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Rheological and DSC studies of gelatinization of chemically modified starch heated at various temperatures

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Abstract

The effects of the degree of modification and heating temperature on the physico-chemical properties of hydroxypropylated phosphate cross-linked potato starch (HPS) on gelatinization were studied by heating differential scanning calorimetry (DSC), microscopic observation, granule size distribution and dynamic viscoelasticity measurements. The endothermic peak appeared at the temperature from 45 to 46°C for HPS, whereas it appeared at 60°C for native potato starch (NPS) in the heating DSC curves. Dynamic viscoelastic measurements were performed for 5% dispersions of NPS and HPS heated in various temperatures. The HPS granules heated in the temperature range from 50 to 100°C for 30 min did not rupture, and the diameter after heating was strongly dependent on the degree of modification. In contrast NPS granules ruptured gradually on heating above 70°C. The viscoelasticity of heated HPS dispersions were strongly dependent on the degree of modification. The storage shear modulus (G') and the loss shear modulus (G'') of HPS dispersions decreased and became more frequency dependent with an increasing degree of modification. The viscoelasticity of these dispersions heated in the temperature range from 50 to 100°C were almost independent of the heating temperature. On the contrary, the viscoelasticity of NPS dispersions decreased with increasing heating temperature.

Keywords: Chemically modified starch; Gelatinization; Rheological properties; Differential scanning calorimetry

1. Introduction

Starch is a major plant source used widely in the food, paper and textile industry. The texture of starch pastes prepared in food process sometimes changes the physical and/or chemical properties of starch pastes because they are strongly dependent on heat, pH, freeze–thaw and shear conditions.

Chemical modification of starch has been used to improve the gelatinization and cooking characteristics, and to prevent retrogradation and gelling tendencies. Recently, many types of chemical modification such as acid hydrolysis, oxidation, etherification, esterification and cross-linking have attracted much attention (Rapaille & Vanhemelrijck, 1997; Rutenberg & Solarek, 1984). Chemically modified starch is widely used as a thickening agent in foods such as sauces, custards, pie fillings and desserts where food manufacturers are looking for starches capable of imparting the required viscoelastic characteristics. In addition to these effects, the chemical modification leads to a considerable change in the gelatinization and swelling properties of the starch (Wurzburg, 1995; Yeh & Yeh, 1993).

Several authors have studied the gelatinization characteristics of chemically modified starch and unmodified starch (Bagley & Christianson, 1982; Christianson & Bagley, 1983; Deshpande, Sathe, Rangnekar & Salunkhe, 1982; El-Hinnawy, El-Saied, Fahmy, El-Shirbeeny & El-Sahy, 1982; Kim, Eliasson & Larsson, 1992a; Kim, Hermansson & Eriksson, 1992b; Wu & Seib, 1990). Differential scanning calorimetry (DSC) studies on the gelatinization characteristics of chemically modified starch have been also reported (Hansen, Hoseney & Faubion, 1991; Hari, Garg & Garg, 1989; Kim & Eliasson 1993; Wootton & Manatsathit, 1984; Yook, Pek & Park, 1993). Eliasson (1986) studied the viscoelastic behavior of some unmodified starch dispersions, which were gelatinized under several different heating conditions. Dail and Steffe (1990) characterized the rheological behavior of gelatinized cross-linked waxy maize starch dispersions and reported their shear-thickening behavior. Hoover, Hannouz and Sosulski (1988) and Kim et al. (1992a,b)) studied structural characteristics of hydroxypropyl starches. They concluded that the endothermic peaks

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of chemically modified starches were shifted to lower temperatures and the enthalpy decreased as the degree of molar substitution increased. Okechukwu and Rao (1996) showed that granule size distribution and mean diameter of cowpea starch dispersions gelatinized at 80°C affected the flow behavior.

Systematic studies on the rheology of chemically modified starch have not been performed sufficiently to develop further applications. The aim of the present work is to examine the effects of degree of modification on the physicochemical properties, and gelatinization characteristics of hydroxypropylated potato di-starch phosphates. Hydroxypropylated potato di-starch phosphates were chosen because they have good heat stability in the sense that these granules are not ruptured at water boiling temperatures.

