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Gelatinization mechanism of potato starch

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Abstract

The non-Newtonian behavior and dynamic viscoelasticity of potato starch (Jaga kids red '90, 21.0% amylose content) solutions after storage at 25 and 4°C for 24 h were measured with a rheogoniometer. The flow curves, at 25°C, of potato starch showed plastic behavior >1.0% (w/v) after heating at 100°C for 30 min. A gelatinization of potato starch occurred above 1.0% at room temperature. A very large dynamic viscoelasticity was observed when potato starch solution (3.0%) was stored at 4°C for 24 h and stayed at a constant value with increasing temperature. A small dynamic modulus of potato starch was observed upon addition of urea (4.0 M) at low temperature (0°C) even after storage at 25 and 4°C for 24 h. A small dynamic modulus was also observed in 0.05 M NaOH solution. Possible models of gelatinization and retrogradation mechanism of potato starch were proposed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Potato starch; Gelatinization mechanism; Retrogradation mechanism

1. Introduction

As reported previously (Tako & Hizukuri, 1995), the flow curves at 25°C, of potato amylose aqueous solution approximated to plastic behavior above 1.4%. A curious flow behavior was observed in a solution at 1.6%; the shear stress decreased rapidly with an increase in shear rate up to 9.5 s^{-1}, then it increased gradually with increasing shear rate. The phenomenon, showing a decrease of shear stress with increasing shear rate up to 9.5 s^{-1}, might be caused by a rapid breakdown of an intermolecular hydrogen bonding of potato amylose molecules. Gelation occurred at a concentration of 1.2% at room temperature (25°C). From the results and discussions, we have proposed a possible gelation mechanism of potation amylose molecules in aqueous solution (Tako & Hizukuri, 1995). Intramolecular hydrogen bonding might take place between OH-6 and the adjacent hemiacetal oxygen atom of the D-glucosyl residues within the amylose molecule. In addition, intermolecular hydrogen bonding might take place between the OH-2 and the adjacent O-6 of the D-glucosyl residues on different molecules to make gel.

On the other hand, we have recently discussed the molecular origin for the thermal stability of rice amylopectin in aqueous solution and concluded that the molecules are involved in intramolecular hydrogen bonding (Tako, 1996; Tako & Hizukuri, 1997) and van der Waals forces of attraction (Tako & Hizukuri, 2000a). The intramolecular hydrogen bonding and van der Waals forces of attraction may play a dominant role in the thermal stability of viscosity and dynamic viscoelasticity of rice amylopectin molecules in aqueous solution. However, the flow curves of potato amylopectin (Jaga kids red '90) solution approximated to shear-thinning behavior even at a concentration of 4.0% (Tako 1998). This indicates that a secondary association (intra- and intermolecular) of potato amylopectin molecules is not involved in aqueous solution.

Furthermore, we have proposed possible gelatinization (Tako & Hizukuri, 1999) and retrogradation (Tako & Hizukuri, 2000b) mechanism for rice starch in aqueous solution. An intermolecular hydrogen bonding of rice starch might take place between O-6 of the amylose and OH-2 of the amylopectin molecules. The short amylopectin side-chains (A and B1), which are not involved in intramolecular associations, may take part in the intermolecular associations. Intermolecular hydrogen bonding between amylose and amylopectin molecules is thermally stable. This bonding is liable to dissociate with increasing temperature under shearing flow, but stable under angular flow. However, intermolecular hydrogen bonding, together with intramolecular association within long chains (B3–4) of amylopectin molecules, dissociates above the transition temperature (>50°C) in solutions of 4.0 M urea and 0.05 M NaOH. The dynamic viscoelasticity increased when rice starch

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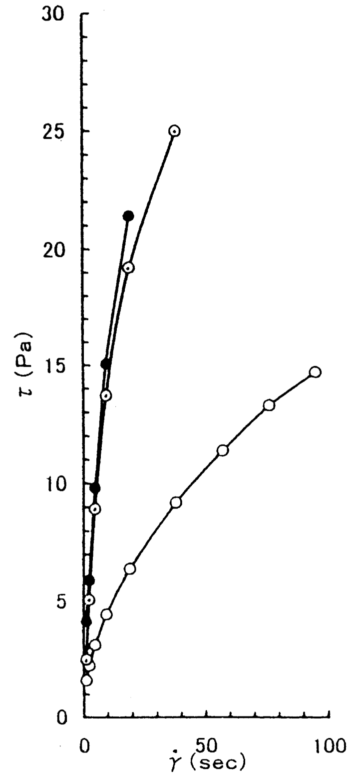


