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Rheological Characteristics of Potato Amylopectin*

Masakuni TAKO

*Department of Bioscience and Biotechnology, Faculty of Agriculture, University of the Ryukyus
(1 Senbaru, Nishihara, Okinawa 903-0213, Japan)*

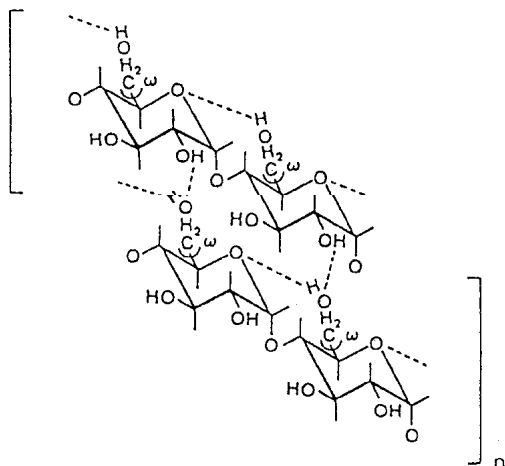
The non-Newtonian behavior and dynamic viscoelasticity in aqueous solution of potato amylopectin were measured with a rheogoniometer, and the molecular origin for the rheological characteristics were discussed in comparison with those of rice amylopectin. The flow curves, at 25°C, of potato amylopectin showed shear-thinning behavior at 2.0 and 4.0% concentration, but plastic behavior at 6.0%, the yield value of which was estimated to be 0.8 Pa. Although the dynamic viscoelasticity of rice amylopectin showed a constant value, it decreased in potato amylopectin solution when the temperature was increased. The $\tan \delta$ value was 1.15 at a concentration of 6.0% even at 0°C. The dynamic modulus decreased with the addition of urea (4.0 M) and in alkaline solution (0.05 N and 0.10 N NaOH) during an increase in the temperature. An increase of the dynamic modulus, however, was observed in 85% DMSO. A slight intramolecular association in potato amylopectin molecules seems to be involved in aqueous solution. The phosphate groups attached at C-6 seem to prevent intramolecular associations of potato amylopectin molecules in aqueous solution.

Amylopectin comprises branched glucans in which linear chains containing on average 18-25 (1-4)- α -linked D-glucopyranosyl residues that are interlinked by (1-6)- α -D-glucopyranosidic linkages to form a multiple branched structure. The arrangement of chains within amylopectin molecules is still not clear. NIKUNI¹⁾ and FRENCH²⁾ proposed the cluster model, whereby the shorter chains (A-chains) are arranged in tightly packed clusters throughout a basic structure composed of long chains (B-chains). The model "cluster" is most widely accepted and not only explains the high viscosity and dynamic viscoelasticity, but it also accounts for the high crystallinity of amylopectins.^{3,4)}

We have proposed possible models of intra- and intermolecular hydrogen bondings of amylose molecules in aqueous solution, as illustrated in Scheme 1.⁵⁾ An intramolecular hydrogen bonding might take place between OH-6 and adjacent hemiacetal oxygen atom of the D-glucosyl residues within amylose molecule. This bonding is likely because of the flexibility

of α -(1-4)-linkage and the extended conformation at a high temperature range. In addition, an intermolecular hydrogen bonding might occur between the OH-2 and the adjacent O-6 of the D-glucosyl residues on different molecules to make gel, as in a solid state.⁶⁾ A part of the intermolecular hydrogen bonding, side-by-side association, breaks down above a transition temperature, 25-35°C, during an increase in the temperature under a steadily shearing force. Residual intermolecular and intramolecular hydrogen bonding are lost above another transition temperature, 80-90°C, under a steady shearing force. Under frequency, however, both intra- and intermolecular hydrogen bondings of amylose molecules are stable until the temperature reached 65-80°C. Although this model corresponds to a double-stranded helix, a single helix also seems to exist in part with the formation of side-by-side intermolecular hydrogen bondings in aqueous solution. A tertiary structure of amylose molecules may consist of two identical left-handed, sixfold helices in aqueous solutions as in the solid state.⁶⁾ Amylose molecules, however, in aqueous solution are notoriously unstable and retrogradation results in an

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Scheme 1. Possible mode of intra- and intermolecular hydrogen bonding of amylose in aqueous solution.

