J Food Sci Nutr
Vol 14, p 233~239 (2009)
DOI: 10.3746/jfn.2009.14.3.233

J Food Science and Nutrition

Rheological Properties of Waxy Rice Starch-Gum Mixtures in Steady and Dynamic Shear

Do-Dan Kim[1], Young Seung Lee[2], and Byoungseung Yoo[1†]

[1]*Department of Food Science and Technology, Dongguk University, Seoul 100-715, Korea*
[2]*Nutrition & Culinary Science Team, Nong Shim Co., Ltd., Seoul 156-709, Korea*

Abstract

The effects of guar gum (GG) and xanthan gum (XG) at different concentrations (0, 0.2, 0.4, and 0.6% w/w) on the rheological properties of Korean waxy rice starch (WRS) pastes were evaluated under both steady and dynamic shear conditions. The flow properties of WRS-gum mixtures were determined from the rheological parameters of the power law model. The addition of GG and XG to WRS resulted in an increase in the apparent viscosity ($\eta_{a,100}$) and consistency index (K) values obtained from power law model. The flow behavior index (n) values of the WRS-XG mixtures decreased with an increase in gum concentration while there was only a marginal difference between n values for the WRS-GG mixtures. Dynamic moduli (G', G'', and η^*) values in the WRS-gum mixture systems also increased with an increase in gum concentration. WRS-XG mixtures had higher dynamic moduli and lower tan δ (ratio of G''/G') values than WRS-GG mixtures, indicating that the higher dynamic rheological properties of WRS-XG can be attributed to an increase in the viscoelasticity of the continuous phase in the starch-gum mixture systems, which was due to the higher viscoleastic properties of XG compared to GG. The dynamic (η^*) and steady shear (η_a) viscosities of the WRS-XG paste at a 0.2% gum concentration followed the Cox-Merz superposition rule.

Key words: rheology, waxy rice starch, guar gum, xanthan gum, dynamic moduli, Cox-Merz rule

INTRODUCTION

Mixtures of starches and gums have been used in the food industry to modify and control the rheological properties of starch-based products. The specific adjustment of their rheological properties is highly important for regulating the production processes and for optimizing the applicability, stability, and sensory properties of food products (1). Much information on the effects of gum on rheological properties of starch pastes has been reported. In general, guar gum (GG) and xanthan gum (XG) have been widely used by the food industries as a favorable thickening agent in food systems and also the addition of GG and XG influences the rheological properties in a wide variety of starch-based products. GG is a water soluble non-ionic polysaccharide, which consists of a chain of (1→4)-linked β-D-mannopyranosyl units with single branching α-D-galactopyranosyl units connected (1→6) linkage, on average, to every second main chain unit. The more extensive branching of GG has been known to be responsible for its easier hydration properties as well as its greater hydrogen-bonding activity, which may also take place within and/or between polysaccharides, proteins, and starches and which could enhance complex formation (2). XG is a high molecular weight extracellular polysaccharide produced by the fermentation of the bacterium *Xanthomonas campestris*. XG is composed of a (1→4) linked β-D-glucan (cellulose) backbone that is substituted on the O-3 position of alternating glucose residues by charged trisaccharide side chains of β-D-mannospyranosyl-(1→4)-β-D-glucuronopyranosyl-(1→2)-6-O-acetyl-β-D-mannospyranosyl. XG is known to exhibit peculiar flow properties with pronounced shear-thinning and weak gel-like behavior due to its unique rigid, rod-like conformation, which is more responsive to shear than a random-coil conformation (3).

The presence of gum in starch-gum mixture systems is known to increase the viscosity of starch and influence the gelatinization and retrogradation of starch. In the literature, there are discrepancies in regards to the enhancements in overall viscosity of starch-gum mixtures. It has been suggested that the observed enhancement of viscosity could be attributed to the incompatibility phenomena (4), the interactions between gelatinized granules (5), and the strong associations of amylose with gum (6). However, it has been known that the starch-gum mixtures were complicated by interactions of leached amylose molecules and gums occurring before and during

[†]Corresponding author. E-mail: bsyoo@dongguk.edu
Phone: +82-2-2260-3368, Fax: +82-2-2264-3368

pasting (6). Therefore, in this study waxy starch (little to no amylose) was used to avoid complications associated with the release of amylose into the surrounding polymer matrix. Recently, a few studies have been conducted on the rheological properties of waxy corn starches mixed with gums (5,7-10). However, no study has yet been conducted regarding the rheological properties of waxy rice starch (WRS) paste mixed with GG and XG under both steady and dynamic conditions. In addition, there have been no reported detailed studies comparing the rheological differences between WRS-GG and WRS-XG mixtures at various gum concentrations.

