

Rheological and Pasting Properties of Naked Barley Flour as Modified by Guar, Xanthan, and Locust Bean Gums

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ABSTRACT: To understand the effects of adding different gums (guar, xanthan, and locust bean gums) on naked barley flour (NBF), the rheological and pasting properties of NBF-gum mixtures were measured at different gum concentrations (0, 0.3, and 0.6% w/w). Steady shear rheological properties were determined by rheological parameters for power law and Casson models. All samples showed a clear trend of shear-thinning behavior ($n=0.16\sim0.48$) and had a non-Newtonian nature with yield stress. Consistency index, apparent viscosity, and yield stress values increased with an increase in gum concentration. Storage modulus values were more predominant than loss modulus values with all concentrations of gums. There is a more pronounced synergistic effect of elastic properties of NBF in the presence of xanthan gum. Rapid visco analyser pasting properties showed that the addition of gums resulted in a significant increase in the peak, breakdown, setback, and final viscosities, whereas the pasting temperature decreased.

Keywords: naked barley flour, gum, rheological property, pasting property, viscoelastic property

INTRODUCTION

Barley, which primarily contains starch, is the fourth largest cereal crop in the world after wheat, corn, and rice (1). In addition, it is the second staple crop in Korea followed by rice (2). Barley contains much more protein, calcium, and dietary fiber than other cereal crops (3). In particular, main component of barley contains about 70% or more starch, like other cereals. Using only barley flour has limitations for making various barley flour-based food products due to the unsuitable physical properties given by barley flour. Recently, barley flour has been recognized as an alternative composite flour to wheat flour, which can be utilized in the processing of various starch-based products like bread, confectionary, snacks, and noodles (4). Accordingly, previous studies on the development of barley flour-based foods have mainly focused on improving processing quality by utilizing composite powders and examining the physical properties of composite powders composed of barley and wheat flours. Therefore, studies on the rheological properties of barley flour in the presence of gums are necessary because materials, which have improved the cereal powder's physical properties by adding gum, are being recently developed. It is also known that starch- or flour-gum mixtures

have been widely used in the food industry because they can modify and control rheological and textural properties, improve moisture retention, control water mobility, reduce cost, and maintain overall product quality during processing and storage of food products (5). However, there are no studies on the comprehensive rheological properties of barely flour in the presence of gums even though only a few studies examined the effects of gum addition on the rheological properties of cereal flours, such as rice and wheat flours (6,7). In this study, naked barley was selected to investigate its rheological properties due to the superior processing suitability compared to other breeds of barley in Korea. Three different gums [guar gum (GG), xanthan gum (XG), and locust bean gum (LBG)] were also selected because they are widely used in the food industry to improve or control the physical and rheological properties of starch-based food products.

The main objectives of this study is to understand the effects of adding three different gums on naked barley flour (NBF) at different gum concentrations by measuring steady and dynamic rheological properties and investigating pasting properties affecting gelatinization and retrogradation. This study can be utilized to improve and control processing quality and end use quality of NBF-based food products.

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MATERIALS AND METHODS

Materials

Naked barley was purchased from the Goseong Agricultural Cooperative (Goseong, Korea). Its proximate composition was: 12.5% moisture, 11.3% protein (N×5.7), 1.78% fat, 1.12% ash, 73.3% carbohydrate (by difference), and the amylose content was 21.7%. GG was supplied from Korea Carrageenan Co., Ltd. (Seoul, Korea), and XG and LBGs were supplied from Jupiter International Co., Ltd. (Seoul, Korea).

Preparation of NBF-gum mixture dispersions

For the preparation of NBF, naked barley was ground and passed through a 120-mesh standard sieve (Chung Gye Inc., Seoul, Korea). NBF-gum mixture dispersions (5% w/w) were prepared by adding three different gums to NBF and distilled water with three different concentrations (0, 0.3, and 0.6% w/w). The dispersions were moderately stirred for 60 min at room temperature and heated at 95°C for 30 min with mild agitation using a magnetic stirrer. After the heating period, the hot NBF-gum mixture was immediately transferred to the rheometer plate.

