PHYSICAL PROPERTIES OF POLYSACCHARIDES (CORNSTARCH AND CURDLAN)

EFFECTS OF TASTE SUBSTANCES ON THE VISCOELASTICITY FOR CORNSTARCH PASTES & THE GELATION MECHANISM OF CURDLAN AQUEOUS DISPERSIONS

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多糖類（澱粉およびカードラン）の諸特性

澱粉糊の粘弾性に及ぼす呈味物質の影響と
カードラン水懸濁液のゲル化機構

大阪市立大学大学院
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生活科学専攻

平島 円

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The effects of sodium chloride (NaCl) on the physical properties for cornstarch pastes

The effects of sour substances on the physical properties for cornstarch pastes

The effects of caffeine on the physical properties for cornstarch pastes

The effects of sodium L-glutamate (MSG) on the physical properties for cornstarch pastes

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</table>
LIST OF SYMBOLS AND ABBREVIATIONS

Symbols

$A_2$ second virial coefficient
$c$ concentration of the solute
$C$ concentration of cornstarch
$C_c$ caffeine concentration
$C_{cu}$ curdlan concentration
$C_m$ sodium L-glutamate (MSG) concentration
$C_n$ sodium chloride (NaCl) concentration
$C_s$ sucrose concentration
$CT$ centrifugation time
$DP$ degree of polymerization
$DS$ degree of syneresis
$G'$ storage modulus
$G'_{i}$ increments $G'$ of around 40 °C on cooling
$G'_{\text{max}}$ maximum values of $G'$ below 50 °C on cooling
$G'_{s}$ saturated value of $G'$
$G'_{50}$ values of at 50 °C on cooling
$G''$ loss modulus
$k$ Huggins constant
$K$ rate constant
$ST$ storage time
$t$ time
$tan\delta$ loss tangent
$t_o$ latent time
$T$ temperature
$T_c^1$ conclusion temperature of mainly amylose–lipid complex disintegration
$T_c^2$ conclusion temperature of mainly amylopectin gelatinization
$T_o$ onset temperature
$T_p$ peak temperature
$T_p^1$ higher peak temperature for curdlan on cooling
$T_p^2$ lower peak temperature for curdlan on cooling
$WH$ water holding capacity of starch or taste substances
$\Delta H$ gelatinization enthalpy
$\Delta H_{cu}$ swelling enthalpy for curdlan dispersion
\(\Delta H_{cu}^l\) enthalpy for lower peaks of curdlan dispersion on reheating
\(\Delta H_{cu}^h\) enthalpy for higher peaks of curdlan dispersion on reheating
\(\Delta H_{cu}^c\) enthalpy for two peaks of curdlan dispersion on cooling
\(\Delta H_s\) enthalpy for exothermic peaks of sucrose solution
\(\Delta T\) temperature range for peaks
\(\gamma\) strain
\(\dot{\gamma}\) shear rate
\(\eta_0\) viscosity of the solvent
\(\eta_1\) shear viscosity at shear rate of 1 s\(^{-1}\)
\(\eta_{10}\) shear viscosity at shear rate of 10 s\(^{-1}\)
\(\eta_{100}\) shear viscosity at shear rate of 100 s\(^{-1}\)
\(\eta_r\) relative viscosity increment
\(\eta_s\) viscosity of sucrose solution
\(\eta_\dot{\gamma}\) shear viscosity
\(|\eta^\ast|_o\) complex viscosity
\([\eta_\dot{\gamma}]\) intrinsic viscosity
\(\sigma\) shear stress
\(\omega\) angular frequency

**Abbreviations**

Ag pans silver pans
CMC carboxymethylcellulose
DDSC differentiated of the DSC
DMSO dimethyl sulfoxide
DSC differential scanning calorimetry
glucose chains amylose and amylpectin chains
MC methylcellulose
MSG sodium L-glutamate
NaCl sodium chloride
potassium sorbate potassium 2,4-hexadienoate
1. INTRODUCTION

POLYSACCHARIDES IN FOODS

Food hydrocolloids, such as polysaccharides and proteins, are often used to impart product stability to a food system. Food polysaccharides from many kinds of plants or animals are consumed by humans, and are essential for the maintenance of life and good health. As the food industry is the largest among various industries in all developed countries, the future holds interesting possibilities to technological advances and the marketing of many new stable, safe and palatable low-fat or nutritious commodities.

It is not surprising that the wide range of sources and functions of polysaccharides in nature has led to a correspondingly wide and expanding range of uses and applications in foods.

<table>
<thead>
<tr>
<th>Polysaccharides</th>
<th>Function</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch</td>
<td>Stabilizer, Thickener, Gelling agent, Binder, Filler</td>
<td>Bakery products, Confectionery, Desserts, Soups, Sauces,</td>
</tr>
<tr>
<td>Carboxymethylcellulose</td>
<td>Stabilizer, Thickener, Water retention agent</td>
<td>Bakery products, Dairy products, Meat products, Syrup</td>
</tr>
<tr>
<td>Guar and Locust bean gums</td>
<td>Stabilizer, Water retention agent</td>
<td>Bakery products, Dairy products, Desserts,</td>
</tr>
<tr>
<td>Gum arabic</td>
<td>Stabilizer, Thickener, Emulsifier, Encapsulating agent</td>
<td>Bakery products, Beverages, Confectionery, Sauces</td>
</tr>
<tr>
<td>Gum tragacanth</td>
<td>Stabilizer, Thickener, Emulsifier</td>
<td>Confectionery, Dairy products, Dressings, Sauces</td>
</tr>
<tr>
<td>Pectins</td>
<td>Gelling agent, Thickener, Stabilizer</td>
<td>Bakery products, Beverages, Confectionery, Dairy products, Jams, Preserves,</td>
</tr>
<tr>
<td>Agars</td>
<td>Gelling agent</td>
<td>Confectionery, Dairy products, Meat products</td>
</tr>
<tr>
<td>Carrageenanans</td>
<td>Stabilizer, Thickener, Gelling agent</td>
<td>Dairy products, Desserts, Dressings, Instant puddings, Meat products</td>
</tr>
<tr>
<td>Alginates</td>
<td>Stabilizer, Gelling agent</td>
<td>Beverages, Dairy products, Instant puddings,</td>
</tr>
<tr>
<td>Xanthan gum</td>
<td>Stabilizer, Thickener</td>
<td>Beverages, Dairy products, Dressings,</td>
</tr>
</tbody>
</table>
Chapter 1

Table 1.2 Terms of applications used in Chapter 1.

<table>
<thead>
<tr>
<th>Industry</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakery products</td>
<td>Bread doughs and mixes, Bun and doughnut glazes, Cake batters and mixes, Dense syrup, Flat icing, Flavor emulsions, Fruit fillings, Meringue, Pastry fillings</td>
</tr>
<tr>
<td>Beverages</td>
<td>Beer, Dietetic beverages, Dry mixes, Fruit juices, Wine</td>
</tr>
<tr>
<td>Confectionery</td>
<td>Caramels, Chewing gum, Dietetic confections, Fruit centers, Gums, Acidic gums (fruit, etc.), Glazes and coatings, Hard sweets, Jellies, Lozenges, Nougat, Taffy</td>
</tr>
<tr>
<td>Dairy products</td>
<td>Cheeses, Cheese spreads, Chocolate milk, Coffee whitener, Custards, Flans, Flavorings, Ice creams, Ice pops, Instant puddings, Milk gels, Milk shakes, Processed cheeses, Puddings, Sherbets, Whipped cream, Whipped toppings, Yogurt,</td>
</tr>
<tr>
<td>Dressings</td>
<td>Syrup and toppings, French salad dressings, Other acidic salad dressings</td>
</tr>
<tr>
<td>Meat products</td>
<td>Canned foods, Ground meat products, Grave-based pet food, Low-fat meats, Patés, Sausages</td>
</tr>
</tbody>
</table>

Examples are listed in Table 1.1. The terms used for applications are collected in Table 1.2

Among many kinds of polysaccharides, starch is the most important source of nutrient and energy in human diets, and besides, starch is often at low cost because starch has been got from many kinds of cereal grains and tubers such as corn, wheat, rice, potato, sweet potato, cassava, sago, etc. There are two types of starches: normal starches, which are the mixture of amylose and amylepectin, and waxy starches, which are made of only amylepectin (See Chapter 3). Normal starches contain roughly 25 % amylose. Mutant varieties of corn, called high-amylose corn, produce starch with amylose contents ranging up to 85 %, although commercial varieties usually have a maximum of 65 % amylose 3). Starches from different sources show individual patterns of the viscosity development that are influenced by the concentration, other substances present and the pattern of heating and cooling rates. Starches are widely used as a thickener, a binder, a stabilizer, a filler and a gelling agent in many kinds of foods by selecting the appropriate starch for each food. Typical applications are in soups, sauces, gravies and pie fillings (Table 1.1) 2). However, the use of native starches in foods is limited by their physical and chemical properties.

To overcome the disadvantages of native starches, such as a gummy and cohesive texture, a loss of viscosity, a lack of clarity and syneresis on storage, starches have been modified. There are many kinds of modified starches such as acid-hydrolyzed starches, oxidized starches, dextrins,
crosslinked starches, starch acetates, starch phosphates (monoester), etc. \(^4\). Some properties of acid-hydrolyzed starches include the decreased paste viscosity, the decreased gel strength and the increased gelatinization temperature \(^3\). In cornstarch, acids hydrolyze amylopectin more extensively than amylose \(^3\). Oxidized starches have quicker drying characteristics, and are produced in a wide range of fluidities. In most cases, as the level of oxidant increases, the fluidity increases \(^4\). Dextrins can be dissolved in water at room temperature. The film properties of dextrins are an important factor governing their usage as a binder, an adhesives and a coating \(^4\). Crosslinked starches were developed to minimize or prevent granule rupture during the cooking process, thus providing starches that give better ultimate viscosity. This means that they exhibit better stability to heat, low pH, shear, conditions of mechanical agitation and freeze-thaw cycles \(^3\), \(^5\), \(^6\). They also play an important role in suspending other food ingredients to provide nutritionally uniform foods \(^4\). Starch acetates are fairly stable chemically under mild to moderately acidic conditions and perform well in most foods. Starch phosphates provide fairly clear, stable dispersions, and suitable for use in thickening food systems having improved freeze-thaw stability. However, because of their anionic character and sensitivity to polyvalent cations, they work best in foods that are salt-free or acidic \(^4\).

Table 1.3 provides a brief summary of the manufacturing processes and an indication of present trends as reflected in modern patents for modified starches.

<table>
<thead>
<tr>
<th>Process</th>
<th>Function/Property</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid conversion</td>
<td>Viscosity lowering</td>
<td>Gum candies, Formulated liquid food</td>
</tr>
<tr>
<td>Oxidation</td>
<td>Stabilization/Adhesion</td>
<td>Formulated foods, Batters, Gum confectionery</td>
</tr>
<tr>
<td>Dextrins</td>
<td>Gelling, Clarification</td>
<td>Confectionery, Flavorings, Baking (gloss), Spices, Oils, Fish pastes</td>
</tr>
<tr>
<td>Dextrins</td>
<td>Binding, Coating, Encapsulation/High solubility</td>
<td></td>
</tr>
<tr>
<td>Crosslinking</td>
<td>Thickening, Stabilization, Suspension, Texturizing</td>
<td>Pie fillings, Breads, Frozen, Bakery products, Puddings, Infant foods, Soups, Gravies, Salad dressings, Baby foods</td>
</tr>
<tr>
<td>Esterification</td>
<td>Stabilization, Thickening</td>
<td>Candies; Emulsions; Products gelatinated at lower temperatures</td>
</tr>
<tr>
<td>Esterification</td>
<td>Clarification/Combined with crosslinking, Alkali sensitive</td>
<td>Soups, Puddings, Frozen foods</td>
</tr>
<tr>
<td>Etherification</td>
<td>Stabilization/Resistance to low-temperature</td>
<td></td>
</tr>
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</table>
As the same origin of starch, cellulose is the most abundant polysaccharide, which is the principal structural component of cell walls, but the use of cellulose in foods is limited by its insolubility and indigestibility. Therefore, the chemically modified cellulose such as carboxymethylcellulose (CMC), methylcellulose (MC) and its derivatives, is used as a stabilizer, a thickener and a water holding agent in foods. Sodium CMC is the most common for use since it is a water-soluble polymer, though the free acid form is insoluble in water. Solutions are stable at pH 5–10, with maximum stability at pH 7–9 \(^3\)). Moreover, CMC does not build up the viscosity in products with high salt concentrations \(^7\). When MC and its derivatives are dissolved in water, they give clear and smooth flowing solutions. They form gels on heating, then return to the solution state at their original viscosity on cooling \(^7\). The commercially available MC has gel temperature ranging from 50 to 80 ºC and gel strength varying from firm to weak \(^7\). From the reason mentioned above, CMC and MC and its derivatives have been widely used in protein-based food (fish and meat), sauces, soup, syrups, dressings, whipped toppings, baked goods and frozen desserts (Table 1.1).

Galactomannans and xyloglucans are the cell wall storage polysaccharides in seeds of most plant species. All these polysaccharides modify the behavior of water in food systems in a highly efficient manner and help in the control of crystal size in saturated sugar solutions \(^6\), \(^8\)). The galactomannans from the seeds of fast-growing guar (guar gum) and carob or locust bean (locust bean gum) have been widely used in the food industry. Both guar gum and locust bean gum are legume-seed galactomannans. Locust bean gum is totally soluble when warmed at 80 ºC in water, and shows a synergy with wheat starch, kappa-carrageenan and xanthan gum, forming gels that are elastic, very cohesive and relatively free from syneresis \(^3\), \(^9\)). On the other hand, guar gum does not form a gel with xanthan gum \(^9\)). However, both guar gum and locust bean gum are excellent as a stabilizer for ice cream, in which they contribute body, chewiness, resistance to heat shock and binding water \(^3\)). The other principal uses of galactomannans are in dairy products, fruit-based water gels, powdered products, bakery products, coffee whitener, baby milk formulations, seasonings, sauces, soups and meat products, such as tinned meats, frozen and cured meat foods (Table 1.1). Xyloglucans are known as tamarind gum or tamarind seed polysaccharides. Xyloglucans normally dissolve in water, yielding high viscous solutions, but do not form a gel \(^10\)). They have been used in the preparations of soups and baked goods. In Europe and the United States, the use of xyloglucans has lapsed, however, in Japan, it is used in food products such as soups and baked goods \(^9\)).

Other polysaccharides, which are isolated from plants, are gum arabic, gum tragacanth,
gum karaya, pectins and konjac-glucomannans. Among the plant exudate polysaccharides, gum arabic is the oldest and the best known. Most commercial gum arabic is the exudate from African *Acacia Senegal* trees. The special importance of gum arabic in food processing and formulation stems from its extremely high solubility in water (50 wt%), coupled with its low viscosity of solutions at the concentrations normally used in food products\(^{11}\). It has been used in confectionary, bakery products, beverages, sauces and meat products as a stabilizer, a thickener, an emulsifier, a film-forming and encapsulating agent and an adhesive (Table 1.1). Gum tragacanth is the gummy exudation from the stems of several species of *Astragalus*, belonging to the subgenus *Tragacantha*. Gum tragacanth contains two fractions, one is soluble in water and the other is insoluble\(^3\). Aqueous dispersions of gum tragacanth have a high viscosity at concentrations as low as 0.5 %. It has been included in dairy products, dressings, sauces, bakery products, confectionery frozen foods and beverages as a stabilizer, a thickener, an emulsifier, a water-biding agent and a crystallization inhibitor (Table 1.1). Gum karaya, sometimes known as *Sterculia* gum, is the dried exudation of the *Sterculia Urens* tree and other species of *Sterculia*. It is the least soluble and forms true solutions only at very low concentrations (< 0.02 % in cold water, 0.06 % in hot water)\(^{12}\), but colloidal dispersions are produced at concentrations up to ~5 %\(^{11}\). A large part of the gum karaya has been used in dairy products such as sherbets. Pectins are one of the most familiar polysaccharides. The texture of fruits and vegetables during growing, ripening and storage is strongly influenced by the amount and nature of the pectin present. HM pectin and LM pectin are terms used for commercial pectins of high and low methoxyl content, respectively, and they have been applied mainly in the food industry as a gelling agent. Pectins form gels under certain circumstances, and this property has made them a very important additive in jams, jellies and marmalade, as well as in the confectionery industry (Table 1.1). Pectins have also been found wide application as a stabilizer in acid milk products\(^{13}-^{15}\). Pectin solutions are most stable at lower pH (pH 3–4) and even at lower temperatures\(^{14},^{15}\). Furthermore, pectins command the interest of nutritionists as dietary fiber\(^{15}\).

Konjac-glucomannans are the main component of the tuber of *Amorphophallus Konjac* C. Koch. They form a thermally stable gel, which is called *Konnyaku* in Japan, upon the addition of an alkaline coagulant. Almost all konjac-glucomannans have been processed to *konnyaku* and *shirataki*, which is a kind of noodle made of konjac-glucomannans in Japan. They have also been used without an alkaline coagulant in confectionary, especially in jelly.

Polysaccharides, which are extracted from seaweeds and used as food ingredients, are
agars, carrageenans and alginates. Agars are members of a class of galactan polysaccharides that occur as intercellular matrix material in numerous species of red seaweeds (marine algae of the class Rhodophyta). Japan continues to be far ahead of any other countries in the production of agars. However, the agar production in other countries is showing a gradual increase. Agars are composed of two major fractions: agarose and agaropectin. It is said that agarose is the gelling portion of agars. Agars have the unique gelation property that occur at low temperatures (30–40 ºC), which are also far below the gel melting points (70–90 ºC). This hysteresis phenomenon of gelation is useful for many applications\(^6\),\(^{16}\). Uses of agars in foods fall mainly within bakery products, confectionery, Japanese desserts and confectionery, meat, fish, poultry products, dairy products and beverages (Table 1.1). Carrageenans also derived from red seaweeds (marine algae of various species of the Rhodophyta). Three basic types are available: kappa, iota and lambda carrageenans, which differ in the number and location of sulfate ester substitution, and differ in the physical properties (Table 1.4). Commercial carrageenans are mixtures of various types; it is approximately 60 % kappa and 40 % lambda\(^3\). The practical utility of the carrageenans derives mainly from their ability to form salt- or cold-setting reversible gels in an aqueous environment and to stabilize milk\(^{17}\). Using carrageenans in milk products is very effective, because carrageenans are incorporated along with milk or milk solids during manufacture of the products\(^{18}\). Carrageenans are also effective in thickening and stabilizing foods, and uses of carrageenans include improved palatability and appearance, and they have also been used in dessert gels, syrup, fish gels, sauces, pet foods, imitation milk and coffee whitener (Table 1.1). Occurring as a structural component in marine

<table>
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<tr>
<th>Carrageenan</th>
<th>Viscosity</th>
<th>Gel type</th>
<th>Solubility</th>
<th>Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kappa</td>
<td>Low</td>
<td>Brittle</td>
<td>Soluble in hot water</td>
<td>Polyol and Protein reactive</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Strong and Firm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Strongest gel with potassium ions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iota</td>
<td>Thixotropic</td>
<td>Elastic</td>
<td>Soluble in cold water</td>
<td>Polyol and Protein reactive</td>
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<td></td>
<td></td>
<td>Weak</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Strongest gel with calcium ions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lambda</td>
<td>High</td>
<td>Non-gelling</td>
<td>Soluble in hot water</td>
<td>Polyol and Protein reactive</td>
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</tr>
</tbody>
</table>

Table 1.4 Physical properties of various carrageenans\(^20\).

6
brown algae (*Phaeophyceae*) and as capsular polysaccharides in soil bacteria, alginates are quite abundant in nature. Alginates form water-soluble sodium alginates by the extraction of alginates from algal materials by using sodium carbonate or sodium hydroxide. Solutions of alginates are in general highly viscous, in particular sodium alginates, and their viscosity is stable in the pH 5–10 for long period at room temperature \(^3\). Alginates have been used in both food and non-food systems as a thickening and a stabilizing agent. When calcium chloride is introduced into a solution of sodium alginates, a gel is formed instantaneously \(^{19}\). By utilizing these high viscosity and gelling ability, alginates and sodium alginates have been used as an additive to improve, modify and stabilize the texture of certain foods such as sauces, dressings, ketchup, mayonnaise, dairy products, confectionary, frozen foods, desserts, jams, pie fillings and mashed potatoes (Table 1.1).

Many microorganisms produce extra-cellular polysaccharides \(^{21}\). Bacterial polysaccharides attract considerable attention, recently. The advantages of these polysaccharides are reproducible chemical and physical properties and a regular source of products. There are curdlan, xanthan gum, gellan gum and pullulan among them. Curdlan is an example of an interesting bacterial polysaccharide that has been developed commercially. This polysaccharide was discovered in 1964, which is prepared from a mutant strain of *Alcaligenes faecalis* var. *myxogenes* \(^{10C3}\) \(^{21}\). It was found to have unusual and interesting gelling properties. Gels are bland in taste, color, and odor, which is valuable in certain food systems such as dairy applications and desserts, especially in Japan, where curdlan is considered a natural product (See Chapter 2). For example; dried *tofu*, which is soybean curd, and *tofu* noodles \(^{21}\). Xanthan gum has been widely used in the food industry, and has triggered further interest in microbial polysaccharides. Beside the use in the food industry, xanthan gum is one of the most studied polysaccharides. Its common and commercial source is the bacterium *Xanthomonas campestris*. Xanthan gum is readily soluble in hot or cold water and produces highly viscous solutions at low concentrations \(^3\). The thixotropy of xanthan gum dispersions has led to the development of a number of dry mix formulations such as sauces and desserts, which can be heated or refrigerated without losing their desirable textural characteristics \(^{22}\) (Table 1.1). Moreover, xanthan gum improves processing and storage of batters and doughs, and it has been suggested that xanthan gum can be used as a gluten replacement in the development of gluten-free breads \(^{23}\). In addition to food applications, xanthan gum has also been used widely in non-food applications, such as non-drip paints, jet-printing, agricultural foams and fire-fighting liquids and oil recovery \(^{22}\). Gellan gum is likely to become the second bacterial polysaccharide to be widely used in the food
industry. Gellan gum is secreted by the microorganism *Sphingomonas elodea* (previously known as *Pseudomonas elodea* of *Auromonas elodea*). The native acylated products show high viscosity at low concentrations and form soft elastic gels after heating and cooling, which are thermoreversible. Whereas, the deacylated products form hard brittle gels similar to agars and carrageenans. Mixture of native and deacylated gellan gum can be used to produce a variety of gel texture, so that gellan gum can be used in a variety of food applications, which include confectionary, jams and jellies, fabricated foods, water-based gels, pie fillings and puddings, icing and frostings and dairy products. Pullulan is the exocellular polysaccharide from *Aureobasidium pullulans*. It is odorless and tasteless, and it dissolves readily in cold water to give a clear and colorless liquid. Pullulan is reported to have the important physiological property of improving the environmental condition in the human intestinal tract; therefore, it is useful in the formulation of special dietary foods.

**PALATABILITY AND TEXTURE**

Eating tasty foods throughout our lives is not only joyful event but also very important to our health. When we add polysaccharides mentioned above to foods for improving texture, the foods should be tasty. Even if they have good physical properties, when they are not delicious, they are absolutely useless. The palatability of foods is evaluated by many factors as shown in Figure 1.1. Among the many factors, food attributes, which represent the direct factors, including chemical factors such as tastes and flavors and physical factors such as texture can be controlled in the food industry, i.e., preparation and processing of foods. Moreover, the large percentage for direct factors contributes to the palatability. Polysaccharides have been added to stabilize the emulsions and the suspensions, and to give the physical structures required for packaging or distribution. More often, the thickening and gelling properties of these polysaccharides are exploited to enhance or standardize the eating quality of products. This means that polysaccharides are the food additives, which can control the texture of foods.

Szczesniak and Kleyn investigated the consumer’s awareness of texture examined by one hundred Americans. One of the most important factors in evaluating the palatability of foods is texture, and it is receiving increasingly more attention. Matsumoto and Matsumoto researched the rate of chemical and physical factors, which contribute to the palatability of foods. They
revealed that solid foods were evaluated mainly by physical properties such as texture, while liquid foods were evaluated mainly by chemical properties.

Many researchers have studied texture-related terms even before investigating the texture itself. Yoshikawa et al. \(^{30, 31}\) collected Japanese terms relating to texture and found more than 12,600 words, many of which were onomatopoetic and mimetic words as compared with English words, and classified them according to the condition of foods. Szczesniak \(^{32}\) divided texture-related terms into three types of texture parameters: mechanical, geometrical and other characteristics. Sherman \(^{33}\) suggested a texture profile that correlated with the process of food intake.

Many researchers have also studied the methods for evaluating texture such as instrumental methods \(^{34-40}\), sensory methods \(^{36-41}\) and intra-oral instrumental methods \(^{34, 42-45}\), which are evaluated by human responses. When we try to evaluate texture, we may face with the problem of measuring texture of foods and we can easily become bewildered by the voluminous literature on texture and the multiplicity of instruments and procedures used to measure textural quality. Bourne \(^{46}\) argued that the reason why so many tests to measure the texture, and concluded that the...
complication of the consumer perspective would make it more difficult to solve than to contend with physical systems alone. We have to use the proper method for various types of foods such as liquid, semi-liquid and solid.

The texture of foods is controlled mainly by polysaccharides and proteins. There are many kinds of gel-like foods in Japan, which contain polysaccharides, and texture control is the one of the most important studies in the food industry.

**TASTE SUBSTANCES**

Foods contain intricate mixtures of tastes. Products made of polysaccharides are no exception.

There are five basic tastes: sweetness, saltiness, sourness, bitterness, and umami. The sense of taste is a chemical stimulus and it is sensed at the taste buds on our tongue. Most people have tens of thousands of taste buds, each containing 50 to 100 taste receptor cells that distinguish the five tastes. Sweet tastes are produced by a large number of substances, which include mono- and oligosaccharides, sugar alcohols, amino acids, peptides, proteins and terpene glycosides. Salty tastes are produced by inorganic and organic salts. Not all salts have the same salty taste: Cl\(^{-}\) ions have a strong salty taste, SO\(_4^{2-}\) ions show an unpleasant taste, Na\(^{+}\) ions exhibit a slightly bitter taste, K\(^{+}\) ions and NH\(_4^{+}\) ions have weak bitter tastes, Mg\(^{2+}\) ions have a strong bitter taste and Ca\(^{2+}\) ions present an unpleasant bitter taste\(^{47}\). Only sodium chloride has pure salty taste and it is simply called salt or cooking salt. Sour tastes are dependent upon hydrogen ions in water. Many kinds of organic acids have refreshing sour tastes. The quality of sour tastes depends on the anions. Almost all foods are acidic, though we are aware of sourness at pH below 4.8\(^{48}\). Bitter tastes are generally not something we are fond of, but they appear to be closely related to sweetness from a molecular structure-receptor relationship\(^{49}\). A natural aversion to bitter tastes can save people from swallowing toxic substances, but some bitter things may actually be healthy, and bitter flavors contribute to the palatability of foods and beverages. We have twenty-four bitter taste receptors to perceive thousands of different bitter substances\(^{50}\). Among bitter compounds in foods are amino acids and peptides, esters and lactones, phenols and polyphenols, flavonoids and terpenes, sulfimides (saccharin), organic and inorganic salts and methylxanthines (caffeine)\(^{51}\). A limited
degree of bitterness is expected and enjoyed\(^{52}\), and the blends of the bitterness and other tastes provide a refreshing gustatory stimulation\(^{49}\). *Umami* tastes, produced by amino acids or nucleic acids, had been thought to be a mixture of sweet and salty tastes\(^{53}\). In the beginning of the 20th century, Japanese researchers, Dr. Ikeda and Dr. Kodama, found *umami* taste substances from kelp and dried bonito, respectively. Subsequently, another Japanese researcher, Dr. Kuninaka, found *umami* taste substances from *shiitake* mushrooms\(^{54}\). Soon afterwards, *umami* taste substances were brought into production and have since been used to prepare soup stocks in Japan. Thus, the Japanese word, *umami*, became an international word.

There are three subsidiary tastes: astringency, acridity and pungency. Subsidiary tastes are accompanied by neurostimulation in addition to the stimulus of tongue by some substances. The definition of astringency is the ability to contract or draw together soft body tissues to check blood flow or to restrict the secretion of fluids. Astringent tastes are the sensation that results when taste buds in the tongue and throat convey information about the chemical composition of a soluble stimulus. It is perceived as a dry feeling in the mouth\(^{49}\). Tannins such as catechin in tea, chlorogenic acid in coffee and ellagic acid in chestnuts have astringent tastes\(^{48}\). We are also generally not fond of astringent tastes, but they are important for tea and wine, both caused by polyphenols. Acrid tastes are unpleasantly sharp, pungent or bitter in taste such as the taste of lye. Homogentisic acid, tannins, oxalic acid and alkaloids have these tastes\(^{48}\). Pungent tastes are defined as tastes that affect the organs of taste or smell with a sharp acrid sensation. Substances with pungent tastes are contained in many kinds of spices and vegetables, have physiological functions and can be used to improve appetites as a secretion of digestive juice, an antibacterial agent and a food preservative\(^{49}\). Some pungent substances found in red (chili) peppers, black pepper and ginger are not volatile and they exert their effects on oral tissues. They are capsaicin in red pepper, piperine in black pepper and gingerol or shogaol in ginger. Other spices and vegetables contain pungent substances that are somewhat volatile, and produce both pungency and characteristic aromas\(^{49}\). They are included in mustard, horseradish, vegetable radishes, onions, garlic, watercress and the aromatic spice, clove. Pungent tastes of *wasabi* (Japanese horseradish) and *sansho* (Japanese pepper) are characteristic tastes in Japan.
**OBJECTIVES IN THIS STUDY**

Starch (corn) and curdlan were selected among numerous polysaccharides in the present thesis. They have a few similar properties. One of them is that both of starch and curdlan consist of D-glucose residues linked. The former has $\alpha$- (1, 4) and $\alpha$- (1, 6) linkages and the latter has $\beta$- (1, 3) linkage (See Chapter 2 and 3). It is generally said that $\beta$- linked configuration results in a rigid backbone or extended chain \(^{55}\), and their dispersions show higher viscosity, e.g., cellulose with $\beta$-(1, 4) linkages, polysaccharides found in the cell walls such as oat, barley, rye and wheat with $\beta$-(1, 3) linkages \(^{55}\). On the other hand, $\alpha$- linked configuration results in a flexible structure, e.g., pullulan with $\alpha$-(1, 4) and $\alpha$-(1, 6) linkages \(^{56}\) and dextran, which is fermented sucrose by *Leuconostoc mesenteroides*, with $\alpha$-(1, 4) and $\alpha$-(1, 3) linkages \(^{57}\). As the linkages of cornstarch and curdlan are different, they may have different physical properties. Another similar properties of cornstarch and curdlan are insoluble in water, and the endothermic events occur upon heating of their aqueous dispersions. Although it is generally difficult to add insoluble polysaccharides to foods, starch is the most widely used polysaccharide in the food industry, and curdlan is expected to be more used. Therefore, their viscoelasticities at various conditions were investigated to develop their further utilization in food industry.

