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Rheological Properties of Hot Pepper-soybean Pastes Mixed with Acetylated Starches

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Abstract Effect of acetylated starches (acetylated rice starch and acetylated tapioca starch) on rheological properties of hot pepper-soybean paste (HPSP) at different mixing ratios of rice flour (RF) and acetylated starch (AS) (10/0, 9/1, 8/2, and 7/3) was evaluated in steady and dynamic shear. All HPSP samples at 25°C exhibited shear-thinning (n=0.31-0.36) and thixotropic behavior with high yield stresses and their steady flow curves were well described by power law and Casson models. The presence of AS resulted in the decrease in consistency index (K), apparent viscosity ($\eta_{a,100}$), and yield stress (σ_{oc}), and their predominant decreases were noticed at higher ratio of RF to AS (7/3 ratio). Arrhenius temperature relationship represents variation with temperature in the range of 5-35°C with the high determination coefficients (R^2=0.97-0.99). Dynamic moduli (G', G", and η^*) values of HPSP samples mixed with AS were lower than those of HPSP with no added AS within the experimental range of frequency (0.63-62.8 rad/sec). Steady and dynamic shear rheological properties of HPSP samples seem to be greatly influenced by the presence of acetylated starch.

Keywords: hot pepper-soybean paste, acetylated starch, viscosity, rheology, dynamic modulus

Introduction

Hot pepper-soybean paste (HPSP), which is called *kochujang*, is a popular condiment consumed in Korea. It is produced from fermentation of mixed ingredients, consisting of malt flour, fermented soybean starter (*meju*), red pepper powder, salt, water, and cereal flours such as rice, soybean, wheat, or barley (1). HPSP, like other food dispersions, exhibits a non-Newtonian, shear-thinning flow behavior with high yield stress and viscosity (2). It has been known that this flow behavior is affected mainly by rheological properties of starch (or cereal flour) dispersions mixed with red pepper power (3). From a consumer point of view, the rheological properties of HPSP are very important attributes with respect to eating characteristics of the product and its quality is often determined by the change of rheological properties that can occur through a long period of fermentation or storage (2,4). During storage, HPSP tends to lose its rheological properties due to hydrolysis and syneresis (serum separation) which lower its quality and sensory acceptance (5). Therefore, the structure stability of HPSP during storage is of primary importance to the manufactures, especially if products are stored at refrigeration temperatures. These disadvantageous phenomena of HPSP products can be reduced by the addition of gums and modified starches which are used as thickening and gelling agents in the food industry.

In general, it has been known that modified starches and gums play an important role in modifying the rheological properties of food products. Therefore, in order to control and improve the rheological properties of HPSP, it is necessary to study the effect of these ingredients on the rheological properties of HPSP (6). Recently, Choi and Yoo (5,6) have studied the rheological properties of HPSP mixed with various gums. They reported that the presence of gums in the HPSP-gum mixture systems, in general, modified and increased the rheological properties, depending on the gum type. They also found that in the HPSP-xanthan mixture systems the addition of xanthan gum increased the elastic properties with an increase in gum concentration form 0.3 to 0.9%. Despite HPSP being extensively studied, little is found in the literature about its rheological properties when mixed with modified starches. Acetylated starch, which is one of the most common modified starches, is used primarily as a thickening agent in variety of food products because of its stability and clarity, thus making baby foods and cream pie fillings in cans and jars meet the requirement of long shelf-life under various temperature conditions (7). In particular, the addition of acetylated starch in the food systems also causes the stability to retrogradation and improved freeze-thaw stability. Therefore, the acetylated starch can be used to stabilize and improve the rheological properties of HPSP products. Specific adjustments of the rheological properties are also important for optimizing the applicability, storage stability, and sensory properties of HPSP. However, there is no information on the effect of acetylated starches on rheologcial properties of HPSP. The main objective of the present study was to investigate the steady and dynamic shear rheological properties of HPSP in the presence of acetylated starches.

