

Factors affecting gel formation of inulin

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Abstract

Inulin gel can be made from shearing or heating–cooling of inulin suspension. Heating of inulin suspension solubilized inulin, cooling caused precipitation of dissolved inulin, especially when a less hydrophilic solvent such as ethanol or glycerol is added. For gel made from heating–cooling process, volumetric gel index (VGI), i.e. the ratio of gel to total volume, was a function of heating temperature, inulin concentration, pH, and solvent added. Minimal inulin concentration required for gel formation increased with increasing heating temperature. High heating temperature ($>80^{\circ}\text{C}$) causes some degree of hydrolysis of dissolved inulin molecules leading to lower VGI's. A low degree of hydrolysis of inulin and a critical concentration of inulin are important for gel formation. The heating–cooling process formed gels with stronger strength, smoother texture, more uniform and smaller particle size as compared to that obtained with a shearing process. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Inulin is an energy reserving material in various plants such as chicory root, dahlia tuber and Jerusalem artichoke. Chemically, inulin consists of a long chain made up of 22–60 fructose molecules and one glucose molecule at one end. The fructose molecules are connected by β -(2-1) bonds. The last fructose is linked with a glucose by an α -(1-2) bond as in sucrose (Roberfroid, 1999a). The average molecular weight and degree of polymerization of inulin depend on the source of inulin, the time of harvest and the process of production. Industrially, inulin is produced from the flaked chicory root (including 16% inulin, wet basis) by extraction at high temperature followed by an ion exchange process (Dysseleer & Hoffem, 1995).

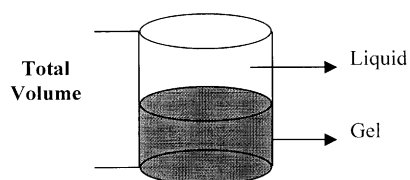
Inulin has been used in food industry to produce fructose syrup or fructo-oligosaccharide (FOS) by acid or enzymatic hydrolysis (Niness, 1999; Yamazaki & Matsumoto, 1993). Inulin also has been studied for non-food applications with the modification of native inulin either by enzymatic or chemical treatment. Modified inulins have shown the potential as a carrier for drug delivery (Molteni, 1985), a vaccine adjuvant (Cooper & Steele, 1988), a chelating agent (Verraest, Peters, Kuzze, Raaijmakers, & van Bakkum,

1998) and a builder or co-builder of detergents (Besemer & van Bakkum, 1994).

From the physiological point of view, since inulin is non-digestible by the alimentary enzymes in the human body, it has the basic benefits of a dietary fiber. It has been reported to reduce lipid and cholesterol levels in blood. Inulin also regulates gastrointestinal transit time and stool weight and enhance the adsorption of calcium (Roberfroid, 1993). Another benefit of inulin is its prebiotic function. Inulin stimulates the growth of *Bifidobacterium* sp. which helps in increasing the population of good bacteria in the colon (Havenaar, Bonnin-Marol, Dokkum, Petit, & Schaafsma, 1999). Considering that the calorie of inulin is much lower than that of regular carbohydrates when metabolized in human (Roberfroid, 1999b), inulin can be used not only as a functional food or as a dietary fiber, it can also be used as a fat substitute in various food systems.

Carbohydrates or proteins are considered to be the main ingredients for making food gels. Generally, gels made from biopolymers, including food gels can be classified into either associative or particulate gels according to the mechanism of networking between polymer molecules (Clark, 1996). In the associative case, random coils of polysaccharides undergo three-dimensional transitions from coil to helix shape during gelation. This helps polymer chains form a network structure between molecules. Thermoreversible gelations of polysaccharides (agar, carrageenan and alginate) and fibrous protein are included

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Volumetric Gel Index

$$= \frac{\text{Volume of gel}}{\text{Total volume}} * 100$$

Fig. 1. Definition of VGI.

in this category. The other type, the particulate gel, is made through large, random aggregation between polymer chains. The formation of gel from association of milk casein micelles (cheese, yogurt) is included in this particulate gel-type.

Gel can also be defined as an insoluble semi-rigid form of solid dispersion in a liquid. As mentioned earlier, carbohydrates or proteins are considered to be the main ingredients for food gels. Soluble polymers become insoluble to form semi-solid structure (gel) due to association of polymer molecules in a polymer solution (sol) (Funami, Funami, Yada, & Nkao, 1999; Piculell, 1995). Sol–gel transition in food system is often found in carbohydrate-gels. Gel formation from carbohydrates is affected by many factors such as the concentration of reactant, heating temperature, pH, and salts. These factors also decide the gel strength and rheological properties (viscosity, storage and loss moduli) of the gel.

As far as the processing of inulin as a fat substitute is concerned, high shearing process has been suggested to make a fat mimetic gel structure by a manufacturer of inulin (de Leenheer, 1993). Gel formation can be a key step to produce carbohydrate based fat substitutes including inulin. As of present, mechanism of gel formation and factors affecting gel formation of inulin have not been published

yet. The objective of this research is to study factors affecting gel formation from inulin.

2. Materials and methods

2.1. Materials

Inulin (Raftilin[®] HP) from Orafiti (Malvern, PA) was used throughout the experiments. According to the company (Niness, 1999), Raftilin[®] HP was made from chicory root. The average particle size of inulin is 30 μm based on our measurement under a microscope.

