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Structure of potato starch pastes in the ageing process by the measurement of their dynamic moduli

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The effect of ageing on the rheological properties of potato starch pastes was investigated by measurement of dynamic viscoelasticity. The value of the storage modulus (G') increased rapidly with time for the first few hours, but attained equilibrium after a long period of ageing. The relation between the concentration and the storage modulus showed a $c^{1\cdot 6}$ dependence. The Avrami exponent (n) obtained in this study was 0·66 and deviated significantly from the value ($n = 1$), corresponding to rod-like growth of crystal. The rate of storage modulus increase decreased with increasing concentrations up to 10%, and at higher concentrations little or no increase was observed. In addition, the rate of storage modulus increase increased dramatically when the NaCl concentration was raised to levels of 0·01 M or above. An even greater increase in rate occurs on addition of $AlCl_3$.

INTRODUCTION

Starch pastes are formed by heating an aqueous suspension of starch granules above the gelatinisation temperature. On subsequent cooling and ageing retrogradation occurs which is due to the aggregation and partial crystallisation of starch molecules (Whistler, 1964). From this viewpoint, a large body of experimental data on the crystallinity of starch molecules has been accumulated by using different experimental techniques; e.g. X-ray diffraction (Katz & van Itallie, 1930), DSC (Jankowski & Rha, 1986), turbidity (Ring *et al.*, 1987), solubility (del Rosario *et al.*, 1983). However, the most directly important properties of starch pastes are the rheological characteristics (Bechtel & Fischer, 1949) and these can change dramatically during ageing.

The rheological properties of starch pastes are often characterised by empirical methods where the range of shear rates is very broad and poorly defined. Fundamental methods in which information about the structure of starch can be obtained, have been used to characterise the viscosity of starch suspensions (Evans & Haisman, 1979; Doublier, 1981; Wong & Lelievre, 1981). Shear stress relaxation has also been used to study more concentrated gels (Eliasson & Bohlin, 1982; Bohlin *et al.*, 1986). In addition, a number of papers has been published on rheological changes on ageing of starch (Wong & Lelievre, 1982; Miles *et al.*, 1985; Orford *et al.*, 1987) and its components (Ring *et al.*, 1987; Clark *et al.*, 1989).

Generally, the structure breakdown caused by the shear forces applied by oscillatory measurements in the linear viscoelastic range can be considered to be negligible (Svegmark & Hermansson, 1990), thus, the determination of dynamic moduli has been shown to be a useful means of studying the change in the structure occurring with time (te Nijenhuis & Dijkstra, 1975). With this in mind, the author undertook the current work to investigate the change in the structure on ageing of starch from dynamic rheological measurements of potato starch pastes. The present report deals with an attempt to estimate the effect of starch concentration and addition of salts through continuous dynamic measurement. From these observations, a relation between the chain entanglement and the crystal formation of starch in the ageing process is also proposed.

EXPERIMENTAL

Materials

The potato starch used in this study was a commercial sample (Wako Pure Chemicals Co., Japan). Other

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chemicals were of the highest purity available, used without further purification.

Preparation of starch pastes

Weighed amounts of starch were slurried with an appropriate volume of water. These suspensions were then heated to 90°C at a constant rate of 1·5°C min^{-1} in the Brabender Amylograph (Brabender OHG, Germany), and held at the maximum temperature for 5 min. Concentrations were measured by drying aliquots of the pastes to constant weights at 105°C, and expressed on a dry weight/weight percentage basis.

Measurement of dynamic viscoelasticity

The dynamic shear characteristics of the starch pastes were examined with a Rheometer RM-1 (Shimadzu Manufacturing Co., Japan) using cone and plate geometry. This instrument is generally similar to a Weissenberg Rheogoniometer, in which rotational and vibrational stresses are combined. In this instrument, oscillatory torque is sensed through the small movement of the cone supported by a torsion bar. Deflection of the cone is followed with an electrical detector and is registered on the recorder. The radius of the cone was 4·0 cm and the cone angle (θ) was 0·07 rad. A constant temperature (22 ± 0·5°C) was controlled by running water in the cone-plate system surrounded by a water jacket and was regulated by a Cool Mate (TE-105 M, Toyo Seisakusho Co., Japan). After the hot paste prepared had been immediately transferred to the lower plate and gap width had been set, the system was quickly cooled to 22°C and the excess material was cut off with a spatula. The sample at the edge of the cone-plate system was covered by silicone oil to prevent evaporation during ageing. In order to relax, all sample pastes were then allowed to rest at 22°C for 20 min before tests began.