Rheological measurements

Steady flow properties of NBF-gum mixture dispersions were determined by the Haake RotoVisco-1 (Haake GmbH, Karlsruhe, Germany) at 25°C having a parallel plate geometry of 3.5 cm in diameter at a gap of 500 μm. Flow measurements were performed over the range of shear rate from 0.4 to 500 1/s. The power law (Eq. 1) and Casson (Eq. 2) models were fitted to the flow curves (shear stress versus shear rate):

$$\sigma = K\dot{\gamma}^n \quad (1)$$

$$\sigma^{0.5} = K_{oc} + K_c\dot{\gamma}^{0.5} \quad (2)$$

where σ (Pa) is the shear stress, $\dot{\gamma}$ (1/s) is the shear rate, K ($\text{Pa}\cdot\text{s}^n$) is the consistency index, n is the flow behavior index, and $(K_c)^2$ is the Casson plastic viscosity. The apparent viscosity ($\eta_{a,50}$) at 100/s was calculated from the magnitudes of K and n , and Casson yield stress (σ_c) was determined as the square of the intercept (K_{oc}).

Dynamic shear rheological properties were carried out using an AR 1000 rheometer (TA Instruments, New Castle, DE, USA) at 25°C. The plate-plate geometry was used (diameter 4 mm; gap 500 μm). An oscillatory frequency sweep test was performed in the range of 0.63 ~ 62.8 rad/s at 2% strain in order to determine the storage modulus (G'), loss modulus (G''), complex viscosity (η^*), and loss tangent ($\tan \delta = G''/G'$). TA rheometer Data Analysis software (version VI. 1.76, TA Instruments) was

used to calculate the G' , G'' , and η^* .

Pasting properties measurements

The pasting properties of NBF-gum mixtures (7% w/w) were measured on a Rapid Visco Analyser (RVA) (Model RVA-4, Newport Scientific PTY Ltd., Warriewood, Australia). All NBF-gum mixture dispersions (5% w/w) containing 0, 0.3, and 0.6% (weight basis) gum concentrations were prepared, as previously described. The dispersions (28 g) were then poured into aluminum canisters and stirred manually using a plastic paddle for 20 ~ 30 s prior to insertion into the RVA machine. The heating and cooling cycles were programmed in the following manner. All samples were held at 50°C for 1 min, and then heated to 95°C at a rate of 7.5°C/min and held at 95°C for 5 min, cooled to 50°C at a rate of 7.5°C/min, and finally held at 50°C for 5 min, while maintaining a rotation speed of 160 rpm. Then, the peak viscosity (maximum viscosity during pasting), breakdown viscosity (the difference between the peak viscosity and the minimum viscosity during pasting), setback viscosity (the difference between the maximum viscosity during cooling and the minimum viscosity during pasting), final viscosity (the viscosity at the end of the RVA run), and pasting temperature (temperature indicating an initial increase in viscosity) of the NBF-gum mixture dispersions were determined.

Statistical analysis

Results are expressed as the mean ± standard deviation. An analysis of variance (ANOVA) was performed using the Statistical Analysis System software version 9.1 (SAS Institute, Cary, NC, USA). Differences in means were determined using Duncan's multiple-range test. $P < 0.05$ was considered to be significant.

RESULTS AND DISCUSSION

Steady shear rheological properties

Rheograms of the NBF-gum mixtures in the presence of the gums at different concentrations (0, 0.3, and 0.6%) indicated non-Newtonian (pseudoplastic) natures (Fig. 1), and the σ versus $\dot{\gamma}$ data were well fitted to the simple power law and Casson models with high determination coefficients ($R^2 = 0.95 \sim 0.99$), and their flow parameters used to describe the flow curves are summarized in Table 1. All samples showed shear thinning behaviors with values of flow behavior index ($n = 0.16 \sim 0.48$). When comparing the NBF-gum mixture samples, the mixtures prepared with GG and XG had higher shear-thinning behavior with values of n as low as 0.16 ~ 0.34 as compared to the NBF-LBG mixture ($n = 0.41 \sim 0.48$), which were higher than the control ($n = 0.35$). The n values of