2. Materials and methods

2.1. Materials

Native potato starch (NPS) and hydroxypropylated phosphate cross-linked potato starches (HPS) were provided by Lyckeby Stärkelsen (Kristianstad, Sweden), and further purified by washing three times with 80% (v/v) methanol. The degree of hydroxypropyl substitution and phosphate cross-linking in NPS and HPS are shown in Table 1.

2.2. DSC analysis

DSC measurements were performed with a Micro DSC III (Setaram Co., Caluire, France). Each 40 mg (d.b.) of starch and 760 mg of distilled water (5% (w/w)) were directly weighed into a DSC cell and dispersed by a needle. After sealing, a cell was left for 1 h to equilibrate. A cell containing an equal amount of distilled water was used as a reference. The temperature was raised from 20 to 90°C at 0.2°C/min.

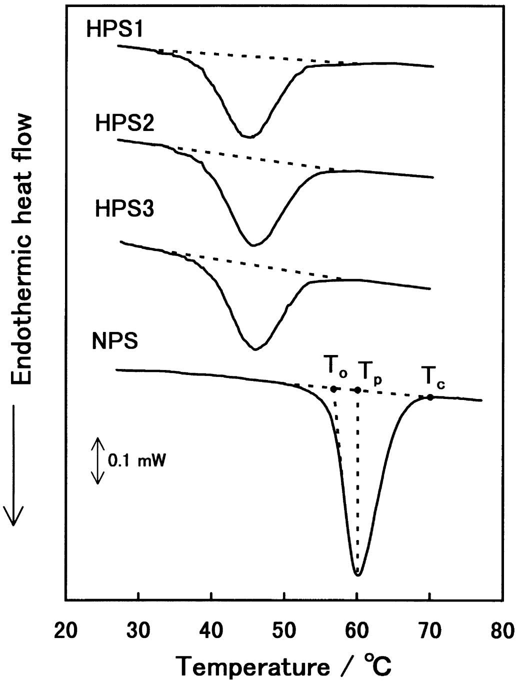

Fig. 1. The heating DSC curves of NPS and HPS. Heating rate: 0.2°C/min.

2.3. Microscopic observation and size distribution of starch granules

One percent (w/w) dispersions of NPS and HPS1, 2 and 3 were prepared in distilled water using a motorized stirrer. The dispersions were stirred at 200 rpm for 30 min at 20°C, and heated in an oil bath to 30, 40, 50, 60, 70, 80, 90 and 100°C for about 10 min and then kept at each temperatures for 30 min. The hot samples of NPS and HPS were suspended with distilled water and observed immediately using a light microscope TMD-2S (Nikon Co., Tokyo, Japan), respectively.

The size distribution analysis was also carried out. Granule size distributions of the unheated and heated samples of NPS and all HPS were determined with a computer controlled laser diffraction particle size analyzer SALD-2000J (Shimadzu Co., Kyoto, Japan).

2.4. Viscoelasticity measurement

Three percent (w/w) dispersions of NPS and HPS1, 2 and 3 were prepared in distilled water using a motorized stirrer. The dispersions were stirred at 200 rpm for 30 min at 20°C, and heated in an oil bath to 95°C for about 10 min and then kept at 95°C for 30 min. The distilled water was added to the hot dispersion to adjust the concentration. The dispersions were kept at 20°C for 24 h, and the storage shear modulus (G') and the loss shear modulus (G'') of NPS and HPS dispersions were measured as a function of frequency using a cone and plate geometry (50 mm diameter and cone angle 0.4 rad) on a dynamic stress rheometer DSR (Rheometrics Co., NJ, USA).