Materials and Methods

Materials and preparation of acetylated rice starch

Experimental studies on rheological properties of HPSP-acetylated starch mixtures were conducted with acetylated

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rice starch and acetylated tapioca starch. Acetylated tapioca starch (0.43% acetyl content) was provided by Deasang Co. (Seoul, Korea). Acetylated rice starch was prepared in our laboratory from native rice starch which was obtained from Bangkok Starch Industrial Co., Ltd. (Nakornprathom, Thailand). Analytical grade acetic anhydride was obtained from Samchun Pure Chemical Co., Ltd. (Pyongtack, Korea) for preparation of acetylated rice starch. Acetylated rice starch was prepared by reacting native rice starch with acetic anhydride according to the procedure of Wurzburg (8) with minor modifications, by described by Shon and Yoo (9). About 500 g of rice starch were dispersed in 750 mL of distilled water and stirred at 30°C to obtain a uniform suspension. The pH of the suspension was adjusted to 8.0 with 4% NaOH. Acetic anhydride was added drop-wise to the stirred slurry at 1.5% level, based on dry weight of starch, while maintaining the pH within the range 7.8-8.2 with the continuous addition of 4% NaOH solution during reaction. The reaction was allowed to proceed for 10 min after the completion of acetic anhydride addition. The slurry was then adjusted to pH 5.5 with 15% HCl. After sedimentation, it was washed free of acid, 3 times with distilled water, and then dried in a vacuum drier at 40°C. The dried acetylated starch was ground and then passed through a 100 mesh standard sieve (Chung Gye Inc., Seoul, Korea) with 150 mm openings using an analytical sieve shaker (AS200; Retsch GmbH & Co., Haan, Germany). Acetylated rice and tapioca starches used in this study had the same percent acetyl content (0.43%). Percent acetyl content was determined according to the method of Smith (10).

Preparation of fermented hot pepper-soybean paste (HPSP) For the preparation of traditional fermented HPSP rice flour, malt flour, *meju* flour, red pepper powder and salt were purchased in a local supermarket. The rice flour (RF) was mixed with different quantities of acetylated starch (AS). The RF-AS mixture was prepared by mixing AS to obtain 0, 10, 20, and 30% (weight basis) AS levels. Therefore, the mixing ratios of RF and AS are RF/AS=10/0, 9/1, 8/2, and 7/3. Malt flour was soaked in water for 1 hr, cooked at 60°C for 1 hr and filtered for the preparation of malt extract. The RF-AS mixture with malt extract was heated at 60°C for 90 min and mixed with other ingredients (*meju* flour, red pepper powder, and salt) to obtain HPSP, as described earlier (3). The recipe for the preparation of HPSP was 23% RF-AS mixture flour, 8.7% *meju*, 17.3% red pepper powder, 8.2% salt, and 8.5% malt flour. Predetermined amount of water was added to adjust the final moisture level of HPSP sample to 53%. HPSP samples were poured into the plastic jars and incubated at 25°C for 12 weeks fermentation.

Rheological measurements A TA rheometer (AR 1000; TA Instruments, New Castle, DE, USA) was used to conduct steady and dynamic shear experiments at 25°C using a parallel plate system (4 cm dia.) at a gap 1,000 μm. After loading the rheometer plate, each sample was allowed 5 min to recover its structure and reach the measurement temperature before conducting rheological measurements.

Steady shear data were obtained by the shear stress recorded by increasing the shear rate continuously from 0.4 to 1,000 1/sec. To analyze time-dependent flow behavior, the samples were sheared first in ascending order (0.4-1,000 1/sec) and then in descending order. The relationship between shear stress and shear rate for all samples at 25°C was analyzed by using the well-known power law model (Eq. 1) and Casson (Eq. 2) model which is a structure-based flow model that has been used for a number of food dispersions containing yield stress.

