Rheological Characteristics of Waxy Rice Starch Modified by Carboxymethyl Cellulose

Hyundo Lee and Byoungseung Yoo
Department of Food Science and Biotechnology, Dongguk University-Seoul, Gyeonggi 10326, Korea

ABSTRACT: The effects of carboxymethyl cellulose (CMC) at different concentrations (0, 0.2, 0.4, and 0.6% w/w) on the rheological properties of waxy rice starch (WRS) pastes were evaluated under both steady and dynamic shear conditions. The flow properties of WRS-CMC mixtures were determined from the rheological parameters of power law and Casson models. All samples demonstrated a clear trend of shear-thinning behavior (n=0.33 ∼ 0.34), with a marginal difference shown between n values. The addition of CMC to WRS increased the apparent viscosity (\( \eta_a,100 \)), consistency index, and Casson yield stress values. The dynamic moduli [storage modulus (\( G' \)), loss modulus (\( G'' \)), and dynamic viscosity (\( \eta^* \))] and ratio of \( G''/G' \) values of WRS-CMC mixtures also increased with an increase in CMC concentration; the higher dynam- ic rheological properties observed at higher CMC concentrations may be attributed to an increase in the viscoelasticity of the continuous phase in the starch-gum mixture system. Dependence of \( \eta_a,100 \) on temperature followed the Arrhenius model for all samples. The Cox–Merz rule was not applicable to WRS-CMC pastes with different CMC concentrations, demonstrating that there was a deviation between \( \eta^* \) and steady shear viscosities for all samples. Therefore, the synergistic effect of CMC on the rheological properties of WRS pastes appeared to be the result of coacervation.

Keywords: CLSM, waxy rice starch, carboxymethyl cellulose, synergistic effect, coacervation

INTRODUCTION

Waxy rice starch (WRS) is widely used in food products, either as a raw material or as a food additive. Similar to other starches, WRS has disadvantages, such as retrogradation, either from extended cooking, high shear, or acidic conditions, and may produce weak-bodied, cohesive, rubbery pastes, and undesirable gels (Shi and BeMiller, 2002). However, the addition of proper non-starch polysaccharides (gums) can overcome these limitations of starches (Kim et al., 2009). In general, starches modified by mixing with gums have improved rheological and textural properties. Previous studies have modified the rheological properties of WRS by adding small amounts of gums, such as guar gum, locust bean gum, and xanthan gum, which are widely used by the food industry as a favorable thickening agent in food systems (Kim et al., 2009; Kulicke et al., 1996). However, no comprehensive information is available about the effect of carboxymethyl cellulose (CMC) on the steady and dynamic rheological properties of WRS. CMC, which is a water-soluble heteropolysaccharide with a high molecular weight, is often used together with starches to provide a desirable texture, control water mobility, and improve overall product stability by forming macromolecular structures through inter- and intra-molecular hydrogen bonds (Sun et al., 2017). Therefore, the main objective of this study was to investigate the rheological properties of WRS-CMC pastes supplemented with different concentrations of CMC under both steady and dynamic conditions. An understanding of phase separation and rheological properties of WRS-CMC mixtures could lead to improvements in the formulations of WRS-based products for further applications in product development.

MATERIALS AND METHODS

Materials and preparation of WRS-CMC mixtures
Commercial WRS was provided by the SMS Corporation (Pathum Thani, Thailand). The proximate composition of WRS was: 13.6% moisture, 0.7% protein (N×6.25), 0.8% fat, 0.2% ash, 84.7% carbohydrate (by difference), and the amylose content was 6.30%. CMC was purchased...
from Shanghai Shenguang Edible Chemicals Co., Ltd. (Shanghai, China). WRS-CMC mixtures (5% w/w) for rheological measurements were prepared by dispersing WRS with distilled water and CMC to obtain 0%, 0.2%, 0.4%, and 0.6% (weight basis) CMC; 0% CMC (100% WRS) was used as the control. The dispersion was moderately stirred for 60 min at room temperature and heated at 95°C for 30 min with mild agitation using a magnetic stirrer (HS15-26P, Misung Scientific Co., Ltd., Daejeon, Korea). The hot paste samples were immediately transferred to a rheometer plate at 25°C to measure the rheological properties.

Rheological analysis

The steady and dynamic shear rheological properties of the WRS-CMC mixtures were investigated using a Haake RheoStress 1 rheometer (Haake GmbH, Karlsruhe, Germany) and controlled stress rheometer (AR 1000, TA Instruments, New Castle, DE, USA), respectively. Plate-plate geometries with diameters of 35 mm (RheoStress 1) and 40 mm (AR1000) were used. Each sample was loaded between the parallel plates at 25°C and compressed to obtain a gap of 500 μm. After 5 min of equilibration to reach the measurement temperature of 25°C, rheological outcomes were measured.

