freeze-thawed for 5 cycles to form a solid or semi-solid state with a size of 1.5 × 2.0 cm (height × diameter). The texture profile of the samples was analyzed using a TA-XT Plus texture analyzer (Texture Technologies, Scarsdale, NY, USA) with the P/36R compression platen (36 mm diameter). The samples were compressed to 40 % of the original height and the test speed was set at 1.0 mm/s.

2.7. Low field-nuclear magnetic resonance (LF NMR)

Water distribution of corn starch-galactomannans mixture gels was analyzed using the LF NMR (Xie, Zhang, Xia, & Ai, 2020). The mixture gels (5 mL) were weighed into a test tube (stored at −20 °C for 24 h), and then the spin–spin relaxation time (T2) signals were recorded at 32 °C using an NMR analyzer (PQ001, Niumag Co., ltd., Shanghai, China).

2.8. Viscoelastic properties of CS-galactomannans mixture pastes

Viscoelastic properties (G′ and G″) of corn starch-galactomannans mixture pastes were determined in the angular frequency range of 0.1 to 100 rad/s (1.0 Hz) with the rotary rheometer at 50 °C. Afterward, the storage modulus (G′) of the pastes was collected with an angular frequency at 10 rad/s during the cooling process from 50 to 5 °C (5 °C/min).

2.9. Scanning electron microscope (SEM)

After the texture analysis, the starch gels were cut into a slice (0.1 mm) and placed on a specimen holder. Then liquid nitrogen was used to quickly quench and freeze-dry the samples. Microstructure of the samples was analyzed using scanning electron microscopy (VEGA3, TECAN, Czech).

2.10. Statistical analysis

All the data were listed as mean ± standard deviation (SD) ($n \geq 2$) in this study. SPSS software (SPSS for Windows, 16.0, 2007, SPSS Inc., USA) was used to conduct Pearson's correlation (r) and significant difference analysis (Tukey test).

3. Results and discussion

3.1. Molecular weight and conformational characteristics

Molecular weight and conformational characteristics of FG, GG, LBG, and TG are presented in Fig. 1(AB) and Table 1. The M_n of FG, GG, LBG, and TG were 0.80 × 10^6, 2.37 × 10^6, 3.52 × 10^6, and 2.43 × 10^6 Da, respectively. The M_w of FG, GG, LBG, and TG was 0.89, 2.71, 3.61, and 2.77 × 10^6 Da, respectively. The M_n and M_w of GG, LBG, and TG were higher than those of FG ($P < 0.05$). The M_w range for galactomannans evaluated herein was similar with that reported by Gillet et al. (2017). Polydispersity indexes (PDI) of FG, GG, LBG, and TG were 1.13, 1.15, 1.03, and 1.14, respectively, suggesting that the galactomannans had a narrow M_w distribution (Cui et al., 2020; Zhang, Zhang, Liu, Ding, & Ye, 2015). The R_{hz} values of FG, GG, LBG, and TG were 72.01, 101.3, 111.6, and 100.2 nm, respectively. The R_{gz} values of FG, GG, LBG, and TG were 80.00, 152.00, 170.40, and 151.45 nm, respectively, which is consistent with molecular size values of polysaccharides reported by Sébastien, Christophe, Mario, Pascal, Michel, and Aurore (2014). The R_{hz} and R_{gz} values of GG, LBG, and TG were higher than those of FG, which could be due to the more branched structure of FG decreased its molecular size in solution. The $[\eta]_w$ (intrinsic property) refers to the shape and volume of a polymer in solution, and a larger $[\eta]_w$ value reflects an extended rigid chain of a polymer (Huang, Huang, Li, and Zhang, 2009; Wu et al., 2014). The $[\eta]_w$ values of FG, GG, LBG, and TG were 1649.88, 2047.95, 2356.09, and 1944.59 mL/g, respectively, indicating that galactomannans possess a semi-flexible chain (Ma, Wang, & Zhang, 2008). Moreover, the structure of GG, LBG, and TG was more extended than that of FG, and LBG had the most remarkable extended structure in solution.