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

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

where, σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (1/sec), K is consistency index (Pa · sec^n), and n is the flow behavior index (dimensionless). Casson yield stress (σ_{oc}) and Casson plastic viscosity (η_c) based on the Casson model (Eq. 2) were determined as $(K_{oc})^2$ and $(K_c)^2$, respectively, that was obtained from linear regression of the square roots of shear rate-shear stress data. Using magnitudes of K and n according to the power law model (Eq. 1), apparent viscosity ($\eta_{a,100}$) at 100 1/sec was calculated. For the study of the influence of temperature on viscosity, the $\eta_{a,100}$ values were also obtained at different temperatures of 5, 15, 25, and 35°C. Arrhenius equation (Eq. 3) was used to investigate the temperature dependency of the $\eta_{a,100}$ values of all samples.

$$\eta_{a,100}=A\cdot\exp(Ea/RT) \tag{3}$$

where, $\eta_{a,100}$ is the apparent viscosity (Pa · sec) at 100 1/sec, A is a constant (Pa · sec), T is the absolute temperature (K), R is gas constant (8.3144 J/mol · K), and Ea is the activation energy (kJ/mole).

Dynamic shear data were obtained from frequency sweeps over the range of 0.63-62.8 rad/sec at a strain of 3% using small-amplitude oscillation measurements. The 3% strain was in the linear viscoelastic region for each sample. The values of storage modulus (G'), loss modulus (G"), and complex modulus (η^*) as a function of frequency (ω) were calculated using TA rheometer Data Analysis Software (version VI.1.76). All experiments were conducted in triplicate. Results reported were an average of 3 measurements.

Results and Discussion

Steady shear properties Plots of shear stress (σ) vs. shear rate ($\dot{\gamma}$) data for HPSP-AS mixtures at different mixing ratios of RF to AS (10/0, 9/1, 8/2, and 7/3) at 25°C showed the non-Newtonian nature with yield stress (Fig. 1). Table 1 shows the magnitudes of rheological parameters from the power law and Casson models, which were used to describe the flow curves of HPSP samples (Fig. 1). Experimental data of σ vs. $\dot{\gamma}$ for HPSP-AS mixtures were fitted well to 2 models (Eq. 1 and 2) with high determination coefficients (R^2=0.95–0.99) in describing the steady shear rheological properties of all HPSP samples. HPSP-AS mixture samples had shear-thinning behavior with values of flow behavior indices of n=0.34–0.36 which were a little higher than that (0.31) found in HPSP with no added AS (the control) (Table 1). The observed shear-thinning behavior can be due to the particle aggregation as a result of the particle-particle interaction (11) because HPSP is composed of solid particles (red pepper powder and

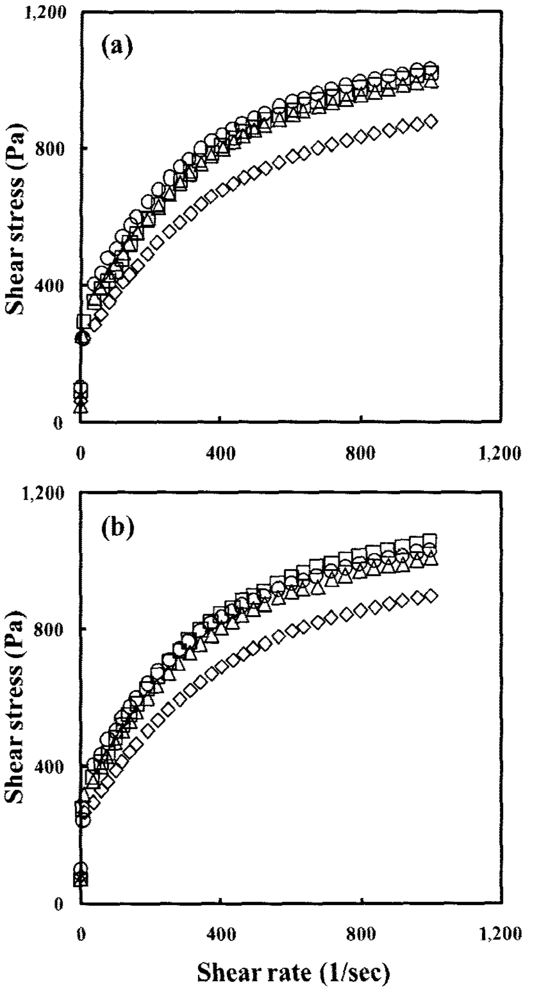

Fig. 1. Shear rate-shear stress plots for HPSP samples at different ratios of rice flour (RF) to acetylated starch (AS). RF/AS ratios were: (○) 10/0, (△) 9/1, (□) 8/2, and (◇) 7/3. (a) Acetylated rice starch and (b) acetylated tapioca starch.

soybean power) dispersed in a continuous liquid phase, and due to the high molecular weight substance (starch dispersions) which plays a major role in stable network structure of HPSP (12).

