

Thermal and Rheological Properties of Hydrogels Prepared with Retrograded Waxy Rice Starch Powders

Won-Jun Jung, Jung-Ah Han, and Seung-Taik Lim

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Abstract Waxy rice starch dispersed in water (50% solids) was gelatinized by heating the dispersion at 121°C for 20 min, and retrograded by storing the paste at 4°C for 2 days. The starch gel was then freeze-dried and ground into powders. The retrograded starch powders were hydrated at 20-30% solid concentration at different temperatures (4 and 23°C), and then thermal and rheological properties were analyzed using the hydrogels. The gel hydrated at 4°C had an onset temperature of melting at 34.9°C, which was approximately 10°C lower than that observed for the gel hydrated at 23°C. The enthalpy value was greater for the gel hydrated at 4°C (14.2 J/g) than the gel hydrated at 23°C (8.8 J/g). The yield stress and consistency of the hydrogels were proportional to the solid concentration. The hydrogel prepared with 30% retrograded starch powders at 4°C displayed a thick creamy texture with retrograded starch crystals that could melt at a temperature range of 35-51°C. The thermal and rheological properties of the hydrogels exhibited the possibility for the retrograded starch powders to be used as fat mimetic in foods.

Keywords: waxy rice starch, retrograded starch, hydrogel, rheology, onset temperature, fat mimetic

Introduction

High fat-intake increases the risks for obesity and cardiovascular diseases; thus, dietary habits that include consumption of less fat have been recommended. To satisfy health conscious consumers, many kinds of fat replacer have been developed for this purpose. As a fat replacer, the fat mimetic partially replaces fat while still retaining the sensory qualities of fat (taste and mouthfeel). Currently, most fat replacers are mainly based on carbohydrates or proteins that display water soluble characteristics.

Carbohydrates-based fat mimetics have been especially used in baked products such as cookies, biscuits, and cakes (1-3). They act by binding to extra water, creating a sense of creaminess and lubricity similar to full fat products (4,5). For instance, gums, starches, pectin, cellulose, and other carbohydrate ingredients provide some of the functions of fat in foods by the hydrophilic interaction with water. These polymeric substances also provide a texture and mouthfeel that similar to fat, which is a prerequisite of a fat replacer (6,7).

Retrogradation has been used to describe the changes in physical behavior due to the association of starch chains following gelatinization. These changes may result in the formation of double helices of starch chains, and variably ordered crystalline arrays of the helices (8,9). The reordering of amylopectin is more responsible for the recrystallization process than that of amylose. Retrograded starches usually show an endothermic peak at temperatures lower than that for native starches (10), and this peak is often near human body temperature. The lower melting temperature allows the retrograded starch to be favorably used as a fat mimetic in some food systems.

When water was added to retrograded starch powders, viscoelastic hydrogels could be formed by rapid water adsorption. The hydrogels consist of hydrophilic polymer

Seung-Taik Lim (✉)
Graduate School of Life Sciences and Biotechnology, Korea University,
Seoul 136-701, Korea
Tel: +82-2-3290-3435; Fax: +82-2-927-5201
E-mail: limst@korea.ac.kr

Won-Jun Jung
R&D Center, Daesang Co., Icheon, Gyeonggi 467-813, Korea

Jung-Ah Han
Department of Food Service Management and Nutrition, Sangmyung
University, Seoul 110-743, Korea

networks, which may contain a water weight that is up to thousands times larger than their dry weight. These gels may degrade and eventually disintegrate by thermal or mechanical force, and the texture and rheology of the hydrogels are important physical characteristics that determine their use in foods. In this study, hydrogels with retrograded waxy rice starch were prepared and the thermal and rheological properties of the gels were evaluated. The fat-mimetic characteristics of the retrograded waxy rice hydrogel were also examined.

