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Influence of cross-linked potato starch treated with $POCl_3$ on DSC, rheological properties and granule size

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Abstract

Differential scanning calorimetry (DSC), rheological measurements and granule size analyses were performed to characterize the influence of phosphorylation substitution levels on the properties of cross-linked potato starch. Phosphorus oxychloride ($POCl_3$) was used to produce the cross-linked potato starch. The levels of the reagent used for the reaction ranged between 40 and 5000 ppm (dwb). Storage (G') and loss (G'') moduli were measured for a 5% (w/w) gelatinized starch dispersion stored at 20 °C for 24 h after heating at 85 °C for 30 min. The samples from 80 to 500 ppm were recognized as 'strong gel'systems, whereas native potato starch showed 'weak gel'behavior. Steady shear and dynamic viscoelastic properties of gelatinized starch dispersion were compared. Furthermore, granule mean diameter was measured by laser scattering for a 1% (w/w) dispersion heated at 85 °C for 30 min. The granules in the 100 ppm sample swelled to a maximum of about 2.6 times the native starch granule mean diameter.

Keywords: Cross-linked potato starch; Differential scanning calorimetry; Steady shear and dynamic viscoelastic properties; Granule mean diameter

1. Introduction

Native starches generally contain small amounts ($<0.1\%$) of phosphorus. Although present in small quantities, phosphorus can affect the properties and behavior of the starch, and has gained a great deal of attention. In root and tuber starches, phosphorus is covalently linked to the starch in the form of phosphorus esters (Hizukuri, Tabata, & Nikuni, 1970), whereas in cereal starches it occurs mostly as contaminating phospholipids (Meredith, Dengate, & Morrison, 1978; Schoch, 1942). Inorganic phosphate may also be present.

Craig, Maningat, Seib, and Hoseney (1989) reported that the phosphorus content in native potato starch (NPS) is 0.052% (w/w), or one phosphate monoester per 370 glucosidyl residues, mainly in the form of phosphate monoesters. The presence of phosphate monoesters linked directly to amylopectin molecules is one of the unique features of potato starch (Muhrbeck, Svensson, & Eliasson, 1991). Phosphate monoester increases paste clarity and viscosity, whereas phospholipids make starch paste opaque and decrease viscosity (Kasemsuman & Jane, 1994).

Starch phosphates, which are prepared by chemical methods, have been reported to give clear pastes of high consistency, with good freeze–thaw stability and emulsifying properties. The preparation, properties and uses of phosphorylated starches were reviewed by Solarek (1986). Starch phosphates may be grouped into two classes: monostarch phosphates and distarch phosphates (cross-linked starches). In general, monoesters are introduced at a higher level of substitution than diesters on starch because even a very few cross-links can drastically alter the paste and gel properties of starch. Formation of cross-linked starches is generally considered the most important reaction used in the preparation of modified food starches and to overcome the disadvantages which limit or prevent the utilization of native starches in food applications.

Currently, there is little information on the rheology of chemically modified potato starches that can be used to develop further applications. Hence, the objective of this study is to examine the influence of different degrees of

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phosphorylation on the physicochemical, thermal properties and rheological characteristics of cross-linked potato starches (CPS).

2. Materials and methods

2.1. Materials

Commercial NPS was obtained from Minami Tokachi Noukouren Starch Factory (Hokkaido, Japan). The starch was washed with distilled water, and then dried at 35–40 °C.

2.2. Preparation of cross-linked potato starch and phosphorus content

Phosphorus oxychloride ($POCl_3$) was used to produce CPS in which a phosphate diester bonds covalently with NPS molecules. The products also contain some monophosphate groups (Solarek, 1986).

Cross-linking of starch was done with $POCl_3$ in alkali containing sodium hydroxide (Na_2SO_4, 2% based on dry weight of starch) as described by Zheng, Han, and Bhatty (1999). The concentration of the dry starch in a slurry was 33.3%. Four independent variables were selected: pH of the reaction mixture (pH 10.5), amount of $POCl_3$ (40–5000 ppm based on dry weight of starch), reaction temperature (40 °C), and reaction time (1 h). The levels of the reagent used for the reaction were 40 ppm (0.004%), 60 ppm (0.006%), 80 ppm (0.008%), 100 ppm (0.01%), 250 ppm (0.025%), 500 ppm (0.05%), 1000 ppm (0.1%), 2000 ppm (0.2%) and 5000 ppm (0.5%), based on dry weight of starch.

For cross-linking, starch (250 g, db) was suspended in 224 ml of distilled water and then 224 ml of 0.5 M NaCl solution was added to the slurry. After adjusting to pH 10.5 with 1 M NaOH, 10–1250 μg of $POCl_3$ was added to the slurry using a microsyringe. The reaction mixture was stirred at 40 °C for 1 h, then adjusted to pH 6.8–7.0 with 1N HCl solution. Modified starch was recovered by filtering it on a fritted glass funnel with suction and washed with distilled water. It was then dried at 35–40 °C. A control sample was treated in the same way, but the substituting reagent was omitted.

The phosphorus content in NPS and CPS was measured using the vanado-molybdate method (Yamamoto, 1998). Reported values are averages of at least three determinations of each sample.

2.3. DSC measurement

Differential scanning calorimetry (DSC) measurements were performed with a Micro DSCII (Setaram Co., Caluire, France). Each 50 mg (d.b.) of starch and 950 mg of distilled water (5% (w/w)) was directly weighed into a DSC pan. After sealing, a pan was left for 24 h to equilibrate before measurement. A pan containing an equal amount of distilled water was used as a reference. The temperature was kept at 30 °C for 20 min and then raised from 30 to 100 °C at a heating rate of 1.2 °C/min.

The enthalpy of gelatinization (ΔH) of each sample was obtained from the peak area of the endotherm following the DSC standard procedure. In addition, the onset temperature (T_o), peak temperature (T_p) and conclusion temperature (T_c) were determined. The gelatinization temperature range (R) was calculated as $2(T_p - T_o)$, as described by Krueger, Knutson, Inglett, and Walker (1987). Data were calculated from at least three determinations of each sample.