Five percent dispersions of NS and HPS were prepared by the method mentioned above, and heated at 50, 60, 70, 80, 90 and 100°C for 30 min. Dynamic viscoelastic measurements were performed using a DSR and steady shear viscosity measurements were performed using a fluid spectrometer RFSII (Rheometrics Co., NJ, USA). The hot sample was poured directly onto the plate of the instrument, which had been kept at 20°C. Frequency dependence of G' and G'' for these starch dispersions was measured at 20°C by a DSR after heated the dispersions at each temperature for 30 min. Apparent viscosity was measured at shear rates ranging from 0.1 to 100 s^{-1} by RFSII at 20°C.

3. Results and discussion

3.1. DSC analysis

Heating DSC curves for 5% (w/w) dispersions of NPS

Table 1
The ratio(%) of hydroxypropyl groups and phosphate cross-linkages

	Hydroxypropyl groups[a]		Phosphate cross-linkages[b]	
	(C_3H_7O) (%)	DS[c]	(PO_4H) (%)	PCL[d]
NPS	0.00	0.000	0.00	0.000
HPS1	0.61	0.018	0.96	0.016
HPS2	1.28	0.047	0.88	0.015
HPS3	2.51	0.097	0.86	0.015

[a] Measured by modified Zeisel method.

[b] Measured by spectrophotometric method using molybdenum blue.

[c] Degree of substitution.

[d] Phosphate cross-linkages = number of cross linkages/number of glucose residues.

and HPS are shown in Fig. 1. Onset temperature (T_o), peak temperature (T_p) and conclusion temperature (T_c) for 5% (w/w) dispersions of NPS and HPS are shown in Table 2. T_p of HPS1, 2 and 3 ranged from 45 to 46°C, and were about 15°C lower than that of NPS, and the enthalpy (ΔH) did not differ between the three HPS samples. Wootton and Manatsathit (1984) reported that T_p decreased with increasing degree of hydroxypropylation, in contrast to our work probably because in our case, phosphate cross-linking content was almost equal. Quan, Kweon and Sosulski (1997) reported that the degree of phosphate cross-linking affected the ΔH in heating DSC curves showing that the effects of phosphate

Table 2
Thermal transition characteristics of native and chemically modified starches (T_o, T_p and T_c are the onset, peak and conclusion temperatures, respectively)

	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
NPS	56.7	60.1	70.1	14.0
HPS1	39.1	45.2	66.8	9.9
HPS2	39.2	45.9	65.6	9.8
HPS3	40.3	45.9	68.0	10.0