Dynamic shear rheological tests have been used to characterize or classify the viscoelastic properties of starch pastes (11). In a dynamic test, the storage modulus (G′), loss modulus (G″) and complex viscosity (η^*) are determined using a sinusoidal strain cycle. Often there is a correlation between the steady shear and dynamic rheological properties of macromolecular dispersions. The Cox-Merz (12) superposition rule (Eq. 1), involving the frequency (ω) dependence of complex dynamic viscosity (η^*) and shear rate ($\dot{\gamma}$) dependence of steady shear apparent viscosity (η_a), has been confirmed experimentally for several macromolecular dispersions, but not for starch pastes or starch-gum mixtures.

$$\eta^*(\omega) = \eta_a(\dot{\gamma}) \mid_{\omega=\dot{\gamma}} \quad (1)$$

Several researchers have evaluated the validity of the Cox-Merz rule in a variety of starch pastes and found that the Cox-Merz rule is not applicable to all samples (13-16). However, a study on the applicability of the Cox-Merz rule in WRS pastes, especially in the presence of gums, has not been performed. The principal objectives of the present study were 1) to investigate the effect of GG and XG concentration on the rheological properties of Korean WRS pastes as a function of gum concentration in both steady and dynamic shear, 2) to determine the synergistic effect of GG and XG on the rheological properties of WRS-gum mixtures, and 3) to compare rheological properties of WRS-XG and WRS-GG mixtures.

MATERIALS AND METHODS

Materials and starch isolation

Guar gum (GG) and xanthan gum (XG) were purchased form Sigma Co. (St. Louis, MO, USA). Korean waxy rice was obtained from a rice growing farm in Jeongnam, Korea. It was milled and ground to flour at a local miller. Waxy rice starch (WRS) was isolated from the waxy rice flour according to the alkaline method reported by Juliano (17). The isolated starch was washed three times with distilled water, and then dried in an oven drier at 40°C. The dried starch was ground and then passed through a 100-mesh standard sieve (Chung Gye Inc., Seoul, Koea) with 150 μm openings using an analytical sieve shaker (Model AS200, Retsch GmbH & Co., Haan, Germany).

Preparation of WRS-gum mixture pastes

WRS-gum mixtures (5% w/w) were prepared by mixing WRS with distilled water, and GG and XG to obtain 0%, 0.2%, 0.4%, and 0.6% (weight basis) gum levels. These gum concentrations were selected based on the levels that are commonly used for product formulations in the food industry. The mixture was allowed to hydrate by stirring for 1 hr at room temperature, and then heated at 95°C in a water bath for 30 min with mild agitation in order to avoid air entrainment into the mixture. At the end of the heating period, the hot sample mixture was immediately transferred to the rheometer platen and the rheological properties were measured.

Rheological measurements

Steady and dynamic shear rheological properties of WRS-gum mixtures were determined using a Carri-Med CSL^2 100 rheometer (TA Instruments, New Castle, DE, USA) with a measuring system having a plate-plate geometry (4 cm dia.) at a gap of 500 μm. Each sample was transferred to the rheometer plate at 25°C. Steady shear (shear stress and shear rate) data were obtained over a shear rate range of 1.0～1000 1/sec. In order to describe the steady shear rheological properties of the samples, the data were fitted to the well-known power law (Eq. 2).

$$\sigma = K\dot{\gamma}^n \quad (2)$$

where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (1/sec), K is the consistency index (Pa s^n) and n is the flow behavior index (dimensionless).