2.2. Water solubility of inulin

Solubilities of inulin were measured with 300 ml water in a beaker immersed in a water bath at 25, 50, 60, 70, 80 and 90°C. Temperature regulator and water circulator in the water bath controlled the temperature throughout the experiment. Inulin–water mixture was stirred to make a homogeneous solution at 150 rpm. At each temperature, 0.1 g of inulin was added to water slowly (0.1 g/min) until undissolved particles were found in the solution after 2 min of continuous stirring to find out saturation concentration of inulin at that particular temperature.

2.3. Definition of volumetric gel index (VGI)

As a parameter for the optimization of inulin-gel formation, VGI was employed to express the degree of gel formation (Fig. 1). It is expressed as the volume of gel (V_G) over the total volume (V_T) multiplied by 100. For example, if there were no gel formed, VGI of the system would be 0. VGI would be between 0 and 100% for partial gel formation.

2.4. Shear induced gel formation

In this study, inulin gel was formed through shearing or heating of inulin–water mixture followed by cooling. For shear induced gel, two shear conditions were used to see effect of shear on gel formation. A specified concentration of inulin–water mixture was mixed at relatively low or high shear conditions for 5 min. For relatively low shear mixing, the water–inulin mixture was mixed with a magnetic stirrer at 250 rpm in a 250 ml beaker. For relatively high shear experiment, an Osterizer mixer (approx. 5000 rpm) was utilized to mix the samples. The sheared inulin solution was allowed to set for a day at 25°C.

2.5. Thermally induced gel formation of inulin

First, a specified amount of inulin powder was dissolved in water at a particular temperature with stirring at 150 rpm. The dissolved inulin was poured into a volumetric flask and made up to 100 ml. After mixing it again, the inulin solution was poured into a bottle, and allowed to cool down for a day

Table 1

Conditions of heating temperature and inulin concentration to determine the possibility of thermally induced gel formation

| Heating temperatures (°C) ^a | Inulin concentrations (% w/v) |
|--|-------------------------------|
| 25 | 5, 10, 15 |
| 30 | 5, 10, 15 |
| 40 | 5, 10, 15 |
| 50 | 5, 10, 15 |
| 60 | 5, 10, 15 |
| 70 | 5, 10, 15, 20 |
| 80 | 5, 10, 15, 20, 25 |
| 90 | 5, 10, 15, 20, 25, 30, 35 |
| 100 | 5, 10, 15, 20, 25, 30, 35, 40 |

^a Samples are thermally treated at each temperature for 5 min.

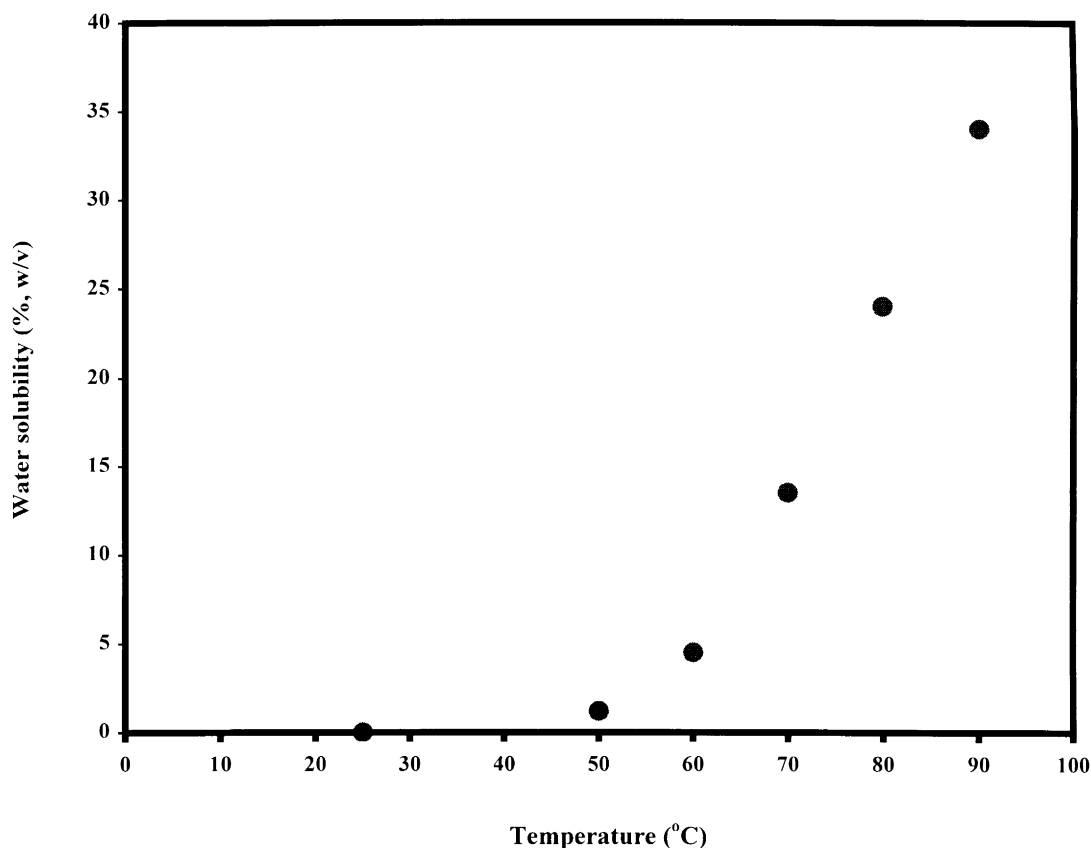


Fig. 2. Water solubility of inulin.

at 25°C under gravity to set the gel structure. Each VGI presented in this paper is the average value of at least three trials. Pictures were taken of the samples for the initial and the final stages of gel formation.

