小麦アミロペクチンのレオロジー的性質

Rheological Properties of Wheat Amylopectin☆

Masakuni TAKO*, Ikuko SHIROMA and Shuntoku UECHI

Department of Bioscience and Biotechnlogy, Faculty of Agriculture, University of the Ryukyus

Abstract: The non-Newtonian behavior and dynamic viscoelasticity of wheat (Rosella) amylopectin in aqueous solution were investigated. The flow curves, at 25℃, of Rosella amylopectin showed shear-thinning behavior at various concentrations (3.0, 5.0 and 7.0%). The storage modulus of Rosella amylopectin showed a little high values and decreased gradually during increase in temperature even at 7.0% solution. The tan δ showed a value of 2.0 at 7.0% even at low temperature (0℃) and increased a little with increase in temperature. The storage modulus of Rosella amylopectin (7.0%) increased a little upon addition of urea (4.0 M) and decreased gradually with increase in temperature. The storage modulus was a little higher in 0.05 M NaOH solution (7.0%) than in aqueous solution. The results obtained suggested that the wheat (Rosella) amylopectin molecules might be involved in little secondary association in aqueous solution.

Key words: wheat amylopectin, shear-thinning behavior, little secondary association

Introduction

Amylopectin is a highly branched polysaccharide consisting of linear (1→4)-α-D-glucose chains linked through α-(1→6) branched points on every 18-25 residues.[1,2] Several models have been proposed for its molecular structure, the cluster models presented by Nikuni,[3] French[4] and Hizukuri[5] appearing to be accepted as its most probable.

We have proposed the molecular origin for thermostability of the viscosity and dynamic viscoelasticity of rice amylopectin (Kogane,[6] Reimei, Takanari[7] and Koshihikari[8]) in aqueous solutions. The thermal stability of rice amylopectin molecules might be attributed to intramolecular hydrogen bonding between a OH-6 and an adjacent hemiacetal oxygen atom of D-glucosyl residues. An intramolecular association might also take place between a OH-6 and an adjacent H-1 of D-glucosyl residues with van der Waals forces of attraction. The intramolecular associations (hydrogen bonding and van der Waals forces of attraction) of rice amylopectin molecules seemed to be involved in inner long chains ($B_{2\text{-}4}$ and super long chains) in part. Particularly, Koshihikari amylopectin molecules might adopt more expanded conformation than those of the other rice (Kogane, Reimei and Takanari) amylopectins in aqueous solution[8] which might be attributed by intramolecular associations.

However, as reported previously,[9] potato amylopectin (Jaga Kids Red) molecules might adopt a random conformation where phosphate groups located at C-6 (613 ppm) of B-chains, which carry the A or other B-chains, might prevent intramolecular associations in aqueous solution.

We have also reported that a wheat (Halberd) amylopectin molecules were involved in little secondary association in aqueous solution which might be due to different molecular structure with that of rice amylopectin molecule.[10]

In the present paper, we report on the flow behavior and dynamic viscoelasticity of a wheat (Rosella) amylopectin, and its rheological properties are analyzed with respect to its association characteristics in aqueous solution in comparison with those in rice and Halberd wheat amylopectin.[6-8,10]

Materials and Methods

1. Materials.

The wheat (Rosella) amylopectin used in the experiments was provided by Susumu Hizukuri of Kagoshima University, Japan and the same as reported by Shibanuma.[11] The Rosella amylopectin had number-average chain length

☆Presented at the Joint Meeting of the Branch of 252nd Nishinippon, 421st Kansai and 1st Chyugoku-Shikoku, the Society for Bioscience, Biotechnology, and Agrochemistry, Okayama, October 12-13, 2001.

*Correspndong author. (Tel; +81-98-8814: Fax, +81-98-8814, E-mail: tako @agr.u-ryukyu.ac.jp).

($\overline{CLn}$) and the hydrolysis limit with β-amylase was 19.2 ± 1.7 and 57 ± 4.3 %, respectively. The $\overline{CLn}$ of the amylopectin (Rosella) was a little longer than that of rice amylopectins (18.0-19.0), which were used in our previous papers,[6-8] but almost agreed as that of Halberd wheat amylopectin.[11] The iodine affinity of the Rosella amylopectin (0.40 ± 0.005) was higher exclusively than that of rice amylopectins (0.071-0.075)[12] and potato amylopectin (0.08),[13] but had almost same value with that of Halberd amylopectin. The λ max (nm) and phosphorus content (ppm) was 537 ± 1.7 and 4.0, respectively. The average degree of polymerization ($\overline{DPn}$) was estimated to be 18,000 ± 2,200 which was also in agreement with that of Halberd amylopectin.[11]

Aqueous solutions were obtained by heating mixtures of wheat (Rosella) amylopectin in distilled water at 100℃ for 30 min.