2.4. Microscopic observation and mean diameter of starch granules

One percent (w/w) dispersions were prepared in distilled water using a motorized stirrer. The dispersions were stirred for 30 min at 20 °C, and heated in a water bath to 85 °C and then kept at 85 °C for 30 min. The gelatinized dispersions, heated to 85 °C and then kept at 85 °C for 30 min, were observed immediately using a digital camera system HC-300Z (Fujifilm Co., Tokyo, Japan).

A laser scattering particle size distribution analyser LA-300 (Horiba Co., Kyoto, Japan) was used to measure the mean diameter of the gelatinized dispersions, heated to 85 °C and then kept at 85 °C for 30 min. A relative refractive index of 1.20 (= refractive index of starch/refractive index of water) was used. The values were averages of at least two determinations of each sample.

2.5. Viscoelasticity measurement

Five percent (w/w) dispersions of NPS and CPS were prepared in distilled water using a motorized stirrer. The dispersions in Erlenmeyer flasks were stirred mildly for 30 min at 20 °C. Ungelatinized dispersions in Erlenmeyer flasks were heated in a water bath to 85 °C and then kept at 85 °C for 30 min under mild agitation. The gelatinized dispersions were held at 20 °C for 24 h before transferring to the rheometer plate.

Frequency sweep and shear flow tests were then performed at 20 °C with a Rheometrics Dynamic Analyser (RDA) II (Rheometrics Inc., Piscataway, NJ, USA) and a cone and plate geometry (50 mm diameter, cone angle 0.04 rad and 65 μm gap). In each test, a fresh sample was used. After loading it was allowed to rest for 900 s to restore structures that might have been disturbed (Rao, Okechukwu, Da Silva, & Oliveira, 1997). Silicon oil was applied to the edges of the sample to prevent any loss of moisture during the experiment. Each curve presented is typical of at least two runs.

2.5.1. Frequency sweep test

Samples were subjected to a frequency sweep test at a strain of 3.0%. At this strain, a linear viscoelastic behavior was observed for all samples. For strain values within the linear range of deformation, the material functions are independent of strain. The storage shear modulus (G'), loss shear modulus (G'') and loss tangent ($\tan\delta$) of NPS and CPS gelatinized dispersions were measured at an oscillation frequency (ω) ranging from 0.0628 to 100 rad s^{-1} in a logarithmic manner. Tan δ is given by

$$\tan\delta = G''/G' \tag{1}$$

where $\delta(\omega)$ is the phase angle between stress and strain.

At a given oscillation frequency, the values of G' and G'' can be combined in the following formula to yield the complex viscosity (η^*) :

$$\eta^* = ((G')^2 + (G'')^2)^{1/2}/\omega \tag{2}$$

2.5.2. Shear flow test

Upon completion of the frequency sweep test, shear flow tests (steady shear tests) were performed over the shear rate range (0.0628–300 s^{-1}) at 20 °C. The steady shear viscosity (η) of NPS and CPS gelatinized dispersions was measured in a logarithmic manner as a function of shear rate ($\dot{\gamma}$). η is given by

$$\eta = \sigma/\dot{\gamma} \tag{3}$$

where σ is the shear stress.

Measurements of normal stress differences during the shear flow test were performed. The first normal stress difference (N_1) and the first normal stress difference coefficient (Ψ_1) were calculated from the vertical thrust force using measurements of Total Thrust (Ferry, 1980a).

$$\Psi_1(\dot{\gamma}) = N_1(\dot{\gamma})/\dot{\gamma}^2, \qquad N_1(\dot{\gamma}) = 2F/\pi R^2 \tag{4}$$

where F is the vertical thrust force tending to separate the two surfaces, and R is the radius of the plate.

An empirical rule (Lapasin & Pricl, 1999; Ross-Murphy, 1994a) was determined for the correlation of Ψ_1 to a corrected storage modulus function, proportional to G'/ω^2, as well as the Cox–Merz rule (Cox & Merz, 1958). Recently, an empirical rule has been suggested for the correlation of Ψ_1 to $2G'/\omega^2$. The rule is given by the following equation (Coleman & Markovitz, 1964; Menard, 1999):

$$2G'/\omega^2|_{\omega\to 0} = N_1/\dot{\gamma}^2|_{\dot{\gamma}\to 0} = \Psi_1|_{\dot{\gamma}\to 0} \tag{5}$$

This correspondence demonstrates that a strong association exists between the normal stress difference and the elastic properties of a fluid.

3. Results and discussion

3.1. Influence of POCl$_3$ concentrations on mean diameter of starch granules and calculated swelling power

According to Atwell, Hood, Lineback, Varriano-Marston, and Zobel (1988), gelatinization refers to the collapse of molecular orders within the starch granule manifested in irreversible changes in properties such as granular swelling, native crystalline melting, loss of birefringence, and starch solubilization.

In the present study the calculated swelling power, based on the measurements of granular mean diameter, was defined as $(D_{85\,°\mathrm{C}})^3/(D_{20\,°\mathrm{C}})^3$, where $D_{85\,°\mathrm{C}}$ is the mean diameter after heating at 85 °C for 30 min, and $D_{20\,°\mathrm{C}}$ is the mean diameter after heating at 20 °C for 30 min. The mean diameter of starch granules (D_p) and the calculated swelling power $(D_{85\,°\mathrm{C}})^3/(D_{20\,°\mathrm{C}})^3$ versus POCl$_3$ concentrations profiles are shown in Fig. 1. Ziegler, Thompson, and Casasnovas (1993) developed the maximum swelling power to differentiate the swelling behavior of common corn starch, waxy maize starch, and cross-linked waxy maize starch. The maximum swelling power provides a numerical value that describes the ratio of the maximum volume to the initial volume, calculated as the ratio of the maximum diameter cubed to the initial diameter cubed: e.g. a higher swelling has higher values of the maximum swelling power than does a lower swelling.