2.6. Major variables for thermally induced gel formation of inulin

Inulin concentration and heating temperature were chosen as key variables for thermally induced gel formation in this study. Table 1 shows sets of experimental conditions of heating temperature and inulin concentration to see whether inulin–water mixture forms gel at each specific condition. This experiment is also designed to determine the minimal concentration of inulin for thermally induced gel formation. A few other sets of experiments were performed to see the effects of pH and solvent at specified conditions.

2.7. Measurements of particle sizes

Particle sizes of inulin were measured after shear induced and thermally induced gel formation. About 0.5 g of inulin gel was re-dispersed in 100 ml water for 15 min with stirring at 150 rpm, then a droplet of the suspension was used to measure the particle sizes under a microscope. Sizes of 200–300 particles were measured for each sample using

an Olympus America Inc. (Melville, NY) transmission microscope BH2. A standard micrometer was used for the measurement of sizes.

2.8. Measurements of reducing sugar concentration

The concentrations of soluble reducing sugars were measured using 3,5-dinitrosalicylic acid (DNS) (Chaplin, 1986). Immediately after heating in the making of the inulin solution, the solution was diluted with water ten times to quench the hydrolysis. A 0.2 ml of diluted sample was transferred to a test tube, where it was mixed with 2 ml of the DNS reagent. After mixing it with vortex, the samples were heated in the water bath at 100°C for 10 min followed by rapid cooling in cold water. The optical densities (OD) of the samples were measured at 570 nm using a Bausch and Lomb (Rochester, NY) spectrophotometer 601. Fructose was used for the establishment of a standard curve.

2.9. Gel strength (hardness)

The gel strengths of inulin-gels were measured using a texture analyzer TA.XT2 from Texture Technologies Corporation (Scarsdale, NY) at 25°C. The gel samples were placed under the texture analyzer with a cylindrical probe (5 mm i.d.). The depth of punching the samples was 15 mm, and the probe speed was 1 mm/s. The maximal peak

Table 2
Effect of shearing on VGI and gel strength

| Concentration of Inulin (%) ^a | VGI (%) | | Gel strength (g) ^b | |
|--|---------------|-----------------|-------------------------------|-----------------|
| | Low (250 rpm) | High (5000 rpm) | Low (250 rpm) | High (5000 rpm) |
| 5 | 0 | 0 | N/A ^c | N/A |
| 10 | 0 | 0 | N/A | N/A |
| 15 | 0 | 100 | N/A | 4.51 |
| 20 | 0 | 100 | N/A | 8.91 |
| 25 | 0 | 100 | N/A | 22.26 |
| 30 | 100 | 100 | 11.14 | 50.34 |
| 35 | 100 | 100 | 20.05 | 97.56 |

^a Samples are mixed at 25°C for 5 min.

^b Gel strength was measured only for samples with 100% VGI.

^c Not available because the product did not show 100% VGI.

value after punching the sample 15 mm down was considered as gel hardness of the gel.

2.10. Effect of pH on thermally induced gel formation

To see the effect of pH on the gel formation of inulin, pH 1, 2, 3, 4, 6, 8, 10, and 12 were chosen. For this study, 25% (w/v) inulin was dissolved in water at 80°C for 5 min with stirring at 150 rpm. VGI and gel strengths of different pH-related samples were compared to see the differences among them.

2.11. Effect of solvent addition

To see the effect of solvent on the gel formation, ethanol and glycerol were added to inulin solution with a ratio of 1:9 (solvent: inulin solution). Samples with 20 and 25% (w/v) inulin solution dissolved at 80°C were used for this study.

3. Results and discussion

3.1. Water solubility of inulin

Fig. 2 shows the effect of temperature on water solubility

of inulin. At 25°C, inulin was almost insoluble. Even at 50°C, solubility of inulin was only 1.2% (w/v). But with further increases in temperature, solubility increases significantly and reaching 34% (w/v) at 90°C.

3.2. Shear induced gel formation

Table 2 shows the comparative formation of gel after stirring using two different shear conditions. At 5, 10, 15, 20, and 25% (w/v) inulin concentrations, the suspension did not form gel after low stirring (250 rpm), but, 30 and 35% (w/v) suspension made 100% gel structure. Unlike this result, at high shearing condition (5000 rpm) with a mixer, inulin–water mixture formed gel at or higher than 15% (w/v) inulin concentration. Inulin gel made with lower shearing showed a sandy texture due to aggregation of large inulin particles. But with the help of better dispersion of inulin particles at high shearing, a smoother texture similar to that of butter was obtained. These results tell us that gel-formation of inulin can be done with suspension of “small” inulin particles. The particle sizes of these shear-treated gels are reported later.

