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The effects of concentration and sodium hydroxide on the rheological properties of potato starch gelatinisation

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Abstract

The effects of starch concentration on the gelatinisation of starch in the presence of sodium hydroxide (NaOH) were studied in dispersions containing either fixed NaOH/water ratios or fixed NaOH/starch ratios. Microscopic studies revealed that addition of NaOH to a starch dispersion induced immediate and rapid swelling of the starch granules at room temperature. On heating, granule swelling was more pronounced in the presence of NaOH. At high temperature, the granule remnants were smaller and more disperse in the presence of NaOH. Dynamic rheological measurements revealed a change in gel properties as the ratio of NaOH/water was increased. The storage modulus (G') showed a c^2-concentration dependence (where c is the wt% of starch as a percentage of the total sample weight), at high starch concentrations, in the absence of NaOH. As the NaOH/water ratio was increased, G' decreased for equivalent starch concentrations, probably due to the combination of effects of the size and strength of the filler particles, the influence of ionic strength on solvent quality and charge screening, and the hydrolytic effect of NaOH on the starch chains. In the presence of NaOH and at high starch concentrations, deviations from the c^2-dependence were observed. These may be linked to incomplete chemical gelatinisation by the NaOH. In dispersions with a fixed NaOH/starch ratio of 5:95 measurements of the steady shear (η) and complex viscosities (η^*) were fitted to power law equations and the fitting parameters were then plotted versus starch concentration, c. These data can then be used in the prediction of the viscosity of starch dispersions.

Keywords: Potato starch; Sodium hydroxide; Rheology; Microscopy; Gelatinisation

1. Introduction

Starch is used in numerous industrial and food applications, including as a thickening and gelling agent, as a sizing agent in textiles and as an adhesive for paper and paper products. It can also be used as a backbone for partially biodegradable superabsorbent materials. In its native form, starch exists as semi-crystalline granules, with the extent of crystallinity being around 15–45% (Zobel, 1988). In the majority of applications, the functional properties of starch are obtained by gelatinisation and loss of the crystal structure.

In cold water, starch granules undergo limited reversible swelling, but the integrity of the crystal structure is such that they do not dissolve. Heating a dispersion of starch granules above a characteristic gelatinisation temperature causes them to swell and form gel particles. The swollen particles are generally enriched in amylopectin due to the essentially linear amylose molecules diffusing out of the swollen granules, dissolving and forming a continuous phase outside the granules (Hermansson & Svegmark, 1996). Gelatinisation in foods is normally achieved by thermal treatments. However, low temperature swelling and gelatinisation of starch, can be induced by the addition of aqueous alkali (Wooton & Ho, 1989). This is of limited use in the food industry but can be exploited in non-food applications, such as the adhesives and corrugated cardboard industry, where alkali gelatinisation of starch is of great importance.

The gelatinisation of starch dispersions in water has been studied by a number of authors using rheological techniques (Eliasson, 1986; Hsu, Lu, & Huang, 2000; Janas, 1991; Morikawa & Nishinari, 2000; Rao, Okechukwu, Da Silva, & Oliveira, 1997; Svegmark & Hermansson, 1990, 1991; Tattiyakul & Rao, 2000). Wooton and Ho (1989) investigated the gelatinisation of wheat starch in the presence of alkali using microscopy and rheology. They reported differences in mechanism between alkali and thermal gelatinisation. They also noted that available moisture was a limiting factor in alkali