A constant oscillation was applied and maintained during ageing, and the moduli were measured as a function of time. The ageing time was defined as the time elapsed after applying the oscillation. In order to avoid the effect of shearing, the dynamic measurements were made at a small rotating angle (α) of $1{\cdot}753 \times 10^{-2}$ rad and at a very low frequency of $6{\cdot}55 \times 10^{-3}$ rad s^{-1}. The maximum shear strain ($\gamma = \alpha/\theta$) used was 0·25. At this shear strain all samples were in the linear viscoelastic range (Moritaka *et al.*, 1980; Bohlin *et al.*, 1986). Furthermore, Evans & Haisman (1979) have postulated that the frequency-dependence of storage and loss moduli for potato starch over the range $3{\cdot}3 \times 10^{-4}$–$4{\cdot}0 \times 10^{-1}$ rad s^{-1} is slight, so that no major relaxation processes can be occurring in this frequency range. Hence, the viscoelastic behaviour can be compared by taking the moduli at a constant frequency of $6{\cdot}55 \times 10^{-3}$ rad s^{-1} in this study. The storage and loss moduli were determined by using the Markovitz equation (Markovitz, 1952). Each part of the experiments was made at least in duplicate.

RESULTS AND DISCUSSION

Dynamic moduli of starch pastes

The complex shear modulus ($G*$) at a given frequency, in terms of the stress/strain ratio, is

$$G* = G' + iG'' \quad (i^2 = -1) \tag{1}$$

where G', the ratio of the stress component in phase with the strain/strain, is the storage modulus, and G'', the ratio of stress component out of phase with the strain/strain, is the loss modulus. The loss tangent ($\tan\delta$), a measure of the ratio of energy lost to energy stored in a cyclic deformation is also given by

$$\tan\delta = \frac{G''}{G'} \tag{2}$$

Figure 1 shows typical changes in G', G'', and $\tan\delta$ as a function of ageing time for a 12·5% (w/w) potato starch paste at 22°C. The value of G' increased rapidly with time for the first few hours, settled down to a slow increase, and data at long times (not shown) suggest that equilibrium will be attained after a long period, while the value of G'' decreased very little within the observed period. On the other hand, $\tan\delta$ decreased very rapidly for the first few hours, but the decrease then slowed and $\tan\delta$ eventually approached the value of 0·1.

If $\tan\delta \gg 1$, the material will behave as a liquid (i.e. the energy used to deform the material will be viscously dissipated), whereas if $\tan\delta \ll 1$, the material will behave as a solid (i.e. deformation within the linear

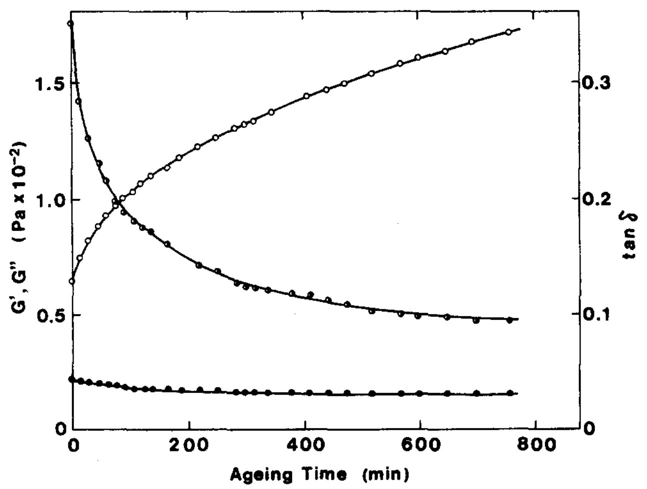

Fig. 1. Plots of the storage (G') and loss (G'') moduli, and $\tan\delta$ as a function of ageing time for a 12·5% (w/w) potato starch paste at 22°C and at an angular frequency of $6{\cdot}55 \times 10^{-3}$ rad s^{-1}. ○, G'; ●, G''; ◑, $\tan\delta$.

range will be essentially elastic) (Evans & Haisman, 1979). Crystalline polymers have values of tan δ in the general neighbourhood of 0·1 (Ferry, 1970). There are numerous examples of random coil polymers forming network junction points as a result of specific interchain aggregation, e.g. interchain hydrogen bonding. In other systems there is substantial evidence that the junction points involve micro-crystallites, although their nature is not always clearly established (Mandelkern, 1982). Hence, the changes of G', G'', and tan δ may be attributable to the level of micro-crystalline junction zones increasing gradually with time and a change in the number of junction points due to chain entanglements. The relative importance of these two factors will be discussed below.

