Effects of Granule Size and Size Distribution on Rheological Behaviour of Hydroxypropylated and Cross-linked Potato Starch

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The effects of granule size and size distribution on rheological behaviour of hydroxypropylated and phosphate cross-linked potato starch (HPPS) were studied by steady and dynamic viscoelasticity measurements. The rheological behaviour of starch dispersions was strongly influenced by granule size and granule-granule interaction. The HPPS granules heated at the temperature range from 50°C to 100°C for 30 min were not ruptured. Average granule size of HPPS dispersion at high concentration was smaller than that at low concentration because HPPS granule could not be sufficiently swollen above this critical concentration. As concentration of starch increased, the viscosity rises dramatically and the flow curves became non-Newtonian over the whole shear rate range. HPPS dispersions tended to show a more solid-like mechanical spectrum with increasing concentration.

Key Word: Starch, Rheology, Granule Size, Size Distribution

1. INTRODUCTION

Starch is used widely in the food industry as a thickening, stabilizing and gelling agent. Starch granules are insoluble in cold water. On heating starch dispersions in water above a certain temperature, gelatinization occurs, i.e., starch granules swell, disintegrate and are well dispersed. On cooling heated starch dispersions, a gel is formed and syneresis begins to occur. This phenomenon is called retrogradation. The elastic modulus of starch gel increases with storage time, and it causes difficulty sometimes in the food industry.

Chemical modification of starch has been used to reduce the change in rheological properties induced by heat treatment and shear and to prevent retrogradation. Recently, there are many types of chemically modified starch, such as starches modified by acid hydrolysis, oxidation, etherification, esterification and cross-linking [1-3]. In addition to these effects, the chemical modification produces considerable change in the gelatinization and swelling properties of the starch [4].

Many studies of modified starch have been performed [5-8], but the rheological studies of chemically modified starch have not been performed sufficiently to develop further applications. The aim of the present work is to examine the role of granule size and granule mass fraction on the rheological behaviour of dispersions of chemically modified potato starch.

2. EXPERIMENTAL

2.1. Materials

The commercial powders of hydroxypropylated phosphate cross-linked potato starch (HPPS) were given by Lyckeby Stärkelsen (Kristianstad, Sweden). The moisture content of HPPS was 8.4 w/w %. The ratio of hydroxypropyl groups and the ratio of phosphate cross linkages in HPPS are 0.61 and 0.96, w/w %, respectively [4].

2.2. Analysis of granule size

1 w/w % dispersions of HPPS and native potato starch (NPS) were prepared in distilled water using a motorized stirrer. The dispersions were stirred at 200 rpm for 30 min at room temperature, and heated in an oil bath to 50, 60, 70, 80, 90 and 100°C for 15 min and then kept at each temperature for 30 minutes. The hot sample dispersions of HPPS and NPS were diluted with distilled water and immediately granule size distributions were determined with a computer controlled laser diffraction particle size analyzer SALD-2000J (Shimadzu Co., Kyoto, Japan).

2.5 and 5 w/w % dispersions of HPPS were prepared by the method mentioned above. Hot samples of HPPS dispersions were cooled to room temperature and were diluted with 50 v/v % methanol. The size distribution analysis was carried out immediately with suspending a sample. When concentrated heated starch dispersion was diluted with alcohol, the granule was contracted. The present work was carried out using 50 v/v % methanol in which starch granules were found neither to swell nor contract during the measurements of size distribution.

2.3. Rheological measurements

HPPS dispersions with six different concentrations of 1, 2, 2.5, 3, 4 and 5 w/w % were prepared in distilled water using a motorized stirrer. Dispersions were stirred at 200 rpm for 30 min at room temperature. Then the dispersion was heated in an oil bath to 60°C for 15 min and then kept at 60°C for 30 min.