The dotted lines refer to hydrogen bonding.

increase in turbidity and eventually precipitation.⁷⁾ Therefore, the retrogradation seems to occur by shrinkage of the amylose molecules which was caused by a decrease of the kinetic energy and Brownian motion of the polymer and water molecules and results in new intra- and intermolecular hydrogen bonding. Much more intense intra- and intermolecular hydrogen bonding (Scheme 1) may result in a precipitation of the amylose molecules in aqueous media.

We have recently discussed molecular origin of the thermal stability for viscosity and dynamic viscoelasticity of three types of rice amylopectin, the number-average chain length (\overline{CLn}) of which was estimated to be 18.8–19.0.^{8,9)} An intramolecular hydrogen bonding may take place between the hemiacetal oxygen atom and the adjacent OH-6 of the D-glucosyl residues, as formed in amylose molecule (Scheme 1). Intramolecular van der WAALS forces of attraction may also take place in part between the hemiacetal oxygen atom and the adjacent hydroxymethyl groups of the D-glucosyl residues because a slight decrease of the dynamic modulus was observed whenupon urea (4.0 M) was added and a large dynamic modulus was maintained during an increase in the temperature up to 80°C. The intramolecular hydrogen bonding and van der WAALS forces of attraction

may have thermostable characteristics even at a high temperature range >80°C.

Potato starch contains a small proportion of covalently bound phosphate in its amylopectin component,¹⁰⁾ and the phosphate groups are mainly located at C-6 of the B-chains of D-glucosyl residues.^{11,12)} The number-average chain length of potato amylopectin molecules are estimated to be 23.5–24.0, and a smaller number of A-chains is substituted than those of rice amylopectin.³⁾

We report herein the flow behavior and dynamic viscoelasticity of a potato amylopectin, and its rheological properties are analyzed with respect to its association characteristics in comparison with those of potato amylose and rice amylopectins.

MATERIALS AND METHODS

Materials. Potato amylopectin, *Jaga kids red '90*, was provided by Professor Emeritus Susumu HIZUKURI of Kagoshima University, Japan. The number-average chain length (\overline{CLn}) of the amylopectin was 23, and the hydrolysis limit with β -amylase was 56%. These values were the normal values of potato amylopectin.¹³⁾ The phosphorus has been found exclusively in the amylopectin (840 ppm) so that the amylopectin linked abundant phosphate, of which 73% (613 ppm) was found as glucose 6-phosphate.¹³⁾ The iodine affinity of the amylopectin (0.08)¹³⁾ was higher than that of rice amylopectins (0.071–0.075), which were used in our previous papers.^{8,9)} The average degree of polymerization (\overline{DPn}) was estimated to be 4,290.

Methods. Aqueous solutions were obtained by heating mixtures of potato amylopectin and distilled water at 100°C for 20 min. Viscosity at various shear rates (1.19–95.03 s⁻¹) and dynamic viscoelasticity at a fixed frequency (3.77 rad s⁻¹) were determined with a rheogoniometer consisting of a coaxial cylinder (1.8 cm diam.) with a rotating outer cylinder (2.2 cm diam.) 6.0 cm long (IR-103, Iwamoto Seisakusho Co., Ltd., Japan). The temperature of the sample was controlled by circulating oil from a Thermo-cool (LCH-130F, Toyo Co., Ltd., Japan) from 0

to 80°C, raised at a rate of 1°C/min by steps. Shear rate ($\dot{\gamma}$), shear stress (τ), and apparent viscosity (η) were calculated with the equation of MARGULES.¹⁴ Dynamic viscosity (η') and elasticity (G') were calculated by a modification of MARKOVITZ's equation.¹⁵ The loss tangent was calculated from the relationship, $\tan \delta = G''/G'$, where G'' is the loss modulus.

