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Shear-induced aggregate formation in starch solutions☆

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Abstract

Shear-thickening behavior and shear-induced pattern formation have been observed in semidilute starch solutions. While the shear-thickening behavior is due to breaking up of highly concentrated gel-like structures dispersed in dilute starch solutions, the pattern-forming behavior is not well understood. The pattern formation, observed when the starch solution is exposed to a high shear field, is a consequence of shear-induced aggregation and is not related to shear-thickening behavior. The patterns have been observed above a certain critical threshold shear rate regardless of the starch type.

In this report, it is shown that the product of shear time and fourth power of shear rate is a controlling factor for the formation of shear-induced aggregates in starch solutions. Since starch solutions prepared under harsh conditions did not show shear-induced aggregate formation, it is suggested that the aggregates are formed from incompletely solubilized starch residues in its apparent solution.
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Keywords: Starch solutions; Shear-induced aggregate; Shear microscopy

1. Introduction

Rheological measurements of semidilute starch solutions have revealed a shear-thickening behavior when the solutions are prepared in a certain procedure (Carriere, 1998; Dintzis & Bagley, 1995a; Dintzis & Bagley, 1995b; Dintzis, Bagley, & Felker, 1995). This phenomenon was observed only with waxy starches, which are composed of a single component, amylopectin. On the other hand, normal maize which is composed of both amylopectin and amylose did not show this behavior. Furthermore, microscopic observation of the starch solution showed pattern formation after the viscosity measurement. This unusual behavior of starch solutions was studied in more detail with various kinds of starches (Dintzis et al., 1996) and with emphasis on rheological behavior (Carriere & Loffredo, 1997; Carriere, 1998). In a previous report (Kim, Willett, Carriere, & Felker, 2002), we focused our efforts on the following issues: (1) What is the relationship between shear-thickening and pattern formation?; (2) What causes shear-thickening behavior?; (3) Why is gentle preparation required for shear-thickening?; (4) Why is shear-thickening irreversible?; (5) What is the entity of the formed pattern in the sheared solution? As a result of this research, the following conclusions were presented: (1) Gently prepared starch (both waxy and normal maize) solutions are macroscopically heterogeneous with regions of highly concentrated gel-like structures dispersed in dilute starch solution; (2) Shear breaks up these heterogeneous regions, increasing viscosity (shear-thickening) as a result of an increase in the concentration of dissolved starch; (3) Pattern formation, observed when the solution is exposed to higher shear rate, is the result of a separate shear-induced aggregation process; (4) Aggregations are not induced below a certain critical threshold shear rate and time is also a factor in the formation of aggregates.

Although it was found that the pattern formation is caused by the aggregation of starch particles, the exact relationship between the degree of aggregation and the two controlling factors, shear time and shear rate, is not known. To understand this relationship, a shear microscope is utilized to monitor the shear-induced patterns that are formed during the application of shear field. The pattern-forming process is analysed as a function of shear time and shear rate.

In the latter part of this report, the origin of constituent material of the shear-induced aggregates is discussed.

☆ Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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2. Experimental

2.1. Materials

Waxy Maize starch and regular corn (normal maize) starch were purchased from Sigma Chemical Co. (St. Louis, MO). Waxy Maize is essentially pure amylopectin that contains only trace amount of amylose, and normal maize contains ca. 73% amylopectin and 27% amylose. Hylon VII, which contains ca. 70% amylose, was obtained from National Starch and Chemical Co. (Bridgewater, NJ). Waxy potato starch was a gift from Dr. Lawton in NCAUR (National Center for Agricultural Utilization Research, Peoria, IL). Sodium Hydroxide (NaOH) and hydrochloric acid were purchased from Fisher Scientific Co. (Fairlawn, NJ). Dimethylsulfoxide (DMSO) was purchased from Aldrich (Milwaukee, WI). All materials were used as received.

2.2. Solution preparation

Starch solutions were prepared as follows: 2.5 g starch was first mixed thoroughly with 40 g of distilled water to dampen all granules; then 40 g of 1 N NaOH was added to the mixture which was stirred vigorously with a magnetic spin bar for 10–20 min to disrupt all granules and dissolve them. Then the solution was neutralized with 3 N Hydrochloric acid to prevent degradation. Distilled water was slowly added to the starch solution while stirring to achieve 100 g of 2.5% starch solution in 0.4 N NaCl.