Rheological measurements were performed on a fluid

spectrometer RFS II (Rheometrics Co., NJ, USA) using a parallel plate geometry (50mm diameter, 1mm gap). In steady shear measurements in the shear rate range from 10^{-3} to 10^2/s, the viscosity η, the shear stress σ and the shear rate $\dot{\gamma}$ were measured. All the flow curves were approximated well by the Herschel-Bulkley equation (Equation 1),

$$\sigma - \sigma_0 = k\dot{\gamma}^n \quad (1)$$

where σ is shear stress (Pa), σ_0 is yield stress (Pa), k is consistency coefficient (Pa s^n), $\dot{\gamma}$ is shear rate (1/s) and n is flow behaviour index.

In dynamic oscillatory measurements, the storage shear modulus G', the loss shear modulus G'', mechanical loss tangent $\tan\delta$ ($=G''/G'$) and the complex viscosity η^* ($=(G'^2 + G''^2)^{1/2}/\omega$), (where ω is angular frequency), were observed in the frequency range from 10^{-2} to 10^2 rad/s using the RFS II.

3. RESULTS AND DISCUSSION
3.1. Size distribution

The granule size distribution and average granule diameter are important properties of the dispersed phase which govern the viscoelasticity of gelatinized dispersions of unruptured starch granules. The average diameters of the granules heated at various temperatures are shown in Fig.1. Granule size of NPS increased with heating temperature up to 50°C then leveled off at 70°C. Further increase in heating temperature caused the rupture of granules. The granule size distribution could not be measured when heated at above 80°C because almost all granules were ruptured. This indicates that NPS granules could swell up to a certain volume, and when the granule size reached a limiting value, the granules would rupture. On the other hand, there were scarcely ruptured granules in HPPS dispersions under all heating conditions. The granule size distributions of all HPPS dispersions became similar after being heated at various temperatures and the average diameter of these granules converged to a constant value. There should be an upper limit of granule size for HPPS to swell because cross-linking and hydroxypropylation prevented starch granules to swell, which prevented the granule from rupture [3,4].

Granule size measurements for concentrated starch dispersions after being heated have never been reported because accurate value of granule size was not measured; if concentrated starch dispersions after being heated are suspended with excess water, granule is swollen up to a certain size. When concentrated starch dispersion after being heated was suspended with alcohol such as methanol or ethanol (<40 v/v %), granule was swollen extensively. On the contrary, the granule was contracted if alcohol concentration was higher. The present work was carried out using 50 v/v % ethanol to suspend a concentrated starch sample. The granule size distribution of HPPS dispersions with various concentrations unheated and heated at 60°C for 30 min is shown in Fig.2. Size distribution of unheated granule was not different between 2.5 w/w % and 5 w/w %. The average granule size of unheated dispersions was 28.6 μm irrespective of HPPS

concentration. The average granule size of heated starch dispersions at a concentration of 2.5 and 5 w/w % was 102.2 and 79.2 μm, respectively. Granule size in heated dispersions decreased with increasing concentration, and granule size distribution was shifted to a much smaller size with increasing starch concentration. Granules of HPPS after being heated were fully swollen to fill the space completely over a concentration of 3 w/w %. This indicated that starch granules were prevented to swell because of a lack of sufficient water for gelatinization [3].
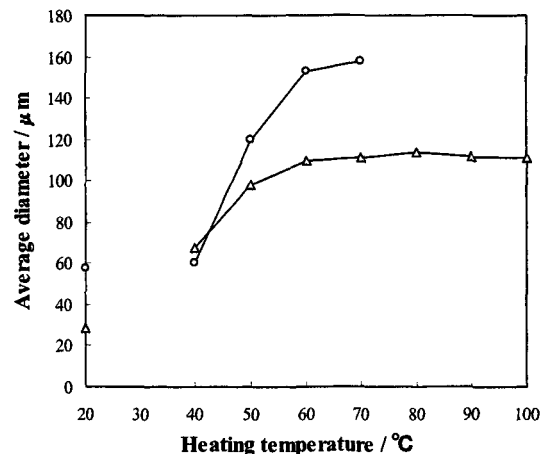