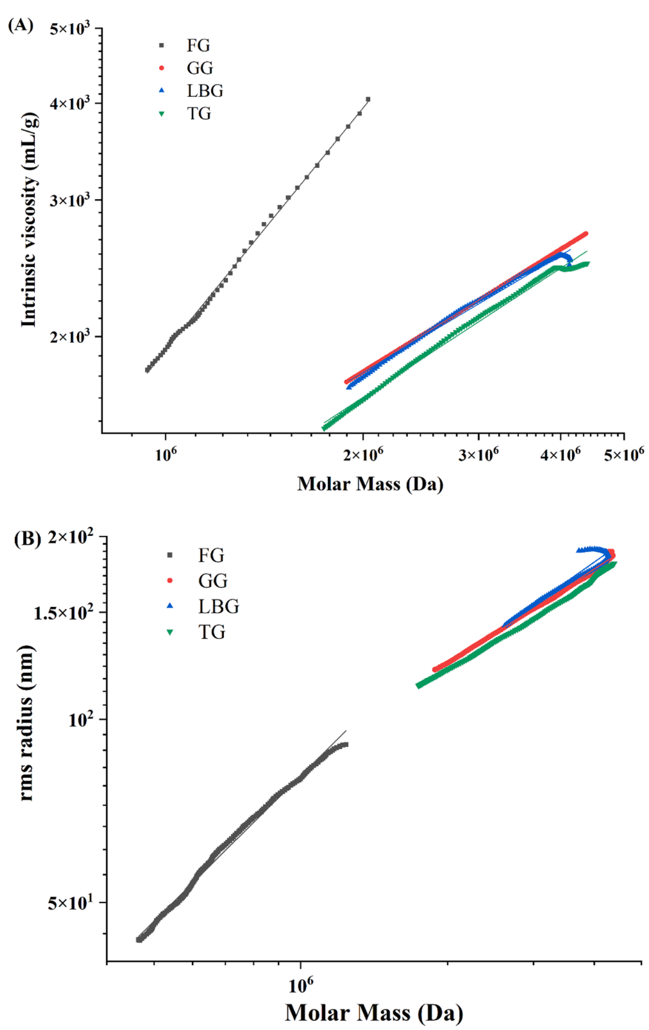

Fig. 1. Structural and conformational characteristics of the galactomannans. (A), the Mark-Houwink-Sakurada; (B) the Power-law plots.

Table 1
Structural and conformational characteristics, monosaccharide composition, and power law parameters of the galactomannans.

	FG	GG	LBG	TG
Structural and conformational characteristics				
M_n (×10^6 Da)	0.80 ± 0.24[c]	2.37 ± 0.11[b]	3.52 ± 0.13[a]	2.43 ± 0.17[b]
M_w (×10^6 Da)	0.89 ± 0.20[c]	2.71 ± 0.09[b]	3.61 ± 0.13[a]	2.77 ± 0.17[b]
PDI = (M_w/M_n)	1.13 ± 0.08[a]	1.15 ± 0.01[a]	1.03 ± 0[b]	1.14 ± 0.01[a]
R_{hz} (nm)	72.01 ± 6.44[c]	101.32 ± 1.29[b]	111.58 ± 2.49[a]	100.20 ± 2.76[b]
R_{gz} (nm)	80.00 ± 12.16[c]	152.00 ± 4.53[b]	170.40 ± 1.13[a]	151.45 ± 2.33[b]
$[\eta]_w$ (mL/g)	1649.88 ± 353.62[c]	2047.95 ± 50.08[b]	2356.09 ± 65.93[a]	1944.59 ± 88.85[b]
α_s	0.93 ± 0.07[a]	0.49 ± 0.03[b]	0.55 ± 0.02[b]	0.50 ± 0.00[b]
α_η	0.92 ± 0.17[a]	0.56 ± 0.01[b]	0.51 ± 0.04[b]	0.55 ± 0.02[b]
Monosaccharide compositions (mg/L)				
Gal	4.08 ± 0.03[a]	8.01 ± 0.38[b]	6.38 ± 0.37[c]	5.50 ± 0.09[d]
Man	5.59 ± 0.76[c]	15.72 ± 0.13[b]	19.06 ± 1.49[a]	19.01 ± 0.71[a]
Man/Gal	1.37	1.96	2.99	3.46
Power law parameters (1.0 % w/w at 25 °C)				
k (Pa·s^n)	0.03 ± 0.00[d]	2.63 ± 0.48[b]	1.50 ± 0.16[c]	5.81 ± 1.59[a]
n	0.55 ± 0.03[a]	0.48 ± 0.00[b]	0.49 ± 0.01[b]	0.40 ± 0.01[c]
R^2	0.99	0.99	0.99	0.99

Note: FG, Fenugreek gum; GG, Guar gum; LBG, Locust bean gum; TG, Tara gum. Different letters in each row presented a significant difference ($P < 0.05$).

The Mark-Houwink-Sakurada equation ($[\eta] = k\,M_w^{\alpha_\eta}$) and the Power-Law equation ($R_g = k\,M_w^{\alpha_s}$) are usually used to reflect conformation of polymer in solution. According to exponent α_η and α_s values, the conformation can be described as a globular chain shape (α_η 0.22, α_s 0.33), a semi-flexible chain (α_η 0.5–0.8, α_s 0.40–0.60), and rigid rods (α_η 1–2, α_s 1.0), respectively (Guo et al., 2020; Xu et al., 2021). Therefore, conformational behaviors of GG (α_η 0.56, α_s 0.49), LBG (α_η 0.51, α_s 0.55), and TG (α_η 0.55, α_s 0.50) in solution were identified as a semi-flexible chain. Conversely, FG (α_η 0.92, α_s 0.93) showed a rigid rod structure in solution, which could be attributed to a highly branched structure of FG.