2. Methods.

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 (Iwamoto Seisakusho Co., Ltd, Japan) consisting of a coaxial cylinder (1.8cm diam.) with a rotating outer cylinder (2.2cm diam.). The temperature of the sample was controlled by circulating oil from a thermo-cool instrument (LCH-130F, Toyo Co., Ltd., Japan), over the temperature range of 0-70 ℃ and raised at a stepwise rate of 1 ℃ min^{-1}. Shear rate ($\dot{\gamma}$), shear stress (τ), and apparent viscosity (η) were calculated with the equation of Margules.[14] Dynamic viscosity (η') and storage modulus (G') were calculated by modification of Markovitz's equation.[15] The loss tangent (tan δ) was calculated from the relationship, tan δ = G"/G', where G" = $\omega\eta'$ is the loss modulus, and ω is the angular velocity of the outer cylinder.

Results and Discussion

1. Characteristics of wheat amylopectin.

The chain length distribution pattern[11] of Rosella amylopectin was largely trimodal with peaks at dp. 11, 18 and 40, but shoulders were observed at these peaks. Furthermore, small amounts of super long chains (LC) and a long chain (B_3) component were present. The shortest chain fraction ($A+B_1$) was predominant (78.0 mol%) the total value of which, however, is smaller than that of rice amylopectin (Akihikari, 89.7 mol%).[16]

2. Flow characteristic.

The flow curves, at 25 ℃, of Rosella wheat amylopectin at various concentrations (3.0, 5.0 and 7.0%) are shown in Fig. 1. The flow curves approximated that of shear-thinning behavior which was in agreement with that of Halberd amylopectin solution.[10] As reported in the preceding papers,[6-8] rice amylopectin solutions showed plastic behavior where yield values were estimated at various concentrations (2.0, 4.0 and 6.0%). The result suggests that Rosella wheat amylopectin molecules are involved in less secondary association (intra- or intermolecular) because yield values were not observed at all concentrations.[6-8,17]

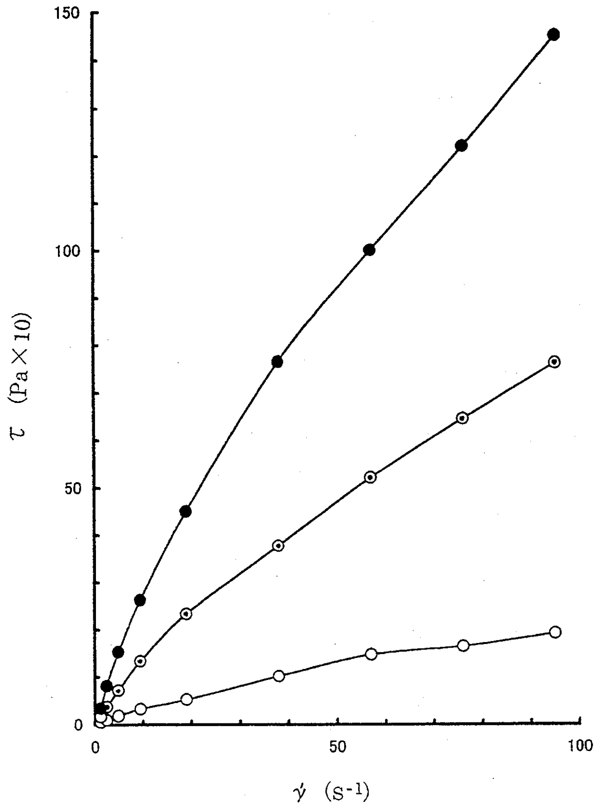

Fig. 1. Flow curves, at 25 ℃, of Rosella amylopectin at various concentrations.
Concentration: ○ 3.0%; ⦿, 5.0%; ●, 7.0%.

