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# Effect of Shear Rate on the Viscosity of Rice Starch Suspensions with and without Annealing during Gelatinization

Kazumi Tsutsui[1], Keiko Katsuta[1], Teruyoshi Matoba[1], Takahiro Funami[2], Makoto Takemasa[3], and Katsuyoshi Nishinari[3]

[1]Department of Food Science and Nutrition, Nara Women's University, Kitauoyanishi-machi, Nara 630-8263, Japan

[2]Hydrocolloid Laboratory, San-Ei Gen F.F.I., Inc., 1-1-11, Sanwa-cho, Toyonaka, Osaka 561-8588, Japan

[3]Department of Food and Human Health Sciences, Graduate School of Human Life Science, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

Fax: 81-6-6605-3086, e-mail: nisinari@life.osaka-cu.ac.jp, nishinari@hydrocolloids.org

Effect of shear rate on the temperature dependence of viscosity for rice starch suspension with and without annealing was investigated by steady shear viscosity and Rapid Visco-Analyzer (RVA) measurements. In the steady shear viscosity measurements, shear thinning was observed in the non-annealed sample, the control, and the sample annealed at 62 °C for 15 min in the temperature range from 65 to 97 °C, although the viscosity of the annealed sample showed less dependence of the shear rate due to the amylose leached out from starch granules. In the RVA measurements, shear thinning-like behavior was also observed in the temperature range from 70 to 95 °C while shear thickening-like behavior occurred in the temperature range from 50 to 70 °C for the control and the annealed sample. At temperatures higher than about 70 °C, in both the steady shear viscosity and the RVA measurements, shear thinning appeared which resulted in the structural change from the suspension into the polymer solution by the increase of the amount of amylose leached out during starch gelatinization. The possible origins of shear thickening-like behavior observed in the RVA measurements are (i) a shear degradation caused by destruction of the structure of the sample with high stress and (ii) a jamming of the swollen starch granules at high shear rates. Our study suggested that processing conditions including geometry and rotation speed should be the important factor to govern the rheological properties of annealed starch.

**Keywords:** shear thinning, shear thickening, starch, gelatinization, annealing, steady shear viscosity, Rapid Visco-Analyzer (RVA)

## 1. INTRODUCTION

Starch is a main energy source for us, and exists in many diet foods such as bread [1], noodle, cake [2], and snack. Starch granule is the semi-crystalline particle consisting of two main polysaccharides, amylose and amylopectin [3, 4]. Amylose is an essentially linear (1-4)-linked α-D-glucan while amylopectin is a highly branched macromolecule consisting of short chains of α-D-glucose with (1-6)-α-linked branches [3, 4]. Starch-water system is a so called "suspension". That is, starch is not dissolved, and precipitates in water. However, when the starch granule is heated in the excess water, the crystalline structure is disrupted by the breakage of hydrogen bonds, and starch granule is swollen [5]. Amylose will be leached out from the starch granules, and the heated sample becomes the polymer solution. This process, structural change from the suspension to the polymer solution during heating, is called as "the starch gelatinization".

In the processing of starch foods, the processing conditions such as stirring and extrusion sometimes play a key role on the final texture of starch products [6]. For example, it is known that the texture of the biscuits depends on the mixing time of the wheat flour dough [7]. Shear stress is an important factor to control the rheological properties of starch foods. At the same time, when this dough is mixed and hold even at the room temperature, the starch granule is annealed. In general, annealing is well known as a hydrothermal treatment which changes the physicochemical properties of starch granules, i.e., the increase of the gelatinization temperature and that of the degree of the starch crystallization [8-10]. Annealing is defined as the incubation in the excess water (60%) or in the intermediate water content (40-55%) at a temperature between the glass transition and the gelatinization temperature [8-10].

However, the effects of shear rate (or shear stress) on the rheological properties of the annealed starch foods during gelatinization are not completely understood. Therefore, the steady shear viscosity and the Rapid Visco-Analyzer (RVA) measurements were carried out to investigate and clarify these effects in terms of the structure of starch such as suspension or solution, and to get more insight which is helpful to control the final texture of the annealed starch products.