The texture of foods is not only controlled by polysaccharides but also by taste substances, since some of taste substances have been found to affect the rheological properties of polysaccharides. In other words, the chemical factors of foods have effects on the physical factors of foods, and vice versa the physical factors influence the chemical factors (Figure 1.1).

To confirm the effects of taste substances on the physical properties, cornstarch and five basic taste substances were used in this thesis. The following taste substances were selected: sucrose of sweet substances; sodium chloride (NaCl) of salty substances; citric acid, acetic acid, lactic acid, malic acid, tartaric acid and ascorbic acid of sour substances; caffeine of bitter substances and sodium L-glutamate (MSG) of *umami* substances. Sucrose, sodium chloride, citric acid, caffeine and sodium L-glutamate are important as basic substances for difference tests in the sensory evaluation \(^{58}\). Products made of starch contain these taste substances. The function of starch includes stabilizing and thickening foods or dishes. Some taste substances are believed to interact with starch and thereby may change the texture to an undesirable one in starch products.

Therefore, it is worthwhile to investigate the effects of taste substances on the physical
properties of cornstarch pastes since it may lead us to understanding how to control the viscosity of starch products.
2. GELATION MECHANISM OF CURDLAN

INTRODUCTION

Curdlan is a microbial polysaccharide, which has been produced by *Alcaligenes Faecalis var. myxogenes* 10C3 \(^2\). Curdlan consists of the linear β-(1, 3) D-glucose residues (Figure 2.1). Curdlan is insoluble in water, while it is soluble in dimethyl sulfoxide (DMSO) or in alkaline solutions. When an aqueous dispersion of curdlan is heated, the curdlan can swell in water and the dispersion forms a gel. It forms a so-called low-set gel, which is thermo-reversible, by heating at around 60 °C. On the other hand, it forms a thermo-irreversible gel, which is called high-set gel, by heating at above 80 °C. It is said that thermo-reversible gels are formed by hydrogen bonds, and hydrophobic interactions contribute for the formation of thermo-irreversible gels \(^5\). The swelling of curdlan accompanies with the endothermic reaction on heating \(^5\), and the exothermic reaction occurs by the formation of hydrogen bonds on cooling \(^6\). Konno et al. \(^6\) showed that the gels formed by dispersions heated in the temperature range from 60 to 120 °C were thermo-reversible, and gels formed by heating at above 145 °C were thermo-irreversible. Funami et al. \(^6\) investigated the effects of heating rate on the formation of thermo-reversible gels. They reported that thermo-reversible gelation was inhibited with decreasing heating rate. Harada et al. \(^6\) demonstrated by X-

![Figure 2.1](image_url)  
*Figure 2.1* Chemical structure of curdlan.
ray diffraction analysis that the single stranded helices in curdlan were converted to triple stranded helices by heating at higher temperatures and then cooling. Zhang et al. 63), 64) also concluded by NMR results that the formation of gels based on the formation of triple helices. Moreover, a dilute alkaline solution of curdlan can form a gel without heating when it is neutralized with acid 65). This gel is also formed by hydrogen bonds. Funami et al. 61) found that the viscoelasticity for curdlan in an alkaline solution was greater than that in an aqueous dispersion. Watase and Nishinari 66) reported that curdlan in DMSO aqueous solutions could form gels, which were very stable, when they were heated at between 50 and 60 °C.

In this chapter, the gelation mechanism and properties of curdlan aqueous solutions were investigated for the further development in the industrial utilization. Curdlan has been used for controlling the texture of various foods such as udon, which is Japanese noodles, surimi, which is fish paste, hams and sausages, jellies, jams, tofu, which is soybean curd 67). Some of them have successfully been used in the food industry. For example, spherical jelly containing fruit juice; when dispersions of curdlan containing fruit juices are heated, the gel formation occurs from the outer surface of the spheres. Frozen tofu containing curdlan has a smooth texture because curdlan gels are stable even if they are treated with freeze-thawing 68), 69). Moreover, curdlan will attract more attention because it consists of β-glucose residues. It is said that β-glucose residues have an anticancerous property 70), 71).

The objectives of this chapter are to investigate the differences in the viscoelasticity between the solution and the dispersion of curdlan, and the effects of heating temperature on the gelation mechanism for curdlan aqueous dispersions.

MATERIALS AND METHODS

Materials

A curdlan sample (Lot. DL–15A) was kindly provided by Takeda Chemical Industries, Ltd. (Osaka, Japan). Chemical analyses of curdlan sample are listed in Table 2.1*. The concentration of curdlan (C_{cu}) varied between 2 and 4 wt% for curdlan aqueous dispersions, and between 1 and 3 wt% for dimethyl sulfoxide (DMSO) solutions, between 2 and 10 wt% for differential scanning

* Data were provided by Takeda Chemical Industries, Ltd.
calorimetry (DSC) measurements. DMSO was purchased from Wako Pure Chemical Industries, Inc. (Osaka, Japan).

**Preparation of curdlan DMSO solutions**

Powders of curdlan were dissolved in DMSO, stirring with a magnetic stirrer at room temperature. After curdlan was dissolved completely in DMSO, the solutions were kept at 40 ºC overnight, stirring with a magnetic stirrer.

**Preparation of curdlan aqueous dispersions**

Powders of curdlan were dispersed in distilled water at room temperature, followed by homogenization with a rate of 1200 rpm at 0 ºC. A plunger (18.5 mm diameter) of the homogenizer was made of PTFE (polytetrafluoroethylene). Then the dispersions were transferred into vials, which were soaked in the mixture of ice and water, and sonicated for 10 min. The dispersions were stirred with a magnetic stirrer at 40 ºC overnight.

**Steady shear and dynamic oscillatory measurements**

Steady shear and dynamic oscillatory measurements for curdlan DMSO solutions and aqueous dispersions were carried out using a Fluids Spectrometer RFS II (Rheometrics Co. Ltd., New Jersey, U.S.A.) with a 25 mm diameter plate geometry. From steady shear measurements, the shear stress ($\sigma$) at 40.0 ºC was obtained, and from dynamic oscillatory measurements, the storage

<table>
<thead>
<tr>
<th>Item</th>
<th>Standard value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic ($\text{As}_2\text{O}_3$) / $\mu$g/g</td>
<td>below 2</td>
</tr>
<tr>
<td>Heavy metal (Pb) / $\mu$g/g</td>
<td>below 20</td>
</tr>
<tr>
<td>Water content / %</td>
<td>6.2</td>
</tr>
<tr>
<td>Ash content / %</td>
<td>5.8</td>
</tr>
<tr>
<td>Turbidity 660nm T%</td>
<td>97</td>
</tr>
<tr>
<td>(Dispersion of 2 % curdlan)</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.3</td>
</tr>
<tr>
<td>Viable bacteria / g</td>
<td>560</td>
</tr>
<tr>
<td>Mold and Yeast / g</td>
<td>below 10</td>
</tr>
<tr>
<td>Coliform bacteria</td>
<td>negative</td>
</tr>
</tbody>
</table>
modulus ($G'$), the loss modulus ($G''$), loss tangent ($\tan\delta = G''/G'$) and the complex viscosity ($|\eta^*|_\omega = \sqrt{G'^2 + G''^2}/\omega$) were obtained. The frequency dependence measurements at 40.0 and 70.0 °C, time dependence measurements at 70.0 °C and temperature dependence measurements in temperature ranges from 20.0 °C to various temperatures between 50.0 and 90.0 °C were conducted. The heating and cooling rate was 1.0 °C/min. Strains for dynamic oscillatory measurements were chosen in the plateau range of each sample on the strain dependence test.

**Steady stress measurements**

Steady stress measurements for curdlan aqueous dispersions were carried out using a Dynamic Stress Rheometer DSR (Rheometrics Co. Ltd., New Jersey, U.S.A.) with a 25 mm diameter plate geometry. $\sigma$ dependence of the strain ($\gamma$) measurements were used to determine the yield stress of curdlan aqueous dispersions. $\sigma$ was applied from 0 to 5 Pa for 2 and 3 wt% curdlan dispersions or from 0 to 10 Pa for 4 wt% curdlan dispersions with the different time of 60, 120 and 180 sec. Measurements were made at 40.0 °C.

**DSC measurements**

DSC measurements were conducted using a PTC-10D, 8240A (Rigaku Corporation, Tokyo, Japan) with 70 μl silver (Ag) pans. Curdlan (5, 7.5 and 10 wt%) and distilled water were mixed in the Ag pans. They were added up to total sample weights of 45 mg, then sealed. The pans were stored at room temperature overnight for the curdlan sample immersing in water. Samples were heated from 25 °C to various temperatures between 40 and 110 °C at a heating rate of 1.0 °C/min (first scanning), and they were kept at the temperature for 60 min. Then, the samples were cooled to 10 °C by using liquid nitrogen, and they were reheated from 10 °C to 80 °C at the same heating rate mentioned above (second scanning). From DSC curves, the onset temperature ($T_o$), the peak temperature ($T_p$), the conclusion temperature ($T_c$), swelling temperature range for peaks ($\Delta T = T_c - T_o$) and the swelling enthalpy for curdlan dispersion ($\Delta H_{cw}$) could be obtained.

A micro DSCIII (Setaram Inc., Caluire, France) was also used for DSC measurements to investigate the thermal properties of curdlan on cooling with 1000 μl stainless steel pans. Curdlan (2 wt%) and distilled water were mixed in the pans. They were added up to total sample weights of 900 mg, then sealed and they were kept overnight as mentioned above. Samples were also heated from 20 °C to various temperatures between 50 and 115 °C at a heating rate of 1.0 °C/min, and they
were kept at the temperature for 30 min. Then, the samples were cooled to 10 °C at a cooling rate of 1.0 °C/min. From cooling DSC curves, the onset temperature \( (T_o) \), the higher peak temperature \( (T_p^1) \), the lower peak temperature \( (T_p^2) \), the conclusion temperature \( (T_c) \), temperature range for peaks \( (\Delta T = T_c - T_o) \) and the enthalpy for two peaks \( (\Delta H_{cu}^1) \) could be obtained.

Distilled water was used as a reference for all DSC measurements.

RESULTS AND DISCUSSION

The viscoelasticity of curdlan dimethyl sulfoxide (DMSO) solutions

Curdlan is insoluble in water, while it is soluble in DMSO, so that the viscoelasticity for curdlan aqueous solutions and curdlan DMSO solutions should be quite different (Compare, e.g., Figure 2.2 and Figure 2.3). At first, the property of DMSO solutions for curdlan is discussed.

Figure 2.2 illustrates angular frequency \( (\omega) \) dependence of storage modulus \( (G') \) and loss modulus \( (G'') \) for curdlan DMSO solutions with various concentrations between 1 and 3 wt%.

![Figure 2.2: Angular frequency (\(\omega\)) dependence of storage modulus (\(G'\), left) and loss modulus (\(G''\), right) for curdlan DMSO solutions with various concentrations between 1 and 3 wt%. Measurements were made at 40.0 °C. The strain for 1, 1.5, 2, 2.5 and 3 wt% curdlan solutions, was 25, 15, 15, 15 and 3.5 %, respectively.](image-url)
modulus ($G''$) for curdlan DMSO solutions with various curdlan concentrations ($C_{cu}$) at 40.0 °C. Samples with $C_{cu} < 2.5$ wt% showed a typical behavior known for the concentrated solutions of flexible polymers, i.e., $G'$ is less than $G''$ at lower $\omega$ and $G'$ is greater than $G''$ at higher $\omega$. The values of $G'$ and $G''$ increased with increasing $C_{cu}$ and the cross points of $G'$ and $G''$ shifted to lower $\omega$ with increasing $C_{cu}$. This characteristic behavior reflects the timescale of the molecular entanglements. At higher $\omega$, where entanglements of interchains do not have sufficient time to come apart within the period of oscillation, the network behaves like crosslinked gels, while at lower $\omega$, the chains do have sufficient time to disentangle and flow, and the solutions behave like liquid. $G'$ predominated over $G''$ at all $\omega$ examined and $G'$ and $G''$ increased slightly with increasing $\omega$ for solutions with $C_{cu} > 2.5$ wt%. This behavior is classified as a weak gel. Weak gels may undergo conformational disorder-to-order transitions accompanied by the set up of three-dimensional networks. The junction zone formations are believed to occur via associations of ordered regions, though, in some cases, the junction zones are much less stronger than true gels, so that the networks formed would be essentially transient and are therefore called weak gels. It was found that junction zones and entanglements in curdlan DMSO solutions increased with increasing $C_{cu}$, then curdlan DMSO solutions with $C_{cu} > 2.5$ wt% behaved like weak gels.

Yield stress of curdlan aqueous dispersions

Next, aqueous dispersions for curdlan, which are insoluble states, are discussed.

Figure 2.3 shows $\omega$ dependence of $G'$ and $G''$ for curdlan aqueous dispersions with various $C_{cu}$ at 40.0 °C (left) and 70.0 °C (right). $G'$ was greater than $G''$ at all $\omega$ examined, and $G'$ and $G''$ did not depend on $\omega$ so much. This is one of the characteristics for the viscoelastic solid. Although the samples at 40.0 °C could flow and the gelation did not occur visibly, the aqueous solutions of curdlan behaved as solid-like. The similar rheological behavior for dispersions has been also reported, for example; solutions of a mixture for alkyltrimethylaminoxides and hexane, dispersions of monodisperse polystyrene lattices, ovalbumin aqueous colloids and xanthan-konjacmannan dispersions.

The values of $G'$ and $G''$ for samples at 70.0 °C were greater than those for samples at 40.0 °C. Loss tangent (tan$\delta$) at 70.0 °C was far less than that at 40.0 °C (Figure 2.4). This indicates that the dispersions have changed into more solid-like state by heating at 70.0 °C.

Figure 2.5 indicates the complex viscosity ($|\eta^*|_\omega$) for aqueous dispersions of curdlan with
Figure 2.3 Angular frequency ($\omega$) dependence of storage modulus ($G'$, solid) and loss modulus ($G''$, hollow) for curdlan aqueous dispersions with various concentrations between 2 and 4 wt%. Measurements were made at 40.0 ºC (left) and 70.0 ºC (right). The strain for 2, 3 and 4 wt% curdlan dispersions, was 3.5, 2.5 and 2.5 %, respectively.

Figure 2.4 Angular frequency ($\omega$) dependence of loss tangent ($\tan\delta$) for curdlan aqueous dispersions with various concentrations between 2 and 4 wt%. Measurements were made at 40.0 ºC (solid) and 70.0 ºC (hollow). The strain for 2, 3 and 4 wt% curdlan dispersions, was 3.5, 2.5 and 2.5 %, respectively.
Figure 2.5 Complex viscosity ($|\eta^\ast|_\omega$) for curdlan aqueous dispersions with various concentrations between 2 and 4 wt% as a function of angular frequency ($\omega$). Measurements were made at 40.0 °C. The strain for 2, 3 and 4 wt% curdlan dispersions, was 3.5, 2.5 and 2.5 %, respectively.

Various concentrations as a function of $\omega$ at 40.0 °C. $G'$ and $G''$ did not depend on $\omega$, however, the magnitude of $|\eta^\ast|_\omega$ tended to infinity for lower $\omega$: $\lim_{\omega \to 0} |\eta^\ast|_\omega = \infty$; this can be regarded as an indication for the existence of yield stress \(^{72}\).

Figure 2.6 shows the shear stress ($\sigma$) for curdlan dispersions with various concentrations and distilled water as a function of shear rate ($\dot{\gamma}$) at 40.0 °C. $\sigma$ for distilled water showed the Newtonian flow behavior, i.e., $\sigma$ increased proportionally with increasing $\dot{\gamma}$. While, all curdlan dispersions showed the shear-thinning behavior and $\sigma$ had a plateau region at lower $\dot{\gamma}$. The values of $\sigma$ at lower $\dot{\gamma}$ increased with increasing $C_{cu}$. It is thought that this behavior is observed for the dispersions with crystal like structures of the dispersing particle \(^{75}\). This also indicates that curdlan dispersions have a yield stress \(^{75}\).

Then, the yield stress was determined by the method, which Hoffmann et al. used \(^{72}\). They obtained the yield stress from different values of strain ($\dot{\gamma}$) by stress applied at different times. In this study, 60, 120 and 180 sec were used as different times. $\sigma$ and $\dot{\gamma}$ were linear at lower $\sigma$ and $\dot{\gamma}$,
indicating the elastic response, but a deviation was observed above a certain stress, which is yield stress (Figure 2.7). The dispersions of curdlan behaved as an elastic solid below the yield stress, and it began to flow above the yield stress. The values of the yield stress for 2, 3 and 4 wt% curdlan dispersions were determined to be 0.1, 0.12 and 1.2 Pa, respectively. The yield stress increased with increasing $C_{cu}$, and increased sharply for curdlan dispersions with $C_{cu}$ above 4.0 wt%. The yield stress is originated from the ordered arrangements of the molecules, and it is a certain measure of the strength of the solid structure and strongly correlates to the rigidity of the system \(^{78}\). This indicates that curdlan aqueous dispersions have an elastic solid behavior.

The difference in the mechanical spectra of true gels and these dispersions cannot be distinguished only by the measurement of the $\omega$ dependence in the small deformation range \(^{79}\). These dispersions, having a yield stress, flow under the shear, which is higher than the yield stress, while the true gels break beyond a certain deformation.
Chapter 2

Figure 2.7 Strain ($\gamma$) for 2 (left), 3 (center) and 4 (right) wt% curdlan aqueous dispersions as a function of shear stress ($\sigma$). $\sigma$ was changed from 0 to 5 Pa for 2 and 3 wt% dispersions and from 0 to 10 Pa for 4 wt% dispersions in different times of 60, 120 and 180 sec. Measurements were made at 40.0 °C.

The gelation rate for curdlan aqueous dispersions at 70 °C

The curdlan aqueous dispersions could form gels by heating at 70.0 °C. During gelation, the magnitude of both $G'$ and $G''$ increases, however, in most cases, the increase in $G'$ is much higher than that in $G''$. Therefore, $G'$ alone can be used to quantitatively determine the structure development rates. Then, the changes in $G'$ for curdlan aqueous dispersions with various $C_{cu}$ at 70.0 °C were examined (Figure 2.8). The values of $G'$ increased sharply in 1000 sec and approached the certain values. All these curves were approximated well by a first-order reaction equation:

$$G'(t) = G'_s \left[1 - \exp\left(-K(t-t_0)\right)\right] \quad (2.1)$$

where $G'_s$ is the saturated value of $G'$ after a sufficient long time, $K$ is the rate constant, $t$ is time and $t_0$ is the latent time. In the present case, curdlan dispersions were kept at 70.0 °C, therefore, $t_0$ was almost negligible, i.e., the gelation began to occur almost without delay.

Then, Equation 2.2 is changed to a logarithm:

$$K(t-t_0) = -\log(1 - G'/G'_s) \quad (2.2)$$

$K$ was calculated from the slope of $-\log(1 - G'/G'_s)$ as a function of $(t-t_0)$. The values of $K$ for 2, 3 and 4 wt% curdlan aqueous dispersions were $0.9 \times 10^{-3}$, $1.2 \times 10^{-3}$ and $1.3 \times 10^{-3}$, respectively. It was found that the gelation proceeded faster with increasing $C_{cu}$.
Gelation mechanism of curdlan

Figure 2.8 Time ($t$) dependence of storage modulus ($G'$) for curdlan aqueous dispersions with various concentrations between 2 and 4 wt%. Measurements were made at 70.0 °C. The angular frequency was 1.0 rad s$^{-1}$. The strain for 2, 3 and 4 wt% curdlan dispersions, was 3.5, 2.5 and 2.5 %, respectively.

The temperature dependence of the gelation for curdlan aqueous dispersions

The temperature ($T$) dependence of $G'$ for curdlan aqueous dispersions with various $C_{\text{cu}}$ were demonstrated in Figure 2.9 (left). The samples were heated from 20.0 °C to 70.0 °C and were kept at 70.0 °C for 30 min, then they were cooled to 20.0 °C. All samples showed the similar tendency. Upon heating, $G'$ decreased with increasing $T$, where $T$ was below 55 °C, indicating a liquid behavior. $G'$ began to increase with increasing $T$, where $T$ was above 55 °C. It is thought to be due to the swelling of curdlan$^{59,60}$. The values of $G'$ increased during keeping samples at 70.0 °C, indicating the gelation of curdlan. $G'$ decreased with decreasing $T$ down to around 40 °C on cooling, but $G'$ for 2 wt% samples did not depend on decreasing $T$. Then $G'$ increased remarkably at 40 °C. It reflected the gelation by the formation of hydrogen bonds$^{60,81}$. $T$ at the sharp increases of $G'$ for 2, 3 and 4 wt% dispersions were 41.3, 42.8 and 44.7 °C, respectively. This result signifies that the number of hydrogen bonds in curdlan dispersions increases with increasing $C_{\text{cu}}$, and the gelation can occur at higher temperatures for dispersions with higher $C_{\text{cu}}$. The samples described in Figure
Figure 2.9 Temperature ($T$) dependence of storage modulus ($G'$) for curdlan aqueous dispersions with various concentrations between 2 and 4 wt%. Samples were heated from 20.0 ºC to 70.0 ºC, then samples were cooled from 70.0 ºC to 20.0 ºC. The measurements were repeated 2 times. First measurements were illustrated on left, and second ones were on right. The angular frequency was 1.0 rad s$^{-1}$. The strain for 2, 3 and 4 wt% curdlan dispersions, was 3.5, 2.5 and 2.5 %, respectively.

2.9 (left) were heated and cooled again in the same temperature range and at the same heating and cooling rate (Figure 2.9 right). $G'$ decreased gradually at $T < 50$ ºC, and decreased sharply at 50 ºC on reheating, indicating the breaking hydrogen bonds, which were formed by cooling. The values of $G'$ at 70.0 ºC were almost same as those of $G'$ at 70.0 ºC, when the samples were heated at first. $G'$ of 4 wt% dispersion increased with increasing $T$, where $T \geq 60$ ºC. It is thought to be due to the gelation by the hydrophobic interactions, which is thermo-irreversible $^{60,81}$. When $C_{cu}$ increases, the number of hydrophobic interactions of curdlan increases, so that this tendency could be observed only in 4 wt% curdlan aqueous dispersion. $G'$ decreased with decreasing $T$ on recooling, and increased sharply at around 40 ºC again because of the formation of hydrogen bonds. Hydrogen bonds were broken at 50 ºC on reheating and they were formed at 40 ºC on recooling. This hysteresis is often observed in gels formed by hydrogen bonds $^7$. The values of $G'$ at 20.0 ºC were almost same as those of $G'$ at 20.0 ºC after first heating and cooling. The hydrogen bonds formed by
heating at 70.0 °C and cooling, were thermo-reversible. This process may be repeated continuously with no anticipated loss of properties.

Here, the increments of $G'$ at around 40 °C on cooling ($G'_i$) were examined by changing heating temperatures and were calculated from the following equation:

$$G'_i = \frac{G'_{\text{max}}}{G'_{50}} \quad (2.3)$$

where $G'_{\text{max}}$ is the maximum values of $G'$ below 50 °C on cooling and $G'_{50}$ is the values of at 50 °C on cooling.

$G'_i$ increased with increasing heating $T$ (≤ 70 °C), in particular, sharp increment of $G'_i$ could be observed at heating $T = 60$ °C (Figure 2.10). These higher values of $G'_i$ means that many hydrogen bonds are formed by heating at around 70 °C. $G'_i$ decreased inversely with increasing heating $T$ (> 70 °C). The curdlan dispersions form gels on heating at higher $T$, their main molecular forces, which are responsible for the formation of junction zones, are considered as hydrophobic interactions. This indicates that the formation of hydrophobic interactions is promoted by heating at higher $T$, i.e., $T > 70$ °C. It is thought that the formation of hydrogen bonds is prevented by the

![Figure 2.10](image-url)

**Figure 2.10** Effects of heating temperature ($T$) on the increment of $G'$ at around 40 °C on cooling ($G'_i$) for 2 wt% curdlan aqueous dispersions.
formation of hydrophobic interactions.

The effects of heating temperature for the gelation are discussed in the next section.

**Differential scanning calorimetry (DSC) measurements**

Figure 2.11 shows heating DSC (first scanning) curves for 5, 7.5 and 10 wt% curdlan aqueous dispersions. Endothermic peaks were observed at around 58 °C because of the swelling of curdlan. Peak temperatures and enthalpy ($\Delta H_{cu}$) did not depend on the $C_{cu}$ so much in the concentration range examined (Figure 2.12). These tendencies were in good agreement with a previous study 59. The sharpness of the peak was estimated from the peak height and the temperature range ($\Delta T$):

\[
\text{Sharpness of the peak (mW °C}^{-1}\text{)} = \frac{\text{peak height (mW)}}{\Delta T (^{\circ}C)} \tag{2.4}
\]

**Figure 2.11** Heating (first scanning) DSC curves for curdlan aqueous dispersions with various concentrations between 5 and 10 wt%. Characters beside each curve represent the curdlan concentrations. The heating rate was 1.0 °C/min.
The sharpness of the peak for 5, 7.5 and 10 wt% curdlan dispersions were $3.0 \times 10^{-3}$, $4.6 \times 10^{-3}$ and $5.4 \times 10^{-3}$ mW °C$^{-1}$, respectively. The peaks became sharper with increasing $C_{cu}$.

Cooling DSC curves for 2.0 wt% curdlan dispersions are illustrated in Figure 2.13. Heating $T$ varied between 50 and 115 °C. No peak could be observed in the cooling DSC curves for dispersions heated at $T \leq 50$ °C, while double exothermic peaks at around 38 and 31 °C appeared for dispersions heated at $T > 50$ °C. These exothermic peaks were attributed to the structure ordering due to the formation of hydrogen bonds $^{60,81}$. The curdlan dispersion, which was heated at 70 °C, had a maximum value of endothermic enthalpy ($\Delta H_{cu}^{c}$) (Figure 2.14). It is thought that many hydrogen bonds in curdlan dispersions are formed by heating at 70 °C, and the hydrophobic interactions become stronger with increasing heating $T$ (> 70 °C). These results coincided with that of $G'$ (Figure 2.10). From the results in Figure 2.10 and 2.14, it is thought that the formation of hydrogen bonds are prevented by heating at higher $T$ since the gels formed by hydrophobic interactions might be a rigid structure, in which the molecular motions are restricted, although hydrophobic interactions are weak interactions in comparison with hydrogen bonds or covalent bonds. Then, the
Figure 2.13 Cooling DSC curves of 2 wt% curdlan aqueous dispersions. Measurements were made after heating samples up to various temperatures (T) between 50 and 115 °C and keeping at various T for 30 min. Characters beside each curve represent the heating T, at which the dispersions were kept. The cooling rate was 1.0 °C/min.

Figure 2.14 Effects of heating temperature (T) on the exothermic peaks of T and enthalpy (ΔH_{cu}) of 2 wt% curdlan aqueous dispersions on cooling. T_o: onset temperature; T_{p1}: higher peak temperature; T_{p2}: lower peak temperature; T_c: conclusion temperature; ΔT: peak temperature range T_c – T_o and ΔH_{cu}: enthalpy for mg curdlan.
rearrangement of molecular chains was inhibited for the dispersions heated at higher $T$ (above 70 °C)\(^{82}\).

Figure 2.15 demonstrates the reheating (second scanning) DSC curves for 5, 7.5 and 10 wt% curdlan dispersions, which had been heated at various $T$ between 40 and 110 °C for 60 min. When the curdlan dispersions were heated at $T \leq 50$ °C, there were no differences between reheating and heating (first heating) DSC curves. Therefore, heating at $T \leq 50$ °C did not affect curdlan dispersions. The endothermic peaks became smaller and shifted to higher temperature with increasing heating $T$, where $T > 50$ °C, and the endothermic peaks inversely shifted to lower temperature for the curdlan dispersions, which had been heated at $T \geq 60$ °C.

Two endothermic peaks were observed in the DSC curves for the dispersions, which had been heated at 50 °C $< T \leq 62$ °C (Figure 2.16). It is thought that two kinds of structural disordereding with different thermal energies may occur in the dispersions heated in this $T$ range. The main endothermic peaks around 58 °C were shifted to higher temperatures with increasing first heating $T$ up to 60 °C, and these peaks disappeared by heating at $T > 62$ °C. These peaks were thought to be
Figure 2.16 Reheating (second scanning) DSC curves of 10 wt% curdlan aqueous dispersions. Measurements were made after heating samples up to various temperatures ($T$) between 50 and 63 ºC, keeping at various $T$ and cooling to 10 ºC. Characters beside each curve represent the heating $T$, at which the dispersions was kept. The heating rate was 1.0 ºC/min.

due to the swelling of curdlan. Curdlan could swell completely by heating at $T > 62$ ºC, and the swelling of curdlan was thermo-irreversible. Therefore, these peaks could not be observed by heating samples again. The endothermic peaks at lower $T$ around 53 ºC became larger with increasing first heating $T$ up to 70 ºC and became smaller with increasing first heating $T$ above 70 ºC. This tendency is similar to that for exothermic peaks on cooling (Figure 2.14). From the reheating DSC curves, the enthalpy for lower peaks of curdlan dispersion ($\Delta H_{cu}^l$) and the enthalpy for higher peaks (swelling) of curdlan dispersion ($\Delta H_{cu}^h$) were estimated.

Figure 2.17 shows the changes in $\Delta H_{cu}^l$ and $\Delta H_{cu}^h$ on reheating and exothermic peaks ($\Delta H_{cu}^c$) on cooling for the curdlan dispersions. The changes in $\Delta H_{cu}^l$ and $\Delta H_{cu}^c$ were almost the same, therefore, lower endothermic peaks on reheating were caused by breaking hydrogen bonds.
Figure 2.17 Changes in the enthalpy ($|\Delta H_{cu}|$) of 2 wt% curdlan aqueous dispersions on cooling and 10 wt% curdlan dispersions on reheating. Samples were heated at various temperatures ($T$) between 40 and 115 °C and keeping at various $T$ for 30 and 60 min, respectively. $\Delta H_{cu}^c$: the exothermic enthalpy of mg curdlan on cooling and $\Delta H_{cu}^l$ and $\Delta H_{cu}^h$: the endothermic enthalpy for lower and higher peaks of mg curdlan on reheating, respectively. The heating and cooling rate was 1.0 °C/min.