Effect of starch concentration on ageing

When changes in the storage modulus of starch pastes as a function of time are measured, it is difficult to estimate the value at the state near equilibrium, since syneresis occurs after a long period of ageing. We have found that changes in the storage modulus as a function of time for a gel can be approximated by the equation for an orthogonal hyperbola (Mita, 1990). That is

$$G'_t - G'_0 = \frac{(G'_\infty - G'_0)t}{t_{1/2} + t} \qquad (3)$$

where $G'\infty$, G'_t, and G'_0 are the respective storage moduli after infinite time, after a time t, and at $t = 0$. $t_{1/2}$ is the time corresponding to $(G'_\infty - G'_0)/2$. The value of G'_0 was calculated by extrapolating the values of G' at the beginning of ageing to $t = 0$, since it was impossible to estimate directly the value of G'_0. The following equation can be obtained by inverting eqn (3):

$$\frac{1}{G'_t - G'_0} = \frac{t_{1/2}}{G'_\infty - G'_0}\frac{1}{t} + \frac{1}{G'_\infty - G'_0} \qquad (4)$$

Plots of the reciprocal of the storage modulus against the reciprocal of time are linear, giving the values of G'_∞ from the intercept on the ordinate. Figure 2 shows plots of the increment of the storage modulus, $G'_t - G'_0$, against time t for a 12·5% (w/w) potato starch paste at 22°C. It can be seen that the calculated curve is compatible with the experimental one, except for the first few hours of ageing. The calculated curves were also fitted to the experimental data (not shown) over at least a 24 h period. In this manner, the values of G'_∞ for starch pastes were determined. Table 1 shows the values of G'_0 and G'_∞ at different concentrations of starch pastes.

As has been mentioned, the moduli of many polymer gels are proportional to the square of concentration. Then, the concentration-dependence of potato starch paste was calculated from the values of G'_0 and G'_∞, producing the following empirical relationships:

$$G'_0 = 1{\cdot}71 \times c^{1{\cdot}5} \quad \text{(Pa)}$$

and

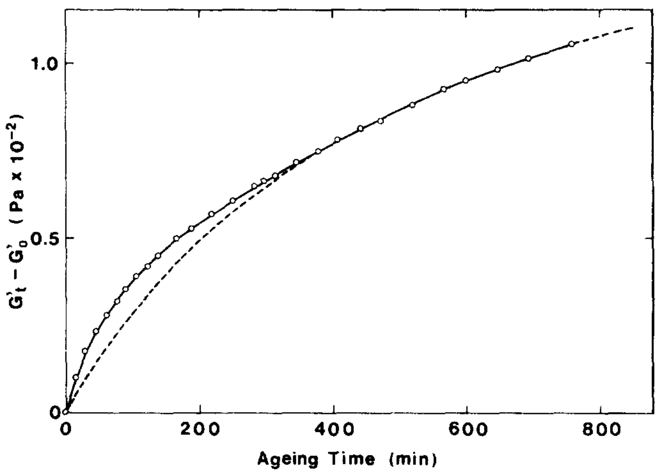

Fig. 2. Plots of the increment of the storage modulus ($G'_t - G'_0$) as a function of ageing time for a 12·5% (w/w) potato starch paste at 22°C and at an angular frequency of $6{\cdot}55 \times 10^{-3}$ rad s^{-1}. —○— , Experimental; ----, calculated from eqns (3) and (4).

Table 1. Concentration-dependence of the storage moduli, the Avrami exponent, the rate constant, and the half-increment time for potato starch gels stored at 22°C

Concentration (% w/w)	G'_0[a] (Pa)	G'_∞[b] (Pa)	Avrami exponent n	Rate constant K (min^{-1})	$t_{1/2}$[c] (min)
4·2	13·1 ± 0·1	42·3 ± 0·3	0·64	$1{\cdot}74 \times 10^{-2}$	311 ± 4
6·2	26·9 ± 0·2	81·6 ± 2·0	0·64	$1{\cdot}48 \times 10^{-2}$	408 ± 14
8·3	38·0 ± 0·6	123·7 ± 2·4	0·65	$1{\cdot}26 \times 10^{-2}$	479 ± 15
10·4	48·5 ± 1·3	177·1 ± 1·1	0·66	$1{\cdot}12 \times 10^{-2}$	533 ± 13
12·5	65·4 ± 1·8	229·1 ± 3·9	0·66	$1{\cdot}07 \times 10^{-2}$	550 ± 8
14·6	84·0 ± 0·3	316·7 ± 3·3	0·66	$1{\cdot}10 \times 10^{-2}$	517 ± 5
16·7	108·6 ± 3·8	406·1 ± 1·1	0·66	$1{\cdot}12 \times 10^{-2}$	524 ± 4