The mean diameters and standard deviations of granules heated to 85 °C for 30 min and the corresponding percent increase with respect to NPS are given in Table 1. The mean diameter (D_o) and the standard deviation (σ_o) for NPS were 81.8 and 54.1 μm, respectively. Among the studied starches, after the dispersions were heated at 85 °C for 30 min, the corresponding diameters (D) of the granules ranged from 73.4 μm for the 5000 ppm sample to 215.5 μm for the 100 ppm sample, and the corresponding standard deviations (σ) from 42.3 μm for the 5000 ppm sample to 98.4 μm for the 60 ppm sample. Granules in the 100 ppm sample swelled to a maximum of about 2.6 times the native starch granule mean diameter. The coefficient of variation (CV) value for NPS was the maximum value (66.1%) among the starches studied, while CV for the 100 ppm sample was the minimum value (44.8%).

Increasing the degree of substitution gradually until 100 ppm increased both the calculated swelling power and D_p of CPS. This is due to the inclusion of phosphate cross-links inside the starch granules. However, above 100 ppm both values decreased. This implies that there were stronger association forces in the granules of CPS above 100 ppm than those lower than 100 ppm POCl$_3$. The decrease in these two parameters (the calculated swelling power and D_p) is due to the presence of more cross-links.

In addition, NPS began to rupture at 70 °C. When heated at 85 °C most granules were ruptured according to microscopic observations (data not shown). On the contrary,

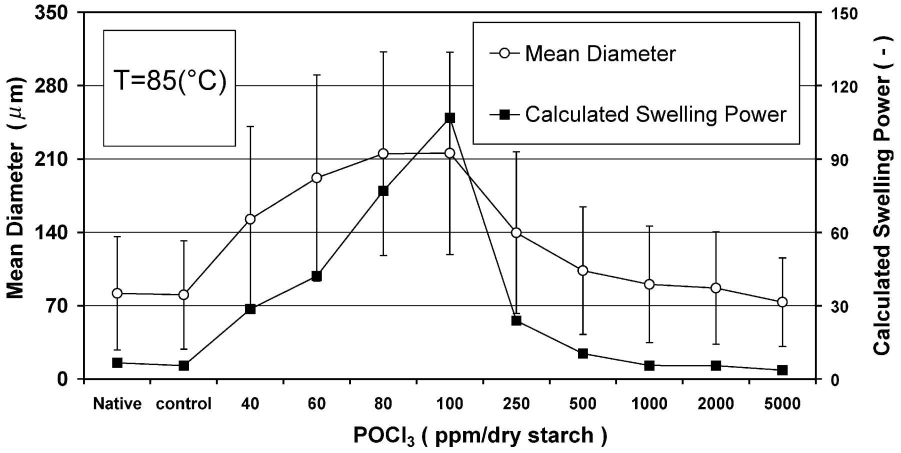

Fig. 1. Mean diameter of starch granules (D_p) (○) and calculated swelling power ($(D_{85\ ^\circ C})^3/(D_{20\ ^\circ C})^3$) (■) dependent on the levels of phosphorus oxychloride ($POCl_3$) used for the cross-linking reaction for all samples. The samples were heated to 85 °C and then kept at 85 °C for 30 min: vertical bars indicate range of standard deviations at least in duplicate in the range of D_p profiles.

there were scarcely any ruptured granules in CPS under all examined $POCl_3$ concentration conditions.

3.2. DSC analysis

The phosphorus content and ΔH versus $POCl_3$ concentration profiles for all samples in Fig. 2 indicate a strong correlation between the phosphorus content and ΔH. In addition, the T_o and T_p versus $POCl_3$ concentration profiles and thermal properties for NPS and CPS are shown in Fig. 3 and Table 2. The T_o, T_p and ΔH of the 100 ppm sample (61.11 °C, 65.45 °C and 15.38 J/g, respectively) were significantly lower than for NPS (62.76 °C, 66.77 °C and 16.70 J/g, respectively). Additionally, Table 2 indicates that the 100 ppm sample displayed a lower gelatinization temperature and lower enthalpy to melt the starches than other treated samples. As the gelatinization temperatures such as T_o and T_p reflect the degree of ordered molecular structure in the starch granules (Gebre-Mariam & Tübinger, 1996), it may be assumed that the 100 ppm sample was more fragile than any of the other samples. These results agree with previous work on NPS (Muhrbeck & Eliasson, 1991). As suggested earlier, the decrease in ΔH values is due to the inclusion of phosphate cross-links inside the starch granules. In contrast, D_p and the calculated swelling power for the 100 ppm sample were the highest for all the samples examined, as shown in Fig. 1.

However, further increasing the degree of phosphate cross-links caused a gradual increase in T_o, T_p and ΔH of CPS samples compared to those in the 100 ppm sample. Thus, highly associated starch granules with a strongly bonded micellar structure might display higher T_o, T_p and ΔH.

The T_o and T_p of starches is reportedly a measure of the perfection of starch crystallites, while ΔH is a measure of the degree of crystallinity (Tester & Morrison, 1990). ΔH (measured by DSC) results more from the loss of molecular (amylopectin double-helical) order than from the loss of crystallinity (measured by X-ray crystallography) (Cooke & Gidley, 1992). Similarly, DSC monitors both crystallite melting and conformational disordering of helices for amylose–lipid complexes. The latter appears to make the greater contribution to ΔH for the transition (Biliaderis, 1991, 1992).

3.3. Viscoelasticity analysis

3.3.1. Frequency sweep test

G' (elastic part) and G'' (viscous part) plotted as a function of frequency can provide information on gel

Table 1

Mean starch granule diameter (D), standard deviation of size distribution (σ), change in average diameter (ΔD) and standard deviation ($\Delta\sigma$), CV, and degree of substitution (DS) due to heating at 85 °C for 30 min

$POCl_3$ (ppm starch, dwb)	D (μm)	σ (μm)	ΔD[a] (%)	$\Delta\sigma$[b] (%)	CV[c] (%)	DS[d] (–)
Native	81.8	54.1	NA	NA	66.1	0.00378
Control[e]	80.3	51.8	− 1.83	− 4.25	64.5	0.00369
40	152.5	88.5	86.4	63.6	58.0	0.00380
60	191.9	98.4	134.6	81.9	51.3	0.00385
80	215.0	97.3	162.8	79.9	45.3	0.00397
100	215.5	96.6	163.4	78.6	44.8	0.00375
250	139.6	77.3	70.7	42.9	55.4	0.00384
500	103.5	61.0	26.5	12.8	58.9	0.00386
1000	90.3	55.5	10.4	2.59	61.5	0.00393
2000	86.8	53.7	6.11	− 0.74	61.9	0.00413
5000	73.4	42.3	− 10.3	− 21.8	57.6	0.00522

NA: not applicable.