2.3. Shear microscopy

A custom-built phase-contrast microscope was used for taking images under shear field. The shear cell was composed of cone and plate both made of quartz. The shear rate was controlled by a computer terminal, which was serially interfaced with the motor. Since the images under shear field are in motion, a custom-built flash was used as a light source to avoid smearing. Detailed structure of the instrument is described in a separate publication (Kim & Willett, 2001). During the experiment, shear fields were applied as a step-by-step format.

2.4. Agitator

For observing shaking effect on the aggregates formed in the starch solution, a sample solution was sheared with Brookfield Programmable Rheometer (Model DV-III) equipped with coaxial cylinder cell. Shear field was applied at 230 s^{-1}. Then the sheared solution were shaken with a custom-built agitator which vibrates 15($\pm$1) times a second with an amplitude of ca. 2.5 cm. 10 mL of the solution was shaken in a vial (volume, 21 mL) at a time.

2.5. Microwave heating

For the preparation of starch solutions in harsh condition, a microwave oven (Ethos MicroSYNTH 1600 microwave lab station from Milestone, Shelton, CT) was used. Normal Maize and Hylon VII were examined. 25 mL of 2% starch solutions

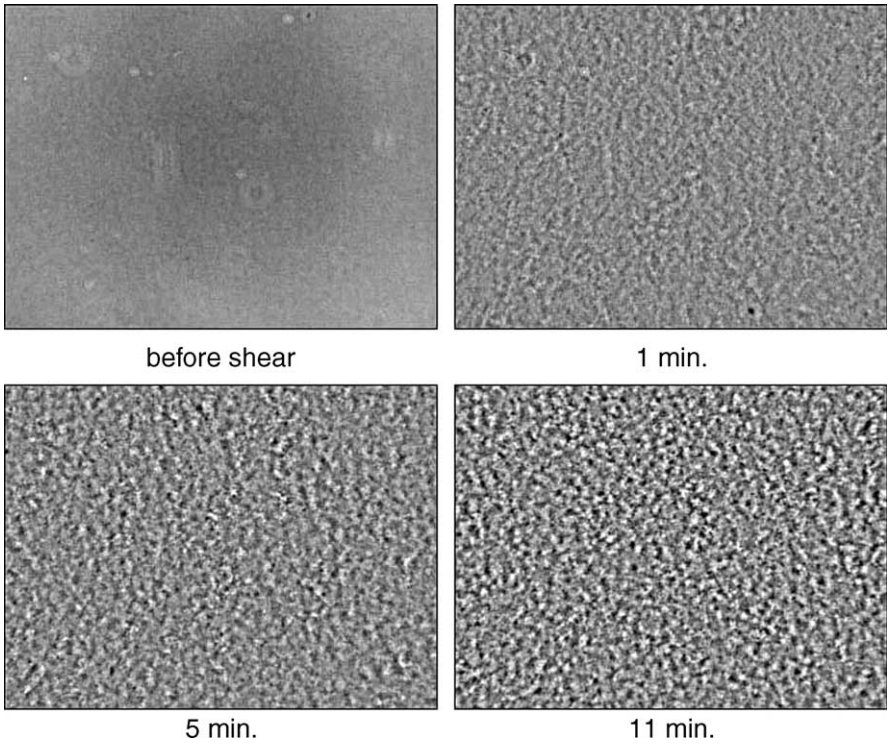

Fig. 1. Pattern development with increaseing shear time observed with a phase-contrast microscope. 2.5% waxy maize in 0.5% NaOH solution was sheared at 500 s^{-1}. (a) before shear; (b) sheared for 1 min.; (c) sheared for 5 min.; (d) sheared for 11 min.

were heated in a 50 mL quartz pressure vessel (Model QRS1550 from Milestone) for 5 min at each preset temperature. Temperature settings were 70, 90, 110, 130, 150, 170, 190, 210, and 230 °C.