[a] Storage modulus at $t = 0$.
[b] Storage modulus after infinite time.
[c] Time at the half-increment of storage modulus.

$$G'_\infty = 4{\cdot}28 \times c^{1{\cdot}6} \text{ (Pa)} \tag{5}$$

In this way, it was found that the storage modulus of potato starch paste was weakly dependent on concentration, compared to that of the other polymer gels. Evans & Haisman (1979) have reported that there is a linear relationship between the concentration and the dynamic moduli by using a freshly prepared potato starch paste, although it depends on the starch sources. Miles *et al.* (1985) have reported that the gels from wheat and corn starch show a linear increase in shear modulus as starch concentration rises from 6 to 30%. On the other hand, Svegmark & Hermansson (1990) have reported that the characteristics of the concentration-dependence differs due to the shear history of the sample during gelatinisation and even moderate shear treatment after gelatinisation gives rise to structural changes. Such a change in structure due to shearing may take place during the preparation of pastes in the Brabender Amylograph using this study.

Effect of structure of starch on ageing

If the storage modulus (G') is linearly related to the extent of starch crystallisation, the changes of the storage modulus of starch pastes can be described according to the Avrami equation (Avrami, 1940), as follows:

$$\frac{G'_\infty - G'_t}{G'_\infty - G'_0} = \exp(-Kt^n) \tag{6}$$

where K is the rate constant and n is the Avrami exponent (Sherman, 1970). Equation (6) can be expressed in the following logarithmic form

$$\log\left(-\ln\frac{G'_\infty - G'_t}{G'_\infty - G'_0}\right) = n \log t + \log K \tag{7}$$

Changes in the storage modulus of starch pastes at different concentrations were measured at 22°C. Typical fits of the storage modulus measurements to the double logarithmic form of eqn (7) are shown in Fig. 3. Approximately linear relationships were obtained for all concentrations studied. In Fig. 3, the Avrami exponent (n) can be obtained from the slope and the rate constant from the intercept on the ordinate at $\log t = 0$. Table 1 shows the respective values of n, K, and $t_{1/2}$ at different concentrations of starch pastes. The times at half-increment of the storage modulus ($t_{1/2}$) were determined by substituting 0·5 for $(G'_\infty - G'_t)/(G'_\infty - G'_0)$ in eqn (7). The value of $t_{1/2}$ increased with increasing concentration up to 10·4%, but did not vary at concentrations above 10·4%. A similar behaviour was observed for the rate constant (K). They suggest that the rate of storage modulus increase decreases significantly as the concentration rises to about 10%.

In general, retrograded starches are partially crystalline with B-type hydrated crystalline regions in which water molecules constitute an integral structural part of the crystal unit cell (French, 1984). A 'fringed micelle' model has been proposed to describe the morphology of partially crystalline polymer. This consists of a three dimensional network composed of micro-crystallites crosslinking amorphous regions of random-coil chain segments (Stein, 1969; Levine & Slade, 1987). This model may be applied to explain the effect of starch concentration on ageing as follows. The number of junction points caused by chain entanglement at zero time increase as the concentration rises, however the increase in the number of junction points caused by successive entanglement with time will be restricted as the concentration rises, since the increase in concentration leads to a decrease of topological movement of starch itself. Such behaviour may be retarded further by the formation of 'fringed micelles'.

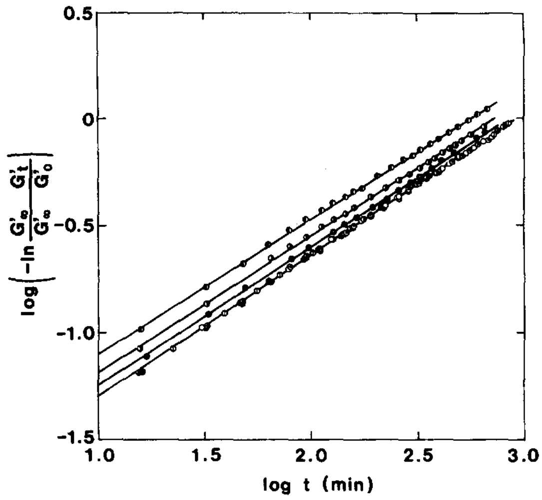

Fig. 3. Plots of the storage modulus measurements of potato starch pastes at different concentrations according to the double logarithmic form of the Avrami equation (eqn (7)). ◐, 4·2%; ◑, 6·2%; ◎, 8·3%; ⊙, 10·4%; ○, 12·5%; ⦶, 14·6%; ●, 16·7%.

