Rheological Differences of Waxy Barley Flour Dispersions Mixed with Various Gums

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ABSTRACT: Rheological properties of waxy barley flour (WBF) dispersions mixed with various gums (carboxyl methyl celluleose, guar gum, gum arabic, konjac gum, locust bean gum, tara gum, and xanthan gum) at different gum concentrations were examined in steady and dynamic shear. WBF-gum mixture samples showed a clear trend of shear-thinning behavior and had a non-Newtonian nature with yield stress. Rheological tests indicated that the flow and dynamic rheological parameter (apparent viscosity, consistency index, yield stress, storage modulus, and loss modulus) values of WBF dispersions mixed with gums, except for gum arabic, were significantly higher than those of WBF with no gum, and also increased with an increase in gum concentration. In particular, konjac gum at 0.6% among other gums showed the highest rheological parameter values. Tan δ values of WBF-xanthan gum mixtures were lower than those of other gums, showing that there is a more pronounced synergistic effect on the elastic properties of WBF in the presence of xanthan gum. Such synergistic effect was hypothesized by considering thermodynamic compatibility between xanthan gum and WBF. These rheological results suggest that in the WBF-gum mixture systems, the addition of gums modified the flow and viscoelastic properties of WBF, and that these modifications were dependent on the type of gum and gum concentration.

Keywords: waxy barley flour, gum, rheological property, viscoelastic property, synergistic effect

INTRODUCTION

Gums (hydrocolloids) are high molecular-weight hydrophilic biopolymers used as functional ingredients in the food industry for the control of microstructure, texture, and shelf-life (1). In general, they are often incorporated into starches or flours in food systems to achieve specific rheological properties of starches or flours in the food industry. It is also known that the synergistic interactions between starch and the added gum may improve the rheological and sensory properties of starch-based foods (2). The changes in rheological properties of starches occur as a result of the high molecular weight polymeric nature of the gums and the interactions between two polymer chains. Therefore, selective use of gums can allow the manipulation of rheological properties of starches and also lead to improvements in the formulation of starch-based products.

Barley is the fourth largest cereal crop in the world after wheat, corn, and rice (3). Even though barley is inferior compared to other cereal crops, it contains much higher dietary fiber content, particularly β -glucans which are beneficial to human health. There are many different

kinds of commercially available processed barley products, such as breakfast cereals, stews, soups, porridge, bakery flour blends, snack, baby foods, breads, and noodles (4). In Korea, barley, which primarily contains starch (approximately 70% starch), is the second most important cereal crop after rice and is mainly used as a rice substitute or as a component of wheat products, such as breads and noodles (5). However, in case of developing processed foods by using barley flour, it has shown limitations for making various barley-based products with barley flour only due to its unacceptable taste, color, and texture for making breads and noodles. Recently, barley flour is recognized as alternative composite flour to wheat flour which can be utilized in processing of various starch-based products, such as breads, confectionary, and noodles. Accordingly, previous researches on the development of barley-based foods have focused mainly on improving processing quality by utilizing composite flours and examining the physical properties of composite flours which are composed of barley and wheat flours in making bread and noodle products (3). However, there are no studies on the physical and rheological properties of barley flour itself as a food ingredient to improve the quality of barley flour-based products.

It is well known that the knowledge of starch-gum mixtures is very important and necessary for developing new textures and enabling substitutions of ingredients (6). Currently, the starch-gum mixtures are receiving much attention from many researchers due to concerns regarding the effect of gum addition on the physical and rheological properties of starches during processing. Therefore, many studies have been conducted to investigate the effect of various gums on the physical and rheological properties of starches in order to improve the sensory and textural properties of starch-based products (6-8). However, only a few studies examined the effect of gum addition on the rheological properties of cereal flours, such as rice and wheat flours (9,10). They observed an efficient synergism for flour-gum mixtures, indicating that the addition of gums to flour dispersions had a great effect on the rheological properties of flourgum mixtures, and their rheological properties depended on the type and concentration of gum. However, no studies as yet have been published regarding the rheological properties of barley flour in the presence of various gums. In this study, we selected the waxy barley flour (WBF) to investigate the rheological properties of WBF-gum mixtures because it is commonly used as a rice substitute or as a component of wheat products in Korea.