Fig. 1. Flow curves, at 25°C, of potato starch at various concentrations; ○, 1.0%; ⊙, 2.0%; ●, 3.0%.

solution was stored at 25 and 4°C for 24 h (Tako & Hizukuri, 2000b). We have concluded that, after formation of intermolecular hydrogen bonding between O-6 of the amylose and OH-2 of the amylopectin molecules, another intermolecular hydrogen bond may form between OH-2 of a D-glucose residue of the former molecule and O-6 of a short side chain (A and B1) of the latter molecule. Two or more short side-chains (A and B1) of an amylopectin molecule may associate with an amylose molecule. After saturation of intermolecular hydrogen bonding between amylose and amylopectin molecules, an intermolecular association may also take place between amylopectin molecules through hydrogen bonding, because the molar ratio of amylose to amylopectin was 1:5 (Tako & Nakamura, 1986b, 1988; Tako, Qi & Toyama, 1998). This bonding may be caused by a decrease of Brownian motion and kinetic energy of amylopectin and water molecules during storage at 25 and 4°C for 24 h. At this stage, side-by-side association between O-3 and OH-3 of D-glucosyl residues on different amylopectin molecules may also take place.

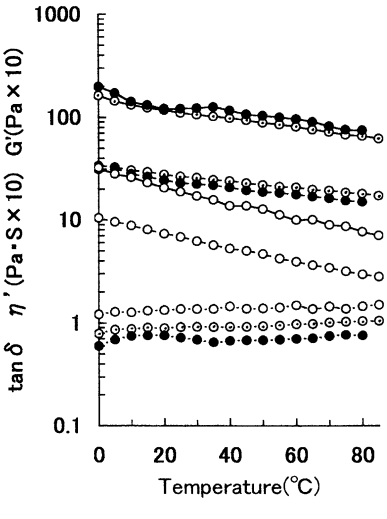


Fig. 2. Effects of temperature on dynamic viscoelasticity and tan δ of potato starch at various concentrations; ○, 1.0%; ⊙, 2.0%; ●, 3.0%.

We previously reported that a potato amylopectin (Jaga kids red '90) molecule might adopt a random conformation in aqueous solutions (Tako, 1998). Thus, we report herein the flow behavior and dynamic viscoelasticity of a solution of potato starch and its rheological properties were analyzed with respect to its association characteristics in comparison with those of potato amylose, potato amylopectin and rice starches. This work may offer a new concept of the gelatinization and retrogradation mechanism of potato starch in aqueous solution.

2. Materials and methods

2.1. Materials

Potato starch (Jago kids red '90) was a gift from Dr Ayako Suzuki (Osaka Women's University). The potato starch contained 21.0% of amylose, 800 ppm of phosphate (Suzuki, Shibanuma, Takeda, Abe & Hizukuri, 1994). The $\overline{\text{d.p.n}}$ and $\overline{\text{d.p.w.}}$ of amylose molecule were 2110 and 5130, respectively. The amylopectin molecules had an average chain length of 23. The hydrolysis limit with β-amylase and iodine affinity of the amylopectin was 56% and 0.08 (g/100 g), respectively (Suzuki et al., 1994).

2.2. Viscosity and dynamic modulus measurements

Viscosity at various shear rates (1.19–95.03 s^{-1}) and dynamic viscoelasticity at 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.). The temperature of the sample was controlled by circulating oil from a thermo-cool instrument (LCH-130F, Toyo Co., Ltd), over the temperature range of 0–90°C and raised at a stepwise rate of 1°C min^{-1}. Shear rate ($\dot{\gamma}$), shear stress (τ), and viscosity (η) were calculated with the equation of Margules (Harris, 1977). Dynamic viscosity (η') and elasticity (G') were calculated by modification of Markovitz's equation (Markovitz, 1952). The loss tangent (tan δ) was calculated from the relationship, $\tan\delta = G''/G'$ where $G'' = \omega\eta'$ is the loss modulus, and ω is the angular velocity of the outer cylinder. Values reported are the means of two determinants.

