Effect of Tara Gum Addition on Steady and Dynamic Shear Rheological Properties of Rice Starch Isolated from the Korean Rice Variety 'Boramchan'

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ABSTRACT: The present study was performed to investigate the influence of tara gum (TG) addition on the steady and dynamic shear rheological properties of rice starch (RS) isolated from the Korean rice variety 'Boramchan' flour. From X-ray diffraction and Fourier transform infrared spectra of RS, it was found that RS was purely isolated. All RS+TG pastes (4.7:0.3, 4.5:0.5, and 4.3:0.7, w/w) showed shear-thinning fluid characteristics. Adding TG significantly increased the values of apparent viscosity and consistency index of RS. In the dynamic shear rheological analysis, the dynamic moduli and complex viscosity of RS+TG pastes were significantly greater than those of the RS paste, indicating that RS+TG pastes had significantly higher viscoelastic properties than the RS paste. Light microscopy images of RS+TG pastes showed that the addition of TG can inhibit the RS granule from swelling.

Keywords: rice starch, Boramchan, tara gum, rheological properties

INTRODUCTION

Rice (*Oryza sativa* L.) is a staple food for almost half of the world's population. Rice kernel mainly contains starch which is almost 90% of the total kernel weight (1). Rice starch (RS) has many advantages such as small granular size (3～5 μm), white color, bland flavor, hypoallergenicity, and easy digestibility (2). However, the inherent properties of RS have some disadvantages, which limit its applications in the food industry. For example, RS showed lower rheological properties than potato, corn, and wheat starches (3).

These limitations can be controlled by chemical modifications. However, recently, due to consumers' preference for natural food ingredients, there has been a growing interest in the mixture of RS and hydrocolloids to overcome the shortcomings of native RS. According to previous studies reported by Choi and Chang (4) and Kim et al. (5), hydrocolloids such as guar gum (GG), tara gum (TG), locust bean gum (LBG), and xanthan gum can improve the steady and dynamic shear rheological properties of starch and starch-based food systems. Moreover, the addition of hydrocolloids can improve the structural stability and sensory properties of starch-based food products during distribution and storage.

TG is obtained from the endosperm of *Caesalpinia spinosa* tree. TG is a galactomannan polysaccharide that mainly consists of a linear chain of mannose linked β (1→4) bonds and galactose units as side chains with α (1→6) linkages. The ratio of mannose to galactose in TG is 3:1, which is similar to that of GG (2:1) and LBG (4:1). Due to its structural similarity, TG exhibits high viscosities in water within a few minutes like GG and synergistic interactions with agar and xanthan to improve gel strength like LBG (6).

Up to now, many researchers have studied the effect of hydrocolloids (GG and LBG) on the physicochemical and rheological properties of starch (corn starch and potato starch). However, there has not been an attempt to isolate RS from Boramchan and improve the rheological properties of RS in addition to TG. Therefore, the objectives of the present study were to analyze the structural properties of the isolated RS from Boramchan and elucidate the influence of TG addition on the steady and dynamic shear rheological properties of RS.

MATERIALS AND METHODS

Materials
Rice flour from 'Boramchan' was purchased from Nongshim Co., Ltd. (Seoul, Korea). TG was obtained from Jupiter international Co. (Seoul, Korea). Potato amylose and maize amylopectin were purchased from Sigma (St. Louis, MO, USA).

Isolation of RS
RS was isolated by the alkaline steeping method with slight modification (7). Rice flour (500 g) was dispersed in 0.2% sodium hydroxide solution (1.5 L), while constantly stirring at 30°C for 1 h. Then, the suspension was centrifuged at 1,800 g for 10 min using a centrifuge (Combi 408, Hanil Science Industrial Co., Ltd., Incheon, Korea). The supernatant was discarded and the protein extract was removed from the precipitate. The alkaline extraction was repeated until traces of the protein extract were no longer found. Afterward, the starch precipitates were mixed with distilled water (1 L) and neutralized at pH 7.0 with 0.1 M hydrochloric acid. The starch dispersion was centrifuged, washed twice using distilled water, and then washed with 95% ethanol. The purified starch was dried at 40°C for 24 h, pulverized, screened through 150 μm mesh sieve, and stored in a sealed container at 4°C before use.

Chemical composition, amylose content, and structural properties of RS
RS was analyzed for its chemical composition. The standard AACCI approved methods were used to determine the contents of moisture (44-15A), ash (08-01), protein (46-12A), and lipid (30-10).

