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RESEARCH NOTE

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Dynamic Rheological Studies on Mixtures of Hot Pepper-Soybean Paste and Xanthan Gum

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Abstract Dynamic rheological properties of hot pepper-soybean paste (HPSP) mixed with xanthan gum were evaluated at different gum concentrations (0.3, 0.6, and 0.9%) and fermentation times (12 and 24 week). Magnitudes of storage (G') and loss moduli (G") in the HPSP-xanthan gum mixture systems increased with an increase in frequency (ω), while complex viscosity (η*) decreased. G' values were higher than the G" values over most of the frequency range (0.63-63 rad/sec), and were frequency-dependent. The dynamic moduli (G', G", and η*) of the HPSP-xathan mixtures were lower than those of the control (0% gum). The differences between the dynamic moduli values at 12-week and 24-week fermentation decreased with increasing gum concentration, showing that xanthan gum can be used to stabilize and improve the viscoelastic rheological properties of HPSP. The G' value of the HPSP-xathan mixtures increased with an increase in gum concentration from 0.3 to 0.9%, whereas the G" decreased. The ability of xanthan gum to increase the elastic properties in the HPSP-xanthan mixture systems seemed to be the result of the incompatibility phenomena existing between xanthan gum and glutinous rice starch.

Keywords: hot pepper-soybean paste, xanthan gum, fermentation time, rheology, dynamic modulus

Introduction

Hot pepper-soybean paste (HPSP), which is called *kochujang*, is a fermented seasoning sauce popular in Korea. HPSP, like other food dispersions, is considered to be composed of solid particles dispersed in a continuous medium due to the addition of red pepper and soybean powders (1). It also has a homogeneous texture with a stable network structure due to the gelatinization of starch through processing and the particle-particle interaction of raw materials during fermentation (1-3). The quality of HPSP is determined by the changes in the physicochemical, microbiological, and rheological characteristics that develop through a long period of fermentation. The rheological properties, in particular, determine the overall texture of HPSP and influence the intensity of its flavor (4). These properties are of significance in order to quantify, predict, maintain, and control their quality, and to ensure product acceptability, as products with improper textural properties may be unacceptable (5). The addition of gum to HPSP can be used to modify and control its rheological properties (6). Specific adjustments of the rheological properties are also important for optimizing the applicability, storage stability, and sensory properties of HPSP. In a recent study, Choi and Yoo (6) examined the effect of gum additions [carboxylmethylcellulose (CMC), guar gum, hydroxypropylmethylcellulose (HPMC), and tara gum] on the rheological properties of HPSP at a gum concentration of 0.5%. They found that the HPSP-gum mixture systems modified and increased the steady and dynamic rheological properties, depending on the gum type. However, the effect of xanthan gum on the rheological properties of HPSP samples has not yet been studied in detail.

Xanthan gum, a well-known extracellular microbial polysaccharide produced by the bacterium *Xanthomonas compestris*, is used as a stabilizer or thickener in food systems. When added to food dispersions, xanthan gum increases the low shear-rate viscosity while having little effect on the viscosity of the food at high shear rates. This shear-thinning character of xanthan gum makes food products easy to pour, mix, or pump. Such flow behavior is more pronounced with xanthan gum than with other gums due to its rigid and rod-like conformation which is more responsive to shear than a random-coil conformation (7). In addition, xanthan gum is not degraded by shear, and it recovers its original 'at rest' viscosity upon cessation of shearing (8). Therefore, the unique flow behavior of xanthan gum can allow easy extrusion of HPSP products from tubes, maintenance of its position on solid foods, and easy mixing with other food materials.