Dynamic shear properties were evaluated using small-amplitude oscillatory rheological measurements. The sample was oscillated in the range of 0.63～62.8 rad/sec at 3% strain. The 3% strain was in the linear viscoelastic region. Frequency sweep tests were also performed at 25°C. Carri-Med software (version 3.1) was used to obtain the experimental data and to calculate storage modulus (G′), loss modulus (G″), complex viscosity (η^*), and tan δ (ratio of G″/G′). In order to relax the samples before the rheological measurements, all samples were allowed to rest at 25°C on the plate for 5 min. All rheological measurements were performed in triplicate. The reported results were an average of the three measurements.

RESULTS AND DISCUSSION

Steady shear properties

The shear stress (σ) versus shear rate ($\dot{\gamma}$) data for WRS pastes mixed with guar gum (GG) and xanthan gum (XG) at different gum concentrations at 25°C are shown in Fig. 1. Experimental data of σ and $\dot{\gamma}$ were well fitted to the power law model with high determination coefficients (R^2=0.98～0.99) (Table 1). WRS-XG mixtures exhibited a highly shear-thinning behavior with flow behavior index values (n) as low as 0.24～0.36, which were lower than those (0.50～0.52) of both the WRS paste without gum (control) and WRS-GG mixtures, indicating that the WRS-XG mixtures displayed a more pseudoplastic behavior. Such higher shear-thinning behavior may be attributed to the higher amount of breakage of the intra- and inter-molecular associative bonds in the WRS-XG mixtures at higher shear rates. The n values of the WRS-XG mixtures decreased with an increase in gum concentration, showing a dependence on XG concentration, while no effect of gum concentration on n values for the WRS-GG mixtures was observed. This tendency is in good agreement with those reported for other starch-XG mixtures (15,18). Such high shear- thinning behaviors of the WRS-XG mixtures can be attributed to the unique rigid, rod-like conformation of XG (19).

The consistency index (K=4.26～20.5 Pa.sec^n) values of WRS-gum mixtures were, in general, much higher than that (3.25 Pa.sec^n) of the control (0% gum) (Table 1) and increased with an increase in gum concentration, indicating a higher synergism with gum due to starch-gum interaction. The synergistic effect of gum on WRS paste can be described by an increase of gum concentration in the continuous phase of the medium. According to Alloncle and Doublier (4), the gum is located within the continuous phase, and thus the volume of this phase is reduced, which causes a dramatic increase in gum concentration in the continuous phase, thereby resulting in a very high viscosity. The WRS-XG mixture also showed higher K values (7.49～20.5 Pa.sec^n) than the WRS-GG mixture (4.26～7.42 Pa.sec^n), indicating that the addition of XG caused the formation of a weak gel-like structure in the mixtures. It has been known that the flow properties of GG in a solution system showed an entanglement solution behavior due to the flexibility of the GG chain (20). From these observations, it was found that the XG had a strong influence on the steady shear properties of the WRS pastes at the gum concentration range examined in this study as compared to GG.