Fig. 1 Average diameter (μm) of NPS and HPPS granules after being heated at different temperatures for 30 min. ○, NPS (1%); △, HPPS (1%). Measurement temperature: 25°C.
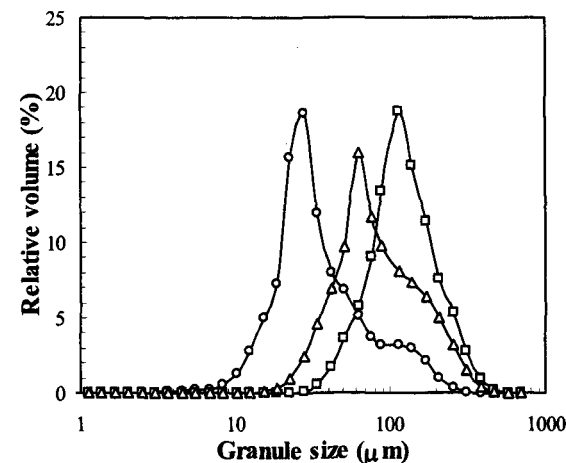

Fig. 2 Granule size distribution of HPPS dispersions after being heated at 60°C for 30min. ○, before heated; □, 2.5%; △, 5%. Measurement temperature: 25°C.

3.2. Steady shear and dynamic oscillatory experiments

It is well known that the viscosity of some suspensions in steady shear flow tends to a constant value at low shear rates (the Newtonian region). By increasing the shear rate, the viscosity approaches a power law dependence with $\eta \propto \dot{\gamma}^{n-1}$ (the power law region), where n is the flow behaviour index [9, 10].

Fig.3 shows the shear rate dependence of the viscosity for 1, 2, 2.5, 3, 4, and 5 w/w % dispersions of HPPS at 25 ℃. The magnitude of viscosity increased with increasing concentration. At high concentration, HPPS dispersions after being heated scarcely showed a Newtonian region and were power law fluids that exhibit yield stress at low shear rates. Above a shear rate of 10^{-2}/s, 3, 4, and 5 w/w % HPPS dispersions showed shear thinning behaviours clearly. The Herschel-Bulkley model (equation 1) was found to best describe the shear stress versus shear rate data with r^2 values greater than 0.96 (data not shown). The power law parameters and yield stress for HPPS dispersion heated at various concentrations are shown in Table I. Yield stress increased with increasing concentration of starch. The value of consistency index k also increased with increasing concentration, however, the value of flow behaviour index n decreased with increasing concentration. The consistency index and flow behaviour index were strongly influenced by starch concentration. HPPS dispersion after being heated has little entanglement of network. Okechukwu and Rao [11,12] reported that shear thinning behaviour for starch dispersions after being heated was changed by the heating temperature and time. At higher concentration, the slope of the flow curve was close to − 0.76 that of 'random coil' polysaccharide [10] which entangles each other because the granule-granule interaction increased.
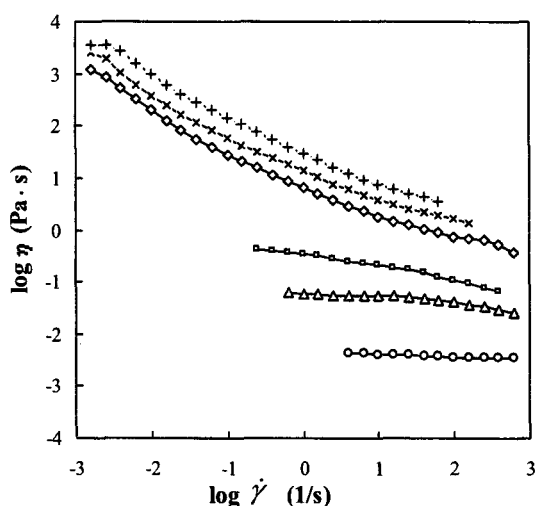

Fig. 3 The flow curves of 1% (◯), 2% (△), 2.5% (□), 3% (◇), 4% (×), 5% (+) of HPPS dispersions heated at 60℃ for 30 min. Measurement temperature: 25℃.

Table I Rheological parameters of Herschel-Bulkley model for HPPS dispersions heated at 60℃.