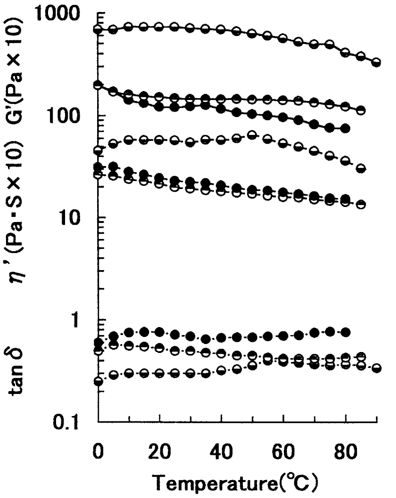


Fig. 3. Effects of temperature on dynamic viscoelasticity and tan δ of potato starch (3.0%; ●) after storage at 25°C (◓) and 4°C (◒) for 24 h.

3. Results

To compare the rheological behavior of potato starch with that of potato amylose potato amylopectin and rice starches, the viscosity and dynamic viscoelasticity were measured under the same conditions as those of previous studies (Tako, 1998, 2000; Tako & Hizukuri, 1995, 1999, 2000b). A gelatinization of Jaga kids potato starch occurred at a concentration above 1.0% (w/v) in aqueous solution.

The flow behavior, at 25°C, of Jaga kids potato starch at various concentrations is shown in Fig. 1. The flow curves approximated that of plastic behavior and the yield values were estimated to be 1.2, 2.0 and 2.7 Pa at 1.0, 2.0 and 3.0% concentration, respectively. As reported previously (Tako, 1998), Jaga kids red potato amylopectin solutions showed shear-thinning behavior, even at a concentration of 4.0%. This indicates that the very intensive intermolecular association has been accomplished in potato starch molecules (Tako & Hizukuri, 1999, 2000b), though the molar ratio of amylose to amylopectin of the starch is 1.5 (Suzuki et al., 1994).

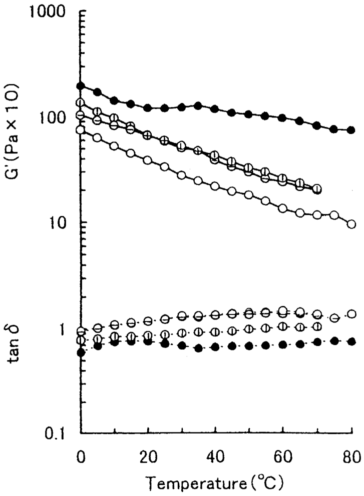


Fig. 4. Effects of temperature on dynamic modulus and tan δ of potato starch (3.0%; ●) after addition of 4.0 M urea (○); after storage at 25°C (⊖); after storage at 4°C (⦶) for 24 h.

As shown in Fig. 2, the dynamic modulus of the potato starch increased with increasing concentration up to 2.0% and showed very large values during increasing temperature. However, almost the same values were observed at a concentration of 3.0%. This indicates that intermolecular association of the potato starch has been saturated at a concentration above 2.0%. A weak sigmoid curve was observed in a solution of potato starch at 3.0% during increasing temperature and stayed at a large value. On the other hand, dynamic viscosity at a concentration of 2.0% showed a larger value than that in a solution of 3.0% and was constant during increasing temperature. The tan δ values of potato starch solution decreased from 1.2 to 0.67 when concentrations were increased from 1.0 to 3.0% at low temperature (0°C). The tan δ value for a 3.0% solution showed a weak sigmoid curve during increasing temperature. As reported previously (Tako, 1998), the dynamic modulus of a potato amylopectin (Jaga kids) showed low value even at a concentration of 6.0% and decreased gradually with increasing temperature. The tan δ value of the potato amylopectin solution showed a very large value (1.02) even at a concentration of 6.0% and at low temperature (0°C).

Though the dynamic modulus of the potato starch (3.0%) had almost the same values during increase in temperature after storage at 25°C as that immediately after preparation, it increased greatly after storage at 4°C (Fig. 3). This indicates that much more intense intermolecular association of the potato starch molecules has been accomplished when the solution has been stored at 4°C. A small increase in dynamic modulus was observed with increasing temperature up to 25°C, then it stayed at a constant value in a solution of 3.0%. A weak sigmoid curve was observed in 3.0% solution after storage at 25°C for 24 h, a phenomenon which was also observed in a rice starch solution (Tako & Hizukuri, 2000b). On the other hand, the dynamic viscosity of the 3.0% starch solution increased with increase in temperature up to 50°C, then it decreased gradually with further increase in temperature when the solution was stored at 4°C for 24 h. The tan δ value decreased from 0.67 to 0.23 after storage at 4°C for 24 h and was constant up to 45°C, then it increased slightly with further increase in temperature.