3.2. Monosaccharide compositions analysis

Monosaccharide composition analysis of FG, GG, LBG, and TG is presented in Table 1. Gal and Man were detected in FG, GG, LBG, and TG. Gal content of FG, GG, LBG, and TG was 4.08, 8.01, 6.38, and 5.50 mg/L, respectively. The Man content of FG, GG, LBG, and TG was 5.59, 15.72, 19.06, and 19.01 mg/L, respectively. Different galactomannans have varying molar ratios of galactose to mannose (Man/Gal ratio), which is the key factor determining chemical properties of galactomannans (Prajapati et al., 2013). The Man/Gal ratio of FG, GG, LBG, and TG was 1.37, 1.96, 2.99, and 3.46, respectively. The Man/Gal ratio of FG, GG, LBG, and TG is reportedly within the range of 1.0:1.0–1.1, 1.0:1.6–1.8, 1.0:3.0, and 1.0:3.9–4.0, respectively. The Man/Gal ratio of GG, LBG, and TG in this study was similar with previously reported values (Liu, Lei, He, Xu, & Jiang, 2020). Further, the Man/Gal ratio of FG was lower than that reported in the literature (Srivastava & Kapoor, 2005), which could be due to FG obtained from different cultivars might possess different Man/Gal ratios.

3.3. Rheological properties analysis of galactomannans solution

3.3.1. Steady shear properties

Flow curves of FG, GG, LBG, and TG solution (1.0 %, w/w) are shown in Fig. 2(A). The viscosity of the galactomannans solution decreased with the shear rate increases, which can be defined as the non-Newtonian fluid behavior. The viscosity of TG solution was significantly higher than that of FG, GG, and LBG solution ($P < 0.05$). Also, the viscosity of GG solution was slightly higher than that of LBG solution, and FG solution had the lowest viscosity.

The behavior of FG, GG, LBG, and TG solutions was in line with previous studies (Liu, Chang, Chen, Xu, Ma, & Zhong, 2020). Gadkari, Tu, Chiyarda, Reaney, and Ghosh (2018) also found that, at the same concentration, the apparent viscosity of GG solution was higher than that of FG solution. Shear-thinning behavior of TG, GG and LBG solution at low shear rate could be due to dis-entanglement of polysaccharide chains in solution or orientation of polysaccharide coils in the direction of flow during shear (Wei, Lin, Xie, Xu, Yao, & Zhang, 2015; Wu, Ding, Jia, & He, 2015), indicating that TG, GG, and LBG molecules could easily entangle other molecules in solution to achieve a certain viscosity (Wu, Ding, Jia, & He, 2015).

The TG has a larger number of hydroxyl groups, which can form hydrogen bonds to increase solution viscosity (Wu, Ding, Jia, & He, 2015). With more galactose substitution, the formation of intermolecular hydrogen bonds of galactomannans decreased. Hence, FG with a higher Gal content showed the lowest viscosity (Liu, Lei, He, Xu, & Jiang, 2020). Furthermore, the conformational structure of FG, GG, LBG, and TG solutions as determined by AFM could offer a better explanation.

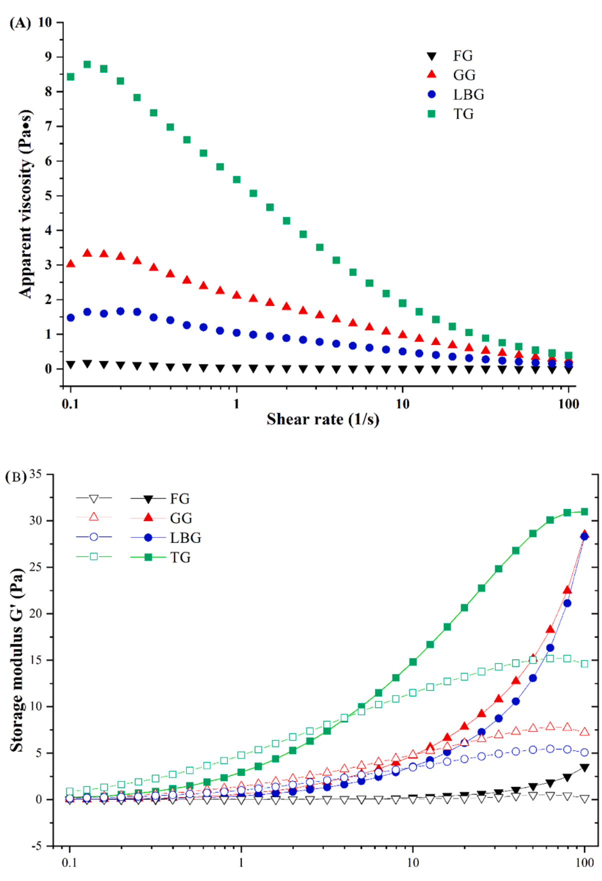

Fig. 2. Flow curves of the galactomannan solution with concentration at 1.0% (w/w) (A); viscoelastic properties of the solution at 1.0% (w/w) (B); the solid sign, storage modulus; the hollow sign, loss modulus.