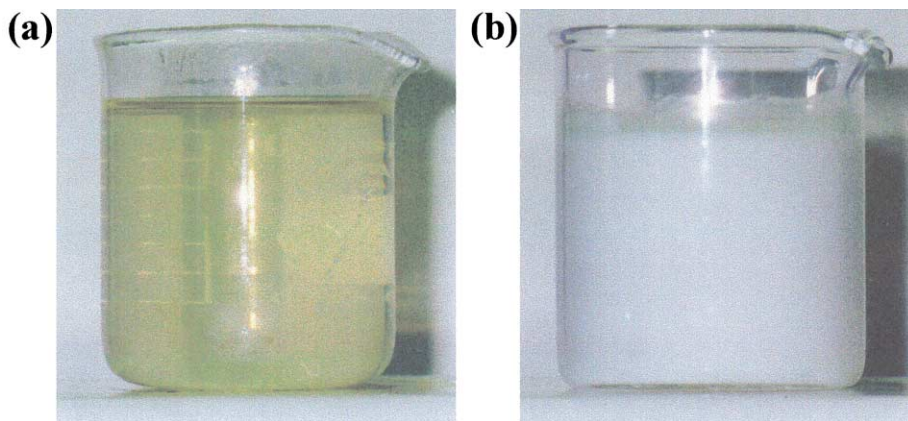


Fig. 3. Sol–gel transition of inulin solution. 30% (w/v) inulin heated at 90°C for 5 min and cooled down at 25°C for 1 day. (a) Before cooling; and (b) after cooling.

Table 3
Effect of heating temperature on VGI

| Concentration of Inulin (%) ^a | VGI (%) | | | | | | | | |
|--|---------|------|------|------|------|------|-------|-------|--------|
| | 25°C | 30°C | 40°C | 50°C | 60°C | 70°C | 80°C | 90°C | 100°C |
| 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0.0 | 0.0 | 0.00 |
| 10 | 0 | 0 | 0 | 0 | 80 | 100 | 12.5 | 0.5 | 0.25 |
| 15 | 0 | 0 | 100 | 100 | 100 | 100 | 75.0 | 15.0 | 7.50 |
| 20 | | | | | | 100 | 100.0 | 75.0 | 13.25 |
| 25 | | | | | | | 100.0 | 100.0 | 30.00 |
| 30 | | | | | | | | 100.0 | 45.00 |
| 35 | | | | | | | | 100.0 | 98.75 |
| 40 | | | | | | | | | 100.00 |

^a Samples are thermally treated at each temperature for 5 min.

3.3. Thermally induced gel formation

Fig. 3 shows the pictures before and after inulin-gel formation as an example. Fig. 3 displays the typical sol–gel transition of inulin solution as observed. After 30% inulin was dissolved in water at 90°C, inulin solution started to form gel slowly as the temperature dropped down to 15°C. Sol–gel transition is often found in carbohydrate-gels. Soluble polymers become insoluble to form a semi-solid structure (gel) due to association of polymer molecules in polymer solution (sol).

Before gel formation, inulin solution showed a whitish or yellowish color depending on the concentration of inulin and heating temperature. As the temperature dropped, the inulin solution started to form gel slowly. After a certain setting time, inulin solution formed a white gel as seen in Fig. 3(b). Setting time for inulin gel varies according to inulin concentration, heating temperature and solvent added. The texture of this gel was similar to that of butter or yogurt depending on concentration. But as seen in Table 3, gel formation was not observed at every experimental condition studied. Solutions with low concentrations such as 5% (w/v) did not show any gel structure at all temperature studied. This fact indicates that there must be a critical inulin concentration for the formation of gel structure.

3.4. Effect of concentration of inulin on gel formation

As seen in Table 3, different combinations of inulin concentration and heating temperature were used to relate heating temperature and inulin concentration to gel formation. The pH and heating time were maintained at pH 6 and 5 min throughout these experiments. VGI was used to show the degree of gel formation. As mentioned in the previous section, at a concentration of 5% (w/v), the solution did not form gel regardless of heating temperature, showing 0% VGI. As concentration increased, VGI increased gradually and finally reached 100%. For example, at 80°C, as shown in Table 3, 5% (w/v) inulin solution did not form gel. As the concentration of inulin increased, VGI started to increase gradually. By increasing the concentration to 20 and 25%

(w/v), the solutions formed 100% gel through sol–gel transition. This trend was also found at higher heating temperatures such as 90 and 100°C. At low concentrations such as 5 and 10% (w/v), the solution did not show gel network after heating and cooling. But as inulin concentration increased, the solution started to form gel, which led to an increase in VGI.

Another interesting result was found by heating at low temperatures. Inulin–water mixture did not form gel at 25, 30, 40, and 50°C with 10% (w/v) inulin. This is probably due to the fact that inulin is only sparingly soluble at these temperatures. The formation of partial gel was observed at 60°C and 100% gel was formed at 70°C. With further increase in temperature, VGI decreased. At moderate temperature (60–70°C), the polymer chains may have more active movement in the solution due to higher kinetic energy. This may help the inulin chain dispersed better in the solution. Thus the better contact between inulin chains becomes easier during cooling to form gel structure. Since the solubility of polymer is a complex issue, this hypothesis need to be proven with other experiments.

But, at high temperatures between 70 and 80°C, the chain may start to degrade into shorter chains by hydrolysis, which makes it harder to form a gel. Results of inulin hydrolysis will be discussed later. Notice that inulin formed 100% gel with 10, 15 and 20% inulin concentrations at 70°C as seen in Table 3. That is 10% inulin concentration is the minimum or close to the minimum concentration required for gel formation for sample heated at 70°C for 5 min. Similarly, at 40, 50 and 60°C, the minimum concentration is 15% as shown in Table 3.