The shear stress (σ, Pa) versus shear rate (γ̇, s⁻¹) dependence was determined at γ̇ values in the range of 0.4 ~500 s⁻¹. Further, to evaluate the time-dependent flow behavior, the samples were sheared first in ascending order and then in descending order. The up-flow curves were described by the power law model (Eq. 1) and the Casson model (Eq. 2):

\[
\sigma = K \gamma^n
\]

(1)

\[
\sigma^{0.5} = K_c + K_{c0.5}^{0.5}
\]

(2)

where K is the consistency index (Pa·sⁿ), n is the flow behavior index (dimensionless), and Kc is the Casson plastic viscosity. The Casson yield stress (σ₀) according to the Casson model [Eq. (2)] was determined as the square of the intercept (KC) that was obtained from linear regression of the square roots of the γ̇-σ data. By using the magnitudes of K and n, we calculated the apparent viscosity (ηₐ) at 100 s⁻¹. The temperature dependence was assessed by fitting the Arrhenius model (Eq. 3) to the experimental data using ηₐ at different temperatures (25~70°C) for all samples:

\[
\eta_a = A \cdot \exp \left( \frac{E_a}{RT} \right)
\]

(3)

where A is a constant (mPa·s), T is the absolute temperature (K), R is the gas constant (8.3144 J/mol/K), and Ea is the activation energy (J/mol).

Dynamic rheological tests were conducted using small-amplitude oscillatory rheological measurements at 25°C. A dynamic oscillatory test was performed as a function of the angular frequency (ω) (0.63 ~62.8 rad·s⁻¹) at 2% strain. The 2% strain was within the linear viscoelasticity limit. The TA rheometer data analysis software (version VI. 1.76, TA Instruments) was used to obtain the experimental data and calculate the storage (or elastic) modulus (G'), loss (or viscous) modulus (G''), complex viscosity (η*), and loss tangent (tan δ=G''/G'). The tan δ value allows the evaluation of viscoelastic behavior: tan δ<1, predominantly elastic behavior; tan δ>1, predominantly viscous behavior. All rheological measurements were performed in triplicate.

Correlations between the values of dynamic shear parameters (η* and ω) and steady shear parameters (η₀ and γ̇) were estimated using the Cox-Merz rule (Eq. 4). To examine the applicability of the Cox-Merz rule, the η₀ and η* of all WRS-CMC mixtures were plotted versus γ̇ and ω₀, respectively (Cox and Merz, 1958).

\[
\eta^* (\omega) = \eta_0 (\gamma^*) \exp \left( \frac{E_a}{RT} \right)
\]

(4)

Statistical analysis

All experiments were conducted in triplicate, with data are reported as the mean±standard deviation (SD). For multiple comparison analysis, analysis of variance (ANOVA) followed by Duncan’s multiple range test was performed using the Statistical Analysis System program (version 9.2; SAS Institute, Cary, NC, USA). P<0.05 was considered statistically significant.

RESULTS AND DISCUSSION

Steady shear properties

The results of σ versus γ̇ of WRS-CMC mixtures containing different CMC concentrations (0.2% ~0.6%) fitted well to the power law (Eq. 1) and Casson (Eq. 2) models with high R² (0.98 ~0.99) values (Table 1). All samples had a non-Newtonian (pseudoplastic) nature and demonstrated shear-thinning behavior with flow behavior index (n) values as low as 0.33 ~0.34 (Fig. 1). This type of flow behavior is typical of starch-gum mixture systems (Kim et al., 2009; Lee et al., 2017; Kim and Yoo, 2011; Kim and Yoo, 2006; Yoo et al., 2005). There were no significant differences between the n values of the control (0% CMC) and WRS-CMC mixtures, indicating that the presence of CMC in the WRS-CMC mixtures had no effect on the n values. Similar results were reported in a previous study of WRS-guar gum mixtures (Lee et al.,
Table 1. Apparent viscosity ($\eta_{a,100}$), consistency index (K), flow behavior index (n), and Casson yield stress ($\sigma_{oc}$) of waxy rice starch-carboxymethyl cellulose (CMC) mixtures with different CMC concentrations

| Concentration (%) | $\eta_{a,100}$ (Pa·s) | K (Pa·s^n) | n | $\sigma_{oc}$ (Pa) |
|-------------------|------------------------|------------|---|------------------|
| 0 (control)       | 0.84±0.05^d            | 17.7±0.84^d| 0.34±0.01^a | 23.7±0.71^d |
| 0.2               | 1.14±0.03^c            | 25.4±2.11^c| 0.33±0.02^a | 31.5±0.65^c |
| 0.4               | 1.35±0.03^b            | 28.5±1.36^b| 0.34±0.01^a | 38.9±0.59^b |
| 0.6               | 1.57±0.01^a            | 34.7±1.50^a| 0.33±0.01^a | 46.9±0.50^a |