## 2. EXPERIMENTAL

### 2.1 Material

Non-waxy rice starch was kindly supplied by Shimada Kagaku Kogyo. Co. Ltd. (Niigata, Japan). The composition of dry starch was as follows; moisture 13.2%, protein 0.3%, lipid 0.5%, ash 0.1%, amylose 9.7%, and mean granular diameter 5.77μm.

### 2.2 Annealing

The annealing temperature was 62 °C because the annealing effect on the rheological properties of the sample annealed at 62 °C was remarkably observed as reported previously [11]. For example, the storage and the loss moduli, $G'$ and $G''$, of the sample annealed at 62 °C were the smallest values, and the onset temperature of $G'$ and $G''$, the temperature where $G'$ and $G''$ started to increase, was the highest in the samples annealed in the temperature range from 48 to 73 °C [11]. Since the peak temperature of lower temperature DSC peak for 10 wt% rice starch is 62 °C, the annealing temperature used in the present study is the temperature of the starch gelatinization. Further, the annealing time was fixed at 15 min.

### 2.3 Sample preparation

To make 10 wt% rice starch suspension based on the moisture content (13.2%), distilled water (88.5g) and starch (11.5g) were put into a 300 mL Erlenmeyer flask, and starch was dispersed at 25 °C for 90 min with degassing under vacuum to remove the air. A part of soaked sample was taken out with stirring, and was immediately used for steady shear viscosity and RVA measurements. This was written as "the control" or "25 °C" in the present study. Further, the other soaked sample was heated from 25 to 62 °C keeping stirred to make the sample annealed at 62 °C. After the temperature of sample had reached to 62 °C, the sample was held at this temperature with continued stirring for 15 min. After the annealed sample was taken out in the same way as the control, it was immediately used for the measurements.

### 2.4 Measurements

<u>Steady shear viscosity measurements.</u> The steady shear viscosity measurements were carried out by a strain controlled rheometer (Rheosol G-3000, UBM Co., Kyoto, Japan). Four shear rates, 1.0, 3.0, 5.0, and 10.1 $s^{-1}$, were selected. The prepared suspension was placed in the gap (51μm) between the cone (angle, 3.964deg; diameter, 39.95mm) and the plate. The sample between the cone and the plate was covered by a semi-hermetic case, and a small amount of 100 cSt silicone oil was put around the sample to prevent the evaporation of water in the sample on heating. It was heated from 25 to 97 °C at 1 °C/min, and this was written as "the control" or "25 °C". In the case of the sample annealed at 62 °C, since the temperature of sample was lowered during setting the sample on the plate, the temperature at which we started to measure was 50 °C.

<u>Rapid Visco-Analyzer (RVA) measurements</u>. The characteristics of viscosity for starch suspension during gelatinization were investigated by RVA (Super 3, Newport Scientific Pty. Ltd, Australia). The non-annealed sample (the control) or the sample annealed at 62 °C for 15 min (25.00g) was put into an aluminum cup (diameter, 35mm; height, 65mm), and was mixed with a paddle being a twisted board [12] at 960 rpm for 10 sec. The mixing temperature of the control was 25 °C, and that of the annealed sample was 50 °C. The rotation speeds after mixing, 160, 320, and 800 rpm, were selected, and the control and the annealed sample were heated to 95 °C at 1 °C/min. It is known that the viscosity-like characteristic value obtained by RVA is shown by Rapid Visco Unit (RVU), and depends on the detail of the sample.