	1%	2%	2.5%	3%	4%	5%
k (Pa s^n)	0.01	0.07	0.38	10.3	20.1	38.4
n	0.87	0.87	0.72	0.39	0.36	0.32
r^2	1.00	0.99	0.98	0.99	0.99	0.96
σ_0 (Pa)	0.01	0.04	0.33	2.02	3.76	10.1

Fig.4 shows frequency dependence of G' and G'' for HPPS dispersions with various concentrations. At lower concentrations ($\leqq$2.5 w/w%), G' was smaller

than G'' at lower frequencies and the situation was reversed at higher frequencies (>44.7 rad/s for 1 w/w % dispersion; > 0.02 rad/s for 2.5 w/w % dispersion) and both moduli were strongly frequency dependent, whereas at higher concentrations (>2.5 w/w %), both moduli tended to be frequency independent. The viscoelasticity of starch dispersions was primarily governed by a combination of the volume fraction of the granule. The tan δ of HPPS dispersions at a concentration of above 3 w/w % showed the same magnitude and tendency (Fig.5), indicating that HPPS granules were fully swollen to fill the space completely above a certain concentration, and they could not be sufficiently swollen above this critical concentration [3].
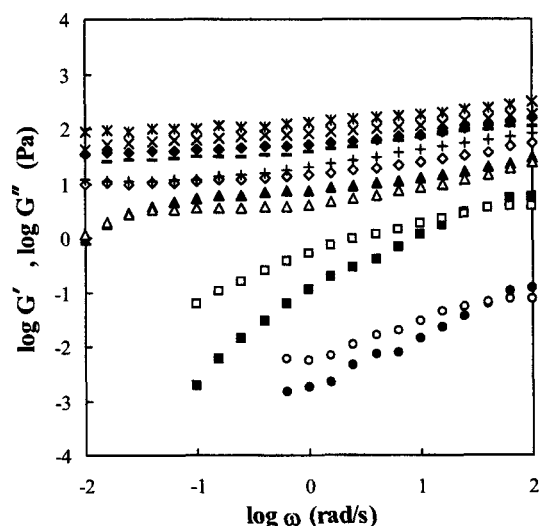

Fig. 4 Frequency dependence of G' and G'' for 1% (●, ◯), 2% (■,□), 2.5% (▲,△), 3% (◆,◇), 4% (×,+), 5% (∗,—) HPPS dispersions heated at 60℃ for 30 min. Measurement temperature: 25℃.
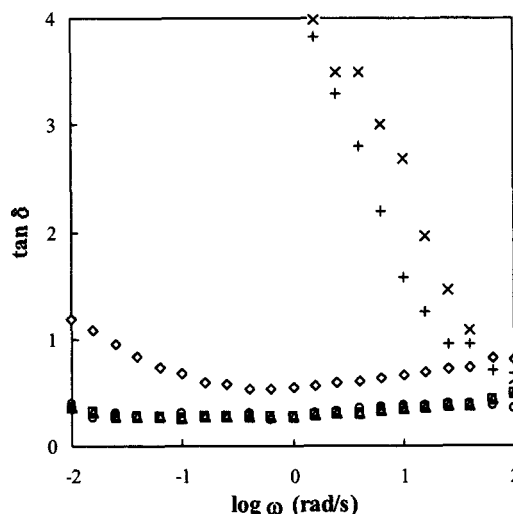

Fig. 5 Tan δ of 1% (×), 2% (+), 2.5% (◇), 3% (△), 4% (□), 5% (◯) HPPS dispersions heated at 60℃ for 30 min. Measurement temperature: 25℃