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

2017). The K, $\eta_{a,100}$, and $\sigma_{oc}$ values of WRS-CMC mixtures were much higher than those of the control (without CMC) and increased with increased CMC concentration from 0 to 0.6% (Table 1), indicative of a higher synergism with CMC. These results demonstrate that WRS-CMC mixtures were high shear-thinning fluids with high magnitudes of K and $\sigma_{oc}$.

Temperature dependence (Arrhenius equation)

The temperature dependence of $\eta_{a,100}$ of the WRS-CMC mixtures was determined by fitting the data to the Arrhenius model (Eq. 3), where $\eta_{a,100}$ decreases to an exponential function with temperature. The Arrhenius temperature relationship has been confirmed experimentally in previous studies of starch-gum mixtures (Lee et al., 2017; Kim and Yoo, 2011; Kim and Yoo, 2006; Yoo et al., 2005). From a plot of ln $\eta_{a,100}$ (ordinate) versus (1/T) (abscissa), Ea=(slope×R), and A is the exponential of the intercept. Ea values were determined from regression analysis of 1/T versus in $\eta_{a,100}$ (Fig. 2), and were in the range of 5.71~8.70 kJ/mol with high determination coefficients ($R^2=0.96~0.98$) (Table 2). The Ea values (5.71~7.59 kJ/mol) of the WRS-CMC mixtures were much lower than the value (8.70 kJ/mol) of the control; further, Ea values decreased with increased CMC concentration, indicative of a lower effect of temperature on the rheological parameter at higher CMC concentrations. Similar patterns between Ea variation and concentration have been previously observed for the rice starch-xanthan gum (Lee et al., 2017) and rice starch-tara gum mixtures (Kim and Yoo, 2011). Therefore, the Ea values of WRS-CMC mixtures in a temperature range of 25~70°C were significantly affected by the concentration of CMC.

Time-dependent flow behavior

Measurement of increasing and decreasing $\gamma$ of WRS-CMC mixtures showed a hysteresis loop pattern in the range of 0.4~500 s$^{-1}$, indicating that all samples exhibited time-dependent shear-thinning (thixotropic) flow behavior (Fig. 3). The area enclosed by the hysteresis loop is known to indicate the degree of breakdown due to shearing (Weltmann, 1943). Thixotropic flow behavior was less pronounced in the presence of CMC based on the area of the loop between the up and down flow curves (Fig. 3), demonstrating that CMC addition enhanced re-association after structure breakdown accelerated by high $\gamma$. The hysteresis loop area of WRS-CMC mixtures de-
increased with increased concentration of CMC. Specifically, the loop area of WRS with 0.6% CMC was markedly decreased compared with that of WRS alone, suggesting that the addition of CMC at high concentrations enhanced the formation of the shear-induced network structure of the WRS-CMC mixtures and reduced the breakdown of the network at a high $\dot{\gamma}$ (Lee et al., 2017). This may be attributed to the synergistic effects between WRS and anionic CMC molecules in the formation of typical cross-linkages found in biopolymer gels (Michailova et al., 1999). Similar findings have also been reported for other starch-gum mixtures (Lee et al., 2017; Sikora et al., 2008; Korus et al., 2004).

**Dynamic rheological properties**

Fig. 4 shows the changes in $G'$ and $G''$ as a function of the $\omega$ for WRS-CMC mixtures at 25°C. The $G'$ and $G''$ values were increased with increasing $\omega$, and the $G'$ was much higher than $G''$ depending on the frequency, demonstrating weak gel-like behavior of the WRS-CMC mixtures. This type of behavior has been interpreted as an entangled network among macromolecules (Doublier and Curvelier, 1996) and is in good agreement with that observed for other waxy starch pastes mixed with gums (Michailova et al., 1999).