Materials and Methods

Preparation of retrograded waxy rice starch powders

An aqueous dispersion of waxy rice starch (50% dry solids), which was obtained from Remy Industries (Remyline-AXDR, Belgium), was gelatinized by heating the dispersion at 121°C for 20 min, and the gelatinized paste was then retrograded by storing in a cold chamber (4°C) for 48 hr. After retrogradation, the starch gel was freeze-dried, ground, and sieved through a 200 mesh screen.

Preparation of hydrogels Hydrogels were prepared by hydrating the retrograded waxy rice starch powders at different solid contents (20, 25, and 30%) and different temperatures (4 or 23°C). Distilled water was slowly added to the starch powders while homogenizing (30 sec, Ultra turrax T25; IKA Works Inc., USA). The dispersion was then stored for 24 hr at the hydration temperature (4 or 23°C) to stabilize the gel matrices.

Thermal properties Both native and retrograded starches were thermally analyzed using a differential scanning calorimeter (DSC, DSC6100; Seiko, Japan). Water (50% based on total weight) was added to the starch (about 3 mg) in an aluminum pan, and the dispersion was heated from -10 to 180°C at a heating rate of 5°C/min. To retrograde, the heated DSC sample pan was stored at 4°C for 2 days, and then analyzed using the same procedure as the native starch. The endothermic melting of the hydrogels prepared with the retrograded starch powders was also measured. A portion of the hydrogels (about 10 mg, 30% dry solids) prepared at different temperatures (4 and 23°C) was directly analyzed using DSC from -10 to 180°C at a heating rate of 5°C/min. All thermograms were recorded using an empty aluminum pan as the reference.

Photomicrographs and flowing properties Photomicrographs of retrograded waxy rice starch powders and hydrogels were taken with a light microscope (CX-40 MDBH2-RFCA; Olympus, Japan). Retrograded waxy rice

starch powder was dispersed in ethanol (95%) for microscopic observation. To compare plasticity and creaminess of crystallized waxy rice starch hydrogel, spoon test was conducted. Hydrogels were scooped up and the shape was compared.

Rheological measurement Rheological measurements were performed using an oscillatory rheometer (Rheostress 150; Haake, Germany) equipped with a plate and plate fixture (35-mm diameter, 1,000- μ m gap). Hydrogels (5 g, each) were carefully loaded onto the fixed plate and the extra sample was gently removed. To prevent water evaporation, the edge of the plate was covered with silicon oil. The temperature was fixed at 4 or 23°C, and oscillatory shear (1.0 Hz frequency) was applied. The rotational tests were carried out to determine the yield stress and viscosity. For the yield stress of the hydrogels, a controlled shear rate test was performed; the range of shear rate was controlled from 0.1 to 150/sec for 180 sec. To test the fluid properties, the results from this test were applied to the Herschel-Bulkley model and Casson model. The Herschel-Bulkley model assumes that the material has consistency and flow behavior. Parameters from the Casson model can be used to calculate the yield stress. In these mathematical models, σ is shear stress, σ_y is yield stress, $\dot{\gamma}$ is shear rate, k is the consistency index, and n is the flow behavior index.

Herschel-Bulkely model

$$\sigma = \sigma_y + k \dot{\gamma}^n \quad (1)$$

Casson model

$$\sigma^{0.5} = \sigma_y^{0.5} + \eta_1^{0.5} \dot{\gamma}^{0.5} \quad (2)$$

The oscillation stress sweep study to scan the material was conducted over the range of 0.1-150 Pa and at a frequency of 1.0 Hz. The resulting viscoelastic parameters were monitored and the linear viscoelastic region was measured. The influence of temperature on sample structure was studied over the temperature range of 4-80°C. Shear stress was fixed at 2 Pa, which was the value in the linear viscoelastic region.