It was found that the gels formed by heating at $50 \, ^\circ C < T \leq 115 \, ^\circ C$ were partially thermo-reversible, because exothermic peaks on the cooling DSC curves and endothermic peaks in the reheating DSC curves could be observed. This thermo-reversible networks were formed by hydrogen bonds \(^7, \, ^{81}\). The thermo-irreversible gels might be formed by heating at $T > 115 \, ^\circ C$. It seems that they have more rigid structure, and show no exothermic peaks on cooling, because the more rigid structure does not allow the rearrangement of molecular chains by the formation of hydrogen bonds on cooling. Then the degree of thermo-irreversible gelation ($dG$) was calculated from $\Delta H_{cu}^l$ and $\Delta H_{cu}$.

$$dG (\%) = \left\{1 - \frac{\Delta H_{cu}^l}{\Delta H_{cu}}\right\} \times 100 \quad (2.5)$$

Figure 2.18 shows $dG$ for aqueous dispersions of curdlan with various concentrations. When gels are completely thermo-irreversible, endothermic peaks for the breaking of hydrogen bonds can be observed.
bonds cannot be observed on the reheating DSC curves, then $dG$ becomes 100 %. $dG$ was zero at heating $T \leq 45 \, ^\circ C$, indicating that gels did not form. As it is clear from Figure 2.18, $dG$ increased steeply with increasing heating $T$ up to 70 \, ^\circ C, and continued to increase gradually with increasing heating $T$ above 70 \, ^\circ C. This indicates that the aqueous dispersions of curdlan heated at $45 \, ^\circ C < T < 110 \, ^\circ C$ forms partially irreversible gels, and tends to become almost irreversible gels at heating $T \geq 110 \, ^\circ C$. $dG$ did not depend on $C_{cu}$ so much.

The thermo-irreversible gel could be formed completely by heating at $T \geq 110 \, ^\circ C$ from the results of $dG$ on reheating DSC measurements, however, it was found from cooling DSC measurements that thermo-irreversible gel could not form by heating at $T \leq 115 \, ^\circ C$. This gap of the results might be the differences in sensitivity of instruments, therefore, the thermo-irreversible gel might be formed by heating at $T > 115 \, ^\circ C$.

**Figure 2.18** The degree of thermo-irreversible gelation ($dG$) for curdlan dispersions with various concentrations as a function of heating temperature ($T$). The concentration of curdlan was 5, 7.5 and 10 wt%. 

![Graph showing the degree of thermo-irreversible gelation (dG) for curdlan dispersions with various concentrations as a function of heating temperature (T). The concentration of curdlan was 5, 7.5, and 10 wt%.](image-url)
CONCLUSIONS

The mechanical spectra for the curdlan DMSO solutions and curdlan aqueous solutions were quite different. The former showed a typical behavior known for the concentrated solutions of flexible polymers and weak gels, where the concentration of curdlan ($C_{cu}$) was below 2.5 wt% and $C_{cu}$ was more than 2.5 wt%, respectively, and the latter showed a solid-like behavior, where $C_{cu}$ was between 2 and 4 wt%. This behavior of curdlan dispersions could be observed at all temperature examined, and The dispersions behaved more solid like with increasing temperature. Moreover, aqueous dispersions of curdlan had the yield stress.

Endothermic peaks at around 58 ºC on heating (first scanning) DSC curves of curdlan dispersions were observed because of the swelling of curdlan Exothermic peaks at around 38 ºC on cooling DSC curves for the sample heated at more than 50 ºC were observed. These exothermic peaks were caused by the formation of the hydrogen bonds. When samples were heated up to between 50 and 110 ºC and were cooled, two endothermic peaks appeared on reheating (second scanning) DSC curves. These endothermic peaks indicate that curdlan samples prepared by heating at less than 110 ºC have formed thermo-reversible gels and partially thermo-irreversible gels, and the curdlan aqueous dispersions need to be heated at more than 115 ºC to form completely thermo-irreversible gels.
3. PHYSICAL PROPERTIES OF CORNSTARCH

INTRODUCTION

Starch is among the most abundant of plant products. Starch, both native and modified, has been widely used as a thickener, a stabilizer or a gelling ingredient in the food industry. The main constituents of starch are amylose and amylopectin, which consist of the linear $\alpha$- (1, 4) D-glucose residues linked and branched $\alpha$- (1, 6) D-glucose residues linked that make large polysaccharide molecules (Figure 3.1). Amylose and amylopectin play a significant role in dictating the functional properties of starch. The ratio of amylose to amylopectin depends on the botanical origin. Starch is

![Figure 3.1 schematic structures of amylose (top) and amylopectin (bottom).](image-url)
present in the form of granules, which is partially crystalline and birefringent. The form, size and crystalline structure of starch granules also depend on their botanical origin.

When starch is heated in water at a higher temperature (about 80 °C), the starch granules swell. Starch granules lose their crystallinity, birefringence and double helical structures. Amylose and amylopectin can be leached out from the granules, and starch granules rupture. This process is an endothermic melting or dissociation known as the gelatinization. It depends on temperature, the amount of water present, agitation during heating, heating rate, etc. As a result of the gelatinization, starch pastes develop the viscosity, which make them technically useful as an ingredient in many kinds of foods. However, starch granules are not soluble in water because both amylose and amylopectin are high in molecular weight and tend to aggregate. These properties make the usage in foods difficult. It is also difficult to measure the functional properties of starch in neutral aqueous solution, because rheological properties of starch pastes and gels are determined by both the dispersed swollen granules and the continuous phase. Furthermore, gelatinized starch regains some of their structural orders during storage, and aggregations are observed. It is known as the retrogradation. It makes more difficult to measure the functional properties of starch. Besides the difficulties of the measurements, textural changes become apparent, and the phenomena of hardening and staling occur during retrogradation. These changes are not generally desirable for starch products.

In this study, cornstarch was selected among numerous types of starches because cornstarch has been used the most in the food industry. There are many reports concerning the gelatinization and the retrogradation of native starches. Many researchers have studied the viscosity of pastes or the strength of gels \( 83-99 \) or the gelatinization temperature and the enthalpy \( 86-88, 93, 94, 96-104 \) for starch. However, they have used many types of starch such as potato \( 87-90, 103, 104 \), wheat \( 84, 87-90, 100, 102-104 \), rice \( 101, 104 \), various beans \( 85, 86, 91, 97 \), cassava \( 103 \), sago \( 103 \), oat \( 98 \), barley \( 102 \) and corn \( 91, 93-96, 99, 102-104 \), and the samples were prepared in their methods. Consequently, the physical properties of cornstarch have not been completely known yet. It should be useful to know the properties of cornstarch pastes for making the best use in foods as a thickener.

The objectives of this chapter are to know the physical properties of cornstarch used in this research and to make reproducible samples.
MATERIALS AND METHODS

Materials

A cornstarch sample (cornstarch Y) was kindly provided by Sanwa Cornstarch Co., Ltd. (Nara, Japan). The moisture (water) content of the cornstarch was determined to be 13.4 % by drying it at 130 °C in atmospheric pressure. The lipid content of the cornstarch was determined to be 0.67 % by extracting it with methanol at 45 °C. See the following details on the methods for determining the lipid content. The concentration of cornstarch varied between 0.5 and 4.0 wt%. The distilled water, which was made by ion exchanging and distilling, was used for the preparation of starch samples.

Potassium 2,4-hexadienoate (potassium sorbate, 0.05 wt%) was used to prevent microbial growth. The use of potassium sorbate as a preservative is allowed by the Sanitation Law of Food in Japan. Potassium sorbate was purchased from Wako Pure Chemical Industries, Inc. (Osaka, Japan). Acetone and methanol were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan).

Determination of lipid content in cornstarch sample

Powders of cornstarch (30 g) were dispersed in 85 vol% methanol, then stirred with a magnetic stirrer in a triangle flask (300 mL) for 60 min at room temperature. Stirring in the same way, the sample was then extracted in a water bath and later in an incubator for at least 5 hours at 45 °C. After extracting at 45 °C, the dispersion was cooled to room temperature and 85 vol% methanol was aspirated. This extraction procedure was repeated four times. Next, 100 % methanol was used to extract the sample. The dispersion was heated and cooled twice using the same methods mentioned above.

Methanol was washed with acetone. The sample was filtered with a glass filter, and then acetone was filtered using 1 μm filter paper (No.5C ADVANTEC).

The lipid was removed from the filter paper into a vat, using acetone and distilled water. Then it was frozen at −80 °C and freeze-dried. This freeze-dried residue was weighed to determine the amount of lipid.

Preparation of cornstarch pastes

Powders of cornstarch were dispersed in distilled water. Cornstarch pastes were prepared
using an agitator illustrated in Figure 3.2 (See Steady shear measurements in RESULTS AND DISCUSSION). After stirring the dispersions at 200 rpm for 30 min at 25 °C, the cornstarch dispersions were heated up to 97 °C, stirring at the same rate and maintained at 97 °C for 60 min. Then the hot dispersions were poured into glass vessels (140 mL volume) and cooled in a water bath (5 L volume) at 25 °C for 60 min equipped with a temperature regulator, stirring with a magnetic stirrer. The temperature of samples reached 25 °C in 30 min. The sample preparation diagram is illustrated in Figure 3.3.

The viscoelasticity of starch pastes made by these procedures did not change at least 250 min. Therefore, the changes in the viscosity of starch pastes by the retrogradation could be ignored.

**Steady shear and dynamic oscillatory measurements**

Steady shear and dynamic oscillatory measurements of starch pastes were carried out using a Fluids Spectrometer RFS II (Rheometrics Co. Ltd., New Jersey, U.S.A.) with a 50 mm diameter plate geometry. The gap was adjusted to 1.00 mm. All measurements were made at 25.0 °C. From these measurements, the shear viscosity ($\eta_\gamma$), the storage modulus ($G'$), the loss modulus ($G''$), and the complex viscosity ($|\eta^*|_\omega = \sqrt{G'^2 + G''^2}$) were obtained. Strains for dynamic oscillatory measurements were chosen in the plateau range of each sample on the strain dependence test.

**Figure 3.2** Schematic diagram of an apparatus for the preparation of cornstarch pastes.
Measurements were made after around 200 min from the preparation of samples, and it took about 20 min to conduct each measurement (Figure 3.3).

**Differential scanning calorimetry (DSC) measurements**

DSC measurements were conducted using a DSC6100S (Seiko Instruments Inc., Chiba, Japan) with 70 μl silver (Ag) pans. Cornstarch (3.0 wt%) and distilled water were mixed in the Ag pans. They were added up to total sample weights of 70 mg, then sealed. Samples were heated from 25 °C to 130 °C at a heating rate of 1.0 °C/min. From DSC curves, the onset temperature \( T_o \), the peak temperature \( T_p \), the conclusion temperature of amylopectin gelatinization \( T_c^1 \), the conclusion temperature of amylose–lipid complex disintegration \( T_c^2 \) and the gelatinization enthalpy \( \Delta H \) could be obtained.

A micro DSCIII (Setaram Inc., Caluire, France) was also used for DSC measurements to investigate \( T_o, T_p, T_c^1 \) and \( \Delta H \) as a function of stirring time for starch dispersions before measurements. The pans for this DSC instrument, which is made of 500 μl stainless steel, are larger than those for other DSC instruments. Therefore, it should give us fine data. Cornstarch (12 wt%)
was dispersed in distilled water and the dispersions were stirred with a magnetic stirrer at room temperature for arbitrary times, then the samples were put in the pans.

RESULTS AND DISCUSSION

Steady shear measurements

The viscosity of starch pastes generally depends remarkably on the stirring methods of the starch dispersion and the heat history. In this study, an agitator shown in Figure 3.2 was made to prepare reproducible samples. This agitator is composed of a cylinder vessel made of PYREX® glass (50 mm diameter, 2.5 mm thickness and 320 mm height) (C), a stirring motor (M), a stirring propeller made of stainless steel (SUS304) coated with fluoro plastic (P), a circulator for temperature control (Refrigerated Circulator Model 9110 Poly Science, Illinois, U.S.A.) (T) and a jacket made of TPX® (polymethylpenten) (J). The top of the cylinder was covered with a cap made of PTFE (polytetrafluoroethylene), which was drilled for the bar of the stirring propeller. Evaporation of water from the hole of the cap could be disregarded. The temperature inside the cylinder vessel was controlled by the circulator, which controls the temperature inside the jacket. Under these conditions, it was possible to stir the samples uniformly.

Figure 3.4 shows the shear viscosity \( \eta_\dot{\gamma} \) of cornstarch pastes with various concentrations as a function of shear rate \( \dot{\gamma} \). Starch pastes have been reported to exhibit the shear-thickening behavior \(^{83},^{91},^{106}\), i.e., \( \eta_\dot{\gamma} \) increases with increasing \( \dot{\gamma} \), or the shear-thinning behavior \(^{83},^{84},^{91},^{107}–^{109}\), i.e., \( \eta_\dot{\gamma} \) decreases with increasing \( \dot{\gamma} \), or both the shear-thickening and the shear-thinning behavior \(^{83},^{91},^{107}\), i.e., shear-thickening behavior at higher \( \dot{\gamma} \) and shear-thinning behavior at lower \( \dot{\gamma} \). These behaviors depend on the type of starches, the size of granules, the concentration of starches, heating temperatures and measuring temperatures. Cornstarch pastes used in this study showed a typical shear-thinning behavior, where cornstarch concentration \( C \) is higher than 1.0 wt%. The Newtonian plateau did not appear. This means that the Newtonian plateau would appear at lower \( \dot{\gamma} \) than that used in this measurement, because amylose and amylopectin chains (glucose chains) leached out from starch granules have high molecular weights, which have wide range. Moreover, as swollen starch granules behave like dispersed molecules in the glucose chain solution, \( \eta_\dot{\gamma} \) depends on \( \dot{\gamma} \) strongly at lower \( \dot{\gamma} \).
Figure 3.4 Shear viscosity ($\eta_\gamma$) of cornstarch pastes with various concentrations between 1.0 and 4.0 wt% as a function of shear rate ($\dot{\gamma}$). Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.

It was observed that $\eta_\gamma$ became greater and the shear-thinning behavior became remarkable with increasing $C$ (Figure 3.4). On the other hand, for the samples with $C < 1.0$ wt%, the values of $\eta_\gamma$ were very small and it was almost limit for the instrument to make measurements. $\eta_\gamma$ did not depend on $\dot{\gamma}$ so much. This behavior is not the Newtonian flow but it may be a dilatant behavior. Such dilatant behavior occurs when high concentrations of rigid particles are sheared. This is because for the system to flow its volume must expand.

$C$ dependence of $\eta_\gamma$ observed at the same condition as in Figure 3.4 is illustrated in Figure 3.5. Some values of $\eta_\gamma$, where $\dot{\gamma}$ are 1, 10 and 100 s$^{-1}$, were chosen. Although $\eta_\gamma$ increased with increasing $C$ at all $\dot{\gamma}$ examined, the increase was non-linear. It is because there are strong interactions between gelatinized starch granules. It is found that $C$ should be at least 2.0 wt% to obtain higher viscosity. However, when $C$ was above 4.0 wt%, gelation occurred partly in the starch pastes. From these reasons, the concentration of 3.0 wt% cornstarch was chosen to investigate the effects of taste substances for the cornstarch pastes (See Chapter 4–9). This concentration is widely used to increase the viscosity for foods and it is possible to conduct
Chapter 3

Figure 3.5 Concentration ($C$) dependence of the shear viscosity ($\eta_\gamma$) for cornstarch pastes at shear rates of 1, 10 and 100 s$^{-1}$. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.

rheological measurements with wide range.

Dynamic oscillatory measurements

Complex viscosity ($|\eta^*|_\omega$) of cornstarch pastes with various concentrations as a function of angular frequency ($\omega$) is shown in Figure 3.6. Comparing $|\eta^*|_\omega$ in Figure 3.6 with $\eta_\gamma$ in Figure 3.4, $|\eta^*|_\omega$ and $\eta_\gamma$ of all samples did not obey the Cox-Merz rule: $\eta_\gamma = |\eta^*|_\omega$\textsuperscript{110}. The Cox-Merz rule was found to be applicable for several synthetic and biopolymer dispersions\textsuperscript{111}, but not for biopolymer dispersions with either hyperentanglements or aggregates or complex food systems\textsuperscript{5,91,108,112–118} and some synthetic polymers\textsuperscript{119}. The reason that cornstarch pastes did not obey the Cox-Merz rule is that starch pastes contain swollen granules and glucose chains. The values of $|\eta^*|_\omega$ were not coincidental with those of $\eta_\gamma$, while $|\eta^*|_\omega$ had a similar tendency to $\eta_\gamma$. The values of $|\eta^*|_\omega$ increased with increasing $C$. $|\eta^*|_\omega$ was less than $\eta_\gamma$ on samples with $C < 4.0$ wt%. This could be attributed to the heterogeneous nature of starch dispersions that undergo aggregation\textsuperscript{108}. This behavior is not very common in biopolymer systems, but it has been found for some semidilute
Figure 3.6 Complex viscosity ($|\eta^*|_\omega$) of cornstarch pastes with various concentrations between 2.0 and 4.5 wt% as a function of angular frequency ($\omega$). Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 ºC. The strain for 2.0, 3.0, 3.5 and 4.0 wt% cornstarch concentrations, was 50, 30, 12 and 3 %, respectively.

solutions of polysaccharides\textsuperscript{108), 116). On the other hand, $|\eta^*|_\omega$ was greater than $\eta_\gamma$ on samples with $C \geq 4.0$ wt%. It is high enough in steady shear to break down structures of inter- and intra-molecular associations. In this case, $|\eta^*|_\omega$ is usually greater than $\eta_\gamma$\textsuperscript{5), 91), 112)–115), 118), 119)}. As $|\eta^*|_\omega$ is characteristic of the network structures, which are not destroyed by shear, it is suggested that the network structures became stronger with increasing $C$.

Figure 3.7 illustrates angular frequency ($\omega$) dependence of storage modulus ($G'$) and loss modulus ($G''$) of cornstarch pastes with various $C$. Samples with $C < 4.0$ wt% showed a behavior known for the concentrated solutions of flexible polymers, i.e., $G'$ is less than $G''$ at lower $\omega$ and $G'$ is greater than $G''$ at higher $\omega$ (See Chapter 2). The values of $G'$ and $G''$ increased with increasing $C$. $G'$ with $C \geq 3.0$ wt%, did not depend on $\omega$ at lower $\omega$ and the long-time relaxation was observed. $G'$ is greater than $G''$ at lower $\omega$, $G'$ is less than $G''$ at intermediate $\omega$ and $G'$ is greater than $G''$ at higher $\omega$ again for the samples with 3.0 wt% $< C < 4.0$ wt%. This plateau, similar in shape to the rubber plateau, appears in same dispersed systems of spherical particles, where no entanglement
coupling occurs\textsuperscript{111},\textsuperscript{119}. In the case of starch pastes, it is thought that the entanglements of glucose chains, which leached out from starch granules, increase, and the aggregation of starch granules occurs. The values of $G'$ were greater than those of $G''$ at all $\omega$ examined and $G'$ and $G''$ increased with increasing $\omega$ for pastes with $C \geq 4.0$ wt%. This behavior resembles that for a weak gel (See Chapter 2). Starch granules and glucose chains that leach out from starch granules formed entangled three-dimensional networks at higher $C$.

From the results mentioned above, it is found that the cornstarch pastes with $C \geq 4.0$ wt% behave as weak gels, which have many entanglements by glucose chains, while the cornstarch pastes with $C < 4.0$ wt% have less entanglements and behaved like the concentrated solutions of flexible polymer. The results of dynamic oscillatory measurements also supported that $C = 3.0$ wt% would be appropriate to investigate the viscoelasticity of cornstarch pastes in this study, because this concentration should make possible to conduct measurements with wide range.

![Diagram](Figure 3.7) Angular frequency ($\omega$) dependence of storage modulus ($G'$, left) and loss modulus ($G''$, right) for cornstarch pastes with various concentrations between 2.0 and 4.0 wt%. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. The strain for 2.0, 3.0, 3.5 and 4.0 wt% cornstarch concentrations, was 50, 30, 12 and 3 %, respectively.
Differential scanning calorimetry (DSC) measurements

It is well known that starch containing higher concentrations of lipid, such as cornstarch, has two endothermic peaks in heating DSC curves\(^{(101), (120)}\). The lower temperature peak reflects the amylopectin gelatinization and the higher temperature peak is attributed to the disintegration of the amylose–lipid complex. Figure 3.8 shows a typical heating DSC curve of a cornstarch dispersion and a differentiated line of the DSC curve (DDSC line). The onset temperature \(T_o\), the peak temperature \(T_p\), the conclusion temperature of amylopectin gelatinization \(T_c^1\) and the conclusion temperature of amylose–lipid complex disintegration \(T_c^2\) were determined from the DDSC line in this work, i.e., \(T_o\) is a point, where the DDSC line swerves from a base line of the DDSC line. A base line of the DDSC line is drawn from the values of DDSC of zero, which mean there was no change in DSC curve.

\(T_p\) is a point, where DDSC is zero. \(T_c^1\) and \(T_c^2\) are points, where the DDSC line returns the

![Figure 3.8](image)

**Figure 3.8** A heating DSC curve and a differentiated line of the DSC curve (DDSC line) for a 3.0 wt% cornstarch dispersion. The heating rate was 1.0 °C/min. \(T_o\): onset temperature, \(T_p\): peak temperature, \(T_c^1\): conclusion temperature for amylopectin gelatinization and \(T_c^2\): conclusion temperature for amylose–lipid complex disintegration.
Chapter 3

base line. The gelatinization enthalpy ($\Delta H$) was estimated from the area, which is closed by the $T_o$ and $T_c^1$ line and DSC curves.

When cornstarch samples were dispersed in distilled water and stirred at room temperature before putting samples in pans for DSC measurements, gelatinization temperatures ($T_o$, $T_p$ and $T_c^1$) and $\Delta H$ depended on the stirring time of the starch dispersions (Figure 3.9). Gelatinization temperatures were shifted to lower temperatures and $\Delta H$ decreased with increasing stirring time. These shifts and decreases indicate that the gelatinization occurs easily by stirring the starch dispersions because of the enhancements of the swelling for starch granules. $T_p$ and $\Delta H$ generally reported by many researchers are around 70 °C and 11 mJ/mg, respectively, which coincide with $T_p$ and $\Delta H$ without stirring the sample (stirring time = 0). Therefore, DSC measurements were made as soon as samples were prepared by mixing samples in the pans from this time forward, so that gelatinization temperatures should not shift lower temperatures and $\Delta H$ should not decrease.

Figure 3.9 Onset temperature ($T_o$), peak temperature ($T_p$), conclusion temperature of amylopectin gelatinization ($T_c^1$) and gelatinization enthalpy ($\Delta H$) of 12.0 wt% cornstarch dispersion as a function of stirring time for the cornstarch dispersion.
CONCLUSIONS

The viscoelasticity of cornstarch pastes increased with increasing cornstarch concentration ($C$). This increase was non-linear. It is found that $C$ should be more than 2.0 wt% to obtain higher viscosity, but gelation occurred partly in the starch pastes with $C > 4.0$ wt%. The pastes with $C \geq 4.0$ wt% showed a behavior of weak gels because entangled networks increased, while the pastes with $C < 4.0$ wt% behaved as the concentrated solutions of flexible polymers. It was decided that $C = 3.0$ wt% was used to investigate changes in the viscoelasticity of starch pastes because it would conduct rheological measurements with wide range.

The gelatinization temperature shifted to lower temperatures and the gelatinization enthalpy decreased with prolonging the stirring time of the cornstarch dispersion before putting samples in pans for DSC measurements. From this reason, it was decided that DSC measurements were made as soon as sample were prepared by mixing samples in the pans.
4. EFFECTS OF SUCROSE ON THE PHYSICAL PROPERTIES FOR CORNSTARCH PASTES

INTRODUCTION

Starch products contain intricate mixtures of tastes. The tastes are mainly controlled by seasoning substances, some of which are known to have effects on the physical properties of starch pastes and gels. In Chapter 4–9, the effects of various taste substances on the physical properties for cornstarch pastes were investigated.

The sweet substances are the most widely added to starch products. In Japan, sugar has been used with powders of rice to make various traditional Japanese sweets, many of which are higher starch concentrations and are gel-like. Sugar is also contained in soups and sauces, which have lower concentrations of starch. It is thought that lower concentrations of starch is affected more sensitively by adding taste substances as compared with higher concentrations of starch.

Many researchers have reported concerning the effects of sweet substances on the gelatinization and the retrogradation of starches. They have used various types of starch such as potato\(^{121)-(125)}\), wheat\(^{109), (121), (125)-(130)}\), sweet potato\(^{131)}\), rice\(^{132)-(135)}\), sago\(^{136), (137)}\), amaranth\(^{138)}\), acorn\(^{139)}\), modified starch\(^{140)}\) and corn\(^{122), (124), (125), (141), (142)}\). They have also used many kinds of methods such as amylogram\(^{121), (126), (127), (141)}\), DTA or DSC\(^{123)-(125), (128), (131)-(133), (136)-(140), (142)}\), X-ray analysis\(^{142)}\), microscopic observations\(^{128), (141)}\), NMR\(^{130)}\) and viscosity or viscoelasticity measurements\(^{109), (122), (129), (133) -(136), (139), (140)}\). Regarding to the viscoelasticity of starch pastes in the presence of sweet substances, Cheer and Lelievre\(^{129)}\) reported that the viscosity of 3.5 or 4.0 wt% wheat starch pastes increased with increasing sucrose concentration\(C_s\) up to 15 w% and decreased inversely with increasing\(C_s\) above 15 wt%. On the other hand, the result of Ahamad and Williams\(^{136)}\) was that the viscoelasticity of 6 wt% sago starch pastes in the presence of sucrose decreased with increasing\(C_s\). Takahashi and Kikura\(^{122)}\) studied the shear viscosity and the rigidity of 12.5 wt% cornstarch pastes in the presence of 15 wt% sucrose. They found that both shear viscosity and rigidity for starch pastes with sucrose were greater than those for pastes without sucrose. Thus, the
viscoelasticity of starches depends greatly on the origins of starches, the concentration of starch and $C_s$. Moreover, sweet substances have been added before heating starch dispersions, i.e., before gelatinization, to investigate the effects of sweet substances on the gelatinization and the retrogradation of starch. By adding sucrose after heating starch dispersions, i.e., after gelatinization, the effects of sucrose on the viscoelasticity of starch should change, in comparison with those by adding before gelatinization.

In this chapter, cornstarch and sucrose were selected. Cornstarch is the most widely used among many types of starch in the food industry as mentioned in Chapter 3. Sucrose is widely used for an ingredient or a seasoning of sweetness in the food industry and in home cooking. $C_s$ of foods is 0–10 % in soups and sauces, about 15 % in starch jellies and below 30 % in baked cakes. Therefore, the wide $C_s$ range was used to examine the effects of sucrose on the physical properties of cornstarch pastes.

The objective is to investigate how sucrose affects the physical properties of starch pastes and contributes to the effect of increasing the viscosity for starch pastes by adding sucrose before and after gelatinization.

MATERIALS AND METHODS

Materials

The concentration of cornstarch was fixed at 3.0 wt%; this is the concentration generally used as a thickener in sauces or soups. The determination of the concentration of starch is described in Chapter 3. Sucrose (granulated sugar, Taito Co., Ltd., Hyogo, Japan) was of a commercial grade. Chemical analyses of sucrose sample are displayed in Table 4.1*. The concentration of sucrose varied between 0 and 55 wt%. Potassium 2,4-hexadienoate (potassium sorbate, 0.05 wt%) was used to prevent microbial growth. Iodine solution was used to dye starch granules and amylose chains. Potassium sorbate and 10 mM iodine solution were purchased from Wako Pure Chemical Industries, Inc. (Osaka, Japan).

* Data were provided by Taito Co., Ltd.
**Effects of sucrose on the physical properties for cornstarch pastes**

<table>
<thead>
<tr>
<th>Table 4.1 Chemical analyses of sucrose sample*.</th>
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<td><strong>Item</strong></td>
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<tr>
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<tr>
<td>Sugar content</td>
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<tr>
<td>Sucrose content</td>
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<tr>
<td>Reducing sugar content</td>
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<tr>
<td>Ash content</td>
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<tr>
<td>Others</td>
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<tr>
<td>Granularity</td>
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<tr>
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<td>Property of solution</td>
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<td>Color value C.I.** 420 nm</td>
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<tr>
<td>Heavy metal as Pb</td>
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<td>Arsenic</td>
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**color index

Preparation of sucrose solutions and cornstarch pastes

1. Preparation of sucrose solutions

Sucrose was dissolved in distilled water, and the solutions were stirred with a magnetic stirrer for 30 min at 25 °C. Then, they were heated at 97 °C for 60 min and were cooled in a water bath at 25 °C for 60 min, stirring by the same way mentioned above.

2. Preparation of cornstarch pastes in the presence of sucrose

Powders of cornstarch were dispersed in distilled water or in sucrose aqueous solutions prepared beforehand by adding various concentrations of sucrose to distilled water. A control sample was made of cornstarch and distilled water. The stirring rate, heating rate and heating time for the samples were the same as described in preparation of cornstarch pastes in Chapter 3 (See Figure 3.3). The samples were also prepared, which were added sucrose after heating, i.e., after gelatinization of starch, and then the starch pastes were cooled by the same methods mentioned in Chapter 3. The final concentration of cornstarch was 3.0 wt%. The time, when sucrose was added before and after gelatinization, was also noted in Figure 3.3.
Chapter 4

Steady shear and dynamic oscillatory measurements

Steady shear and dynamic oscillatory measurements of starch pastes were carried out using a Fluids Spectrometer RFS II (Rheometrics Co. Ltd., New Jersey, U.S.A.) with a 50mm diameter plate geometry. The details are described in Chapter 3, and the same parameters could be obtained.

Microscopic observations

Microscopic observations were made using an OPTIPHOTO (Nikon Co. Ltd., Tokyo, Japan) equipped with 2D-color CCD (1280 × 960 pixels). Pastes prepared by the method mentioned above were diluted with 2 times of distilled water. Starch granules and amylose chains of cornstarch were dyed with a 10 mM iodine solution.