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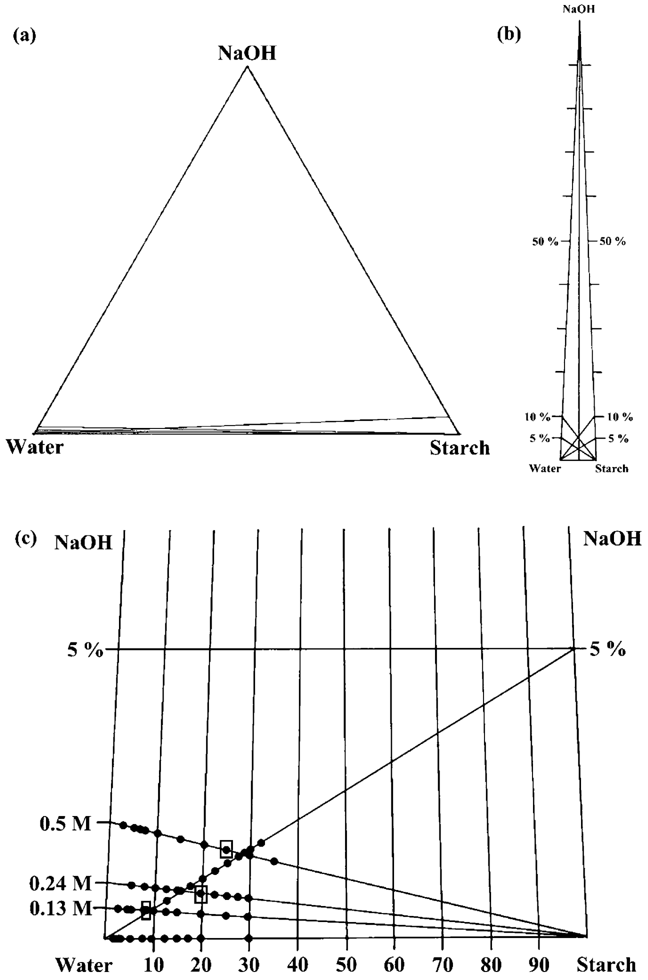

Fig. 1. (a) Phase diagram and (b) modified phase diagram, with extended NaOH axis, of the starch/water/NaOH system. The tie lines in (a) show the conditions for the fixed NaOH/water and fixed NaOH/starch experiments. (c) Magnified view of modified phase diagram showing the tie lines for the fixed NaOH/water and fixed NaOH/starch experiments. Individual experimental points are indicated by the circles. Boxes indicate the points at which the concentration dependence of G' deviated from a c^2-dependence.

gelatinisation, but that there was a scarcity of information concerning the effects of temperature on the starch/water/alkali system. The effect of different alkali solutions on the gelatinisation of rice, maize and wheat starch, was investigated by Ragheb, Abd El-Thalouth, and Tawfik (1995) using rheological techniques. They reported that the treatment of starch with sodium hydroxide was accompanied by some physicochemical changes in the structure of the starch. Their work also showed that the nature and concentration of alkali used had an effect on the rheological properties of the starch pastes.

The aim of the current work is to examine the rheological properties of starch gelatinisation in the starch/water/sodium hydroxide (NaOH) system. The effects of increasing starch concentration in dispersions with fixed NaOH/water ratios, and fixed NaOH/starch ratios will provide a greater understanding of the alkali gelatinisation process.

2. Materials and methods

2.1. Materials

Native potato starch was kindly supplied by AVEBE (Foxhol, The Netherlands). Sodium hydroxide (NaOH) pellets were purchased from BDH and used in the preparation of the NaOH solutions. Distilled water was used in the preparation of starch dispersions. The starch dispersions used in the rheological study were prepared containing either a fixed ratio of NaOH/water, or a fixed ratio of NaOH/starch. In each case the overall concentration of starch (wt%) was varied. The relationship between these two studies can be illustrated using a ternary phase diagram of the type shown in Fig. 1. Fig. 1c shows the sample compositions studied in this paper.

2.2. Microscopic observation of starch gelatinisation

A light microscope (James Swift, UK) fitted with a crossed polar analyser was used to observe the gelatinisation of starch. The starch was dispersed in distilled water on a microscope slide and placed onto a Linkam TC92 hot stage (Linkam Scientific Instruments, UK) in the optical path. The temperature of the hot stage was increased incrementally between 25 and 80 °C and the qualitative extent of granule swelling was noted. The effect of NaOH on the gelatinisation process was observed by adding a drop of 0.5 M NaOH solution to the starch dispersion in distilled water on the microscope slide. The effect of the NaOH solution on the starch dispersion was then recorded at 25 °C, and subsequently at progressively higher temperatures, as the hot stage temperature was raised.

2.3. Rheological observation of starch gelatinisation at a fixed NaOH/water ratio

Starch dispersions were prepared using distilled water, 0.13, 0.24 and 0.5 M NaOH, which gave NaOH wt% in water of 0, 0.52, 0.96 and 2.0%, respectively. Starch dispersions were prepared from these solutions for a range of starch concentrations between 1 and 35 wt%. The dispersions were prepared at room temperature, by addition of dry starch powder to the required amount of stirred distilled water, or NaOH solution.