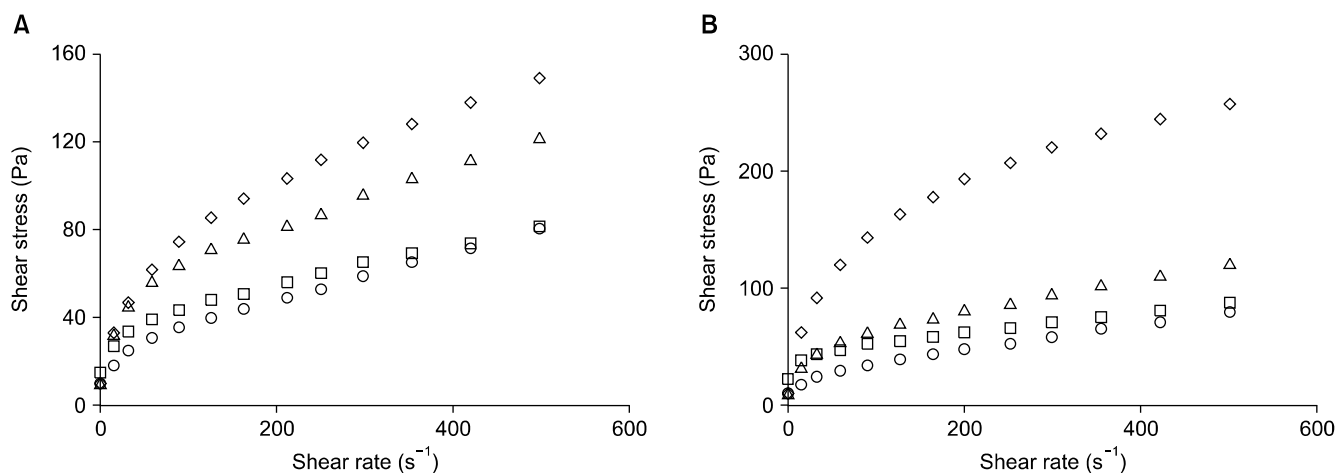


Fig. 1. Shear stress-shear rate plots of naked barley flour-gum mixtures with 0.3% (A) and 0.6% (B) gum concentrations at 25°C. ○, control; △, GG; □, XG; ◇, LBG.

Table 1. Effect of gum addition on steady shear rheological properties of naked barley flour-gum mixtures at 25°C

Gum type	Gum concentration (%)	$\eta_{a,100}$ (Pa·s)	K (Pa·s ⁿ)	n (-)	σ_{oc} (Pa)
Control (no gum)	0	0.37±0.00 ^g	7.52±0.08 ^g	0.35±0.00 ^c	9.81±0.41 ^f
GG	0.3	0.67±0.02 ^d	13.8±0.35 ^e	0.34±0.00 ^c	20.8±0.74 ^c
	0.6	1.23±0.02 ^b	29.3±0.08 ^a	0.31±0.00 ^d	43.3±1.24 ^a
XG	0.3	0.43±0.01 ^f	15.0±0.11 ^d	0.23±0.00 ^e	17.1±0.58 ^d
	0.6	0.54±0.01 ^e	26.1±0.32 ^b	0.16±0.00 ^f	28.6±0.44 ^b
LBG	0.3	0.75±0.04 ^c	11.3±0.28 ^f	0.41±0.01 ^b	10.4±0.81 ^e
	0.6	1.65±0.05 ^a	18.3±0.15 ^c	0.48±0.00 ^a	11.0±1.31 ^e

GG, guar gum; XG, xanthan gum; LBG, locust bean gum.

$\eta_{a,100}$, apparent viscosity; K, consistency index; n, flow behavior index; σ_{oc} , yield stress.

Mean values in the same column with different letters (a-g) are significantly different ($P < 0.05$).

the NBF mixed with GG and XG decreased with an increase in gum concentration, indicating that these mixtures became more pseudoplastic, showing a dependence on gum concentration. In particular, the NBF-XG mixture at 0.6% exhibited greater pseudoplasticity than other mixtures due to the unique flow behavior of XG, i.e., a high viscosity at low shear rates and a low viscosity at high shear rates. Such high shear-thinning behaviors can be due to the great extended conformation of GG, and the unique rigid, rod-like conformation of XG with a high molecular weight (8). Similar observations were made by Choi and Yoo (9) and Kim and Yoo (10) for sweet potato starch-XG and acorn starch-GG mixtures, respectively.