To analyze flow behavior of galactomannans, the Power-Law model was used (Eq. (2)):

$$\sigma = k \cdot r^{n} \quad (2)$$

where k is the consistency and n is the flow behavior index, respectively.

Flow behavior of FG, GG, LBG, and TG solutions was well described by the model ($R^2 \geq 0.99$), and the k values of TG solution were significantly higher than that of FG, GG, and LBG solutions ($P < 0.05$) (Table 1). Also, the n value of TG solution was lower than those of FG, GG, and LBG, and the n values of all evaluated solutions were below 1, demonstrating the shear-thinning nature of galactomannans (Wu, Ding, Jia, & He, 2015).

3.3.2. Viscoelastic properties

Frequency sweeps for FG, GG, LBG, and TG solution at a concentration of 1.0 % (w/w) are shown in Fig. 2(B). The FG solution showed G′ > G″ in the angular frequency range without cross points, thus indicating the solution presented a weak gel behavior; conversely, GG, LBG, and TG solutions showed a liquid-like behavior (G′ < G″) in the low angular frequency range (Gadkari, Tu, Chiyarda, Reaney, & Ghosh, 2018). Wei, Lin, Xie, Xu, Yao, and Zhang (2015) also found the storage modulus (G′) to be higher than the loss modulus (G″) of FG solution at different concentrations. With the increase in angular frequency, a crossover point (G″ = G′) was created for GG, LBG, and TG solutions, and the crossover point of TG solution was lower than that of GG and LBG solution, demonstrating that GG, LBG, and TG solution behaved more like a gel after the crossover point (Wu, Ding, Jia, & He, 2015). Overall, the TG solution showed strong rheological properties and the FG solution presented weaker rheological properties, an observation that is similar with apparent viscosity analysis.

3.4. AFM analysis

AFM images of FG, GG, LBG, and TG are shown in Fig. 3(ABCD). The heights and morphologies of FG, GG, LBG, and TG differed significantly. Heights of FG, GG, and TG were within the range of 0–5 nm, which were lower than that of LBG (0–6 nm), which could be due to the higher molecular weight and molecular size of LBG. There are several conformations for polysaccharides, including polymer (P), linear strands (LS), single branch (SB), and multiple branches (MBR) (Xie, Zhang, Lan, Gong, Wu, & Wang, 2018; Zhang, Zhang, Liu, Ding, & Ye, 2015). AFM analysis of FG revealed the presence of polymer structures, whereas, for GG, some linear strands, polymers, and multiple branch structures were observed. For LBG, linear strands, polymer, and multiple branch structures can also be found. Interestingly, AFM analysis of TG revealed a regular network structure with linear strands, polymers, and multiple branch structures. In solution, the more extended structure of TG was entangled or cross-linked to form a network structure. These results corroborated observations in structure and conformation analysis.

3.5. Freeze-thaw stability

Syneresis of CS gel in the presence of FG, GG, LBG, and TG in three and five cycles is listed in Table 2. After three cycles, CS gel showed a higher syneresis value (27.87 %) than that of CS + GG (18.17 %), CS + LBG (13.21 %), or CS + TG gels (0.46 %) ($P < 0.05$); the latter showed the lowest syneresis value. No significant difference was found between CS gel and CS + FG gels (31.45 %) ($P > 0.05$). After five cycles, syneresis values of CS + GG (25.20 %), CS + LBG (17.96 %), and CS + TG (3.86 %) gels increased significantly ($P < 0.05$), which were significantly lower than syneresis values of CS gel alone (28.48 %) and CS + FG (32.20 %) ($P < 0.05$). These results indicate that the use of GG, LBG, and TG could enhance the freeze–thaw stability of CS gels. Lee and Chang (Lee & Chang, 2015) also found that LBG, GG, and TG could enhance the freeze–thaw stability of water chestnut starch. The formation and

