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RESEARCH NOTE

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Effect of Modified Starches on Caking Inhibition in Ramen Soup

Hye-Won Wee, Young-Jin Choi[1], and Myong-Soo Chung*
Department of Food Science and Technology, Ewha Womans University, Seoul 120-750, Korea
[1]Department of Food Science and Biotechnology, Seoul National University, Seoul 151-921, Korea

Abstract The effect of the addition of 2 kinds of chemically modified starches (the anti-caking agents; tapioca starch and corn starch) on caking of ramen soup was observed using a low-resolution proton-pulsed nuclear magnetic resonance (NMR) technique. After storing ramen soup samples with diverse compositions of modified starch at 20-40% relative humidity for 4 weeks, changes in the spin-spin relaxation time constant (T_2) were measured as a function of temperature. T_2-Temperature curves for ramen soup containing modified starches showed that the caking initiation temperature (glass transition temperature) was increased by 5°C following the addition of only 0.5% modified cornstarch. The results indicate that the modified corn starch used in this study would be an effective anti-caking agent for ramen soup, thus prolonging the shelf life of the product.

Keywords: anti-caking agent, ramen soup, caking phenomenon, low-resolution proton-pulsed nuclear magnetic resonance (NMR), spin-spin relaxation time constant (T_2), glass transition temperature (T_g)

Introduction

The strict control of moisture content, storage at low temperatures, handling at low humidity, and packaging in moisture-barrier materials, when possible, are key factors in preventing or minimizing powder caking (1, 2). Another effective method to prevent or minimize the caking of hygroscopic food powders is the addition of flow conditioners or anti-caking agents to improve their flowability and/or inhibit their tendency to cake. The most commonly used food-grade commercial anti-caking agents are phosphates, talcum, salts of stearic acid, silicon dioxide, silicates, starches, and modified carbohydrates, which are usually chemically and physically inert, and are effective at concentrations of up to 2% (3). In other words, if the amount of available moisture is so large that it exceeds the water-holding capacity of anti-caking agents, they are ineffective. Peleg and Mannheim (4) showed that 2 kinds of anti-caking agents, 1% aluminum silicate and 1% calcium stearate, had no effect on powdered onion because the conditioned powder adsorbed moisture freely and reached equilibrium at a high relative humidity (RH).

In general, the storage stability of powders can be determined by measuring the period over which flowability is maintained without caking. Many quantitative methods to observe caking and conditions under which it occurs have been utilized to verify the flowability of powders and to characterize caking phenomena. These include the measurement of hardness and compressibility using a texture analyzer (5, 6), sieving method using sieves (7), the determination of the changes in bulk volume and density (8, 9), and the measurement of cohesion using Jenike flow factor tester (1, 10). In addition, the temperature of caking onset has been measured with the aid of various tools: Lazar *et al.* (11) measured the sticky-point tempe-rature; Tsourouflis *et al.* (12) developed a method to determine the collapse temperature; indirect methods for detecting the chemical changes using differential scanning calorimetry (13, 14), electron-spin resonance (15), and nuclear magnetic resonance (NMR) (14, 16).

Our recent studies using low-resolution proton-pulsed NMR have shown that caking of food powders is closely associated with their physical state transition and molecular mobility (17-21). The resistance or sensitivity of food powders to caking varies with their state transition and molecular mobility properties. In these studies, the state transition and molecular mobility properties as measured by spin-spin relaxation time (T_2) of food powders were analyzed using NMR techniques. Through NMR analysis, a quantitative relationship between temperature and molecular mobility for each powder was determined, and a connection between this relationship and caking characteristics of powders was further established. We found that caking temperature is related to glass transition temperature (T_g). Powders exhibited 4 different patterns of the temperature-T_2 curves and that pattern depends on powders' chemical composition, molecular weight, water activity, and so on (17-21).

In this study, the effect of chemically modified starches (tapioca and corn starches) as anti-caking agents on the caking of instant ramen soup under several environmental humidity conditions was investigated by NMR techniques.

Materials and Methods

Materials Twenty g of instant ramen soup (Table 1) was placed in an aluminum container with no top together with 0, 0.5, 1.0, 2.0, 3.0, or 4.0 wt% of chemically modified tapioca starch (CRISPIOCA® PLUS, National Starch, Cambridge, UK) and chemically modified corn starch (DRY-FLO®, National Starch). Each sample was placed in a vacuum desiccator adjusted to an RH from 20 to 40% using various saturated salt solutions (Table 2). These samples were kept for 4 weeks in an incubator maintained

*Corresponding author: Tel: 82-2-3277-4508; Fax: 82-2-3277-4508
E-mail: mschung@ewha.ac.kr
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Table 1. Recipe of ramen soup

Ingredients	Percentage by weight
Garlic powder	1.9
Hydrolyzed animal protein	6.2
Hydrolyzed vegetable protein (HVP)	1.3
Seasoning (HVP + Lactose)	3.7
Beef extract powder-3	2.5
Powdered soy sauce	6.2
Seasoning (glucose + corn syrup)	5.0
Onion powder	5.0
Disodium succinate	0.6
Glucose	1.3
Beef extract powder-1	7.5
Beef extract powder-2	2.5
Red pepper	3.7
Corn powder	1.4
Black pepper	1.9
Seasoned red pepper	1.3
Dried green onion	1.4
Salt	28.0
Sucrose	9.3
Monosodium glutamate	9.3
Total	100.0