In comparison to the control (10/0 ratio), HPSP-AS mixtures showed lower values of yield stress (σ_{oc}) in the range of 296-421 Pa. Among the all samples examined, 7/3 ratio caused the greatest decrease in σ_{oc}. From these observations, it was found that the HPSP-AS mixtures were highly shear-thinning fluids with high yield stresses, and their yield stress values were decreased by the addition of AS. The magnitudes of apparent viscosity ($\eta_{a,100}$) and consistency index (K) of HPSP-AS mixtures were lower than those of the control, indicating that there was a lower viscosity with the addition of AS in the HPSP-AS mixture systems. There were also no noticeable changes in their values between 9/1 and 8/2 ratios. Such lower $\eta_{a,100}$ and K values of the HPSP-AS mixtures can be explained by the stability to retrogradation of starch in HPSP. Yoo and Choi (3) reported that K, $\eta_{a,100}$, and σ_{oc} values of HPSP increased with an increase in fermentation time, and the steady shear rheological data at 12-week fermentation also were much higher than those at 0-week fermentation. This indicates that the addition of AS to HPSP caused a more pronounced effect on retrogradation stability, resulting in lower steady shear rheological data. From these observed results, it can be concluded that the steady shear rheological properties of HPSP-AS mixture samples appear to be significantly affected by the presence of AS and the ratio of RF to AS. However, there was not much difference between steady shear data of acetylated rice starch and acetylated tapioca starch.

The investigation of the effect of the temperature on rheological properties of HPSP products is important because they can be processed and stored in a wide range of temperatures. Effect of temperature (5-35°C) on the apparent viscosity ($\eta_{a,100}$) at a specified shear rate (100 1/sec) of HPSP-AS mixture samples can be calculated by using the Arrhenius equation (Eq. 3), in which the apparent viscosity decreases to an exponential function with temperature. We have experimentally confirmed the Arrhenius temperature relationship with high determination coefficients for HPSP samples in previous studies (1,2,6). The magnitudes of Ea and A were determined at each concentration from regression analysis of 1/T vs. ln $\eta_{a,100}$. The calculated values of Ea and constant A were in the range of 11.8-15.0 kJ/mole and $0.92\text{-}4.44\times10^{-2}$ Pa · sec, respectively, with the high determination coefficients (R^2=0.97-0.99) (Table 2), showing that the Ea increased with an increase in the ratio of RF to AS and the Ea value (11.8 kJ/mole) of the control also was relatively lower than those (12.6-15.0 kJ/mole) of HPSP-AS mixture samples. In addition, acetylated rice starch had higher Ea values than acetylated tapioca starch. These

Table 1. Power law model parameters, apparent viscosity, and Casson model parameters of HPSP samples at different ratios of rice flour (RF) to acetylated starch (AS)

Sample	RF/AS ratio	Apparent viscosity	Power law model			Casson model		
		$\eta_{a,100}$ (Pa · sec)	K (Pa · sec^n)	n (-)	R^2	σ_{oc} (Pa)	η_c (Pa · sec)	R^2
Control	10/0	5.46±0.14	134±1.87	0.31±0.01	0.99	495±8.77	0.14±0.00	0.96
Acetylated rice starch	9/1	4.82±0.04	103±1.74	0.34±0.00	0.99	400±1.77	0.15±0.00	0.95
	8/2	4.84±0.01	102±6.30	0.34±0.01	0.99	396±4.04	0.16±0.01	0.96
	7/3	3.84±0.11	74.1±1.15	0.36±0.01	0.99	296±4.61	0.15±0.01	0.96
Acetylated tapioca starch	9/1	4.97±0.01	110±0.98	0.34±0.00	0.99	411±1.01	0.14±0.02	0.96
	8/2	5.09±0.15	109±3.33	0.34±0.01	0.99	421±2.98	0.16±0.01	0.96
	7/3	4.02±0.06	77.7±1.38	0.36±0.01	0.99	311±4.73	0.16±0.01	0.96