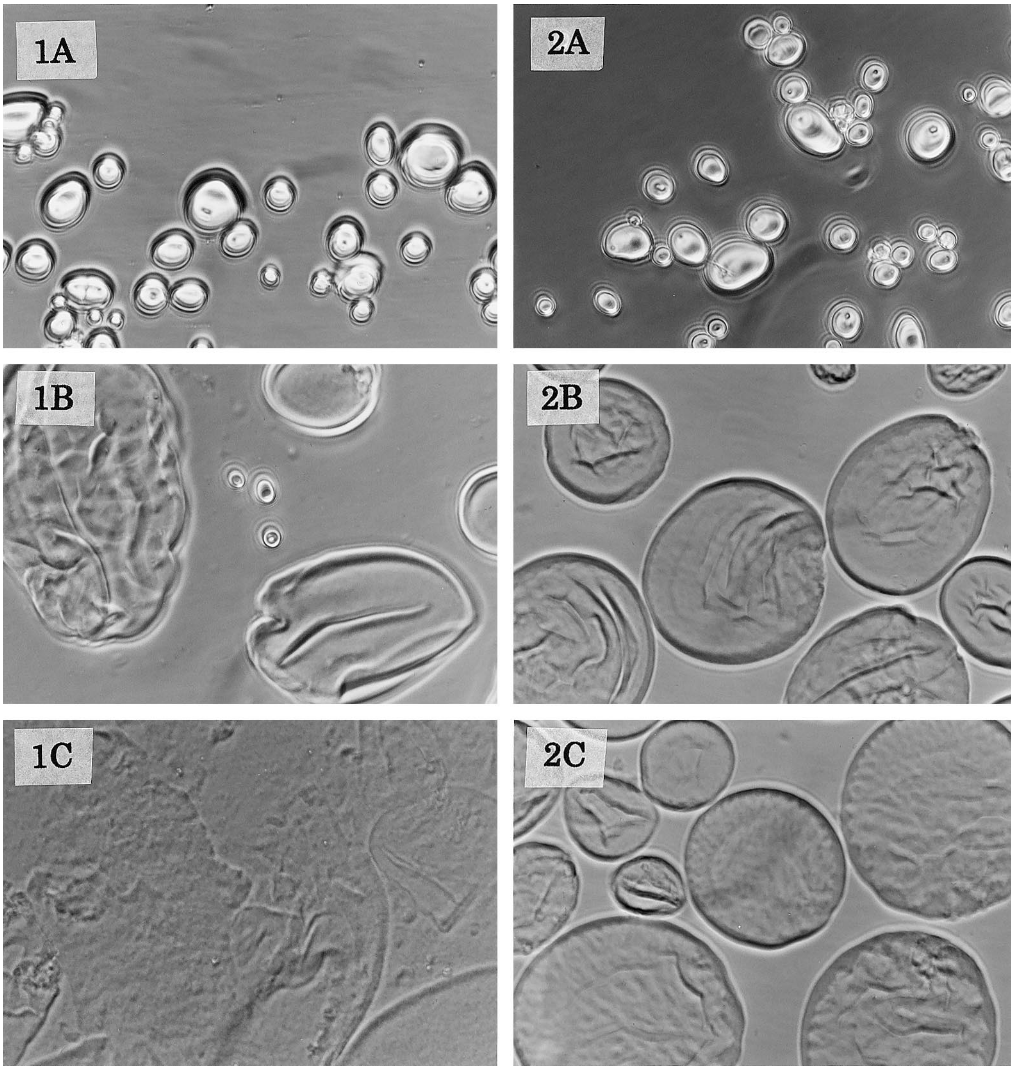

Fig. 2. Micrographs of NPS and HPS1 granules taken before heating and just after heating at 70 and 100°C for 30 min. (× 400). 1A, NPS 20°C; 1B, NPS 70°C; 1C,NPS 100°C; 2A, HPS1 20°C; 2B, HPS1 70°C; 2C, HPS1 100°C.