The dynamic rheometry for small-deformation oscillatory measurements provides valuable information on the viscoelastic properties of food dispersions, including HPSP samples, without causing damage to their structural elements. Therefore, dynamic rheological measurements can be used to observe the potential structural properties of food dispersions, using dynamic moduli that relate to molecular changes (9). It is important to understand the role of gums in food dispersions with regard to their structural properties. For this reason, recent rheological studies on food dispersions have been conducted using nondestructive dynamic oscillatory measurements. However, no attempt has been made to study the effect of xanthan gum on the dynamic rheological properties of HPSP. In the present study, our aim was to elucidate the dynamic rheological properties of HPSP-xanthan gum mixtures at different concentrations and fermentation times using dynamic oscillatory measurements.

Materials and Methods

Materials and preparation of fermented hot pepper-

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soybean paste (HPSP) To prepare traditional HPSP, glutinous rice flour, malt flour, *meju* flour, red pepper powder, and salt were purchased at a local supermarket. The malt flour was soaked in water for 1 hr, cooked at 60°C for 1 hr, and filtered for preparation of the malt extract. The glutinous rice flour and malt extract mixture was heated at 60°C for 90 min and mixed with the other ingredients (*meju* flour, red pepper powder, and salt) to obtain HPSP, as described previously (6). The recipe for the preparation of HPSP was 23% glutinous rice flour, 8.7 % *meju* flour, 17.3% red pepper powder, 8.2% salt, and 8.5% malt flour. A predetermined amount of water was added to adjust the final moisture level of HPSP sample to 53%. Finally, the sample was immediately divided into four samples of 300 g sample portions. Xanthan gum at different concentrations (0.3, 0.6, and 0.9%) were then added into each sample and mixed them for 5 min at 1,000 rpm using a mixer having a rotational blade with a diameter of 50 mm (type Z-1000; Eyela, Tokyo, Japan). The exception was the sample control, which had no added gum. The HPSP samples were poured into plastic jars and incubated at 25°C for 12- and 24-week fermentations.

Rheological measurements A TA rheometer (AR 1000; TA Instruments, New Castle, DE, USA) was used to conduct the steady and dynamic shear experiments at 25°C using a parallel plate system (4 cm diameter) at a gap of 1,000 μm. After the sample was loaded onto the rheometer plate, it was allowed to rest for 5 min before rheological measurements were conducted.

The dynamic shear data were obtained over the range of 0.63-62.8 rad/sec at a strain of 3%. The linear viscoelastic range of each sample was determined from stress sweeps at 6.28 rad/sec. The values of G', G", and η^* as a function of the frequency were calculated using TA rheometer Data Analysis Software (version VI.1.76). All experiments were conducted in triplicate, and the results are reported as the average of the three measurements.

Results and Discussion

Figure 1 shows changes in storage modulus (G'), loss modulus (G"), and complex viscosity (η^*) as a function of the frequency (ω) for the HPSP-xanthan gum mixtures at 12-weeks fermentation. The magnitudes of G' and G" increased with an increase in ω, and G' was greater than G" at all values of ω, showing a slight frequency dependency. Log η^* versus log ω plots also showed shear-thinning behavior that followed the power law model. This behavior is similar to those observed in other HPSP-gum mixtures (6). Table 1 shows G', G", and η^* values at 30 rad/sec for the HPSP-gum mixtures with different gum concentrations (0.3, 0.6, and 0.9%) at 12- and 24-week of fermentation. From the dynamic rheological data (Table 1 and 2), it was found that the HPSP-xanthan mixtures displayed weak gel-like behavior because the slopes (G'= 0.14-0.16 kPa·sec; G"= 0.21-0.23 kPa·sec) are positive and the magnitudes of G' (3.54-5.26 kPa) are higher than those of G" (1.62-2.84 kPa); therefore, the G"/G' ratio ($\tan \delta$) is in the range of 0.39-0.54. This indicates that the elastic properties are dominant over viscous properties. The dynamic moduli