The amylose content of RS was measured according to the method of Williams et al., with slight modifications (8). RS (20 mg) was continuously mixed with 0.5 M potassium hydroxide (10 mL) for 5 min. The suspension was transferred to a 100 mL volumetric flask, and the final volume was made up to 100 mL using distilled water. Then, 10 mL of the solution was transferred to a 50 mL volumetric flask containing 0.1 M hydrochloric acid (5 mL) and 0.2% I_2/2% KI (0.5 mL). The final volume was made up to 50 mL using distilled water. After 5 min, the absorbance of the samples was measured at 620 nm. The amylose contents of RS were calculated from a standard curve prepared with mixtures of potato amylose and maize amylopectin.

X-ray diffraction (XRD) patterns of RS were analyzed by an X-ray diffractometer (D8 Advance, Bruker AXS GmbH, Karlsruhe, Germany). The X-ray generator tension and current were 40 kV and 40 mA, respectively. The samples were scanned through the range of 2θ from 6° to 30°.

The Fourier-transform infrared (FT-IR) spectrum of RS was obtained by using a Fourier-transform infrared spectrophotometer (Spectrum One System, Perkin-Elmer, Waltham, MA, USA). RS was ground with potassium bromide and pressed into a disc. Spectral scanning range was 4,000 to 500 cm^{-1}.

Preparation of RS-TG pastes
To prepare the RS paste alone, RS (5%, w/w) was dispersed in distilled water under magnetic stirring for 1 h at room temperature and heated in a water batch at 95°C for 30 min with constant gentle mixing.

The mixtures of RS and TG (4.7:0.3, 4.5:0.5, and 4.3:0.7, w/w) were mixed. These samples were marked as RS+TG0.3, RS+TG0.5, and RS+TG0.7, respectively. TG was first dissolved in distilled water, heated in a water bath at 95°C for 5 min, and cooled to room temperature. Then, RS was added to the flask containing the TG suspension to make a total weight of 100 g. Once dispersed, magnetic stirring was continued for 1 h at room temperature. Then, the heating treatment of RS+TG pastes was the same as that of RS. At the end of the heating period, the hot pastes were immediately transferred to measure their microscopic observations and rheological properties.

Microscopic observations of RS-TG pastes
The RS, RS+TG0.3, RS+TG0.5, and RS+TG0.7 pastes were obtained from the preparation of RS-TG pastes. Each sample was placed on a glass slide, and stained with 1% (w/w) Lugol's iodine solution. In order to minimize evaporation, the samples were covered with a coverslip. The samples stained with Lugol's iodine solution were analyzed by ECLIPSE Ci-L optical microscope (Nikon, Tokyo, Japan).

Steady shear and dynamic shear rheological properties of RS-TG pastes
Steady shear rheological properties of all samples were conducted with a controlled stress rheometer (MCR-102, Anton Paar, Graz, Austria), using a plate to plate system (diameter: 5 cm, gap: 0.5 mm). Samples were transferred to the rheometer plate. Steady shear data were obtained at 25°C over the shear rate in the range of 0.1~1,000 s^{-1}. To describe the steady shear rheological properties of the samples, data were fitted to the well-known power law model [1]. The following equation was used:

$$\sigma = K\dot{\gamma}^n \qquad [1]$$

where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency index (Pa·s^n), and n is the flow behavior index (dimensionless). Using the magnitudes of K and n, the apparent viscosity at 500 s^{-1} ($\eta_{a,500}$) was

calculated.

Dynamic shear data were obtained from angular frequency (ω) sweeps over the range of 0.628~62.8 rad/s. The strain amplitude for the frequency sweep measurements was selected as 2% according to the strain sweep results (data not shown) in order to be in the linear viscoelastic region for all samples. Frequency sweep tests were also conducted at 25°C. A RheoPlus/32 software (V 3.40, Anton Paar) was used to obtain the data and to calculate the storage modulus (G'), loss modulus (G"), complex viscosity (η*), and tan δ (G"/G').

Statistical analysis
All statistical analyses were performed using the Statistical Analysis System program (version 9.4) (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 using Fisher's least significant difference (LSD). Significance was defined at the 5% level.

RESULTS AND DISCUSSION

Chemical composition
The moisture, ash, protein, lipid, and total starch contents of RS from Boramchan were 3.60%, 0.17%, 0.33%, 0.90%, and 93.32%, respectively (Table 1), suggesting that protein, lipid, and ash in rice flour were almost entirely removed. The amylose and amylopectin contents of RS were 22.11 and 77.78%, respectively (Table 1). Similarly, You et al. (9) found that the amylose content of RS from Boramchan was 23.6%.