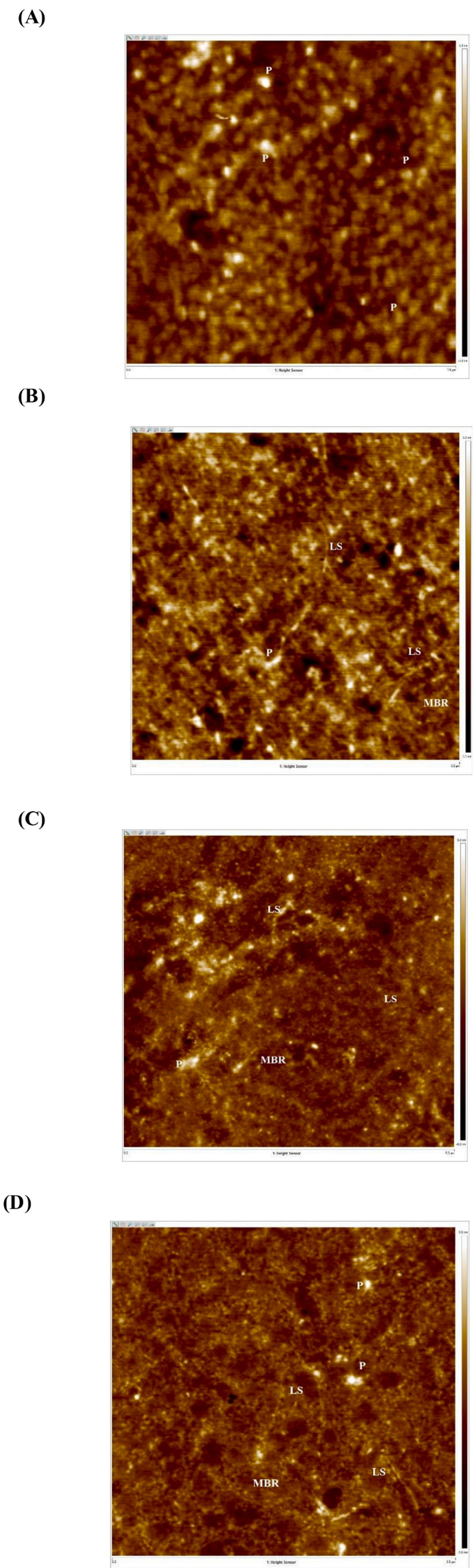

Fig. 3. AFM images of the galactomannans. (A), FG; (B), GG; (C), LBG; (D), TG. P, polymer; LS, linear strands; SB, single branch; MBR, multiple branches.

melting of ice crystals in the freeze–thaw process can damage the network structure and lead to the loss of hydrogen bonds among starch molecules (Zhang, Bai, Pan, Li, Cheng, & Chen, 2018). The GG, LBG, or TG has a large number of hydroxyl groups in their structure, which easily form hydrogen bonds with starch molecules, especially for TG (Liu, Chang, Chen, Xu, Ma, & Zhong, 2020). Another explanation for the above-mentioned observations was that the presence of GG, LBG, and TG increased the viscosity of the binary gels, which limited water release (Gadkari, Tu, Chiyarda, Reaney, & Ghosh, 2018; Liu, Lei, He, Xu, & Jiang, 2020). Due to their excellent freezing resistance, GG, LBG, and TG are commercially used in ice creams to enhance quality. Since FG has a higher Gal content, which could weaken existing intermolecular hydrogen bonds (Maity, Saxena, & Raju, 2018). Also, the freeze–thaw stability of CS + FG gel was comparable to that of CS gel alone.

3.6. *Retrogradation of CS gels during storage under refrigeration*

After refrigerated storage, the DSC curves including the retrogradation melting enthalpy (ΔH_r) of CS or CS-galactomannans binary gels are presented in Fig. 4(A). An endothermic peak in DSC curves can be defined as the endothermic peak of the starch gels after refrigerated storage. The ΔH_r of starch gels was higher in CS (0.34 J/g), followed by CS + FG (0.33 J/g), CS + GG (0.27 J/g), CS + LBG (0.25 J/g), and CS + TG 0.19 J/g) (Table 2). Also, the endothermic peak temperature of CS + GG (63.50 °C), CS + LBG (63.50 °C), and CS + TG (63.55 °C) was higher than that of CS (60.65 °C) ($P < 0.05$) (Table 2). Higher melting enthalpy and peak temperature are correlated with more energy to gelatinize recrystallized starch granules during retrogradation. These results indicate that the presence of LBG, GG, and TG could inhibit retrogradation of CS gels, especially TG. Chen, Xiong, and Gao (2018) also found that GG, TG, and LBG significantly retarded recrystallization of starch molecules. In general, the presence of gums at large proportions in the formulation of starch gels has been reported to inhibit retrogradation, which could be associated with increased viscosity of binary gels determined by the presence of gums, thus limiting water mobility and starch chain migration. Another explanation is related to many hydroxyl groups in the structure of galactomannans, which form more hydrogen bonds with starch molecules, thus recrystallization of the starch molecule is limited. This phenomenon is likely related to the Man/Gal ratio of galactomannans. These results demonstrate that the Man/Gal ratio and apparent viscosity of galactomannans are related to their effect on the retrogradation of starch gels.