Table 2. Water activity (a_w) of the saturated salt solutions used in this study

Salt	a_w	Solubility (g/mL water)
$CH_3COO^-K^+$	0.23	2.00
$MgCl_2$	0.33	1.67
K_2CO_3	0.44	1.00

at a temperature of 25°C (i.e., until no more moisture adsorption or desorption occurs). Water activity of each sample was then measured using an Aw sprint (TH-500; Novasina, Pfäffikon, Switzerland).

NMR study After the 4 weeks of storage, each sample exhibited different water activity. The change in T_2 with changing temperature was measured for each of the samples by placing 3 g of each into the magnetic field of a 20-MHz low-field NMR analyzer (minispec-mq20; Bruker, Rheinstetten, Germany) installed with a temperature controller. T_2 measurements were made in the range from -20 to 110°C, and the average heating rate was adjusted to 0.67°C/min. Using a single, 90°, one-pulse sequence, as in the studies by Chung *et al.* (19, 20), the free induction decay (FID) curve was obtained at each temperature. Likewise, the specific measurement process used in the present study was similar to that used in the studies of Chung *et al.* (19, 20). On the other hand, NMR parameters were

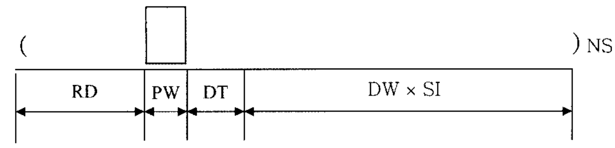

Fig. 1. Schematic of a 90° one-pulse nuclear magnetic resonance (NMR) sequence. The following parameters were used in the study: RD (recycle delay between scans) = 1.0 sec, PW (pulse width or pulse length) = 2.32 μsec, DT (variable delay between the pulse and acquisition) = 10.0 μsec, DW (dwell time or tau delay) = 5 μsec, SI (size of data) = 1,000, NS (number of scans) = 16.

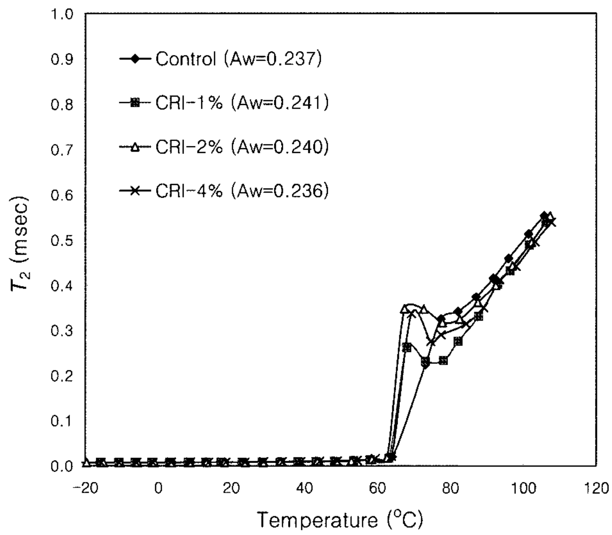

Fig. 2. Effect of the addition of modified tapioca starch (CRISPIOCA® PLUS; CRI) to ramen soup stored at low relative humidity (23-24%) on the spin-spin relaxation time constant (T_2), as a function of temperature. Data were acquired with the aid of a low-field NMR technique.

adjusted in the present study as shown in Fig. 1, since the optimal conditions for the sequence are machine-dependent (17). The one-component exponential model was used for the curve fitting of the FID curve, as in the studies by Chung *et al.* (17, 19, 20), to calculate T_2 at each temperature for the preparation of the T_2-temperature curves.

Results and Discussion

Figure 2-5 show the T_2 data as a function of temperature, as measured by proton-pulsed NMR, for instant ramen soup after the addition of various quantities of 2 kinds of anti-caking agent and varying the water activity. As shown in Fig. 2 and 3, significant differences were not found when CRISPIOCA® PLUS was used as the anti-caking agent, regardless of anti-caking agent content and water activity. This tapioca starch is thus not useful as an anti-caking agent for instant ramen soup. However, in the case of DRY-FLO®, we found that with increasing concentration in the sample, there were tendencies toward an increasing transition temperature point (T_{Trans}) of T_2; that is, T_g or the caking temperature (Fig. 4 and 5). This tendency is more apparent at relatively higher water