Structural properties of RS
The XRD pattern of RS showed strong diffraction peaks at 15, 17, 18, and 23° (2θ) (Fig. 1A). These patterns were

Table 1. Chemical composition of rice starch

Chemical composition	Rice starch (%)
Moisture	3.60±0.23
Ash	0.17±0.01
Protein	0.33±0.00
Lipid	0.90±0.10
Total starch	93.32±1.03
Amylose	22.22±0.21
Amylopectin	77.78±0.21

the typical type-A starch pattern (10). The result of the present study was consistent with previously reported results (11,12).

The FT-IR spectrum of RS is shown in Fig. 1B. RS showed peaks at 3,350 cm^{-1} and 2,932 cm^{-1}, which were ascribed to the inner- and intro-hydrogen-bonded OH stretching vibration and CH bond stretching vibration, respectively (13). The OH bending vibration and CH$_2$ scissoring vibration were observed at around 1,647 cm^{-1} and 1,416 cm^{-1}, respectively (14). RS had three distinctive peaks observed for the vibration of C-O bond stretching (C-O-C and C-O-H) between 1,019 and 1,154 cm^{-1} (15). Similar spectral results for RS have been observed (16,17). Therefore, in the present study, it would be confirmed that the XRD and FT-IR spectra of RS exhibited typical peaks of a starch backbone, and RS was purely isolated.

Microscopic observations of RS-TG pastes
Fig. 2 depicts light microscopy images of RS with and without TG. In the RS paste, after heating at 95°C, the swollen granules were eventually ruptured, resulting in a loss of granule integrity. However, when RS granules were gelatinized in the presence of TG, the integrity of the starch granules was maintained, and the extent of starch swelling was significantly decreased (18). Moreover, this effect was more pronounced when the amount of TG was increased from 0.3 to 0.7%.
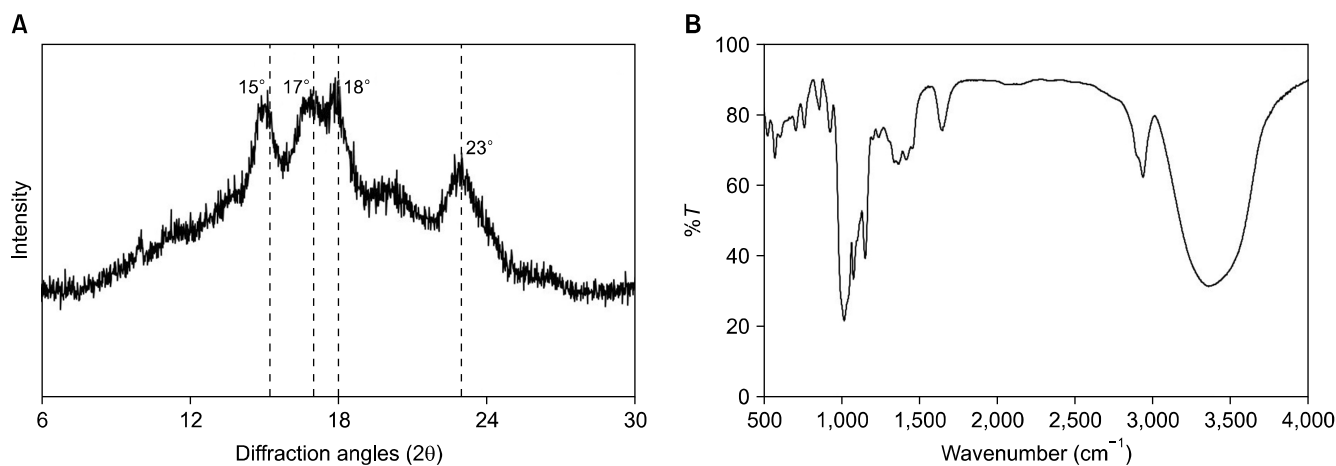