Results and Discussion

Thermal properties of retrograded starches Waxy rice starch were gelatinized with water (1:1 ratio) in a DSC sample pan and the melting properties are shown in Table 1. The onset and conclusion temperature (T_o and T_c) were 58.1 and 91.2°C, respectively. The melting enthalpy of waxy rice starch was measured 15.5 J/g in this experiment and this is slightly higher than those in literatures (7-12 g/J) (11). The reason could be explained that the sample with

Table 1. Thermal properties of native and retrograded waxy rice starch (starch:water=1:1)

	Day	To ¹⁾ (°C)	Tc (°C)	Tc-To (°C)	ΔH (J/g)
Native		58.1 ^{a2)}	91.2 ^a	33.1 ^d	15.5 ^{ab}
Retrograded	1	-	-	-	-
	2	22.4 ^c	66.5 ^b	44.1 ^a	13.9 ^c
	3	27.6 ^b	66.5 ^b	38.9 ^c	15.1 ^b
	5	27.2 ^b	66.7 ^b	39.5 ^b	16.3 ^a

¹⁾To, gelatinization onset temperature; Tc, conclusion temperature; ΔH, melting enthalpy

²⁾Different letters on data indicate differences in statistical significance ($p < 0.05$).

50% water content showed dual peak, resulting in slight over-estimate in measuring melting enthalpy. After gelatinization, the starch in the pan was retrograded by storing at 4°C for 2 days. The onset for crystal melting started between 22–28°C for the retrograded starch, which was lower than that (58.1°C) of the native starch (Table 1). During retrogradation, new crystals are formed, which have lower thermal stability than those in native starch (12). Retrogradation of amylopectin involves a crystallization process of the outer branches (DP 14–18), and the crystals melt in a lower temperature range than recrystallized amylose (13). The endotherm associated with the melting of recrystallized amylopectin also depends on the storage temperature. This may be attributed to the temperature-dependency of polymer crystallization, which influences the ‘perfectness’ of the crystals produced: the lower the storage temperature is, the less perfect the formed crystallites will be, resulting in lower melting temperatures and broader endothermic transitions (14).

As a fat mimetic, the onset for melting is considered important to provide a fat-like ‘mouthfeel’, because the sample with lower onset temperature is more readily hydrated or can form dispersions in the food matrix to give fat-like texture and viscosity (15). The onset temperature of the starch retrograded at 4°C for 2 days was 22.4°C and the conclusion temperature was 66.5°C, which indicates that some of the crystals could melt at body temperature. The enthalpy for melting of retrograded waxy rice starch (13.9–16.3 J/g) was comparable to that of native starch crystals (15.5 J/g). The melting temperature range of the retrograded starch became slightly broader than the gelatinization range for native starch (Table 1). The melting temperature of retrograded waxy rice starch was 4–8°C lower than the waxy corn starch retrograded under identical conditions (data not shown). The waxy rice starch is expected to provide a better mouthfeel because the granule size is much smaller (about 5 μm) than that of other starches (16).

The water content in the starch paste affects the rate of retrogradation of starch. Longton and LeGrys (17) reported that no retrogradation was observed at 4°C if the starch concentration was below 10% or above 80%. In this study, no endotherm for the retrograded starch was observed

Table 2. Thermal properties of hydrogels (30%) of retrograded waxy rice starch hydrated at different temperatures

Hydration temp.	To ¹⁾ (°C)	Tc (°C)	Tc-To (°C)	ΔH (J/g)
4°C	34.9±0.2	51.0±0.1	16.1±0.3	14.2±1.5
23°C	44.2±0.2	58.0±0.9	13.8±0.9	8.8±0.7

¹⁾To, gelatinization onset temperature; Tc, gelatinization end temperature; ΔH, melting enthalpy

when the water content was less than 35% over a period of 5 days at 4°C (data not shown). Over 3-day storage, as the retrogradation period increased, no significant increase in the melting temperature was observed, but the melting enthalpy continually increased (Table 1). It was assumed that during the early stage of retrogradation, less stable crystals might have formed, and then as recrystallization continued, the crystals became more perfect and stable, which resulted in the increased enthalpy.