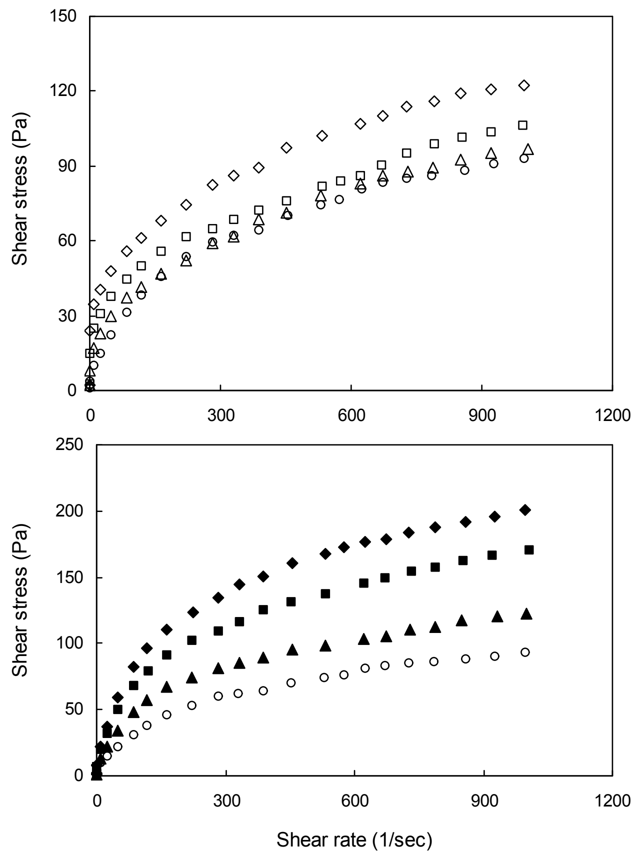

Fig. 1. Shear stress-shear rate plots for waxy rice starch pastes mixed with guar and xanthan gums at 25°C: (○) 0%, (△, ▲) 0.2%, (□, ■) 0.4%, and (◇, ◆) 0.6% gum concentration. Open symbol: guar gum, closed symbol: xanthan gum.

Dynamic shear properties

Fig. 2 shows the changes in G' and G" as a function

Table 1. Flow rheological properties of waxy rice starch pastes mixed with guar and xanthan gums at different gum concentration

Gum type	Concentration (%)	Power law		
		n (-)	K (Pa.sec^n)	R^2
Control	0 (no gum)	0.50±0.00	3.25±0.07	0.99
Guar	0.2	0.52±0.00	4.26±0.03	0.99
	0.4	0.51±0.01	6.38±0.05	0.99
	0.6	0.51±0.00	7.42±0.30	0.99
Xanthan	0.2	0.36±0.00	7.49±0.08	0.99
	0.4	0.28±0.00	13.5±0.29	0.99
	0.6	0.24±0.00	20.5±0.35	0.98

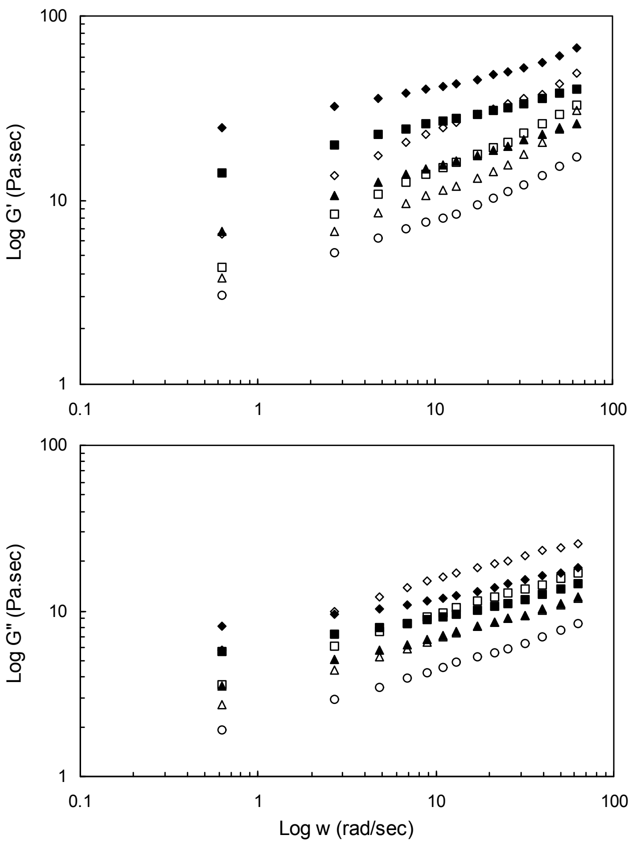

Fig. 2. Plot of log G' and log G" versus log ω of waxy rice starch pastes mixed with guar and xanthan gums at 25°C: (○) 0%, (△, ▲) 0.2%, (□, ■) 0.4%, and (◇, ◆) 0.6% gum concentration. Open symbol: guar gum, closed symbol: xanthan gum.