RESULTS AND DISCUSSION

To compare the rheological behavior of potato amylopectin with that of rice amylopectins, the viscosity and dynamic viscoelasticity were measured under the same conditions as those of previous studies.^{8,9} The flow curves, at 25°C, of potato amylopectin at various concentrations are shown in Fig. 1. The flow curves were approximated to shear-thinning behavior at 2.0 and 4.0%, but to plastic behavior at 6.0%, the yield value of which was estimated to be 0.8 Pa. As reported previously,^{8,9} the flow curves for rice amylopectins showed plastic behavior even at a concentration of 2.0%. This might be caused by the formation of intramolecular hydrogen bonding and van der WAALS forces of attraction. Thus a little secondary (intra- or intermolecular) association

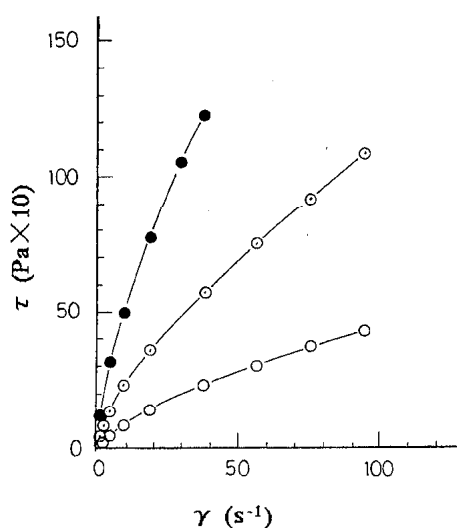


Fig. 1. Flow curves of potato amylopectin at various concentrations and 25°C.

Concentration: ○, 2.0%; ◐, 4.0%; ●, 6.0%.

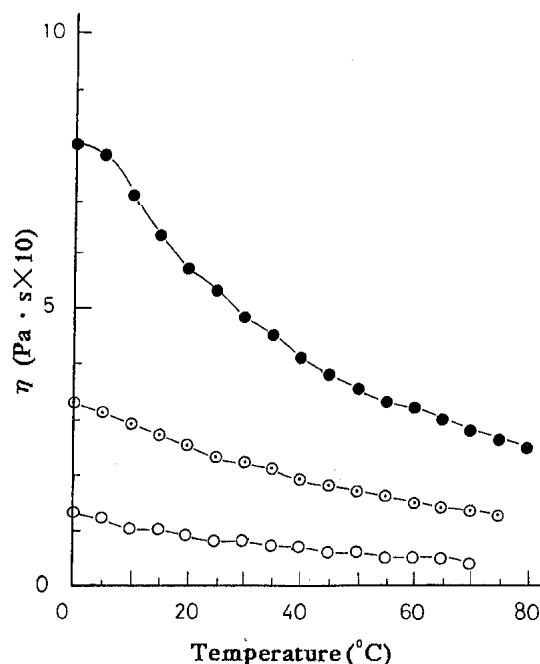


Fig. 2. Effects of temperature on viscosity of potato amylopectin at various concentrations.

Concentration: ○, 2.0%; ◐, 4.0%; ●, 6.0%.

seems to be involved in the potato amylopectin molecules in aqueous solution, since the yield value was observed at high concentration > 6.0%.

As shown in Fig. 2, the viscosity of potato amylopectin at 2.0 and 4.0% decreased gradually with an increase in temperature at a shear rate of 9.5 s^{-1} . A rapid decrease in the viscosity was observed in the solution at 6.0%. The viscosity of rice amylopectins, however, increased with increases in temperature up to 5–15°C: then the viscosity stayed at a constant value with further increase in the temperature.^{8,9} On the other hand, an increase in the viscosity with increasing temperature from 20 to 30°C, which was estimated to be the first transition temperature, was observed in an aqueous solution of potato amylose:⁵ then a small decrease in the viscosity occurred, but showing large values, and a constant viscosity was kept with further increase in the temperature up to 90°C, which was estimated to be the second transition temperature: then it decreased rapidly. The results and discussion