Fig. 1. X-ray diffraction (A) and Fourier-transform infrared (B) spectra of rice starch.
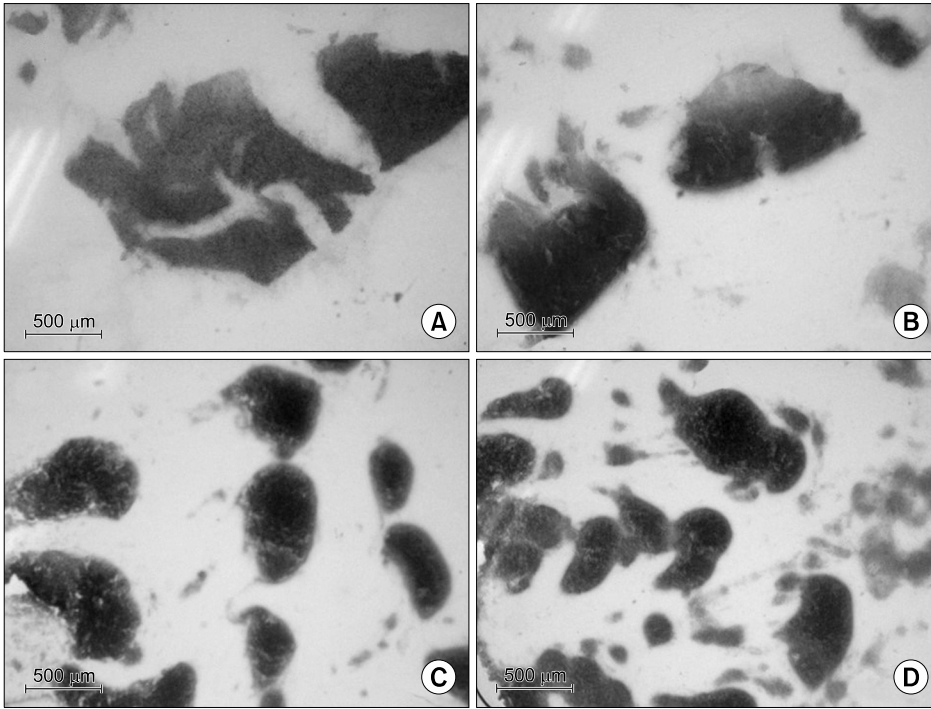
Fig. 2. Light microscopy images of the mixture of rice starch (RS) and tara gum (TG) with different amounts of TG at 25°C. (A) RS, (B) the mixture of RS and TG (4.7:0.3, w/w), (C) the mixture of RS and TG (4.5:0.5, w/w), and (D) the mixture of RS and TG (4.3:0.7, w/w).
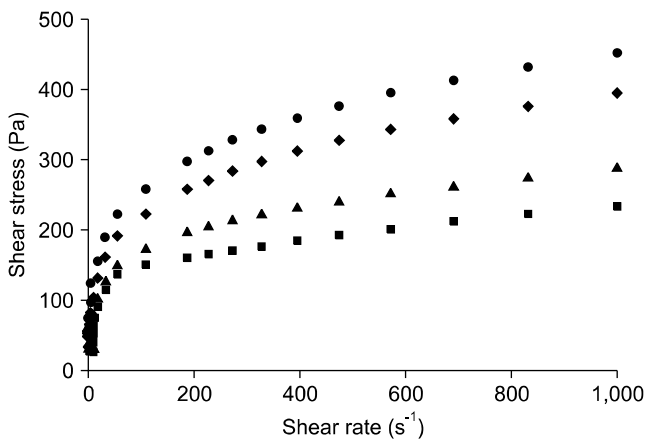

Fig. 3. Log shear stress–apparent viscosity plots of the mixture of rice starch (RS)–tara gum (TG) with different amounts of TG at 25°C. ■, RS; ▲, the mixture of RS and TG (4.7:0.3, w/w); ◆, the mixture of RS and TG (4.5:0.5, w/w); ●, the mixture of RS and TG (4.3:0.7, w/w).

Table 2. Apparent viscosity ($\eta_{a,500}$), flow behavior index (n), and consistency index (K) of the mixture of rice starch (RS) and tara gum (TG) with different amounts of TG at 25°C

Sample	$\eta_{a,500}$ (Pa·s)	n (−)	K (Pa·s^n)	R^2
RS	0.42±0.07^a	0.24±0.00^a	46.80±7.23^a	0.99
RS+TG0.3	0.49±0.03^a	0.23±0.01^a	58.18±7.10^b	0.99
RS+TG0.5	0.66±0.01^b	0.27±0.00^b	60.38±1.95^b	0.99
RS+TG0.7	0.78±0.06^b	0.28±0.01^b	66.66±0.21^c	0.99

Values with different letters (a–c) within the same column differ significantly ($P<0.05$).
RS, rice starch; RS+TG0.3, the mixture of rice starch and tara gum (4.7:0.3, w/w); RS+TG0.5, the mixture of rice starch and tara gum (4.5:0.5, w/w); RS+TG0.7, the mixture of rice starch and tara gum (4.3:0.7, w/w).