of the frequency (ω) for WRS-gum mixtures at 25°C. G' and G" values increased with increasing ω, and G' was much higher than G" at all ω values tested (0.63～62.8 rad/sec) with a small frequency dependency, confirming the viscoelastic nature of the WRS-gum mixture pastes. Such behavior is in good agreement with those found in other waxy starch pastes mixed with gums (5,7-10). Table 2 shows G', G", and η^* at 6.28 rad/sec for the WRS-gum mixtures at 25°C. In general, the dynamic moduli (G', G", and η^*) of the WRS-gum mixtures were higher than those of the control (0% gum) and increased with an increase in gum concentration, indicating that the addition of gum to WRS pastes had a synergistic effect on the viscoelastic properties. Such synergistic effect of gum on the rheological properties of WRS pastes can be interpreted as an increase in the viscoelastic properties of the gum due to the increase in its local concentration in the continuous phase of the starch-gum mixture systems (4). In particular, the dynamic moduli values of the WRS-XG mixtures were much higher those of the WRS-GG mixtures, indicating that XG were very effective in increasing the viscoelastic properties of the mixture. The higher viscoelastic properties of the WRS-XG mixtures can also be related to the higher stiffness of XG compared to GG. This rigidity implies a much more limited mobility of the chains and hence much longer relaxation times, resulting in higher elastic properties. In addition, the tan δ (ratio of G"/G') values (0.30～0.46) of the WRS-XG mixtures were lower than those (0.57～0.71) of the WRS-GG mixtures and the control (no gum), indicating that the WRS-XG mixtures were much more elastic than the other samples. This effect was more pronounced when the concentration of XG increased. Such elastic properties of the WRS-XG mixtures can merely be related to the associations of ordered chain segments of XG, resulting in a weak three-dimensional network, as described by Doublier and Cuvelier (21). However, the tan δ values (0.61～0.71) of the WRS-GG mixtures were higher than those of the control (0.57) and WRS-XG mixtures (0.30～0.46), demonstrating an effect of GG on the viscous properties of WRS paste. This is in good agreement with results reported for waxy corn starch pastes mixed with gums (7). From these observations, we found that there was a more pronounced synergistic effect of XG on the elastic properties of WRS compared to GG.

The dynamic rheological data of log (G', G") versus log ω were also subjected to linear regression; slope values of log (G', G") versus log ω of WRS-gum mixtures with different gum concentrations at 25°C are shown in Fig. 3. The slopes of G' (GG=0.42～0.45; XG=0.21～

Table 2. Storage modulus (G'), loss modulus (G"), complex viscosity (η^*), and tan δ at 6.28 rad/sec for waxy rice starch pastes mixed with guar and xanthan gums at different concentrations

Gum type	Concentration (%)	G' (Pa)	G" (Pa)	η^* (Pa·sec)	Tan δ
Control	0 (no gum)	6.78±0.02	3.84±0.01	1.24±0.01	0.57±0.01
Guar	0.2	9.41±0.31	5.76±0.06	1.76±0.05	0.61±0.01
	0.4	13.5±0.77	8.59±0.27	2.35±0.14	0.64±0.02
	0.6	18.3±0.69	12.8±0.27	3.53±0.15	0.71±0.02
Xanthan	0.2	13.3±0.01	6.06±0.26	2.32±0.02	0.46±0.02
	0.4	24.0±0.49	8.50±0.04	4.06±0.08	0.35±0.01
	0.6	36.7±1.26	11.2±0.05	6.10±0.19	0.30±0.01