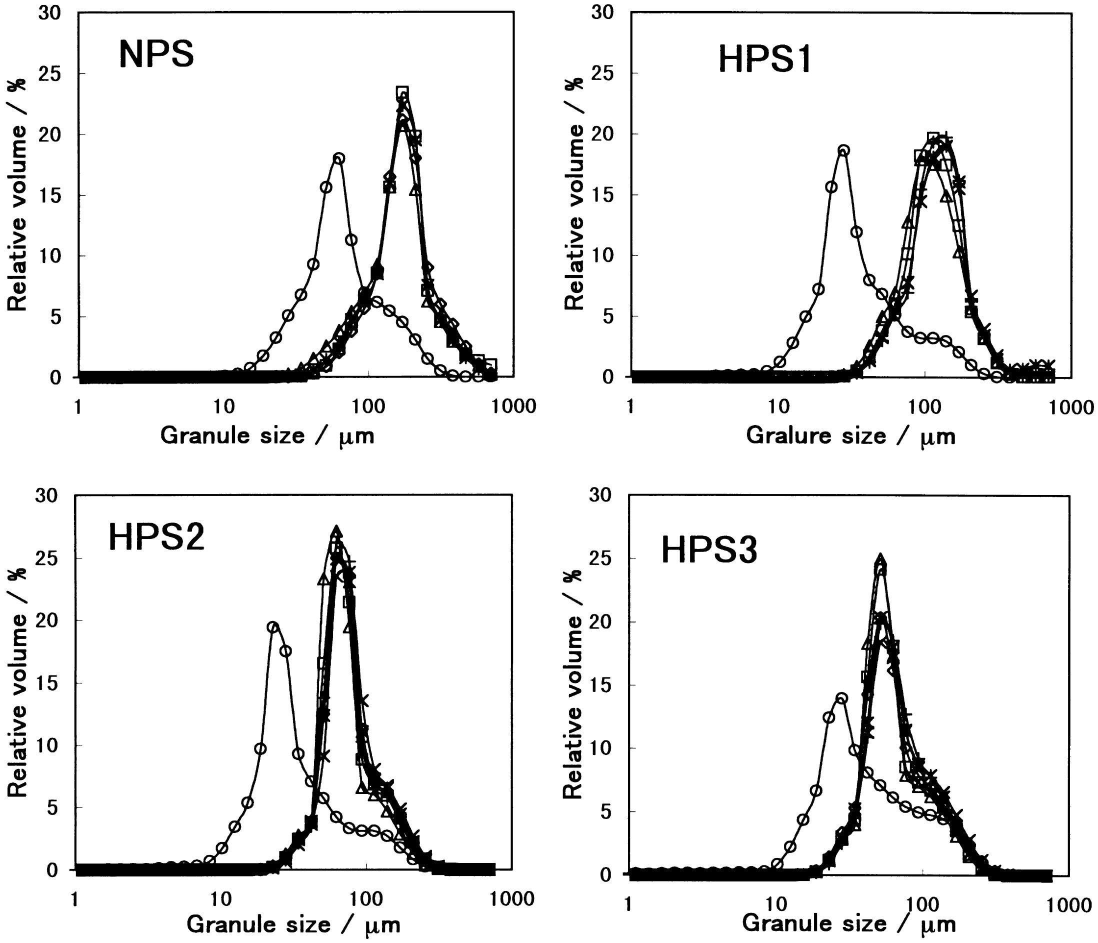

Fig. 3. Granule size distribution of NPS and HPS heated at various temperatures for 30 min. Refractive index = $1.60-0.1i$. Temperature: ○, before heating △, 50°C; □, 60°C; ◇, 70°C; *, 80°C; ×, 90°C; +, 100°C.

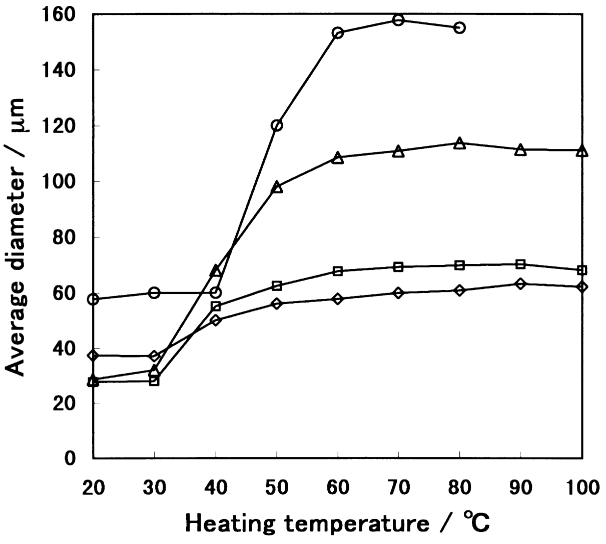

Fig. 4. Average diameter (μm) of NPS and HPS granules after heating at various temperatures for 30 min. ○, NPS; △, HPS1; □, HPS2; ◇, HPS3.

cross-linking are larger than that of hydroxypropylation. As the Δ*H* of HPS is smaller than that of NPS, it is possible that the modification (especially cross-linking) prevents gelatinization. Some loss of structural order during the process of chemical modification may also occur. It is not possible to conclude which possibility is more important at present. This should be explored in the future.