Table 2. Activation energies (Ea) of HPSP samples at different ratios of rice flour (RF) to acetylated starch (AS)

Sample	RF/AS ratio	A ($\times 10^{-2}$ Pa · sec)	Activation energy (kJ/mol)	R^2
Control	10/0	4.44	11.8	0.97
Acetylated rice starch	9/1	1.73	13.9	0.99
	8/2	1.39	14.5	0.99
	7/3	0.92	15.0	0.98
Acetylated tapioca starch	9/1	3.15	12.6	0.98
	8/2	2.82	13.0	0.99
	7/3	1.06	14.7	0.98

indicate that the increase in viscosity with temperature was more pronounced at higher RF/AS ratios and acetylated rice starch. Therefore, these results suggest that the addition of AS decreased the heat stability of HPSP. The Ea values seem to be related to the flow behavior index (n), showing that the more pseudoplastic the HPSP, the less the effect of temperature on its apparent viscosity. These results confirm an earlier observation that the values of Ea depend on the flow behavior index (13).

Time-dependent flow behavior It has been known that time-dependent flow properties in food dispersions provides a means to evaluate their structural changes. As shown in Fig. 2 and 3, thixotropic behaviors were observed in all shear stress-shear rate curves obtained by first increasing and then decreasing shear rates in the range of 0.4-1,000 1/sec. If the sample is shear sensitive, the 2 flow curves do not coincide, thus causing a hysteresis loop. Such time-dependent characteristic could be explained by the orientation or deformation of structure of dispersed solids caused by the shearing action (14). Classical approach to characterizing structural breakdown is the measurement of the hysteresis loop, as noted by Weltman (15). The area enclosed by the hysteresis loop is an indication of the degree of structural breakdown due to shearing. The loop areas seem to decrease with an increase of mixing ratio, even though there was not much difference between the loop areas at 9/1 and 8/2 ratios (Fig. 3 and 4). In particular, the loop area at 7/3 ratio was much smaller than those of other samples. Such small loop area means that there is a low degree of structural breakdown during shearing. Therefore, it could be concluded that the structure loss of HPSP could be reduced in the presence of AS. Similar time-dependent flow behaviors were also observed for commercial HPSP products (16).

Dynamic shear properties Figure 4 shows changes in storage modulus (G'), loss modulus (G"), and complex viscosity (η^*) as a function of the frequency (ω) for all HPSP samples at 25°C. The magnitudes of G' and G" increased with an increase in ω, and G' was higher than G" at all values of ω, which showed a frequency dependency. Log η^* versus log ω plot shows shear-thinning behavior following power law model. Table 3 shows that the dynamic moduli (G', G", and η^*) of the HPSP-AS mixtures were lower than those of the control. Such higher dynamic