The value for the Avrami exponent (n) was 0·66, although n is slightly lower than 0·66 at concentrations below 8·3% (Table 1). This suggests that the mechanism of crystal growth is independent of the concentration of starch. The Avrami exponent deals with the kinetics of phase changes during crystal growth around randomly distributed nuclei in terms of the change in dynamic modulus (Sherman, 1970). The value of n is also a constant whose value lies between 1 and 4, depending on the nucleation mechanism (Mandelkern, 1964). It has been demonstrated that the basic mechanism of retrogradation of starch is instantaneous nucleation followed by rod-like growth of crystals (i.e. $n = 1$) (McIver *et al.*, 1968; Kim & D'Appolonia, 1977; Wong & Lelievre, 1982). Roulet *et al.* (1988) have studied the changes during ageing of concentrated wheat starch system applying the Avrami equation to X-ray scattering and DSC data as well as to the compression modulus and dynamic mechanical properties. If the increase in the storage modulus with time is therefore expressed by the instantaneous nucleation followed by rod-like growth of crystal, the Avrami exponent should give $n = 1$. However, the value obtained in this study was approximately 0·7.

In order to explain the above conflict, we assume the following two processes occur during the ageing of starch pastes.

(1) The rapid increase in storage modulus at the early stage of ageing will depend mainly on the chain entanglement of starch molecules in the amorphous regions, since the entanglements behave as crosslinks with short life-times (Slade *et al.*, 1989).
(2) The slow increase in storage modulus over a long period of ageing will be brought about by the increase in the rod-like growth of crystals which is attributable to the entanglement junction points developed on ageing being replaced by the micro-crystalline junction zones. Accordingly, the overall increase in the storage modulus will be expressed as the combination of two increases due to the entanglement and the rod-like growth of crystals.

In a study of the kinetics of chain entanglement in amorphous polymer gels such as wheat protein, it has been proposed that the increase in the storage modulus attains near equilibrium after 48 h of ageing (Mita, 1990). The results shown in Fig. 3 were analysed, based on the assumption that the entanglement junction points developed on ageing would be completely replaced by micro-crystallites after 48 h of ageing and that the nucleation would be followed only by rod-like growth of crystal (i.e. $n = 1$). Figure 4 shows typical increases in the storage modulus of 12·5% starch as a function of ageing time and the components of this modulus that can be attributed to entanglement and crystal growth. The component of storage modulus due to the chain entanglement increased rapidly with time for the first 200 min, to be followed by a much slower rate of decrease and approached the value of zero after 48 h of ageing. On the other hand, the increment of storage modulus due to the crystal growth increased slowly with time, and attained an equilibrium state after a long period. By using the above analysis, the rate constants of the storage modulus increase caused by the crystal growth were $9{\cdot}66 \times 10^{-4}$, $8{\cdot}32 \times 10^{-4}$, $7{\cdot}59 \times 10^{-4}$, and $7{\cdot}24 \times 10^{-4}$ min^{-1} for 4·2, 6·9, 8·3, and 10·4–16·9% starch pastes, respectively. In this way, the rate of storage modulus increase decreased with increasing concentration up to 10%, similar to the concentration-dependence of the rate constant (K) as shown in Table 1.

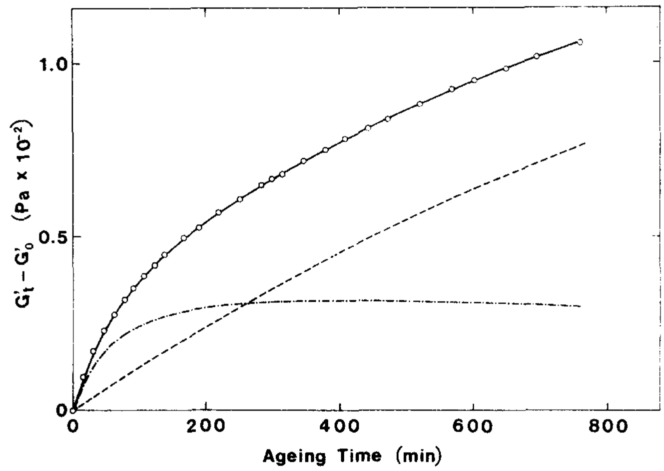

Fig. 4. Typical increases in the storage modulus ($G'_t - G'_0$) of starch paste (12·5%) as a function of ageing time (—O—) and for the entanglement component (—•—) and crystal growth component (----), based on the assumption that the entanglement junction points are completely replaced by the micro-crystallites after 48 h of ageing.

