JOURNAL OF
AGRICULTURAL AND
FOOD CHEMISTRY

Effects of Citric Acid on the Viscoelasticity of Cornstarch Pastes

Madoka Hirashima, Rheo Takahashi, and Katsuyoshi Nishinari*

Department of Food and Human Health Sciences, Graduate School of Human Life Science,
Osaka City University, Sumiyoshi, Osaka 558-8585, Japan

The effects of citric acid on the rheological properties of cornstarch pastes were studied by steady shear and dynamic oscillatory viscoelasticity, intrinsic viscosity measurements and microscopic observation. The pH of cornstarch dispersion was adjusted between 6.0 and 3.0. The viscosity of the pastes was increased by lowering the pH (between 5.5 and 3.6), while the viscosity of samples with pH below 3.5 decreased further than that of the control (pH = 6.3). Citric acid promoted the collapse of starch granules; however, adding excessive citric acid led to the hydrolysis of glucose chains. No decrease in the viscoelasticity was observed for cornstarch pastes by adding acid at 25 °C after gelatinization.

KEYWORDS: Cornstarch; viscoelasticity; citric acid; pH

INTRODUCTION

Starch has been widely used as a thickener, stabilizer, or gelling ingredient in the food industry. The main constituents of starch are amylose and amylopectin, which consist of linked α-D-glucose residues that make large polysaccharide molecules. Starch is present in the form of granules, which are not soluble in water. When starch is heated in water, the starch granules swell and rupture. Amylose and amylopectin can be leached out from the granules, and the starch suspension becomes a viscous paste. This process is known as gelatinization. Starch has been added to many kinds of food using this property.

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. Because starch is hydrolyzed by acid, aqueous hydrochloric acid is used to make acid-hydrolyzed starch by compulsorily causing hydrolysis of amylose and amylopectin chains (*1–4*). However, sour substances (various acids) are included in many foods and are added to many foods as acidulents or preservatives. It is necessary to investigate the effects of acids on the viscoelasticity of starch because it may lead to understanding how to control the viscosity of starch products.

In this study, cornstarch and citric acid were selected as the model for actual starch food products. Cornstarch is the most widely used starch in the food industry. Citric acid is contained in citrus fruits and is added to foods as a sour seasoning. It is also important as a sour basic substance for difference tests on the sensory evaluation.

There are many reports concerning the effects of acids or pH on gelatinization and retrogradation of starch (*5–11*) while there are no report concerning the viscoelasticity of cornstarch to our knowledge.

Our objective is to investigate how citric acid affects the rheological properties of starch pastes and contributes to the effect of increasing the viscosity for starch pastes.

MATERIALS AND METHODS

Materials. A cornstarch sample (cornstarch Y) was kindly provided by Sanwa Starch Co. Ltd. (Nara, Japan). The concentration of cornstarch was fixed at 3.0 wt %; this is the concentration generally used for thickeners in sauces or soups. The moisture (water) content of the cornstarch was determined to be 13.4% by drying it at 130 °C in atmospheric pressure. Citric acid (anhydrous) and dimethyl sulfoxide were of reagent grades. The pH was adjusted between 6.0 and 3.0. Sorbic acid potassium salt (0.05 wt %) was used to prevent microbial growth.

Preparation of Cornstarch Pastes. Powders of cornstarch were dispersed in distilled water or in citric acid solutions with pH adjusted beforehand. A control sample of pH 6.3 was made of cornstarch and distilled water. Cornstarch pastes were prepared using the agitator illustrated in **Figure 1**. After stirring the dispersions at 200 rpm for 30 min at 25 °C, the cornstarch dispersions were heated 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 and cooled in a water bath at 25 °C equipped with a temperature regulator, stirring with magnetic stirrers. The samples were also prepared, which were then adjusted to the pH after heating and cooling the starch dispersions (i.e., after gelatinization of starch). The final concentration of cornstarch was 3.0 wt %.