The dynamic modulus of a Jaga kids red potato starch 3.0% solution was small and decreased gradually with increasing temperature upon addition of 4.0 M urea (Fig. 4). Almost the same dynamic modulus was observed when the solution was stored at 25 and 4°C for 24 h. In contrast, the tan δ value increased upon addition of urea and increased a little with increasing temperature. The result indicates that an intermolecular association of potato starch molecules associates with hydrogen bonding.

The dynamic modulus of a Jaga kids red 3.0% solution

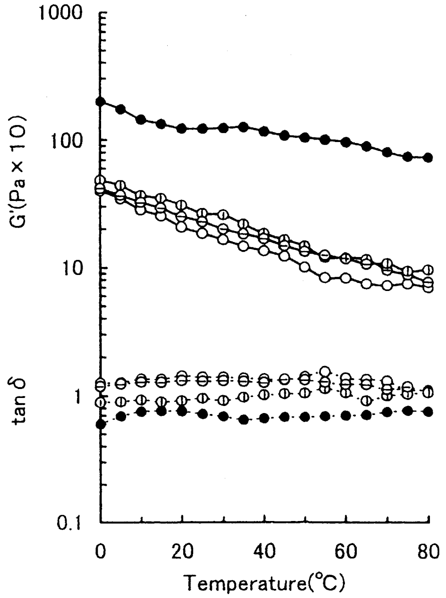
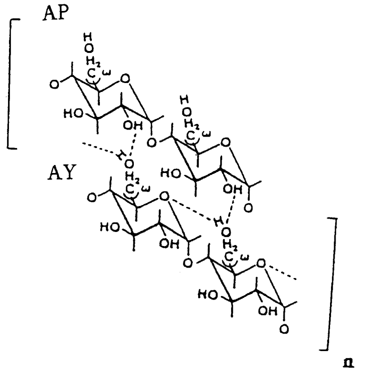


Fig. 5. Effects of temperature on dynamic modulus and tan δ of potato starch (3.0%; ●) in alkaline solution (0.05 M NaOH; ○); after storage at 25°C (⊖); after storage at 4°C (⦶) for 24 h.

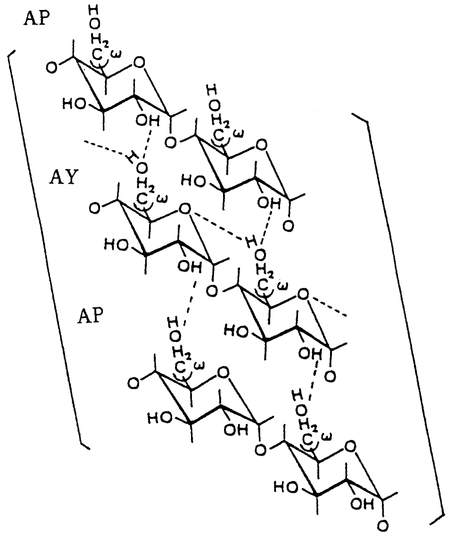
remained low in alkaline solution (0.05 M NaOH) at low temperature (0°C) and decreased gradually with increasing temperature (Fig. 5). After storage at 25 and 4°C for 24 h, the dynamic modulus was slightly larger and decreased gradually with increased temperature. The result is in agreement with that of potato amylopectin solution (Tako, 1998).