The changes on ageing of starch has been suggested to consist of two reactions with different rates of increase in shear modulus. Miles *et al.* (1985) have found no direct relation between the kinetics of crystal formation and the small deformation behaviour of amylose gels. They have also reported that the crystallisation of the amylose gel is limited by storage and lagged behind the shear modulus increase, whereas the crystallisation of the starch gel closely follows the shear modulus, and postulated that the short-term increase in shear modulus is attributed to gelation of solubilised amylose in the continuous phase and the long-term increase to crystallisation of amylopectin within the granules. By using this hypothesis in studies of gelation and retrogradation of starch with regard to concentration and botanical source, Orford *et al.* (1987) have suggested that the initial rate of development of stiffness of the gels is related to the amount of amylose solubilised during gelatinisation and the long-term increase in crystallisation involving amylopectin. Consequently, the rapid increase of storage modulus at the early stage of ageing may be attributed to the entanglement of solubilised amylose and the slow increase of storage modulus over a long period of ageing to the crystal formation of amylopectin. In addition, the concentration-dependence of the rate of storage modulus increase may be attributable to the solubility of amylose component being saturated at concentrations above 10% because of the very low solubility of amylose (Miles *et al.*, 1985).

On the other hand, interesting studies of gelation mechanism of pure amylose have been made by Clark *et al.* (1989). They have found that the relative rate of turbidity and modulus increase for amylose gels are dependent on the chain length, i.e. for short chains the turbidity precedes gelation, whereas for longer chains gelation occurs before a significant increase in turbidity. This suggests that the molecular weight of amylose, which is one of the major components of starch, plays an important role in determining the storage modulus increase on ageing. A more detailed discussion is not possible, since the amylose in the potato starch used is not well-defined.

Effect of sodium chloride on ageing

Changes in the storage modulus of starch paste (12·5%) at different concentrations of sodium chloride were measured at 22°C. Typical fits of the storage modulus measurements to the double logarithmic form are shown in Fig. 5. This procedure gives two values of the Avrami exponent at NaCl concentrations above 0·01 M,

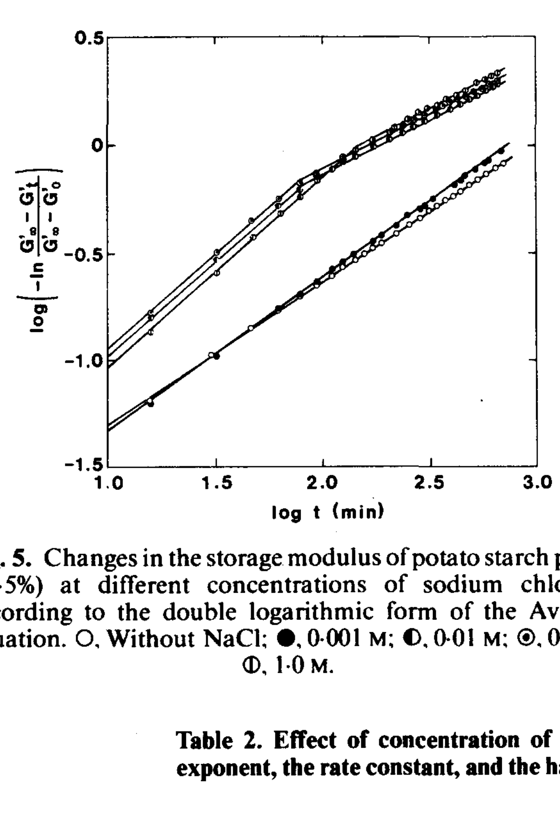

Fig. 5. Changes in the storage modulus of potato starch paste (12·5%) at different concentrations of sodium chloride according to the double logarithmic form of the Avrami equation. O, Without NaCl; ●, 0·001 M; ◐, 0·01 M; ⊙, 0·1 M; ⦶, 1·0 M.

suggesting that the behaviour of NaCl-containing pastes was more complex, compared with NaCl-free starch pastes. Table 2 shows the respective values of G'_0, G'_∞, n, K, and $t_{1/2}$ for starch paste (12·5%) containing NaCl at different concentrations. The value of G'_0 increased as the NaCl concentration increased. On the other hand, the value of G'_∞ was almost independent of NaCl concentration up to 0·001 M, and decreased to a minimum value at 0·01 M, and increased again above 0·1 M. By using DSC, Wootton & Bamunuarachchi (1979) have reported an increase in the temperature at which the endotherm on addition of 1·5 M NaCl, and a subsequent decrease as NaCl levels are raised further. Furthermore, it is reported that a significant increase in the consistency of the starch is observed as the NaCl concentration increases (D'Appolonia, 1972). Such behaviour may be related to the increase of G'_0 by adding NaCl. The effect of NaCl on the values of G'_∞, however, is still obscure.