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., Piscataway, NJ) 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, shear viscosity ($\eta_{\dot{\gamma}}$), storage modulus (G'), loss modulus (G''), and complex viscosity ($|\eta^*|_\omega = (G'^2 + G''^2)^{1/2}/\omega$) were

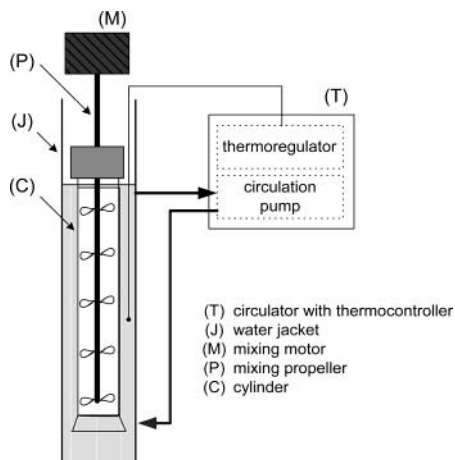**2930** *J. Agric. Food Chem.,* Vol. 52, No. 10, 2004

Hirashima et al.

Figure 1. Schematic diagram of the cornstarch paste agitator.

obtained. Strains for dynamic oscillatory measurements were chosen in the plateau range of each sample on the strain dependence measurements.

Microscopic Observations. Microscopic observations were made using OPTIPHOTO (Nikon Co. Ltd., Tokyo, Japan) equipped with 2D-color CCD (1280 × 960 pixels). Unheated cornstarch dispersions and heated cornstarch pastes were observed. Pastes prepared by the method mentioned above were diluted 2 times with distilled water. Granules of cornstarch were dyed with a 10-mM iodine solution.

Intrinsic Viscosity Measurements. Cornstarch (3.00 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 magnetic stirrers, then cooled in a water bath at 25 °C for 60 min stirring. Dimethyl sulfoxide (DMSO) was then added to the dispersions so that the ratio of DMSO to distilled water became 90:10 (vol). Starch can be solved completely in 90 vol % DMSO aqueous solutions (*12−14*). The solutions were heated and cooled again using the same methods mentioned above. The concentration of starch became 0.28 wt %. 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 ca. 330 s. at 40.0 °C. Intrinsic viscosity ($[\eta]$) was calculated from the Huggins equation[15]

$$\eta_i/c = [\eta](1+k[\eta]c+\cdots)$$

$$\eta_i = (\eta - \eta_0)/\eta_0$$

where η_0 is the viscosity of the solvent, η is the viscosity of the solution, η_i is the relative viscosity increment, c is the concentration of the solute, and k is the Huggins constant.

The relative viscosity increment has previously been called the specific viscosity. The use of the specific viscosity is discouraged by IUPAC Compendium of Chemical Terminology 2nd Edition (1997).

RESULTS AND DISCUSSION

Steady Shear Measurements for Starch Pastes Adding Acid before Gelatinization. Figure 2 shows the shear viscosity ($\eta_{\dot{\gamma}}$) of 3.0 wt % cornstarch pastes as a function of pH. The pH was adjusted by adding citric acid before gelatinization. The viscosity of the control (pH 6.3) is illustrated in mesh. All samples showed typical shear-thinning behaviors. $\eta_{\dot{\gamma}}$ was affected by both $\dot{\gamma}$ and pH. It was observed that $\eta_{\dot{\gamma}}$ became greater, and shear-thinning behavior became remarkable at pH between 5.5 and 3.6 in comparison with the control. On the contrary, $\eta_{\dot{\gamma}}$ for pH above 5.5 and below 3.6 became less than that of the control, and shear-thinning behavior became less pronounced.
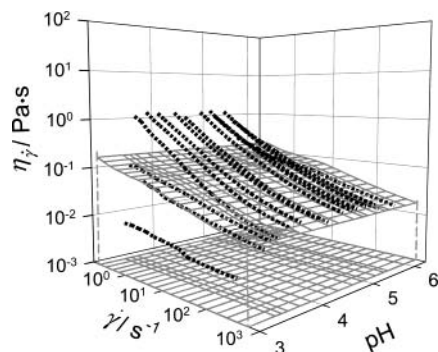