The main objectives of this study were to determine the steady and dynamic shear rheological properties of WBF in the presence of various gums, and to evaluate the effect of gum concentration and type on rheological properties. Information about the modification of the rheological properties of barley flour-gum mixtures will be helpful in developing new textures and enabling substitutions of ingredients.

MATERIALS AND METHODS

Materials and preparation of WBF-gum mixture samples

WBF, Heenchal barley flour, was a commercial product obtained from Goseong National Agricultural Cooperative Federation (Gyeongnam, Korea). The proximate composition of WBF was 12.5% moisture, 11.3% protein, 3.3% fat, 1.1% ash, 71.8% carbohydrate (by difference), and 16.9% amylose. The seven commercial food gums tested were xanthan gum (CP Kelco, Atlanta, GA, USA), guar gum (Habgen Guargums Ltd., Karachi, Pakistan), locust bean gum (Tate & Lyle, Bergamo, Italy), konjac gum (CKAA1220, Hong Kong Sheli Ltd., Chengdu, China), gum arabic (396I, Alland et Robert, Paris, France), carboxyl methyl celluleose (FH3000, Suzhou Co., Ltd., Suzhou, China), and tara gum (E417, Silvateam, Callao, Peru).

For the rheological measurements, WBF-gum mixture

dispersion (5%, w/w) were prepared by mixing WBF with distilled water and gums to obtain 0.3% and 0.6% gum concentrations. A WBF dispersion with no added gum (control) was also prepared. The dispersion was stirred for 1 h at room temperature and then heated at 95°C in a water bath for 30 min. The prepared hot paste was immediately transferred to a rheometer plate at 25°C for the measurement of its flow and dynamic rheological properties.

Rheological properties

Steady shear rheological measurements were carried out using a Haake rheometer (RS-1, Thermo Scientific, Karlsruhe, Germany) at 25° C having a parallel plate geometry of 3.5 cm in diameter at a gap of 500 μ m. Steady shear flow tests were performed over the range of shear rate from 0.4 to 500 s⁻¹. The power law (Eq. 1) and Casson (Eq. 2) models were fitted to the flow curves (shear stress versus shear rate):

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

$$\sigma^{0.5} = K_{oc} + K_{c} \dot{\gamma}^{0.5} \tag{2}$$

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

Dynamic shear rheological properties were carried out using a AR 1000 rheometer (TA Instruments, New Castle, DE, USA) at 25°C. The plate-plate geometry was used (diameter 4 mm; gap 500 μ m). An oscillatory frequency sweep test was performed in the range of 0.63 \sim 62.8 rad·s⁻¹ at 2% strain in order to determine the storage modulus (G'), loss modulus (G"), and loss tangent (tan δ =G"/G'). TA rheometer Data Analysis software (version VI. 1.76, TA Instruments) was used to obtain the experimental data and to calculate the dynamic shear rheological parameters (G', G", and complex viscosity). All rheological experiments were performed in triplicate.

Statistical analysis

All results are expressed as mean±standard deviation. Analysis of variance (ANOVA) was performed using Statistical Analysis System software (version 9.2, SAS Institute, Cary, NC, USA). Differences in means were determined using Duncan's multiple-range test.

RESULTS AND DISCUSSION

The σ versus $\dot{\gamma}$ data for WBF-gum mixture dispersions at

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0.3% and 0.6% gum concentrations at 25°C are shown in Fig. 1. The experimental results of σ and $\dot{\gamma}$ were well fitted to the simple power law model (Eq. 1) and Casson (Eq. 2) models, with high determination coefficients (R² =0.94~0.99) (Table 1). All WBF-gum mixtures exhibited shear-thinning behavior with values of flow behavior index values ($n=0.20\sim0.44$). In particular, the WBF-xanthan mixtures exhibited the lowest n values $(0.20 \sim 0.22)$ at all concentrations among the seven mixture samples (n=0.20~0.44), even though WBF had low shear-thinning behavior with an n value as low as 0.35 when compared to other mixtures. Such high shear-thinning behavior of WBF-xanthan mixtures may be due to the unique rigid, rod-like conformation and high molecular weight of xanthan gum (11). This result is in good agreement with those found in rice flour-gum mixtures (9).