3. Results and discussion

3.1. Shear-induced pattern formation

When the sheared starch solutions are examined with a bright-field microscope, no noticeable particles are observed. However, when a phase-contrast microscope is employed, patterns are observed in the solution. This means the refractive index of the pattern-forming material is close to that of the solvent medium. Shear-induced pattern formation is observed at shear rates higher than 100 s^{-1} regardless of the source of starches, and the contrast of the formed pattern increases as shear time increases. The formed pattern persists for a few days. If the pattern formation was a shear-induced phase-transition, it should disappear as soon as the shear field is removed (Moses, Kume, & Hashimoto, 1994). Hence, it is not a phase-transition but some physical change of starch molecules. Typical images that demonstrate time-dependent evolution of pattern structure are shown in Fig. 1.

Although it is known that the patterns do not form below a critical shear rate and the pattern development is time-dependent (Kim et al., 2002), the relationship between the degree of pattern formation and the two controlling factors—shear rate and shear time—is not well understood. This issue was investigated with a shear microscope and quantitative experimental results are presented in the following sections.

3.2. Quantitative evaluation of shear-induced patterns

As patterns developed in the sheared starch solution, images were captured with a shear microscope. For quantitative evaluation of the formed patterns, a contrast factor for each image was calculated according to the following definition. Although the contrast factor has been defined in the previous report (Kim et al., 2002), it is repeated here again as it is the basis of the quantitative evaluation of images.

The contrast of an image is defined in the literature (Koenig, 1998) as in Eq. (1),

$$C = \frac{(I_{\max} - I_{\min})}{(I_{\max} + I_{\min})} \tag{1}$$

where I stands for intensity of light in the image. However, in practical situations, illumination of the overall field of view is non-uniform. Therefore, intensities are not evenly distributed in the captured images: the center part of the image is always brighter than the circumference. In this situation, $I_{\max}$ will always be in the middle and $I_{\min}$ in the circumference yielding a meaningless contrast factor, C. Noise in the captured images is another problem. To circumvent these problems, a reference image file from each image is generated by smoothing the original image repeatedly until the detailed structure of the image is washed away and only the contour of the illumination remains. The intensity in each pixel of the resulting reference file is then subtracted from that of original image file and the resultant differences are squared to avoid obtaining negative numbers. The sum of the squared differences is used as a measure of contrast. The contrast factor, Δ defined as above is

$$\Delta = \sum\sum \{I_{i,j} I_{\mathrm{ref}}, i, j\}^2. \tag{2}$$

Here, $I(i,j)$ is the light intensity of the actual image at pixel (i,j) and $I_{\mathrm{ref}}(i,j)$ is that of the reference image. As the contrast of the image increases, the numerical value of the contrast factor will also increase.

Following the above definition, a series of data obtained from a 2.5% potato starch solution was processed. Pattern formation was investigated at thirteen fixed shear rates between 80 and 1000 s^{-1} for 10, 15 or 20 min. The resulting data are shown in Fig. 2(a). The processed data yields several conclusions. Shear rates of 80 or 100 s^{-1} are not sufficient to induce pattern formation. It is clear that the patterns form faster at higher shear rate and the contrast factor increases with