Figure 2. Shear viscosity ($\eta_{\dot{\gamma}}$) of 3.0 wt % cornstarch pastes as a function of pH. The pH was adjusted by adding citric acid before gelatinization. The shear viscosity of the control is illustrated in mesh. Measurements were made at 25.0 °C
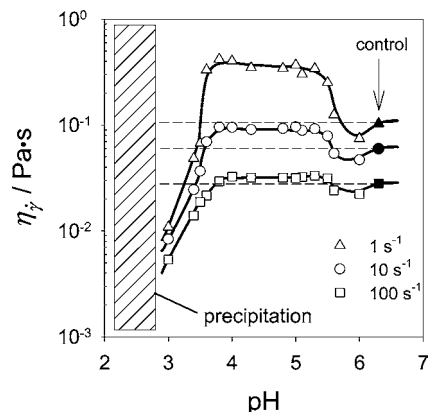

Figure 3. pH dependence of shear viscosity ($\eta_{\dot{\gamma}}$) of 3.0 wt % cornstarch pastes at the shear rates of 1, 10, and 100 s^{-1}, respectively. The pH was adjusted by adding citric acid before gelatinization. Measurements were made at 25.0 °C.

The pH dependence of the shear viscosity observed at the same condition as in **Figure 2** is demonstrated in **Figure 3** to investigate the changes in the viscosity in detail. Some values of $\eta_{\dot{\gamma}}$, where $\dot{\gamma}$ are 1, 10, and 100 s^{-1}, were chosen and represented by η_1, η_{10}, and η_{100}, respectively. η_{100}, which is the viscosity at higher $\dot{\gamma}$, decreased by lowering the pH to 5.6 and increased inversely at 5.6 > pH > 3.6. The values of η_{100} were greater than that of the control at this pH range. When the pH was lowered further, η_{100} decreased again. The values of η_1, which is the viscosity at lower $\dot{\gamma}$, were less than that of the control where the pH is above 5.6 and below 3.6 and were greater for pH between 5.6 and 3.6. The values of η_{10} had a similar tendency to η_1. The viscosity changed depending on the pH because the condition differed (i.e., size or shapes of starch granules and the number of amylose and amylopectin chains (glucose chains) differed).

It was reported that the viscosity of wheat starch pastes decreased in the presence of citric acid (*5*) or ascorbic acid (*6*). It was also reported that the viscosity of cassava starch pastes decreased by adding ascorbic acid (*8−10*). Yamada et al. 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 (*7*). Moreover, when cornstarch was separated from corn kernels by steeping in the aqueous solution containing lactic acid, the viscosity of these cornstarch pastes decreased further than that of cornstarch pastes obtained by steeping in the aqueous solution without lactic acid (*16*). On the other hand, the hardness of various foods observed in texture profile analysis increased by adding acids (e.g., bread
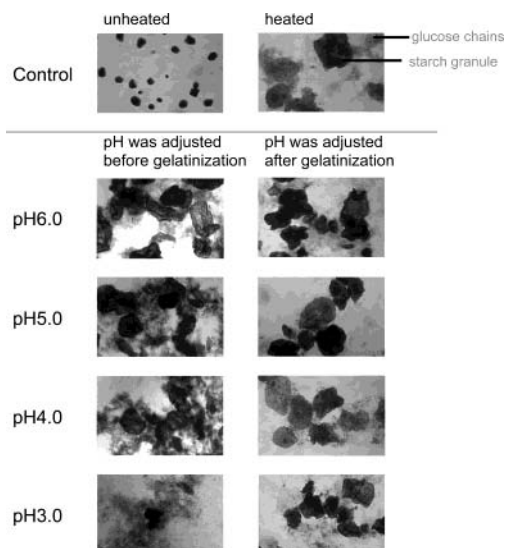
Figure 4. Microscopic photographs of starch granules for 3.0 wt % cornstarch pastes. Pastes were diluted with distilled water and dyed with 10 mM iodine solution. The pH was adjusted by adding citric acid. Image size is 390-μm × 725-μm. Observations were made at ambient temperature.

loaf (*2*, *17*) wheat flour dough (*18*), and peeled potatoes (*19*)) Such firming must be distinguished from softening and cell sloughing (*19*). However, an increase in the viscosity for starch pastes by adding acids has not yet been reported to our knowledge.

Microscopic Observation. The viscosity of starch pastes is affected by the size of starch granules and the number of glucose chains leaching out from starch granules. Microscopic photographs of the cornstarch granules, with pH adjusted before gelatinization, are lined along the left in **Figure 4**. Starch granules can be seen in purple circular lumps and glucose chains, which are mainly amylose chains, in blue mass of strands.