The values of $t_{1/2}$ decreased drastically at NaCl concentrations above 0·01 M, but a further decrease with increasing salt concentration was not observed as the concentration was increased still further (Table 2). The results shown in Fig. 5 were analysed in a similar manner to that used in Fig. 4. Figure 6 shows typical increases in the storage modulus of starch paste (12·5%) at an NaCl concentration of 0·1 M as a function of ageing time for the overall increases of storage modulus and for the two storage modulus increases due to entanglement and crystal formation, respectively. The storage modulus increase due to entanglements increased very rapidly with time for the first 100 min, to be followed by a rapid rate of decrease, and approached the value of zero after 48 h of ageing. A similar behaviour was observed in starch pastes at NaCl concentrations above 0·01 M. By using the above analysis, the rate constants for storage modulus increase caused by the crystal formation were $7{\cdot}24 \times 10^{-4}$, $8{\cdot}91 \times 10^{-4}$, $1{\cdot}38 \times 10^{-3}$, $1{\cdot}48 \times 10^{-3}$, and

Table 2. Effect of concentration of sodium chloride on the storage moduli, the Avrami exponent, the rate constant, and the half-increment time for a 12·5% (w/w) potato starch gel stored at 22°C

Concentration of NaCl (M)	G'_0 (Pa)	G'_∞ (Pa)	Avrami exponent n	Rate constant K (min^{-1})	$t_{1/2}$ (min)
0	65·4 ± 1·8	229·1 ± 3·9	0·66	$1{\cdot}07 \times 10^{-2}$	550 ± 8
0·001	67·7 ± 0·3	244·6 ± 0·3	0·71	$9{\cdot}12 \times 10^{-3}$	446 ± 1
0·01	77·3 ± 1·5	177·1 ± 1·5	0·88[a]	$1{\cdot}40 \times 10^{-2a}$	88 ± 2
			0·50[b]	$7{\cdot}34 \times 10^{-2b}$	
0·1	88·1 ± 1·5	205·5 ± 2·1	0·89[a]	$1{\cdot}41 \times 10^{-2a}$	79 ± 1
			0·50[b]	$7{\cdot}71 \times 10^{-2b}$	
1·0	106·8 ± 2·3	274·9 ± 5·3	0·90[a]	$1{\cdot}10 \times 10^{-2a}$	74 ± 4
			0·50[b]	$7{\cdot}78 \times 10^{-2b}$	

[a]Initial stage of ageing.
[b]Final stage of ageing.

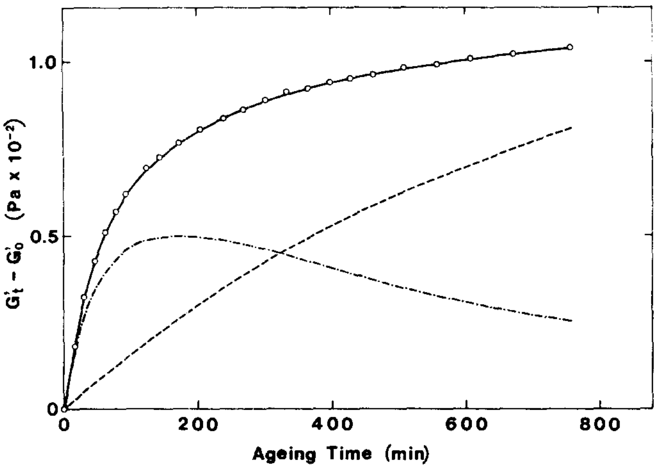

Fig. 6. Typical increases in the storage modulus ($G'_t - G'_0$) of starch paste (12·5%) at the NaCl concentration of 0·1 M as a function of ageing time (—O—) for the entanglement (—•—) and the crystal growth component (----), based on the assumption that the entanglement junction points developed in ageing are completely replaced by the micro-crystallites after 48 h of ageing.