Differential scanning calorimetry (DSC) measurements

DSC measurements were conducted using a DSC6100S (Seiko Instruments Inc., Chiba, Japan) with 70 µl silver (Ag) pans.

1. Sucrose

Sucrose (20, 30, 40 and 50 wt%) and distilled water were mixed in the Ag pans. The weight of distilled water for sucrose solutions was fixed at 40 mg. Distilled water (40 mg) was used as a reference. Samples were heated from 25 °C to 200 °C at a heating rate of 1.0 °C/min. The enthalpy of 1 mg sucrose solution (ΔHs) could be obtained.

2. Cornstarch and sucrose

Cornstarch (3.0 wt%), sucrose (20, 30, 40 and 50 wt%) and distilled water were mixed in the Ag pans. They were added up to total sample weights of 70 mg, then sealed. Each concentration of sucrose solution was used for a reference, because some peaks were observed in DSC curves of sucrose solutions (See Figure 4.2). Samples were heated from 25 °C to 130 °C at a heating rate of 1.0 °C/min. From DSC curves, the onset temperature (To), the peak temperature (Tp), the conclusion temperature of amylpectin gelatinization (Tc1), the conclusion temperature of amylose–lipid complex disintegration (Tc2), the gelatinization temperature range for peaks (ΔT = Tc2 − To) and the gelatinization enthalpy (ΔH) could be obtained.
RESULTS AND DISCUSSION

Steady shear and differential scanning calorimetry (DSC) measurements of sucrose solutions

Figure 4.1 shows the viscosity for sucrose solutions ($\eta_s$) as a function of sucrose concentration ($C_s$). It is well known that sucrose solutions show a behavior of the Newtonian fluid. However, it took a few days for sucrose solutions with higher $C_s$ to behave as a Newtonian fluid. This means that it takes longer time for sucrose to dissolve completely in water, when $C_s$ is higher. Then, the values of shear viscosity at shear rate ($\gamma$) of 100 s$^{-1}$ were taken as $\eta_s$ because sucrose solutions always showed the Newtonian fluid behavior at higher $\gamma$. $\eta_s$ increased with increasing $C_s$, and sharply increased with increasing $C_s$ above 30 wt%. The value of $\eta_s$ with 50 wt% was ten times as great as that of distilled water at 25 °C ($8.90 \times 10^{-4}$ Pa·s).

Two exothermic peaks at around 140 and 200 °C were observed in heating DSC curves for sucrose solutions (Figure 4.2). The enthalpy of 1 mg sucrose solution ($\Delta H_s$) approximately at 140

![Graph showing the viscosity of sucrose solutions (ηs) as a function of sucrose concentration (Cs).](image)

**Figure 4.1** Sucrose concentration ($C_s$) dependence of the viscosity for sucrose solutions ($\eta_s$). Sucrose solutions were heated at 97 °C and were cooled to 25.0 °C. Measurements were made at 25.0 °C.
Figure 4.2 Heating DSC curves of sucrose solutions with various concentrations between 20 and 50 wt%. The heating rate was 1.0 °C/min. Inset: Changes in the enthalpy for exothermic peaks at around 140 °C. The enthalpy for mJ/mg of sucrose solution ($\Delta H_s$) was calculated.

°C increased proportionally with increasing $C_s$ (inset in Figure 4.2). The enthalpy of 1 mg sucrose calculated from the slope was 15 mJ/mg. This value is similar to that of the exothermic enthalpy for the inversion of sucrose (12.3 mJ/mg). Therefore, these exothermic peaks at 140 °C were proved to be induced by the inversion of sucrose, and large exothermic peaks at around 200 °C were found to be due to the caramelization of glucose and fructose, which arose from the inversion of sucrose $^{143}$. Other peaks were observed at about 50 °C for the sample with $C_s = 40$ wt% and at about 80 °C for the sample with $C_s = 50$ wt%. These peaks disappeared by storing the samples in the pans for a few days before starting the measurement. These peaks are thought to be due to the dissolution of sucrose in water.
Steady shear measurements of cornstarch pastes with sucrose added before gelatinization

Figure 4.3 shows the shear viscosity ($\eta_{\dot{\gamma}}$) for 3.0 wt% cornstarch pastes in the presence of sucrose as functions of $\dot{\gamma}$ and $C_s$. Sucrose was added before gelatinization. $\eta_{\dot{\gamma}}$ of the control is illustrated in mesh. All samples showed a typical shear-thinning behavior. It was observed that $\eta_{\dot{\gamma}}$ with $C_s \leq 20$ wt% increased with increasing $C_s$ and the shear-thinning behavior became remarkable in comparison with the control. On the contrary, $\eta_{\dot{\gamma}}$ with $C_s > 20$ wt% decreased with increasing $C_s$ and the shear-thinning behavior became less pronounced.

$C_s$ dependence of $\eta_{\dot{\gamma}}$ observed at the same condition as in Figure 4.3 is demonstrated in Figure 4.4. Some values of $\eta_{\dot{\gamma}}$, where $\dot{\gamma}$ are 1, 10 and 100 s$^{-1}$, were chosen and represented by $\eta_1$, $\eta_{10}$ and $\eta_{100}$, respectively. $\eta_{\dot{\gamma}}$ at a lower $\dot{\gamma}$, $\eta_1$ increased with increasing $C_s$ up to 20 wt% and decreased inversely with increasing $C_s$ above 20 wt%. The values of $\eta_1$ were greater than that of the control at $C_s < 40$ wt% and almost the same at $C_s \geq 40$ wt%. $\eta_{\dot{\gamma}}$ at a higher $\dot{\gamma}$, $\eta_{100}$ had a similar tendency to $\eta_1$, however, $\eta_{100}$ had a maximum value for samples with $C_s$ between 20 and 35 wt%.

**Figure 4.3** Shear viscosity ($\eta_{\dot{\gamma}}$) for 3.0 wt% cornstarch pastes in the presence of sucrose as functions of shear rate ($\dot{\gamma}$) and sucrose concentration ($C_s$). Sucrose was added before gelatinization. Mesh illustrates $\eta_{\dot{\gamma}}$ of the control (3.0 wt% cornstarch paste without sucrose). Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.
Figure 4.4 Sucrose concentration ($C_s$) dependence of the shear viscosity ($\eta_\gamma$) for 3.0 wt% cornstarch pastes at shear rates of 1, 10 and 100 s$^{-1}$. Sucrose was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.

and the values of $\eta_{100}$ at all $C_s$ range examined were greater than that of the control. $\eta_{10}$ showed a similar tendency to $\eta_{100}$. From these results, it is thought that $C_s$ range can be divided into three: I) 0 wt% $\leq C_s \leq$ 20 wt%, II) 20 wt% $< C_s < 40$ wt% and III) $C_s \geq$ 40 wt%. $\eta_\gamma$ changed depending on $C_s$ because the swelling rate of starch granules differed, i.e., size or shapes of starch granules and the number of amylose and amylopectin chains (glucose chains) differed. The changes in size of starch granules and the number of glucose chains are discussed in the next section.

Microscopic observations

Microscopic photographs of starch granules with sucrose added before gelatinization are lined along the left in Figure 4.5. Starch granules can be seen in purple spherical lumps, and glucose chains, which are mainly amylose chains, in blue mass of strands.

The heated cornstarch granules were swollen and partly ruptured. The size distribution of starch granules could be seen in photographs of unheated and heated starch granule for the control (Figure 4.5 top). Rao et al. 91) reported that the standard deviation of the starch granules for samples
Effects of sucrose on the physical properties for cornstarch pastes

**Figure 4.5** Microscopic photographs of starch granules for 3.0 wt% cornstarch dispersions in the presence of sucrose with various concentrations between 0 (control) and 50 wt%. Sucrose was added before and after gelatinization. Samples were prepared as described in Figure 3.3. Pastes were diluted with distilled water and dyed with 10 mM iodine solution. Pictures of the control were taken before and after heating. Image size is 390 μm × 725 μm. Pictures were taken at ambient temperature.
before and after heating were 6.1 and 11.8 µm, respectively.

There were several larger granules of the samples with added 10 and 20 wt% sucrose in comparison with those of the control (Figure 4.5 top, right and middle, left). This result coincides with that of other researchers\textsuperscript{129, 136}. Therefore, $C_s$ range I is a stage of increasing the swelling rate. Thus, $\eta_\gamma$ of starch samples, where $C_s$ is below 20 wt%, increased with increasing $C_s$. There were no glucose chains leaching out from starch granules of samples added 40 and 50 wt% sucrose (Figure 4.5 bottom, left). Similar results have been reported by Savage and Osman\textsuperscript{141}. $C_s$ range III is a stage of preventing the swelling rate. The cause of decreases in $\eta_\gamma$ at this range is thought that there are no entanglements of glucose chains and starch granules are smaller than those of others. The size of starch granules for the sample with $C_s = 30$ wt% were smaller than those with $C_s = 10$ and 20 wt% (Figure 4.5 middle, left). Therefore, $C_s$ range II is a stage of decreasing the swelling rate.

**DSC measurements of cornstarch dispersions**

Figure 4.6 shows heating DSC curves for 3.0 wt% cornstarch dispersions with various $C_s$. Two peaks were observed in the DSC curves for cornstarch dispersions as described in Chapter 3. The following parameters could be obtained from DSC curves: the onset temperature ($T_o$), the peak temperature ($T_p$), the conclusion temperature of amylopectin gelatinization ($T_c^1$), the conclusion temperature of amylose–lipid complex disintegration ($T_c^2$), the gelatinization temperature range for peaks ($\Delta T = T_c^2 - T_o$) and the gelatinization enthalpy ($\Delta H$).

On the other hand, there were lower endothermic peaks in DSC curves for samples with $C_s \geq 30$ wt% as compared with the endothermic peaks for the gelatinization (Figure 4.6). Namely, three peaks were observed in the DSC curves of starch dispersion with $C_s \geq 30$ wt%. These peaks may be caused by dissolution of sucrose since their temperatures were almost coincident with those of the peaks observed in DSC curves for sucrose solutions (Figure 4.2). Although each concentration of sucrose solution was used as a reference, these dissolved peaks appeared. It is thought that starch prevents sucrose from dissolving in water.

Figure 4.7 indicates the changes in $T_o$, $T_p$, $T_c^1$, $T_c^2$, $\Delta T$ and $\Delta H$ determined from Figure 4.6. $T_o$, $T_p$, $T_c^1$ and $T_c^2$ shifted to higher temperatures and $\Delta H$ increased with increasing $C_s$, while $\Delta T$ was not affected by sucrose. Namely DSC curves became sharper with increasing $C_s$. These results are coincident with the results that have ever been reported\textsuperscript{124, 131, 136, 137, 139, 140}. Whistler and
Effects of sucrose on the physical properties for cornstarch pastes

Figure 4.6 Heating DSC curves of 3.0 wt% cornstarch dispersions in the presence of sucrose with various concentrations between 0 (control) and 50 wt%. Characters beside each curve represent sucrose concentrations. The heating rate was 1.0 °C/min.

Figure 4.7 Effects of sucrose on the gelatinization temperature ($T$) and enthalpy ($\Delta H$) for 3.0 wt% cornstarch dispersions. $T_o$: onset temperature; $T_p$: peak temperature; $T_c^1$: conclusion temperature for amylopectin gelatinization; $T_c^2$: conclusion temperature for amylose–lipid complex disintegration; $\Delta T$: gelatinization range $T_c^2 - T_o$; $\Delta H$: enthalpy for mg starch.
Daniels \textsuperscript{3)} reported that high sugar concentration decreases the rate of starch gelatinization, the peak viscosity and gel strength, and disaccharides are more effective in delaying the gelatinization and in reducing the peak viscosity than monosaccharides. The cause of these phenomena is thought that sucrose binds starch chains in amorphous areas and the chains exhibit limited flexibility \textsuperscript{129)} and sucrose acts as an antiplasticizer, since its molecular weight is greater than that of the primary plasticizer of starch, water \textsuperscript{132), 144)}.

In this study, starch pastes were prepared by heating at 97 \degree C for 60 min. $T_e^2$ of samples with $C_s \geq 20$ wt\% was higher than 97 \degree C, $T_e^1$ of samples with $C_s \geq 40$ wt\% was higher than 97 \degree C, and $T_p$ of samples with $C_s > 45$ wt\% was higher than 97 \degree C. Therefore, $\eta_\gamma$ decreased at higher $C_s$ because the starch gelatinization did not occur completely by heating at 97 \degree C and sucrose prevented starch granules from swelling. Nevertheless, $\eta_\gamma$ of the paste with $C_s = 20$ wt\% increased. This increase is thought that the starch gelatinization may occur completely during heating at 97\degree C for 60 min, or the ability of sucrose to enhance swelling of starch granules \textsuperscript{129), 136)}, or both of them.

\textbf{Dynamic oscillatory measurements of cornstarch pastes with sucrose added before gelatinization}

Figure 4.8 illustrates the angular frequency ($\omega$) dependence of the storage modulus ($G'$) and the loss modulus ($G''$) for 3.0 wt\% cornstarch pastes with or without sucrose. Sucrose was added before gelatinization. The paste of the control showed a behavior known for concentrated solutions of flexible polymers, i.e., $G'$ is less than $G''$ at lower $\omega$ and $G'$ is greater than $G''$ at higher $\omega$. $G'$ of samples with $C_s \leq 35$ wt\% did not depend on $\omega$ at lower $\omega$ and the long-time relaxation was observed. $G'$ is greater than $G''$ at lower $\omega$, $G'$ is less than $G''$ at intermediate $\omega$ and $G'$ is greater than $G''$ at higher $\omega$ again. This plateau, similar in shape to the rubber plateau, appears in some dispersed systems of spherical particles, where no entanglement couplings occur \textsuperscript{111), 119)} as mentioned in Chapter 3. The values of this plateau increase with increasing concentration of dispersed particles or size of particles \textsuperscript{119)}. In the case of starch pastes, it is thought that the entanglements of glucose chains, which leached out from starch granules, increased and the aggregation of starch granules occurs. The viscoelasticity at lower $\omega$ reflects the aggregation of starch granules and size of granules, and the viscoelasticity at higher $\omega$ reflects the entanglement of glucose chains. The values of $G'$ were less than those of $G''$ at all $\omega$ examined for pastes with $C_s$ above 40 wt\%. This behavior resembles that for liquid.
Effects of sucrose on the physical properties for cornstarch pastes

Figure 4.8 Angular frequency (ω) dependence of storage modulus (G', left) and loss modulus (G'', right) for 3.0 wt% cornstarch pastes in the presence of sucrose with various concentrations between 0 (control) and 55 wt%. Sucrose was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. The strain for samples with 0 (control), 5, 15, 20, 22.5, 25, 30, 35, 40, 50 and 55 wt% sucrose concentrations, was 30, 20, 5, 3, 8, 10, 10, 15, 30, 20 and 30 %, respectively.
Moreover, the values of $G'$ increased with increasing $C_s$ up to 20 wt% and decreased inversely with increasing $C_s$ above 20 wt%. The values of $G''$ had a same tendency, but there were no difference in the values of $G''$ at 25 wt% $\leq C_s \leq$ 55 wt%. The reason that $G'$ and $G''$ increased with increasing $C_s$ up to 20 wt% is thought that the number of glucose chains leached out from starch granules increase, and the psuedo-networks are formed by binding sucrose to starch chains\textsuperscript{3),128),133}. The cause of decrease for $G'$ and $G''$ at $C_s > 20$ wt% is that sucrose prevents glucose chains from leaching out from starch granules, and starch granules from swelling. A constant value of $G''$ at 25 wt% $\leq C_s \leq$ 55 wt% indicates that there is no change in the number of glucose chains leached out from starch granules. The viscosity of starch pastes is strongly affected by the size of starch granules. The size of starch granules decreased with increasing $C_s$ in this $C_s$ range (Figure 4.5), therefore, it is thought that the viscosity of starch pastes in $C_s$ range III would be affected by the viscosity of sucrose solutions.

Complex viscosity ($|\eta^*|_\omega$) for 3.0 wt% cornstarch pastes in the presence of sucrose as functions of $\omega$ and $C_s$ is shown in Figure 4.9. Sucrose was added before gelatinization. $|\eta^*|_\omega$ of the control is illustrated in mesh. Comparing of $|\eta^*|_\omega$ in Figure 4.9 with $\eta_\gamma$ in Figure 4.3, $|\eta^*|_\omega$ and $\eta_\gamma$ of all samples did not obey the Cox-Merz rule: $\eta_\gamma = |\eta^*|_\omega$\textsuperscript{110} because starch pastes contained swollen granules and glucose chains as mentioned in Chapter 3. The values of $|\eta^*|_\omega$ did not coincide with those of $\eta_\gamma$, while $|\eta^*|_\omega$ had a similar tendency to $\eta_\gamma$. The values of $|\eta^*|_\omega$ for all sample were less than those of $\eta_\gamma$. As $|\eta^*|_\omega$ is characteristic of the network structures, when the number of entanglements of glucose chains increase, $|\eta^*|_\omega$ would become greater than $\eta_\gamma$. These less values of $|\eta^*|_\omega$ indicate that there are not so many entanglements of glucose chains that leach out from starch granules. It is thought that sucrose does not enhance the leaching out of glucose chains from starch granules, though the values of $|\eta^*|_\omega$ increased at $C_s \leq 20$ wt%.

**Effects of cornstarch on increasing viscosity for cornstarch pastes with sucrose added before gelatinization**

Adding much sucrose led to a decrease in $\eta_\gamma$ for starch pastes because the swelling of starch granules was inhibited, although the values of $\eta_\gamma$ was greater than that of the control or almost same. These higher values of $\eta_\gamma$ may be attributed not only to the viscosity of starch pastes
Figure 4.9 Complex viscosity ($|\eta^*|_\omega$) for 3.0 wt% cornstarch pastes in the presence of sucrose as functions of angular frequency ($\omega$) and sucrose concentration ($C_s$). Sucrose was added before gelatinization. $|\eta^*|_\omega$ of the control (3.0 wt% cornstarch paste without sucrose) is illustrated in mesh. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. The strain for samples with 0 (control), 1, 5, 10, 15, 20, 25, 30, 35, 40, 50 and 55 wt% sucrose concentrations, was 30, 15, 20, 15, 5, 3, 10, 10, 15, 30, 20 and 20 %, respectively.

but also to that of sucrose solutions as shown in Figure 4.1. Then, the relative viscosity increment*** ($\eta_{r\gamma}$) was used to examine the contribution of cornstarch to $\eta_{\gamma}$ of cornstarch pastes.

$$\eta_{r\gamma} = \frac{\eta_{\gamma} - \eta_0}{\eta_0}$$  \hspace{1cm} (4.1)

where $\eta_0$ is the viscosity of the solvent. In this case, the values of $\eta_s$ were used as $\eta_0$.

Figure 4.10 indicates $C_s$ dependence of $\eta_{r\gamma}$ at $\gamma = 1$, 10 and 100 s$^{-1}$. Sucrose was added before gelatinization. $\eta_{r\gamma}$ at all $\gamma$, increased with increasing $C_s$ up to 20 wt% ($C_s$ range I) and decreased with increasing $C_s$ above 20 wt% ($C_s$ range II and III). $\eta_{r\gamma}$ at $C_s$ more than 28 wt% was less than that of the control. The values of $\eta_{r\gamma}$ were almost independent of $\gamma$, where $C_s$ was above 40 wt% (Figure 4.3 and 4.4), while the value of $\eta_s$ increased with increasing $C_s$ (Figure 4.1).

*** The relative viscosity increment is previously called the specific viscosity. The use of the specific viscosity is discouraged by IUPAC Compendium of Chemical Terminology 2nd Edition (1997).
Figure 4.10 Relative viscosity increment ($\eta_{i\gamma}$) for 3.0 wt% cornstarch pastes in the presence of sucrose as a function of sucrose concentration ($C_s$). Sucrose was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. Shear rates ($\dot{\gamma}$) are 1, 10 and 100 s$^{-1}$.

Therefore, the effect of cornstarch itself on increasing $\eta_{i\gamma}$ for cornstarch pastes did not display so much at $C_s$ range III.

When sucrose is added to the cornstarch pastes after heating, i.e., after gelatinization, the inhibition of swelling for starch grains can be prevented. Therefore, higher viscosity for starch pastes must be obtained.

Effects of adding sucrose after gelatinization

Figure 4.11 illustrates $\eta_{i\gamma}$ for 3.0 wt% cornstarch pastes as functions of $\dot{\gamma}$ and $C_s$. Sucrose was added after gelatinization. $\eta_{i\gamma}$ of the control is illustrated in mesh. Typical shear-thinning behaviors could be also seen for all samples. There was no difference in the degree of the shear-thinning for all samples.

Figure 4.12 shows $C_s$ dependence of $\eta_{i\gamma}$ at the same condition as in Figure 4.11. Some values of $\eta_{i\gamma}$, where $\dot{\gamma}$ are 1, 10 and 100 s$^{-1}$, were chosen. No decrease in $\eta_{i\gamma}$ was observed even at higher $C_s$ for all $\dot{\gamma}$ examined. $\eta_{i\gamma}$ increased with increasing $C_s$ and the values of $\eta_{i\gamma}$ for all
Effects of sucrose on the physical properties for cornstarch pastes

Figure 4.11 Shear viscosity ($\eta_\gamma$) for 3.0 wt% cornstarch pastes in the presence of sucrose as functions of shear rate ($\gamma$) and sucrose concentration ($C_s$). Sucrose was added after gelatinization. Mesh illustrates $\eta_\gamma$ of the control (3.0 wt% cornstarch paste without sucrose). Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 ºC.

Figure 4.12 Sucrose concentration ($C_s$) dependence of the shear viscosity ($\eta_\gamma$) for 3.0 wt% cornstarch pastes at shear rates of 1, 10 and 100 s$^{-1}$.Sucrose was added after gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0ºC.
samples were greater than that of the control. Many glucose chains could be seen in the microscopic photographs for the samples with 40 and 50 wt% sucrose added after gelatinization as compared with those added sucrose before gelatinization (Figure 4.5 bottom). Moreover, many starch granules collapsed for the samples with 40 and 50 wt% sucrose as compared with those for the control and the samples added 10, 20 and 30 wt% sucrose after gelatinization (Figure 4.5 right). It is supposed that many starch granules contact each other because the starch concentration, when starch dispersions were heated, is higher than that of other samples. The gelatinization occurred completely by adding sucrose after gelatinization.

The same tendencies were observed in the results of dynamic oscillatory measurements. The values of $G'$ and $G''$ were increased with increasing $C_s$ (Figure 4.13). No paste with sucrose added after gelatinization did show the liquid behavior. The plateau region appeared at lower $\omega$ for all pastes in the presence of sucrose, i.e., $G'$ is greater than $G''$ at lower $\omega$, $G'$ is less than $G''$ at

![Figure 4.13](image)

**Figure 4.13** Angular frequency ($\omega$) dependence of storage modulus ($G'$, left) and loss modulus ($G''$, right) for 3.0 wt% cornstarch pastes in the presence of sucrose with various concentrations between 0 (control) and 50 wt%. Sucrose was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0°C. The strain for samples with 0 (control), 5, 20, 30 and 50 wt% sucrose concentrations, was 30, 10, 3, 3 and 3 %, respectively.
intermediate $\omega$ and $G'$ is greater than $G''$ at higher $\omega$ again. This behavior indicates that the aggregation of starch granules and glucose chains are enhanced by the addition of sucrose.

The values of $|\eta^*|_\omega$ also increased with increasing $C_s$ (Figure 4.14). The values of $|\eta^*|_\omega$ in Figure 4.14 were not also coincidental with those of $\eta_\gamma$ in Figure 4.11, and were always less than those of $\eta_\gamma$. In the case of cornstarch alone, the values of $|\eta^*|_\omega$ were greater than those of $\eta_\gamma$ at cornstarch concentration above 4.0 wt% (See Figure 3.4 and 3.6 in Chapter 3). The ratio of cornstarch to water for samples, where $C_s$ was higher than 25 wt%, was higher than that for 4.0 wt% cornstarch pastes during heating (starch/water = 4/96 $\approx$ 0.042). Nevertheless, $|\eta^*|_\omega$ were less than $\eta_\gamma$. It is thought that sucrose prevents glucose chains from entangling because sucrose binds glucose chains.$^{3,129}$

Some values of $\eta_{\gamma}$, where $\gamma$ are 1, 10 and 100 s$^{-1}$, were also greater than those of the control, when sucrose was added after gelatinization (Figure 4.15). The values $\eta_{\gamma}$ of the samples

![Figure 4.14 Complex viscosity ($|\eta^*|_\omega$) for 3.0 wt% cornstarch pastes in the presence of sucrose as functions of angular frequency ($\omega$) and sucrose concentration ($C_s$). Sucrose was added after gelatinization. $|\eta^*|_\omega$ of the control (3.0 wt% cornstarch paste without sucrose) is illustrated in mesh. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 ºC. The strain for samples with 0 (control), 5, 10, 19, 20, 25, 30, 35, 40 and 50 wt% sucrose concentrations, was 30, 8, 4, 3, 3, 3, 3 and 3 %, respectively.](image)
Chapter 4

Figure 4.15 Relative viscosity increment ($\eta_{i\gamma}$) for 3.0 wt% cornstarch pastes in the presence of sucrose as a function of sucrose concentration ($C_s$). Sucrose was added after gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. Shear rates ($\gamma$) are 1, 10 and 100 s$^{-1}$.

With $C_s \leq 50$ wt% were greater than those of the control. However, $\eta_{i\gamma}$ decreased with increasing $C_s$ at $C_s > 20$ wt%, and the values of $\eta_{i\gamma}$ at $C_s > 50$ wt%, were less than those of the control. It seems that the effects of cornstarch on increasing $\eta_{i\gamma}$ for cornstarch pastes are, in fact, decreased by the addition of higher $C_s$, and the higher $\eta_s$ contributes for the higher viscosity of cornstarch pastes.

From these results, adding sucrose after gelatinization was effective in increasing the viscoelasticity of cornstarch pastes as compared with adding sucrose before gelatinization. However, $\eta_{i\gamma}$ at all $\gamma$, increased with increasing $C_s$ up to 20 wt% and decreased with $C_s$ above 20 wt%.
CONCLUSIONS

The viscosity of sucrose solutions increased with increasing sucrose concentration ($C_s$), and sharply increased with increasing $C_s$ above 30 wt%. Two exothermic peaks at around 140 and 200 °C were observed in heating DSC curves of sucrose solutions. It was found that the exothermic peaks at around 140 °C were due to the inversion of sucrose, and large exothermic peaks at around 200 °C were for the caramelization of glucose and fructose, which arose from the inversion of sucrose. Other peaks were observed at about 50 °C for the sample with $C_s = 40$ wt% and at about 80 °C for the sample with $C_s = 50$ wt% because of the dissolution of sucrose in water.

When sucrose was added to cornstarch dispersions before gelatinization, the viscoelasticity of cornstarch pastes increased with increasing $C_s$ up to 20 wt% and decreased with increasing $C_s$ above 20 wt%, although the viscoelasticity of samples in the presence of sucrose was higher than that of the control at higher shear rate and frequency.

It is obvious from microscopic observations that smaller amounts of sucrose enhanced the swelling for starch granules, while larger amounts of sucrose decreased the rate of swelling for starch granules. Then, the gelatinization temperatures of starch dispersions in the presence of sucrose shifted to higher temperatures with increasing $C_s$ and the gelatinization was not completed in the presence of excessive sucrose. Therefore, the viscoelasticity of cornstarch pastes was not increased by the addition of excessive sucrose.

No decrease in the viscoelasticity was noted for cornstarch pastes by adding sucrose after gelatinization and the viscoelasticity of pastes increased with increasing $C_s$. The starch granules could swell and rupture even at a higher content of sucrose. The effect of cornstarch on increasing the viscoelasticity for cornstarch pastes with sucrose was greater than that of the control, when sucrose was added after gelatinization.
5. EFFECTS OF SODIUM CHLORIDE ON THE PHYSICAL PROPERTIES FOR CORNSTARCH PASTES

INTRODUCTION

Salty tastes are produced by inorganic and organic salts, however, only sodium chloride (NaCl) has pure salty tastes, and it is simply called salt or cooking salt. Salt is a necessary seasoning, especially for Japanese dishes. If we don’t have salt itself, it is contained in Japanese traditional seasonings: miso pastes and soybean sauces. Their concentrations of salt are 5–15 % and about 16 %, respectively. They have been widely used in Japanese dishes. For that reason, the average intake of salt for Japanese people (12 g/day) is more than that for American and European people. Japanese government says that the intake of salt should be less than 10 g/day. However, salt is a vital substance and it is essential to control the tastes of foods. The concentration of salt is about 1 % in dishes, which gives a nice salty taste.

Many researchers have studied the effects of sodium salts on gelatinization and retrogradation of starch. They have used various types of starch such as potato (121), wheat (121), 127), 130), 147), 148), 150), 152), rice (132), 151), 153), sago (137), 154), amaranth (138), cassava (155) and corn (122), 146), 147), 156). They have also used many kinds of methods such as amylogram (121), 127), 146), 147), 152), DTA or DSC (123), 130), 132), 137), 138), 154), 156), X ray analysis (151), light scattering (149), NMR (130), 151), 153), ORD (151), ESR (150), microscopic observations (151), 152), 156) and viscosity or viscoelasticity measurements (122), 148), 150), 151), 153–155). The viscoelasticity of starch samples depends greatly on the origins of starches, the concentration of starch and types and concentrations of sodium salts.

In this chapter, sodium chloride (NaCl) was used to examine the effects of salty substance on the viscoelasticity of starch pastes. NaCl has been widely used for an ingredient or a seasoning of saltiness in the food industry and in home cooking as mentioned above.

The objective is to investigate how NaCl affects the physical properties of starch pastes and contributes to the effect of increasing the viscosity for starch pastes by adding NaCl before and after gelatinization.
MATERIALS AND METHODS

Materials

The concentration of cornstarch was fixed at 3.0 wt% as in Chapter 4. Sodium chloride (NaCl, Foundation of the Salt Industry Center of Japan, Tokyo, Japan) was of a commercial grade. The content of sodium chloride was more than 99 %. The concentration of NaCl varied between 0 and 25 wt%. Potassium 2,4-hexadienoate (potassium sorbate, 0.05 wt%) was also used to prevent microbial growth. Iodine solution was also used to dye starch granules and amylose chains.