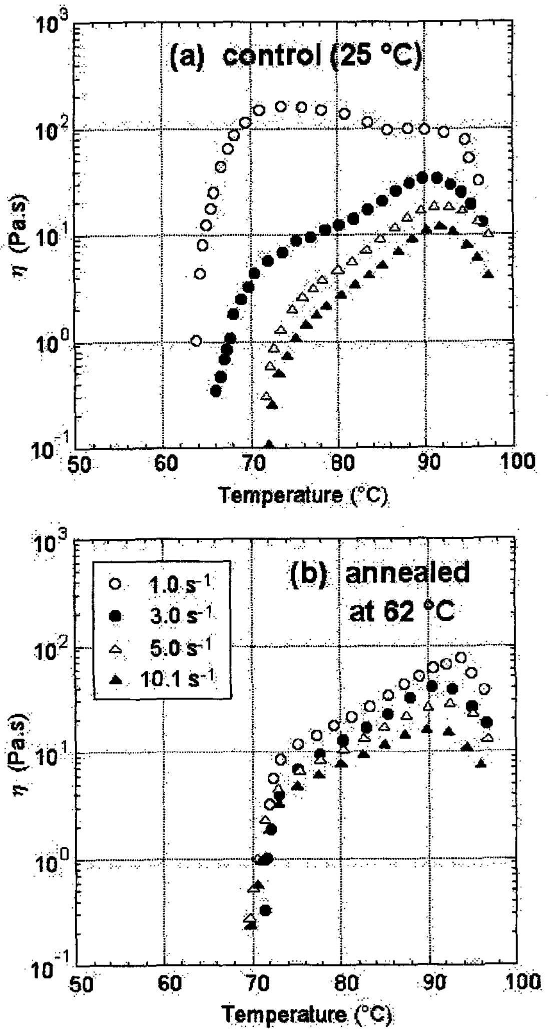


Figure 1. Temperature dependence of steady shear viscosity, $\eta$, measured at four different shear rates for (**a**) non-annealed rice starch suspension (control) and (**b**) sample annealed at 62 °C for 15 min. Shear rates: 1.0, 3.0, 5.0, and 10.1 $s^{-1}$. Concentration of starch suspension: 10 wt%. Heating rate: 1 °C/min.

### 3. RESULTS AND DISCUSSION

3.1 Uniform shear rate: Effect of shear rate on the temperature dependence of steady shear viscosity, $\eta$, for rice starch suspension with and without annealing.
Figure 1 shows the temperature dependence of $\eta$ measured at four different shear rates for (**a**) non-annealed rice starch suspension (control) and (**b**) sample annealed at 62 °C for 15 min. For both samples measured at 1.0 $s^{-1}$, $\eta$ started to increase at about 70 °C, the value increased to $10^2$ Pa.s at 90 °C, and decreased to $10^1$ Pa.s at 97 °C. Since the amount of amylose leached out from the swollen granules increases, the viscosity increases. Further, the melting of amylose-lipid complex decreases the viscosity in the temperature range from about 90 to 97 °C as described previously [11]. Further, when the shear rate increased, at each temperature the viscosity of the control and the annealed sample decreased. In the temperature range from about 65 to 97 °C, shear thinning was observed in both samples. When the starch gelatinization is completed, the amount of leached out amylose increases, and shear thinning occurs. However, although the viscosity of the control depended on the shear rate, shear thinning was hardly observed in the annealed sample.

It is well known that steady shear viscosity, $\eta$, of polymer solutions can be described by $\eta = k\,(d\gamma/dt)^n$ at high shear rates, where $\gamma$ is the strain, and $k$ and $n$ are the empirical characteristic parameters responsible for the shear behavior especially for the structural viscosity. Generally, the exponent, $n$, is not largely affected by concentration and molar mass of the polymer.

However, the exponent, $n$, for the control is much different from that for the annealed sample, and depends on the temperature. This strongly suggests that the origins of the structural viscosity for them are different.

In the case of starch-water system, it is well known that the structure is drastically changed by the gelatinization. That is, at temperatures lower than the gelatinization temperature, the sample is not a solution, but a suspension of starch granules. In contrast, at temperatures higher than the gelatinization temperature, the sample becomes a polymer solution, because the starch granules will be broken by gelatinization, and amylose is leached out from the starch granules. Therefore, the difference of the exponent, $n$, for the control and the annealed sample is probably related to the difference of their structures.

In detail, the most of the starch granule in the control is not gelatinized and broken at the temperatures between 50 and 60 °C. At temperatures lower than the gelatinization temperature (= 62 °C), the amount of leached out amylose in the control is much lower than that in the annealed sample [11]. On the other hand, the annealed sample has both the amylose leached out from the starch granules and the non-broken (not completely gelatinized) starch granule. We previously reported that the leached out amylose prevents the further leaching out of amylose from the starch granules [11].