![Figure 3: Thixotropic flow curves of waxy rice starch-carboxymethyl cellulose (CMC) mixtures with different CMC concentrations at 25°C: (A) 0%, (B) 0.2%, (C) 0.4%, and (D) 0.6%.](image_url)

![Figure 4: Plots of modulus ($G'$) and loss modulus ($G''$) versus $\omega$ for waxy rice starch-carboxymethyl cellulose (CMC) mixtures with different CMC concentrations at 25°C: (○) 0%, (□) 0.2%, (△) 0.4%, and (◊) 0.6%.](image_url)
ties. Table 3 shows $G'$, $G''$, and $\eta^*$ provide useful information about its viscoelastic properties. The dispersed and continuous phases, which could also be determined by the structural properties of the starch paste were determined by the structural properties of the starch-gum mixture system. Therefore, the dynamic rheological properties of the starch paste can be explained by the formation of a thermodynamically incompatible network structure considering that addition of CMC results in a small increase in $G'$ compared with $G''$ with tan $\delta$ values (0.51 ~ 0.66) higher than that of the control (0.49). Therefore, the mechanism of the synergistic effect of CMC in the WRS-CMC mixture system can be predicted by the changes in dynamic rheological parameters, as highlighted by Kim et al. (2009) and Funami et al. (2008).

### Table 3. Storage modulus ($G'$), loss modulus ($G''$), complex viscosity ($\eta^*$), and tan $\delta$ values at 6.28 rad $\cdot$ s$^{-1}$ for waxy rice starch-carboxymethyl cellulose (CMC) mixtures with different CMC concentrations

| Concentration (%) | $G'$ (Pa) | $G''$ (Pa) | $\eta^*$ (Pa $\cdot$ s) | tan $\delta$ |
|-------------------|-----------|------------|------------------------|--------------|
| 0                 | 9.29±0.64$^a$ | 4.54±0.26$^a$ | 1.65±0.08$^b$ | 0.49±0.06$^d$ |
| 0.2               | 14.4±0.77$^a$ | 7.35±0.12$^a$ | 2.57±0.12$^c$ | 0.51±0.02$^c$ |
| 0.4               | 17.0±0.38$^a$ | 10.0±0.16$^a$ | 3.14±0.04$^a$ | 0.59±0.02$^a$ |
| 0.6               | 19.9±0.37$^a$ | 13.0±0.33$^a$ | 3.78±0.07$^a$ | 0.66±0.01$^b$ |

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

The effect of CMC on the viscoelastic properties of WRS pastes can be explained by the formation of a thermodynamically incompatible network structure considering that addition of CMC results in a small increase in $G'$ compared with $G''$ with tan $\delta$ values (0.51 ~ 0.66) higher than that of the control (0.49). Therefore, the mechanism of the synergistic effect of CMC in the WRS-CMC mixture system can be predicted by the changes in dynamic rheological parameters, as highlighted by Kim et al. (2009) and Funami et al. (2008).

### Applicability of Cox-Merz rule

The applicability of the Cox-Merz rule (Cox and Merz, 1958) (equivalence between steady shear rheological properties and small-amplitude dynamic rheological properties at equal frequency values ($\omega$ = 0.63 ~ 62.8 rad $\cdot$ s$^{-1}$) and $\gamma$ (0.4 ~ 100 s$^{-1}$) for WRS-CMC mixtures with different CMC concentrations was evaluated (Fig. 5). The magnitudes of $\eta^*$ were lower than those of $\eta_b$, demonstrating that WRS-CMC mixtures did not obey the Cox-Merz rule over the entire range of $\gamma$ and $\omega$ investigated. This behavior may be attributed to the heterogeneous nature of the polysaccharide dispersions that undergo aggregation and the highly branched structure of the polysaccharides, as noted by Da Silva and Rao (1992) and Xu et al. (2006). In addition, Silva et al. (2017) stated that the $\eta^*<\eta_b$ behavior may be associated with differences in structure formation when samples are subjected to dynamic oscillatory shear and steady shear measurements. This phenomenon was also observed for other starch or gum dispersions (Da Silva and Rao, 1992; Xu et al., 2006; Chun and Yoo, 2007). Similar differences between the two lines ($\eta^*$ and $\eta_b$) were observed for all samples, indicating that the deviation from the Cox-Merz rule was not affected by the CMC concentration. These results suggest that the applicability of the Cox-Merz rule may be dependent on the type of starch or gum used in the starch-gum mixture system.
Fig. 5. Combined plot of apparent viscosity ($\eta_a$, ●) and complex viscosity ($\eta^*$, ○) versus angular frequency/shear rate (Cox-Merz plot) for waxy rice starch-carboxymethyl cellulose (CMC) mixtures with different CMC concentrations at 25°C: (A) 0%, (B) 0.2%, (C) 0.4% and (D) 0.6%.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2019R1H1A2080055). This work was also supported by the Dongguk University Research Fund.