Preparation of cornstarch pastes in the presence of NaCl

The same preparation procedure was used as described in Chapter 4.

Cornstarch pastes were prepared by adding NaCl both before and after gelatinization. A cornstarch sample was made of cornstarch and distilled water.

Measurements

Steady shear and dynamic oscillatory measurements and microscopic observations of starch pastes were carried out as mentioned in Chapter 3 and 4. The same parameters could be obtained.

Differential scanning calorimetry (DSC) measurements were also conducted using the same method in Chapter 4. NaCl concentration (Cn) was 5, 10, 15, 20 and 25 wt%. Each concentration of NaCl solution was used for a reference.

RESULTS AND DISCUSSION

Steady shear measurements of cornstarch pastes with sodium chloride (NaCl) added before gelatinization

Figure 5.1 shows the shear viscosity (ηγ ) for 3.0 wt% cornstarch pastes in the presence of NaCl as functions of shear rate (γ ) and NaCl concentration (Cn). NaCl was added before gelatinization. ηγ of the control is illustrated in mesh. All samples showed a typical shear-thinning behavior. The Newtonian plateau was not observed in ηγ for all samples including the control at
Figure 5.1 Shear viscosity ($\eta_{\dot{\gamma}}$) for 3.0 wt% cornstarch pastes in the presence of sodium chloride (NaCl) as functions of shear rate ($\dot{\gamma}$) and NaCl concentration ($C_n$). NaCl was added before gelatinization. Mesh illustrates $\eta_{\dot{\gamma}}$ of the control (3.0 wt% cornstarch paste without NaCl). Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.

all $\dot{\gamma}$ examined. $\eta_{\dot{\gamma}}$ of samples with $C_n \leq 0.5$ wt% increased sharply and the shear-thinning behavior became remarkable in comparison with the control. On the contrary, $\eta_{\dot{\gamma}}$ for samples, where $0.5$ wt% $< C_n \leq 15$ wt%, decreased with increasing $C_n$ and the shear-thinning behavior became less pronounced. $\eta_{\dot{\gamma}}$ of samples with $C_n > 15$ wt% increased with increasing $C_n$ again and the shear-thinning behavior became remarkable.

$C_n$ dependence of $\eta_{\dot{\gamma}}$ observed at the same condition as in Figure 5.1 is demonstrated in Figure 5.2. Some values of $\eta_{\dot{\gamma}}$, where $\dot{\gamma}$ are 1, 10 and 100 s$^{-1}$, were chosen and represented by $\eta_1$, $\eta_{10}$ and $\eta_{100}$, respectively. The values of $\eta_{\dot{\gamma}}$ at a lower $\dot{\gamma}$, $\eta_1$ were greater than that of the control, where $C_n$ was below 5 wt%, and $\eta_1$ had the maximum value, where $C_n$ was 0.5 wt%. Then the values of $\eta_1$ were not different from that of the control at 5 wt% $< C_n \leq 15$ wt%. $\eta_1$ of pastes with $C_n$ above 15 wt% increased sharply with increasing $C_n$. $\eta_{10}$ had a similar tendency to $\eta_1$, though the values of $\eta_{10}$, where $C_n$ was below 0.1 wt%, were not different from that of the control, and $\eta_{10}$ had a constant value at 1 wt% $\leq C_n < 15$ wt%. $\eta_{\dot{\gamma}}$ at a higher $\dot{\gamma}$, $\eta_{100}$ was not different from that of the
Figure 5.2 Sodium chloride (NaCl) concentration ($C_n$) dependence of shear viscosity ($\eta$) for 3.0 wt% cornstarch pastes at shear rates of 1, 10 and 100 s$^{-1}$. NaCl was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 ºC.

control at $C_n \leq 0.2$ wt% and $\eta_{100}$ increased with increasing $C_n$. $\eta_{100}$ also increased sharply at $C_n$ above 15 wt%.

From these results, the effects of $C_n$ on the viscoelasticity of cornstarch pastes can be divided into three ranges: I) $C_n \leq 5$ wt%, II) 5 wt% $< C_n \leq 15$ wt% and III) $C_n > 15$ wt%.

Differential scanning calorimetry (DSC) measurements of cornstarch dispersions

Figure 5.3 shows heating DSC curves of 3.0 wt% cornstarch dispersions in the presence of NaCl with various concentrations. Two peaks were observed in the DSC curves for cornstarch dispersions as described in Chapter 3. The following parameters could be obtained from DSC curves: the onset temperature ($T_o$), the peak temperature ($T_p$), the conclusion temperature of amylopectin gelatinization ($T_c^1$), the conclusion temperature of amyllose–lipid complex disintegration ($T_c^2$), the gelatinization temperature range for peaks ($\Delta T = T_c^2 - T_o$) and the gelatinization enthalpy ($\Delta H$). The gelatinization temperatures and enthalpy of cornstarch in the
Figure 5.3 Heating DSC curves for 3.0 wt% cornstarch dispersions in the presence of sodium chloride (NaCl) with various concentrations between 0 (control) and 25 wt%. Characters beside each curve represent NaCl concentrations. The heating rate was 1.0 °C/min.

The presence of NaCl did not increase or decrease proportionally with increasing $C_n$.

Figure 5.4 indicates the changes in $T_o$, $T_p$, $T_{c1}$, $T_{c2}$, $\Delta T$ and $\Delta H$ determined from Figure 5.3. $T_o$, $T_p$, $T_{c1}$ and $T_{c2}$ shifted to higher temperatures and $\Delta H$ increased with increasing $C_n$ up to 10 wt% and $T_o$, $T_p$, $T_{c1}$ and $T_{c2}$ shifted to lower temperatures and $\Delta H$ decreased with increasing $C_n$ above 10 wt%. $\Delta T$ had the same tendency as $\Delta H$, though $\Delta T$ did not change so much at lower $C_n$. Namely, the gelatinization temperatures and the enthalpy had a maximum value in the $C_n$ range II (5 wt% < $C_n$ ≤ 15 wt%). These results are coincident with those that have ever been reported $^{123, 130, 137, 138, 145, 146, 149}$. In this study, cornstarch pastes were prepared by heating at 97 °C. $T_{c2}$ at $C_n$ range II was higher than 97 °C, so that the gelatinization could not occur completely and $\eta_g$ of pastes with this $C_n$ range decreased. The reason for shifting the gelatinization temperatures to higher temperatures and increasing the gelatinization enthalpy is that free water is not enough for starch granules to
Figure 5.4 Effects of sodium chloride (NaCl) concentration ($C_n$) on the gelatinization temperature ($T$) and enthalpy ($\Delta H$) of 3.0 wt% cornstarch dispersions. $T_o$: onset temperature; $T_p$: peak temperature; $T_c^1$: conclusion temperature for amylopectin gelatinization; $T_c^2$: conclusion temperature for amylose–lipid complex disintegration; $\Delta T$: gelatinization range $T_c^2 - T_o; \Delta H$: enthalpy for mg starch.

gelatinize\textsuperscript{123–125, 128, 131, 136, 138, 140, 142, 145}. Jane\textsuperscript{156} reported that Na\textsuperscript{+} ions particularly decreased free water. In the case of adding sucrose, sucrose binds amylose and amylopectin chains (glucose chains) in amorphous areas and the chains exhibit limited flexibility\textsuperscript{128, 132, 144} (See Chapter 4). The effects of NaCl on the gelatinization were different from those of sucrose. The results of DSC measurements reveal that the changes in the gelatinization temperatures and the enthalpy for starch dispersions with NaCl do not depend necessarily on the decrease of free water, but the reason for these changes can not be evidenced by the results of DSC measurements alone.

**Microscopic observations**

Microscopic photographs of the starch granules with NaCl added before gelatinization are displayed in Figure 5.5. There were several larger granules of the samples with $C_n \leq 5$ wt% ($C_n$ range I) and there were many glucose chains leached out from starch granules as compared with
Figure 5.5 Microscopic photographs of starch granules for 3.0 wt% cornstarch pastes in the presence of sodium chloride (NaCl) with various concentrations between 0 (control) and 25 wt%. NaCl was added before gelatinization. Samples were prepared as described in Figure 3.3. Pastes were diluted with distilled water and dyed with 10 mM iodine solution. Image size is 390 μm × 725 μm. Pictures were taken at ambient temperature.
those of the control. Therefore, the increase of $\eta$ in $C_n$ range I was affected by the size of starch granules and the number of glucose chains leached out from starch granules.

If NaCl promotes the starch gelatinization, $\eta$ should increase with increasing $C_n$. In fact, there were no differences in $\eta$ between the control and the pastes with $5 \text{ wt}\% < C_n \leq 15 \text{ wt}\%$ ($C_n$ range II). It is supposed that a large number of glucose chains would leach out from starch granules in the pastes at $C_n$ range II as compared with the control, although the size of starch granules for samples at this $C_n$ range is smaller than that of the control. In the case of $C_n > 15 \text{ wt}\%$ ($C_n$ range III), the size of starch granules was almost same or smaller than those of the control, while the number of glucose chains leached out from starch granules obviously increased with increasing $C_n$ in this $C_n$ range. It seems that the effects of NaCl on increasing $\eta$ in $C_n$ range III are fundamentally equal to those in $C_n$ range II. However, $\eta$ increased sharply with increasing $C_n$ in $C_n$ range III. It is thought that the increase of $\eta$ at $C_n$ range III is due to leaching out of many glucose chains from starch granules as compared with those in $C_n$ range II.

The effects of Cl$^-$ ions on the gelatinization of starch

The effects of NaCl or other ions on the gelatinization of starch are collected from many reports\textsuperscript{145–147), 150), 151), 154), 156), 157).}

1. Cations ($X^+$) are weak acid ion exchangers, namely $X^+$ ions dissociate the hydroxyl group of starch ($\text{OH} \rightarrow \text{OX}$)\textsuperscript{146), 151).}

2. Some of OX displace for OH again at higher temperatures\textsuperscript{146).}

3. Divalent cations are stronger than monovalent cations\textsuperscript{145), 146), 154), 156).}

4. Anions can penetrate the starch granules and promote the starch gelatinization\textsuperscript{146), 151).}

5. Anions can rupture hydrogen bonds in starch granules and promote the swelling of starch granules\textsuperscript{145), 146), 150), 151), 157).}

From these considerations, the effects of NaCl on the viscosity for cornstarch pastes are discussed below.

1. $C_n$ range I ($C_n \leq 5 \text{ wt}\%$)

As the major axes of cornstarch granules increase 9 % by swelling upon sorption of water\textsuperscript{3), 158), the volume of the granules increases about 30 %. After starch granules swell, electrolytes with small size such as Na$^+$ ions and Cl$^-$ ions can penetrate easily into starch granules, if there are no effect of electrostatic repulsion in starch granules and surfaces of starch granules. When starch is dispersed
in water at room temperature, imbalance of ions comes out inside the starch NaCl aqueous dispersion. It is called Donnan effect\(^{146},159\). For dissolving this imbalance of ions, –OH of glucose residues in starch granules substitutes –ONa, and H\(^+\) ions are excluded into NaCl aqueous solution. The penetration of Cl\(^-\) ions is repelled by Donnan potential on the surface of starch granules at the same time. This repellent means that the concentration of Na\(^+\) ions in the starch granules may be almost equal to that in the NaCl aqueous solution and the concentration of Cl\(^-\) ions in the starch granules may be lower than that in the NaCl aqueous solution, because of the lower \(C_n\) at \(C_n\) range I. When the starch dispersions with \(C_n\) range I were heated and gelatinized, the volume of the starch granules also increased greatly by swelling (Figure 5.5 middle, left). This increase of the volume on the gelatinization might bring new imbalance of ions in starch NaCl aqueous dispersion, and some of –ONa in glucose residues inside starch granules would displace –OH again. As the result, Donnan potential would decrease and repelling of Cl\(^-\) ions would decrease, namely the penetration of Cl\(^-\) ions into starch granules would be promoted. These hypotheses might be true from the results of changes in pH for the cornstarch pastes (Figure 5.6) and Oosten’s report\(^{146}\). The pH of cornstarch pastes with \(C_n \leq 5\) wt\% was lowered by the addition of NaCl, because many Na\(^+\) ions were absorbed in the starch granules, and H\(^+\) ions were excluded into NaCl solution. However, the pH did not change among before, during and after gelatinization. It is thought that the movements of Cl\(^-\) ions are controlled by the decrease in the charge density inside starch granules, rather than the exchange of –ONa to –OH. The increase of \(\eta_{\gamma}\) in this \(C_n\) range indicates that there is no effect of Donnan potential and starch granules can swell and the anions contribute to starch gelatinization as a gelatinization agent.

2. \(C_n\) range II (5 wt\% < \(C_n\) ≤ 15 wt\%)

The effects of NaCl on the swelling of starch granules and glucose chains leached out from starch granules are fundamentally same as the effects in \(C_n\) range I. However, the degree of the gelatinization for starch by heating at about 100 °C, which is used for general gelatinization, decreased in comparison with that in \(C_n\) range I. This is because the structure of water are changed due to the higher concentrations of NaCl, in particular, Na\(^+\) ions act on water as a structure maker and decrease free water\(^{156}\). Therefore, starch dispersions did not gelatinize completely because gelatinization temperatures shifted to higher temperatures, which were higher than 97 °C used for preparation of starch pastes (Figure 5.4). However, Cl\(^-\) ions, which have penetrated starch granules, have the effect on rupturing the hydrogen bonds inside starch granules\(^{146},151\), and glucose chains
leached out from starch granules. $\eta_{\gamma}$ did not depend on $C_n$ or $\eta_{\gamma}$ increased with increasing $C_n$ at higher $\gamma$ in $C_n$ range II, although the values of $\eta_{\gamma}$ were less than those in $C_n$ range I at lower $\gamma$, (Figure 5.2).

The reason for greater values of $\eta_{\gamma}$ as compared with that of the control is that there would be many glucose chains leached out from starch granules, which have higher molecular weights, in the pastes at this $C_n$ range as compared with those of the control, in spite of smaller size of the starch granules.

3. $C_n$ range III ($C_n > 15$ wt%)

In the starch aqueous dispersion with higher $C_n$, Na$^+$ ions and H$^+$ ions can exchange each other on the surface of starch granules and Cl$^-$ ions can penetrate starch granules even before gelatinization. Chiotelli et al.\textsuperscript{150} reported that the gelatinization temperature of wheat and potato starch with above 7 % NaCl decreased, and they concluded that the driving force of anions exceeded the repulsing force of the Donnan potential, and anions entered the granules and started the gelatinization process by rupturing the hydrogen bonds between the starch molecules. Thus,
when the starch dispersions with Cl\(^-\) ions inside starch granules, are heated, many glucose chains leached out from starch granules because Cl\(^-\) ions break the hydrogen bonds. However, the swelling of starch granules is controlled by the changes in the structure of water, because of the existence of many electrolytes in starch pastes. The less values of \(\Delta H\) in this range (Figure 5.4) suggest that ordered regions of starch would be destabilized by NaCl\(^{150}\). The reason for smaller size of starch granules and the existence of many glucose chains (Figure 5.5) is thought that glucose chains leached out from starch granules faster than starch granules swelled. No change in pH for starch pastes with \(C_n > 15\) wt\% revealed that there were excessive electrolytes in this \(C_n\) range (Figure 5.6).

**Dynamic oscillatory measurements of cornstarch pastes with NaCl added before gelatinization**

Figure 5.7 illustrates the angular frequency (\(\omega\)) dependence of the storage modulus (\(G'\))

**Figure 5.7** Angular frequency (\(\omega\)) dependence of storage modulus (\(G'\), left) and loss modulus (\(G''\), right) for 3.0 wt\% cornstarch pastes in the presence of sodium chloride (NaCl) with various concentrations between 0 (control) and 25 wt\%. NaCl was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. The strain for samples with 0 (control), 0.2, 0.5, 5, 10 and 25 wt\% NaCl concentrations, was 30, 10, 3, 30, 30 and 30 %, respectively.
and the loss modulus ($G''$) for 3.0 wt% cornstarch pastes with or without NaCl. NaCl was added before gelatinization. The paste of the control showed a behavior known for concentrated solutions of flexible polymers, i.e., $G'$ is less than $G''$ at lower $\omega$ and $G'$ is greater than $G''$ at higher $\omega$ as described in Chapter 3 and 4. The mechanical spectra for starch pastes depend on the size of starch granules, the number of glucose chains leached out from starch granules after gelatinization and coexisting substances. $G'$ for all samples did not depend on $\omega$ at lower $\omega$ and the long-time relaxation was observed. For starch pastes in the presence of NaCl, there were also the entanglements of glucose chains accompanied with starch granules (See Chapter 4). $G'$ at $C_n$ range I ($C_n \leq 5$ wt%) was greater than that of the control, and $G'$ had the maximum values at $C_n = 0.5$ wt%. It coincided with the results of $\eta_\gamma$. When the number of glucose chains leached out from starch granules are almost constant, the size of starch granules should affect the values of $G'$ and $G''$. Therefore, the maximum values of $G'$ and $G''$ in this range may be due to the largest size of starch granules. Contrary to these results, $G'$ and $G''$ decreased with increasing $C_n$ at $C_n$ range II (5 wt% < $C_n \leq 15$ wt%), because the swelling of starch granules were prevented in this range, especially at $C_n = 10$ wt%. $G'$ for samples with $C_n$ range III ($C_n > 15$ wt%) increased with increasing $C_n$ again. It was too difficult to compare the size of starch granules, but the values of $G'$ were greater than those of $G''$ at all $\omega$ examined for pastes with 20 wt% ≤ $C_n$ ≤ 25 wt%. This is the behaviour for a weak gel. This result supports the assumption that there would be many glucose chains in $C_n$ range III as compared with other $C_n$ ranges.

Complex viscosity ($|\eta^*|_\omega$) for 3.0 wt% cornstarch pastes in the presence of NaCl as functions of $\omega$ and $C_n$ is shown in Figure 5.8. NaCl was added before gelatinization. $|\eta^*|_\omega$ of the control is illustrated in mesh. Comparing of $|\eta^*|_\omega$ in Figure 5.8 with $\eta_\gamma$ in Figure 5.1, $|\eta^*|_\omega$ and $\eta_\gamma$ of all samples did not obey the Cox-Merz rule because starch pastes contained swollen granules and glucose chains as described in previous chapters. The values of $|\eta^*|_\omega$ did not coincide with those of $\eta_\gamma$, while $|\eta^*|_\omega$ had a similar tendency to $\eta_\gamma$. The values of $|\eta^*|_\omega$ where 0.4 wt% ≤ $C_n$ ≤ 1 wt% and $C_n \geq 20$ wt%, were greater than those of $\eta_\gamma$, while the values of $|\eta^*|_\omega$ for other samples were less than that of $\eta_\gamma$. As $|\eta^*|_\omega$ is characteristic of the network structures, which are not destroyed by shear, it is suggested that the network structures for the samples with 0.4 wt% ≤ $C_n$ ≤ 1 wt% and $C_n \geq 20$ wt% are stronger than those for other samples (See Chapter 3).

From these results, it is found that it is easier for glucose chains to leach out from starch granules and to form the entangled networks at 0.4 wt% ≤ $C_n$ ≤ 1 wt% and $C_n \geq 20$ wt%.
Figure 5.8 Complex viscosity (|\(\eta^*\)|) for 3.0 wt% cornstarch pastes in the presence of sodium chloride (NaCl) as functions of angular frequency (\(\omega\)) and NaCl concentration (\(C_n\)). NaCl was added before gelatinization. Mesh illustrates |\(\eta^*\)| of the control (3.0 wt% cornstarch paste without NaCl). Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. The strain for samples with 0 (control), 0.2, 0.4, 0.5, 0.8, 1, 2, 4, 5, 5.5, 7, 9, 10, 12.5, 15, 17.5, 20, 22.5 and 25 wt% NaCl concentrations, was 30, 10, 3, 3, 5, 12, 30, 30, 20, 15, 10, 50, 30, 3, 4, 5, 3, 3 %, respectively.

Effects of adding NaCl after gelatinization

Figure 5.9 illustrates \(\eta_\dot{\gamma}\) of 3.0 wt% cornstarch pastes as a function of \(\dot{\gamma}\). NaCl was added after gelatinization. Typical shear-thinning behaviors could be also seen for all samples. No decrease in \(\eta_\dot{\gamma}\) could be observed even at \(C_n\) range II by adding NaCl after gelatinization. The values of \(\eta_\dot{\gamma}\) increased with increasing \(C_n\). However, the values of \(\eta_\dot{\gamma}\) for pastes, to which NaCl was added after gelatinization, were less than those for pastes with NaCl added before gelatinization at \(C_n\) range III. There was no difference in the values of \(\eta_\dot{\gamma}\) at higher \(C_n\), i.e., 10 wt% \(\leq C_n \leq 20\) wt%; this constant value is supposed that the driving force of Cl\(^-\) ions for rupturing the hydrogen bonds may be enhanced by heating, and Cl\(^-\) ions do not have any effects on \(\eta_\dot{\gamma}\) of starch pastes without heating so much. It is thought that the reason for increasing \(\eta_\dot{\gamma}\) of samples by adding NaCl after gelatinization is just due to the decrease of the concentration of water, which leads to the
increase of the ratio of cornstarch to water.

There was also no difference in the microscopic photographs for the samples with $C_n < 15$ wt% (Figure 5.10). Many glucose chains could be observed by adding NaCl after gelatinization in the $C_n$ range II (Figure 5.10 top, right). Many starch granules collapsed for the samples with $C_n = 15$ wt% as compared with those for other samples. It is supposed to be that many starch granules contact each other because the ratio of starch to water, when starch dispersions were heated, is higher than that of other samples. The collapse of starch granules could be also observed in the case of adding sucrose after gelatinization (See Figure 4.5 bottoms, right in Chapter 4).

The same tendencies were observed in the results of dynamic oscillatory measurements. The values of $G'$ and $G''$ were increased with increasing $C_n$ (Figure 5.11). $G'$ was greater than $G''$ at all $\omega$ examined for all samples with NaCl. Namely, all samples behaved like weak gels. Although the values of $G'$ and $G''$, where $C_n$ is above 20 wt%, were less than those of samples adding NaCl before gelatinization, the entangled networks formed by adding NaCl after gelatinization.

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**Figure 5.9** Shear viscosity ($\eta/\gamma$) for 3.0 wt% cornstarch pastes in the presence of sodium chloride (NaCl) with various concentrations between 0 (control) and 20 wt%. as a function of shear rate ($\gamma$. NaCl was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 ºC.
**Figure 5.10** Microscopic photographs of starch granules for 3.0 wt% cornstarch pastes in the presence of sodium chloride (NaCl) with various concentrations between 0 (control) and 15 wt%. NaCl were added after gelatinization. Samples were prepared as described in Figure 3.3. Pastes were diluted with distilled water and dyed with 10 mM iodine solution. Image size is 390 $\mu$m $\times$ 725 $\mu$m. Pictures were taken at ambient temperature.

**Figure 5.11** Angular frequency ($\omega$) dependence of storage modulus ($G'$, left) and loss modulus ($G''$, right) for 3.0 wt% cornstarch pastes in the presence of sodium chloride (NaCl) with various concentrations between 0 (control) and 20 wt%. NaCl was added after gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 ºC. The strain for samples with 0 (control), 5, 10, 15 and 20 wt% NaCl concentrations, was 30, 3, 3, 3 and 3 %, respectively.
The values of $|\eta^*|_\omega$ also increased with increasing $C_n$ (Figure 5.12), although the values of $|\eta^*|_\omega$ were not coincidental with those of $\eta_{\gamma}$ in Figure 5.9. All values of $|\eta^*|_\omega$ were greater than those of $\eta_{\gamma}$. These higher values of $|\eta^*|_\omega$ would be due to many entanglements by glucose chains or due to the higher ratio of cornstarch to water, when the cornstarch dispersions were heated (See Chapter 3).

![Figure 5.12](image.png)

**Figure 5.12** Complex viscosity ($|\eta^*|_\omega$) for 3.0 wt% cornstarch pastes in the presence of sodium chloride (NaCl) with various concentrations between 0 (control) and 20 wt% as a function of angular frequency ($\omega$). NaCl was added after gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. The strain for samples with 0 (control), 5, 10, 15 and 20 wt% NaCl concentrations, was 30, 3, 3, 3 and 3 %, respectively.
CONCLUSIONS

When sodium chloride (NaCl) was added to cornstarch dispersions before gelatinization, the viscoelasticity of the cornstarch pastes changed complicatedly by NaCl concentration ($C_n$). The viscoelasticity of cornstarch pastes, where $C_n$ was below 5 wt% and more than 15 wt%, was greater than that of the control. The increase of viscoelasticity for pastes with $C_n$ below 5 wt% was due to the increasing of the swelling rate for starch granules. When Donnan potential decreases, the penetration of Cl$^-$ ions into starch granules is promoted. Then, Cl$^-$ ions rupture the hydrogen bonds between starch molecules. Thus, the viscoelasticity of pastes with $C_n \leq 5$ wt% and $C_n > 15$ wt% increased.

On the other hand, the viscoelasticity of the samples with 5 wt% < $C_n \leq 15$ wt% was less than that of the pastes, where $C_n$ was below 5 wt% and more than 15 wt%. The gelatinization temperatures of cornstarch dispersions in the presence of NaCl shifted to higher temperatures and the enthalpy increased with increasing $C_n$ up to 10 wt%, and the gelatinization temperatures shifted to lower temperatures and the enthalpy decreased with increasing $C_n$ above 10 wt%. Namely, the gelatinization of starch dispersions was prevented by adding NaCl with 5 wt% < $C_n \leq 15$ wt%, and hence the viscoelasticity could not be enhanced. It was obvious from microscopic observations that smaller amounts of NaCl enhanced the swelling for starch granules, while starch granules with intermediate $C_n$ were smaller than those of other $C_n$ ranges.

No decrease in the viscoelasticity was noted for cornstarch pastes by adding NaCl after gelatinization and the viscoelasticity of pastes increased with increasing $C_n$, though the viscoelasticity of pastes added NaCl above 15 wt% after gelatinization was less than that of pastes added NaCl before gelatinization.
6. EFFECTS OF SOUR SUBSTANCES ON THE PHYSICAL PROPERTIES FOR CORNSTARCH PASTES

INTRODUCTION

Sour tastes are produced by many kinds of organic acids, and they are contained in many kinds of foods. Sour substances have been used as a sour seasoning, an acidulent and a preservative. It is well known that starch is hydrolyzed by strong acids, for example, aqueous hydrochloric acid. To overcome the disadvantages of native starches such as its gummy or cohesive texture and the formation of rigid and opaque gels, many kinds of modified starches have been designed. Acid-hydrolyzed starch is one of them. Aqueous hydrochloric acid is used to make acid-hydrolyzed starch by compulsorily causing hydrolysis of amylose and amyllopectin chains \(^4\), \(^86\), \(^108\), \(^160\), \(^161\). However, sour substances (various organic acids) are included in many foods and are added to many dishes as an acidulent or a preservative as mentioned above. It is necessary to investigate the effects of various acids on the viscoelasticity of starch since it may lead to understanding how to control the viscoelasticity of starch products.

Many researchers have reported about the effects of acids or pH on gelatinization and retrogradation of starch. They have used various types of starch such as potato \(^121\), \(^122\), \(^163\), \(^164\), wheat \(^121\), \(^126\), \(^127\), cassava \(^155\), \(^165\), \(^166\), rice \(^167\) and corn \(^122\), \(^163\), \(^164\), and many types of sour substances such as citric acid \(^126\), \(^164\), acetic acid or vinegar \(^121\), \(^122\), \(^164\), ascorbic acid \(^127\), \(^155\), \(^165\), \(^166\). They have also used many kinds of methods such as amylogram or RVA \(^121\), \(^126\), \(^127\), \(^163\), \(^164\)–\(^167\), X-ray analysis \(^165\), and viscosity or viscoelasticity measurements \(^122\), \(^155\), \(^165\), \(^166\), while there are few reports \(^122\) concerning the viscoelasticity of cornstarch in the presence of sour substances.

In this chapter, citric acid, acetic acid, lactic acid, malic acid, tartaric acid and ascorbic acid were used to examine the effects of sour substances on the viscoelasticity of starch pastes as the model for actual starch food products. Citric acid is contained in citrus fruits and is added to foods as a sour seasoning. It is also important as a basic sour substance for difference tests on sensory
evaluation\(^{58}\)). Acetic acid is the main sour component of vinegar. Lactic acid is included in cheese and yogurt. Malic acid and tartaric acid are in many kinds of fruits and are used as an acidulent. Ascorbic acid is an important source of vitamin C; it is also contained in many kinds of vegetables and fruits and is used as an antioxidant. Table 6.1 is the list of sour substances, which were used in this study, and their chemical formulas and foods including them.

The objective is to investigate how sour substances affect the physical properties of starch pastes and contribute to the effect of increasing the viscosity for starch pastes by adding acids before and after gelatinization. Powders of sour substances are generally added to foods before and after gelatinization and liquid of them are generally added to foods or cooking after gelatinization.

### Table 6.1 Sour substances and their whereabouts

<table>
<thead>
<tr>
<th>Sour substance</th>
<th>Chemical formula</th>
<th>Foods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric acid</td>
<td>COOH</td>
<td>Citric fruits, Ume (Japanese apricot)</td>
</tr>
<tr>
<td></td>
<td>HOOCCH₂CCH₂COOH</td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH₃COOH</td>
<td>Vinegar, Pickled vegetables</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>CH₃CHOHCOOH</td>
<td>Yogurt, Cheeses, Pickled vegetables</td>
</tr>
<tr>
<td>Malic acid</td>
<td>HOOCCH₂CHOHCOOH</td>
<td>Apples, Peaches, Grapes</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>HOOC(CHOH)₂COOH</td>
<td>Grapes, Pineapples</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>COCOH=COHCHHOHCH₂OH</td>
<td>Citric fruits, Vegetables</td>
</tr>
</tbody>
</table>

**MATERIALS AND METHODS**

**Materials**

The concentration of cornstarch was fixed at 3.0 wt% as in Chapter 4 and 5. Citric acid (anhydrous), acetic acid, DL-lactic acid, DL-malic acid, L(+)-tartaric acid and L(+)-ascorbic acid were of reagent grades. All these samples were purchased from Wako Pure Chemical Industries, Inc. (Osaka, Japan). The pH was adjusted between 6.0 and 3.0 by using these acids. Potassium 2,4-hexadienoate (potassium sorbate, 0.05 wt%) was also used to prevent microbial growth. Iodine
solution was also used to dye starch granules and amylose chains. Dimethyl sulfoxide (DMSO, Wako Pure Chemical Industries, Inc., Osaka, Japan) was used to make solutions of cornstarch.