3.2. Microscopic observation and size distribution of starch granules

Fig. 2 shows photomicrographs obtained for dispersions of starch granules (NPS and HPS1) at 20°C and the dispersions heated at 70 and 100°C, respectively. The photographs of HPS2 and 3 are not shown because these are very similar to HPS1 except granule size. All starch granules at 20°C revealed lamellae like a shell (Sathe & Salunkhe, 1981), and showed a similar appearance (photographs not shown). NPS granules began to rupture when heated at 70°C. At 100°C, they ruptured completely and the remains of granules existed. On the contrary, there were scarcely any

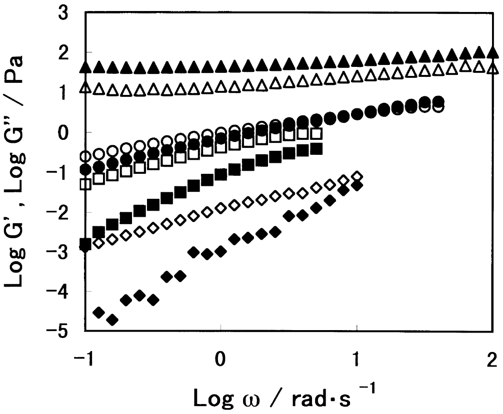

Fig. 5. Frequency dependence of G' (closed) and G'' (open) for 3% dispersions of NPS (○) HPS1 (△), HPS2 (□) and HPS3 (◇) stored at 5°C for 24 h after heating at 95°C for 30 min.

ruptured granules in HPS dispersions under all heating conditions.

The granule size distribution of all dispersions showed a small shoulder at large granule sizes before heating (Fig. 3). Granule size of NPS increased with heating temperature up to 50°C then leveled off at 70°C. Further increase in heating temperature (>80°C) caused the rupture of granules. The average diameter of NPS granules which were not ruptured after heating at 80°C was smaller than that heated at 70°C because the large granules were ruptured preferentially, and when heated at above 90°C, the granule size distribution could not be measured because all granules were ruptured. This indicates that NPS granules could swell up to a certain volume, and when the granule size reached a limit value, the granule would rupture. The heating DSC curves of NPS dispersion began to deviate from the baseline at 50°C (Fig. 1), then NPS granules began to swell at this temperature. When 1% (w/w) dispersions of NPS were stirred at 200 rpm for 30 min at 50°C, granule size of NPS swelled up to twice the size of that obtained before heating (Fig. 4).

The granule size distributions of all HPS dispersions became similar after heating at various temperatures, and the average diameter of these granules converged to a constant value (Fig. 4). Okechukwu and Rao (1996) showed that only unheated dispersions of native cowpea starch had a shoulder, however, in the present study, all heated dispersions of HPS2 and 3 also, had a small shoulder at large granule sizes. This indicates that these granules did not swell homogeneously probably because at the higher degrees of modification, substitution was not uniform. The granule diameter after heating above 50°C showed a smaller value with increasing degree of modification.