The granule sizes and shapes before heating for all samples with adjusted pH were similar to those of the control (**Figure 4**, top left). There were no differences among all samples (data not shown).

The heated cornstarch granules were swollen and partly ruptured. The granule sizes of the samples at pH 6.0, 5.0, and 4.0 with pH adjusted before gelatinization were almost the same as those of the control; however, the number of glucose chains at pH5.0 and 4.0 was apparently more than that of the control. Therefore, there are many entanglements of glucose chains as compared with those of the control, and these networks of glucose chains lead to higher viscosities. Thus, the viscosity of starch samples, where the pH is between 5.6 and 3.6, was greater than that of the control. Almost all granules were broken at pH 3.0 when the pH was adjusted before gelatinization, and more glucose chains were observed compared to other samples. Decreases in the viscosity at lower pH ranges may be due to the collapse of many starch granules or the hydrolysis of glucose chains by adding acid.

Intrinsic Viscosity Measurement. If the hydrolysis of glucose chains were to occur by adding acid, the degree of polymerization (DP) for glucose chains should decrease. Intrinsic viscosity ([η]) was then measured to confirm that the hydrolysis of glucose chains did occur. Because [η] corresponds to DP, the size of glucose chains can be estimated from changes in [η]. **Figure 5** shows the results of intrinsic viscosity measurements. The pH of the *x*-axis is equivalent to the pH in the preparation for cornstarch pastes. [η] decreased slightly at pH
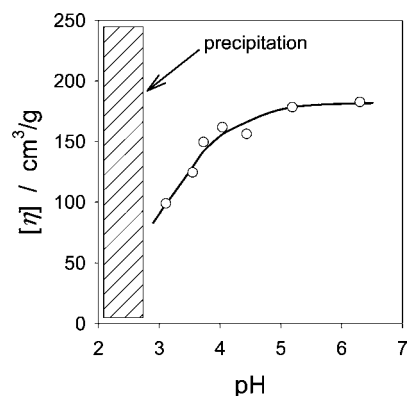

Figure 5. Intrinsic viscosity ([η]) of cornstarch at various pH in 90 vol % DMSO aqueous solution. The pH was adjusted by citric acid before gelatinization. Measurements were made at 40.0 °C.
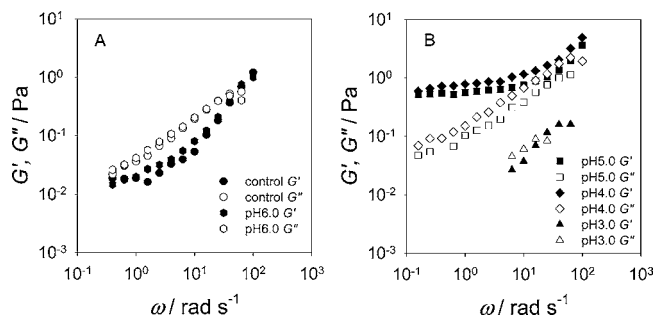

Figure 6. Frequency (ω) dependence of *G*′ and *G*″ for 3.0 wt % cornstarch paste. The pH was adjusted by adding citric acid before gelatinization. (**A**) Control and at pH 6.0 and (**B**) at pH 5.0, 4.0 and 3.0. Measurements were made at 25.0 °C. The strain for the samples at pH 6.3 (control), 6.0, 5.0, 4.0, and 3.0, was 30, 30, 3, 3, and 20%, respectively.

$\geq$ 4.0. This decrease indicates that few glucose chains were hydrolyzed by adding acid. However, increases in the viscosity were observed, where the pH is between 5.5 and 3.6, as shown in **Figure 3**. It is thought that citric acid enters the starch granules, causing the hydrolysis of glucose chains inside starch granules, then leads many glucose chains to leach into the starch pastes. Therefore, the entanglements of glucose chains increase further than those of the control. [η] decreased sharply at pH < 4.0. This indicates that hydrolysis of glucose chains occurred by adding acid, and DP decreased further than that at pH $\geq$ 4.0. Decreases in the viscosity were observed, where the pH is below 3.5, because the entanglements of glucose chains were less than those at pH $\geq$ 4.0. Precipitation of starch in starch pastes occurred at pH < 2.7 (**Figures 3** and **6**). It is known that the solubility of amylose with various DP increased considerably with shorter and longer molecules (*20*, *21*) 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 (*20*), and amylose exhibited a sharp minimum of solubility for DP between 75 and 80 (*21*). Amylose with DP between 40 and 660 were found to precipitate, although the precipitation depended on the concentration of amylose (*22*). The precipitation of starch is thought to be caused by many glucose chains with low *DP* in starch pastes.