Small deformation measurements of storage modulus (G'), loss modulus (G'') and complex dynamic viscosity ($\eta^* = (G'^2 + G''^2)^{1/2}/\omega$, where ω is the frequency in rad s^{-1}) were made using a Rheometrics DSR 200 stress controlled rheometer (Rheometrics Scientific Ltd., UK), with a 25 mm diameter, 1 mm gap parallel plate geometry. Temperature control was achieved via an electrically heated lower plate. Starch dispersions were transferred to the rheometer plate, which was held at 25 °C, and their periphery was coated with light silicone oil to minimize evaporation. Following loading onto the rheometer plate, the starch dispersions were heated, at a rate of 1 °C min^{-1}, from 25 to

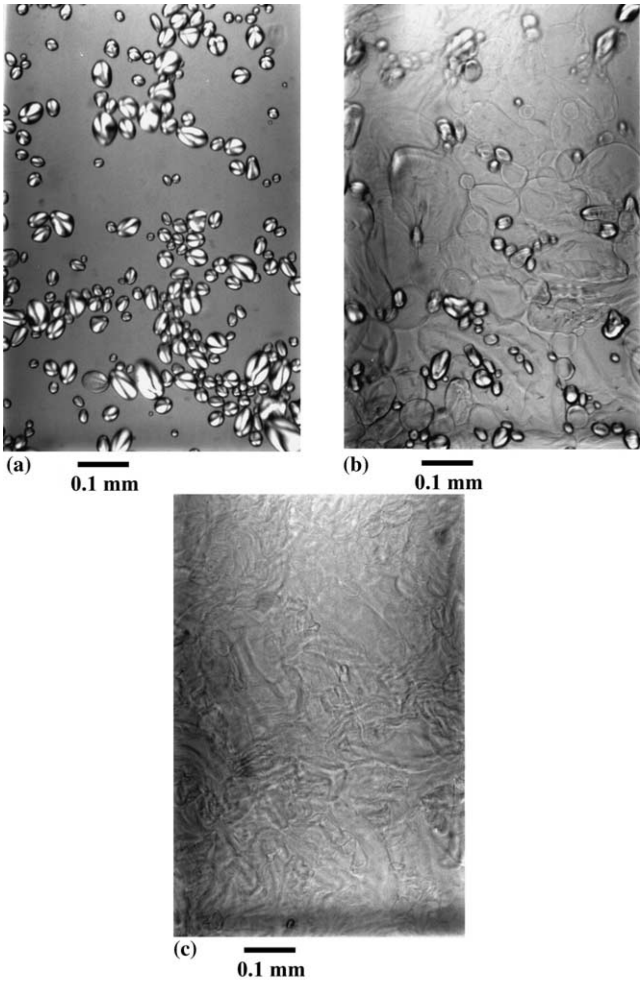

Fig. 2. Starch granules dispersed in distilled water at: (a) 25 °C, (b) 60 °C and (c) 80 °C.

70 °C (80 °C for the dispersions prepared in the absence of NaOH). They were then held for 60 min at the elevated temperature, prior to being cooled to 40 °C. Throughout this heating regime measurements of G' and G'' were recorded. This procedure provides a rheological picture of the gelatinisation process. Following gelatinisation, the frequency dependence of G', G'' and η^* were recorded between 0.1 and 100 rad s^{-1}, at 1% strain and 40 °C.

2.4. Rheological observation of starch gelatinisation at a fixed NaOH/starch ratio

Starch dispersions were prepared with a fixed NaOH/starch ratio of 5:95. The required amount of NaOH, 5 wt% based on the dry weight of starch, was dissolved in a small amount of distilled water and was then added to a stirred dispersion of starch in the remaining distilled water. The starch concentration in the dispersions was varied between 10 and 35 wt% of the total weight of the sample.

The starch dispersions were loaded onto the rheometer plate, held at 25 °C, and their periphery was coated with silicone oil to minimize evaporation. The frequency dependence of G', G'' and η^* were recorded between 0.1 and 100 rad s^{-1} (1% strain), and the shear rate dependence of the steady shear viscosity (η) was recorded between 0.01 and 100 s^{-1}. The dispersions were then heated up to 70 °C, at 1 °C min^{-1}, and held for 15 min, while measurements of G' and G'' were recorded. The measurements of frequency dependence and shear rate dependence were then repeated at 70 °C. The temperature of the lower rheometer plate was then adjusted to 40 °C and measurements of G' and G'' were recorded while the gelatinised starch cooled. A final measurement of the frequency dependence and shear rate dependence was then recorded at 40 °C.