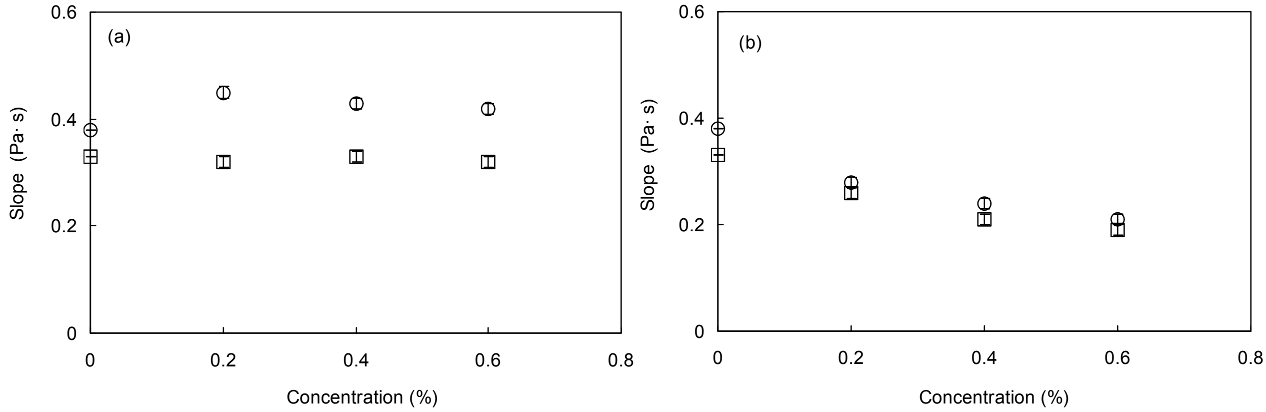

Fig. 3. Plot of slope values versus gum concentration in the waxy rice starch-gum mixture systems at 25°C: (a) guar gum, (b) xathan gum, (○) slope of G', (□) slope of G". Error bars represent standard deviation of the mean.

