Prev Nutr Food Sci
Vol 17, p 192~196 (2012)
http://dx.doi.org/10.3746/pnf.2012.17.3.192

Steady and Dynamic Shear Rheological Properties of Buckwheat Starch-galactomannan Mixtures

Dong Won Choi and Yoon Hyuk Chang†

Department of Food Science and Engineering, Daegu University, Gyeongbuk 712-714, Korea

Abstract

This study investigated the effects of galacomannans (guar gum, tara gum, and locust bean gum) on the rheological properties of buckwheat starch pastes under steady and dynamic shear conditions. The power law and Casson models were applied to describe the flow behavior of the buckwheat starch and galactomannan mixtures. The values of the apparent viscosity ($\eta_{a,100}$), consistency index (K), and yield stress (σ_{oc}) for buckwheat starch-galactomannan mixtures were significantly greater than those for the control, indicating that there was a high synergism of the starch with galactomannans. The magnitudes of storage modulus (G′) and loss modulus (G″) for the starch-galactomannan mixtures increased with increasing frequency (ω). The dynamic moduli (G′, G″), and complex viscosity (η*) for the buckwheat starch-galactomannan mixtures were significantly higher than those for the control.

Key words: buckwheat starch, galactomannan, steady shear properties, dynamic shear properties

INTRODUCTION

Starch and gum (hydrocolloids) mixtures are frequently used in food systems to provide desirable texture, moisture control and water mobility, as well as to enhance overall product quality (1-4). In general, starch by itself is widely used as a thickening agent in the food industry, and adding gums strongly influences the rheological properties of the starch. Steady and dynamic shear rheological tests have been frequently used to investigate the rheological properties of starch-gum mixture systems (5-12). It has been reported that the rheological properties of starch-gum mixture solutions are dependent on the type, structure, molecular weight, and concentration of the gums added to the starch solution (8-12).

Buckwheat (*Fagopyrum esculentum* Moench) is widely cultivated in many countries, including India, China, Russia, Poland, Brazil, Japan, United States, and Korea. Buckwheat starch is frequently used as an ingredient of processed buckwheat products, such as noodles, curds, pasta, porridges, and soups (13).

Galactomannans are water-soluble polysaccharides found in seed endosperms of various legumes and are widely used in food industry, mainly as thickening agents. They have a lower cost than carrageenan and xanthan, and their synergistic interaction with starches increases the feasibility of a new functionality with wide industrial importance (14-16). Galactomannans are essentially composed of a straight chain backbone of 1-4-linked β-D-mannopyranose units with a side-branching unit of galactopyranose. The most popular galactomannans include guar gum (GG), tara gum (TG), and locust bean gum (LBG). These three gums differ basically in the mannose: galactose ratio, which is around 2:1 for GG, 3:1 for TG, and 4:1 for LBG (14).

Many researchers have studied the effect of the addition of gums on the rheological properties of wheat (4), corn (6), sweet potato (11), acorn (3), and rice (8) starch pastes. However, there is no report in the literature, as far as the authors are aware, on the effects of galactomannans such as GG, TG, and LBG on the rheological properties of buckwheat starch pastes. Moreover, to apply buckwheat starch-galactomannan mixtures in food and non-food systems, it is necessary to evaluate the detailed rheological properties of the mixtures. Therefore, the objective of the present study was to investigate the rheological properties of buckwheat starch and galactomannan mixtures under steady and dynamic shear conditions.

MATERIALS AND METHODS

Materials

Buckwheat starch and GG were obtained from Muksarang (Goheung, Korea) and from Sigma (St. Louis, MO, USA), respectively. TG and LBG were purchased from Silvateam (Piedmont, Italy) and CP Kelco (Lille

†Corresponding author. E-mail: changyh@daegu.ac.kr
Phone: +82-53-850-6537, Fax: +82-53-850-6539

Skensved, Denmark), respectively.