In general, the magnitudes of $\eta_{a,100}$, K, and σ_{oc} of WBF mixed with gums, except for gum arabic, were much higher than those of the control (0% gum) (Table 1), indicating a higher synergism with gum due to starch-gum interaction. The flow parameters ($\eta_{a,100}$, K, and σ_{oc}) of all mixture samples increased with an increase of gum concentration from 0 to 0.6%. On the contrary, the flow parameter values of gum arabic were much lower than those of the control, showing no particular trend. This is in good agreement with that found in tapioca starch-gum arabic mixture (12). These results confirmed that the WBF-gum mixtures, except for gum arabic, are shearthinning fluids with higher magnitudes of $\eta_{a,100}$, K, and σ_{oc} when compared to the control. Comparison of the K and σ_{oc} values for WBF-gum mixture samples showed the WBF-konjac mixture at 0.6% to have higher values

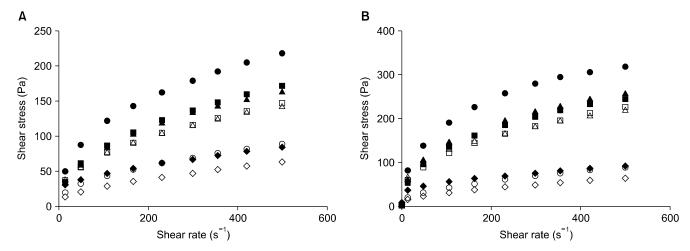


Fig. 1. Shear stress-shear rate plots for waxy barley flour-gum mixtures with different gum concentrations at 25°C. A, 0.3%; B, 0.6%. \bigcirc , control; \square , carboxyl methyl celluleose; \triangle , guar gum; \diamondsuit , gum arabic; \blacksquare , konjac gum; \blacksquare , locust bean gum; \blacktriangle , tara gum; \spadesuit , xanthan gum.

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

Gum type	Concentration (%)	η _{a,100} (Pa·s)	K (Pa·s ⁿ)	n (—)	σ_{oc} (Pa)
Control (no gum)	0	0.43±0.01 ⁱ	8.38±0.15 ^j	0.35±0.01 ^e	9.27±0.28 ^l
CMC	0.3	0.76±0.01 ^f	15.2±0.14 ⁹	0.35±0.01 ^e	20.7±0.06 ^h
	0.6	1.14±0.04 ^d	23.3±0.36 ^c	0.35±0.01 ^e	26.5 ± 0.07^{d}
G G	0.3	0.78±0.01 ^{ef}	15.4±0.33 ^g	0.35±0.01 ^e	18.7±0.04 ⁱ
	0.6	1.29 ± 0.03^{c}	28.8±0.09 ^b	0.32±0.01 ^f	34.1±0.21 ^b
GA .	0.3	0.30±0.01 ^j	5.31±0.05 ¹	0.38±0.01 ^d	7.66 ± 0.84^{m}
	0.6	0.34 ± 0.01^{j}	7.69 ± 0.28^{k}	0.32±0.01 ^f	8.88±0.52 ^l
K G	0.3	1.13 ± 0.02^{d}	17.7±0.30 ^f	0.40±0.01 ^c	21.1±0.01 ^{gh}
	0.6	1.85±0.03°	31.5±0.60°	0.38±0.01 ^d	40.5±0.32°
_BG	0.3	0.81 ± 0.02^{e}	11.2±0.24 ⁱ	0.43±0.01 ^a	13.9±0.02 ^k
	0.6	1.30±0.01 ^c	17.3±0.49 ^f	0.44±0.01 ^a	21.5±0.11 ^g
ΓG	0.3	0.82±0.01 ^e	13.7±0.56 ^h	0.39 ± 0.01^{d}	14.6±0.60 ^j
	0.6	1.41±0.03 ^b	21.1±0.26 ^d	0.41±0.01 ^b	24.3±0.40 ^e
K G	0.3	0.51±0.02 ^h	18.8±0.55 ^e	0.22±0.01 ^g	22.8±0.41 ^f
	0.6	0.59±0.01 ^g	23.7±0.09 ^c	0.20±0.01 ^h	31.3±0.03 ^c

Values in the same column with different letters (a-m) are significantly different (P<0.05).

CMC, carboxyl methyl celluleose; GG, guar gum; GA, gum arabic; KG, konjac gum; LBG, locust bean gum; TG, tara gum; XG, xanthan gum.

