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RESEARCH NOTE

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Dynamic Rheological Investigation of Hot Pepper-soybean Paste Mixed with Acetylated Starch: Effect of Storage Time and Temperature

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Abstract The effects of storage time (0, 1, and 2 month) and temperature (5, 15, and 25°C) on the dynamic rheological properties of hot pepper-soybean paste (HPSP) mixed with acetylated starches (AS) were studied by small-deformation oscillatory measurements. Dynamic moduli (G', G", and η*) values of HPSP-AS mixtures increased with an increase in storage time and also decreased with increasing storage temperature. However, dynamic moduli values of the control (no added AS) were independent on storage time and temperature. Tan δ values (ratio of G"/G') in all HPSP samples did not change much with an increase in storage time and temperature. After 2 months of storage, the dynamic moduli of the HPSP-AS mixture samples were much lower than those of the control, indicating that the addition of AS can inhibit the retrogradation that developed over a long period of storage. Structural and rheological properties of HPSP samples seem to be stabilized by the presence of AS.

Keywords: hot pepper-soybean paste, acetylated rice starch, acetylated tapioca starch, rheological property, dynamic modulus

Introduction

Hot pepper-soybean paste (HPSP), a pungent sauce used as a popular seasoning in Korea, is made from the fermentation of a mixture of 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). It has a homogeneous texture with a stable network structure due to the gelatinization of starch that occurs during processing and the particle-particle interaction of the raw materials during fermentation (2,3). However, a very significant change in the rheological properties of HPSP products is observed over a longer storage time. This loss of the rheological properties of HPSP may be attributed to syneresis (the release of serum) lowering its quality and sensory acceptance (4). In general, it has been shown that gums and modified starches, which are used as thickening and gelling agents in the food industry, play an important role in reducing the syneresis of food products. Therefore, in order to control the rheological properties of HPSP products during storage, it is necessary to study the effect of these ingredients on the rheological properties of HPSP (5). In addition, manufactures currently have the limited rheological data on the structural stability of HPSP mixed with modified starches.

Recently, several researchers have studied the dynamic rheological properties of HPSP with the addition of modified starches and gums using small-deformation oscillatory measurements (4-6). They reported that the presence of gums or modified starches, in general, modified and influenced the rheological properties of HPSP, depending on the gum or starch type and storage conditions. However, there is no information on the dynamic rheological properties of HPSP-acetylated starch mixtures in terms of their structural stability during storage. In general, the dynamic rheological experiments conducted using small-deformation oscillatory measurements provide a suitable means for observing the potential structural properties of raw materials and formulated final products. These studies can also be applied to industrial quality control in terms of structure and stability control, including texture and sensory evaluation (7). Therefore, understanding the dynamic rheological properties of HPSP-acetylated starch mixtures under different storage conditions with regard to their structural properties will lead to improvements in the formulation of HPSP products.

The main objective of the present study was to investigate the effect of storage time and temperature on the dynamic rheological properties of HPSP mixed with acetylated starches by small-deformation oscillatory measurements.

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Materials and Methods

Materials and preparation of HPSP mixed acetylated starches Experimental studies on rheological properties of HPSP-acetylated starch mixtures were conducted with acetylated rice starch and acetylated tapioca starch. Acetylated tapioca starch was supplied by Deasang Co. (Seoul, Korea). Acetylated rice starch was prepared in our laboratory from native rice starch obtained from Bangkok Starch Industrial Co., Ltd. (Nakornprathom, Thailand), as described by Shon and Yoo (8). Acetylated rice and tapioca starches used in this study had the same percent acetyl content (0.43%). For the preparation of traditional fermented hot pepper-soybean paste (HPSP), rice flour, malt flour, *meju* flour, red pepper powder, and salt were purchased at a local supermarket. The rice flour (RF) mixed with acetylated starch (AS) was prepared by adding AS to a final concentration of 10%(w/w). A HPSP sample with no added starch (control) was also prepared. 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 the other ingredients (*meju* flour, red pepper powder, and salt) to obtain the HPSP. The recipe for the preparation of HPSP was 23% RF-AS mixture, 8.7% *meju*, 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%. HPSP samples were poured into plastic jars and incubated at 25°C for 12 weeks to allow fermentation to take place. Finally, the HPSP sample (0 month) was portioned into 3 samples of 100 g each and then stored at different temperatures (5, 15, and 25°C) for 2 months. The rheological properties of HPSP samples were measured on the first day following the 12-week fermentation period and also once a month thereafter.