Retrograded waxy rice starch powders were hydrated (30% solid content) at 2 different temperatures, 4 and 23°C, and the thermal transition properties of the hydrogels were examined by DSC. As shown in Table 2, the starch gel hydrated at 4°C had an onset temperature of 34.9°C, and that hydrated at 23°C had an onset temperature of 44.2°C. The enthalpy value was also greater in the gel hydrated at 4°C (14.2 J/g) than the gel hydrated at 23°C (8.8 J/g). This may have occurred because some starch crystals, which may have relatively low thermal stability, melted during the hydrogel preparation at 23°C. In practical applications, the starch crystals in the hydrogels of retrograded starch powders are expected to undergo some melting when they are consumed, providing a smooth fat-like mouthfeel, as suggested by Roller and Jones (18). Under light microscopy, the retrograded waxy rice starch powders appeared as swollen particles that were densely packed in the starch hydrogel (30% solid content).

Flowing properties and photomicrographs Flowing texture of retrograded waxy rice starch hydrogels with various concentrations was compared (Fig. 1). When it was scooped up, a hydrogel containing 20% retrograded starch

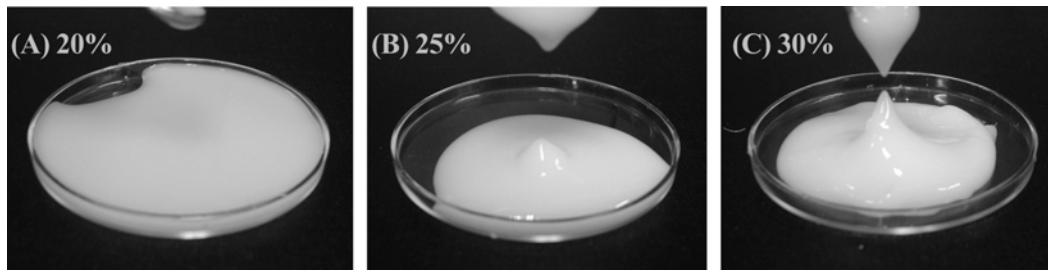


Fig. 1. Photographs of hydrogel with different concentrations.

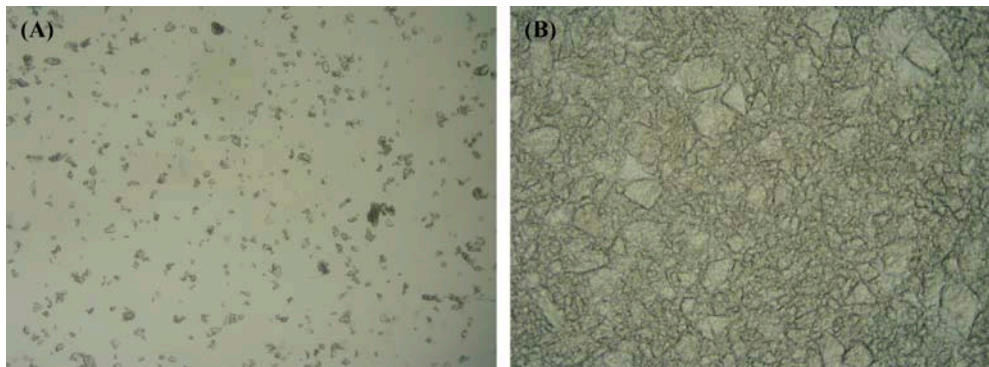


Fig. 2. Microscopic photographs (100 \times) of retrograded waxy rice starch particles in alcohol (A) and 30% solid starch gel hydrated at 4 $^{\circ}$ C (B).

behaved like a liquid. The paste viscosity increased with solid concentration, so the hydrogel of 30% starch had viscoelastic behavior than that of 25% starch. The 30% hydrogel had plastic behavior; when it was scooped up, it kept shape changed.