3. Viscosity

The viscosity of Rosella amylopectin at 7.0% decreased gradually with increase in the temperature at a shear rate of 9.5 s^{-1} (not shown in figure). As reported in our preceding papers,[6-8] a slight increase in the viscosity with increasing temperature was observed up to 20℃, then decreased a little even at high temperature range (70~80℃) in rice amylopectins, but almost the same phenomenon, decreasing viscosity, was observed in Halberd wheat amylopectin solution.[10]

4. Dynamic viscoelasticity.

Effect of temperature on storage modulus of the Rosella amylopectin at angular velocity of 3.77 rad · s^{-1} at various concentrations are shown in Fig. 2. The storage modulus increased proportionally with an increase in

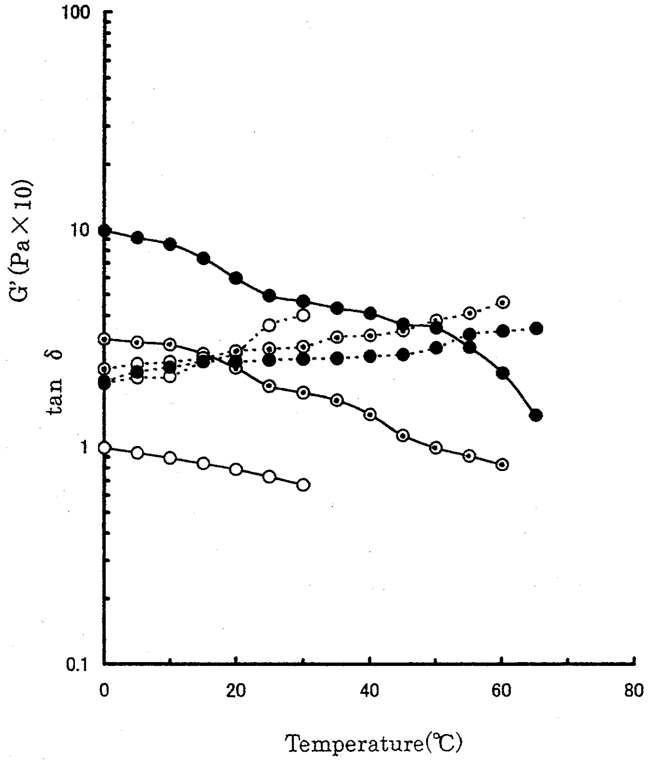

Fig. 2. Effect of temperature on storage modulus of Rosella amylopectin at various concentrations and 3.77 r ad・s^{-1}. Concentration: ○, 3.0%; ⊙, 5.0%; ●, 7.0%
——, storage modulus; ……, tan δ.

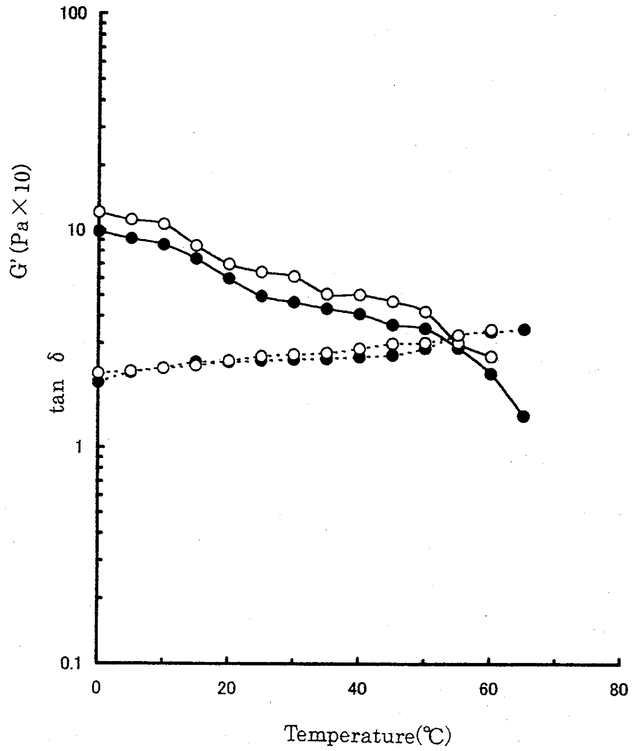

Fig. 3. Effect of temperature on storage modulus of Rosella amylopectin (7.0%) after preparation in aqueous solution (●) and after preparation with addition of urea (4.0 M) (○).

concentration from 3.0 to 7.0%. The storage modulus, however, was only 1.0 Pa even at low (0℃) temperature and at a concentration of 7.0%, the value of which was a little lower than that of Halberd amylopectin solution.[10] The storage modulus decreased gradually with increase in temperature, the phenomenon of which was in agreement with that of Halberd amylopectin solution. However, as reported in our preceding papers,[6-8] the storage modulus showed very high value (10~12 Pa) and stayed at a constant value with increase in the temperature in rice amylopectin solutions. The dynamic viscosity also increased with an increase in concentration and decreased gradually with increase in temperature (not shown in figure). On the other hand, tan δ showed a value of 2.0 at 7.0% at low temperature (0℃), the value of which was higher than that of rice amylopectins (0.2~0.4), but almost the same with that of Halberd amylopectin solution (1.8). The tan δ of Rosella amylopectin increased a little with increase in temperature. The result indicates that little secondary associations are involved in Rosella amylopectin molecules even at low temperature (0℃) in a solution of 7.0%. The result also indicates that Rosella amylopectin is more viscous than elastic in aqueous solution.