The difference between the viscosity at the lowest shear rate, 1.0 $s^{-1}$, and that at the highest shear rate, 10.1 $s^{-1}$, for the control was larger than that for the annealed sample in all the temperature range. The exponent, $n$, for the control was larger than that for the annealed sample. These results demonstrate that annealing can control this exponent, $n$. This means that annealing is useful to make the texture of starch food stable against the shear.

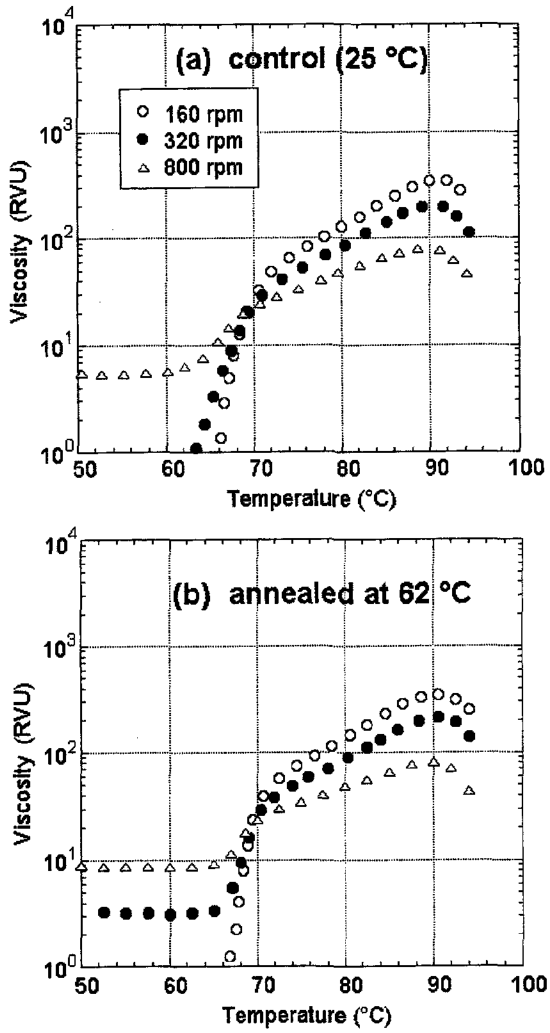


Figure 2. Effect of rotation speed on the temperature dependence of the viscosity observed by RVA for (**a**) 10 wt% rice starch suspension (control) and (**b**) sample annealed at 62 °C for 15 min. Heating rate: 1 °C/min.

3.2 Non-uniform shear rate: Effect of rotation speed on the temperature dependence of the viscosity for the sample with and without annealing observed by RVA.
Figure 2 shows the effect of rotation speed on the temperature dependence of the viscosity observed by RVA for (**a**) the control and (**b**) the sample annealed at 62 °C for 15 min. The RVA viscosity for the control and the annealed sample increased with increasing rotation speed in the lower temperature range from 50 to 70 °C. However, this decreased with increasing rotation speed in the higher temperature range from 70 to 95 °C. Since the geometry used for the RVA measurements is complex [12], the shear rate is not

uniform in the sample. Moreover, the distribution of the shear rate also depends on the detail of the rheological properties of the sample such as viscosity and structure, i.e, suspension or polymer solution. However, the average value of shear rate will increase, when the rotation speed of the paddle increases. Therefore, these two phenomena, "the increase of viscosity with increasing rotation speed in the lower temperature range" and "the decrease of that in the higher temperature range" as described above, do not directly mean "shear thickening" and "shear thinning", respectively, and we call them "shear thickening-like behavior" and "shear thinning-like behavior", respectively.

Moreover, the flow behavior of the control and the annealed sample changed "shear thickening-like behavior" into "shear thinning-like behavior" at 70 °C. It was suggested that the crossover temperature (drastic change observed at 70°C) was caused by the completion of the starch gelatinization, because this temperature, 73 °C, was the conclusion temperature of the lower temperature DSC peak ($T_{c1}$) for the control and the annealed sample, as reported previously [11]. The temperature, $T_{c1}$, generally means the completion of starch gelatinization for the melting of amylopectin. The structural viscosity of starch with and without annealing at temperatures lower than 70 °C is dominated by starch granules without gelatinization, and that at temperatures higher than 70 °C by leached out amylose.