Dynamic rheological measurement A TA rheometer (AR 1000; TA Instruments, New Castle, DE, USA) was used to conduct dynamic shear experiments at 25°C using a parallel plate system (4 cm diameter) at a gap of 1,000 μm. Each sample was allowed to rest for 5 min following the loading of the sample on the rheometer plate before dynamic rheological measurements were conducted. Dynamic shear data were obtained over a range of 0.63-62.8 rad/sec at a strain of 3%. The linear viscoelastic range was determined for each sample from stress sweeps at 6.28 rad/sec. Storage (or elastic) modulus (G'), loss (or viscous) modulus (G"), complex viscosity (η*), and loss factor (tan δ=G"/G') data as a function of frequency were obtained directly from the TA rheometer Data Analysis Software (version VI.1.76). All experiments were conducted in triplicate. The average of the 3 measurements was reported as the measured value.

Results and Discussion

Table 1 and 2 show changes in the magnitudes of G', G", η*, and tan δ of HPSP-AS mixtures including the control, following storage at different temperatures (5, 15, and 25°C) for different lengths of time (0, 1, and 2 month). G' is a measure of the energy that is stored in the material or recoverable per cycle of deformation, while G" is a measure of the energy that is lost as viscous dissipation per cycle of deformation. η* is a measure of the overall resistance to flow. The tan δ is a measure of the differences in the viscoelastic behavior. Dynamic moduli (G', G", and η*) of HPSP-AS mixtures decreased with an increase in storage temperature from 5 to 25°C while they increased

Table 1. Storage modulus (G'), loss modulus (G"), complex viscosity (η*), and tan δ at 6.28 rad/sec of HPSP samples without acetylated starch at different storage times and temperatures[1)]

Storage time (month)	Storage temp. (°C)	G' (kPa)	η* (kPa)	G" (kPa·sec)	Tan δ
0	25	3.45±0.02	1.50±0.02	0.58±0.02	0.43±0.01
1	5	2.99±0.03	1.25±0.02	0.52±0.01	0.42±0.00
	15	3.00±0.04	1.25±0.03	0.52±0.01	0.42±0.00
	25	3.00±0.04	1.26±0.02	0.49±0.05	0.42±0.01
2	5	3.43±0.07	1.45±0.03	0.60±0.01	0.42±0.00
	15	3.43±0.05	1.48±0.02	0.60±0.01	0.43±0.00
	25	4.49±0.08	1.87±0.02	0.76±0.01	0.42±0.01

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

Table 2. Effect of storage time and temperature on storage modulus (G'), loss modulus (G"), complex viscosity (η*), and tan δ at 6.28 rad/sec of HPSP samples mixed with acetylated starches[1)]

Acetylated starch	Storage time (month)	Storage temp. (°C)	G' (kPa)	G" (kPa)	η* (kPa·sec)	Tan δ
Rice starch	0	25	2.30±0.02	0.99±0.01	0.40±0.02	0.43±0.01
	1	5	2.91±0.01	1.26±0.05	0.51±0.00	0.43±0.00
		15	2.86±0.04	1.16±0.02	0.50±0.01	0.41±0.00
		25	2.52±0.04	1.05±0.02	0.44±0.01	0.42±0.00
	2	5	3.23±0.04	1.40±0.04	0.56±0.01	0.43±0.01
		15	3.00±0.05	1.27±0.03	0.53±0.01	0.42±0.00
		25	2.90±0.01	1.19±0.01	0.50±0.00	0.41±0.00
Tapioca starch	0	25	2.50±0.07	1.07±0.04	0.43±0.01	0.43±0.01
	1	5	3.14±0.05	1.36±0.01	0.55±0.01	0.43±0.00
		15	3.13±0.03	1.33±0.01	0.55±0.00	0.42±0.00
		25	2.78±0.02	1.16±0.01	0.48±0.00	0.42±0.00
	2	5	3.39±0.09	1.48±0.01	0.59±0.01	0.44±0.00
		15	3.18±0.01	1.33±0.01	0.55±0.00	0.42±0.00
		25	3.12±0.05	1.31±0.01	0.54±0.01	0.42±0.00