3.7. *Textural profile*

The textural parameters, including hardness, chewiness, and springiness of CS gels were analyzed and are presented in Table 2. The CS + GG gel showed a higher hardness (346.20 g) than the other gels ($P < 0.05$), suggesting that GG could form stronger gels with starch molecules (Liu & Xu, 2019). These results were consistent with data previously reported (Dangi, Yadav, & Yadav, 2019; Lee & Chang, 2015; Loser, Iturriaga, Ribotta, & Barrera, 2021). In short, the presence of polysaccharides leads to the immobilization of water molecules in starch gels (Dangi, Yadav, & Yadav, 2019). Moreover, gums could entangle or interact with starch molecules to increase gel strength (Loser, Iturriaga, Ribotta, & Barrera, 2021). Interestingly, the hardness of CS + GG (429.80 g) and CS + TG (417.19 g) gels increased significantly ($P < 0.05$) after repeated freeze–thaw cycles. However, the hardness of CS + FG (205.49 g) gels decreased significantly ($P < 0.05$). Charoenrein and Preechathammawong (2012) also found the increased hardness of gum-starch binary gels, which could be because galactomannans in aqueous solution form hydrogel or showed phase transition behavior induced by the freezing and thawing process (Naoi, Hatakeyama, & Hatakeyama, 2002).

Chewiness means the masticated energy of gels (Liu & Xu, 2019). With the addition of galactomannans in gel formulation, chewiness of CS

Table 2
Effects of the galactomannans on freeze–thaw stability, retrogradation, and textural properties of corn starch gels.

	Syneresis (%)		Thermal properties		Textural properties (fresh/frozen)		
	3 cycles	5 cycles	T_p (°C)	ΔH_r (J/g)	Hardness (g)	Chewiness	Springiness
CS	27.87 ± 1.07^{b}	28.48 ± 1.04^{b}	60.65 ± 0.07^{b}	0.34 ± 0.02^{a}	$295.17^{bA}/282.35^{bA}$	$197.84^{bA}/236.91^{aA}$	$0.95^{aA}/0.95^{aA}$
CS + FG	31.45 ± 2.23^{a}	32.20 ± 1.88^{a}	61.40 ± 0.42^{b}	0.33 ± 0.01^{a}	$298.16^{bA}/205.49^{cB}$	$235.40^{abA}/170.61^{bB}$	$0.96^{aA}/1.01^{aA}$
CS + GG	18.17 ± 0.93^{c}	25.20 ± 0.38^{c}	63.50 ± 0.14^{a}	0.27 ± 0.04^{b}	$346.20^{aB}/429.80^{aA}$	$257.11^{aA}/114.21^{cB}$	$0.96^{aA}/0.72^{cB}$
CS + LBG	13.21 ± 3.06^{d}	17.96 ± 4.64^{d}	63.50 ± 0.14^{a}	0.25 ± 0.06^{b}	$292.31^{bA}/276.08^{bA}$	$227.80^{abA}/161.65^{bB}$	$0.96^{aA}/0.81^{bB}$
CS + TG	0.46 ± 0.00^{e}	3.86 ± 0.27^{e}	63.55 ± 0.49^{a}	0.19 ± 0.05^{b}	$326.15^{abB}/417.19^{aA}$	$211.34^{abA}/170.28^{bB}$	$0.94^{aA}/0.78^{bB}$

Note: CS, corn starch; FG, Fenugreek gum; GG, Guar gum; LBG, Locust bean gum; TG, Tara gum; ΔH_r, retrogradation melting enthalpy. The lowercase in each column or the capital letter in each row presented a significant difference ($P < 0.05$).

and galactomannans binary gels was higher than that of CS gel alone, especially for CS + GG gel (257.11) ($P < 0.05$). Huang, Kennedy, Li, Xu, and Xie (2007) found that the presence of polysaccharides increased the chewiness of starch gels, thus indicating that more energy is needed to masticate the starch gels. After freeze–thaw treatment, the chewiness of the binary gels was decreased significantly ($P < 0.05$).

Springiness refers to gel rubberiness in the mouth, i.e. how much the structure of gels is broken down by the initial compression (Huang, Kennedy, Li, Xu, & Xie, 2007; Teng, Chin, & Yusof, 2013). For freshly prepared gels, no significant difference in springiness of CS gels was observed. After freeze–thaw cycles, springiness of CS + GG (0.72), CS + LBG (0.81), and CS + TG (0.78) gels decreased significantly ($P < 0.05$). Wang et al (2013) also described decreased springiness of rice, ginkgo, Chinese water chestnut, and potato starch gels after freeze-thawing. These results indicate that freeze–thaw applied to CS + GG, CS + LBG, and CS + TG gels yielded more easily masticated gels, which might be due to galactomannans inducing more viscous regions in the gel structure and decreased springiness (Dangi, Yadav, & Yadav, 2019).

3.8. Water distribution of CS-galactomannans mixture gels

Water distribution can reflect the stability of starch gel in the freeze–thaw process, which was analyzed using LF NMR and listed in Table S1. The major peak proportion of CS-galactomannans mixture gels was in the range of 200–1000 ms (A_{22}), which indicated the free water in the gels (Xie, Zhang, Xia, & Ai, 2020). No significant difference in A_{22} value was found between CS and CS + FG gel, but the value of CS + GG (25.20 %), CS + LBG (17.96 %), and CS + TG (3.86 %) gels was lower than that of CS gel ($P < 0.05$). Furthermore, the A_{21} value, which reflects the limited water (Xie, Zhang, Xia, & Ai, 2020), of CS + GG (25.20 %), CS + LBG (17.96 %), and CS + TG (3.86 %) gels was higher than that of CS gel ($P < 0.05$). This could be due to GG, LBG, and TG forming network structures tightly with starch molecules and their higher water affinity. These results were consistent with the freeze–thaw stability of CS-galactomannans mixture gels.