[a] $\Delta D\ (\%) = ((D - D_o)/D_o) \times 100$: D is the mean diameter after heating at 85 °C for 30 min, and D_o is the mean diameter after heating at 85 °C for 30 min using NPS.

[b] $\Delta\sigma\ (\%) = ((\sigma - \sigma_o)/\sigma_o) \times 100$: σ is the standard deviation of the granules after heating at 85 °C for 30 min, and σ_o is the standard deviation after heating at 85 °C for 30 min using NPS.

[c] Coefficient of variation.

[d] Degree of substitution: DS was calculated using the following equation $DS = 162P/(3100 - 124P)$, where P = % phosphorus (dry basis) of starch.

[e] Under the same conditions of phosphorylation without adding phosphorus oxychloride ($POCl_3$).

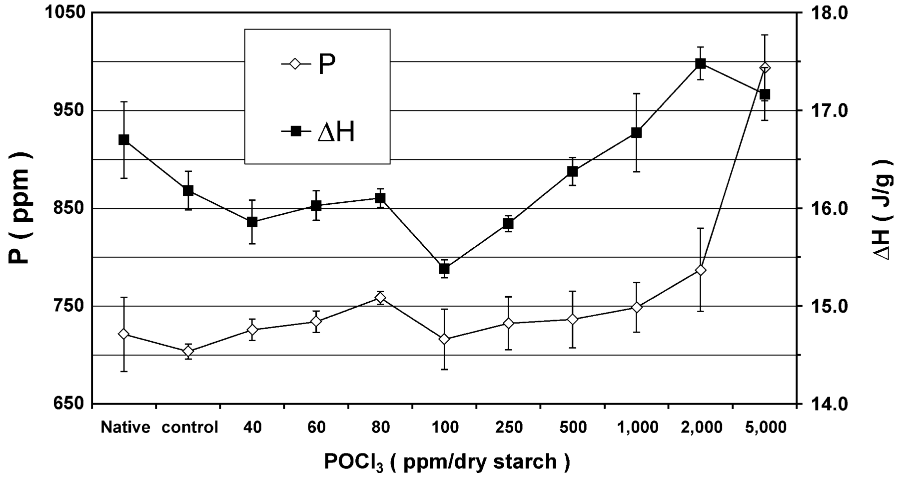

Fig. 2. Phosphorus content (*P*) (◇) and enthalpy of gelatinization (ΔH) (■) dependent on the levels of phosphorus oxychloride ($POCl_3$) used for the cross-linking reaction for all samples: vertical bars indicate range of standard deviations at least in triplicate.

structure. This plot is usually known as the mechanical spectrum or the frequency sweep and can be used to determine the difference between entangle networks, covalently cross-linked materials, and physical gels (Clark & Ross-Murphy, 1987; Doucet, Gauthier, & Foegeding, 2001).

The frequency dependence of G' and G'' for NPS and CPS samples is shown in Figs. 4 and 5. In the present study, the strain amplitude was fixed at 3.0%. The degree of frequency dependence can be determined by Power law parameters proposed by Ramkumar and Bhattacharya (1996):

$$G' = A\omega^B \tag{6}$$

where G' is the storage modulus, ω is the oscillation frequency, and A is a constant. The constant B is the slope in a log–log plot of G' versus ω. Power law parameters ($G' = A\omega^B$) are given in Table 3. It is known that $B = 0$ for a covalent gel, whereas for a physical gel $B > 0$. The B value can be used to compare the gel to a covalent gel. Also, B is related to the material strength factor of the gel (Hsu, Lu, & Huang, 2000).

3.3.1.1. Starches of native, 40 and 100 ppm $POCl_3$ samples. Fig. 4 shows that G' increased with ω, and there was a gradual increase in G' in the range of $0.0628 < \omega < 1.0$, followed by a plateau in the range of $1.0 < \omega < 100$. As shown in Fig. 4, G' was higher than G'' for all three samples, and for NPS, G' had a higher dependence on ω. This type of spectrum is sometimes associated with a ‘weak gel’ structure (Clark & Ross-Murphy, 1987).

In contrast, the spectrum of the 40 ppm sample was typical for numerous gel structures (Clark & Ross-Murphy, 1987). G' was higher than G'' throughout the frequency range, and G' was almost independent of ω. G'' showed a spectrum parallel to G', but half a decade lower. On the other hand, G'' increased with ω for NPS, reached a maximum, and then decreased. This maximum in G'' is often observed for soft polymers such as lightly cross-linked rubber (Ferry, 1980b).

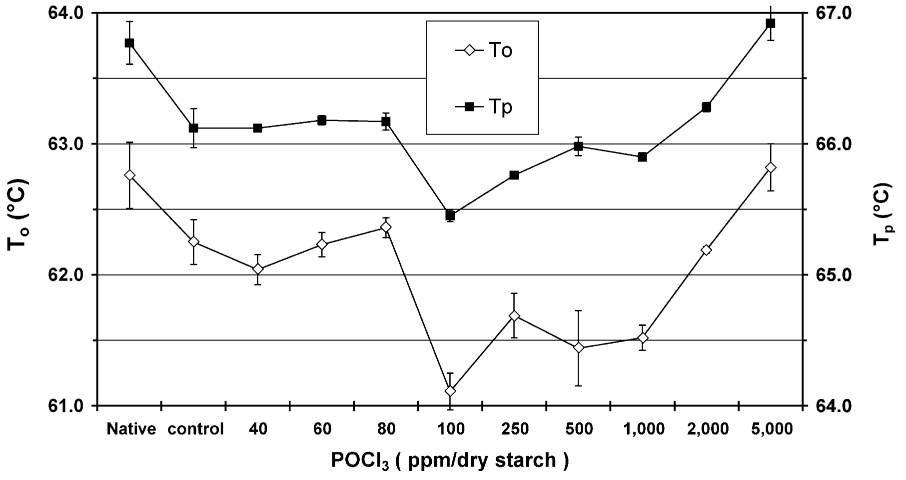

Fig. 3. Onset temperature (T_o) (◇) and peak temperature (T_p) (■) dependent on the levels of phosphorus oxychloride ($POCl_3$) used for the cross-linking reaction for all samples: vertical bars indicate range of standard deviations at least in triplicate.