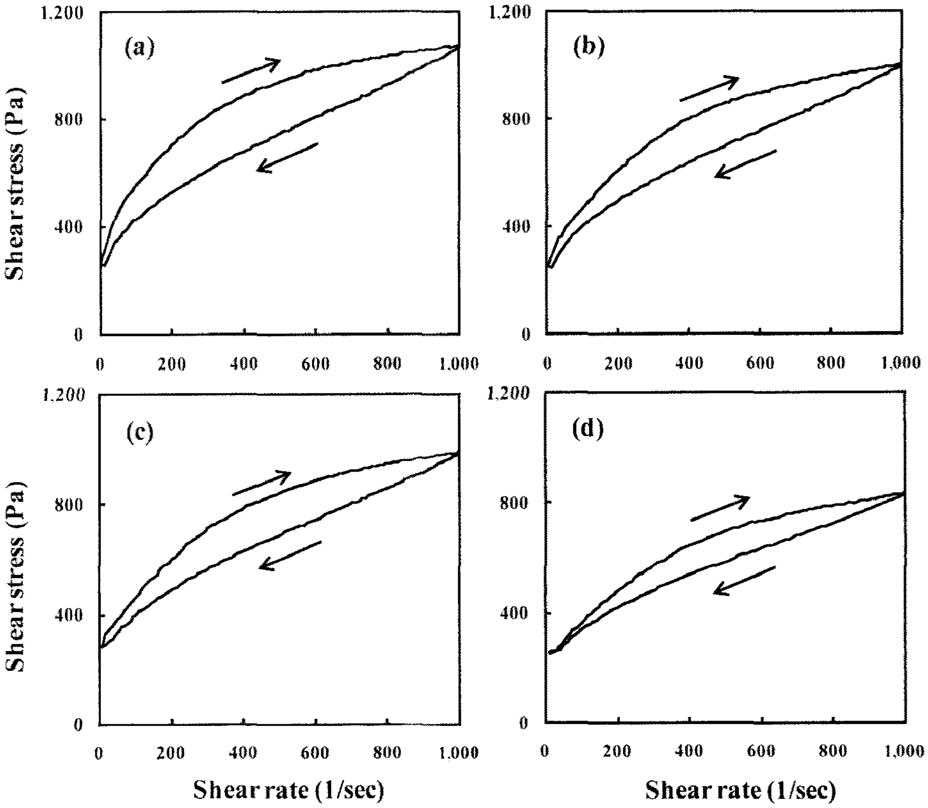

Fig. 2. Thixotropic flow curves for HPSP samples at different ratios of rice flour (RF) to acetylated rice starch. RF/ARS ratios were: (a) 10/0, (b) 9/1, (c) 8/2, and (d) 7/3.

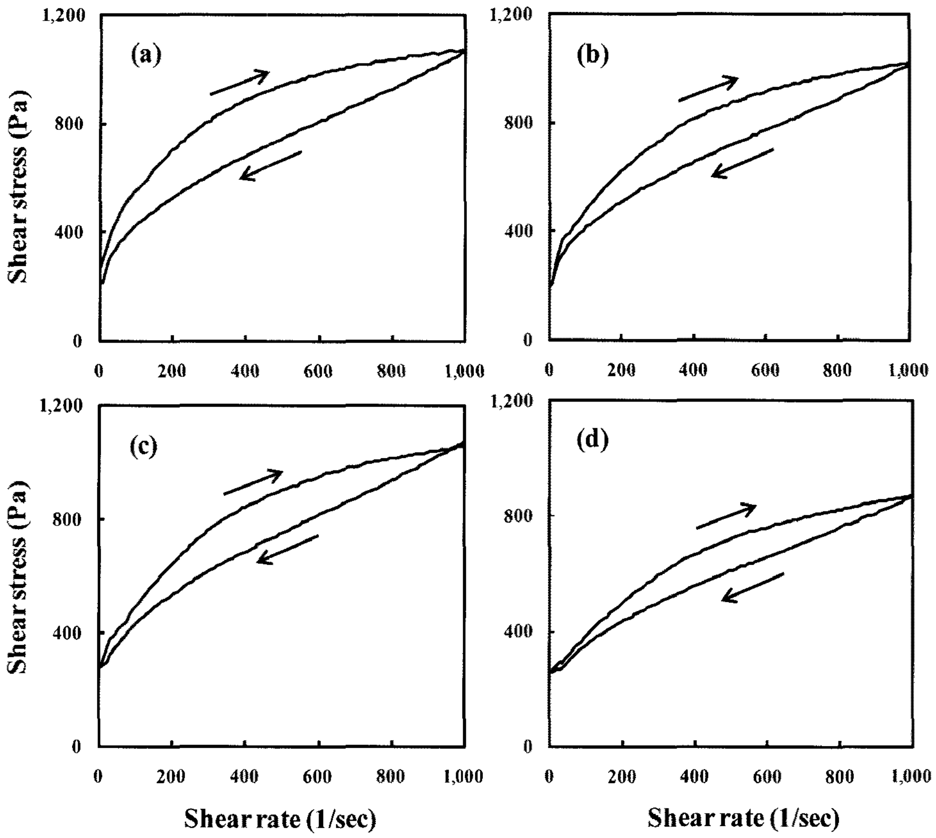

Fig. 3. Thixotropic flow curves for HPSP samples at different ratios of rice flour (RF) to acetylated tapioca starch. RF/ARS ratios were: (a) 10/0, (b) 9/1, (c) 8/2, and (d) 7/3.