Steady shear rheological properties

The plots of apparent viscosity versus shear rate at 25°C for the RS and RS+TG pastes are shown in Fig. 3. When the shear rate increased, the apparent viscosities of all samples decreased, which suggested that all samples exhibited non-Newtonian behavior. Furthermore, the apparent viscosities of RS+TG pastes were higher than that of the RS paste and increased with increasing the amounts of TG. Similar results regarding the apparent viscosity of the mixture of RS and TG was reported by Lee et al. (19).

Confirming the flow properties of all samples, the experimental data of shear stress and shear rate was well described by the power law model with high determination coefficients ($R^2=0.99$) (Table 2). The flow behavior index (n) of all samples was less than 1, which can be characterized by the shear-thinning behaviors. Furthermore, the K and $\eta_{a,500}$ of all RS+TG pastes were significantly higher than those of RS with increasing amounts of TG. Similar findings were observed by Kim and Yoo (20). They observed that the addition of TG to waxy barley flour dispersions had a significant increase in the K and $\eta_{a,100}$ values of waxy barley flour dispersions.

Dynamic shear rheological properties

Dynamic rheological tests are the most common methods used to obtain the dynamic moduli on rheological behaviors such as elastic and viscous characteristics of materials (21). The storage modulus (G') is a measure of the energy stored in the material and recovered from it per cycle of oscillation and it accounts for molecular events of an elastic property. The loss modulus (G") is a
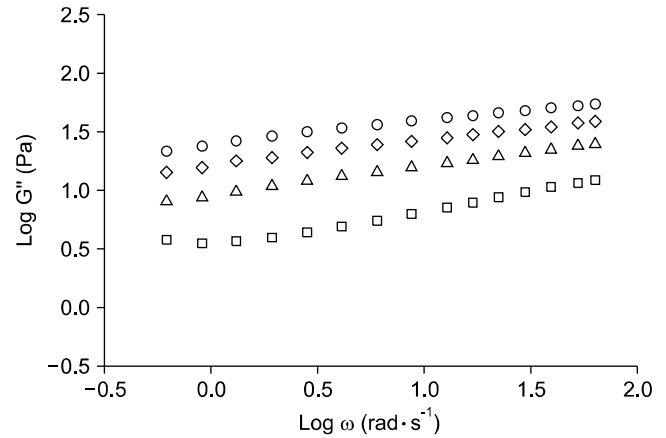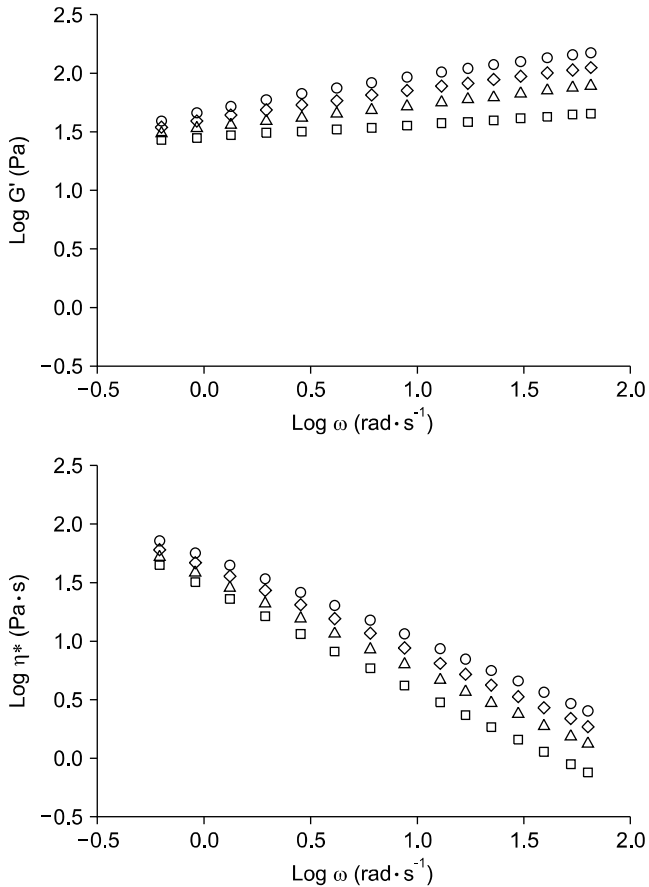
Fig. 4. Plots of log storage modulus (G'), loss modulus (G"), and complex viscosity (η^*) versus log ω of the mixture of rice starch (RS) and tara gum (TG) with different amounts of TG at 25°C. □, RS; △, the mixture of RS and TG (4.7:0.3, w/w); ◇, the mixture of RS and TG (4.5:0.5, w/w); ○, the mixture of RS and TG (4.3:0.7, w/w).