Table 2
Thermal properties of native and CPS

$POCl_3$ (ppm starch, dwb)	Gelatinization temperature[a] (°C)				Enthalpy, ΔH[b] (J/g)
	T_o	T_p	T_c	R	
Native	62.76 ± 0.25	66.77 ± 0.16	75.40 ± 0.40	8.02 ± 0.24	16.70 ± 0.39
Control	62.25 ± 0.17	66.12 ± 0.15	74.65 ± 0.26	7.75 ± 0.42	16.18 ± 0.20
40	62.04 ± 0.12	66.12 ± 0.02	75.34 ± 0.89	8.15 ± 0.23	15.86 ± 0.22
60	62.23 ± 0.09	66.18 ± 0.04	74.90 ± 0.99	7.91 ± 0.21	16.03 ± 0.15
80	62.36 ± 0.08	66.17 ± 0.07	75.48 ± 0.86	7.61 ± 0.02	16.10 ± 0.10
100	61.11 ± 0.14	65.45 ± 0.04	74.77 ± 0.71	8.69 ± 0.28	15.38 ± 0.09
250	61.69 ± 0.17	65.76 ± 0.01	74.59 ± 0.44	8.15 ± 0.31	15.84 ± 0.08
500	61.44 ± 0.29	65.98 ± 0.07	74.32 ± 0.30	9.07 ± 0.56	16.38 ± 0.14
1000	61.52 ± 0.10	65.90 ± 0.03	74.21 ± 0.65	8.77 ± 0.25	16.77 ± 0.40
2000	62.19 ± 0.03	66.28 ± 0.04	75.15 ± 0.61	8.17 ± 0.11	17.48 ± 0.17
5000	62.82 ± 0.18	66.92 ± 0.13	75.90 ± 0.78	8.20 ± 0.15	17.17 ± 0.27

Values are the means ± standard deviations of the means of at least three determinations.

[a] T_o = onset temperature, T_p = peak temperature, T_c = conclusion temperature, R = gelatinization range $2(T_p - T_o)$.

[b] ΔH = enthalpy of gelatinization (dwb, based on starch weight).

The 100 ppm sample was typical of a gel as well as the 40 ppm sample. However, G' was a decade higher than G'' for the 100 ppm sample, which showed significant differences in their respective curves. G' showed no dependence of ω, whereas G'' increased slightly with increasing frequency. Therefore, this spectrum can be taken to designate a 'true gel' (Clark & Ross-Murphy, 1987) and reflected the existence of a three-dimensional network with junction zones having a longer lifetime than other observation times.

3.3.1.2. Starches of 500, 1000 and 5000 ppm $POCl_3$ samples. Fig. 5 shows the curves for these three samples. The 500 ppm sample displayed the gel with the highest G' and G'' of all examined samples. For the 500 ppm sample, the A value of the power law constants ($G' = A\omega^B$) amounted to 1777.5 Pa s at $\omega = 1.0$ rad s^{-1}, and the B value amounted to 0.0661 in the range of $1.0 < \omega < 100$, as shown in Table 3. The value of B (slope) in Fig. 5 for the 500 ppm sample was slightly higher than that of the 100 ppm sample, indicating that the 500 ppm sample, as a covalent gel like cross-linked starch, was not stronger than the 100 ppm sample mentioned earlier. Also, G' was a decade higher than G'' for the 500 ppm sample in the range of $1.0 < \omega < 100$, whereas in the range of $0.0628 < \omega < 1.0$, G' was about half a decade higher than G''.

On the other hand, for the 1000 ppm sample, G' was half a decade lower than the 500 ppm sample. G' was about half a decade higher than G'' over the range of frequencies. For the 5000 ppm sample, both G' and G'' were a decade lower than for the 500 ppm sample.

3.3.1.3. Frequency dependence of tan δ. The frequency dependence of tan δ for NPS and CPS samples is shown in Figs. 6 and 7. Tan δ decreased with ω for uncross-linked samples such as NPS and control samples. There was a sharp increase in the range of $0.0628 < \omega < 0.158$, followed by a sharp decrease in the next frequency range. At low frequency, tan δ is higher for uncross-linked polymers (Ferry, 1980b) and inversely proportional to

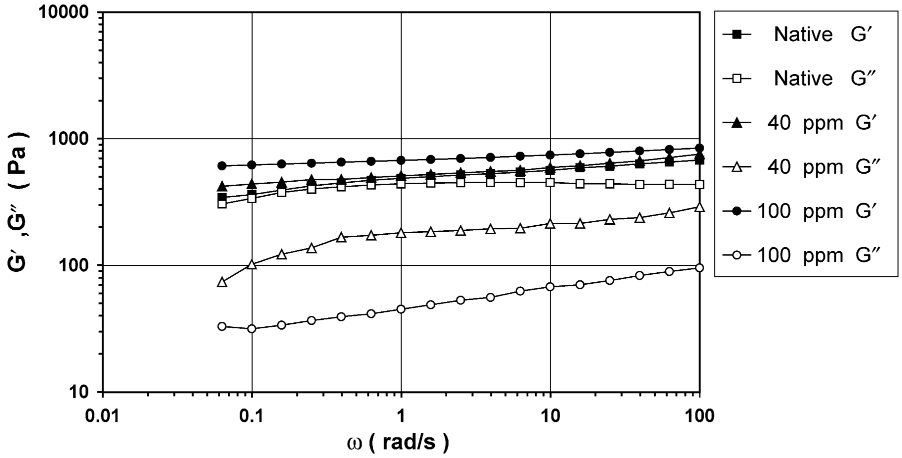

Fig. 4. Frequency dependence of G' (closed) and G'' (open) for NPS (□) and CPS at 40 ppm (△), 100 ppm(○) of $POCl_3$ used for the cross-linking reaction: 5% (w/w) dispersions stored at 20 °C for 24 h after heating at 85 °C for 30 min.