moduli can be attributed to the high viscoelasticity due to the retrogradation of starch during fermentation. In particular, G' values, which reflect the elastic property of sample, were more pronounced at the control as compared to HPSP-AS mixtures. Decrease of dynamic moduli with increasing the ratio of RF to AS can also be explained by a weakened gel network structure caused by greater water uptake in the swollen granules of AS. In our previous study, acetylated rice starch had a more pronounced effect on the swelling power as compared to the native starch (9). In general, it has been known that such increased swelling of AS is attributed to the reduction of interaction between starch chains due to the increase in hydrophilicity of starch due to the introduction of acetyl groups. Therefore, the addition of AS seems to stabilize the rheological properties of the final products, resulting in the decrease of retrogradation of starch in HPSP.

In relation to structure, log (G', G") vs. log ω plots of weak gels have positive slopes and G' is greater than G" over a wide range of ω. As shown in Fig. 4 and Table 3, it was found that all samples displayed weak gel-like behavior because the slopes of G' and G" are positive and the magnitudes of G' (1.82-3.45 kPa) are higher than those of G" (0.82-1.50 kPa) at 6.3 rad/sec, showing that the G"/G' ratio (tan δ) is in the range of 0.43-0.44. These results suggest that all samples are more elastic than viscous. This tendency is in good agreements with results reported on HPSP-gum mixtures (4,6). It was also found that there was not much difference between tan δ values of all samples. In general, dynamic moduli tended to decrease with an

Table 3. Storage (G') and loss (G") moduli, complex viscosity (η*), and tan d at 6.3 rad/sec of HPSP samples at different ratios of rice flour (RF) to acetylated starch (AS)

Sample	RF/AS ratio	G' (kPa)	G" (kPa)	η* (kPa · sec)	Tan δ
Control	10/0	3.45±0.02	1.50±0.02	0.58±0.02	0.43±0.01
Acetylated rice starch	9/1	2.30±0.02	0.99±0.00	0.40±0.02	0.43±0.01
	8/2	2.28±0.07	0.99±0.01	0.40±0.01	0.43±0.01
	7/3	1.82±0.04	0.80±0.01	0.32±0.01	0.44±0.01
Acetylated tapioca starch	9/1	2.50±0.07	1.07±0.04	0.43±0.01	0.43±0.01
	8/2	2.53±0.08	1.11±0.03	0.44±0.02	0.44±0.01
	7/3	1.92±0.06	0.82±0.01	0.33±0.02	0.43±0.01