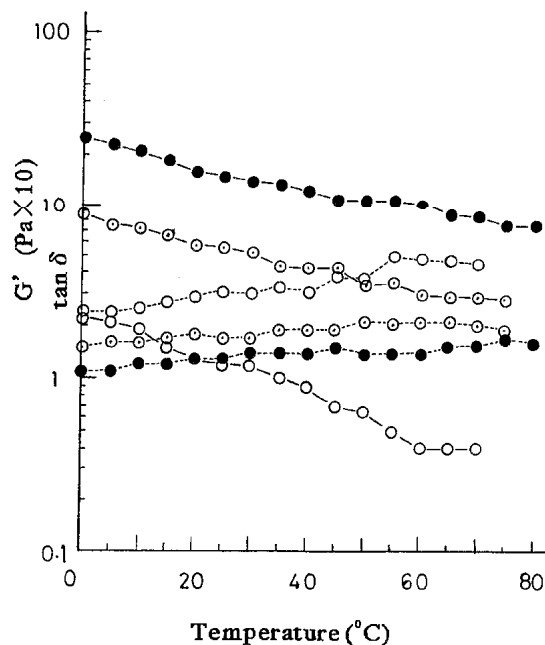


Fig. 3. Effects of temperature on the dynamic modulus of potato amylopectin at various concentrations.

—, Dynamic modulus; ---, $\tan \delta$. Concentration: \circ , 2.0%; \odot , 4.0%; \bullet , 6.0%.

suggest that only a slight secondary association may be involved in the potato amylopectin molecules even at a low temperature range in aqueous solution.

The effects of temperature on dynamic viscoelasticity of the potato amylopectin at various concentrations are shown in Fig. 3. The dynamic modulus increased with an increase in concentration and showed slightly large values in comparison with those of rice amylopectins at 6.0%, where a very large dynamic modulus was observed. The dynamic viscoelasticity, however, decreased gradually with increases in temperature at various concentrations. The $\tan \delta$ value showed a very large value (2.40) at a concentration of 2.0% at a low temperature (0°C) and decreased slightly with an increase in the concentration to a value of 1.15 at 6.0%. The $\tan \delta$ values increased gradually with increases in temperature. But to the contrary, the $\tan \delta$ for rice amylopectins showed low values of 0.38–0.42 and stayed at a constant value during in the temperature increase at a

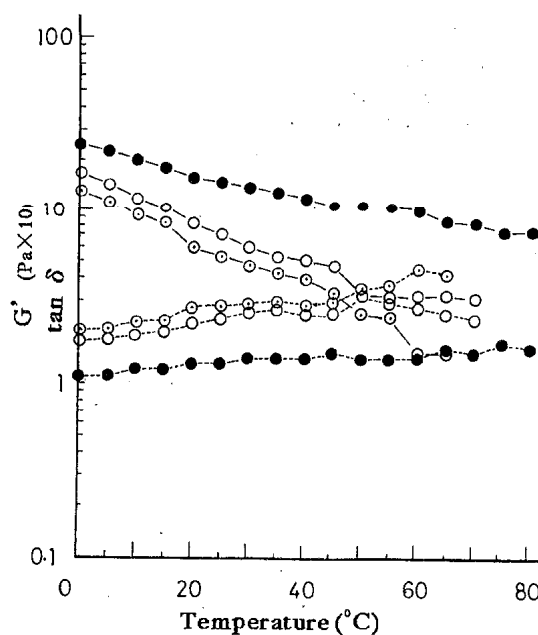


Fig. 4. Effects of temperature on the dynamic viscoelasticity of potato amylopectin at a concentration of 6.0% in an NaOH solution.