Dynamic Oscillatory Measurements for Starch Pastes, Adding Acids before Gelatinization. Figure 6 illustrates the frequency (ω) dependence of storage modulus (*G*′) and loss modulus (*G*″) of cornstarch pastes with or without adjusting the pH before gelatinization. Samples with pH6.3 (control) and 6.0 showed behaviors known for concentrated flexible polymer solutions (i.e., *G*′ is less than *G*″ at lower ω, and *G*′ is greater
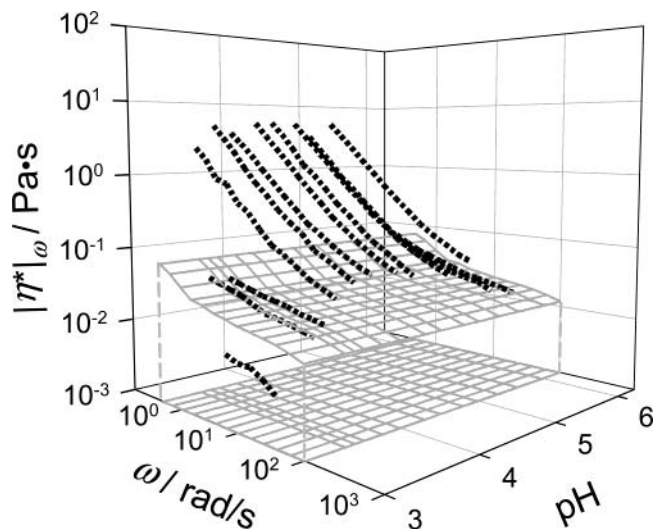
Figure 7. Complex viscosity ($|\eta^*|_\omega$) of 3.0 wt % cornstarch pastes as a function of pH. The pH was adjusted by adding citric acid before gelatinization. The complex viscosity of the control is illustrated in mesh. Measurements were made at 25.0 °C. The strain for the sample at pH6.3 (control), 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.
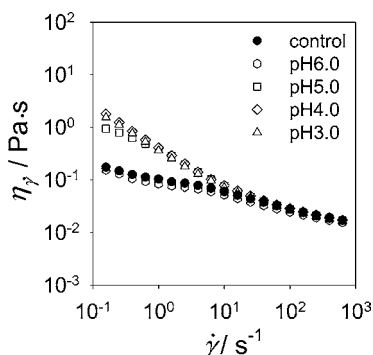

Figure 8. Shear viscosity ($\eta_{\dot\gamma}$) of 3.0 wt % cornstarch pastes. The pH was adjusted by adding citric acid after gelatinization. Measurements were made at 25.0 °C.

than G'' at higher ω). The values of G' and G'' for a paste with pH 6.0 were not different from those of the control (pH 6.3) (**Figure 6A**). The values of G' were greater than those of G'' at all ω examined, and G' and G'' increased with increasing ω for pastes with pH 5.0 and 4.0. This behavior resembles that of a weak gel (**Figure 6B**). Starch granules and glucose chains that leach out from starch granules formed entangled networks at these pH. The paste behaved as a concentrated solution where the pH is 3.0. The values of G' and G'' were less than those of the control at all ω examined (**Figure 6B**). This suggests that the size of starch granules and DP for glucose chains both decreased.