Photomicrographs of retrograded waxy rice starch powder and retrograded waxy rice starch hydrogel (30% solid content) are shown in Fig. 2. Various sizes of particles were found from powder (Fig. 2A), and in the gel hydrated at 4 $^{\circ}$ C, there was a matrix formation by swelled particles (Fig. 2B). It assumes that small size particles are self-gelling and forming gel matrix, however a big size of particles was not gelatinized and seemed rather swelled. So, the hydrogel consists of swelled particles and gel network. The melting behavior of swelled retrograded starch could attribute the fatty nature as suggested by Roller and Jones (18). Mechanical function of gel matrix and temperature function of swollen particles of retrograded starch may be useful as fat mimetic.

Rheological properties The rheological properties of the hydrogels were assessed using the Herschel-Bulkley and Casson models. The consistency indices (k), flow behavior indices (n), and yield stresses (σ_y) were determined at 2 different temperatures (4 or 23 $^{\circ}$ C) and 3 different concentrations (20, 25, or 30%). The consistency index increased as the solid content in the hydrogel increased (Table 3). When the gel was hydrated at 23 $^{\circ}$ C, a larger

increase in consistency was observed than when the gel was hydrated at 4 $^{\circ}$ C: 8.4, 36.6, and 279.5 (Pa \cdot sec n), respectively at 20, 25, and 30% solids. The higher consistency index for the gel hydrated at 23 $^{\circ}$ C compared to that at 4 $^{\circ}$ C might have occurred due to the partial melting of the starch crystals during hydration at 23 $^{\circ}$ C. The flow behavior indices (n) showed the reverse tendency relative to the consistency index; it slowly decreased with the solid concentration. The same reasoning behind the trend observed for the consistency indices can also be used to explain the trend observed for the flow behavior indices. The yield stress (σ_y) increased with an increase in the solid concentration and was also affected by the hydration temperature (Table 3). The hydrogels prepared at 4 $^{\circ}$ C showed a slightly lower yield stress value than those hydrated at 23 $^{\circ}$ C. Haighton (19) reported that the yield stress ranged from 100 to 200 Pa, indicating that the gels have a soft and spreadable texture, whereas the yield stress was less than 100 Pa, indicating that the gels were too soft to be spreadable. In this study, the yield stress values of the hydrated waxy rice starch gels (30% solid content) (113 Pa hydrated at 4 $^{\circ}$ C and 175 Pa at 23 $^{\circ}$ C) were sufficient for the gels to have a soft texture and spreadability.

Dynamic rheological properties Excess water and heating induce starch granules swelling. The swelling attributes destabilizing the crystalline lamellae leading to its disruption and progressive melting. The crystals in the granule are not

Table 3. Rheological parameters of retrograded waxy rice starch hydrogels

Temp.	Solid content (%)	Herschel-Bulkley model			Casson model		G' at peak temp.
		k ¹⁾ (Pa·sec ⁿ)	n	R ²	σ _y (Pa)	R ²	
4°C	20	4.9±0.39	0.73±0.038	0.99	4.3±2.73	0.98	3,652
	25	19.3±0.42	0.68±0.002	0.99	22.1±2.99	0.99	4,135
	30	137.1±1.10	0.56±0.004	0.99	113.6±3.97	0.97	4,914
23°C	20	8.4±0.02	0.71±0.001	0.99	6.9±0.05	0.99	912
	25	36.6±0.01	0.66±0.001	0.99	29.1±0.42	0.98	1,100
	30	279.5±1.50	0.48±0.004	0.99	175.1±1.08	0.96	1,335

¹⁾k, consistency index; n, flow behavior index; σ_y, yield stress; R², correlation coefficient