$\eta_{a,100}$, K, and σ_{oc} values of NBF-gum mixtures were significantly higher than those of the control, and also increased with an increase in concentration of gums from 0 to 0.6% (Table 1), suggesting that there was a high synergism in the presence of gums. The synergistic effect of gums on starch paste viscosity in the starch-gum mixture systems has been described by various mechanisms, including interactions between starch exudates (amylose) and gum, a great increase in the concentration of gum in the continuous phase (amylose), and the influence of gum

on the physical properties of starch granules, such as size, shape, and granule integrity, as well as the amount of exudate from starch granules (11). The order of effectiveness in increasing the $\eta_{a,100}$ at all concentrations was as follows: LBG > GG > XG. Such lower $\eta_{a,100}$ values (0.43 ~ 0.54 Pa·sⁿ) of the NBF-XG mixtures when compared to those of the other mixtures might be due to the low n values (0.16 ~ 0.23) of the NBF-XG mixtures. When comparing the K and σ_{oc} values of the NBF-gum mixtures, the NBF-GG mixture at 0.6% showed significantly higher K and σ_{oc} values than the other mixtures due to the greater hydration capacity and thickening properties of GG. The same effect of flow properties in the starch-gum mixture systems was also observed in sweet potato starch-gum mixtures (12). Therefore, it can be concluded that the flow properties of NBF-gum mixtures were apparently influenced by the type of gum as well as gum concentration.

Dynamic shear rheological properties

Changes in the G' and G'' as a function of frequency (ω) in the NBF-gum mixtures at 25°C are presented in Fig. 2. G' and G'' values increased with an increase in the ω , whereas complex η^* decreased, depending on ω . From