Complex viscosity ($|\eta^*|_\omega$) of 3.0 wt % cornstarch pastes as a function of pH is shown in **Figure 7**. $|\eta^*|_\omega$ of the control is illustrated in mesh. The pH was adjusted before gelatinization. Comparing $|\eta^*|_\omega$ in **Figure 8** with $\eta_{\dot\gamma}$ in **Figure 2**, $|\eta^*|_\omega$ and $\eta_{\dot\gamma}$ of all samples did not obey the Cox−Merz rule, $\eta_{\dot\gamma} = |\eta^*|_\omega$, because starch pastes contained swollen granules and glucose chains. The values of $|\eta^*|_\omega$ were not coincidental with those of $\eta_{\dot\gamma}$, while $|\eta^*|_\omega$ had a similar tendency to $\eta_{\dot\gamma}$. $|\eta^*|_\omega$ of samples with 6.0 > pH > 3.4 and 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 3.0 was less than that of the control. $|\eta^*|_\omega$ was greater than $\eta_{\dot\gamma}$ on samples with 5.3 ≥
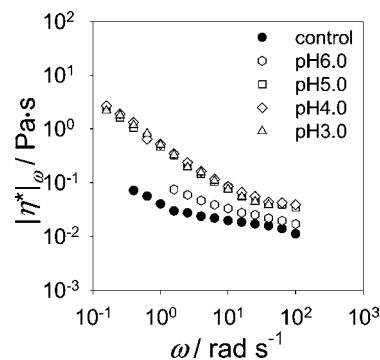

Figure 9. Complex viscosity ($|\eta^*|_\omega$) of 3.0 wt % cornstarch pastes. The pH was adjusted by adding after gelatinization. Measurements were made at 25.0 °C. The strain for the samples at pH 6.3 (control), 6.0, 5.0, 4.0, and 3.0, was 30, 30, 3, 3, and 3%, respectively.

pH ≥ 3.6. The cornstarch pastes with this pH range behave as a weak gel. On the other hand, the cornstarch pastes for pH above 5.3 and below 3.6 had the behavior of a liquid.

From the results mentioned above, adding much acid leads to a decrease in the viscosity 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 viscosity for starch pastes must be obtained.

The Effects of Adding Acids after Gelatinization. Figure 8 shows $\eta_{\dot\gamma}$ of 3.0 wt % cornstarch pastes with pH adjusted after gelatinization. There were no differences between the control sample and samples with pH 6.0. Moreover, decreases in the viscosity could not be observed even at lower pH (pH = 3.0). Many starch granules could be seen in the microscopic photograph for the sample adjusted to pH 3.0 after gelatinization, compared with those adjusted to pH before gelatinization (bottoms in **Figure 4**). The values of $\eta_{\dot\gamma}$ for all samples were greater than that of the control, except for the samples at pH 6.0.

The same tendencies were observed in dynamic oscillatory measurements. The values of $|\eta^*|_\omega$ for all samples with pH adjusted after gelatinization were greater than that of the control (**Figure 9**).

Conclusions. When citric acid was added before gelatinization, the viscosity of cornstarch pastes increased by adjusting the pH between 5.6 and 3.6, while the viscosity of pastes with pH below 3.5 decreased further than that of the control (pH = 6.3) on the steady shear and dynamic oscillatory measurements.

It is obvious from intrinsic viscosity measurements that the hydrolysis of glucose chains occurs by adding acid before gelatinization. However, increases in the viscosity could be seen by adding small amounts of acids (5.6 > pH > 3.5), because many glucose chains leached out from starch granules, indicating that there were many entanglements of glucose chains. On the other hand, adding large amounts of acids (pH ≤ 3.5) leads to the fracture of starch granules, and thus, a decrease in the viscosity was observed.

No decrease in the viscoelasticity was noted for cornstarch pastes by adding citric acid after gelatinization. The hydrolysis of glucose chains could be prevented.

Citric Acid and Cornstarch Pastes

J. Agric. Food Chem., Vol. 52, No. 10, 2004 **2933**

LITERATURE CITED

(1) Wurzburg, O. B. Modified Starches. In Food Polysaccharides and Their Applications; Stephen, A. M., Ed.; Marcel Dekker Inc.: New York, 1995; pp 67−97.

(2) Plata-Oviedo, M.; Camargo, C. Effect of Acid Treatments and Drying Processes on Physicochemical and Functional Properties of Cassava Starch. *J. Sci Food Agric.* **1998**, *77*, 103−108.

(3) Chamberlain, E. K.; Rao, M. A. Effect of Concentration on Rheological Properties of Acid-Hydrolyzed Amylopectin Solutions. *Food Hydrocolloids* **2000**, *14*, 163−171.

(4) Li, J. H.; Vasanthan, T.; Rossnagel, B.; Hoover, R. Starch from Hull-less Barley: II. Thermal, Rheological, and Acid Hydrolysis Characteristics. *Food Chem.* **2001**, *74*, 407−415.