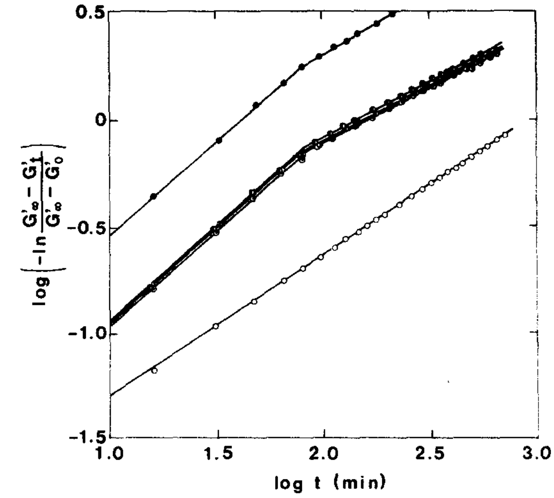

Fig. 7. Plots of the storage modulus measurements of potato starch paste (12·5%) containing the different salts at the level of 0·1 M according to the double logarithmic form of the Avrami equation. O, Without salt; ◉, LiCl; ◑, NaCl; ◐, $CaCl_2$; ●, $AlCl_3$.

$1{\cdot}62 \times 10^{-3}$ min^{-1} for 0, 0·001, 0·01, 0·1, and 1·0 M NaCl, respectively. In this way, the behaviour of starch pastes containing NaCl was quite different from that of starch paste without NaCl, suggesting faster entanglement and crystal formation.

Effect of other salts on ageing

Changes in the storage modulus of starch paste (12·5%) containing the various salts at the constant level of 0·1 M were measured at 22°C. Typical fits of the storage modulus measurements to the double logarithmic form are shown in Fig. 7. The above procedure gives two values of the Avrami exponent for all salts as well as NaCl. Table 3 shows the respective values of G'_0, G'_∞, n, K, and $t_{1/2}$ for starch paste (12·5%) containing the various salts at the constant level of 0·1 M. The data in Table 3 show that the addition of $AlCl_3$ has a large effect on the ageing of starch paste. That is, both the values of G'_0 and G'_∞ were much larger than those of other salts, and the value of $t_{1/2}$ was considerably smaller, indicating that the storage modulus increase for starch pastes is significantly accelerated by adding $AlCl_3$. By using the same procedure as used in Figs 4 and 6, the rate constant for the storage modulus increase caused by the crystal formation were $1{\cdot}40 \times 10^{-3}$, $1{\cdot}48 \times 10^{-3}$, $1{\cdot}53 \times 10^{-3}$, and $4{\cdot}52 \times 10^{-3}$ min^{-1} for LiCl, NaCl, $CaCl_2$, and $AlCl_3$, respectively.

In general, the rate of flocculation or aggregation is influenced by the valency of the ions which are oppositely charged to the colloidal particles, whereas the specific nature of these ions is far less important. The flocculation values for monovalent, bivalent, and trivalent electrolytes differ too greatly, and contain the

Table 3. Effect of various salts on the storage moduli, the Avrami exponent, the rate constant, and the half-increment time for a 12·5% (w/w) potato starch gel stored at 22°C. The concentration of salts was 0·1 M

Salt	G'_0 (Pa)	G'_∞ (Pa)	Avrami exponent n	Rate constant K (min^{-1})	$t_{1/2}$ (min)
LiCl	79·5 ± 1·4	191·9 ± 2·7	0·89[a] 0·51[b]	$1{\cdot}38 \times 10^{-2}$[a] $7{\cdot}32 \times 10^{-2}$[b]	86 ± 4
NaCl	88·1 ± 1·5	205·5 ± 2·1	0·89[a] 0·50[b]	$1{\cdot}40 \times 10^{-2}$[a] $7{\cdot}34 \times 10^{-2}$[b]	79 ± 1
$CaCl_2$	88·6 ± 2·7	204·2 ± 4·2	0·89[a] 0·52[b]	$1{\cdot}47 \times 10^{-2}$[a] $7{\cdot}41 \times 10^{-2}$[b]	74 ± 1
$AlCl_3$	156·7 ± 4·5	284·1 ± 7·3	0·88[a] 0·57[b]	$3{\cdot}80 \times 10^{-2}$[a] $1{\cdot}43 \times 10^{-1}$[b]	27 ± 1

[a]Initial stage of ageing.
[b]Final stage of ageing.

reciprocal valency of the counter-ions to the power of six (Verwey & Overbeek, 1948). Consequently, the rate of storage modulus increase due to the aggregation may be strongly influenced by trivalent electrolytes such as $AlCl_3$.

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