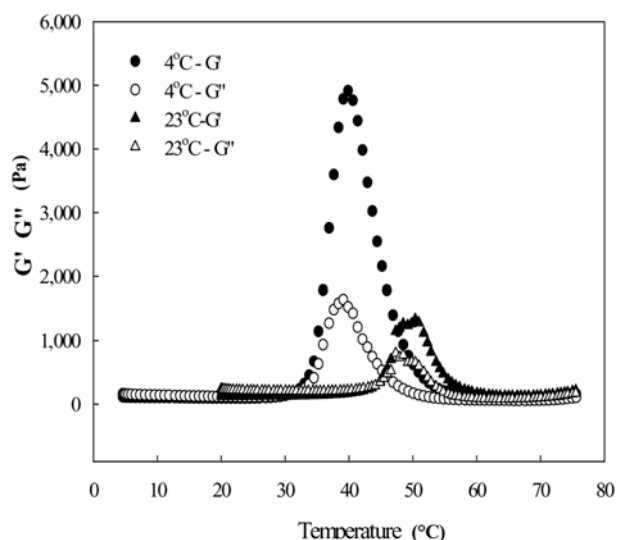


Fig. 3. Storage (G') and loss moduli (G'') in the temperature ramping test with hydrogels containing retrograded waxy rice starch (30% solids).

homogeneous and the thermal disruption of starch crystals is expected to occur over a wide range of temperatures. In dynamic rheology, storage (G'), and loss moduli (G'') are the key parameters in characterizing the viscoelastic properties of semi solid hydrogels. The G' is a measure of the energy stored in the material and recovered, which is an estimate of solid behavior. The G'' measures the energy dissipated or lost (as heat) per cycle of sinusoidal deformation, and indicates liquid or viscous behavior (20).

The storage (G') and loss moduli (G'') of the starch hydrogels prepared at different hydration temperatures and concentrations were recorded during a temperature ramping at 2 Pa (Fig. 3). Both modulus values of the gel (30%) hydrated at 4°C displayed rapid increases at temperatures around 30°C. The G' was maximal around 40°C and then rapidly decreased. An increase in G' and G'' were induced by starch melting (21). The crystal melting of starch is associated with an increase in viscosity as the linear chains diffuse out of the granules, which subsequently induce the

formation of a gel network. The decreases in modulus and viscosity after reaching the maximum values are associated with the loss or collapse of the swollen granules. At this point, the system is transformed into a mixture of leached amylose, amorphous amylopectin, and granule fragments (22,23). For the gel hydrated at 23°C, starch melting started at 45°C and the maximum G' value was observed around 50°C. The difference in rheological properties between the gels hydrated at different temperature was in agreement with the DSC results: the starch hydrogel stored at 4°C had a lower melting temperature than the starch hydrogel stored at 23°C.

The solid content in the hydrogels also induced different rheological properties. As expected, both modulus values were positively related with the solid concentration. However, even at the same concentration, the effect of the hydration temperature was still observed (Table 3). The maximum G' values for 30% recrystallized starch gel hydrated at 4 and 23°C were 4,914 and 1,335 Pa, respectively. This difference between hydrogels formed at different hydration temperatures might have resulted from the change in thermal properties of the recrystallized starch. The higher G' indicates that more crystals may have been formed. A higher content of starch crystals, which may melt at lower temperatures, may be more favorable for applications as fat substitutes. Thus, the hydrogels fabricated with a 30% solid concentration and hydrated at a low temperature (4°C) were most suitable for use as fat mimetics.

Starch powders prepared by lyophilizing retrograded starch paste may readily hydrate into gels without heating, which contain crystals that may melt in a temperature range lower than that for the gelatinization of native starch. The rheological properties of the hydrogels of retrograded starch powders depend on hydration temperature. At the same solid concentration, the gels of retrograded waxy rice starch powders hydrated at 4°C contained crystals that had a lower melting temperature and showed a lower consistency than the gels hydrated at 23°C. Thus, these retrograded starch powders hold promise for used as fat mimetics since the hydrogels had a smooth mouthfeel.

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