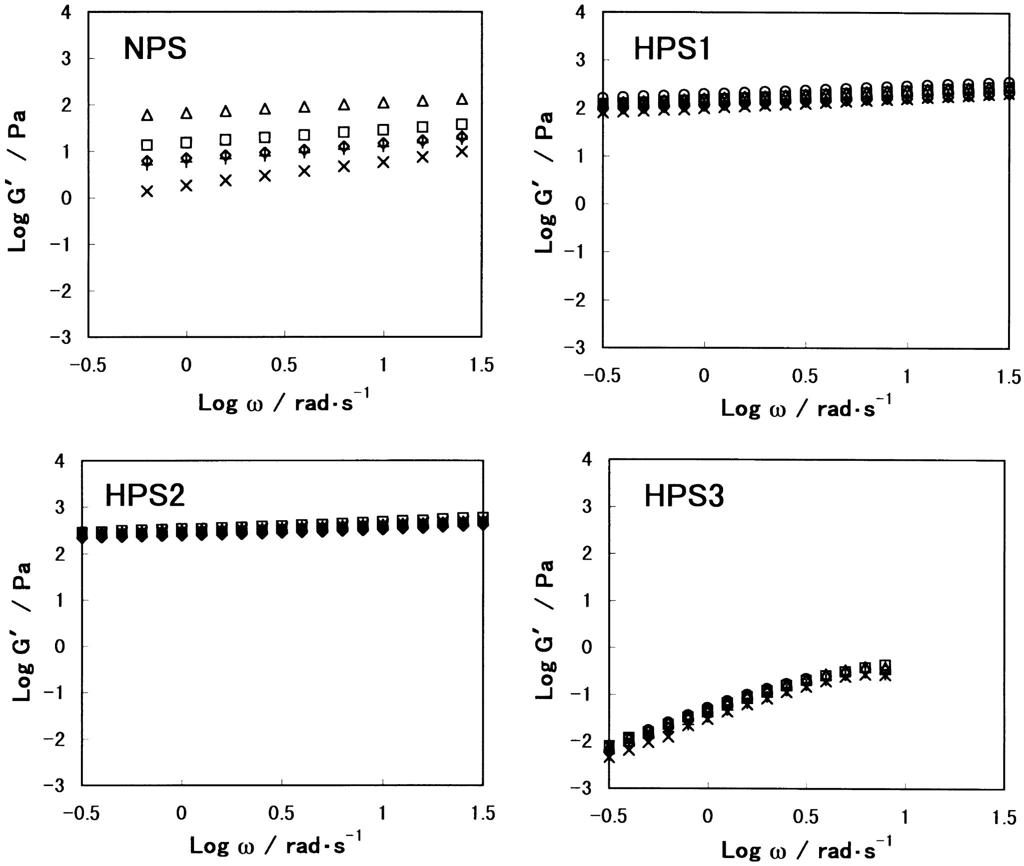

Fig. 6. Frequency dependence of G' for 5% dispersions of NPS and HPS heated at various temperatures for 30 min. Temperature: ○, 50°C; △, 60°C; □, 70°C; ◇, 80°C; +, 90°C; ×, 100°C.