3.5. Effect of heating temperature on gel formation

As pointed out in the previous section, heating temperature is an important factor in determining VGI. At the same inulin concentration, VGI increased initially with increasing temperature and then started decreasing as temperature increased further. For example, although 15% (w/v) inulin solution did not form gel at 25 and 30°C, it formed a 100% gel (VGI) at 40, 50, 60 and 70°C. But the VGI's decreased

Table 4
Effect of heating temperature on soluble reducing sugar content

| Concentration of Inulin ^a (%,w/v) | Reducing sugar (%, w/v) | | | |
|---|-------------------------|--------|-------|-------|
| | 70°C | 80°C | 90°C | 100°C |
| 5 | 0.032 | 0.0489 | 0.080 | 0.200 |
| 10 | 0.091 | 0.1178 | 0.167 | 0.310 |
| 15 | 0.162 | 0.2156 | 0.275 | 0.370 |
| 20 | | 0.2665 | 0.358 | 0.510 |
| 25 | | 0.3414 | 0.447 | 0.630 |
| 30 | | | 0.559 | 0.850 |
| 35 | | | | 1.000 |
| 40 | | | | 1.160 |

^a Samples are thermally treated at each temperature for 5 min.

with further increase in temperature. The VGI's at 80 and 90°C were 75 and 15%, respectively; the higher the temperature the less the VGI, indicating hydrolysis of inulin which is supported by the reducing sugar data shown later.

Table 3 shows the requirements of a minimum (critical) inulin concentration to form gel at different temperature. The critical concentration increases with increasing heating temperature. At 40, 50 and 60°C, the required inulin concentration is 15%: at 70°C, it is 20%: 80 and 90°C, 25% and at 100°C, 40%.

What causes this kind of trend? As mentioned earlier, it may be due to the hydrolysis of inulin during heating. Reaction rate is a function of the reaction rate constant and the concentration of reactant as seen in Eq. (1) unless the reaction follows zeroth order kinetics.

Reactant → Product

$$-r_{\text{reactant}} = r_{\text{product}} = k(T)[\text{reactant}]^n \quad (1)$$

where r is the reaction rate; k , the reaction rate constant; T , temperature; and n , the reaction order. As temperature increases, hydrolysis of inulin increases because the reaction rate constant, k increases with increasing temperature, usually according to Arrhenius equation.

Table 5
Effect of heating temperature on gel strength

| Concentration of Inulin (%,w/v) ^a | Gel strength (g) | | | | | |
|---|------------------|-------|-------|-------|--------|--------|
| | 40°C | 50°C | 60°C | 70°C | 80°C | 90°C |
| 5 | N/A ^b | N/A | N/A | N/A | N/A | N/A |
| 10 | N/A ^b | N/A | N/A | 14.26 | N/A | N/A |
| 15 | 12.47 | 14.91 | 28.07 | 45.26 | N/A | N/A |
| 20 | | | | 68.61 | 7.43 | N/A |
| 25 | | | | | 158.60 | 28.51 |
| 30 | | | | | | 264.41 |
| 35 | | | | | | 300.25 |

^a Samples are thermally treated at each temperature for 5 min.

^b Not available because the product did not show 100% VGI.

3.6. Concentration of reducing sugar

We monitored the change of reducing sugar as a parameter to help prove that hydrolysis of inulin does occur during the heating of inulin. Table 4 shows the amount of reducing sugar at different conditions. These data shows different degrees of hydrolysis of inulin during heating. At 80°C with 5% (w/v) inulin, reducing sugar content was 0.0489% (w/v) after five minutes heating. As the heating temperature and concentration of inulin increased, higher amount of reducing sugar was produced. Thus, these data are supporting the fact that hydrolysis is happening during thermal treatment and leading to the increases in non-gel forming components, i.e. the hydrolyzed products. Even though reducing sugar content does not relate directly to molecular weight distribution of the non-gel forming components (hydrolyzed products) in the solution, it tells us indirectly that the average molecular weight of the material has decreased.

The increases in reducing sugar content indirectly suggest that the degrees of polymerization (DP) of the inulin chain are decreasing because only the last fructose molecule which possess the reducing end can participate in reacting with the DNS reagent. In other words, during hydrolysis, long inulin chains are broken into smaller chains. And smaller chains that have relatively low DP cannot form gel.

3.7. Gel strength of thermally induced gel

Table 5 shows the gel strengths of thermally induced gels. Gel strength is a strong function of inulin concentration. For example, for gels made with 70°C heating, the hardness of gel is 14.26 g at 10% (w/v) concentration, 45.26 g at 15% and 68.61 g at 20% (w/v). This trend is also applicable to different heating temperatures. At low heating temperatures such as 40, 50, 60, and 70°C, the gel hardness increases with increasing temperature. But at higher temperature such as 80 and 90°C, the gel hardness decreases with increases in temperature. The higher kinetic energy associated with higher temperatures and significant hydrolysis of inulin at these temperatures may explain these observations.