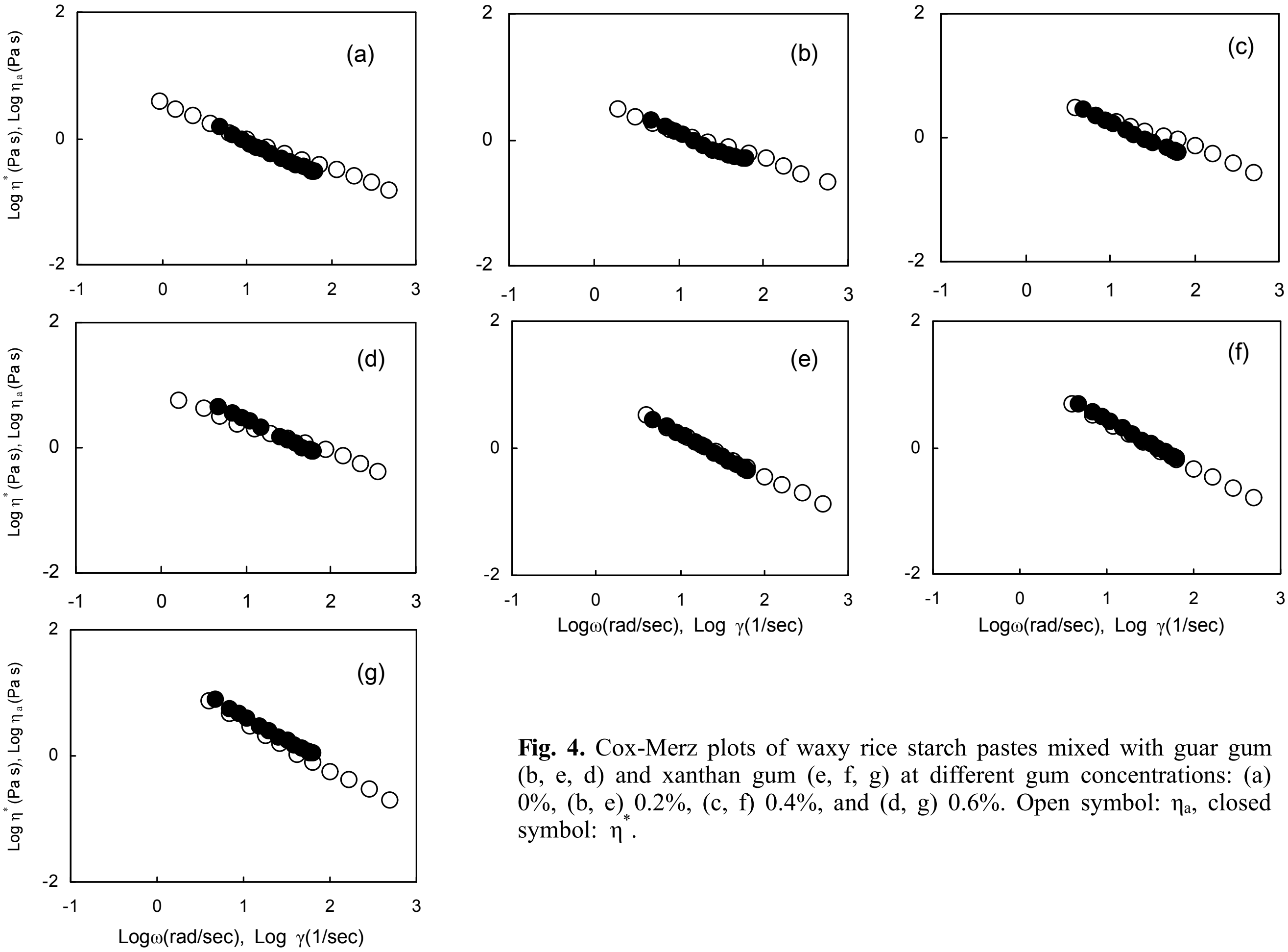

Fig. 4. Cox-Merz plots of waxy rice starch pastes mixed with guar gum (b, e, d) and xanthan gum (e, f, g) at different gum concentrations: (a) 0%, (b, e) 0.2%, (c, f) 0.4%, and (d, g) 0.6%. Open symbol: η_a, closed symbol: η^*.

0.28; control=0.38) and G" (GG=0.32～0.33; XG=0.19～0.26; control=0.33) of all samples were positive with high R^2 (0.98～0.99). The slopes of G' for the WRS-GG mixtures were relatively higher than those of G". These observed results show that the elastic properties of WRS pastes can be decreased through the addition of GG. The slopes of G' and G" for the WRS-XG mixtures were relatively lower than those for the WRS-GG mixtures, indicating that the WRS-XG mixtures were more elastic and G' and G" were less dependent on the frequency in comparison to the WRS-GG mixtures. Choi et al. (19) reported that in the gum solution system the slope values of G' and G" of XG were much lower than those of other gums, suggesting that XG is more elastic than viscous. Such more pronounced elastic properties of XG can be related to its relatively higher stiffness when compared to other gums, as previously described. The difference in the dynamic rheological properties between the WRS-XG and WRS-GG mixtures suggests that their synergistic effects are influenced by the chemical structure of GG and XG in the continuous phase. From these dynamic rheological data (Fig. 2), it was also found that the WRS mixed with GG and XG in the concentration range of 0.2～0.6% exhibited a weak gel-like behavior because for weak gels log (G', G") versus log ω plots have positive slopes and G' has a higher magnitude than G", which is frequency dependent. This same behavior was observed earlier in other starch pastes mixed with GG and XG (4-9,14,15).

Based on the above statement, it can be concluded that the synergistic effect of GG and XG on the rheological properties of WRS pastes may be attributed to the increased viscoelasticity of the continuous phase in which the gum is concentrated in the WRS-gum mixture systems due to the swelling of starch granule during gelatinization. Finally, these observations indicate that the viscoelastic properties of the WRS-gum mixtures seem to be dependent on the gum concentration, and are affected by the viscoelastic properties of the added gum.

Correlation between complex and apparent viscosity

The Cox-Merz rule was used to compare the experimental data obtained under steady and dynamic shear conditions. In order to examine the applicability of the Cox-Merz rule, the η_a and η^* of the WRS pastes mixed with XG and GG at different concentrations must be presented as functions of $\dot{\gamma}$ and ω, respectively (Fig. 4). An obvious deviation from the Cox-Merz rule was found for all samples, except for the WRS-XG at 0.2% concentration, which showed a coincidence between the curve of $\eta^*(\omega)$ and that of $\eta_a(\dot{\gamma})$; thus, obeying the empirical Cox-Merz rule. In our previous studies, it was found that there were many exceptions to this rule in the starch pastes or starch-gum mixtures, suggesting that the deviations from the Cox-Merz rule may be strongly influenced by the starch or gum concentration (14-16). These observed results indicate that the applicability of the Cox-Merz rule may be closely related to the type of gum and gum concentrations used in this system.

ACKNOWLEDGEMENTS

This work was supported by the research program of Dongguk University.