3. Results and discussion

3.1. Microscopic observation of starch gelatinisation

Fig. 2 shows the photographs obtained for a dispersion of starch granules in water. At 25 °C (Fig. 2a) the granules are birefringent due to the lamellar structure. Raising the temperature of the dispersion to 60 °C causes some of the granules to swell and lose their birefringence (Fig. 2b). Further heating results in swelling of all the starch granules, and eventually leads to granule rupture. Remnants of the granule structure are left behind in the gelatinised starch dispersion and can be seen in Fig. 2c, which shows the starch dispersion at 80 °C.

The behaviour of the starch granules in the presence of NaOH is somewhat different. Fig. 3 shows the effects of addition of a drop of 0.5 M NaOH to a dispersion of starch in water. Prior to the addition of the NaOH, the starch granules are birefringent as before (Fig. 3a). Addition of the NaOH solution to the dispersion at 25 °C promotes immediate and rapid swelling of the starch granules, resulting in the photograph shown in Fig. 3b. On heating, the granules continue to swell as can be seen in Fig. 3c, which shows the starch dispersion at 50 °C. Comparing Fig. 3c with Fig. 2b reveals that the extent of swelling is much greater in NaOH than in water, despite the lower temperature. Further heating to 70 °C gives the image shown in Fig. 3d. Almost all of the starch granules have now ruptured, leaving behind remnants of their structure. The gelatinisation of the starch occurs at a lower temperature in the presence of NaOH, and the granule remnants are smaller and less structured than those seen in the water dispersions (compare Figs. 2c and 3d).

3.2. Rheological observation of starch gelatinisation at a fixed NaOH/water ratio

3.2.1. The gelatinisation process

The gelatinisation process was monitored by recording the values of G' and G'' during the heating of the starch suspensions to 70 °C (80 °C for the dispersion in pure water), holding at the elevated temperature and subsequent

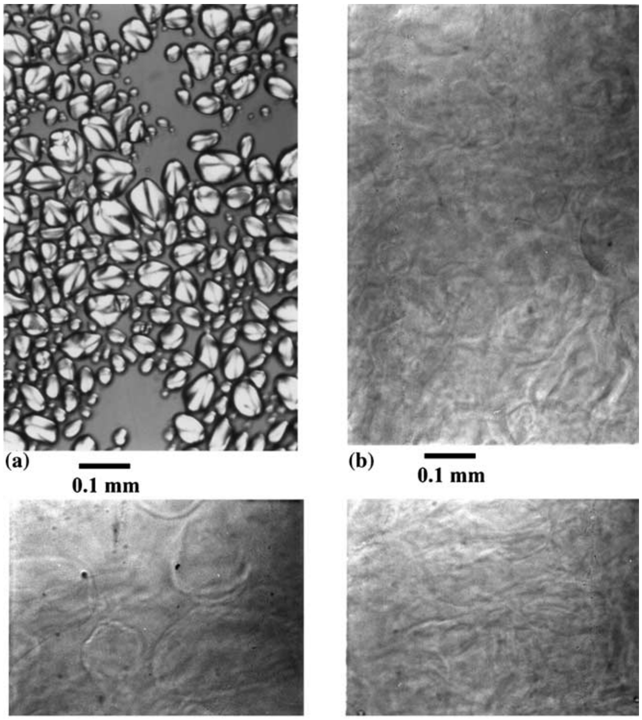

Fig. 3. Starch granules dispersed in distilled water (a) at 25 °C, (b) at 25 °C following addition of a drop of 0.5 M NaOH, (c) following addition of 0.5 M NaOH and heating to 50 °C and (d) following addition of 0.5 M NaOH and heating to 70 °C.

cooling to 40 °C. The temperature profiles of G' and G'' for starch suspensions prepared in distilled water and in 0.13 M NaOH are shown in Fig. 4 and those for suspensions prepared in 0.24 and 0.5 M NaOH are shown in Fig. 5.