From comparison of data in Tables 2 and 5 we can

conclude that thermally induced gel shows stronger gel hardnesses than shear induced gel at the same inulin concentration under our experimental condition. Shear induced gel forms gel with hydrogen bond and van der Waals interactions among particles (aggregates of molecules) in dispersion. But thermally induced gel can form the network structure among the molecular chains through entanglement of molecules into smaller particles as compared to that of shear gels during cooling. These arguments are supported by the particle size analysis presented later. This rationale can also help explain the differences of gel hardness between thermally induced and shear induced gels. However, we may have to be careful to draw the conclusion about effect of shearing on gel formation of inulin. With very high shearing which can provide enough energy equivalent to thermal energy to inulin–water mixture, shear induced gel may be as strong as thermally induced gel.

3.8. Distribution of particle size

Fig. 4 shows the microscopic images of particle sizes of inulin gels suspended in water. The particle sizes of the re-suspended gel are easily seen under microscope. Thermal-induced inulin gel shows relatively smaller and more uniform particle sizes as compared to that of shear induced gels. Fig. 5 shows the differences in particle sizes between low shearing, high shearing and thermally induced gels. The average particle size of low shear induced gel is $29.88 \pm 14.04 \mu\text{m}$. With increasing shearing at higher RPM, the particle size decreased to $9.95 \pm 9.79 \mu\text{m}$. The distributions of particle sizes of shear induced gels was broad and very large particles were still found under microscopic observations. The average particle size of thermally induced gel is $2.31 \pm 0.78 \mu\text{m}$ which is about ten times smaller than the size of inulin gel made by low shear induced gel. The thermally induced gel also showed a narrower distribution of particle sizes than the two shear-induced gels.

Viscoelastic materials undergo elastic or plastic deformation according to the amount of shear stress applied to the material. Plastic deformation unlike elastic deformation is permanent and the material does not recover its original shape when the stress is removed. In plastic deformation, the material starts flowing when stress higher than yield strength, σ_y or flow stress, σ_{flow} is applied. Stronger materials require higher stress to make dislocation happen. The stress needed to sustain flow increases as the grain size (d) decreases according to the following relationship between shear stresses and grain sizes (Gerberich, 1997):

$$\sigma_{\text{flow}} \propto d^{-1/2} \quad (2)$$

Shear stress required to deform the material is inversely proportional to square root of the particle diameter. In other words, material that consists of smaller particle sizes has stronger structure than that with larger particle size

Table 6
Effect of pH on the VGI and gel strength

| pH ^a | VGI (%) | Reducing sugar (% w/v) | Gel strength (g) |
|-----------------|---------|------------------------|------------------|
| 1 | 0 | 25.00 | Not available |
| 2 | 0 | 15.72 | Not available |
| 3 | 100 | 2.12 | 132.55 |
| 4 | 100 | 0.41 | 147.01 |
| 6 | 100 | 0.34 | 158.59 |
| 8 | 100 | 0.33 | 154.29 |
| 10 | 100 | 0.36 | 156.81 |
| 12 | 100 | 0.26 | 170.37 |

^a 25% (w/v) samples are thermally treated at 80°C for 5 min.

assuming the same density for both. This fundamental theory can be applied to our inulin gel system presented here. The smaller size of inulin particles in thermally induced gel can be the cause of the smoother texture and higher mechanical strength when compared to shear induced gels. Another factor is the distribution of the particle sizes. A broad distribution leads to increased probability of weak spots in a structure.

3.9. Effect of pH on the gel formation

As seen in Table 6, at low pH's such as 1 and 2, inulin solution did not show any gel structure after the heating–cooling process designed to make gels. This may be due to severe hydrolysis of inulin at low pH conditions because hydrogen ions have been known to catalyze hydrolysis. The gel strength of inulin gel made with 25% (w/v) inulin and heating at 80°C was not affected by pH larger than 4 and smaller than 10. But at pH 3 and 4, gel strengths were a little lower than the control value at pH 6 due to possible hydrolysis of inulin during heating.

3.10. Effect of solvent on the thermally induced gel formation of inulin

Table 7 shows the setting time for gel formation from inulin solution when the solution was diluted with water, ethanol or glycerol. The inulin solution diluted with water takes longer time to form gel than those diluted with other diluents. The setting times were about 3 and 2 times quicker than that of control (water) when ethanol and glycerol were added to the inulin solution, respectively. Table 7 also shows that the setting time of inulin solution is a function of inulin concentration in the solution. The higher the concentration, the shorter is the setting time.

In these experiments, after adding solvent to inulin solution, as the solutions are allowed to cool naturally, it can be assumed that the cooling rate is similar for all three cases. So the effect of temperature can be neglected during precipitation. Then, the polarity of solution may be a factor in deciding setting time of inulin gel. Dielectric constants of water, ethanol and glycerol are 80.0, 24.6 and 42.5, respectively, at 25°C (Furniss, Hannaford, Smith, & Tatchell,