(5) Campbell, A. M.; Briant A. M. Wheat Starch Pastes and Gels Containing Citric Acid and Sucrose. *Food Res.* **1957**, *22*, 358−366.

(6) D'Appolonia, B. L. Effect of Bread Ingredients on Starch-Gelatinization Properties as Measured by the Amylograph. *Cereal Chem.* **1972**, *49*, 532−543.

(7) Yamada, T.; Morimoto, Y.; Hisamatsu, M. Effect of Citric Acid on Potato Starch Gelatinization. *Starch/Stärke*. **1986**, *38*, 264−268.

(8) Vallès-Pàmies, B.; Barclay, F.; Hill, S. E.; Mitchell, J. R.; Paterson, L. A.; Blanshard, J. M. V. The Effects of Low Molecular Weight Additives on the Viscosities of Cassava Starch. *Carbohydr. Polym.* **1997**, *34*, 31−38.

(9) Sriburi, P.; Hill, S. E.; Mitchell, J. R. Effects of L-Ascorbic Acid on the Conversion of Cassava Starch. *Food Hydrocolloids* **1999**, *13*, 177−183.

(10) Sriburi, P.; Hill, S. E. Extrusion of Cassava Starch with Either Variations in Ascorbic Acid Concentration or pH. *Int. J. Food Sci. Tech.* **2000**, *35*, 141−154.

(11) Wang, H.-H.; Sun, D.-W.; Zeng, Q.; Lu, Y. Effect of pH, Corn Starch and Phosphates on the Pasting Properties of Rice Flour. *J. Food Eng.* **2000**, *46*, 133−138.

(12) Jackson, D. S. Solubility Behavior of Granular Cornstarches in Methyl Sulfoxide (DMSO) as Measured by High Performance Size Exclusion Chromatography. *Starch/Stärke*. **1991**, *43*, 422−427.

(13) Chamberlain, E. K.; Rao, M. A. Rheological properties of acid converted waxy maize starches in water and 90% DMSO/10% water. *Carbohydr. Polym.* **1999**, *40*, 251−260.

(14) Chamberlain, E. K.; Rao, M. A. Effect of concentration on rheological properties of acid-hydrolyzed amylopectin solutions. *Food Hydrocolloids* **2000**, *14*, 163−171.

(15) Huggins, M. L. The Viscosity of Dilute Solutions of Long-Chain Molecules. IV. Dependence on Concentration. *J. Am. Chem. Soc.* **1942**, *64*, 2716−2718.

(16) Shandera, D. L.; Jackson, D. S. Effect of Corn Wet-Milling Conditions (Sulfur Dioxide, Lactic Acid, and Steeping Temperature) on Starch Functionality. *Cereal Chem.* **1996**, *73*, 632−637.

(17) Piazza, L.; Masi, P. Moisture Redistribution Throughout the Bread Loaf During Staling and Its Effect on Mechanical Properties. *Cereal Chem.* **1995**, *72*, 320−325.

(18) Nakamura, M.; Kurata, T. Effect of L-Ascorbic Acid on the Rheological Properties of Wheat Flour-Water Dough. *Cereal Chem.* **1997**, *74*, 647−650.

(19) Sapers, G. M.; Cooke, P. H.; Heidel, A. E.; Martin, S. T.; Miller, R. L. Structural Changes Related to Texture of Pre-Peeled Potatoes. *J. Food Sci.* **1997**, *62*, 797−803.

(20) Burchard, W. Streulicht- und Viskositätsmessungen an Wäβrigen Amyloselösungen. II. *Makromol. Chem.* **1963**, *59*, 16−27.

(21) Pfannemüller, B. Conformation of Amylose in Aqueous Solution: Optical Rotatory Dispersion and Circular Dichroism of Amylose-Iodine Complexes and Dependence on Chain Length of Retrogradation of Amylose. *Biopolymers* **1971**, *10*, 243−261.

(22) Gidley, M. J.; Bulpin, P. V. Aggregation of Amylose in Aqueous Systems: The Effect of Chain Length on Phase Behavior and Aggregation Kinetics. *Macromolecules* **1989**, *22*, 341−346.