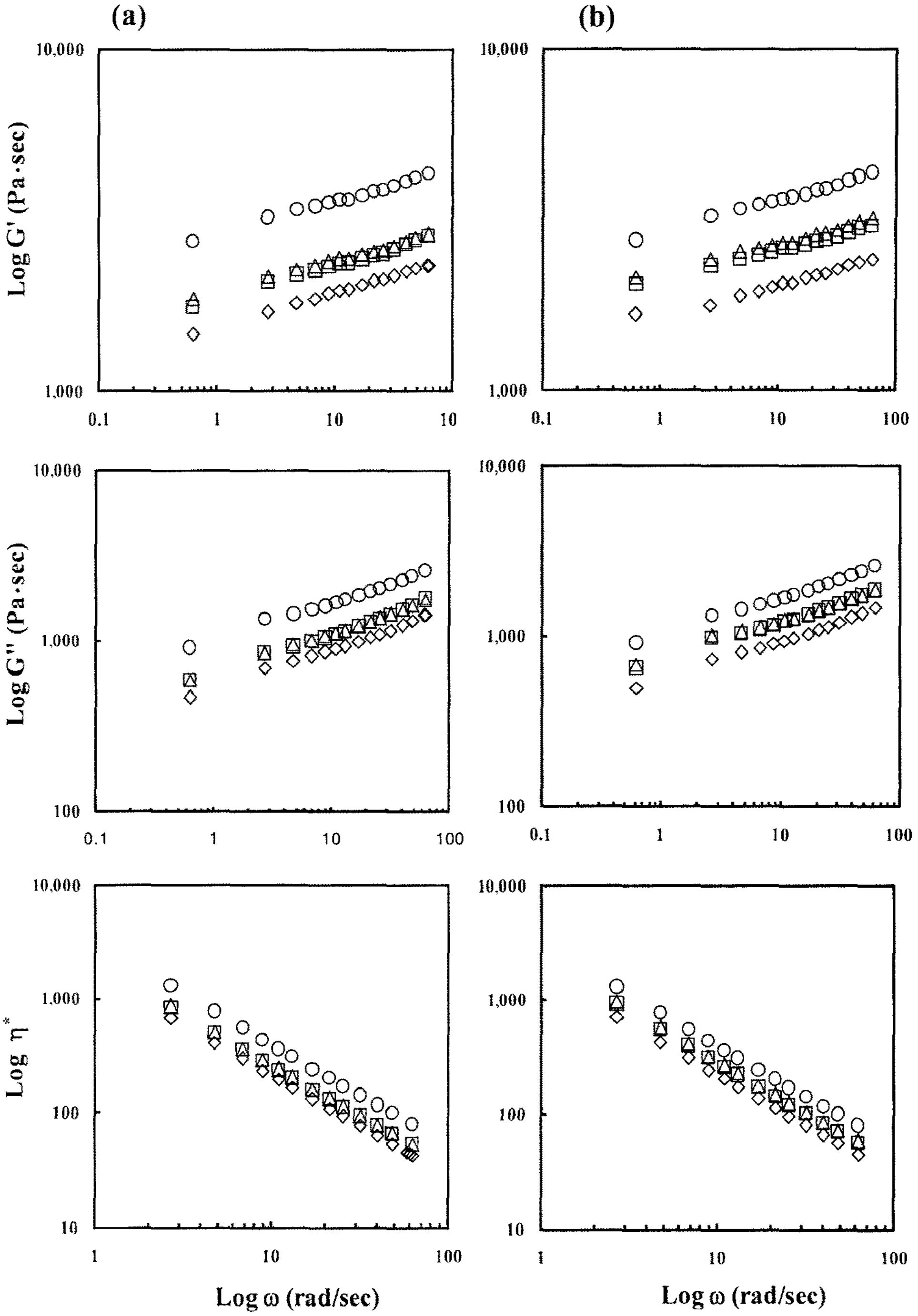

Fig. 4. Plot of log G', G'', η* vs. log ω for HPSP samples at different ratios of rice flour (RF) to acetylated starch (AS). RF/AS ratios were: (○) 10/0, (△) 9/1, (□) 8/2, and (◇) 7/3. (a) Acetylated rice starch and (b) acetylated tapioca starch.

increase in the ratio of RF to AS, even though there were only slight difference between dynamic moduli for HPSP-AS mixtures at 9/1 and 8/2 ratios. However, for the HPSP-AS mixtures, there was not much difference between dynamic moduli values of acetylated rice starch and acetylated tapioca starch. These dynamic moduli values showed similar trends as the values of K, $\eta_{a,100}$, and σ_{oc} obtained from steady shear rheological measurements, as described previously. In the light of rheological data presented in this study, it can be concluded that the steady and dynamic shear rheological properties in the HPSP-AS mixture systems appear to be affected by the presence of AS, and depend on the RF/AS ratio except for lower ratio, i.e., 9/1. However, their rheological properties can also be influenced by storage time or storage temperature after fermentation. Therefore, additional studies are required to determine the effect of storage time and temperature on HPSP-AS mixtures in terms of their structure stability during storage.

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