AUTHOR DISCLOSURE STATEMENT

The authors declare no conflict of interest.

REFERENCES

Achayuthakan P, Suphantharika M. Pasting and rheological properties of waxy corn starch as affected by guar gum and xanthan gum. Carbohydr Polym. 2008. 71:9-17.

Alloncle M, Doublier JL. Viscoelastic properties of maize starch/hydrocolloid pastes and gels. Food Hydrocolloids. 1991. 5:455-467.

Chun SY, Yoo B. Effect of molar substitution on rheological properties of hydroxypropylated rice starch pastes. Starch. 2007. 59:334-341.

Cox WP, Merz EH. Correlation of dynamic and steady flow viscosities. J Polymer Sci. 1958. 28:619-622.

Da Silva JAL, Rao MA. Viscoelastic properties of food hydrocolloid dispersions. In: Rao MA, Steffe JF, editors. Viscoelastic Properties of Foods. Elsevier Applied Science, London, UK. 1992. p 285-316.

Doublier JL, Curvelier G. Gums and hydrocolloids: functional aspects. In: Eliasson AC, editor. Carbohydrates in Food. Marcel Dekker, Inc., New York, NY, USA. 1996. p 283-318.

Funami T, Nakauma M, Noda S, Ishihara S, Asai I, Inouchi N, et al. Effects of some anionic polysaccharides on the gelatinization and retrogradation behaviors of wheat starch: soybean-soluble polysaccharide and gum arabic. Food Hydrocolloids. 2008. 22:1528-1540.

Kim C, Yoo B. Rheological properties of rice starch-xanthan gum mixtures. J Food Eng. 2006. 75:120-128.

Kim DD, Lee Y, Yoo BS. Rheological properties of waxy rice starch-gum mixtures in steady and dynamic shear. J Food Sci Nutr. 2009. 14:233-239.

Kim WW, Yoo B. Rheological and thermal effects of galactomannan addition to acorn starch paste. LWT-Food Sci Technol. 2011. 44:759-764.

Korus J, Juszczak L, Witzczak M, Achremowicz B. Influence of selected hydrocolloids on triticale starch rheological properties. Int J Food Sci Technol. 2004. 39:641-652.

Kulicke WM, Eidam D, Kath F, Kix M, Kull AH. Hydrocolloids and rheology: regulation of viscoelastic characteristics of waxy rice starch in mixtures with galactomannans. Starch. 1996. 48:105-114.

Lai LS, Liu YL, Lin PH. Rheological/textural properties of starch and crude hsian-tao leaf gum mixed systems. J Sci Food Agric. 2003. 83:1051-1058.

Lee HY, Jo W, Yoo B. Rheological and microstructural characteristics of rice starch-tara gum mixtures. Int J Food Prop. 2017. 20:1879-1889.
Michailova V, Titeva ST, Kotsilkova R, Krusteva E, Minkov E. Influence of aqueous medium on viscoelastic properties of carboxymethylcellulose sodium, hydroxypropylmethyl cellulose, and thermally pre-gelatinized starch gels. Colloids Surf A Physicochem Eng Asp. 1999. 149:515-520.

Shi X, BeMiller JN. Effects of food gums on viscosities of starch suspensions during pasting. Carbohydr Polym. 2002. 50:7-18.

Sikora M, Kowalski S, Tomasik P. Binary hydrocolloids from starches and xanthan gum. Food Hydrocolloids. 2008. 22:943-952.

Silva C, Torres MD, Chenlo F, Moreira R. Rheology of aqueous mixtures of tragacanth and guar gums: effects of temperature and polymer ratio. Food Hydrocolloids. 2017. 69:293-300.

Sun J, Zuo XB, Fang S, Xu HN, Chen J, Meng YC, et al. Effects of cellulose derivative hydrocolloids on pasting, viscoelastic and morphological characteristics of rice starch gel: effects of cellulose derivative on characteristics of rice starch. J Texture Stud. 2017. 48:241-248.

Weltmann RN. Breakdown of thixotropic structure as function of time. J Appl Phys. 1943. 14:343.

Xu X, Liu W, Zhang L. Rheological behavior of Aeromonas gum in aqueous solutions. Food Hydrocolloids. 2006. 20:723-729.

Yoo D, Kim C, Yoo B. Steady and dynamic shear rheology of rice starch-galactomannan mixtures. Starch. 2005. 57:310-318.

Zhao W, Wang Y. Coacervation with surfactants: from single-chain surfactants to gemini surfactants. Adv Colloid Interface Sci. 2017. 239:199-212.