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

(K=31.5 Pa.sⁿ; σ_{oc} =40.5 Pa), indicating the higher synergism with konjac due to its greater thickening properties in the mixture system. In contrast, the addition of gum arabic decreased the K and σ_{oc} values of WBF. It is known that gum arabic itself exhibits relatively lower viscosity in solution when compared to other gums. Therefore, the addition of gum arabic to WBF may lead to the adverse effect on increase in flow parameter values of WBF paste. These results are in good agreement with those reported for mixtures of konjac gum with potato starch (2) and gum arabic with rice starch (13). In addition, the xanthan gum showed the largest increase of K and σ_{oc} values at lower gum concentration (0.3%). This result is consistent with a previous report for aqueous xanthan solutions at different concentrations (14). The greater significant increases in σ_{oc} values when compared to $\eta_{a,100}$ and K values also indicate that the elastic properties of WBF were strongly influenced by the addition of gums (15). From the above observations, it can be concluded that changes in the flow parameter values of WBF-gum mixtures were influenced by the type and concentration of gum.

Changes in G' and G" as functions of the frequency (ω)

for WBF-gum mixture dispersions at different gum concentrations (0.3 and 0.6%) are shown in Fig. 2. G' and G" values increased with increasing ω, and G' was much higher than G" at all values of ω. Table 2 also shows dynamic moduli (G' and G") values at 6.28 rad·s⁻¹ of WBFgum mixtures with different gum concentrations at 25°C. The dynamic moduli of all gums, except for gum arabic, were higher than those of control (0% gum), and they also increased with an increase in gum concentrations from 0 to 0.6%, indicating that the addition of gums to WBF has synergistic effect on viscoelastic properties. In particular, the xanthan and konjac showed the higher G' values (26.0 Pa and 51.4 Pa) at 0.3% and 0.6%, respectively, when compared to other gums, and konjac at all concentrations also showed much higher G" (13.5 Pa at 0.3% and 35.5 Pa at 0.6%). Such dynamic behavior of WBF-gum mixture dispersions may be attributed to an increase in the viscoelasticity of the continuous phase in mixture systems due to the thickening properties of added gums as noted by BeMiller (16). However, the dynamic moduli of gum arabic were much lower than those of the control, showing that this trend was a similar to the values of flow rheological parameters ($\eta_{a,100}$, K, and σ_{oc}).

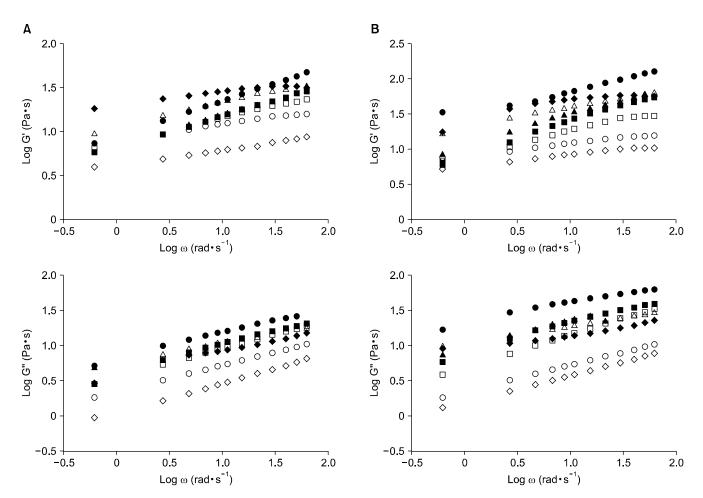


Fig. 2. Plot of G' and G" versus ω of waxy barley flour-gum mixtures with different gum concentrations at 25°C. A, 0.3%; B, 0.6%. \bigcirc , control; \square , carboxyl methyl celluleose; \triangle , guar gum; \diamondsuit , gum arabic; \blacksquare , konjac gum; \blacksquare , locust bean gum; \blacktriangle , tara gum; \spadesuit , xanthan gum.