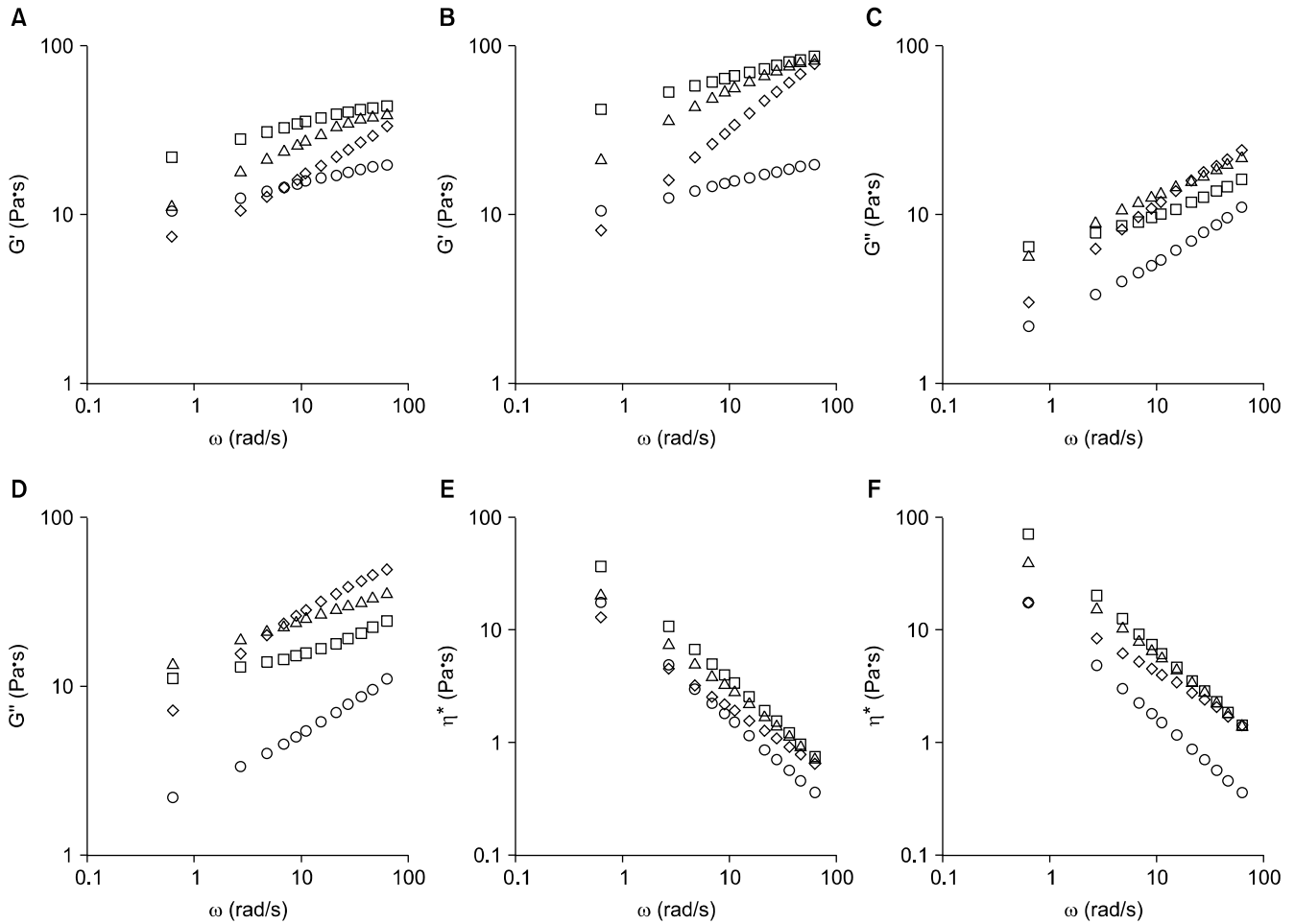


Fig. 2. G' and G'' versus ω of naked barley flour-gum mixtures with 0.3% (A, C, and E) and 0.6% (B, D, and F) gum concentrations at 25°C. ○, control; △, GG; □, XG; ◇, LBG.

the dynamic rheological data, it was found that NBF-gum mixtures exhibited a weak gel-like behavior because their slopes were positive and the G' values (14.5~61.2 Pa) were more predominant than G'' (9.08~24.4 Pa). In particular, in the NBF-XG mixtures, the G' values were much higher than the G'' values at all values of ω , with a small ω dependency confirming their viscoelastic nature. In general, the G' , G'' , and η^* values of NBF-gum mixtures were higher than those of the control, and also in-

creased with an increase in gum concentration from 0 to 0.6% (Table 2). Such behavior is in agreement with those found for other starch-gum mixture systems (13-15). The dependency of gum concentration might be due to the increase of viscoelastic properties by the addition of the gums in the NBF-gum mixture systems. The values of G' at 6.28 rad/s increased in the following order with all gum concentrations: XG > GG > LBG. However, the values of G'' increased in the following order: GG >

Table 2. Storage modulus (G'), loss modulus (G''), complex viscosity (η^*), and $\tan \delta$ at 6.28 rad/s of naked barley flour-gum mixtures at 25°C

Gum type	Gum concentration (%)	G' (Pa)	G'' (Pa)	η^* (Pa·s)	$\tan \delta$
Control (no gum)	0	14.5±0.41 ^f	4.44±0.08 ^a	2.41±0.03 ^f	0.31±0.00 ^d
GG	0.3	23.2±0.58 ^e	11.7±0.35 ^d	4.14±0.01 ^d	0.50±0.00 ^c
	0.6	46.6±0.44 ^b	22.4±0.08 ^b	8.23±0.02 ^b	0.48±0.00 ^c
XG	0.3	32.7±0.37 ^c	9.08±0.11 ^f	5.41±0.04 ^c	0.28±0.00 ^d
	0.6	61.2±0.34 ^a	13.8±0.32 ^c	9.99±0.03 ^a	0.22±0.00 ^e
LBG	0.3	14.5±0.81 ^f	9.81±0.28 ^e	2.79±0.06 ^e	0.68±0.01 ^b
	0.6	26.9±1.31 ^d	24.4±0.15 ^a	5.78±0.03 ^c	0.91±0.00 ^a

GG, guar gum; XG, xanthan gum; LBG, locust bean gum.

Mean values in the same column with different letters (a-g) are significantly different ($P < 0.05$).

LBG > XG at 0.3% and LBG > GG > XG at 0.6%. The difference in viscoelastic properties between NBF-GG and NBF-LBG mixtures suggest that their synergistic effects are influenced by the chemical structure of the galactomannans in the continuous phase (16).