REFERENCES

1. Kulicke WM, Eidam D, Kath F, Kix M, Hamburg AH. 1996. Hydrocolloids and rheology: regulation of visco-elastic characteristics of waxy rice starch in mixtures with galactomannans. *Starch/Starke* 48: 105-114.
2. Bahnassey YA, Breene WM. 1994. Rapid Visco-Analyzer (RVA) pasting profiles of wheat, corn, waxy corn, tapioca and Amaranth starches (*A. hypochondriacus* and *A. cruentus*) in the presence of konjac flour, gellan, guar, xanthan and locust bean gums. *Starch/Starke* 46: 134-141.
3. Urlacher B, Noble O. 1997. Xanthan. In *Thickening and Gelling Agents for Food*. Imeson A, ed. Chapman & Hall, London, UK. p 284-311.
4. Alloncle M, Doublier JL. 1991. Viscoelastic properties of maize starch/hydrocolloid pastes and gels. *Food Hydrocolloid* 5: 455-467.
5. Abdulmola NA, Hember MWN, Richardson RK, Morris ER. 1996. Effect of xanthan on the small-deformation rheology of crosslinked and uncrosslinked waxy maize starch. *Carbohydr Polym* 31: 65-78.
6. Christianson DD, Hodge JE, Osborne D, Detroy RW. 1981 Gelatinization of wheat starch as modified by xanthan gum, guar gum, and cellulose gum. *Cereal Chem* 31: 65-78.
7. Achayuthakan P, Suphantharika M. 2008. Pasting and rheological properties of waxy corn starch as affected by guar gum and xanthan gum. *Carbohydr Polym* 71: 9-17.
8. Achayuthakan P, Suphantharika M, Rao MA. 2006. Yield stress components of waxy corn starch-xanthan concentration and different starches. *Carbohydr Polym* 65: 469-478.
9. Khondkar D, Tester RF, Hudson N, Karkalas J, Morrow J. 2007. Rheological behaviour of uncross-linked gelatinized waxy maize starch with pectin gels. *Food Hydrocolloid* 21: 1296-1301.
10. Rodriguez-Hernandez AI, Durand S, Garnier C, Tecante A, Doublier JL. 2006. Rheology-structure properties of waxy maize starch-gellan mixtures. *Food Hydrocolloid* 20: 1223-1230.
11. Rao MA. 2007. Rheology of food gum and starch dispersions. In *Rheology of Fluid and Semisolid Foods.* Rao MA, ed. Springer, New York, USA. p 153-222.
12. Cox WP, Merz EH. 1958. Correlation of dynamic and steady viscosities. *J Polym Sci* 28: 619-622.
13. Da Silva PMS, Oliverira JC, Rao MA. 1998. Rheological properties of heated cross-linked waxy maize starch dispersions. *Int J Food Properties* 1: 23-34.
14. Chun SY, Yoo B. 2006. Steady and dynamic shear rheological properties of sweet potato flour dispersions. *Eur Food Res Technol* 223: 313-319.
15. Kim C, Yoo B. 2006. Rheological properties of rice starch-xanthan gum mixtures. *J Food Eng* 75: 120-128.
16. Yoo B. 2006. Steady and dynamic shear rheology of glutinous rice starch flour dispersions. *Int J Food Sci & Technol* 41: 601-608.
17. Juliano BO. 1984. Rice starch: production, properties and uses. In *Starch: Chemistry and Technology*. Whistler RL, BeMiller JN, Paschall EF, eds. Academic Press, New York, USA. p 516-528.
18. Choi HM, Yoo B. 2009. Steady and dynamic shear rheology of sweet potato starch-xanthan gum mixtures. *Food Chem* 116: 638-643.
19. Choi SJ, Chun SY, Yoo B. 2006. Dynamic rheological

properties of selected gum solutions. *Food Sci Biotechnol* 15: 474-477.
20. Ross-Murphy SB. 1995. Structure-property relationships in food biopolymer gels and solutions. *J Rheol* 39: 141-1463.
21. Doublier JL, Cuvelier G. 1996. Gums and hydrocolloids: functional aspects. In *Carbohydrate Chemistry for Food Scientists*. Eliasson AC, ed. Marcel Dekker, Inc., New York, USA. p 283-318.

(Received July 14, 2009; Accepted September 9, 2009)