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Table 2. Storage modulus (G'), loss modulus (G''), and tan δ at 6.28 rad·s⁻¹ of waxy barley flour-gum mixtures at 25°C

Gum type	Concentration (%)	G' (Pa)	G'' (Pa)	$tan \ \delta$
Control (no gum)	0	11.1±0.11 ^k	4.49±0.11 ^k	0.40±0.01 ^h
CMC	0.3	12.5±0.20 ^j	7.12±0.46 ^j	0.57±0.01 ^f
	0.6	15.4±0.01 ^h	11.3±0.33 ^f	0.74 ± 0.02^{c}
GG	0.3	19.1±0.07 ^f	9.76±0.08 ^g	0.51 ± 0.01^{g}
	0.6	37.2±0.62 ^c	18.3±0.02 ^c	0.49 ± 0.01^{g}
GA	0.3	5.83±0.01 ^m	2.40±0.05 ¹	0.41±0.01 ^h
	0.6	7.76 ± 0.20^{1}	3.16±0.12 ^l	0.41±0.01 ^h
KG	0.3	17.3±0.05 ⁹	13.8±1.10 ^d	0.80 ± 0.07^{b}
	0.6	51.4±0.60°	35.5±0.67 ^a	0.69 ± 0.01^{d}
LBG	0.3	11.9±0.11 ^j	8.32±0.13 ^{hi}	0.70 ± 0.02^{d}
	0.6	19.9±0.69 ^e	17.5±1.05 ^c	0.88 ± 0.02^{a}
TG	0.3	13.3±0.30 ⁱ	8.69±0.11 ^h	0.65±0.05 ^e
	0.6	26.0±0.42 ^d	19.4±0.37 ^b	0.75±0.01 ^c
XG	0.3	26.0±0.27 ^d	7.75±0.10 ^{ij}	0.30 ± 0.01^{i}
	0.6	47.5±0.10 ^b	12.8±0.29 ^e	0.27±0.01 ⁱ

Values in the same column with different letters (a-I) are significantly different (P<0.05).

CMC, carboxyl methyl celluleose; GG, guar gum; GA, gum arabic; KG, konjac gum; LBG, locust bean gum; TG, tara gum; XG, xanthan gum.

This indicates that there is no synergistic effect of gum arabic on viscoelastic properties. The dynamic moduli values of konjac at 0.6% were relatively higher than those of other gums, indicating a more pronounced effect of konjac on the viscoelastic properties of WBF. In addition, the increase in dynamic moluli from 0.3 to 0.6% was more prominent for konjac compared to other gums, showing that 0.6% konjac was approximately 2.6~2.9fold greater compared to the 0.3% konjac. Such higher dynamic moduli values of WBF-konjac mixtures at a high gum concentration seems to be influenced by the konjac gum. These results suggest that there was higher synergism with konjac gum due to its greater thickening properties as compared to other gums. Yaseen et al. (17) also reported that a konjac gum solution exhibited higher viscoelastic properties compared to other gums solutions.

The tan δ (ratio of G"/G') values (0.27 ~ 0.88) of WBFgum mixtures were less than "1" (Table 2), indicating that all the samples were more elastic than viscous. Among the WBF-gum mixture samples having a synergistic effect of gum on viscoelastic properties of WBF (Table 2), all tan δ values (0.41 ~ 0.88) except for xanthan gum $(0.27 \sim 0.30)$ were higher than those of the control (0.40), showing that $\tan \delta$ increased with gum addition. This means that in the mixtures of WBF with gums except for xanthan, G" increased much more than G' when compared to xanthan. However, no significant change in tan δ was observed gum arabic. The large change in G'' compared to G' as well as the higher tan δ values mean that the addition of gum decreased the solid character of the mixture system, contributing to the viscous properties of the starch dispersion (2). Such viscous properties of WBF-gum mixtures can be explained by thermodynamic incompatibility in which the interactions between polymers of the same type are favored energetically when compared to interactions between different polymers (16,18,19). Therefore, the synergistic effect of gum on rheological properties of WBF dispersion may be attributed to the increased viscoelasticity of the continuous phase, in which gum is concentrated in mixture systems due to the thickening properties and greater hydration capacity of gum. In contrast, a strong synergistic interaction between xanthan and WBF was observed due to lower tan δ values (0.27 ~ 0.30) compared to the control and other mixture samples, suggesting that there was thermodynamic compatibility between xanthan and WBF (20,21). From these observations, it was concluded that the addition of gum to WBF dispersion has a pronounced effect on the dynamic rheological properties in WBF-gum mixtures, and the extent of variation greatly depends on the gum type and concentration. These results will be useful for food manufacturers to select the appropriate gums for the required rheological properties of WBF-based products.

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AUTHOR DISCLOSURE STATEMENT

The authors declare no conflict of interest.

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