3.9. Viscoelastic properties of CS-galactomannans mixture pastes

The viscoelastic properties of CS-galactomannans mixture gels are shown in Fig. 4(B). The loss modulus G″ value was higher than the storage modulus G′ of CS, CS-FG, and CS-LBG pastes in the frequency range (0.1–100 rad/s), demonstrating that the sample pastes exhibited a liquid-like behavior (Xie, Zhang, Xia, & Ai, 2020). Furthermore, the G′ was higher than G″ values in the higher frequency range of CS-TG and CS-GG pastes, and the G′ and G″ values of CS-TG and CS-GG pastes were higher than that of CS paste. This was probably due to the association between amylose and TG or GG molecules to enhance the gel network structure (Xie, Zhang, Xia, & Ai, 2020). However, the values of CS-FG and CS-LBG pastes were lower than that of CS paste. Hussain, Singh, Vatankhah, and Ramaswamy (2017) also found a similar trend between LBG and resistant corn starch mixtures, this could be due to phase separation and thermodynamic incompatibility between gums and starch molecules.

The storage modulus G′ of the starch paste is related to the short-term retrogradation of starch pastes (Li et al., 2016), which is presented in Fig. 4(C). With the temperature decreasing, the G′ values of the sample pastes increased slightly. The G′ values of CS, CS-GG, CS-LBG, and CS-TG pastes increased 54.6 %, 36.9 %, 37.4 %, and 39.9 %, respectively, from 50 to 5 °C. During the short-term retrogradation process of the starch paste, amylose will aggregate to form a three-dimensional network, which resulted in a higher G′ value (Li et al., 2016). Hence, the presence of GG, LBG, and TG inhibited the short-term retrogradation of corn starch paste.

3.10. Microstructure

Microstructural changes in fresh CS gels and CS gels treated with five freeze–thaw cycles after freeze-drying was analyzed by the SEM. As shown in Fig. S1(A-E), the structure of fresh gels was intact and condensed without observable pores on the surface. Wang et al (2013) also observed a similar structure of ginkgo, Chinese water chestnut, potato, and rice starch gels as determined by SEM. Interestingly, certain linear or network structures were found in the intact and condensed structures of CS + LBG and CS + TG gels. According to a previous study (Dangi, Yadav, & Yadav, 2019), the linear or network structures might result from the entanglement or cross-link among TG or LBG molecules and leached amylose molecules. Also, entanglement or cross-link of CS + TG gel was regular and tight, which was consistent with the results of freeze-thawing stability and texture of such gels.

After five freeze-thawing cycles, all evaluated gels presented a spongy structure with ice cells and a fibrillar network (Fig. S1 F-J). Moreover, obvious differences were found between the microstructure of CS gel alone and binary gels with galactomannans. For CS and CS + FG gels, ice cells became larger and certain cells cracked after freeze-thawing, which was consistent with the results reported by Charoenrein and Preechathammawong (2012). Collectively, these microstructural changes indicate that freeze-thawing caused the release of frozen water from the gel network. For CS + GG, CS + LBG, and CS + TG gels, ice cells became smaller and the fibrillar network became thinner. Moreover, linear or network structure could also be observed in CS + GG, CS + LBG, and CS + TG gels. These structures further demonstrate that the presence of GG, LBG, and TG could increase the water holding capacity of CS gels. This could be due to the higher Man/Gal ratio and more extended structure of GG, LBG, and TG, especially TG. According to Ye et al. (2018), certain hydrocolloids with better freeze-thawing stability could also decrease the size of ice cells in starch gels, thus improving freeze-thawing stability.

3.11. Correlation analysis

The result of Pearson's correlation between structural characteristics of galactomannans and their effect on retrogradation, freeze-thawing stability, and texture of CS gels was shown in Fig. S2. Syneresis of starch gels after freeze-thawing cycles showed a significantly negative correlation with the Man/Gal ratio ($P < 0.01$) and k ($P < 0.01$), and a positive correlation with α_s ($P < 0.05$), suggesting that galactomannans