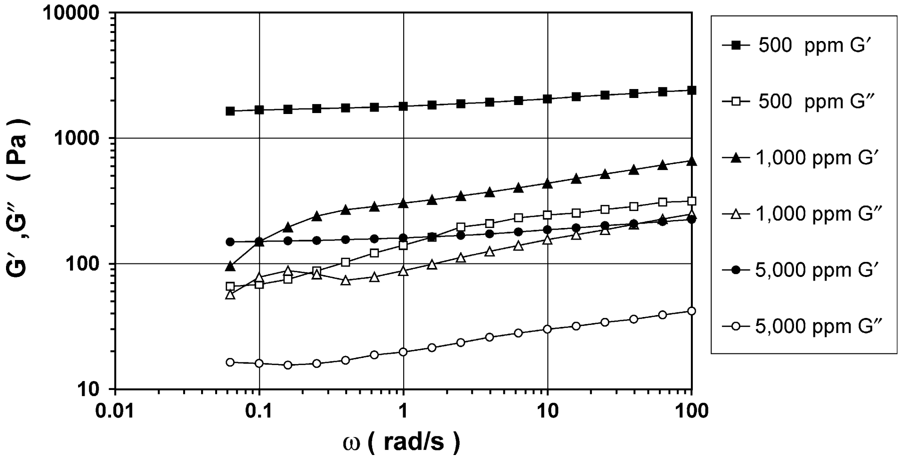

Fig. 5. Frequency dependence of G' (closed) and G'' (open) for CPS at 500 ppm (□), 1000 ppm (△), 5000 ppm (○) of $POCl_3$ used for the cross-linking reaction: 5% (w/w) dispersions stored at 20 °C for 24 h after heating at 85 °C for 30 min.

frequency. In the present study, tan δ was inversely proportional to frequency in the range of $\omega > 0.158$.

In contrast, tan δ generally increased with ω for all examined cross-linked samples. In addition, Figs. 6 and 7 show that tan δ decreased from the 40 ppm sample to the 100 ppm sample, followed by an increase from the 250 ppm sample to the 1000 ppm sample, and then another decrease from the 2000 ppm sample to the 5000 ppm sample.

This suggests that levels of $POCl_3$ concentration affected the structure of starch molecules within the granule, such as the distribution of introduced phosphate cross-links, in ways at present unknown in detail. The position of these introduced phosphate cross-links has significantly different effects on the gelatinization and properties of the starches (Muhrbeck & Eliasson, 1991; Muhrbeck et al., 1991; Muhrbeck & Tellier, 1991). This should be explored in the future.

In general, the increase of G' accompanied by a decrease of tan δ suggests a formation of polymer cross-linking (Berglund, Shelton, & Freeman, 1991). In the present study, two processes may have been involved: strengthening of the cross-linked network at lower $POCl_3$ concentrations until 100 ppm and weakening at higher $POCl_3$ concentrations above 250 ppm. The rice starch gel with high G' (>500 Pa) and low tan δ (<0.2) showed a gelling behavior, as suggested by Lii, Shao, and Tseng (1995). Ross-Murphy (1994b) also reported that for 'strong (true) gel' systems, the ratio G''/G' usually falls in the range of 0.2–0.01, and such a ratio is also seen for many synthetic polymeric networks. Therefore, CPS samples from the 80 ppm sample to the 500 ppm sample could be recognized as having 'strong (true) gel' systems.

3.3.2. Shear flow test and Cox–Merz rule (relationship between $|\eta^*|$ and η)

The empirical Cox–Merz rule (Cox & Merz, 1958) states that η should be the same function of $\dot{\gamma}$ as $|\eta^*|$ is of ω, where $|\eta^*| = ((G')^2 + (G'')^2)^{1/2}/\omega = ((\eta')^2 + (G'/\omega)^2)^{1/2}$, η' being the dynamic viscosity. To establish such a $|\eta^*| - \eta$ relationship, the $|\eta^*|$ and η data were obtained in the same shear rate and frequency range.

Fig. 8 shows that the $|\eta^*|$ for the NPS, 100, 500 and 2000 ppm samples lay above the values of the η, and declined over the frequency range of $\omega = 0.0628$–$100\ \text{rad s}^{-1}$ that is ideally pseudoplastic with a slope of -0.93 for NPS. The observed pseudoplasticity should be ascribed to the disturbance of entanglements which are unable to reform within the period of oscillation.

The result for the 100 ppm sample coincided with the Cox–Merz rule at relatively high $\dot{\gamma}$ and ω. At low $\dot{\gamma}$ and ω a good approximation of $|\eta^*|$ and η could not be seen.

The $|\eta^*|$ was higher than the η over the frequency and shear rate range, and the curves declined with a slope of -0.96, indicating nearly ideal pseudoplastic behavior: the more elastic the behavior, the lower the difference. This was in agreement with the observation of Rao et al. (1997) with gelatinized 5% cross-linked waxy maize starch dispersions.

Table 3
Power law constants for relationship between storage modulus and frequency ($1 \leq \omega$) for all samples investigated ($G' = A\omega^B$)

$POCl_3$ (ppm starch, dwb)	A (Pa s)	B (−)
Native	481.6	0.0730
Control	920.2	0.0426
40	495.9	0.0833
60	604.4	0.0513
80	774.1	0.0468
100	667.4	0.0493
250	1385.2	0.0612
500	1777.5	0.0661
1000	297.0	0.1726
2000	137.5	0.1357
5000	157.4	0.0755

Value is the typical one of at least two runs.