4. Discussion

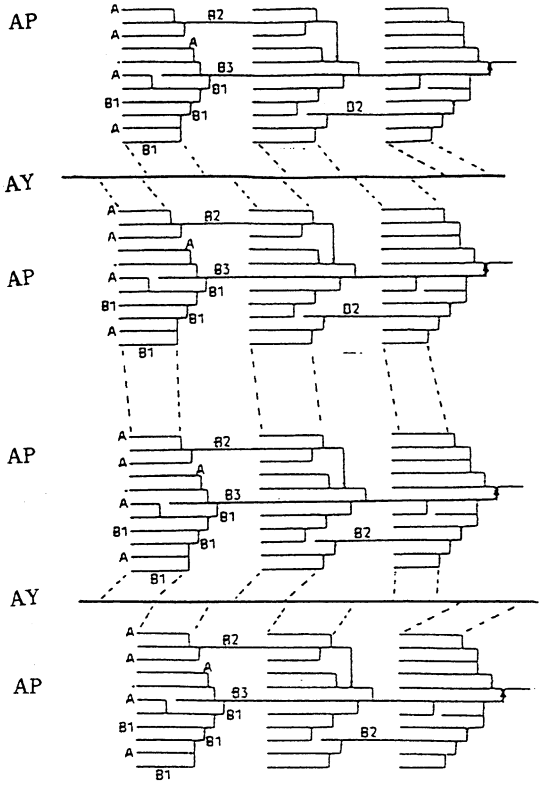
The rheological characteristics of Jaga kids red potato starch differ from those of potato amylose (Tako & Hizukuri, 1995) and Jaga kids red potato amylopectin (Tako, 1998), but were essentially comparable with those of rice starch (Tako, 2000; Tako & Hizukuri, 1999; 2000b). This suggests that intermolecular hydrogen bonding between amylose and amylopectin molecules of Jaga kids potato



Scheme 1. Possible intermolecular hydrogen bonding of potato starch in aqueous solution. Dotted lines represent hydrogen bonding. AY, amylose; AP, short side-chains (A and B1) of amylopectin molecules.



Scheme 2. Possible retrogradation mechanism of potato starch. Dotted lines represent hydrogen bonding. AY, amylose; AP, short side-chains (A and B1) of amylopectin molecules.



Scheme 3. Possible association sites (dotted lines) between amylose and amylopectin molecules of potato starch. Two or more short-chains (A and B1) of amylopectin molecules may take part in the interaction with an amylose molecule. After storage at low temperature (4°C) and for long times, and after saturation of hydrogen bonding between amylose and amylopectin molecules (Scheme 2), self-association within amylopectin molecules may take place.

starch may take place in aqueous solution, as in rice starch solution. Though a little increase in the dynamic modulus was observed after storage at 25°C, it increased greatly when the potato starch solution was stored at 4°C for 24 h.

Thus, we conclude that the gelatinization of potato starch may take place between amylose and short side-chains (A or B1) of amylopectin molecules with hydrogen bonding in aqueous solutions, as illustrated in Scheme 1. Intermolecular hydrogen bonding may occur between O-6 of a D-glucose residue of the amylose and OH-2 of a D-glucose residue of the amylopectin molecules.

After formation of intermolecular hydrogen bonding between O-6 of the amylose and OH-2 of the amylopectin molecules (Scheme 1), another intermolecular hydrogen bonding may form between OH-2 of a D-glucose residue of the former molecule and O-6 of a D-glucose residue of a short side-chain (A or B1) of the latter molecule, as illustrated in Scheme 2.

Much more intense intermolecular hydrogen bonding took place during storage at 4°C for 24 h. Two or more short side-chains (A and B1) of amylopectin molecules may associate with an amylose molecule because Jaga kids potato starch consists of 21.0% amylose and 89.0% amylopectin (Tako, 1991, 1992, 1993, 2000; Tako & Hizukuri, 1999, 2000b; Tako & Nakamura, 1984, 1986a,b, 1988; Tako et al., 1998). After saturation of intermolecular hydrogen bonding between amylose and amylopectin molecules (Scheme 2), an intermolecular association may also take place between amylopectin molecules through hydrogen bonding, as illustrated in Scheme 3. This bonding may be caused by a decrease of Brownian motion and kinetic energy of short side-chains of amylopectin and water molecules during storage at 4°C for 24 h. At this stage, side-by-side association between O-3 and OH-3 of D-glucosyl residues on different amylopectin molecules may also take place with hydrogen bonding (Tako, 2000; Tako & Hizukuri, 2000b).

After gelatinization, Jaga kids potato starch showed more transparent solution than that of rice starches (Tako, 2000; Tako & Hizukuri, 1999, 2000b) and gelatinized at lower concentration (1.0%). This may be due to the high solubility of the amylose (Tako & Hizukuri, 1995) and amylopectin (Tako, 1998) molecules. A slight retrogradation was observed when the potato starch solution was stored at 25°C for 24 h. This may be caused by large kinetic energy and Brownian motion of the amylopectin molecules of Jaga kids potato starch. The results and discussion suggest that potato amylopectin molecules are free from an intramolecular association (Tako, 1998). Accordingly, the amylose molecule of Jaga kids potato starch may adopt a single stranded helix and associate with two or more short side-chains of amylopectin molecules.

Acknowledgements

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