In distilled water, the gelatinisation of starch is a thermal process. Recent research (Waigh et al., 2000) suggests that a side chain liquid–crystalline model may be used to explain the structural and thermal changes on the lamellar length scale. The rheological results presented here provide more general, less mechanistic, information. Examination of Fig. 4a and b reveals that initially the values of G'' are greater than G' and remain so until the temperature reaches ~50 °C, after which $G' > G''$. On reaching this temperature there is a rapid increase in the values of G' and G'' up to a peak value, followed by a slight decrease during further heating, eventually resulting in constant values of G' and G'' on holding at high temperature. These features have been studied before. The rapid increase in G' and G'' is due to the hydration and swelling of the starch granules which results in close packing of the granules (Eliasson, 1986). During the swelling of the granules, amylose is leached out from within the granule structure, changing the rheological properties. The starch granules weaken as they swell, and eventually rupture releasing some amylopectin into the dispersed starch matrix. Small fragments of residual granule structure are left behind in the dispersed starch matrix. These will be largely composed of amylopectin and can act as structured filler particles. This leads to the decrease observed in the values of G' and G''. The amylose and amylopectin released from the granules then form a continuous gelled matrix surrounding the remnants of the ruptured granules. At low starch concentrations (<5 wt%) the peak in the values of G' and G'' occurs at a higher temperature because close packing of the starch granules occurs at a greater degree of swelling, due to the lower volume occupied by the starch granules.

The temperature profiles of G' and G'' for starch dispersions prepared in 0.13 M NaOH are shown in Fig. 4c and d, respectively. At starch concentrations greater than 4 wt% of the total sample weight, the behaviour is similar to that described above for dispersions prepared in distilled water. However, at starch concentrations below 4 wt% there is a change in behaviour. Addition of 0.13 M NaOH solution to starch, at these low concentrations, resulted in a clear weak gel at room temperature. The presence of the NaOH causes the starch granules to gelatinise prior to being heated. This is reflected in the absence of a gelatinisation peak in the traces for G' and G'' at the lowest starch concentration shown (2.4 wt%).

Increasing the concentration of NaOH in the starch dispersions to 0.24 M produces the G' and G'' temperature profiles shown in Fig. 5a and b, respectively. The absence of a gelatinisation peak, that was alluded to previously (for 2.4 wt% starch in 0.13 M NaOH), is clear in the plots of G' and G'' for starch dispersions up to a concentration of 19.8 wt% of the total sample weight. At concentrations greater than 19.8 wt%, the values of G' and G'' initially increase, attaining a maximum value at ~50 °C, followed by a decrease to a constant value. At room temperature the starch dispersions were observed to be clear and gel-like for concentrations up to 20 wt%. Above this, the addition of 0.24 M NaOH solution to the starch produced a viscous white paste. On heating, these paste-like dispersions formed clear gels, confirming the differences observed in the temperature profiles of G' and G'' (Fig. 5a and b).

The absence of an initial rise in the values of G' and G'' at starch concentrations below 20 wt% indicates that the starch granules have already achieved close packing, swelling under the influence of the NaOH. At higher starch concentrations there appears to be insufficient NaOH to promote such extensive swelling, leading to the requirement of additional heating to achieve close packing and rupturing of the starch granules. In order to investigate this, two samples of 25 wt% starch were prepared in 0.24 M NaOH. They were then diluted to 12.5 wt%, one with additional 0.24 M