**Preparation of cornstarch pastes in the presence of various acids**

The same preparation procedure was used as described in Chapter 4.

Cornstarch pastes were prepared with pH adjusted both before and after gelatinization. A control sample of pH 6.3 was made of cornstarch and distilled water. The cornstarch pastes with the pH adjusted by adding various acids, depended slightly on the storage time, i.e., the viscosity decreased slightly with elongating storage time. Therefore, the pastes after 200 min from the preparations were used on the viscoelasticity measurements (See Figure 3.3 in Chapter 3).

**Viscoelasticity measurements and microscopic observations**

Steady shear and dynamic oscillatory measurements and microscopic observations of starch pastes were carried out as mentioned in Chapters 4 and 5. The same parameters could be obtained.

**Intrinsic viscosity measurements**

Cornstarch (3.0 wt%) was dispersed in distilled water or citric acid aqueous solutions with the pH adjusted beforehand. The dispersions were heated in a water bath at 97 °C for 60 min stirring with a magnetic stirrer, then cooled in a water bath at 25 °C for 60 min stirring. DMSO was then added to the dispersions so that the ratio of DMSO to water should become 90:10 (vol). The concentration of starch became 0.28 wt%. DMSO works by breaking associative hydrogen bonds in the polysaccharides and in water \(^{108},161\). Small amounts of water tend to enhance the solubilization of starch in DMSO by temporarily preventing DMSO from swelling the molecules on the surface of starch granule because swelling would prevent DMSO from penetrating the entire granule \(^{168}\). Therefore, 90 vol% DMSO aqueous solutions have been used to dissolve starch completely \(^{108},161,168,169\). The DMSO solutions of cornstarch were heated and cooled again using the same methods mentioned above. The solutions were serially diluted by 90 vol% DMSO aqueous solution to a final concentration of 0.06 wt%. Intrinsic viscosity measurements were made using an Ubbelohde type capillary viscometer at 40.0 ± 0.01 °C. The flow time of the solvent was c.a. 330 sec at 40.0 °C. Intrinsic viscosity \([\eta_f]\) was calculated from the Huggins equation \(^{170}\).
\[
\eta_{i,\gamma} / c = [\eta_{\gamma}] (1+k[\eta_{\gamma}]c^{+\cdots})
\]  
(6.1)

where \(\eta_{i,\gamma}\) is the relative viscosity increment as described in Equation 4.1 in Chapter 4, \(c\) is the concentration of the solute and \(k\) is the Huggins constant.

**RESULTS AND DISCUSSION**

**Steady shear measurements of cornstarch pastes with acids added before gelatinization**

Figure 6.1 shows the shear viscosity (\(\eta_{\gamma}\)) for 3.0 wt% cornstarch pastes as functions of shear rate (\(\dot{\gamma}\)) and pH. The pH was adjusted by adding citric acid before gelatinization. \(\eta_{\gamma}\) of the control (pH = 6.3) is illustrated in mesh. All samples showed typical shear-thinning behaviors. It was observed that \(\eta_{\gamma}\) became greater and the shear-thinning behavior became remarkable at pH between 5.5 and 3.6 in comparison with the control. On the contrary, \(\eta_{\gamma}\) for pH above 5.5 and below 3.6 became less than that of the control, and the shear-thinning behavior became less pronounced.

Figure 6.1 Shear viscosity (\(\eta_{\gamma}\)) for 3.0 wt% cornstarch pastes as functions of shear rate (\(\dot{\gamma}\)) and pH. The pH was adjusted by adding citric acid before gelatinization. Mesh illustrates \(\eta_{\gamma}\) of the control (3.0 wt% cornstarch paste, pH = 6.3). Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.
The pH dependence of $\eta$ at $\dot{\gamma} = 10$ s$^{-1}$ ($\eta_{10}$) is demonstrated in Figure 6.2. The pH was adjusted by adding various acids such as citric acid, acetic acid, lactic acid, malic acid, tartaric acid and ascorbic acid before gelatinization. $\eta_{10}$ decreased by lowering the pH to around 5.6 and $\eta_{10}$ increased inversely at $3.6 < \text{pH} < 5.6$. By lowering the pH furthermore, $\eta_{10}$ decreased again. The values of $\eta_{10}$, where the pH was above 5.5 and below 3.6, were less than that of the control and the values of $\eta_{10}$, where the pH was between 5.5 and 3.6, were greater than that of the control.

Although the pH, where $\eta$ increased or decreased, was slightly different, depending on the types of acids, the tendency of increasing or decreasing $\eta$ of starch pastes was similar. Therefore, $\eta$ of the pastes with the pH adjusted by adding acids depends only on pH and not on types of acids. $\eta$ changed depending on the pH because the condition differed, i.e., size or shapes of starch granules and the number of chains of amylose and amylopectin (glucose chains) differed.

It was reported that the viscosity of wheat starch pastes decreased by the addition of citric acid$^{126}$ or ascorbic acid$^{127}$. It was also reported that the viscosity of cassava starch pastes

![Figure 6.2 pH dependence of shear viscosity for 3.0 wt% cornstarch pastes at the shear rate of 10 s$^{-1}$ ($\eta_{10}$). The pH was adjusted by adding citric acid, acetic acid, lactic acid, malic acid, tartaric acid and ascorbic acid before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.](image-url)

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Chapter 6

decreased by adding ascorbic acid\textsuperscript{155},\textsuperscript{165},\textsuperscript{166}. The results of Takahashi and Kikura\textsuperscript{122} were that \( \eta \) and the rigidity for cornstarch pastes decreased by adding vinegar or acetic acid. Yamada \textit{et al.}\textsuperscript{164} reported that the viscosity of pastes for potato starch decreased by adjusting the pH with citric acid or acetic acid, while that for cornstarch was not affected by acids. Moreover, when cornstarch was separated from corn kernels by steeping in the aqueous solution containing lactic acid, the starch separation became more easily\textsuperscript{171}, and the viscosity of these cornstarch pastes decreased further than that of cornstarch pastes obtained by steeping in the aqueous solution without lactic acid\textsuperscript{172}. Cotyledon tissues of kidney beans were softened by addition of acetic acid and the gelatinization of starch inside tissues was stimulated\textsuperscript{173}. The hardness of cooked rice decreased by adding acetic acid, though the stickiness increased\textsuperscript{174}. On the other hand, the hardness of various foods observed in texture profile analysis increased by adding acids, e.g., bread loaf\textsuperscript{160},\textsuperscript{175}, wheat flour dough\textsuperscript{176} and peeled potatoes\textsuperscript{177}. Such firming must be distinguished from softening and cell sloughing\textsuperscript{177}. However, an increase in the viscosity for starch pastes by adding acids has not yet been reported to the author’s knowledge.

Microscopic observations

Microscopic photographs of the cornstarch granules, with the pH adjusted by adding citric acid before gelatinization, are lined along the left in Figure 6.3.

The granule sizes of the samples at pH 6.0, 5.0 and 4.0 with the pH adjusted before gelatinization were almost the same as those of the control or a little smaller than those of the control, however, the number of glucose chains at pH 5.0 and 4.0 was apparently more than that of the control. It is thought that there are many entanglements of glucose chains as compared with those of the control, and these networks of glucose chains lead to higher \( \eta \). Thus, \( \eta \) of starch samples, where the pH is between 5.6 and 3.6, was greater than that of the control. The granule size of the sample at pH 3.5 was smaller than that of the control, the samples at pH 6.0, 5.0, and 4.0. Almost all granules were broken at pH 3.0, and more glucose chains were observed in comparison with other samples. Decreases in \( \eta \) at the lower pH range may be due to the collapse of many starch granules or the hydrolysis of glucose chains by adding acids.

Intrinsic viscosity measurements

If the hydrolysis of glucose chains were to occur by adding acids, the degree of
**Effects of sour substances on the physical properties for cornstarch pastes**

**Figure 6.3** Microscopic photographs of starch granules for 3.0 wt% cornstarch pastes with or without adjusting pH. The pH was adjusted between 6.0 and 3.0 by adding citric acid before and after gelatinization. Samples were prepared as described in Figure 3.3. Pastes were diluted with distilled water and dyed with 10 mM iodine solution. Image size is 390 $\mu$m × 725 $\mu$m. Pictures were taken at ambient temperature.
polymerization \((DP)\) for glucose chains should decrease. Intrinsic viscosity \([\eta_{\gamma}]\) was then measured to confirm that the hydrolysis of glucose chains did occur. Since \([\eta_{\gamma}]\) depends on \(DP\), the size of glucose chains can be estimated from changes in \([\eta_{\gamma}]\). Figure 6.4 shows the results of intrinsic viscosity measurements. The pH of the x-axis is equivalent to the pH in the preparation for cornstarch pastes. The pH was adjusted by adding citric acid. Huggins constant \((k)\) reflects the interaction of neighboring polysaccharide chains, and it depends on the interaction between macromolecule and solvent. For flexible polymer molecules in good solvent, the value of \(k\) is given between 0.3 and 0.6\(^{178,179}\). The values of \(k\) for the samples with \(6.3 \geq \text{pH} \geq 3.1\) were between 0.4 and 0.6 (Figure 6.4). Therefore, glucose chains were completely dissolved in 90 vol\% DMSO aqueous solutions, and it was found that 90 vol\% DMSO solution was a good solvent for starch.

\([\eta_{\gamma}]\) decreased slightly at \(\text{pH} \geq 4.0\). This decrease indicates that few glucose chains were hydrolyzed by adding acid. However, increase in \(\eta_{\gamma}\) was observed, where the pH is between 5.5 and 3.6 as shown in Figure 6.2. It is thought that acids enter the starch granules, causing the

![Figure 6.4](image.png)

**Figure 6.4** Intrinsic viscosity \([\eta_{\gamma}]\) and Huggins constant \((k)\) of cornstarch in 90 vol\% DMSO aqueous solution as a function of pH. The pH was adjusted by adding citric acid before gelatinization. Measurements were made at 40.0 °C.
hydrolysis of glucose chains inside starch granules, then lead many glucose chains to leach out from starch granules into the starch pastes. Therefore, the entanglements of glucose chains increase further than those of the control. $[\eta_f]$ decreased sharply at pH < 4.0. This indicates that hydrolysis of glucose chains occurs by adding acids and DP for samples at pH < 4.0 decreases further than that for samples at pH ≥ 4.0. Decreases in $\eta_f$ were observed, where the pH is below 3.5, since the entanglements of glucose chains were less than those at pH ≥ 4.0. $\eta_f$ of the paste with pH = 3.0 showed less shear-thinning behavior than that of other samples (Figure 6.1). This behavior is suggested that there are not glucose chains with large DP in the paste. Precipitation of starch in starch pastes occurred at pH < 2.7 (Figure 6.2 and 6.4). It is known that the solubility of amylose with various DP increased considerably with shorter and longer molecules. Amylose with DP 840 had a minimum of the second virial coefficient ($A_2$), which is the index of solubility, while $A_2$ of amylose with DP between 13.5 and 29 could not be determined because of the bad solubility, and amylose exhibited a sharp minimum of solubility for DP between 75 and 80. Amylose with DP between 40 and 660 were found to precipitate, although the precipitation depended on the concentration of amylose. The precipitation of starch occurred in this study may be caused by many glucose chains with low DP in starch pastes.

**Dynamic oscillatory measurements of cornstarch pastes with acids added before gelatinization**

Figure 6.5 illustrates the angular frequency ($\omega$) dependence of the storage modulus ($G'$) and the loss modulus ($G''$) for 3.0 wt% cornstarch pastes with or without adjusting the pH. The pH was adjusted by adding tartaric acid before gelatinization. The paste with pH 6.3 (control) and 6.0 showed a behavior known for concentrated solutions of flexible polymers, i.e., $G'$ is less than $G''$ at lower $\omega$ and $G'$ is greater than $G''$ at higher $\omega$ as described in previous chapters. The values of $G'$ and $G''$ for the paste with pH 6.0 were a little greater than those of the control, but they were not so different from those of the control. The values of $G'$ were greater than those of $G''$ at all $\omega$ examined and $G'$ and $G''$ increased with increasing $\omega$ for pastes with 6.0 > pH > 3.5. This behavior resembles that for a weak gel, which consists of entangled networks formed by starch granules and glucose chains that leach out from starch granules (See Chapter 3). The pastes also behaved as the concentrated solutions of flexible polymers where the pH is below 3.5. $G'$ and $G''$ decreased with lowering pH below 3.5, and the values of $G'$ and $G''$ at pH < 3.5 were less than those of the control.
Figure 6.5 Angular frequency ($\omega$) dependence of storage modulus ($G'$, left) and loss modulus ($G''$, right) for 3.0 wt% cornstarch pastes. The pH was adjusted between 6.0 and 3.0 by adding tartaric acid before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 ºC. The strain for samples at pH 6.3 (control), 6.0, 5.0, 4.0, 3.5 and 3.0, was 30, 30, 3, 3, 15 and 20 %, respectively.

at all $\omega$ examined. This behavior suggests that both the size of starch granules and $DP$ for glucose chains decrease. These behaviors could be observed by adding all types of acids used in this study (data not shown).

Complex viscosity ($|\eta^*|_\omega$) for 3.0 wt% cornstarch pastes as functions of $\omega$ and pH is shown in Figure 6.6. The pH was adjusted by adding citric acid before gelatinization. $|\eta^*|_\omega$ of the control is illustrated in mesh. Comparing $|\eta^*|_\omega$ in Figure 6.6 with $\eta_\gamma$ in Figure 6.1, $|\eta^*|_\omega$ and $\eta_\gamma$ of all samples did not obey the Cox-Merz rule because starch pastes contained swollen granules and glucose chains as described in previous chapters. The values of $|\eta^*|_\omega$ did not coincide with those of $\eta_\gamma$, while $|\eta^*|_\omega$ had a similar tendency to $\eta_\gamma$. $|\eta^*|_\omega$ of samples with $6.0 > pH > 3.4$ was greater than that of the control, and $|\eta^*|_\omega$, where pH is 6.0 and 3.4, was not different from that of the control, while $|\eta^*|_\omega$ at pH < 3.4 was less than that of the control. $|\eta^*|_\omega$ was greater than $\eta_\gamma$ on samples with $5.3 \geq pH \geq 3.6$. The cornstarch pastes with this pH range behave as weak gels. This behavior indicates that there are many entanglements of glucose chains accompanied with starch
Effects of sour substances on the physical properties for cornstarch pastes

Figure 6.6 Complex viscosity ($|\eta^*|_\omega$) for 3.0 wt% cornstarch pastes as functions of angular frequency ($\omega$) and pH. The pH was adjusted by adding citric acid before gelatinization. $|\eta^*|_\omega$ of the control (3.0 wt% cornstarch pastes, pH = 6.3) is illustrated in mesh. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. The strain for samples at pH 6.3 (control), at pH between 6.0 and 5.5, at pH between 5.3 and 3.4 and at pH 3.0, was 30, 30, 3 and 20 %, respectively.

granules in this pH range. On the other hand, the cornstarch pastes at pH > 5.3 and at pH < 3.6 did not have many entanglements by glucose chains. This result coincides with that in Figure 6.5. Similar to Figure 6.2, the tendency of $|\eta^*|_\omega$ for samples with the pH adjusted by adding various acids was not different (Figure 6.7).

From the results mentioned above, adding much acid leads to a decrease in the viscoelasticity for starch pastes because the hydrolysis of many glucose chains occurs. When acids are added to the cornstarch pastes after heating and cooling, i.e., after gelatinization, the hydrolysis of glucose chains can be prevented. Therefore, higher viscoelasticity for starch pastes must be obtained.
Chapter 6

Figure 6.7 pH dependence of complex viscosity for 3.0 wt% cornstarch pastes at the angular frequency ($\omega$) of 10 rad s$^{-1}$ ($|\eta^*|_{10}$). The pH was adjusted by adding citric acid, acetic acid, lactic acid, malic acid, tartaric acid and ascorbic acid before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.

Effects of adding acids after gelatinization

Figure 6.8 shows $\eta_\gamma$ for 3.0 wt% cornstarch pastes with or without adjusting pH as a function of $\gamma$. The pH was adjusted by adding lactic acid after gelatinization. Typical shear-thinning behaviors could be also seen for all samples. There were no differences between the control sample and samples with pH 6.0. Decreases in $\eta_\gamma$ could not be observed even at lower pH (pH = 3.0). The values of $\eta_\gamma$ for all samples were greater than that of the control except for the samples with pH 6.0. The values of $\eta_\gamma$ for samples with the pH adjusted to 5.0 and 4.0 by adding acids after gelatinization were less than those for samples adjusted pH by adding acids before gelatinization. It is thought that leaching out of glucose chains from starch granules is promoted by heating, so that the values of $\eta_\gamma$ adding acids before gelatinization should be greater than those adding acids after gelatinization. This result could be obtained from samples adjusted pH by adding all types of acids used in this work (data not shown). Many starch granules could be observed in the
Effects of sour substances on the physical properties for cornstarch pastes

Figure 6.8. Shear viscosity ($\eta_\gamma$) for 3.0 wt% cornstarch pastes with or without adjusting pH as a functions of shear rate ($\gamma$). The pH was adjusted between 6.0 and 3.0 by adding lactic acid after gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.

The same tendencies were observed on dynamic oscillatory measurements. The behaviors of $G'$ and $G''$ for 3.0 wt% cornstarch pastes, where the pH < 6.0, resembled for a weak gels (Figure 6.9). It is obvious from these results that there are many glucose chains and entangled networks are formed by many glucose chains in the pastes.

No decrease in $|\eta^*|_\omega$ was observed when the pH was adjusted by acetic acid after gelatinization (Figure 6.10). Similar tendencies were observed for all samples with the pH adjusted by adding various acids after gelatinization (data not shown). Comparing $|\eta^*|_\omega$ with $\eta_\gamma$ for pastes with the pH was adjusted by adding each acid, $|\eta^*|_\omega$ was greater than $\eta_\gamma$ on samples with pH < 6.0. Strong structures were formed by adding acids after gelatinization.

The viscoelasticity of the cornstarch pastes adjusted pH by adding acids after gelatinization also depended only on the pH, not on the type of acid.
Figure 6.9 Angular frequency ($\omega$) dependence of storage modulus ($G'$, left) and loss modulus ($G''$, right) for 3.0 wt% cornstarch pastes. The pH was adjusted between 6.0 and 3.0 by adding ascorbic acid after gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 ºC. The strain for samples at pH 6.3 (control), 6.0, 5.0, 4.0, and 3.0, was 30, 30, 3, 3, and 3 %, respectively.

Figure 6.10 Complex viscosity ($|\eta^*|_\omega$) for 3.0 wt% cornstarch pastes as a function of angular frequency ($\omega$). The pH was adjusted between 6.0 and 3.0 by adding acetic acid after gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 ºC. The strain for samples at pH 6.3 (control), 6.0, 5.0, 4.0, and 3.0, was 30, 30, 3, 3, and 3 %, respectively.
CONCLUSIONS

When sour seasonings (various organic acids) were added to cornstarch dispersions before gelatinization, the viscoelasticity of cornstarch pastes increased by adjusting pH to between 5.5 and 3.6, while the viscoelasticity of pastes with pH below 3.5 decreased further than that of the control (pH = 6.3). The changes in the viscoelasticity of starch pastes depended only on the pH, since similar tendencies were observed by adding various acids.

It was obvious from intrinsic viscosity measurements that the hydrolysis of glucose chains occurred by adding acids before gelatinization. However, increases in the viscoelasticity could be observed by adding small amounts of acids (3.5 < pH < 5.6), because many glucose chains leached out from starch granules, inducing entanglements of glucose chains. On the other hand, adding large amounts of acids (pH ≤ 3.5) led to the collapse of starch granules and the decrease of degree of polymerization, thus the decrease in the viscoelasticity was observed.

No decrease in viscoelasticity was noted for cornstarch pastes by adding acids after gelatinization. The values of viscoelasticity were almost same for the samples with pH less than 6.0. The hydrolysis of glucose chains could be prevented by adding acids after gelatinization. The viscoelasticity of the pastes adjusted pH by adding various kinds of acids after gelatinization also showed a similar tendency. The viscoelasticity of the cornstarch pastes also depended on the pH and not on the type of acids.
7. EFFECTS OF CAFFEINE ON THE PHYSICAL PROPERTIES FOR CORNSTARCH PASTES

INTRODUCTION

Since bitter tastes are generally not something we are fond of, bitter substances themselves are not used in foods as seasonings. However, there are many kinds of bitter substances in foods, and they have been studied at the field of chemistry. Bitterness is an important flavor for several beverages consumed in large quantities, including coffee, cocoa and tea \(^{49}\). Bitter substances in foods are listed in Table 7.1. Caffeine and theobromine are alkaloids, which have the effect of the excitement of nerves and are the cardiant. Caffeine is moderately bitter at 150–200 ppm in water (0.015–0.020 %), and it is added in concentrations up to 200 ppm in soft cola beverages, though much of caffeine employed for this purpose is obtained by solvent extraction of green coffee beans, which is carried out in the preparation of decaffeinated coffee \(^{49}\). Theobromine is very similar to caffeine and is present most notably in cocoa. Humulon has a strong antibacterial activity. Large amounts of hops, which include humulon, are employed in the brewing industry to provide unique flavors to beer. A limited bitterness is expected and enjoyed in certain foods such as grapefruits, soybean pastes and soy sauces. They have the effect of giving firmness to the taste for foods \(^{48}, 52\).

<table>
<thead>
<tr>
<th>Bitter substances</th>
<th>Foods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caffeine</td>
<td>Green tea, Black (English) tea, Coffee</td>
</tr>
<tr>
<td>Theobromine</td>
<td>Chocolate, Cocoa</td>
</tr>
<tr>
<td>Humulon</td>
<td>Hops in beer</td>
</tr>
<tr>
<td>Cucurbitacin</td>
<td>Skins of cucumbers</td>
</tr>
<tr>
<td>Naringin</td>
<td>Grapefruits</td>
</tr>
</tbody>
</table>

Table 7.1 Bitter substances and their whereabouts.

There are many reports concerning the effects of sweet, salt and sour substances on gelatinization and retrogradation of starch as mentioned in Chapter 4, 5 and 6, respectively, while
there is no report concerning the effects of bitter substances on the physical properties for starch to
the author’s knowledge. Sweet, salty and sour substances have been widely added to starch products
as a seasoning. Foods including bitter substances such as green tea, coffee, chocolate, citrus fruits,
etc. have been also added to starch products as a flavor or a seasoning; this means that starch
products also contain bitter substances, so that it should be very important to examine the effects of
bitter substances on the physical properties of starch.

In this chapter, caffeine was selected to examine the effects of bitter substance on the
viscoelasticity of starch pastes. Caffeine has been widely used as a flavoring agent that contributes
to the popularity and enjoyment of beverages and foods. It is generally present at low
concentrations (mmol/L) and need not be the major bitter ingredient. Chemical structure of
caffeine and its content in foods and beverages are displayed in Figure 7.1 and Table 7.2,
respectively. It is important as a basic bitter substance for difference tests on sensory evaluation.

Powdered green tea called maccha in Japan has the highest concentration of caffeine among various
foods; caffeine content in powdery maccha is about 2.3 %. When we add maccha to starch products
like starch gels called uiro in Japan as a flavor and a seasoning, the concentration of caffeine may
be the highest. However, the concentrations of caffeine in these starch gels are only around 0.3 %;
this is much lower concentration as compared with the concentration of other taste substances in
starch products.

The objective is to investigate how caffeine affects the physical properties of starch pastes
and contributes to the effect of increasing the viscosity for starch pastes by adding caffeine before
and after gelatinization.

Figure 7.1 Chemical structure of caffeine.
Effects of caffeine on the physical properties for cornstarch pastes

Table 7.2 Caffeine content in foods and beverages.51)

<table>
<thead>
<tr>
<th>Item (serving size)</th>
<th>Caffeine content (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffee (250 mL)</td>
<td></td>
</tr>
<tr>
<td>Brewed, drip</td>
<td>~100</td>
</tr>
<tr>
<td>Instant</td>
<td>~65</td>
</tr>
<tr>
<td>Decaffeinated</td>
<td>~3</td>
</tr>
<tr>
<td>Espresso (30 mL)</td>
<td>~40</td>
</tr>
<tr>
<td>Tea (250 mL)</td>
<td></td>
</tr>
<tr>
<td>Brewed tea – green, black, oolong</td>
<td>~60</td>
</tr>
<tr>
<td>Instant</td>
<td>~28</td>
</tr>
<tr>
<td>Iced</td>
<td>~25</td>
</tr>
<tr>
<td>Soft drinks (250mL)</td>
<td></td>
</tr>
<tr>
<td>Cola and citrus beverages</td>
<td>~24</td>
</tr>
<tr>
<td>Cocoa beverage (250 mL)</td>
<td>~6</td>
</tr>
<tr>
<td>Dark chocolate (30 g)</td>
<td>~20</td>
</tr>
<tr>
<td>Milk chocolate (30 g)</td>
<td>~6</td>
</tr>
</tbody>
</table>

MATERIALS AND METHODS

Materials

The concentration of cornstarch was fixed at 3.0 wt% as in previous chapters. Caffeine monohydrate was of a reagent grade, which was purchased from Wako Pure Chemical Industries, Inc. (Osaka, Japan). Caffeine was added at various concentrations between 0 and 2.3 wt%. Potassium 2,4-hexadienoate (potassium sorbate, 0.05 wt%) was also used to prevent microbial growth. Iodine solution was also used to dye starch granules and amylose chains.

Preparation of cornstarch pastes in the presence of caffeine

The same preparation procedure was used as described in Chapter 4.

Cornstarch pastes were prepared by adding caffeine both before and after gelatinization. A control sample was made of cornstarch and distilled water.

Measurements

Steady shear and dynamic oscillatory measurements and microscopic observations of starch pastes were carried out as mentioned in previous chapters. The same parameters could be obtained.
RESULTS AND DISCUSSION

The viscosity of cornstarch pastes with caffeine added before gelatinization

It is known that caffeine aggregates in water and precipitates\(^{183)-187}\). The caffeine sample used in this study aggregated and then precipitated in water at the concentration above 4.5 wt%. Therefore, cornstarch pastes with caffeine concentration \((C_c)\) of 4.0 wt\% was prepared as the highest \(C_c\) at first, whereas, caffeine aggregated inside cornstarch pastes at \(C_c \geq 2.6\) wt\%. It is thought that caffeine needs more water for dissolving than starch does for gelatinizing. From these consequences, \(C_c\) was settled to be below 2.3 wt\%.

Figure 7.2 shows the shear viscosity \((\eta_\dot{\gamma})\) for 3.0 wt\% cornstarch pastes in the presence of caffeine as a function of shear rate \((\dot{\gamma})\). Caffeine was added before gelatinization. All samples showed typical shear-thinning behaviors. The degree of the shear-thinning behavior was almost same for all samples. The values of \(\eta_\dot{\gamma}\) increased at \(C_c > 1.8\) wt\%. However, it is found that the changes in some values of \(\eta_\dot{\gamma}\), where \(\dot{\gamma}\) are 1, 10 and 100 s\(^{-1}\) were not remarkable (Figure 7.3).

![Figure 7.2 Shear viscosity \((\eta_\dot{\gamma})\) for 3.0 wt\% cornstarch pastes in the presence of caffeine with various concentrations between 0 (control) and 2.3 wt\% as a function of shear rate \((\dot{\gamma})\). Caffeine was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 ºC.](image-url)
Figure 7.3 Caffeine concentration ($C_c$) dependence of shear viscosity ($\eta_\gamma$) for 3.0 wt% cornstarch pastes at shear rates of 1, 10 and 100 s$^{-1}$. Caffeine was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.

Slight increase of $\eta_\gamma$ at higher $C_c$ indicates that aggregated caffeine behaved like dispersed particles in starch pastes, while the effect of aggregated caffeine on $\eta_\gamma$ for starch pastes was not strong so much. From the results of microscopic observations, it was found that there were no changes in the size of starch granules and the number of amylose and amylopectin chains (glucose chains) by adding caffeine before gelatinization (Figure 7.4).

**Dynamic oscillatory measurements of cornstarch pastes with caffeine added before gelatinization**

Figure 7.5 illustrates the angular frequency ($\omega$) dependence of the storage modulus ($G'$) and the loss modulus ($G''$) for 3.0 wt% cornstarch pastes with or without caffeine. Caffeine was added before gelatinization. The paste of the control and the pastes with $C_c \leq 1.8$ wt% showed a behavior known for concentrated solutions of flexible polymers, i.e., $G'$ is less than $G''$ at lower $\omega$ and $G'$ is greater than $G''$ at higher $\omega$ as described in previous chapters. Where $C_c \geq 2.3$ wt%, $G'$ for the pastes did not depend on $\omega$ at lower $\omega$, and $G'$ was greater than $G''$ at lower $\omega$. The values of $G'$
Figure 7.4 Microscopic photographs of starch granules for 3.0 wt% cornstarch pastes in the presence of caffeine with various concentrations between 0 (control) and 1.8 wt%. The caffeine was added before gelatinization. Samples were prepared as described in Figure 3.3. Pastes were diluted with distilled water and dyed with 10 mM iodine solution.

Figure 7.5 Angular frequency ($\omega$) dependence of storage modulus ($G'$, left) and loss modulus ($G''$, right) for 3.0 wt% cornstarch pastes in the presence of caffeine with various concentrations between 0 (control) and 2.3 wt%. Caffeine was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. The strain for samples with 0 (control), 0.069, 0.092, 0.92 and 2.3 wt% caffeine concentrations, was 30, 20, 20, 15 and 15 %, respectively.
and $G''$ for samples with $C_c < 0.092$ wt% were almost same as those of the control, and the values of $G'$ and $G''$ for samples with $C_c \geq 0.092$ wt% were greater than those of the control. $G'$ increased sharply with increasing $C_c$ at lower $\omega$, though $G''$ increased slightly. This behavior appears in some dispersed systems of spherical particles, where no entanglement couplings occur \cite{111, 119} as mentioned in Chapter 4. The values of the plateau region at lower $\omega$ increase with increasing concentration of aggregated particles and the size of the particles\cite{119}. It is found that the slight increase of the viscosity for pastes by adding caffeine is due to the aggregation of caffeine. The reason for the aggregation of caffeine in starch pastes is that the solubility of caffeine may decrease because of the lack of water. This insolubilization means that the strength of water absorption for starch is greater than that for caffeine.