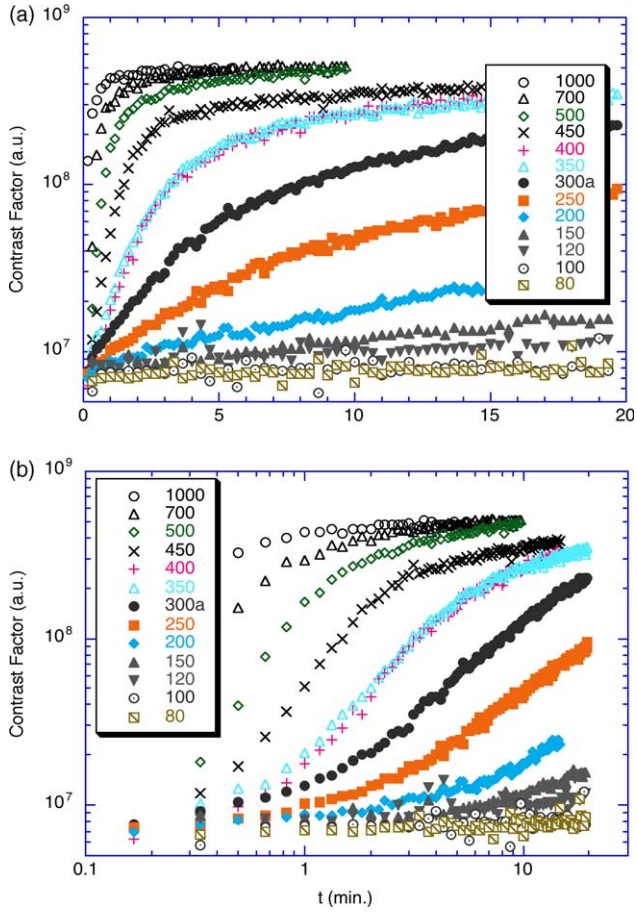

Fig. 2. Time dependence of contrast factor of 2% potato starch solution in 0.5 N NaOH at specified shear rates. The contrast factors were calculated according to Eq. (2) in the text. (a) Semi-log plot of the data. It is clearly shown that the two factors, high shear rates and extended shear time, govern the formation of patterns. Below shear rate of 100 s^{-1}, pattern formation was not noticed. (b) The same data was shown with both axes in log scales. This plot suggests a formation of a universal curve for each data by shifting shear rate curves to the right or left.

extended shear time. Eventually, the degree of pattern formation saturates once a certain level is reached.

3.3. Universal behavior of pattern formation

In Fig. 2(b), the same data shown in Fig. 2(a) are presented with both axes in log scales. This plot suggests possible formation of a universal curve for pattern formation. Shifting shear rate curves to the right or left, it is expected that a universal curve can be constructed. In order to find a shift factor, the following scheme was used.

The data from 400 s^{-1} were used as a reference data. By comparing data at other shear rates with those from 400 s^{-1}, shift factors were found for each shear rate. For example, in the case of 250 s^{-1}, the data curve will be superimposed to that of 400 s^{-1} when multiplied by 0.15. Therefore, 0.15 is assigned as a shift factor for the shear rate of 250 s^{-1}. By repeating this procedure, shift factors for the other shear rates were found and plotted against shear rate. As a result of this plot, a slope of 4 ± 0.1 was obtained (Fig. 3).

The shift factor was obtained for each shear rate as the fourth power of shear rate. This means that we can obtain a universal curve for the formation of shear-induced aggregates by plotting contrast factor (i.e. the degree of aggregate formation) as a function of the product of shear time and fourth power of shear rate. This plot is shown in Fig. 4. There are some deviations of the data from the universal curve. These deviations are serious for the data from 700, 500, 450, and 400 s^{-1}. The reason is that it takes some time for the stepper motor to reach a desired RPM. These delay times cause lower contrast factors than expected at the beginning of the shear experiment. In the case of lower shear rates, variation in contrast factor is too small to be noticed in the plot.

The relationship between shear rate, shear time, and degree of aggregate formation suggests that aggregate formation can

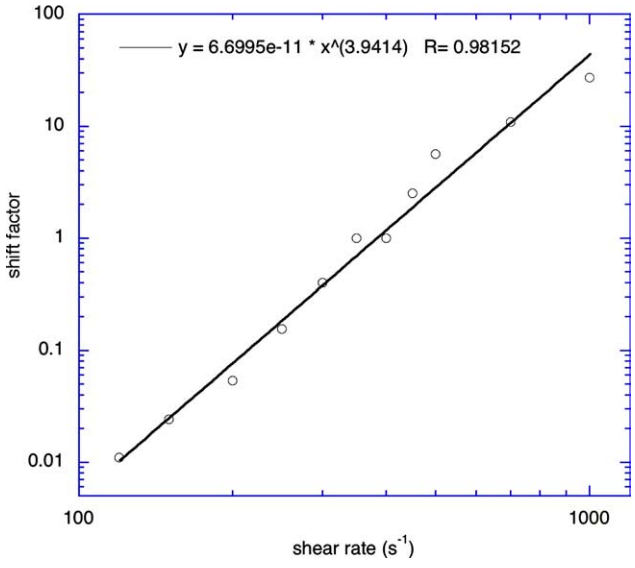

Fig. 3. The shift factors found by using the data from 400 s^{-1} as a reference data were plotted as a function of shear rate. See text for determining shift factor for each shear rate.