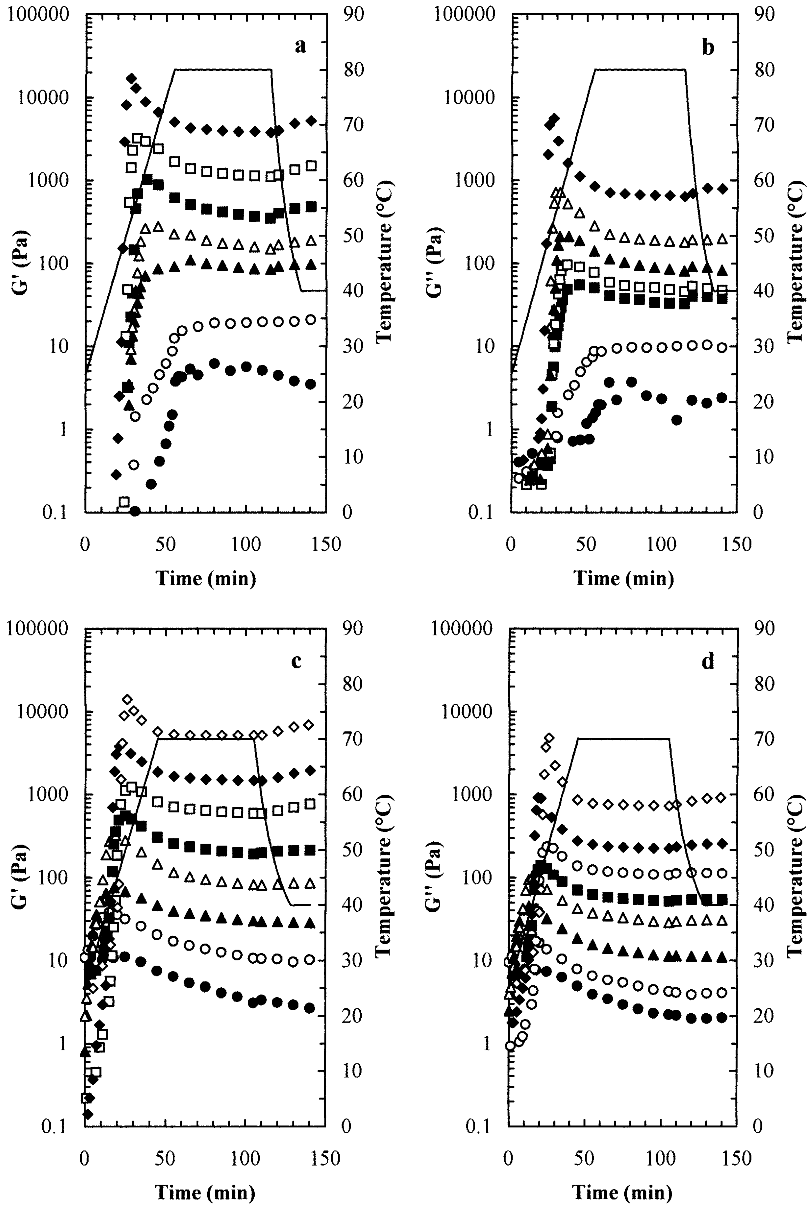

Fig. 4. Temperature profiles of: (a) G' and (b) G'' for starch dispersions in distilled water, at starch concentrations of 2.1 (●), 3.2 (○), 5.5 (▲), 7.8 (△), 12.2 (■), 19.7 (□) and 30.0 (◆) wt%, and temperature profiles of (c) G' and (d) G'' for starch dispersions in 0.13 M NaOH, at starch concentrations of 2.4 (●), 4.2 (○), 5.7 (▲), 8.5 (△), 9.9 (■), 14.3 (□), 19.4 (◆) and 29.3 (◇) wt%, expressed as a percentage of the total weight of the sample. (— Temperature (°C)).

NaOH, and the other with distilled water. The two diluted dispersions were then left at room temperature. Dilution with 0.24 M NaOH produced a clear gel-like sample, whereas the dispersion diluted with distilled water remained white and paste-like. This indicates that the ratio of starch/NaOH influences the room temperature swelling, and gelatinisation of starch by NaOH, and that the differences observed are not solely caused by the changing starch to water ratio.

Raising the concentration of NaOH to 0.5 M resulted in the temperature profiles of G' and G'' shown in Fig. 5c and d, respectively. At all concentrations investigated, the values of G' and G'' decrease on heating. The peak attributable to close packing is not evident in any of the plots. Clear gel-like samples were obtained for all dispersions up to 30 wt% starch. At 35 wt% starch the sample was opaque and gel-like. Although the plots of G' and G'' for this concentration of starch do not have a peak relating to close packing of the granules, they do remain approximately constant during the first 10 min of heating before decreasing to a constant value. There may be a small amount of thermally induced swelling occurring at this high starch concentration, but the effects are somewhat obscured by the high initial values of G' and G'' observed.