A little increase in the storage modulus of Rosella amylopectin (7.0%) was observed on addition of urea (4.0

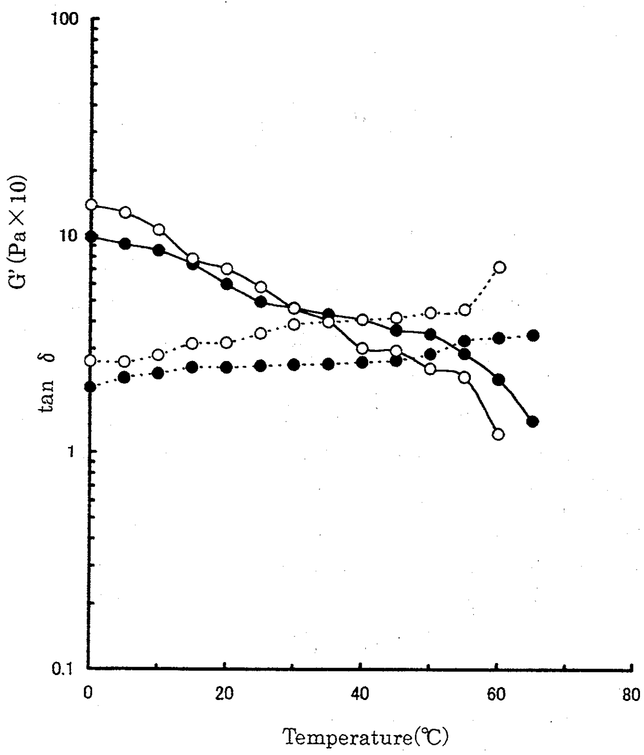

Fig. 4. Effect of temperature on storage modulus of Halberd amylopectin (7.0%) in alkaline solution (○; 0.05 M NaOH) after preparation in aqueous solution (●).

M) and decreased gradually with increase in temperature, as shown in Fig. 3. However, the tan δ showed almost the same value (2.1) even at low temperature (0℃) in comparison with that in aqueous solution (2.0). The value increased gradually with increase in temperature. Such phenomenon, increase in the storage modulus, may be due to salting out effect.[17,18)]

A little higher storage modulus of Rosella amylopectin (7.0%) was observed in 0.05 M NaOH solution than that in aqueous solution and decreased gradually with increase in temperature (Fig. 4). On the contrary, tan δ values in 0.05 M NaOH solution showed higher (2.6) than that of aqueous solution (2.0) even at low temperature (0℃) and increased gradually with increase in the temperature. The result suggests that there is no secondary association in Rosella amylopectin molecules in aqueous solutions because the tan δ value showed almost the same value in alkaline solution. The increase in storage modulus may be attributed to have expanding conformations of wheat (Rosella) amylopectin molecules in alkaline solution.

The flow behavior and dynamic viscoelasticity of solutions of wheat (Rosella) amylopectin were different with those of rice (Kogane,[6)] Reimei, Takanari[7)] and Koshihikari[8)]) amylopectin, but essentially agreed with those of potato and Halberd wheat amylopectin.[10)] The value of first named solution, however, decreased upon addition of urea (4.0 M) and in alkaline solution (0.05 M NaOH).

Conclusions

Thus, we conclude that the molecular origin for the viscosity and dynamic viscoelasticity of Rosella wheat amylopectin molecules seems to be attributed to an entanglement of molecular chains on different molecules, as in Halberd amylopecttin molecules.[10)] The wheat (Rosella and Halberd) amylopectin molecules may be involved in compacted conformations which are caused by a large amount of long chains > B_1 where about 40% of the B chains carried no A chains.[19)] Consequently, a structure of wheat (Rosella and Halberd) amylopectin molecules seems to be different from those of rice amylopectin molecules.

Acknowledgements

The authors wish to thank Professor Emeritus Susumu Hizukuri and Professor Yoshihito Takeda at Kagoshima University for their valuable advices and for the gift of wheat amylopectin. Financial support by Elizabeth Arnold Fuji Foundation, Japan, is gratefully acknowledged.