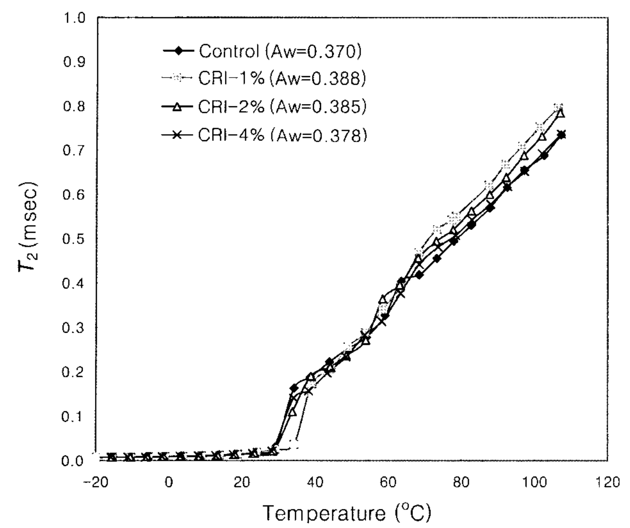

Fig. 3. Effect of the addition of modified tapioca starch (CRI) to ramen soup stored at high relative humidity (37-39%) on T_2 as a function of temperature, as measured by low-field NMR.

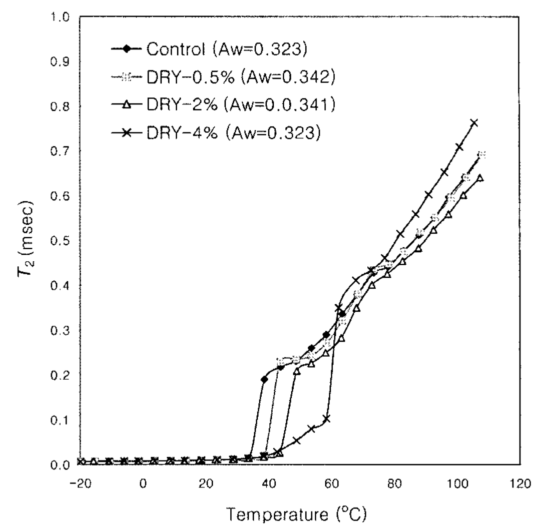

Fig. 5. Effect of the addition of modified corn starch (DRY) to ramen soup stored at low relative humidity (32-34%) on T_2 as a function of temperature, as measured by low-field NMR.

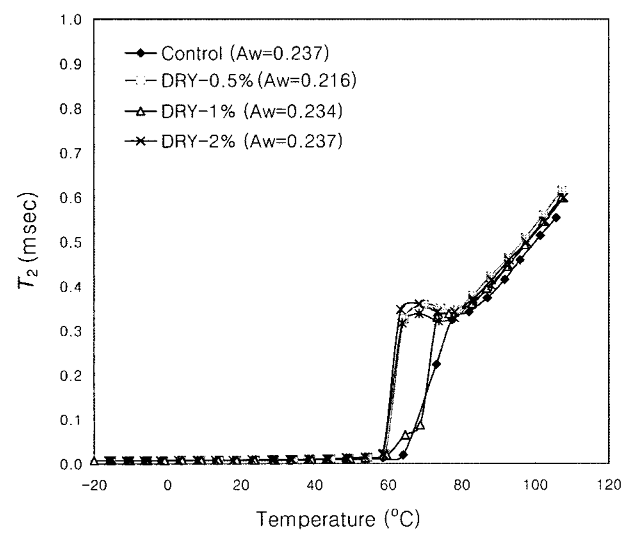

Fig. 4. Effect of the addition of modified corn starch (DRY-FLO®; DRY) to ramen soup stored at low relative humidity (21-24%) on T_2 as a function of temperature, as measured by low-field NMR.

activity. As shown in Fig. 5, T_{Trans} was 35, 40, 45, and 60 °C for DRY-FLO® concentrations of 0, 0.5, 2.0, and 4.0 wt%, respectively. This indicates that in instant ramen soup, the temperature at the onset of caking was significantly increased by the use of this modified corn starch as an anti-caking agent. These results could be explained by a mechanism in which caking can be prevented by increasing the T_g of the amorphous phase in the powder food system (22, 23). This mechanism has been demonstrated for dairy-based infant formula powders with added high-molecular-weight carbohydrates (13). Chuy and Labuza (13) reported that the addition of amylopectin into commercial infant formulas leads to an increase in molecular weight, resulting in an increase in T_g and an improvement in product stability. In protein hydrolyzates, it has been observed that a lower degree of hydrolysis (i.e., a higher average molecular weight) diminishes caking (8). Some lipids have been shown to exert an antiplasticization effect in lipid-compatible polymers plasticized by water, which increases T_g (24).

These results are practically meaningful, since the period of storage stability of instant ramen soup could be prolonged by 2 months under the environmental conditions of 50-60% RH and a storage temperature of 25-30°C if T_{Trans} is increased by 5°C, as evaluated by applying the prediction models designed by Chung *et al.* (20, 21). Moreover, storage stability could be further improved at even higher environmental RHs and temperatures (18).

Future studies into the optimum concentration of modified cornstarch to use as an anti-caking agent, bearing in mind production costs and carrying out a sensory evaluation, may confirm that the addition of DRY-FLO® is beneficial for improving the storage stability and prolonging the shelf life of instant ramen soup.

Acknowledgments

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