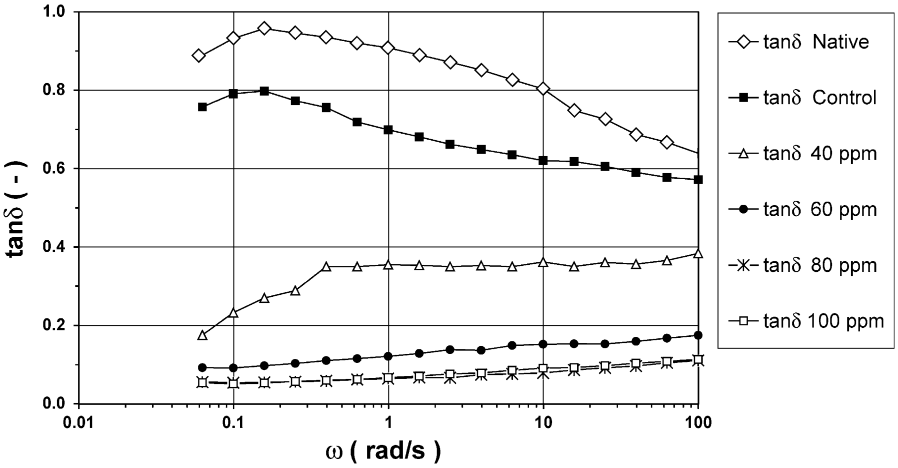

Fig. 6. Frequency dependence of tan δ for NPS (◇), Control (■) and CPS at 40 ppm (△), 60 ppm (●), 80 ppm ($*$), 100 ppm (□) of $POCl_3$ used for the cross-linking reaction: 5% (w/w) dispersions stored at 20 °C for 24 h after heating at 85 °C for 30 min.

The result for the 500 ppm sample does not coincide with the Cox–Merz rule over the frequency and shear rate range. Deviation from the Cox–Merz rule reflects the gel-like nature of gelatinized 5% cross-linked waxy maize starch dispersions (Rao, 1999). It could be assumed the structures increased the junctions caused by mechanical entanglements, and this would lead to the higher observed difference between $|\eta^*|$ and η.

Furthermore, it should be noted that the dilatant behavior of all samples above 250 ppm could be seen at higher shear rates in the range of $\dot{\gamma}$ above 10 s^{-1}. The dilatant behaviors for both the 500 ppm and the 2000 ppm samples are shown in Fig. 8. It was assumed that these structures in Fig. 8 were disrupted on shearing, and this would lead to the observed increase in pseudoplasticity (‘shear thinning’ behavior) (Nuessli, Handschin, Conde-Petit, & Eschen, 2000). Dilatancy (‘shear thickening’ behavior) is sometimes seen in swollen particulate systems such as starch dispersions (Ross-Murphy, 1994c). Dilatancy was reported in dispersions of gelatinized wheat starch (Bagley & Christianson, 1982), corn starch (Christianson & Bagley, 1983), cross-linked waxy maize starch (Dail & Steffe, 1990a,b), and cowpea starch (Okechukwu, Rao, Ngoddy, & McWatters, 1991). As far as we are aware, the dilatant behavior of potato starch has not been reported. The best explanation for these dilatant observations was that the small shear stresses in the fluid could not deform the relatively rigid starch granules. Dilatancy is not a common phenomena in food rheology.

Based on microscopic views (data not shown), the starch granules of CPS samples that showed the dilatant behavior were not deformable. Furthermore, the granular starch size was higher and more closely packed at severe higher shear rates above 10 s^{-1}, whereas that of samples at lower shear rates below 10 s^{-1} was relatively lower and not closely packed.

The magnitudes of $|\eta^*|$ were almost always higher than those of $\eta(\dot{\gamma})$, only converging at higher values of frequency

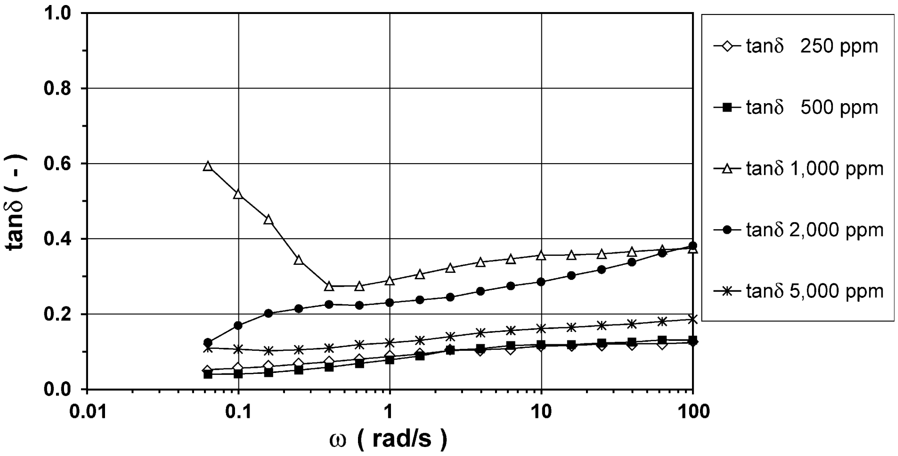

Fig. 7. Frequency dependence of tan δ for CPS at 250 ppm (◇), 500 ppm (■), 1000 ppm (△), 2000 ppm (●), 5000 ppm ($*$) of $POCl_3$ used for the cross-linking reaction: 5% (w/w) dispersions stored at 20 °C for 24 h after heating at 85 °C for 30 min.