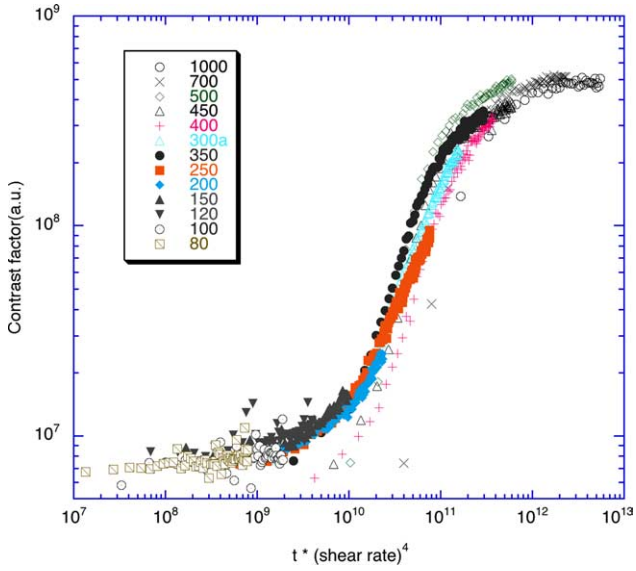

Fig. 4. Experimentally obtained universal curve for the formation of shear-induced aggregates. Contrast factor was plotted as a function of the product of shear time and fourth power of shear rate. Power factor, 4, was obtained from the slope of the plot shown in Fig. 3.

be induced between a microscope slide glass and a cover glass in approximately one second. When a starch solution is placed between the two glass plates and rubbed with a pencil tip (eraser side), the thickness of the solution can be estimated to be around 10 μm. The speed of the motion of the pencil tip can be controlled to be around 5 cm/s. In this condition, the shear rate is estimated to be around 5000 s^{-1}. If the shear field is applied for a second, the product of shear time and fourth power of shear rate is calculated to be around 6.3×10^{14} by definition (Hiemenz, 1984, chp. 2). The universal curve in Fig. 4 shows that the formation of aggregates is already fully accomplished in this experimental condition. This experiment was performed and the result is shown in Fig. 5. The morphology of Fig. 5 is different from that seen in Fig. 1, because the sample is much thinner and the shear was applied in a circular motion. It is noteworthy that the dispersion medium of the starch solution becomes clearer after the induction of aggregate formation. It means that large particles in the solution were removed as a result of aggregate formation.

3.4. Constituent material of aggregates

In the previous paper, it was proposed that the source of shear-induced pattern is the aggregation of starch molecules induced by the applied shear field (Kim et al., 2002). The sheared starch solution (2% Waxy Maize starch in 0.2 N NaOH) was diluted with 0.2 N NaOH solution and observed with a phase-contrast microscope (Fig. 6). Unlike the data shown in the previous report, the starch solution was diluted just after shearing in the shear microscope, and images were taken without moving the sample from the shear cell. Individual aggregates were clearly identified after dilution. In the same report, it was also proposed that this phenomenon

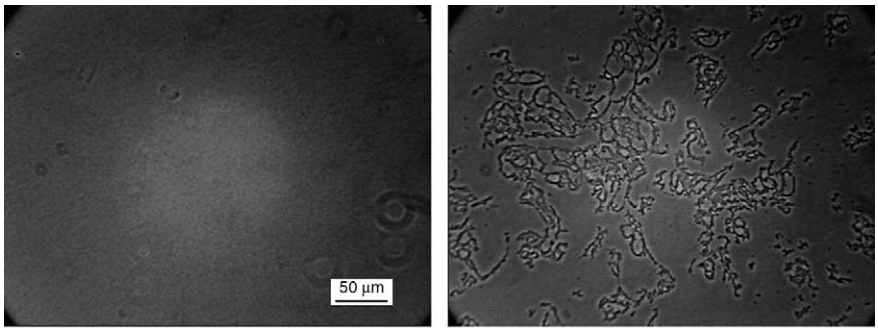

Fig. 5. Shear-induced aggregates formed in between cover glass and slide glass by rubbing the two plates with a rubber tip: (a) before shear, (b) after shear for 1 s.