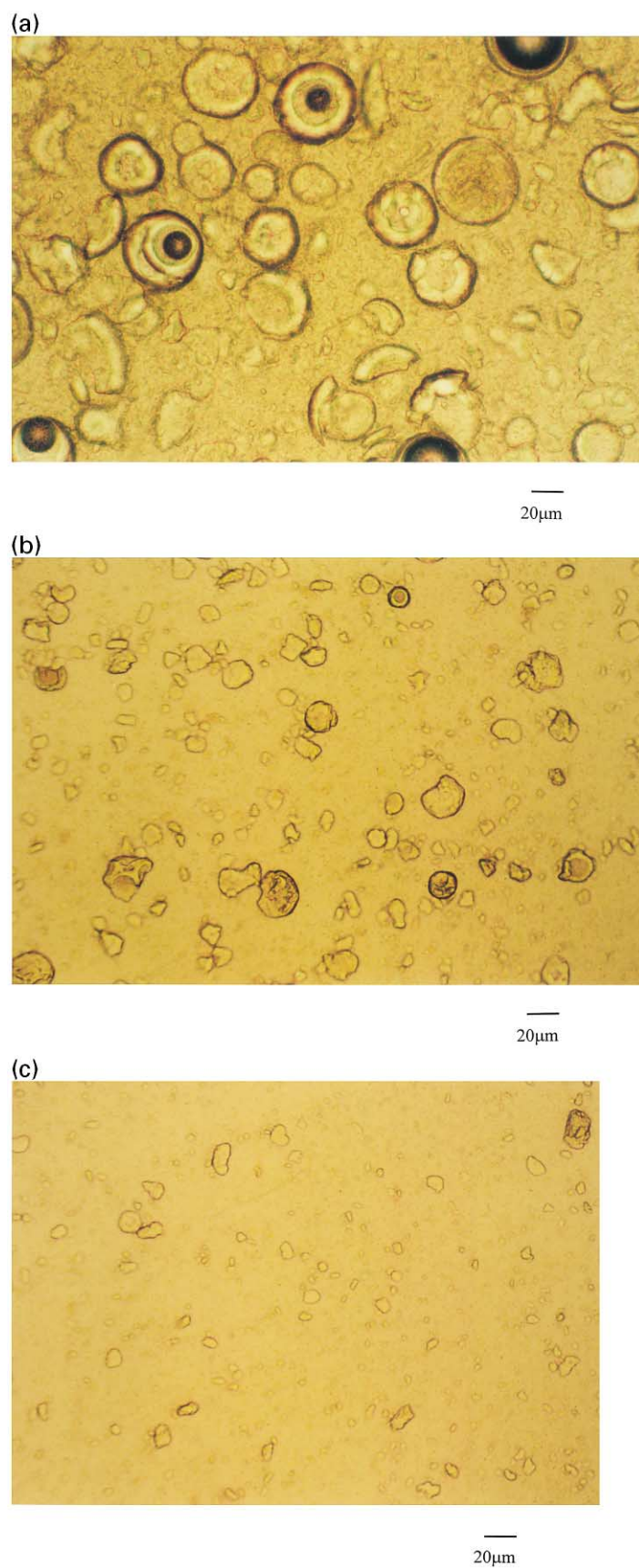


Fig. 4. Microscopic image of inulin gel ($20\times$). (a) Low shear induced gel; (b) high shear induced gel; and (c) thermally induced gel.

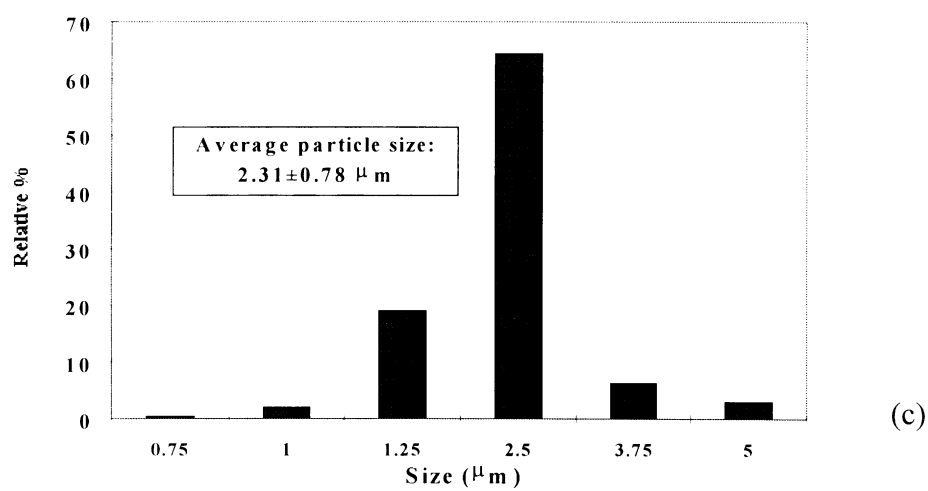
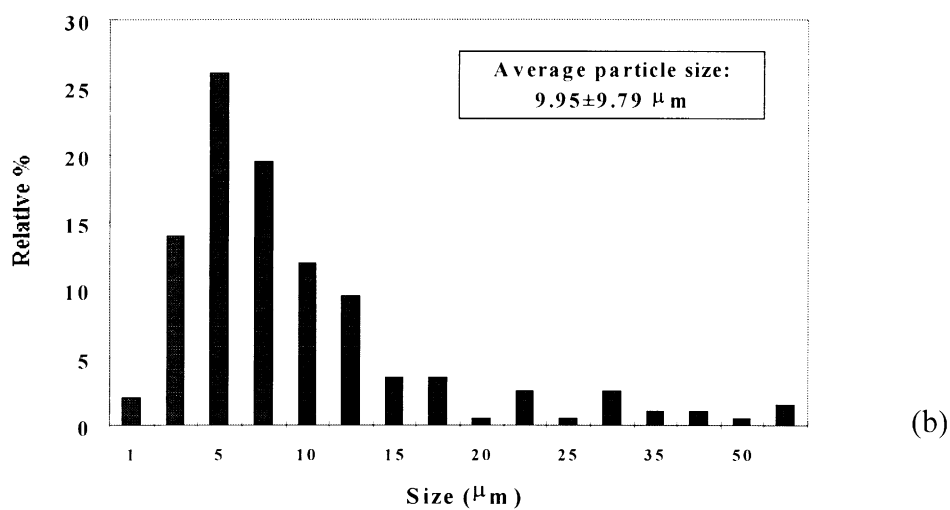
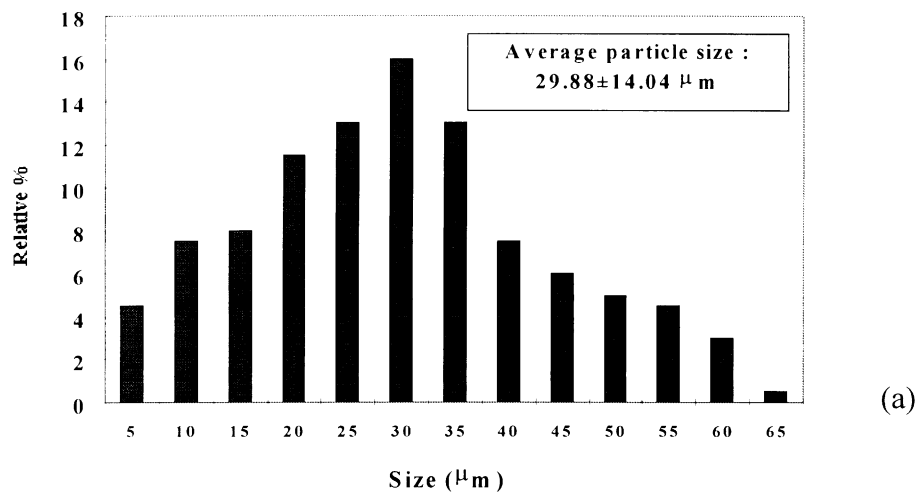