A comparison of the four sets of experiments reveals that

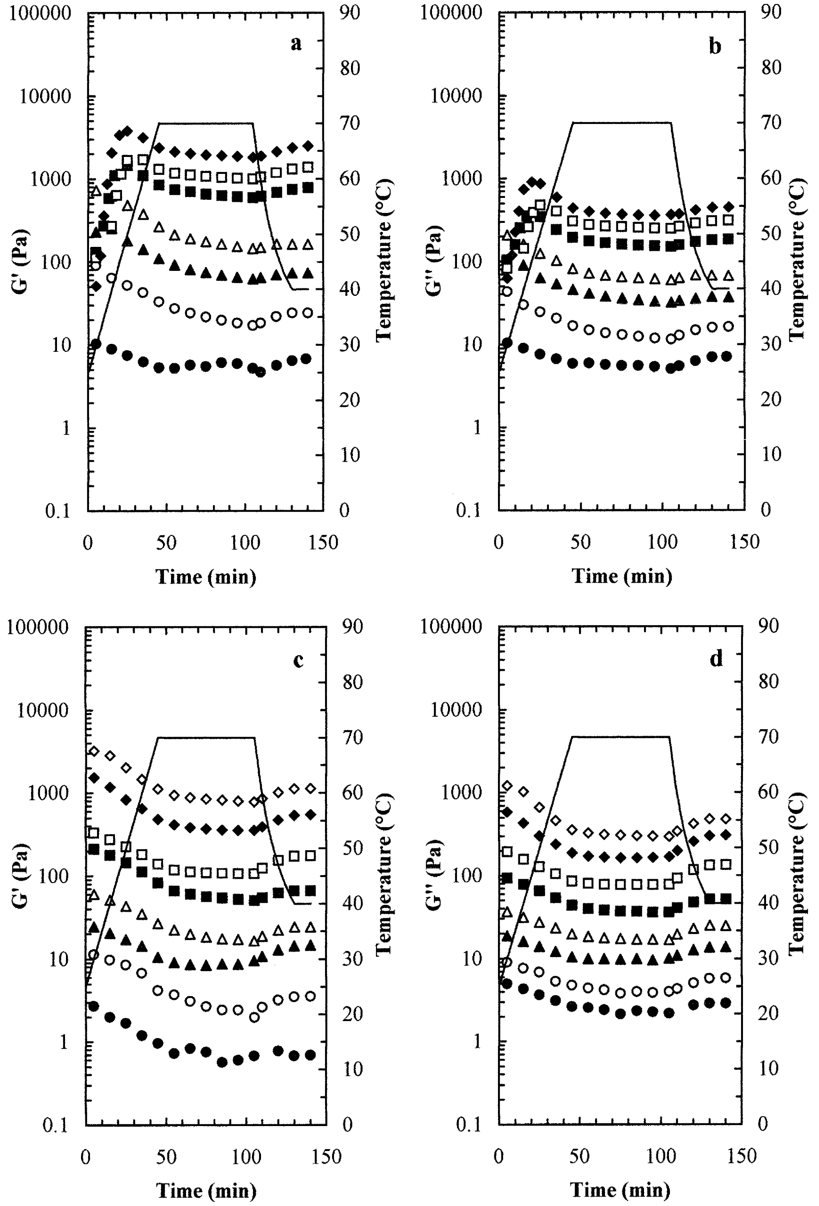

Fig. 5. Temperature profiles of: (a) G' and (b) G'' for starch dispersions in 0.24 M NaOH, at starch concentrations of 7.3 (●), 10.0 (○), 14.7 (▲), 19.8 (△), 22.3 (■), 25.3 (□) and 29.8 (◆) wt%, expressed as a percentage of the total weight of the sample, and temperature profiles of (c) G' and (d) G'' for starch dispersions in 0.5 M NaOH, at starch concentrations of 5.0 (●), 6.2 (○), 10.0 (▲), 14.8 (△), 20.0 (■), 24.8 (□), 30.0 (◆) and 35.0 (◇) wt%, expressed as a percentage of the total weight of the sample. (— Temperature (°C)).

the behaviour on cooling is similar in all cases. The values of G' and G'' increase on cooling due to stiffening of the gel network. It should also be noted that as the concentration of NaOH in the dispersions is increased, the values of G' and G'', for comparative concentrations of starch, decreased. The presence of NaOH in the starch dispersions promotes low temperature gelatinisation of the starch granules, but weakens the resultant gel structure.

In summary, the rheological profile observed on gelatinisation is dependent both on the ratio of starch/NaOH and on the ratio of starch/water. In the absence of NaOH, peaks in G' and G'' are observed on heating, attributable to swelling and rupture of the granules. The more starch, that is per unit of water, the higher and earlier the peak. When the amount of NaOH per starch molecule is relatively high, this peak is entirely lost because granule swelling and rupture occurs on addition of NaOH before heating has begun. At intermediate levels of NaOH, some swelling occurs, but thermal activation is also required and a peak may still be observed on heating.