Complex viscosity ($|\eta^*|_\omega$) for 3.0 wt% cornstarch pastes in the presence of caffeine had the same tendency as $G'$ and $G''$ (Figure 7.6). The values of $|\eta^*|_\omega$ for samples with $C_c < 0.092$ wt%

Figure 7.6 Complex viscosity ($|\eta^*|_\omega$) for 3.0 wt% cornstarch pastes in the presence of caffeine with various concentrations between 0 (control) and 2.3 wt% as a function of angular frequency ($\omega$). Caffeine was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. The strain for samples with 0 (control), 0.069, 0.092, 0.92 and 2.3 wt% caffeine concentrations, was 30, 20, 20, 15 and 15 %, respectively.
were also almost same as those of the control, and the values of $|\eta^*|_\omega$ for samples with $C_c \geq 0.092$ wt% were also greater than those of the control. Comparing $|\eta^*|_\omega$ in Figure 7.6 with $\eta_\gamma$ in Figure 7.2, $|\eta^*|_\omega$ and $\eta_\gamma$ of all samples did not obey the Cox-Merz rule because starch pastes contained swollen granules and glucose chains as mentioned in previous chapters. The values of $|\eta^*|_\omega$ for all samples were less than those of $\eta_\gamma$ at higher $\omega$, while the values of $|\eta^*|_\omega$ at $C_c > 1.8$ wt% were greater than those of $\eta_\gamma$ at lower $\omega$. These higher values of $|\eta^*|_\omega$ indicates that aggregated caffeine affects the network structure of starch or it is easier for $|\eta^*|_\omega$ to be affected by the decrease of water content, which leads to the increase of the ratio of starch to water.

From these results, adding caffeine with higher $C_c$ to cornstarch dispersions before gelatinization led to an increase in the viscoelasticity for starch pastes, however, $C_c$ in foods are very low (below 0.3 wt%) as mentioned above, so that there should be no effect of caffeine included actual starch products on the viscoelasticity for them (inset in Figure 7.3).

The effects of adding caffeine after gelatinization are discussed in next section.

**Effects of adding caffeine after gelatinization**

Figure 7.7 illustrates $\eta_\gamma$ for 3.0 wt% cornstarch pastes with or without caffeine as a function of $\gamma$. Caffeine was added after gelatinization. Typical shear-thinning behaviors could be also seen for all samples. There were no differences in $\eta_\gamma$ for all samples, and no effects were observed by adding caffeine after gelatinization.

The same tendencies were observed on dynamic oscillatory measurements. The values of $G'$ and $G''$ for 3.0 wt% cornstarch pastes in the presence of caffeine were almost same as those of the control, though the values of $G'$ were a little greater than those of the control at lower $\omega$ (Figure 7.8). The values of $|\eta^*|_\omega$ for pastes with caffeine added after gelatinization were a little greater than those of the control (Figure 7.9). These increases might be due to the decrease of water content. This tendency could be observed in the pastes with caffeine added both before and after gelatinization. It is thought that $|\eta^*|_\omega$ is affected by the increase of the ratio of starch to water.
Effects of caffeine on the physical properties for cornstarch pastes

Figure 7.7. Shear viscosity ($\eta_\dot{\gamma}$) for 3.0 wt% cornstarch pastes in the presence of caffeine with various concentrations between 0 (control) and 1.4 wt% as a function of shear rate ($\dot{\gamma}$). Caffeine was added after gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.

Figure 7.8 Angular frequency ($\omega$) dependence of storage modulus ($G'$, left) and loss modulus ($G''$, right) for 3.0 wt% cornstarch pastes in the presence of caffeine with various concentrations between 0 (control) and 1.8 wt%. Caffeine was added after gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. The strain for samples with 0 (control), 0.069, 0.46, 0.92 and 1.8 wt% caffeine concentrations, was 30, 30, 30, 25 and 15 %, respectively.
Figure 7.9 Complex viscosity ($|\eta^*|_\omega$) for 3.0 wt% cornstarch pastes in the presence of caffeine with various concentrations between 0 (control) and 1.8 wt% as a function of angular frequency ($\omega$). Caffeine was added after gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. The strain for samples with 0 (control), 0.069, 0.46, 0.92 and 1.8 wt% caffeine concentrations, was 30, 30, 30, 25 and 15 %, respectively.

CONCLUSIONS

The viscoelasticity of the cornstarch pastes was not affected so much by adding caffeine both before and after gelatinization. Adding caffeine above 2.6 wt% led to the aggregation of caffeine and aggregated caffeine precipitated inside starch pastes. The absorption of water for starch to gelatinize caused the decrease of the solubility for caffeine. However, there was no evident interaction between cornstarch and caffeine, and there was no significant effect of caffeine on the viscoelasticity for cornstarch pastes by adding caffeine.
8. EFFECTS OF SODIUM L-GLUTAMATE ON THE PHYSICAL PROPERTIES FOR CORNSTARCH PASTES

INTRODUCTION

Umami is a taste that one cannot do without in Asian dishes, especially Japanese dishes. Umami substances have the dishes rich, well-rounded, savory and full-bodied, and are necessary in broths and Japanese broths called dashi. Umami tastes probably drive our appetite for protein, just as sweet tastes drive your appetite for carbohydrates and saltiness drives our appetite for salt or minerals. That is why adding umami tastes makes food tastes better and makes you want to eat more (188). It is said that most Americans do not recognize umami tastes when they eat them, though Parmesan cheese, for example, has a very distinctive umami taste (188).

The main substances of umami are sodium L-glutamate (MSG) contained in kelp, theanine, which is added an amido group to L-glutamate, in green tea, inosinic acid in meats and fish, especially dried bonito and guanylic acid in shiitake mushrooms.

There are many reports concerning the effects of sweet, salt and sour substances on gelatinization and retrogradation of starch introduced in Chapter 4, 5 and 6, respectively, while there are few reports regarding the effects of umami substances (122). It is very worth to investigate the effects of umami substances on the physical properties for cornstarch pastes.

In this chapter, MSG was selected as a representative of umami substance. Figure 8.1

\[
\text{HOOC–COOH–CH}_2\text{–CH}_2\text{–COONa} \\
| \\
\text{CH} \\
| \\
\text{NH}_2
\]

**Figure 8.1** Chemical formula of sodium L-glutamate (MSG).
Chapter 8

shows chemical formula of MSG. MSG has been widely used for an ingredient or a seasoning of umami in the food industry and in home cooking. It is also important as a basic umami substance for difference tests on sensory evaluation\(^{58}\). Moreover, MSG enhances the appropriate flavor in the wine, which have only 0.1 to 0.2 % MSG\(^{189}\). The concentrations of MSG in broths are about 1 %, and 1 % solutions of umami substances have thick umami taste\(^{190}\). However, the wide MSG concentration range was used to examine the effects of MSG on the physical properties of cornstarch pastes.

The objective is to investigate how MSG affects the physical properties of starch pastes and contributes to the effect of increasing the viscosity for starch pastes by adding MSG before and after gelatinization.

MATERIALS AND METHODS

Materials

The concentration of cornstarch was fixed at 3.0 wt% as in previous chapters. Sodium L(+)-glutamate monohydrate (MSG) was purchased from Wako Pure Chemical Industries, Inc. (Osaka, Japan). The concentration of MSG (\(C_m\)) varied between 0 and 18 wt%. Potassium 2,4-hexadienoate (potassium sorbate, 0.05 wt%) was also used to prevent microbial growth. Iodine solution was also used to dye starch granules and amylose chains.

Preparation of cornstarch pastes in the presence of MSG

The same preparation procedure was used as described in Chapter 4.

Cornstarch pastes were prepared by adding MSG both before and after gelatinization. A control sample was made of cornstarch and distilled water.

Measurements

Steady shear and dynamic oscillatory, differential scanning calorimetry (DSC) measurements and microscopic observations of samples were carried out as mentioned in the previous chapters. The same parameters could be obtained.

\(C_m\) for DSC measurements was 9, 18 and 40 wt%. Each concentration of MSG solution
Effects of sodium L-glutamate on the physical properties for cornstarch pastes

was used for a reference.

RESULTS AND DISCUSSION

Steady shear measurements of cornstarch pastes with sodium L-glutamate (MSG) added before gelatinization

Figure 8.2 shows the shear viscosity ($\eta_\gamma$) for 3.0 wt% cornstarch pastes with or without MSG as a function of shear rate ($\dot{\gamma}$). MSG was added before gelatinization. All samples showed typical shear-thinning behaviors. $\eta_\gamma$ of the pastes, where MSG concentration ($C_m$) is less than 4.5 wt%, increased slightly at lower $\dot{\gamma}$ and the shear-thinning behavior became slightly remarkable. $\eta_\gamma$ of the pastes with $C_m \geq 4.5$ wt% decreased inversely and the shear-thinning behavior became less pronounced.

![Figure 8.2](image)

**Figure 8.2** Shear viscosity ($\eta_\gamma$) for 3.0 wt% cornstarch pastes in the presence of sodium L-glutamate (MSG) with various concentrations between 0 (control) and 18 wt% as a function of shear rate ($\dot{\gamma}$). MSG was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.
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$C_m$ dependence of $\eta_\gamma$ observed at the same condition as in Figure 8.2 is demonstrated in Figure 8.3. Some values of $\eta_\gamma$, where $\dot{\gamma}$ are 1, 10 and 100 s$^{-1}$, were chosen. Where $C_m < 9$ wt%, there were no differences in the values of $\eta_\gamma$ for all $\dot{\gamma}$ as compared with those of the control. Where $C_m \geq 9$ wt%, the values of $\eta_\gamma$ were less than those of the control, and where $C_m > 18$wt%, starch precipitated inside the pastes. This precipitation indicates that MSG prevents the starch gelatinization.

Differential scanning calorimetry (DSC) measurements of cornstarch dispersions

Figure 8.4 illustrates heating DSC curves of 3.0 wt% cornstarch dispersions in the presence of various $C_m$. Two peaks were observed in DSC curves for cornstarch dispersions as described in Chapter 3. The following parameters could be obtained from DSC curves: the onset temperature ($T_o$), the peak temperature ($T_p$), the conclusion temperature of amylopectin gelatinization ($T_{c1}$), the conclusion temperature of amylose–lipid complex disintegration ($T_{c2}$), the gelatinization

![Figure 8.3](image_url)

**Figure 8.3** Sodium L-glutamate (MSG) concentration ($C_m$) dependence of shear viscosity ($\eta_\gamma$) for 3.0 wt% cornstarch pastes at shear rates of 1, 10 and 100 s$^{-1}$. MSG was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.
Effects of sodium L-glutamate on the physical properties for cornstarch pastes

Figure 8.4 Heating DSC curves of 3.0 wt% cornstarch dispersions in the presence of sodium L-glutamate (MSG) with various concentrations between 0 (control) and 40 wt%. Characters beside each curve represent MSG concentrations. The heating rate was 1.0 °C/min.

Figure 8.4 shows the changes in \(T_o\), \(T_p\), \(T_c^1\), \(T_c^2\), \(\Delta T\) and \(\Delta H\) determined from Figure 8.4. \(T_o\), \(T_p\), \(T_c^1\) and \(T_c^2\) shifted to higher temperatures with increasing \(C_m\). \(T_c^2\) for dispersions in the presence of MSG was higher than 97 °C, at which was used to prepare the cornstarch pastes. \(\Delta H\) also increased with increasing \(C_m\) up to 9 wt%, while \(\Delta H\) decreased with increasing \(C_m\) above 9 wt%.

The tendency of endothermic peaks for cornstarch dispersions in the presence of MSG resembles that for dispersions in the presence of sucrose, while there was no peak for dissolving of MSG in DSC curves for cornstarch dispersions with higher \(C_m\). For example, there was a peak for dissolving of sucrose in the DSC curve of cornstarch dispersion with 40 wt% sucrose (Figure 4.6 in Chapter 4). This indicates that MSG dissolves more easily in water than sucrose does.

temperature range for peaks (\(\Delta T = T_c^2 - T_o\)) and the gelatinization enthalpy (\(\Delta H\)).
Figure 8.5 Effects of sodium L-glutamate (MSG) concentration ($C_m$) on the gelatinization temperature ($T$) and enthalpy ($\Delta H$) for 3.0 wt% cornstarch dispersions. $T_o$: onset temperature; $T_p$: peak temperature; $T_c^1$: conclusion temperature for amylopectin gelatinization; $T_c^2$: conclusion temperature for amylose–lipid complex disintegration; $\Delta T$: gelatinization range $T_c^2 - T_o$ and $\Delta H$: enthalpy for mg starch.

$\Delta T$ had the same tendency as $\Delta H$. This change of $\Delta H$ and $\Delta T$ could be also observed in the DSC curves of starch dispersions with sodium chloride (NaCl). The reason for shifting the gelatinization temperatures to higher temperatures and increasing the gelatinization enthalpy is that the amount of free water is not enough for starch granules to gelatinize\(^1\) as mentioned in Chapter 4 and 5, and MSG may change the structure of water because MSG has Na$^+$ ion like NaCl\(^2\) (See Chapter 5). It is thought that MSG has stronger solubility in water and MSG absorbs free water, which is necessary for starch gelatinization, and this absorption leads to the increase of $\Delta H$ at $C_m \leq 9$ wt%. In the case of NaCl, the decrease of $\Delta H$ for starch dispersions with higher concentration of NaCl, was due to breaking hydrogen bonds by NaCl, which leads to enhancement of gelatinization. However, the reason for the decrease of $\Delta H$ at $C_m > 9$ wt% is that starch cannot gelatinize completely, which means starch gelatinization occurs partially. Because $\eta_f$ decreased at higher $C_m$ as shown in Figure 8.2, and the precipitation of starch at $C_m > 18$ wt% was also observed in Chapter 4.
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occurred. It is thought that starch granules cannot swell and much starch cannot gelatinize because MSG has a strong force to absorb water, and does not bind glucose chains. It seems that the effect of MSG is completely different from that of sucrose or NaCl.

Microscopic observations

Microscopic photographs of the starch granules for 3.0 wt% cornstarch pastes with MSG added before gelatinization are lined along the left in Figure 8.6. There were no differences in the size of starch granules and the number of amylace and amylopectin chains (glucose chains) leached out from starch granules at \( C_m < 9 \) wt%, while the size of starch granules became smaller and the number of glucose chains leached out from starch granules decreased with increasing \( C_m \) above 9 wt%. Therefore, the decrease of \( \eta_\gamma \) at higher \( C_m \) could be observed. Although the change in the gelatinization temperature for starch dispersions with MSG was similar to those with sucrose, MSG did not have the effect on increasing the swelling rate for starch granules.

Dynamic oscillatory measurements of cornstarch pastes with MSG added before gelatinization

Figure 8.7 illustrates the angular frequency (\( \omega \)) dependence of the storage modulus (\( G' \)) and the loss modulus (\( G'' \)) for 3.0 wt% cornstarch pastes with or without MSG. MSG was added before gelatinization. The pastes of all samples with or without MSG showed a behavior known for concentrated solutions of flexible polymers, i.e., \( G' \) is less than \( G'' \) at lower \( \omega \) and \( G' \) is greater than \( G'' \) at higher \( \omega \) as described in previous chapters. \( G' \) for all samples did not depend on \( \omega \) at lower \( \omega \) and the long-time relaxation was observed. There were also the entanglements of glucose chains accompanied with starch granules for pastes in the presence of MSG. \( G' \) at \( C_m \leq 4.5 \) wt% was almost same as that of the control and \( G' \) decreased with increasing \( C_m \) above 4.5 wt%. \( G'' \) for samples with MSG had the same tendency to \( G' \) and the decrease of \( G'' \) at higher \( C_m \) was more remarkable as compared with \( G' \).

Complex viscosity (\( |\eta*|_\omega \)) for 3.0 wt% cornstarch pastes as a function of \( \omega \) is shown in Figure 8.8. MSG was added before gelatinization. Comparing of \( |\eta*|_\omega \) in Figure 8.8 with \( \eta_\gamma \) in Figure 8.2, \( |\eta*|_\omega \) and \( \eta_\gamma \) of all samples did not obey the Cox-Merz rule as mentioned in previous chapters. The values of \( |\eta*|_\omega \) did not coincide with those of \( \eta_\gamma \), while \( |\eta*|_\omega \) had a similar tendency to \( \eta_\gamma \). The values of \( |\eta*|_\omega \) where \( C_m < 9 \) wt%, were a little greater than those of the control,
Figure 8.6 Microscopic photographs of starch granules for 3.0 wt% cornstarch pastes in the presence of sodium L-glutamate (MSG) with various concentrations between 0 (control) and 18 wt%. MSG was added before and after gelatinization. Samples were prepared as described in Figure 3.3. Pastes were diluted with distilled water and dyed with 10 mM iodine solution. Image size is 390 μm × 725 μm. Pictures were taken at ambient temperature.
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Figure 8.7 Angular frequency (ω) dependence of storage modulus (G’, left) and loss modulus (G”, right) for 3.0 wt% cornstarch pastes in the presence of sodium L-glutamate (MSG) with various concentrations between 0 (control) and 18 wt%. MSG was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 ºC. The strain for samples with 0 (control), 0.9, 4.5, 9 and 18 wt% MSG concentrations, was 30, 20, 20, 40 and 80 %, respectively.

Figure 8.8 Complex viscosity (|η*|ω) for 3.0 wt% cornstarch pastes in the presence of sodium L-glutamate (MSG) with various concentrations between 0 (control) and 18 wt%. MSG was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 ºC. The strain for samples with 0 (control), 0.9, 4.5, 9 and 18 wt% MSG concentrations, was 30, 20, 20, 40 and 80 %, respectively.
though there was not a distinguished difference. $|\eta^*|_\omega$ for samples with $C_m \geq 9$ wt% decreased with increasing $C_m$. The values of $|\eta^*|_\omega$ were less than those of $\eta_\gamma$ for all samples. As $|\eta^*|_\omega$ is characteristic of the network structures, which are not destroyed by shear, it is thought that the networks of glucose chains are not strengthened by adding MSG.

From these results, it is found that adding MSG with higher $C_m$ led to the decrease of the viscoelasticity for cornstarch pastes. However, the concentration of MSG in starch products is very low: e.g., about 1 %, there were therefore no effects on the viscoelasticity for pastes with lower $C_m$ (inset in Figure 8.3). In addition, it is known that having excess MSG causes people Chinese restaurant syndrome that is accompanied by headache, palpitation, weakness, dizziness, etc. $^{191}$). It is also reported that about 2 % people over 40 years old in Japan have glaucoma and it is significantly higher percentage as compared with that in Western countries. It is said that the cause of glaucoma may be diets including a large amount of MSG $^{192}$). Adding higher $C_m$ led to the decrease of the viscoelasticity, which was not desirable for cornstarch pastes, however, as it would lead to bad health, it would be better for us not to add excessive MSG to foods.

**Effects of adding MSG after gelatinization**

Figure 8.9 shows $\eta_\gamma$ of 3.0 wt% cornstarch pastes with various $C_m$. MSG was added after gelatinization. A typical shear-thinning behavior could be also seen for all samples. No decrease in $\eta_\gamma$ could not observed even at higher $C_m$ by adding MSG after gelatinization. The values of $\eta_\gamma$ increased with increasing $C_m$, though the values of $\eta_\gamma$ were almost same for the sample with $C_m \geq 9$ wt%. This increase of $\eta_\gamma$ might be due to the decrease of water content; i.e., the increase of the ratio for cornstarch concentration to water. There was also no difference in the microscopic photographs for the samples by adding MSG after gelatinization (Figure 8.4 right). Many glucose chains could be seen by adding MSG after gelatinization even at higher $C_m$.

The same tendencies were observed in the results of dynamic oscillatory measurements. The values of $G'$ and $G''$ were increased with increasing $C_m$ up to 9 wt% (Figure 8.10) and the values of $G'$ and $G''$ for sample with $C_m \geq 9$ wt% were almost same. The values of $G'$ were greater than those of $G''$ at all $\omega$ examined for all samples with MSG added after gelatinization. Namely, all samples behaved like weak gels. This behavior means that the entangled networks are formed by adding MSG after gelatinization. However, these entanglements are not affected by the addition of MSG, but the increase for the number of glucose chains itself in the pastes, because of higher ratio
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**Figure 8.9** Shear viscosity ($\eta$) for 3.0 wt% cornstarch pastes in the presence of sodium L-glutamate (MSG) with various concentrations between 0 and 18 wt%. MSG was added before gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C.

**Figure 8.10** Angular frequency ($\omega$) dependence of storage modulus ($G'$, left) and loss modulus ($G''$, right) for 3.0 wt% cornstarch pastes in the presence of sodium L-glutamate (MSG) with various concentrations between 0 (control) and 14 wt%. MSG was added after gelatinization. Samples were prepared as described in Figure 3.3. Measurements were made at 25.0 °C. The strain for samples with 0 (control), 1.8, 4.5, 9 and 14 wt% MSG concentrations, was 30, 6, 3, 3 and 3 %, respectively.
of cornstarch to water.

The values of \(|\eta^*|_\omega\) also increased with increasing \(C_m\) (Figure 8.11), although the values of \(|\eta^*|_\omega\) were not coincidental with those of \(\eta_r\) in Figure 8.9. The values of \(|\eta^*|_\omega\) were greater than those of \(\eta_r\) at \(C_m > 4.5\) wt%. This behavior also indicates that many glucose chains can entangle due to the higher ratio of cornstarch to water, when cornstarch dispersions are heated (See Chapter 3).

Figure 8.11 Complex viscosity (\(|\eta^*|_\omega\)) for 3.0 wt% cornstarch pastes in the presence of sodium L-glutamate (MSG) with various concentrations between 0 and 18 wt%. MSG was added after gelatinization. Samples were prepared as described in Figure 3.3. The strain for samples with 0 (control), 1.8, 4.5, 9 and 18 wt% MSG concentrations, was 30, 6, 3, 3 and 3%, respectively. Measurements were made at 25.0 °C.
CONCLUSIONS

When sodium L-glutamate (MSG) was added before gelatinization, the viscoelasticity of the cornstarch pastes decreased with increasing MSG concentration ($C_m$) above 9 wt% and starch precipitated in the starch pastes with $C_m > 18$ wt%, though the viscoelasticity for the sample with $C_m < 9$ wt% did not change so much. The gelatinization temperatures shifted to higher temperatures with increasing $C_m$ and the enthalpy increased with increasing $C_m$ up to 9 wt%, while the enthalpy decreased inversely with increasing $C_m$ above 9 wt%. It is thought that the gelatinization does not occur completely because MSG has stronger solubility in water and absorbs free water for starch to gelatinize. It was obvious from microscopic observation that starch granules with $C_m$ above 9 wt% were smaller and the number of amylose and amylopectin chains was less than those of the control. Therefore, the gelatinization of starch dispersions was prevented by adding MSG with higher $C_m$. However, there were no effects of the viscoelasticity for cornstarch pastes with lower $C_m$, which is included in actual foods.

No decrease in the viscoelasticity was noted for cornstarch pastes by adding MSG after gelatinization and the viscoelasticity of pastes increased with increasing $C_m$, though the viscoelasticity of pastes with MSG above 9 wt% after gelatinization was almost same.
9. SYNERESIS OF CORNSTARCH IN THE PRESENCE OF TASTE SUBSTANCES

INTRODUCTION

Syneresis is caused by the physical aggregation of gels formed by macromolecules or solid particles in a solvent. According to Flory\textsuperscript{193}, gels can be classified into four types: (1) well-ordered lamellar structures, including gel mesophases; (2) covalent polymeric networks, completely disordered; (3) polymer networks formed through physical aggregation, predominantly disordered, but with regions of local order; (4) particulate, disordered structures. Syneresis is one of the major properties of gels, which are types of (3) and (4), particularly hydrogels. It is accompanied by a rearrangement of its network and a change in solubility of the polymers. The formation of new bonds leads to a more compact packing of the particles and the expulsion of water from the gel. Factors empirically known to affect syneresis include physical treatments (cutting, stirring and pressing), the shape of the vessels, the position of the vessels, water content, the size (volume) of samples, pH, temperature and heating and cooling rates\textsuperscript{194–198}.

In the case of starch, starch pastes and gels are thermodynamically unstable and undergo changes affecting their technological suitability. Upon cooling, starch molecules reassociate in a complex recrystallization process known as retrogradation, which is often associated with phase separation that is water separation from the gels\textsuperscript{86, 199–201}. The amount of water exuded results from increased inter- and intra-molecular hydrogen bonds due to the aggregation of amylose and amylpectin chains\textsuperscript{86}. This is mainly due to the retrogradation of amylose\textsuperscript{3}.

Syneresis is necessary in manufacturing cheese and cottage cheese; many researchers have studied to enhance syneresis of cheese curd\textsuperscript{194–197, 202–207}. However, syneresis is not desirable in yogurt, starch products and other polysaccharide gels, and numerous studies have been performed to prevent syneresis and instability caused by freeze-thaw\textsuperscript{68, 69, 86, 136, 198, 200, 201, 208–217}. Many methods have been used such as measuring the drying weight\textsuperscript{194}, the shrinkage of gels, i.e., height or volume or the mass of gels\textsuperscript{195, 198, 202–204, 207, 210–215}, the draining of water\textsuperscript{68, 69, 206, 208, 209, 216} and the centrifugation methods\textsuperscript{86, 136, 198, 200, 201, 217}. Budiaman and Fennema\textsuperscript{218, 219} have studied

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about water crystallization as influenced by adding various hydrocolloids. In spite of a large number of researches on syneresis, it is very difficult to measure syneresis of samples accurately, since syneresis might occur at various parts inside test tubes as shown in Figure 9.1. Therefore, methods of estimating the syneresis under various conditions have been examined, and pitfalls and limitations have been discussed \(^{195, 196, 197, 202-204, 206, 209}\).

In this chapter, the effects of taste substances, which were used in Chapter 4–8, on syneresis of cornstarch pastes were examined, i.e., the stability of cornstarch pastes on storage was investigated. Syneresis on storage occurs easily for cornstarch as compared with other starches; wheat, potato, sweet potato, cassava and rice \(^{208}\), in particular starches containing large amount of amylose have poor stability as compared with waxy starches do \(^{3}\). Therefore, it is very difficult to conduct the viscoelasticity measurements for cornstarch pastes to investigate the changes in the viscoelasticity on storage. Then, the changes in syneresis were examined as an index of the retrogradation of starch since the retrogradation of starch pastes or gels is accompanied by the separation of water \(^{86, 201}\).

The objective is to investigate how taste substances affect the syneresis of starch pastes and contribute to the effect of decreasing the syneresis of starch pastes. The concentrations of tastes substances varied widely to examine their effects on the syneresis for cornstarch pastes.

![Figure 9.1 Schemes of types for syneresis in test tubes](image)

**Figure 9.1** Schemes of types for syneresis in test tubes
MATERIALS AND METHODS

Materials

Cornstarch, sucrose, sodium chloride (NaCl), citric acid, caffeine and sodium L-glutamate (MSG) were same samples as used in previous chapters (Chapter 3–8). The concentration of cornstarch was fixed at 3.0 wt% as in previous chapters. The determination of the concentration of cornstarch was mentioned below (Figure 9.3). The degree of syneresis ($DS$) increases with decreasing starch concentration ($C$)\(^{208}\). Therefore, lower $C$, i.e., 3.0 wt%, is proper to investigate the effect of taste substances on syneresis of starch in a shorter period. The concentration of sucrose, NaCl, caffeine and MSG varied between 0 and 50 wt%, 0 and 25 wt%, 0 and 2.7 wt% and 0 and 18 wt%, respectively. The pH was adjusted to between 6.0 and 3.0 by adding citric acid. Potassium 2,4-hexadienoate (potassium sorbate, 0.05 wt%) was also used to prevent microbial growth.

Preparation of cornstarch pastes in the presence of taste substances

Powders of cornstarch were dispersed in distilled water or aqueous solutions of taste substances prepared beforehand by adding various concentrations of taste substances to distilled water. A control sample was made of cornstarch and distilled water (pH = 6.3). After stirring the dispersions at 200 rpm for 30 min at 25 °C, the cornstarch dispersions were heated up to 97 °C, stirring at the same rate and maintained at 97 °C for 60 min. Then 10 g of the hot dispersions was poured into test tubes (10 mL volume, 105 mm height, 13 mm diameter). The height of samples in test tubes was about 90 mm. Then, the tops of test tubes were sealed with Parafilm\textsuperscript{®} and samples and test tubes were weighed. Test tubes containing samples were cooled in a water bath (5 L volume) at 0 °C equipped with a temperature regulator for 30 min. The temperature of the samples reached 5 °C. The cooled samples were stored in a refrigerator at 5 °C for 1, 3, 7, 14, 30 and 45 days. It is said that the increase of crystallinity with time and the crystallization of starch are enhanced at a lower storage temperature (around 4 °C)\(^{100}\). This means that syneresis occurs easily at lower temperatures, therefore, the changes in the degree of syneresis ($DS$) can be observed in a shorter period by storing the samples at 5 °C. The samples in the presence of sucrose were also prepared, which were added sucrose after heating i.e., after gelatinization of starch, and then the starch pastes were cooled by the same methods as mentioned above.
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Syneresis observations

It is very difficult to determine $DS$ accurately as explained above. Many researchers have used the methods of measuring the shrinkage of the samples. When the syneresis occurs in test tubes as described in Figure 9.1A, it is easier to measure syneresis by the changes in the height or volume of the samples. However, the syneresis of cornstarch samples used in this study occurred as shown in Figure 9.1B or C. In such cases, it is difficult to estimate the syneresis by using the methods mentioned above. Therefore, a centrifugation method was used in this study. Samples were centrifuged at $36\times g$ for 60 min. The determination of strength and time for centrifugation is explained below (Figure 9.2). The weight of the supernatant (separated water) and the sediment (cornstarch paste) was determined by removing the supernatant using a pipette. The percentage of separated water was calculated as the $DS$:

$$DS\, (\%) = \frac{\text{the weight of supernatant (g)}}{\text{the weight of whole sample (g)}} \times 100 \quad (9.1)$$

When a large amount of taste substances was added to starch pastes, the water content in the pastes was greatly decreased. Therefore, the ratio of the remaining distilled water in the stored pastes to the distilled water in the pastes, when the pastes were prepared, was calculated as the water holding capacity ($WH$) of the starch or taste substances:

$$WH\, (\%) = 100 - \left(\frac{\text{the weight of supernatant (g)}}{\text{the weight of distilled water in the paste (g)}} \times 100\right) \quad (9.2)$$

Determination of strength and time for centrifugation

To measure the syneresis more accurately, the strength and time for the centrifugation were changed using 3.0 wt% cornstarch pastes (control). The measurements were made as soon as samples were prepared. The strengths for the centrifugation varied between 13 and $1310\times g$, and the times varied between 10 and 120 min. Figure 9.2 shows $DS$ of 3.0 wt% cornstarch pastes at various centrifugation strengths as a function of centrifugation time ($CT$). $DS$ increased with increasing centrifugation strength. This result coincides with that of other researches\textsuperscript{198}. The syneresis of samples did not occur discernibly before the centrifugation since measurements were made immediately after preparing the samples. However, the separation of water at higher centrifugation strengths, i.e., 582 and $1310\times g$, occurred further than that at other centrifugation strengths (Figure 9.2). $DS$ at centrifugation strength of $146\times g$ was also greater than that at lower centrifugation strength, i.e., 13, 36 and $71\times g$ (inset in Figure 9.2). It is found that water is separated from starch
Figure 9.2 Degree of syneresis (DS) for 3.0 wt% cornstarch pastes with various centrifugation strengths between 13 and 1310×g as a function of centrifugation time (CT). Measurements were immediately conducted at room temperature after heating samples at 97 °C and cooling them to 5 °C.