Fig. 5. Particle size distribution of inulin gels. (a) Low shear induced gel; (b) high shear induced gel; and (c) thermally induced gel.

Table 7
Effect of solvent on setting time and gel strength

| Diluents | Inulin concentration (%) ^a | The volume ratio of diluent to inulin solution | Setting time (mm) | Gel strength (g) |
|----------------------|---------------------------------------|--|-------------------|------------------|
| Control ^b | 20 | 1:9 | 160 | 30.29 |
| Ethanol | 20 | 1:9 | 47 | 40.98 |
| Glycerol | 20 | 1:9 | 80 | 37.20 |
| Control ^b | 25 | 1:9 | 47 | 85.53 |
| Ethanol | 25 | 1:9 | 15 | 96.22 |
| Glycerol | 25 | 1:9 | 25 | 89.10 |

^a Inulin was dissolved at 80°C for 5 min.

^b Water was used as a control diluent.

1989). In other words, the dielectric constants of ethanol and glycerol are about one third and one half than that of water, respectively. The dielectric constant of solvent implies its polarity. Generally, the higher the dielectric constant, the more polar the solvent is. In other words, by adding ethanol and glycerol, the polarities of solution decrease. So, water is more polar than those of ethanol and glycerol. When the same amount of diluent (or solvent) was added to the solutions at the same inulin concentration, the time required for the conversion from soluble to insoluble inulin would be affected by the polarity of the diluents. Inulin is a polar compound, its solubility in water is larger than that in ethanol and glycerol. The conclusion here is that by adding ethanol or glycerol, one can speed up the process of gel setting. As to the strength of gels, the added diluents have little effect.

3.11. Proposed model for forming inulin gel

The results obtained in this study show that inulin gel formation is due to precipitation of inulin molecules from solution into particles that form a gel probably through crowding effect. The best range of conditions for gel formation are 20–30% (w/v) inulin concentration, 80–90°C heating for 3–5 min at pH 6–8 and then cool down at room temperature. A severe condition such as high temperature or low pH's (90, 100°C and pH 1 and 2) inulin chains are hydrolyzed into smaller chains during heating and lead to non-gel forming components. A low concentrations ($\leq 5\%$, w/v), inulin–water mixture did not form gel structure because the system does not have enough particle and/or molecular density of inulin chains to reach the critical crowding effect.

3.12. Differences between thermal induced gel and shear induced gel

We can make inulin gel through two different ways, shear or thermal induced method. What are the differences between these gels? First, thermally induced gel shows stronger gel strength than shear induced gel at the same concentration of inulin under condition we studied. Second, with hydrolysis, at higher heating temperature thermally induced gel may have higher content of oligosaccharides

which is a prebiotic material. Third, thermally induced gel shows smaller particle size than that of shear induced gel and so a smoother texture, and also a gel with higher strength.

4. Conclusions

Two different paths have been found to form inulin gel. Gel formation was affected by the concentration of inulin, the heating temperature, the heating time, the solvent used, shear and pH. Thermally induced inulin gel showed stronger gel strength than shear induced gel at the same concentration under our experimental conditions.

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