measure of the energy dissipated or lost per cycle of oscillation and it accounts for molecular events of a viscous property.

Plots of angular frequency (ω) versus storage modulus (G') and loss modulus (G") for RS and RS+TG pastes at 25°C are presented in Fig. 4. The magnitudes of G' of all samples were higher than those of G" with the frequency-dependency of both storage modulus and loss modulus, which was considered as a weak gel (22).

The observed η^* for all samples were decreased with the increase of ω (Fig. 2). In addition, the complex viscosities were significantly higher for all RS-TG pastes than those for RS paste. This finding was in accordance with the result of the steady shear rheological properties (Fig. 1 and Table 1).

The G', G", η^*, and tan δ values of all RS+TG pastes at 6.28 rad/s were significantly higher than those of the RS paste and increased with an increase in the amounts of TG (Table 3). The G" values of RS+TG samples were remarkably increased compared to the values of G' of RS pastes, resulting in the increase of tan δ values of RS+TG pastes. This result was similar to Lee et al. (19) and Kim and Yoo (20). Lee et al. (19) reported that both G" and tan δ values of rice starch were increased in the presence of TG. Furthermore, Kim and Yoo (20) observed that adding galactomannans such as TG and LBG elevated the viscous properties of waxy barley flour.

Table 3. Storage modulus (G'), loss modulus (G"), complex viscosity (η^*), and tan δ of the mixture of rice starch (RS) and tara gum (TG) with different amounts of TG at 25°C

Sample	G' (Pa)	G" (Pa)	η^* (Pa·s)	tan δ
RS	35.55±2.90[a]	6.05±0.34[a]	5.74±0.47[a]	0.17±0.00[a]
RS+TG0.3	52.27±0.02[b]	15.00±0.36[b]	8.66±0.01[b]	0.29±0.01[b]
RS+TG0.5	65.40±1.68[c]	24.31±0.07[c]	11.11±0.25[c]	0.37±0.01[c]
RS+TG0.7	82.97±0.84[d]	35.97±0.40[d]	14.40±0.15[d]	0.43±0.00[d]

Values with different letters (a-d) within the same column differ significantly ($P<0.05$).
RS, rice starch; RS+TG0.3, the mixture of rice starch and tara gum (4.7:0.3, w/w); RS+TG0.5, the mixture of rice starch and tara gum (4.5:0.5, w/w); RS+TG0.7, the mixture of rice starch and tara gum (4.3:0.7, w/w).

Based on the microscopic observations and rheological properties of the RS paste and RS+TG pastes, the addition of TG to the RS paste not only remarkably decreased the extent of swelling in the starch granules but also significantly increased the steady and dynamic shear rheological properties (Fig. 2~4). This result may be due to the fact that TG inhibited the swelling of starch in the continuous phase of RS+TG pastes, when RS gelatinized (23,24).

Furthermore, the effect of TG on the rheological properties of the RS paste might be ascribed to a synergism between RS and TG. According to Pollard and Fischer (25), the galactose-free chain segments, such as in LBG

(mannose : galactose=4:1), generally play a significant role in synergistic interactions with other polysaccharides in solution. Due to the structural similarity between LBG and TG, there would be synergism between RS and TG, thus leading to the increases in the apparent viscosities and complex viscosity of all RS+TG pastes compared to that of RS alone.

In conclusion, both the steady and the dynamic shear rheological parameters for RS were strongly influenced by the addition of TG. The K and $\eta_{a,100}$ values for RS, obtained from the power law model, were significantly increased by the incorporation of TG. The G' and G" values of RS+TG pastes were significantly higher than those of the RS paste alone. The results in the present study could be useful to enhance the rheological properties of RS by the addition of TG. Moreover, these results could contribute to increasing the use of TG for designing RS-based food products.

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AUTHOR DISCLOSURE STATEMENT

The authors declare no conflict of interest.

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