Pastes by compulsion at higher centrifugation strengths. There was no difference in DS at centrifugation strengths between 13 and 71×g, and the centrifugation strength was determined at 36×g, which is the middle strength between 13 and 71×g. Regarding centrifugation time, the separation of water for sample centrifuged for 120 min occurred further than that for other shorter centrifugation times. Then, the centrifugation time was determined for 60 min.

**Determination of concentration for cornstarch**

Figure 9.3 shows DS of cornstarch pastes with various concentrations as a function of storage time (ST). The samples were stored at 5 °C. Lower concentrations of starch (≤ 5 wt%) were used to examine the changes in syneresis during a shorter period. Syneresis of the cornstarch pastes with lowest C used in this study, i.e., $C = 2.0$ wt%, occurred further than other samples did. DS was greater even in shorter ST, and it did not depend on ST so much. Therefore, when 2.0 wt% cornstarch paste is used for syneresis observations, the changes in DS on ST cannot be observed. DS
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Figure 9.3 Degree of syneresis (DS) for cornstarch pastes with various concentrations between 2.0 and 5.0 wt% as a function of storage time (ST). Samples were prepared by heating at 97°C, cooling to 5 °C and storing at 5 °C. Measurements were made at room temperature.

decreased with increasing C, though there were no big differences in DS for sample with C > 2.0wt%, in particular on shorter ST. From these results, C = 3.0 wt% was chosen since it was possible to compare the results of other experiments as described in Chapter 3–8.

RESULTS AND DISCUSSION

The syneresis of cornstarch pastes in the presence of sucrose

Figure 9.4 shows the degree of syneresis (DS) for 3.0 wt% cornstarch pastes in the presence of sucrose as a function of storage time (ST). Sucrose was added before gelatinization. The samples were stored at 5 °C. DS of the control is illustrated by a line. Syneresis of the pastes with sucrose concentration (Cs) below 1 wt% was not different from that of the control (data not shown), DS of samples with 1 < Cs ≤ 20wt% were less than that of the control on shorter ST (≤ 14days) and adding sucrose between 10 and 20 wt% prevented the syneresis of cornstarch pastes (Figure 9.5).
Figure 9.4 Degree of syneresis (DS) for 3.0 wt% cornstarch pastes in the presence of sucrose with various concentrations between 5 and 50 wt% as a function of storage time (ST). Sucrose was added before gelatinization. DS of the control (3.0 wt% cornstarch pastes without sucrose) is illustrated by a line. Samples were prepared by heating at 97 ºC, cooling to 5 ºC and storing at 5 ºC. Measurements were made at room temperature.

Figure 9.5 Degree of syneresis (DS) for 3.0 wt% cornstarch pastes stored at 5 ºC for 1, 3, 30, and 45 days as a function of sucrose concentration (C_s). Sucrose was added before gelatinization. Samples were prepared by heating at 97 ºC and cooling to 5 ºC Measurements were made at room temperature.
On the contrary, syneresis occurred further in the samples with $C_s$ above 40 wt% than in the other samples on shorter $ST$ (≤ 7 days). It is found that $DS$ of pastes, where $C_s \geq 40$ wt%, increased sharply on shorter $ST$. Maezawa and Ohkubo\(^{108}\) reported that $DS$ of starch depended on the swelling rate of starch granules. Adding a small amount of sucrose ($C_s \leq 20$ wt%) promoted the swelling rate of starch granules\(^{129}, 136\), and adding a large amount of sucrose ($C_s > 20$ wt%) prevented the swelling rate of starch granules\(^{141}\) as mentioned in Chapter 4 (See Figure 4.5). This change in size of starch granules indicates that the starch granules for samples with $C_s \leq 20$ wt% can absorb water, and the syneresis is prevented, while the starch granules for pastes with $C_s > 20$ wt% cannot absorb much water, and the water is separated from the pastes. There were no differences in $DS$ on longer $ST$ (≥ 30 days), and reached almost a constant value for all samples with or without sucrose (Figure 9.5). It is thought that $DS$ of around 23 % would be the maximum values for 3.0 wt% cornstarch. It was obvious that the rate of the increase for $DS$ slowed down at $ST \geq 14$ days.

When sucrose was added after gelatinization, $DS$ of samples with $C_s < 30$ wt% had almost same values as that of the control, and $DS$ for 3.0 wt% cornstarch pastes with higher $C_s (\geq 30$ wt%) decreased with increasing $C_s$ at $ST \geq 30$ days. $DS$ of the samples with $C_s \geq 40$ wt% was far less than that of the control. $DS$ for pastes in the presence of sucrose were less than that for the control at $ST < 30$ days (Figure 9.6). The syneresis was prevented by adding sucrose above 30 wt% after gelatinization as compared with that of samples with sucrose added before gelatinization, through the entire $ST$ examined.

According to $DS$, it seems that adding sucrose after gelatinization prevents the syneresis of starch pastes, and it is no problem to store the starch pastes because $DS$ decreased with increasing $C_s$. However, amounts of distilled water in the pastes with higher $C_s$ were far less than that of the control. Therefore, the water holding capacity of starch or sucrose ($WH$) was calculated (Figure 9.7). Although there were no differences in $DS$ by adding sucrose before gelatinization on longer $ST$ (above 30 days), and the decrease of $DS$ for samples with much sucrose added after gelatinization could be observed on all $ST$ examined, $WH$ decreased with increasing $C_s$ on longer $ST$ (≥ 7 days). Sucrose did not have the water holding capacity, and enhanced separating of water from starch pastes.

It was found that adding sucrose after gelatinization was effective in the decease for amount of separated water from cornstarch pastes, though the ratio of separated water to the water
Figure 9.6 Degree of syneresis (DS) for 3.0 wt% cornstarch pastes in the presence of sucrose with various concentrations between 5 and 50 wt% as a function of storage time (ST). Sucrose was added after gelatinization. DS of the control (3.0 wt% cornstarch pastes without sucrose) is illustrated by a solid line. Samples were prepared by heating at 97 °C, cooling to 5 °C and storing at 5 °C. Measurements were made at room temperature.

Figure 9.7 Water holding capacity of starch or sucrose (WH) for 3.0 wt% cornstarch pastes stored at 5 °C for 1, 3, 30 and 45 days as a function of sucrose concentration (C_s). Sucrose was added before (left) and after (right) gelatinization. Samples were prepared by heating at 97 °C and cooling to 5 °C. Measurements were made at room temperature.
in pastes was greater than that of the control.

The syneresis of cornstarch pastes in the presence of sodium chloride (NaCl)

Figure 9.8 shows DS for 3.0 wt% cornstarch pastes in the presence of NaCl as a function of ST. NaCl was added before gelatinization. The samples were stored at 5 ºC. DS of the control is illustrated by a solid line. DS for the samples with NaCl concentration ($C_n$) $\leq$ 1 wt% was not different from that for the control, however, DS for the samples, where $C_n$ was more than 1 wt%, decreased with increasing $C_n$ on longer ST. Syneresis could not be observed in the sample with $C_n$ = 25 wt%. WH had an opposite tendency to DS (data not shown), which means WH for samples with $C_n$ = 25 wt% was almost 100 % on all ST examined.

The changes in DS for pastes with NaCl were very complicated, depending on ST and $C_n$.

Figure 9.8 Degree of syneresis (DS) for 3.0 wt% cornstarch pastes in the presence of sodium chloride (NaCl) with various concentrations between 1 and 25 wt% as a function of storage time (ST). NaCl was added before gelatinization. DS of the control (3.0 wt% cornstarch pastes without NaCl) is illustrated by a solid line. Samples were prepared by heating at 97 ºC, cooling to 5 ºC and storing at 5 ºC. Measurements were made at room temperature.
Syneresis of cornstarch in the presence of taste substances

(Figure 9.9). At $ST \leq 3$ days, the syneresis of pastes, where $C_n \leq 1$ wt% and $5 \text{ wt}\% < C_n \leq 15 \text{ wt}\%$, was promoted (Figure 9.9 left). The increase of $DS$ for pastes with $5 \text{ wt}\% < C_n \leq 15 \text{ wt}\%$ was due to the decrease of the swelling rate for starch granules (See Figure 5.5 in Chapter 5). Although the starch granules could swell enough, $DS$ for pastes with $C_n \leq 1$ wt% increased. The assumption of this result is that the strong networks are formed by amylose and amylpectin chains (glucose chains) leached out from starch granules, and water is separated out of those networks, or the binding of NaCl to starch is stronger than that of water to starch, and water is separated. There were no big differences in $DS$ among the pastes with $1 \text{ wt}\% < C_n \leq 5 \text{ wt}\%$, $15 \text{ wt}\% < C_n \leq 20 \text{ wt}\%$ and the control at $ST \leq 3$ days. It is thought that the balance of absorbing and discharging water would be kept by starch and NaCl. A wonderful decrease of syneresis could be observed by adding NaCl more than 20 wt% through the whole $ST$. This decrease indicates that glucose chains hold water inside their entanglements because there are many glucose chains leached out from starch granules in the paste, and excessive NaCl also binds water. It was revealed from the fact that gelation

Figure 9.9 Degree of syneresis ($DS$) for 3.0 wt% cornstarch pastes stored at 5 ºC for 1 and 3 days (left), 14, 30 and 45 days (right) as a function of sodium chloride (NaCl) concentration ($C_n$). NaCl was added before gelatinization. Samples were prepared by heating at 97 ºC and cooling to 5 ºC. Measurements were made at room temperature.
occurred in the sample with $C_n = 25$ wt% inside the whole test tubes. Different results could be obtained at $ST > 3$ days (Figure 9.9 right). $DS$ for the pastes with $C_n \leq 1$ wt% was almost same as that for the control, and $DS$ for the pastes with $C_n > 1$ wt% was far less than that for the control. Moreover, $DS$ for the pastes with $C_n > 5$ wt% decreased with increasing $ST$. It is thought that water binds to NaCl because a large amount of NaCl can change the structure of water\(^{156}\) (See Chapter 5).

From these results, it is useful for decreasing the syneresis to add NaCl to cornstarch pastes, when samples are stored for longer periods, though there was no effect of adding a small amount of NaCl on the syneresis of cornstarch pastes.

**The syneresis of cornstarch pastes in the presence of citric acid**

Figure 9.10 shows $DS$ for 3.0 wt% cornstarch pastes with or without adjusting pH by adding citric acid as a function of $ST$. The pH was adjusted before gelatinization. The samples were

![Figure 9.10](image)

**Figure 9.10** Degree of syneresis ($DS$) for 3.0 wt% cornstarch pastes with or without adjusting pH as a function of storage time ($ST$). The pH was adjusted to between 6.0 and 3.0 by adding citric acid before gelatinization. $DS$ of the control (3.0 wt% cornstarch pastes, pH = 6.3) is illustrated by a solid line. Samples were prepared by heating at 97 °C, cooling to 5 °C and storing at 5 °C. Measurements were made at room temperature.
stored at 5 °C. *DS* of the control (pH = 6.3) is illustrated by a solid line. *DS* for the samples, where 3.0 < pH ≤ 6.0, was almost same as that for the control, though *DS* was a little greater on shorter *ST* (≤ 7 days). The decrease of the starch granule size (See Figure 6.3) caused these higher values of *DS* on shorter *ST*, and it led to the decrease of absorption of water inside starch granules or the increase of entanglements by glucose chains, which might form tightly packed networks without accompanying with water. On the other hand, a wonderful decrease of syneresis for the sample with pH3.0 was also observed. The hydrolysis occurred remarkably by adding a large amount of acids (pH < 4.0) as mentioned in Chapter 6 (See Figure 6.4). It is thought that hydrolyzed glucose chains form entanglements during storing the sample, and they can hold water inside their networks due to the existence of many glucose chains in the pastes as compared with that in other pastes, in spite of shorter glucose chains. In fact, the gelation was observed for the sample with pH3.0 inside whole test tubes in the same way as the sample with *Cn* = 25 wt%. Adding a large amount of acids was effective in preventing syneresis. The amount of water in the pastes with the pH adjusted by adding citric acid was almost same because the concentration of citric acid was very low (below 0.2 wt%), so that *WH* for the pastes with the pH adjusted to 3.0 was almost 100 %, though *WH* for pastes with pH > 3.0 were not different from that for the control (data not shown).

**The syneresis of cornstarch pastes in the presence of caffeine**

Figure 9.11 shows *DS* for 3.0 wt% cornstarch pastes in the presence of caffeine as a function of *ST*. Caffeine was added before gelatinization. The samples were stored at 5 °C. The *DS* of the control is illustrated by a line. *DS* for samples with caffeine concentration (*Cc*) ≤ 1.8 wt% was almost same as that for the control. *DS* for the samples with *Cc* > 1.8 wt% was less than that for other samples. It is because the aggregation of caffeine occurred in the test tubes at *Cc* ≥ 2.6 wt% (See Chapter 7), and caffeine might absorb much water. But no effects on *WH* for starch pastes in the presence of caffeine could be observed (data not shown). Adding a small amount of caffeine was not affected the syneresis of cornstarch pastes. This result is coincident with the results of the viscoelasticity measurements mentioned in Chapter 7.

**The syneresis of cornstarch pastes in the presence of sodium L-glutamate (MSG)**

Figure 9.12 shows *DS* for 3.0 wt% cornstarch pastes in the presence of MSG as a function of *ST*. MSG was added before gelatinization. The samples were stored at 5 °C. The *DS* of the
Figure 9.11 Degree of syneresis (DS) for 3.0 wt% cornstarch pastes in the presence of caffeine with various concentrations between 0.023 and 2.7 wt% as a function of storage time (ST). Caffeine was added before gelatinization. DS of the control (3.0 wt% cornstarch pastes without caffeine) is illustrated by a line. Samples were prepared by heating at 97 °C, cooling to 5 °C and storing at 5 °C. Measurements were made at room temperature.

Figure 9.12 Degree of syneresis (DS) for 3.0 wt% cornstarch pastes in the presence of sodium L-glutamate (MSG) with various concentrations between 0.9 and 18 wt% as a function of storage time (ST). MSG was added before gelatinization. DS of the control (3.0 wt% cornstarch pastes without MSG) is illustrated by a line. Samples were prepared by heating at 97 °C, cooling to 5 °C and storing at 5 °C. Measurements were made at room temperature.
control is illustrated by a line. MSG concentration ($C_m$) dependence of $DS$ at the same condition as in Figure 9.12 is shown in Figure 9.13. The changes in $DS$ for pastes with MSG were also complicated like samples with NaCl. $DS$ for samples, where $C_m \leq 0.9$ wt% and $C_m \geq 9$ wt%, was greater than that for the control, and $DS$ for samples, where $0.9$ wt% $< C_m < 9$ wt% was almost same as that for the control on shorter $ST$ ($\leq 7$ days), though $DS$ for all samples was no differences on longer $ST$ ($> 7$ days). The decrease of $DS$ at $C_m \geq 9$ wt% was due to the decrease of the size for starch granules (See Figure 8.5 in Chapter 8), which led to the decrease of the absorption of water. However, it is very difficult to explain the reason for the decrease of $DS$ at $C_m \leq 0.9$ wt%, because there was no difference in the viscoelasticity of pastes and in the size for starch granules at this $C_m$ range (See Chapter 8). It is assumed that Na$^+$ ions in MSG bind glucose chains inside starch granules and exclude water from starch granules. When the amount of Na$^+$ ions increases with increasing $C_m$, Na$^+$ ions bind water outside starch granules and change the structure of water. Thus,

![Figure 9.13](image)

**Figure 9.13** Degree of syneresis ($DS$) for 3.0 wt% cornstarch pastes stored at 5 °C for 1, 3, 30 and 45 days as a function of sodium L-glutamate (MSG) concentration ($C_m$). Samples were prepared by heating at 97 °C and cooling to 5 °C. Measurements were made at room temperature.
it would lead to the decrease of the syneresis for samples with $0.9 \, \text{wt}\% < C_m < 9 \, \text{wt}\%$. However, there were no effects by adding MSG to cornstarch pastes for longer $ST$.

$WH$ decreased slightly with increasing $C_m$ for longer $ST$ (Figure 9.14). This decrease indicates that MSG cannot help water separate from starch pastes.

**Figure 9.14** Water holding capacity ($WH$) of starch or sodium L-glutamate (MSG) for 3.0 wt% cornstarch pastes stored at 5 °C for 1, 3, 30 and 45 days as a function of (MSG) concentration ($C_m$). MSG was added before gelatinization. Samples were prepared by heating at 97 °C and cooling to 5 °C. Measurements were made at room temperature.
CONCLUSIONS

The degree of syneresis (DS) for almost all cornstarch pastes in the presence of taste substances reached about 23 % for 45 days storage, which was the same value as the control. It was found that there were no effects of adding taste substances on the syneresis of starch pastes, if pastes were stored for longer time. No samples had the far greater DS than the control did.

However, in the case of adding sucrose, DS of the samples, which were added sucrose between 10 and 20 wt% before gelatinization, was less than that of the control for shorter storage time (ST). It was due to the increase of the size for starch granules. DS of the sample with sucrose added after gelatinization decreased with increasing sucrose concentration because of the decrease of the water content in the pastes.

No syneresis occurred for the sample with 25 wt% sodium chloride (NaCl). The number of amylose and amylopectin chains (glucose chains) leached out from starch granules increased by adding a large amount of NaCl, so that the entangled networks were formed by glucose chains leached out from starch granules, and they could hold water inside their networks, which led to the gelation of samples inside whole test tubes.

The syneresis of sample with pH3.0 did not also occur so much, although the glucose chains were hydrolyzed and became shorter as compared with those for other samples. The number of glucose chains increased by hydrolyzing, and hydrolyzed glucose chains could form the entanglements accompanied with water, so that the samples with pH3.0 formed gels in whole test tubes.
10. CONCLUDING REMARKS

PHYSICAL PROPERTIES OF CORNSTARCH AND CURDLAN

Viscoelasticity of cornstarch pastes and curdlan dispersions

Physical properties of cornstarch pastes and curdlan dispersions were examined by using mainly steady and dynamic oscillatory measurements. It is generally said that \( \beta \)-linked configuration results in a rigid structure and \( \alpha \)-linked configuration results in a flexible structure as mentioned in Chapter 1. Both cornstarch and curdlan consist of glucose residues, but the former has \( \alpha -(1, 4) \) and \( \alpha -(1, 6) \) linkages and the latter has \( \beta -(1, 3) \) linkages. Therefore, their viscoelasticities or gelation mechanisms were greatly affected by the differences in their linkages.

Figure 10.1 shows the mechanical spectra for 3.0 wt% cornstarch paste and 3.0 wt% curdlan aqueous dispersion, both of which were same samples described in Chapter 3 and 2, respectively. Although the differences in the mechanical spectra cannot be compared directly since the measuring temperatures were different, the difference in the glucose residues linked reflects the behavior of their dispersions. The values of storage modulus \( (G') \) and loss modulus \( (G'') \) for the curdlan dispersion were far greater than those of the starch paste, and curdlan dispersion showed a solid like behavior. It indicates that curdlan has a rigid structure and its dispersion shows higher viscoelasticity. Although starch is an exception of polysaccharides with \( \alpha \)-linkage because starch forms granules, starch is more flexible than curdlan, and starch pastes behaved as the concentrated solutions of flexible polymers.

EFFECTS OF TASTE SUBSTANCES ON THE PHYSICAL PROPERTIES FOR CORNSTARCH PASTES

Changes in the viscoelasticity and syneresis of 3.0 wt% cornstarch pastes were investigated by adding taste substances (sucrose, sodium chloride, sour substances, caffeine and sodium L-glutamate). In this study, the point, when taste substances were added to starch dispersions, have
been paid attention, therefore, taste substances were added before and after heating, i.e., before and after gelatinization of starch.

The higher viscoelasticity for cornstarch pastes was obtained and syneresis of pastes tended to decrease by adding taste substances after gelatinization in comparison with adding taste substances before gelatinization. However, there were few exceptions among samples by adding taste substances before gelatinization, which means higher viscoelasticity and lower degree of syneresis could be obtained. The effects of taste substances on the viscoelasticity and the syneresis of cornstarch pastes are summarized below.

**The effects of sucrose on the physical properties for cornstarch pastes**

The higher viscoelasticity for 3.0 wt% cornstarch pastes could be obtained by adding 20 wt% sucrose before gelatinization. These higher values were due to the enhancement of the swelling rate of starch granules. This effect led to decrease the syneresis of cornstarch pastes because starch granules could absorb much water. On the other hand, adding excess sucrose (above

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**Figure 10.1** Angular frequency ($\omega$) dependence of storage modulus ($G'$) and loss modulus ($G''$) for 3.0 wt% cornstarch pastes at 25.0 ºC and 3.0 wt% curdlan dispersions at 40.0 ºC. The strain for cornstarch paste and curdlan dispersion, was 30 and 2.5 %, respectively.
40 wt%) before gelatinization led to the decrease of the viscoelasticity and the swelling rate of starch granules, and syneresis of starch pastes was enhanced.

To avoid the decrease of swelling rate for starch granules, adding sucrose after gelatinization was effective. Starch granules could swell and collapse, and the viscoelasticity and thickness of cornstarch pastes increased with increasing sucrose concentration. Moreover, syneresis of starch pastes was prevented by adding a large amount of sucrose after gelatinization.

**The effects of sodium chloride (NaCl) on the physical properties for cornstarch pastes**

When NaCl was added before gelatinization, the viscoelasticity for cornstarch pastes, where NaCl concentration \( C_n \) ≤ 5 wt% and \( C_n > 15 \) wt%, were greater than those of the control, which is 3.0 wt% cornstarch paste without NaCl. In particular, strong entangled networks were formed in the pastes at 0.4 wt% ≤ \( C_n \) ≤ 1 wt% and \( C_n \) ≥ 22.5 wt%. It was due to Cl⁻ ions, which broke hydrogen bonds between starch molecules. Syneresis of cornstarch pastes with \( C_n \) ≥ 20 wt% was greatly prevented. It indicates that many entanglements are formed by amylose and amylopectin chains (glucose chains) accompanied with water. On the other hand, adding NaCl between 5 wt% and 15 wt% before gelatinization led to the decrease of the viscoelasticity, and syneresis of starch pastes was enhanced on shorter storage time. The higher gelatinization temperatures and the greater value of enthalpy because of the changes in the structure of water resulted in the insufficiency of the gelatinization.

In the case of adding NaCl after gelatinization, the viscoelasticity for cornstarch pastes increased with increasing \( C_n \), although it was better for obtaining the higher viscoelasticity and thickness for starch pastes to add NaCl before gelatinization at 0.4 wt% ≤ \( C_n \) ≤ 1 wt% and \( C_n \) ≥ 22.5 wt%.

**The effects of sour substances on the physical properties for cornstarch pastes**

Adjusting the pH between 5.5 and 3.6 led to the increase of the viscoelasticity for cornstarch pastes, although it has been said that adding acids to starch dispersions led to the decrease of the viscoelasticity because of the hydrolysis of glucose chains. In fact, the hydrolysis of glucose chains occurred slightly at pH ≥ 4.0. This slight hydrolysis resulted in the enhancement of leaching out glucose chains from starch granules and the decrease of granule size, and led to the increase in the viscoelasticity. The syneresis of pastes with this pH range tended to enhance the
syneresis on a shorter storage time because of the smaller size for starch granules. Glucose chains were hydrolyzed obviously at pH < 4.0. The viscoelasticity for cornstarch pastes at pH < 3.6 decreased due to shorter length of glucose chains, however, the syneresis of pastes with lower pH was greatly prevented. It is thought that entangled networks are formed by many glucose chains accompanied with water, though glucose chains become shorter.

The hydrolysis of glucose chains could be prevented by adjusting the pH after gelatinization. Therefore, the higher and stable viscoelasticity could be obtained, though the viscoelasticity for pastes with the pH adjusted after gelatinization was less than that for pastes with the pH adjusted before gelatinization at pH ≥ pH ≥ 4.0.

The effects of caffeine on the physical properties for cornstarch pastes

No effects of caffeine on the viscoelasticity and the syneresis of cornstarch pastes in the presence of caffeine were noted. This means that there was no effect of caffeine on the physical properties for cornstarch pastes; indeed, the solubility of caffeine in water was prevented by starch.

The effects of sodium L-glutamate (MSG) on the physical properties for cornstarch pastes

When MSG was added to cornstarch dispersions before gelatinization, the viscoelasticity for cornstarch pastes with MSG concentration (C_m) ≥ 9 wt% decreased, and syneresis was enhanced at this C_m range on a shorter storage. It is thought that the strong solubility of MSG prevents starch from gelatinizing because MSG absorbs free water for starch to gelatinize. Therefore, the gelatinization of starch dispersions did not occur completely and the decrease of the size for starch granules could be observed at higher C_m. However, adding a small amount of MSG (C_m < 9 wt%) did not affect the viscoelasticity and the thickness for cornstarch pastes, though the syneresis was enhanced on a shorter storage time.

No decrease in the viscoelasticity for cornstarch pastes could not be observed, when MSG was added after gelatinization. Starch could gelatinize completely by adding MSG after gelatinization.

Comparing the effects of taste substances on the viscosity for cornstarch pastes

Which taste substance is the most effective in increasing the viscoelasticity for cornstarch pastes? Figure 10.2 shows the shear viscosity (η̇) for 3.0 wt% cornstarch pastes in the presence of
Concluding remarks

various taste substances. Taste substances were added to cornstarch dispersions both before (left) and after (right) gelatinization. The taste substances that increased $\eta_\dot{\gamma}$ of the pastes the most were collected. When taste substances were added before gelatinization, $\eta_\dot{\gamma}$ of the paste with 25 wt% NaCl was the greatest (Figure 10.2 left). This indicates that the number of amylose and amylopectin chains leached out from starch granules is the most important for increasing the viscosity. When taste substances were added after gelatinization, $\eta_\dot{\gamma}$ of the pastes with 55 wt% sucrose was the greatest (Figure 10.2 right). This is thought that the higher ratio of cornstarch to water in the pastes and higher viscosity of solvent (sucrose solution) contribute to increase $\eta_\dot{\gamma}$, because $\eta_\dot{\gamma}$ of the pastes with 20 wt% NaCl and 18 wt% MSG was almost same.

Comparing $\eta_\dot{\gamma}$ of the paste with 25 wt% NaCl added before gelatinization (Figure 10.2 left) with $\eta_\dot{\gamma}$ of the pastes with 55 wt% sucrose added after gelatinization (Figure 10.2 right), $\eta_\dot{\gamma}$

![Figure 10.2](image-url)

**Figure 10.2** Shear viscosity ($\eta_\dot{\gamma}$) for 3.0 wt% cornstarch pastes in the presence of taste substances. Sucrose was added 20 wt%, sodium chloride (NaCl) was added 25 wt%, pH was adjusted to 4.0 by adding citric acid, caffeine was added 2.3 wt% and sodium L-glutamate (MSG) was added 0.9 wt% before gelatinization (left). Sucrose was added 55 wt%, NaCl was added 20 wt%, pH was adjusted to 4.0 by adding citric acid, caffeine was added 1.4 wt% and MSG was added 18 wt% after gelatinization (right). Samples were prepared as described in Figure 3.3. Measurements were made at 25.0°C.
of the pastes with 55 wt% sucrose was greater than that with 25 wt% NaCl. This also indicates that the higher ratio of cornstarch to water is affected to increase the viscosity and higher viscosity of sucrose solution.

Heating process is the most important for taste substances to increase or decrease the viscoelasticity for starch pastes. When taste substances are not heated with starch dispersions, the ratio of cornstarch to water are affected greatly the viscoelasticity of starch pastes. However, sour substance have a different effect on leaching out glucose chains from starch granules, even if they are added after gelatinization, $\eta_\gamma$ of the paste with adjusted pH to 4.0 before and after gelatinization was almost same (Figure 10.2).
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LIST OF PUBLICATIONS

1. **M. Hirashima**, T. Takaya and K. Nishinari
   DSC and rheological studies on aqueous dispersions of curdlan
   (Chapter 2)

2. **K. Nishinari, M. Hirashima**, E. Miyoshi and T. Takaya
   Rheological and DSC studies of aqueous dispersions and gels of curdlan
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   (Chapter 2)

3. **M. Hirashima**, R. Takahashi and K. Nishinari
   Effects of taste substances on the physical properties of corn starch pastes. I. Sour
   seasonings (citric acid and acetic acid)
   (Chapter 3 and 6)

4. **M. Hirashima**, R. Takahashi and K. Nishinari
   The effects of taste substances on the physical properties of corn starch pastes. II. Sweet
   seasonings (sucrose)
   (Chapter 4)

5. **M. Hirashima**, R. Takahashi and K. Nishinari
   The effects of taste substances on the physical properties of corn starch pastes. III. Saline
   seasonings (sodium chloride)
   (Chapter 5)
6. M. Hirashima, R. Takahashi and K. Nishinari
The effects of tastes substances on the physical properties of corn starch pastes. IV. Bitter (caffeine) and umami (sodium L-glutamate) seasonings
(Chapter 7 and 8)

7. M. Hirashima, R. Takahashi and K. Nishinari
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*Journal of Agricultural and Food Chemistry* (in press)  
(Chapter 6)

8. M. Hirashima, R. Takahashi and K. Nishinari
Effects of adding acids before and after gelatinization on the viscoelasticity of cornstarch pastes.
*Food Hydrocolloids* (submitted)  
(Chapter 6)

Effects of adding sucrose before and after gelatinization on the viscoelasticity of cornstarch pastes.
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