could be explained by either the collision theory or shear-induced phase separation. In those cases, full dissolution of starch molecules in the solvent medium was assumed. However, evidence in this study suggests that starches are not fully solubilized in our experimental condition.

Starch solutions prepared in strong base solution (Dintzis & Bagley, 1995a) or 90% DMSO solution (Carriere, 1998) do not pass through a 5 μm filter. Since the average radius of gyration of starch molecules is smaller than 400 nm (Millard, Wolf, Dintzis, & Willett, 1999), this experimental observation shows that the starch molecules are not fully solubilzed. Starch solutions pass 5 μm filters when the prepared starch solutions are shaken vigorously or when the solutions prepared in strong base are aged for a few weeks. The agitator used for shaking starch solutions is described in the experimental section, and shaking time is 1 min. This observation indicates that harsh conditions are necessary for starch molecules to be fully solubilized. If that is the case, incompletely solubilized starch residues should be on the order of a few microns in size and therefore easily identified with a microscope. However, the refractive index of these residues is too close to that of the solvent medium to be detected even with a phase-contrast microscope. The fact that the starch solution passes through 5 μm filters only after vigorous shaking is firm and direct evidence that the freshly prepared starch solution contains larger residues.

There is more evidence showing that aggregation is due to incompletely solubilized starch residues. Without filtration, shear-induced pattern formation is more prominent. In the case of a month old starch solution that has been prepared in 0.5 N NaOH solution, shear-induced pattern formation is hardly observed and solution viscosity decreased with time, indicating a reduction in the apparent molecular weight of the starch. Another example of applying harsh conditions for solubilization is using a microwave oven. When 2% aqueous starch solutions are heated to 170 °C or higher, microscopically clear solutions are obtained and shear-induced aggregate formation is not observed. Experimental conditions are described in the experimental section.

The examined harsh conditions, i.e. vigorous shaking, strong base solution, and heating to 170 °C, will induce degradation of starch molecules. Therefore, it is believed that complete dissolution of starches is achieved as a result of degradation. However, it is not yet clear whether complete dissolution can be achieved without degradation. Nevertheless, it would be true that the shear-induced aggregation is caused by incomplete solubilization of starches.

The formed pattern disappears after a few days, indicating that the aggregated starch residues are disintegrated by Brownian motion. This means the aggregates are loosely bound together and can be easily disintegrated by applying an

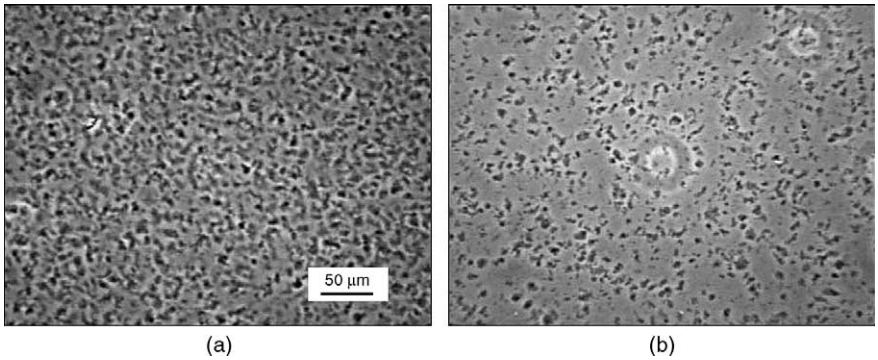

Fig. 6. Shear-induced aggregates observed with a phase-contrast microscope. The formed aggregates were diluted with the same solvent as used for the dissolution of starch molecules: (a) before dilution, (b) after dilution. After dilution, individual particles are visualized. Round circles in (b) are air bubbles in the sample.