—, Dynamic modulus; ---, $\tan \delta$. Symbol: \circ , in 0.05 N NaOH; \odot , in 0.10 N NaOH, \bullet , in aqueous solution.

concentration of 6.0%. The results also suggest that a small secondary association seemed to be involved in potato amylopectin solution even at high concentration (6.0%) and low temperature (0°C), since a high $\tan \delta$ value (1.15) was observed even at a concentration of 6.0% at low temperature (0°C).^{16,17)}

The dynamic modulus showed low values with the addition of urea (4.0 M), which is known as a hydrogen-bonding breaker, in a solution of potato amylopectin (6.0%), and it decreased gradually with increased temperature (not shown in figure). A slight increase of $\tan \delta$ was observed in the presence of urea (1.22), and it increased gradually with increases in temperature at a concentration of 6.0%. The result suggests that a small amount of hydrogen bonding takes part in the amylopectin molecules. Figure 4 shows the effect of temperature on the dynamic modulus of potato amylopectin (6.0%) after being dissolved in 0.05 and 0.10 N NaOH. The dynamic modulus remained

low values in 0.05 N and 0.10 N NaOH solution and decreased gradually with increased temperature. The $\tan \delta$ showed larger values than those in potato amylopectin alone during increases in temperature. On the contrary, the dynamic viscoelasticity showed larger values in a solution of 85% dimethylsulfoxide (DMSO) in comparison with those in aqueous solution (not shown a figure). However, $\tan \delta$ showed almost the same values (1.10 at 0°C) as that of the polymer alone at various temperatures. The increased dynamic viscoelasticity may be due to free from a little secondary association of potato amylopectin molecules in aqueous solution.

As reported in our previous papers,^{8,9)} viscosity and dynamic viscoelasticity of rice amylopectin had very large values and stayed at a constant during increases in temperature. For potato amylopectin, which have average chain length longer (23) than rice amylopectin (18-19), however, the viscosity and dynamic viscoelasticity showed a slightly large values with increasing concentration and decreased gradually with increases in the temperature. Furthermore, $\tan \delta$ values of potato amylopectin showed larger value (1.15 at 6.0%) than that of rice amylopectin (0.33 at 6.0%).^{8,9)} The results suggested that a small secondary association seems to be involved in aqueous solution of potato amylopectin molecules.^{16,17)}

Thus we conclude that the molecular origin for the viscosity and dynamic viscoelasticity of aqueous solution of potato amylopectin seems to be attributed to an entanglement of molecular chains on different molecules where the molecules may essentially adopt a random coil conformation. The potato amylopectin used in this study contains phosphate groups of 840 ppm.¹³⁾ The phosphate groups, however, are mostly located at C-6¹¹⁻¹³⁾ of B-chains, which carry the A or other B-chains.⁹⁾ On the contrary, rice amylopectins contain only a phosphate group of 4-14 ppm.^{18,19)} The results suggest that an intramolecular hydrogen bonding between the hemiacetal oxygen atom and OH-6, as formed in rice amylopectin,^{8,9)} of potato amylopectin molecules seems to be prevented by the phosphate groups.

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ポテトアミロペクチンのレオロジー特性

田幸正邦

琉球大学農学部生物資源科学科
(903-0213 沖縄県中頭郡西原町字千原1番地)

平均重合度 (\overline{DP}_n), 平均鎖長 (\overline{CL}_n), およびリン酸含量がそれぞれ 4290, 23.0, および 840 ppm のポ

テトアミロペクチン (ジャガキッズ, 90, 赤) 水溶液の非ニュートン流動と動的粘弾性をレオゴニオメーターを使用して測定した。ポテトアミロペクチンは2.0および4.0%で擬塑性流動を, 6.0%では降伏値(0.8 Pa)が認められ塑性流動を示した。この結果から, ポテトアミロペクチン分子鎖は水溶液中で二次結合を形成しないことが示唆された。粘性は温度の上昇に伴って徐々に減少した。また, 動的弾性率は濃度の増

大に伴って高い値を有したが, 温度の上昇に伴って減少した。一方, $\tan \delta$ は6.0%低温側(0°C)で1.15であった。動的弾性率は尿素(4.0 M)またはアルカリ溶液(0.05または0.10 N NaOH)で低い値に留まった。しかしながら, 85% DMSO 溶液では逆に増大した。ポテトアミロペクチン分子鎖に置換しているリン酸(C-6, 613 ppm)が, 分子鎖内二次結合を阻害することが示唆された。