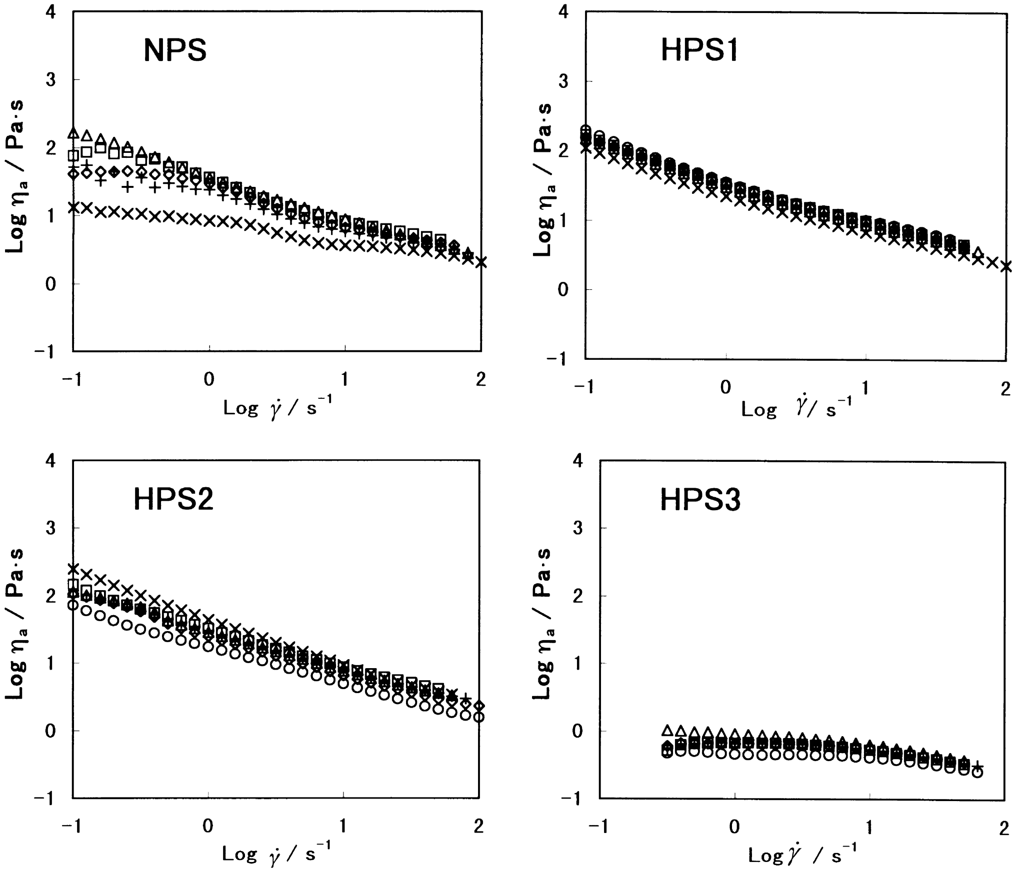

Fig. 7. Apparent viscosities for 5% NPS and HPS dispersions heated at various temperatures for 30 min. Temperature: ○, 50°C; △, 60°C; □, 70°C; ◇, 80°C; +, 90°C; ×, 100°C.

3.3. Dynamic viscoelasticity

Frequency dependence of G' and G'' for NPS and HPS1, 2 and 3 dispersions heated at 95°C for 30 min and then stored at 5°C for 24 h is shown in Fig. 5. Values of G' and G'' of dispersions decreased and became more frequency dependent with increasing degree of modification. The fact that values of G' and G'' for HPS1 dispersions are larger and less frequency dependent than those for NPS is due to the difference in the degree of disintegration of starch granules in HPS1 and NPS observed by light microscopy; starch granules were completely ruptured in NPS after heated at 95°C, whereas all granules of HPS1 remained nearly intact even after such a severe heat-treatment. Eliasson, Finstad and Ljunger (1988) reported that G' of cross-linked waxy maize starch dispersion was larger than that of native one, and this starch gave a more solid-like behavior. Kim et al. (1992a,b) reported that G' and G'' of potato starch dispersions decreased slightly with increasing molar substitution of the hydroxypropyl group. Cross-linking of starch reduces the swelling and increases the rigidity, whereas hydroxypropylation increases hydrophilicity. The ordered structure of starch is disrupted when native starch is modified by cross-linking and hydroxypropylation. Because of the complex interactions between these three factors, the reason why hydroxypropyl substituents should restrict swelling and that dispersions of other modified starch HPS2 and 3 became more liquid-like is not clear at present, and should be explored in the near future.

Frequency dependence of $G'$for NPS and HPS1, 2 and 3 dispersions heated at various temperatures for 30 min was examined (Fig. 6). The measurements of NPS dispersions were carried out only for a short time (74 s) because G' of the dispersion of NPS increases rapidly in comparison with that of HPS (Morikawa & Nishinari, 2000). For HPS3 dispersions, the apparatus could not control the constant stress at above 10 rad/s because 5% dispersion of NPS showed a liquid-like rheological behavior. Values of G' of NPS dispersions were larger at lower heating temperatures and became smaller when heated at 100°C because almost all starch granules were ruptured. On the contrary, all HPS samples were completely gelatinized at 50°C for 30 min, and showed little change on heating at higher temperatures above 50°C. This indicates that these HPS granule was completely gelatinized at 50°C for 30 min.

Fig. 7 shows shear rate dependence of the apparent viscosity for 5% NPS and HPS dispersions heated at various temperatures for 30 min. The flow curves of NPS and HPS dispersions showed shear-thinning behavior at every temperature. HPS dispersions heated at all temperatures showed the same shear thinning behavior, respectively, but apparent viscosity of NPS dispersions became smaller at higher heating temperatures, and tended to show less shear thinning behavior. The network structure for HPS3 dispersions was the weakest in all HPS dispersions after heated because HPS3 dispersions showed a flow behavior closest to a Newtonian fluid and their storage and loss shear moduli were most frequency dependent as shown in Fig. 6.

4. Conclusion

The results of the present study indicate that the HPS granules after heating at high temperatures were not ruptured, and the average diameter of HPS granules and the elastic moduli of HPS dispersions were strongly dependent on the degree of modification. The viscoelasticities and shear thinning behavior for the HPS dispersions after heating at temperatures ranging from 50 to 100°C were almost independent of heating temperature.

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