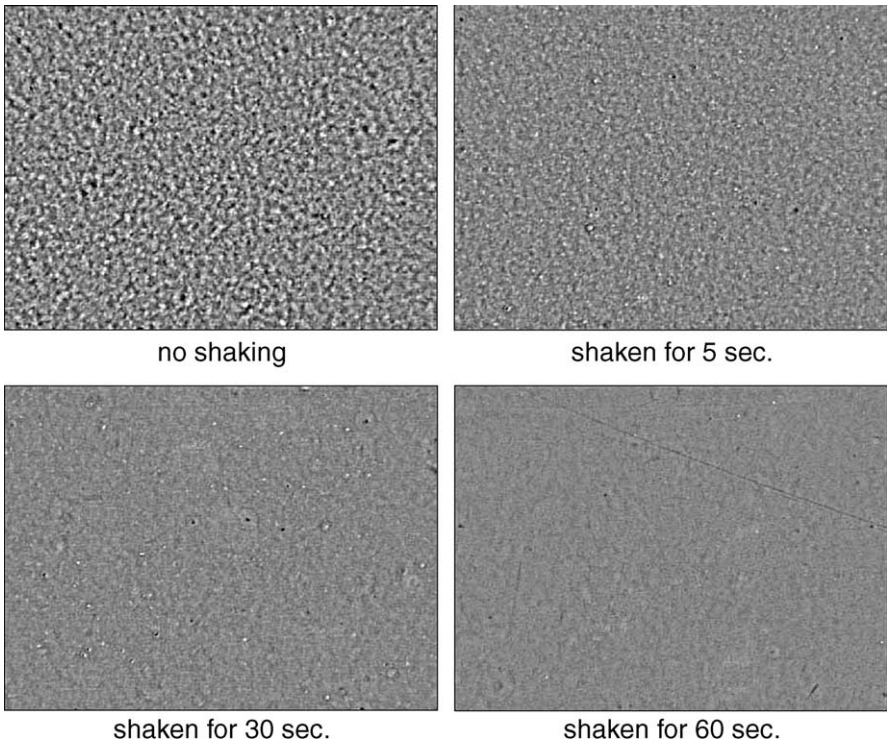

Fig. 7. Shaking effect on the sheared starch solution. Aggregates are disintegrated by shaking the solution. It is also shown that shaking time is another variable for the disintegration of aggregates.

external disturbance e.g. shaking. The experimental result is shown in Fig. 7. Since this experiment requires large quantity of sample, the starch solution was sheared for 30 min at 230 s^{-1} with a Rheometer equipped with coaxial cylinder cell.

4. Conclusions

The goal of this research is to understand the condition for the formation of aggregates that has been observed when they are exposed to high shear fields. It is an intriguing discovery that shear-induced aggregate formation, unlike shear-thickening, does not require gentle solution preparation. This observation confirms the previous finding that these two phenomena are not related to each other (Kim et al., 2002). It also means that the shear-induced aggregation is a common behavior of starch solutions that we have to consider whenever we prepare them.

The universal behavior of aggregate formation is another unforeseen result that allows us to quantitatively analyze the effect of shear rate and shear time on aggregate formation. The fourth power dependence of shear rate means the shear rate is a far more sensitive factor than shear time. The threshold shear rate that is required to form aggregates explains the reason why shear-induced aggregate formation is not commonly observed. The observed minimum shear rate, 100 s^{-1}, is higher than the shear rates normally applied on the starch solutions during solution preparation.

The reason for shear-induced aggregation requires more investigation. For now, we conclude that the aggregates are formed from the incompletely-solubilized starch residues because aggregate formation is not observed when starch solutions are prepared under harsh conditions. Under these conditions, however, amylopectin will degrade to lower molecular weights. Since shear-induced aggregate formation is always observed even in good solvents, it is speculated that the high molecular weight moiety of amylopectin is not fully solubilized by the solvent unless they are under harsh conditions that degrade them. In any case, the starch solutions we used for this experiment are more precisely described as apparent starch solutions.

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