Preparation of buckwheat starch-galactomannan mixtures

The buckwheat starch-galactomannan mixtures were prepared by mixing 4.5 g of the starch with 95 g distilled water and 0.5 g gum (GG, TG and LBG). Furthermore, a dispersion with no added gum was prepared as control. Each mixture was moderately stirred for 1 hr at room temperature to hydrate, and then heated at 95°C for 30 min in a water bath (VS-1205SW1, Vision Scientific, Bucheon, Korea). During heating, a screw-cap Erlenmeyer flask was used to prevent water evaporation.

Steady shear rheological properties

Steady shear rheological properties of buckwheat starch-galactomannan mixtures were determined on a strain controlled Physica MCR 301 Rheometer (Anton Paar, Österreich, Austria). To obtain steady shear (shear stress and shear rate) data, a plate/plate geometry (50 mm diameter, 0.5 mm gap) was used at 30°C with shear rate from 1 to 1,000 s^{-1}. To describe the steady shear rheological properties of the samples, the data were fitted to the well-known power law (Eq. 1) and Casson (Eq. 2) models:

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

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

where σ is the shear stress (Pa), γ is the shear rate (s^{-1}), K is the consistency index ($Pa{\cdot}s^n$), n is the flow behavior index (dimensionless), and $(K_c)^2$ is the Casson plastic viscosity (η_c). Casson yield stress (σ_{oc}) according to the Casson model (Eq. 2) was determined as the square of the intercept (K_{oc}) that was obtained from the linear regression of the square roots of the shear rate-shear stress data. Using the magnitudes of K and n, apparent viscosity ($\eta_{a,100}$) at 100 s^{-1} was calculated. The steady shear rheological measurements were conducted in triplicate. The reported results were expressed as an average of the three measurements.

Dynamic shear rheological properties

Dynamic shear rheological properties [storage modulus (G′), loss modulus (G″), complex viscosity (η^*), and tan δ (G″/G′)] of buckwheat starch-galactomannan mixtures were determined on a strain controlled Physica MCR 301 Rheometer (Anton Paar). Prior to the dynamic shear rheological measurements, a strain sweep test at a constant frequency of 6.3 rad s^{-1} determined the linear viscoelastic region. The dynamic measurements were performed at a strain value of 0.02 (2%) (within the linear viscoelastic region). Frequency sweep tests of all the solutions were performed using a plate/plate geometry (50 mm diameter, 0.5 mm gap) at 30°C and frequency (ω) from 0.63 to 63.8 rad s^{-1}. The dynamic shear rheological measurements were conducted in triplicate. The reported results were expressed as an average of the three measurements.

Statistical analysis

All statistical analyses were performed using SAS version 9.1 (SAS Institute Inc., Cary, NC, USA). Analysis of variance (ANOVA) was performed using the general linear models (GLM) procedure to determine significant differences among the samples. Means were compared by using Fisher's least significant difference (LSD) procedure. Significance was defined at the 5% level.

RESULTS AND DISCUSSION

Steady shear rheological properties

The shear rate versus shear stress data at 30°C were well fitted to the power law model [Eq. (1)] and Casson model [Eq. (2)] with high determination coefficients (R^2 =0.94∼0.99), as indicated in Table 1. All the buckwheat starch and galactomannan mixtures studied had shear-thinning behavior with values of flow behavior indexes (n) as low as 0.24∼0.32, as shown in Table 1 and Fig. 1. GG had the lowest n value among all the buckwheat starch-galactomannan mixtures studied in the present study (Table 1), suggesting that the starch-GG mixture had a more pseudoplastic (i.e. shear-thinning) behavior compared with the starch-TG and the starch-LBG mixtures. This finding was in good agreement with reports in the literature (3,8,11). Kim and Yoo (3) studied the effects of galactomannan addition on the rheological properties of acorn starch, and they found that the acorn starch paste had a more pseudoplastic behaviour in the

Table 1. Effects of gum type on steady shear rheological properties of buckwheat starch pastes at 30°C[1)]