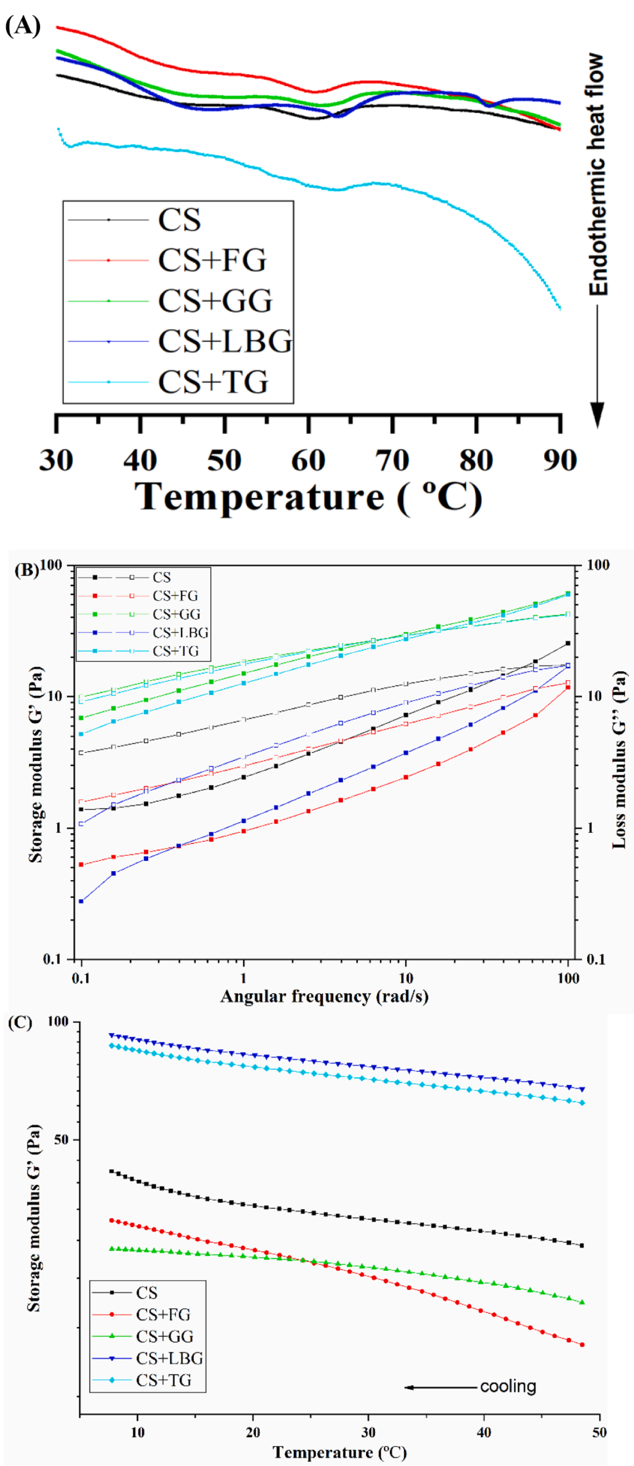

Fig. 4. (A) Differential scanning calorimetry thermograms of corn starch gels without or with the presence of galactomannans; (B) viscoelastic properties of CS-galactomannans mixture gels; (C) storage modulus G′ of CS-galactomannans mixture gels during cooling process.

with higher Man/Gal ratio and apparent viscosity as well as extended structure can enhance freeze–thaw stability of CS gels. The ΔH_r values presented a negative correlation with M_w ($P < 0.05$), Man/Gal ratio ($P < 0.01$), and k ($P < 0.01$) and a positive correlation with α_s ($P < 0.01$) of galactomannans. The results indicated that galactomannans with higher M_w, Man/Gal ratio, apparent viscosity, and extended structure could retard the retrogradation of CS gels. After applying freeze-thawing to CS gels, hardness was positively correlated with k ($P < 0.01$) and negatively correlated with α_s ($P < 0.05$), suggesting that galactomannans with high viscosity and extended structure improved the hardness of CS gels during freeze-thawing. Moreover, springiness was negatively correlated with M_w, Man/Gal ratio, $[\eta]_w$, and k and positively correlated with α_η, suggesting that galactomannans with high M_w, Man/Gal ratio, and apparent viscosity and extended structure could produce more masticable gels after freeze-thawing.

4. Conclusion

In the present work, structural properties of FG, GG, LBG, and TG were investigated as well as their influence on retrogradation induced by storage under refrigeration, freeze-thawing stability, and textural profile after freeze-thawing of CS gels. GG, LBG, and TG showed an extended structure with Man/Gal ratios of 1.96, 2.99, and 3.46, respectively. The effects of galactomannans on the retrogradation of starch gels were mainly related to their M_w, Man/Gal ratio, apparent viscosity, and extended structure. The effects of galactomannans on the freeze-thawing stability of starch gels were related to their Man/Gal ratio, apparent viscosity, and extended structure. Galactomannans with high apparent viscosity and extended structure could help to improve the texture of CS gels submitted to freeze-thawing. These results could be beneficial for the application of galactomannans in starch-based food products, including glue pudding, vermicelli, frozen steam bread, noodles, and dumpling.

CRediT authorship contribution statement

Fan Xie: Conceptualization, Writing – original draft. **Chunmei Yuan:** Data curation. **Hui Zhang:** Methodology. **Yan Wu:** Data curation. **Lianzhong Ai:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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