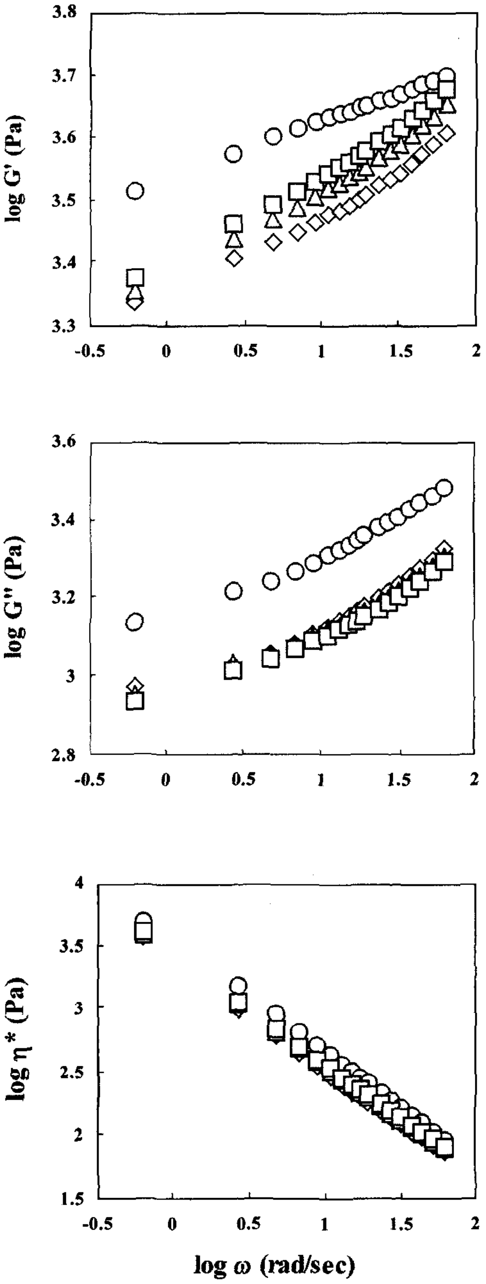

Fig. 1. Plots of log G', G", η^* vs. log ω for HPSP-xanthan gum mixtures at 12-weeks fermentation. (○) control, (◇) 0.3%, (△) 0.6%, (□) 0.9%.

(G', G", and η^*) of the HPSP-xathan mixtures were lower than those of the control (0% gum), indicating that there is no synergistic effect on viscoelastic properties by the addition of xanthan gum to HPSP samples. The G' value of the HPSP-xathan mixtures increased with an increase in gum concentration from 0.3 to 0.9%, whereas the G" decreased. Increase in the dynamic moduli with increasing gum concentration can be attributed to the effective concentration of glutinous rice starch in HPSP, which is increased by the immobilization of water by xanthan gum, resulting in local interactions between starch molecules, as described by Alloncle and Doublier (10) and Yoshimura *et al.* (11). Doublier and Cuvelier (12) also reported that this

Table 1. Storage modulus (G'), loss modulus (G"), and complex viscosity (η^*) at 30 rad/sec of HPSP-xanthan gum mixtures[1)]

Concentration (%)	Fermentation time (week)	G' (kPa)	G" (kPa)	η^* (kPa·sec)
0 (no gum)	12	4.60±0.01	2.59±0.02	0.17±0.01
	24	8.65±0.05	4.48±0.02	0.33±0.01
0.3	12	3.54±0.02	1.72±0.01	0.13±0.01
	24	5.26±0.04	2.84±0.01	0.20±0.01
0.6	12	3.90±0.01	1.65±0.01	0.14±0.01
	24	4.98±0.03	2.40±0.02	0.18±0.01
0.9	12	4.20±0.03	1.62±0.01	0.15±0.01
	24	4.78±0.04	2.12±0.01	0.17±0.01

[1)] Values are mean±SD of triplicate experiments.