Gum type[2)]	Apparent viscosity $\eta_{a,100}$ (Pa·s)	Consistency index K ($Pa{\cdot}s^n$)	Flow behavior index n (-)	Casson yield stress σ_{oc} (Pa)
Control	0.62 ± 0.02^d	19.12 ± 0.67^d	0.25 ± 0.00^c	25.03 ± 1.05^d
GG	1.13 ± 0.05^c	37.60 ± 1.90^a	0.24 ± 0.01^c	53.10 ± 1.60^a
TG	1.36 ± 0.04^a	33.78 ± 2.48^b	0.30 ± 0.01^b	39.54 ± 3.23^b
LBG	1.23 ± 0.08^b	27.83 ± 3.55^c	0.32 ± 0.02^a	28.46 ± 1.84^c

[1)]Values are mean±standard deviation for triplicate measurements.
[2)]GG, guar gum; TG, tara gum; LBG, locust bean gum.

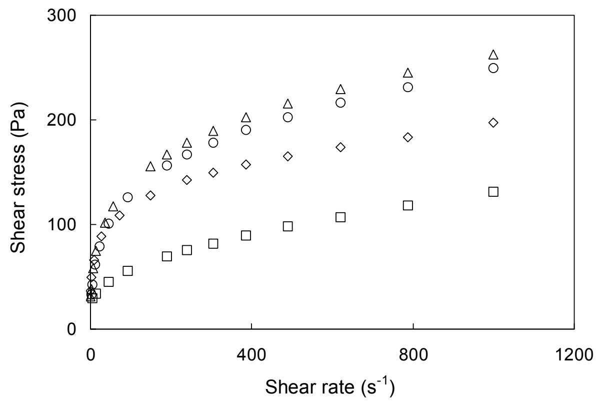


Fig. 1. Shear rate-shear stress plots for buckwheat starch-galactomannan mixtures at 30°C: (□) control, (◇) guar gum, (△) tara gum, (○) locust bean gum.

presence of GG than did LBG. They reported that such higher pseudoplastic behaviour of acorn starch-GG mixture can be related to the gum structure of GG and LBG. GG has a greater extended conformation than LBG, and it is well known that the more extensive branching of GG can be associated not only with its easier hydration properties but also its greater hydrogen-bonding activity, which may also take place within and/or between polysaccharide and starches, therefore improving complex formation (1). The data in this present study also indicate that the more extensive branching of galactomannans (branching ratio: GG>TG>LBG) causes an increase in pseudoplastic behavior of the gums.

The values of the apparent viscosity ($\eta_{a,100}$), consistency index (K), and yield stress (σ_{oc}) for buckwheat starch-galactomannan mixtures were significantly greater than those for the control (Table 1), indicating that there was a high synergism of the starch with galactomannans. According to Lai et al. (7), the synergistic effect of starch with galactomannans during heating can be explained by the interactions between amylose exudates and gum. When comparing the effects of addition of the galacomannans employed in the present study on the K and σ_{oc} values of buckwheat starch pastes, the order of K and σ_{oc} values was GG>TG>LBG. The finding was good agreement with the results observed when other mixtures of galactomannans with wheat starch (4), sweet potato starch (11), and acorn starch (3) were evaluated. A significant increase in K and σ_{oc} values for the starch-GG mixture, as compared with the starch-TG or the starch-LBG mixture, can be explained by a higher synergism of GG with buckwheat starch due to its greater hydration capacity and thickening properties (2).