References

1) Hizukuri, S. 1986. Polymodal distribution of the chain length of amylopectin, and its significants. *Carbohydr. Res.*, 206: 342-347.
2) Manners, D.J. 1989. Recent developements in our understanding of amylopecctin strucure. *Carbohydr. Polym.*, 11: 87-112.
3) Nikuni, J. 1969. Starch and cookery. *Chyouri Kagaku,* 2: 6-10. (in Japanese)
4) French, D. 1972. Fine structure and relationship to the organization of starch granules. *Denpun Kagaku,* 19: 8-25.
5) Hizukuri, S. 1996. in Starch, analytical aspects: in *Carbohydrates in Food,* A.C. Eliasson, ed., Marcel Dekker, Inc, New York, pp. 373-429.
6) Tako, M. 1996. Molecular origin for the thermal stability of waxy-rice (Kogane) starch. *Starch/Stärke,* 48: 414-417.
7) Tako, M and Hizukuri, S. 1997. Molecular origin for the thermal stability of rice amylopectin. J. *Carbohydr. Chem.,* 16: 655-666.
8) Tako, M. and M., Hizukuri, S. 2000. Molecular origin for the thermal stability of Koshihikari amylopectin. *Food Res. Int.,* 33: 15-40.
9) Tako, M. 1998. Rheological characteristics of potato amylopectin. *J. Appl. Glycosci.,* 45: 379-386.
10) Tako, M. and Hizukuri, S. 2003. Rheological characteristics of wheat (Halberd) amylopectin, *Starch/Stärke,* 55: 345-349.
11) Shibanuma, K., Takeda, Y. and Hizukuri, S. 1994. Molecular structure of some wheat starches. *Carbohydr. Polym.,* 25: 111-116.
12) Takeda, Y., Maruta, N., Hizukuri, S. and Juliano, O. 1989. Structures of indica rice starches (IR 48 and IR 64) having intermediate affinities for iodine. *Carbohydr. Res.,* 187: 287-294.
13) Suzuki, A., Shibanuma, K., Takeda, Y., Abe, J. and Hizukuri, S. 1994. Structure and pasting properties of potato starches from Jaga Kids Purple '90 and Red '90. *Oyo Toshitsu Kagaku,* 41: 425-432.
14) Harris, J. 1977. More detail analysis of the coaxial cylinder viscometer: in Rheology and *Non-Newtonian Flow,* Longman, New York., pp. 28-33, 1977.
15) Markovitz, H. 1952. A property of bressel function and its application to the theory of two rheometers. *J. Appl. Phys.,* 23: 1070-1077.
16) Tako, M. and S. Hizukuri, S. 2000. Retrogradation mechanism of ricce starch. *Cereal Chem.,* 77: 473-477.
17) Tako, M. and Nakamura, S. 1988. Gelation mechanism of agarose. *Carbohydr. Res.,* 280: 277-284.

18) Tako, M., A. Sakae, A. and S. Nakamura, S. 1989. : Rheological properties of gellan gum in aqueous media, *Agric. Biol. Chem.,* 53: 771-776.
19) Hizukuri, S. and Maehara, Y. 1990. Fine structure of wheat amylopectin the mode of A to B chain binding. *Carbohydr. Res.,* 206: 145-159.

小麦アミロペクチンのレオロジー的性質

田幸正邦*，城間郁子，上地俊徳

琉球大学農学部生物資源科学科

キーワード：小麦アミロペクチン，レオロジー，粘性，動的粘弾性

要　約

ローゼラ小麦アミロペクチン（平均重合度，18,000±2,200；数平均鎖長，19.2±1.7）水溶液の流動曲線は，広い濃度範囲（3.0～7.0%）で擬塑性流動を示した．ローゼラアミロペクチンの貯蔵弾性率は，濃度の増大に伴って低温側でもそれほど増大しなかった．また，貯蔵弾性率は温度の上昇に伴って徐々に減少した．損失正切（tan δ）は7.0%，0℃でも高い値（2.0）を示した．ローゼラアミロペクチンの貯蔵弾性率は尿素（4.0M）の添加によってわずかに増大し、温度の上昇に伴って徐々に減少した．また、ローゼラアミロペクチンの貯蔵弾性率は，アルカリ溶液（0.05M NaOH）でもわずかに増大し，温度の上昇に伴って徐々に減少した．以上の結果から，ローゼラアミロペクチンの分子鎖は，水溶液で二次結合（分子鎖内または分子鎖間）を形成しない事が示唆された．