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The Cox-Merz rule [13] was not applicable to HPPS dispersion of both concentrations of 2.5 and 5 w/w %. Complex viscosity η^* plotted versus frequency ω was higher than viscosity η plotted versus shear rate $\dot{\gamma}$. A remarkable deviation from the Cox-Merz rule was observed: the complex viscosity was much higher than the viscosity, i.e., $\eta(\dot{\gamma}) < \eta^*(\omega)|_{\omega=\dot{\gamma}}$. In the case of HPPS dispersions, such a deviation might be related to the nature of the suspensions as well as the difference in deformation mode between the oscillatory flow and the shear flow because HPPS dispersion did not have an entanglement between granules. Cox-Merz rule should also be obeyed at high shear rate and high frequency, as has been found experimentally for synthetic random coil polymers [13,14]. At low shear rate and frequency, the curves $\eta(\dot{\gamma})\sim\dot{\gamma}$ and $\eta^*(\omega)\sim\omega$ can be superposed; on increasing the shear rate $\dot{\gamma}$ and/or frequency ω, the slope of $\eta^*(\omega)$ becomes lower than that of $\eta(\dot{\gamma})$. At low shear rate and low frequency, such correspondence is expected since, although different flow patterns are involved, the effects on the molecular re-arrangements cannot be considered significantly perturbative.
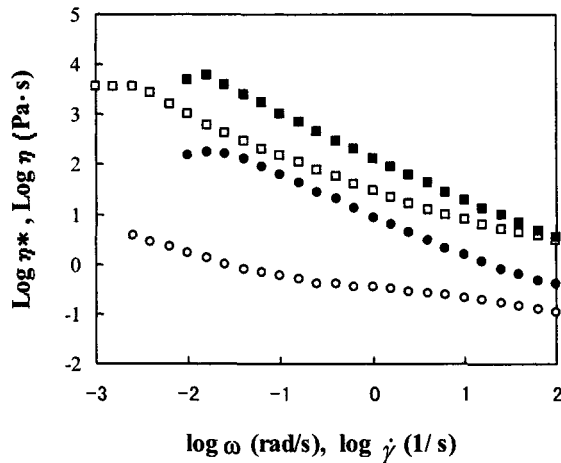

Fig. 6 Cox-Merz plots of complex viscosity η* (closed) and apparent viscosity η (open) for 2.5% (circles) and 5.0% (squares) HPPS dispersions heated 60°C for 30 min. Measurement temperature: 25°C

REFERENCES

[1] M. W. Rutenberg and D. Solarek, "Starch; Chemistry and Technology 2nd ed.", Ed. by R. L. Whistler, J. N. BeMiller and E. F. Paschall, Academic Press, New York (1984) pp. 311-388.

[2] A. Rapaille and J. Vanhemelrijck, "Thickening and Gelling Agents for Food. 2nd ed." Ed. by A. Imeson, Blackie Academic and Professional, London (1997) pp. 199-229.

[3] K. Morikawa and K. Nishinari, *Food Hydrocoll.*, **14**, 395-401 (2000).

[4] K. Morikawa and K. Nishinari, *Carbohydr. Polym.*, **43**, 241-247 (2000).

[5] H. R. Kim and A.-C. Eliasson, *Carbohydr. Polym.*, **22**, 31-35 (1993).

[6] H. R. Kim, A.-C. Eliasson and K. Larsson, *Carbohydr. Polym.*, **19**, 211-218 (1992)

[7] M. A. Rao, E. K. Chamberlain, J. Tattiyakul, W. H. Yang, "Hydrocolloids Part 1", Ed. by K. Nishinari, Elsevier Science B.V., Amsterdam (2000) pp. 291-300.

[8] P. M. S. Da Silva, J. C. Oliveira, M. A. Rao, J. Texture Stud., **28**, 123-138 (1997).

[9] W. W. Graessley, "Physical properties of polymers 2nd ed.", Ed. by J. E Mark et. al., American Chemical Society, Washington DC (1993) pp. 97-143.

[10] E. R. Morris, *Carbohydr. Polym.*, **13**, 85-96 (1990).

[11] P. E. Okechukwu, M. A. Rao, J. Texture Stud., **26**, 501-516 (1995).

[12] P. E. Okechukwu, M. A. Rao, J. Texture Stud., **27**, 159-173 (1996).

[13] W. P. Cox and E. H. Merz, J. Polym. Sci., **28**, 619-622 (1958).

[14] W. W. Graessley, Adv. Polym. Sci. **16**, 1-179 (1974)

4. CONCLUSION

Average granule size of HPPS dispersion at high concentration was smaller than that at low concentration. At higher concentrations, HPPS dispersion showed a non-Newtonian behaviour, and it tended to a Newtonian behaviour when concentration was lowered.