Dynamic shear rheological properties

Small deformation oscillatory rheological tests are useful in examining the molecular origin of the rheological properties of starch and/or gum solutions. The storage modulus (G′) reflects the solid-like properties of a viscoelastic material, while the loss modulus (G″) reflects its liquid-like character (15). In the present study, G′ and G″ values for the buckwheat starch-galactomannan mixtures were greater than those for the control, and the G′ values were much higher than G″ values at all ω values with a small frequency dependency (Fig. 2). Accordingly, it is indicated in the present study that the mixtures were typical of a viscoelastic fluid and exhibited typical "weak gel" properties with G′ exceeding G″ over all of the frequency range investigated. The dynamic moduli (G′ and G″) values at frequency of 6.3 rad s^{-1} of the buckwheat starch-galactomannan mixtures were significantly higher than those of the control (Table 2). The elevation in dynamic moduli can be related to the higher viscoelastic properties of added galactomannans and the new cross-linking between the starch and gums (3).

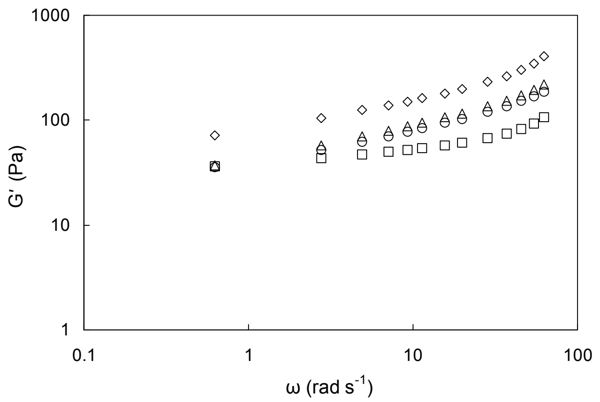
The frequency dependence of complex viscosity (η^*) for the buckwheat starch-galactomannan mixtures is illustrated in Fig. 2. All of the mixtures studied exhibited a shear-thinning flow behavior in accordance with the power law model. The complex viscosity of all the mixtures was higher than that of the control. This speculation is confirmed by the steady shear rheological data (Table 1).

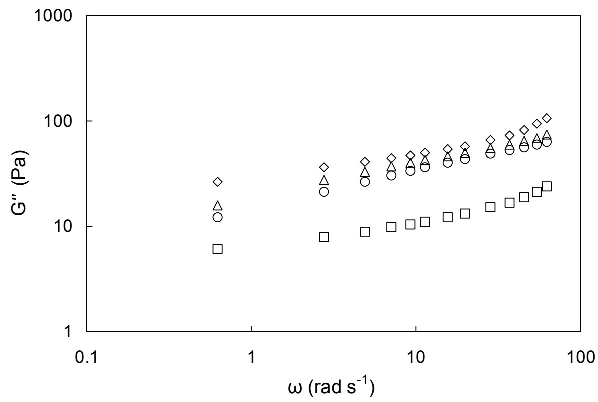
The tan δ values at frequency of 6.3 rad s^{-1} for all the mixtures were significantly higher than the control (Table 2). The values of tan δ, directly obtained from G″/G′ ratio, can be used to elucidate the visocoelastic behavior of polysaccharide solutions. For example, the tan δ values smaller than one indicate predominantly elastic behavior, whereas the tan δ values higher than

Table 2. Storage modulus (G′), loss modulus (G″), complex viscosity (η^*) and tan δ of starch-galactomannan mixtures (measured at 6.3 rad s^{-1} and 30°C)[1)]

Gum type[2)]	Storage modulus G′ (Pa)	Loss modulus G″ (Pa)	Complex viscosity η^* (Pa·s)	Tan δ
Control	149.98±1.38^c	449.85±0.22^c	27.21±0.20^d	0.20±0.00^d
GG	139.12±15.76^a	445.53±3.13^a	20.68±2.26^a	0.32±0.02^c
TG	179.99±3.00^b	436.93±1.32^b	12.48±0.43^b	0.46±0.02^a
LBG	171.46±5.17^b	433.23±2.61^b	10.87±0.21^c	0.43±0.02^b

[1)]Values are mean±standard deviation for triplicate measurements.
[2)]GG, guar gum; TG, tara gum; LBG, locust bean gum.