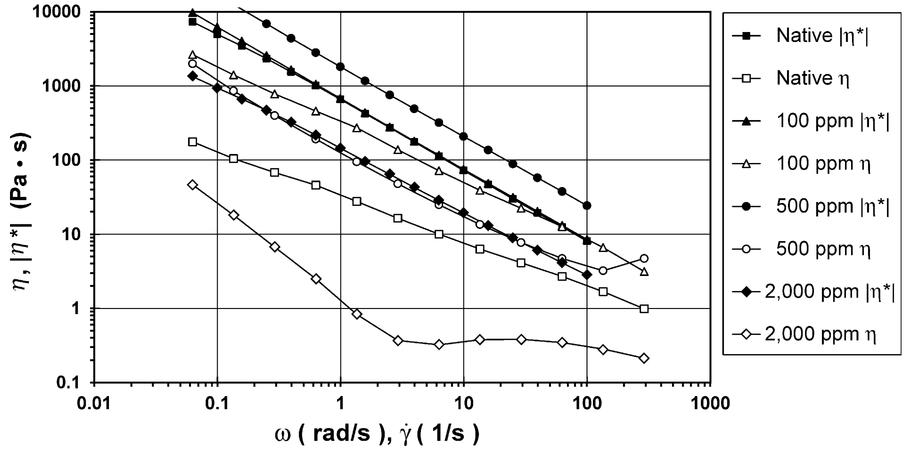

Fig. 8. Cox–Merz rule: shear rate dependence of η (open) and frequency dependence of $|\eta^*|$ (closed) for NPS (□) and CPS at 100 ppm (△), 500 ppm (○), 2000 ppm (◇) of $POCl_3$ used for the cross-linking reaction: 5% (w/w) dispersions stored at 20 °C for 24 h after heating at 85 °C for 30 min.

and shear rate (Fig. 8). Such behavior as $|\eta^*|$ becoming higher than η is very common in biopolymeric systems. This phenomenon is attributed to structure decay in the case of steady experiments whereas such decay is negligible in small amplitude dynamic experiments (Mills & Kokini, 1984).

3.3.3. The first normal stress difference (N_1) and the first normal stress difference coefficient (Ψ_1)

The normal stress differences are due to the elastic component in viscoelastic food materials. In shear flow of elastic fluids, the stress state is completely characterized by the shear stress σ_{21}, the first normal stress difference $N_1 = \sigma_{11} - \sigma_{22}$ and the second normal stress difference $N_2 = \sigma_{22} - \sigma_{33}$. σ_{ij} is the stress component, parallel to the j direction, of the force per unit area acting on the face of a cubical element which is perpendicular to the *i* direction. N_1 can be measured directly in a cone and plate rheometer. Although there is little experimental data about the normal stress differences in gelatinized starch dispersions, interest stems from measurements of N_1 analogue of the Cox–Merz rule given by Eq. (5).

Both the 2000 ppm and the 5000 ppm samples showed that the thrust became negative in magnitude over a range of shear rates (data not shown). This indicates that the entanglements of the chains caused the sample to pull in a direction normal (perpendicular) to the applied stress. Similarly, negative thrust was observed for NPS during shearing, only at low shear rates, $\dot{\gamma} \leq 13.53$ (data not shown). Fig. 9 shows that the thrusts for the 40, 100 and 500 ppm samples were positive in magnitude over a range of shear rates. The different shape of the traces was quite obvious. Ψ_1 as a function of $\dot{\gamma}$ relatively coincided with $2G'/\omega^2$ as a function of ω when compared at $\omega = \dot{\gamma}$ for the 40 ppm sample. However, the results for both the 100 and the 500 ppm samples show a poor agreement between Ψ_1 and $2G'/\omega^2$. Furthermore, for the 100 ppm sample, Ψ_1 was always higher than $2G'/\omega^2$ and parallel to $2G'/\omega^2$. On the other hand, for the 500 ppm sample, Ψ_1 was lower than $2G'/\omega^2$.

It is to be hoped that the experimental measurements of normal stress difference trends might be used to guide future theoretical considerations for the gelatinized starch dispersions.

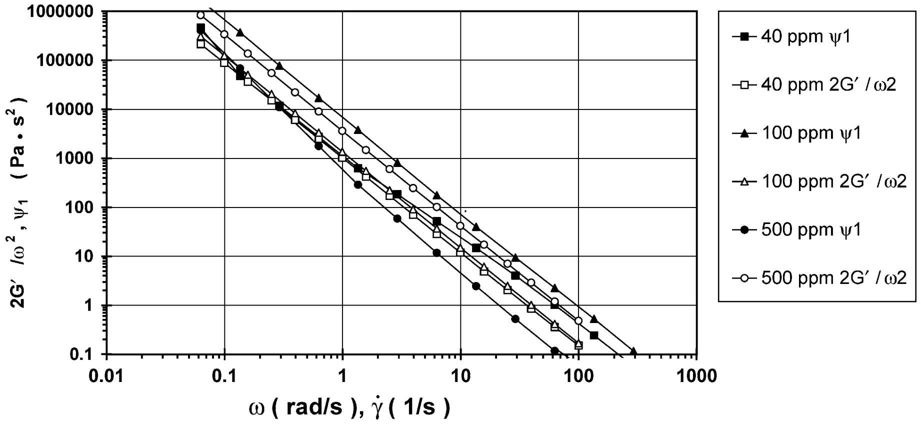

Fig. 9. Another empirical rule: shear rate dependence of Ψ_1 (closed) and frequency dependence of $2G'/\omega^2$ (open) for CPS at 40 ppm (□), 100 ppm (△), 500 ppm (○) of $POCl_3$ used for the cross-linking reaction: 5% (w/w) dispersions stored at 20 °C for 24 h after heating at 85 °C for 30 min.

4. Conclusions

The levels of phosphate cross-links had a strong influence on DSC and rheological properties. The storage shear modulus and granule size of the gelatinized dispersions from CPS between the 40 ppm and the 100 ppm $POCl_3$ starches was markedly increased, followed by a dramatic decrease above the 100 ppm starches. The thermal properties also changed with the $POCl_3$ concentration. The potato starch treated with 100 ppm $POCl_3$ displayed a lower gelatinization temperature, lower enthalpy change, and less phosphorus content than other treated starches. Additionally, the dilatant behavior of all starches treated with above 250 ppm $POCl_3$ could be observed at higher shear rates. Dilatancy is not a common phenomena in food rheology. Further research is necessary to define the role played by the various factors on the thermal and rheological properties of starchy materials, particularly through structural approaches within the granules, such as the distribution of phosphate cross-links that is at present unknown. The position of these phosphate cross-links can have significantly different effects on the gelatinization and physicochemical properties of starches.

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