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

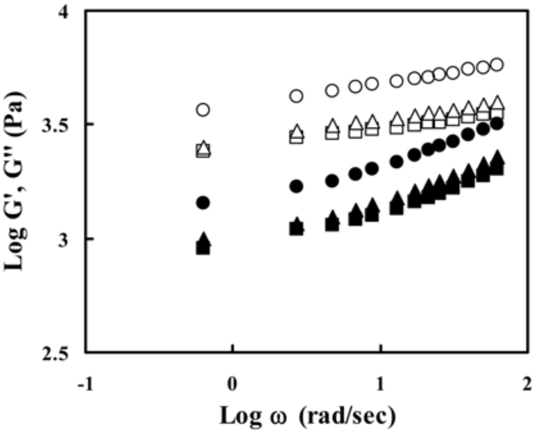

Fig. 1. Plot of log G' and log G" vs. log ω for HPSP-acetylated starch mixtures following 2 months of storage at 25°C. (○, ●) control (without acetylated starch), (□, ■) acetylated rice starch, (△, ▲) acetylated tapioca starch. Open symbol, G'; closed symbol, G".

with an increase in storage time from 0 or 1 to 2 months (Table 2). In contrast, in the case of the control (no added AS) there were considerable variations between dynamic moduli values at different storage times (Table 1), as observed by Yoo and Choi (3). Such large variations in the rheological properties of the control may be attributed to structural changes due to hydrolysis and syneresis occurring over a long period of storage (6). In particular, their values were more pronounced following 2 months of storage at 25°C. In the HPSP-AS mixture systems, there were only slight differences between dynamic moduli after 1 month of storage at 5 and 15°C, suggesting that their viscoelastic properties were affected by the higher storage time and temperature. After 2 months of storage, the dynamic moduli of the HPSP-AS mixture samples were much lower than those of the control, indicating that the lower dynamic moduli may be due to the inhibition of retrogradation during storage in the presence of AS. However, this result is inconsistent with our previous findings that in the HPSP-gum mixture systems, there was a synergistic effect of some gums on the dynamic rheological properties of HPSP (5). Such a reduction of dynamic moduli by the addition of AS to HPSP can also be interpreted as a result of a weakened gel network structure caused by greater water uptake in the swollen granules of AS compared to native starch, as described previously (4,8). In the HPSP-AS mixtures, the decrease in dynamic moduli was more pronounced for the HPSP-rice starch than in the HPSP-tapioca starch, indicating a possible weaker network structure of acetylated rice starch. In addition to the differences observed in the dynamic moduli, the tan δ values of all samples, which were in the range of 0.41-0.44, were less all than one. This means that HPSP-AS mixtures are food dispersions displaying a weak gel-like behavior with elastic properties dominant over viscous properties (9,10). The observed tan δ values did not change much with an increase in storage time and temperature, indicating that there was no appreciable effect of storage conditions on the tan δ values in all samples. This result is consistent with our previous findings that HPSP-AS mixtures with various ratios of rice flour to AS were in the tan δ range of 0.43-0.44 (4).

Figure 1 also shows changes in G' and G" as a function of frequency (ω) for HPSP-AS mixtures following 2 months of storage at 25°C. The magnitudes of G' and G" were found to increase with an increase in ω, and G' was much higher as compared to G" at all values of ω with the small frequency dependence confirming the viscoelastic nature of HPSP. This dependence was more pronounced in the G" values compared to the G' values. A similar trend was observed for HPSP-gum mixtures (4,5). It can be clearly observed from the figure that the addition of AS decreases the viscoelastic properties of HPSP by inhibiting the retrogradation that occurs over a long period of storage. This finding supports the fact that the addition of acetylated starches leads to the structural stability of HPSP during storage at various temperatures, as discussed previously. From these observations, it can be concluded that the structural and rheological properties of HPSP during storage are influenced and stabilized by the addition of acetylated starches.

Acknowledgments

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