Table 2. Slope values of log G' and log G" vs. log ω curve of HPSP-xanthan gum mixtures[1)]

Concentration (%)	Fermentation time (week)	Slope of G' (kPa·sec)	R^2	Slope of G" (kPa·sec)	R^2
0 (no gum)	12	0.09±0.00	0.99	0.21±0.00	0.99
	24	0.12±0.00	0.99	0.22±0.00	0.99
0.3	12	0.15±0.01	0.99	0.23±0.01	0.99
	24	0.14±0.00	0.99	0.22±0.00	0.99
0.6	12	0.16±0.01	0.99	0.22±0.01	0.99
	24	0.15±0.01	0.99	0.22±0.01	0.99
0.9	12	0.16±0.01	0.99	0.21±0.01	0.99
	24	0.16±0.01	0.99	0.22±0.00	0.99

[1)] Values are mean±SD of triplicate measurements.

may be attributed to an increase in the elasticity of the continuous phase in the HPSP-xanthan gum mixture systems as a result of the thickening properties of xanthan gum, which gives rise to a weak three-dimensional network due to the associations of ordered chain segments. They also indicated that the xanthan's viscoelastic properties may be related to its higher stiffness compared to other gums. This rigidity implies a much more limited mobility of the chains and, hence, much longer relaxation times resulting in higher elastic properties. In our previous study, xanthan gum had a more pronounced effect on the elastic properties in the gum solution systems as compared to other gums (9).

As shown in Table 1, the dynamic moduli of all the samples at 24-week fermentation were higher than those at 12-week fermentation. This is in good agreement with the results of Yoo and Choi (1), who found good linear correlations between fermentation times (5-12 week) and dynamic moduli. The higher dynamic moduli at 24-week fermentation can be related to the retrogradation of starch that developed through the long fermentation period. The differences between the dynamic moduli values of 12-week and 24-week fermentation also decreased with an increase in gum concentration, which suggests that the addition of xanthan gum increases the structural stability of HPSP during fermentation. A similar trend was reported for xanthan gum solutions with different concentrations (0.8-1.2%) (9). Therefore, this finding supports that xanthan gum can stabilize and improve the viscoelastic rheological properties of HPSP.

We performed linear regression analyses of the dynamic rheological data of log (G', G") versus log ω, and Table 2 shows the magnitudes of the slopes and determination coefficients (R^2). The slopes of G' (0.14-0.16) and G" (0.21-0.23) of the HPSP-xanthan mixtures were positive with high R^2 values (0.99). In all the samples the slopes of G" (0.21-0.23) were relatively higher than those of G' (0.09-0.16), while the slopes of G' (0.15-0.16 for 12-week and 0.14-0.16 for 24-week) in the HPSP-xanthan mixtures were higher than those of the control (0.09 for 12-week and 0.12 for 24-week). For the control, there was a noticeable difference between the slopes at 12-week fermentation (0.09 of G' and 0.21 of G") and the slopes at 24-week fermentation (0.12 of G' and 0.22 of G"). This result supports the idea that the viscoelastic properties of the control can be decreased over a longer fermentation time. In addition, there were only slight differences between all the slope values for the HPSP-xanthan mixtures at different concentrations (0.3-0.9%), indicating that the gum concentration had no effect on the slope value. From these observations, it was determined that the elastic properties of HPSP could be decreased by the addition of xanthan gum, and the viscoelastic properties in the HPSP-xanthan gum systems did not seem to be influenced by the fermentation time within a gum concentration range of 0.3-0.9%. Although the G' value of the control was higher than those of the HPSP-xanthan mixtures, the network structure of the control can be less stabilized in the light of its lower slope value of G'. A similar trend was observed for rice starch-xanthan gum mixtures at different concentrations (0.2-0.8%) of xanthan gum (13). Kim and Yoo (13) pointed out that the modification of dynamic rheological properties in the rice starch-xanthan gum composite systems could be attributed to phase separation processes in relation to the incompatibility phenomena existing between unlike polysaccharides. Therefore, these results suggest that xanthan's ability to increase the elastic properties in the HPSP-xanthan mixture systems appeared to be the result of the incompatibility phenomena existing between xanthan gum and the glutinous rice starch, as described by Choi and Yoo (6).

Acknowledgments

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