The $\tan \delta$ values of all samples were in the range of 0.22~0.91 (Table 2), indicating that the elastic nature prevailed over the viscous nature. The $\tan \delta$ values (0.37~0.58) of the NBF-galactomannan (GG and LBG) mixtures were higher than that of the control (0.31) whereas those of NBF-XG mixtures was lower (0.22~0.28). This can be attributed to the characteristic of XG which is more elastic and forms strong networks in the NBF-XG mixture. However, the $\tan \delta$ values of NBF were increased by the addition of GG and LBG, indicating that the addition of GG and LBG causes an adverse effect on the elastic properties of the NBF paste. Therefore, it was concluded that the galactomannan gums do not interact synergistically with NBF to form an elastic structure. The mechanism of changes in the viscoelastic properties of starch pastes in the presence of gums can be explained mainly by phase separation (incompatibility phenomena between unlike polysaccharides) or interactions between like and unlike polysaccharides (11,13,14). Based on a similar mechanism, the synergistic effect of GG and LBG on the viscoelastic properties of the NBF paste can be explained by the formation of a thermodynamically incompatible network structure because the NBF pastes mixed with GG and LBG resulted in a small increase in G' compared to G'' with their $\tan \delta$ values (0.48~0.91) higher than the control (0.31). In contrast, the strong synergistic interaction between XG and NBF was observed due to the great increase in G' compared to G'' as well as lower $\tan \delta$ (0.22~0.28) compared to the control (0.31), showing that there was the thermodynamic compatibility between NBF and XG. Therefore, it was concluded that the mechanism of synergistic effects of added gum in the NBF-gum mixture systems can be predicted by the changes in dynamic rheological parameters, and also determined by the chemical structure

of the gums in the continuous phase of the NBF paste, as noted by Kim and Yoo (10) and Funami et al. (17).

Pasting properties

All pasting parameters of NBF in the presence of gums at different concentrations as determined by RVA are summarized in Table 3. There were significant changes in the peak and final viscosities of NBF when various gums were added. Increasing the concentration of gums caused a significant increase in peak and final viscosity values, which may be due to the thickening properties of gums (18-20). This could also be attributed to the possible interactions between starch molecules and gums during the pasting procedure, resulting in the reduced mobility of starch granules (21). The breakdown of the NBF-gum mixtures was significantly higher than that of the control and increased with an increase in gum concentration, which could be due to increases in viscosities leading to much greater shear forces being exerted on the swollen granules in the shear field compared to those encountered in starch dispersions (19). The higher breakdown had also been found in the other starch-gum mixture systems, indicating a degree of granule breakdown (18). The setback values of all mixtures, except for XG at 0.3%, were also higher compared to the control and increased with an increase in gum concentration. The lower setback value of the NBF-XG mixture at 0.3% compared to the control can be explained by a decrease of setback due to the repelling forces between starch granules and the negative charges on the XG molecules (18,21), indicating that retrogradation of NBF might be retarded by XG. NBF-gum mixtures were characterized by slightly lower pasting temperatures compared to the control, and their pasting temperatures also decreased with an increase in gum concentration. Such decrease in pasting temperature in the starch-gum mixture systems can be explained by the increase in the effective concentration of starch in the continuous phase and the enhanced interaction between the granules, as suggested by Galkowska et al. (15) and Funami et al. (17).

Table 3. Pasting properties of naked barley flour-gum mixtures

Gum type	Gum concentration (%)	Peak viscosity (mPa·s)	Breakdown (mPa·s)	Final viscosity (mPa·s)	Setback (mPa·s)	Pasting temperature (°C)
Control (no gum)	0	250±6.08 ^f	174±8.62 ^f	564±18.2 ^g	314±12.6 ^e	64.7±0.25 ^a
GG	0.3	939±26.2 ^c	312±10.0 ^e	1,482±32.0 ^d	543±15.7 ^d	63.5±0.00 ^c
	0.6	1,180±43.6 ^b	773±47.5 ^a	2,707±57.6 ^a	1,527±55.6 ^a	61.7±0.25 ^e
XG	0.3	824±18.7 ^d	379±40.4 ^d	1,102±7.21 ^f	278±19.5 ^f	64.1±0.23 ^b
	0.6	1,161±17.8 ^b	716±13.0 ^b	1,698±48.0 ^c	537±45.2 ^d	62.5±0.00 ^d
LBG	0.3	568±27.0 ^e	327±16.0 ^e	1,232±56.9 ^e	663±30.4 ^c	62.4±0.10 ^d
	0.6	1,334±19.7 ^a	461±26.6 ^c	2,469±41.0 ^b	1,135±24.3 ^b	62.0±0.29 ^e

GG, guar gum; XG, xanthan gum; LBG, locust bean gum.

Mean values in the same column with different letters (a-g) are significantly different ($P < 0.05$).

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AUTHOR DISCLOSURE STATEMENT

The authors declare no conflict of interest.

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