Our results agreed with the reported studies [13-15]. For the starch-water system without annealing, it was reported that shear thickening occurred at temperatures where the starch gelatinization was not completed, and shear thinning was observed at temperatures where the starch gelatinization was completed.

The main reasons why shear thickening occurs at low temperatures are explained as follows.

(I) Shear degradation: Since stirring force is strong enough to destroy the structure of starch sample with and without annealing, it is suggested that the amount of leached out amylose increases by the mechanical destruction of starch granules even at low temperatures where the starch gelatinization is not completed, and the viscosity increases with increasing rotation speed in the temperature range from 50 to 70 °C in the RVA measurements.

(II) Jamming of the swollen starch granules: Starch granules generally swell in the excess water, and the swelling ratio increases during heating, then the volume fraction of starch granules increases [16, 17]. Under the condition that starch granules are enough swollen, and less amylose is leached out from the granules, the structure of the system is similar to the suspension showing shear thickening due to the jamming of the particle under a certain shear rate.

When temperature was raised, shear thinning-like behavior was observed in both the control and the annealed samples in the RVA measurements. Since this phenomenon is similar to the results observed in the steady shear viscosity measurements, the origin of shear thinning-like behavior is the increase of the amount of leached out amylose due to the completion of starch gelatinization.

Although shear thinning in the steady shear viscosity measurement and shear thinning-like behavior in the RVA measurement were observed, shear thickening-like behavior was observed only in the RVA measurements. The observed phenomenon depends on the measurement method, which may be caused by higher shear rate and/or shear stress used for the RVA measurements compared with that used for the steady shear viscosity measurements. In addition, the effect of annealing on the viscosity was hardly observed in the RVA measurements, although that was observed in the steady shear viscosity measurements.

The present study has shown that the stirring condition, geometry and rotation speed, governs the flow behaviors such as shear thinning and shear thickening of the starch suspension with and without annealing during gelatinization. It is closely related with the texture of the annealed starch foods during cooking and extrusion, and the physicochemical characteristics of various processed foods.

REFERENCES

[1] K. D. Nishita and M. M. Bean: *Cereal Chem.*, **56**, 185-189 (1979).
[2] K. Katsuta: *J. Home Econ. Jpn.* **38**, 283-291 (1987) in Japanese.
[3] M. J. Miles, V. J. Morris, S. G. Ring: *Carbohydr. Res.*, **135**, 257-269 (1985).
[4] M. J. Miles, V. J. Morris, P. D. Orford, S. G. Ring: *Carbohydr. Res.*, **135**, 271-281 (1985).
[5] R. Hoover: *Carbohydr. Polym.*, **45**, 253-267 (2001).
[6] C. Mercier, "Food processing systems, Food process engineering Vol. 1", Ed. by P. Linko, Applied Science Publishers press, London (1980) pp. 795-807.
[7] R. Sai Manohar and P. Haridas Rao: *J. Cereal Sci.*, **25**, 197-206 (1997).
[8] I. Larsson and A. C. Eliasson: *Starch*, **43**, 227-231 (1991).
[9] H. Jacobs and J. A. Delcour: *J. Agric. Food Chem.*, **46**, 2895-2905 (1998).
[10] R. F. Tester and S. J. J. Debon: *Int. J. Biol. Macromol.*, **27**, 1-12 (2000).
[11] K. Tsutsui, K. Katsuta, T. Matoba, M. Takemasa, K. Nishinari: *J. Agric. Food Chem.*, **53**, 9056-9063 (2005).
[12] K. P. Lai, J. F. Steffe, P. K. W. Ng: *Cereal Chem.*, **77**, 714-716 (2000).
[13] P. E. Okechukwu and M. A. Rao: *J. Texture Stud.*, **26**, 501-516 (1995).
[14] P. E. Okechukwu and M. A. Rao: *J. Texture Stud.*, **27**, 159-173 (1996).
[15] M. A. Rao, P. E. Okechukwu, P. M. S. Da Silva, J. C. Oliveira, *Carbohydr. Polym.*, **33**, 273-283 (1997).
[16] R. F. Tester and W. R. Morrison: *Cereal Chem.*, **67**, 551-557 (1990).
[17] A. C. Eliasson: *J. Texture Stud.*, **17**, 253-265 (1986).

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