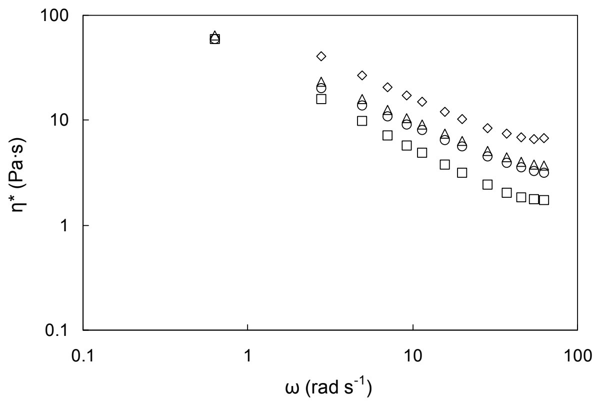


Fig. 2. Plots of log G′, log G″, and η^* versus log ω of buckwheat starch-galactomannan mixtures at 30°C: (□) control, (◇) guar gum, (△) tara gum, (○) locust bean gum.

one indicate predominantly viscous behavior. In the present study, the tan δ values of all the mixtures were lower than one, which means that the mixtures are more elastic rather than viscous.

In general, the dynamic rheological data of ln G′ and ln G″ vs. ln ω were subjected to linear regression, and Table 3 provides the magnitudes of slopes (n′ and n″) and intercepts (K′ and K″) in the following equations (Eq. 3 and 4):

$$G' = K'(\omega)n' \quad (3)$$

$$G'' = K''(\omega)n'' \quad (4)$$

Structurally speaking, for true gels, the plots of ln G′ and ln G″ vs. ln ω have zero slope, whereas for weak gels, the plots have positive slopes and the values of K′ is higher than those of K″ with the frequency dependency as described by Choi and Yoo (9). In the present study, the values of n′ and n″ for all the mixtures were positive, and the K′ values for the same mixtures were substantially higher than the K″ values. Moreover, the values of n′ for the mixtures were significantly higher than those for the control. Thus, the findings indicated that the mixtures had weak gel properties and were more elastic than viscous.

The present study focused on the steady and dynamic shear rheological properties of the buckwheat starch-galactomannan mixtures. The flow behavior index (n), consistency index (K), apparent viscosity ($\eta_{a,100}$), and yield stress (σ_{oc}) values, obtained from the power law and Casson models, for the starch paste were profoundly affected by the type of galactomannan. Among the galactomannan mixtures studied, the starch-GG mixture system had the highest viscoelastic properties, demonstrating a higher synergism of the buckwheat starch with GG, compared to the starch-TG and the starch-LBG mixture

Table 3. Slopes (n′, n″) and intercepts (K′, K″) (Pa·s) of ln (G′, G″) vs. ln ω (frequency, rad s^{-1}) data of buckwheat starch-galactomannan mixtures at 30°C[1)]

Gum type[2)]	G′			G″		
	n′	K′	R^2	n″	K″	R^2
Control	0.28 ± 0.02^{d}	3.82 ± 0.04^{c}	0.96	0.35 ± 0.05^{a}	2.16 ± 0.02^{d}	0.97
GG	0.42 ± 0.12^{a}	4.81 ± 0.07^{d}	0.98	0.32 ± 0.14^{a}	3.70 ± 0.02^{a}	0.97
TG	0.45 ± 0.04^{c}	4.27 ± 0.06^{a}	0.99	0.31 ± 0.03^{a}	3.55 ± 0.04^{d}	0.99
LBG	0.44 ± 0.03^{b}	4.15 ± 0.00^{b}	0.99	0.32 ± 0.01^{a}	3.44 ± 0.04^{c}	0.99

[1)]Values are mean ± standard deviation for triplicate measurements.
[2)]GG, guar gum; TG, tara gum; LBG, locust bean gum.

systems. The effects of additional polysaccharides on steady and dynamic shear rheological properties of buckwheat starch pastes will be presented in a future paper.

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(Received August 29, 2012; Accepted September 6, 2012)