It is not possible to obtain quantitative information concerning critical ratios of starch/water and starch/NaOH from this experiment because of the several factors contributing to the shape and existence of the peak during gelatinisation. However, it is clear that at intermediate levels of NaOH/starch, both thermal and chemical gelatinisation

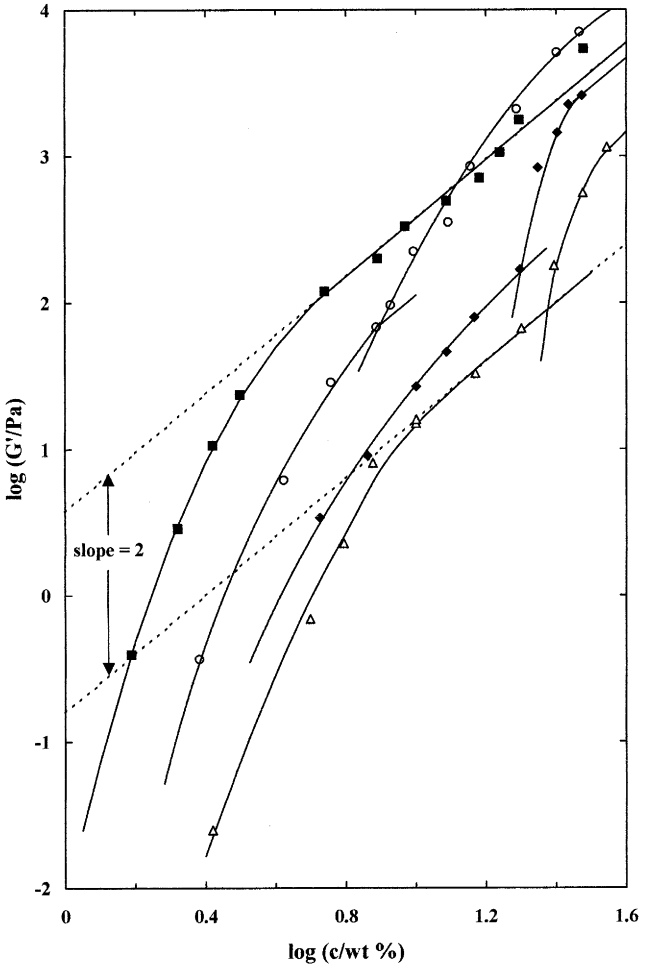

Fig. 6. Concentration dependence of G' (10 rad s^{-1}; 10 Pa stress) for starch gelatinised in distilled water (■), 0.13 M NaOH (○), 0.24 M NaOH (◆) and 0.5 M NaOH (△). Solid lines are guidelines only. Dashed lines have a gradient of 2.

occur, whereas at higher levels, chemical gelatinisation completes the rheological transformation.

3.2.2. The properties of the gelatinised structure

More quantitative information can be gained from a consideration of the properties of the gel when gelatinisation is complete.

For each of the sets of experiments, a plot of log(G'/Pa) versus log(c/wt%), where c is the starch concentration (i.e. the weight of the starch expressed as a percentage of the total weight of the sample), can be used to illustrate the concentration dependence of G' at the end of the heating regime (i.e. at 40 °C when the gelatinisation step is complete). These plots are shown in Fig. 6. The curve for dispersions prepared in distilled water tends towards a slope of ~2 at high concentrations, indicating a c^2-dependence of G'. At the lower concentration end, the slope of the curve increases progressively as the concentration approaches the minimum critical gelling concentration (c_0, the point below which there is insufficient starch to form a continuous network). Curves of this form are typical for gelling biopolymers, and have been shown to occur in a number of systems (Clark & Ross-Murphy, 1985).

The low concentration behaviour of dispersions prepared in NaOH solutions is similar to that observed for dispersions made with distilled water, however the value of c_0 increases as the concentration of NaOH increases. Following the rapid increase in G' above c_0, the three curves are similar in shape but lower in G' than the water values, but then at higher concentrations (>8, 20, and 24 wt% for 0.13, 0.24 and 0.5 M NaOH, respectively) the curves show a second sharp rise in modulus.

The change in the concentration dependence of G' indicates that there is a change in the properties of the final gel structure, as the ratio of NaOH/starch is increased. This can be further illustrated by examining the frequency dependence of G', G'' and η^* for a range of starch concentrations in each set of experiments. The frequency sweep of a concentrated polymer solution would show values of $G'' > G'$, with G'' being proportional to ω and G' proportional to ω^2. The values of η^* would be frequency independent. As the polymer concentration is increased the spectra would show what is known as terminal zone behaviour. The polymer chains begin to interact and η^* values decrease as the chains align themselves under the influence of shear, a process known as shear thinning. The values of G' become greater than G'', as the moduli tend towards a constant value. Once gelation has occurred the values of G' predominate over G'' and are largely frequency independent. The values of η^* decrease linearly with increasing ω, with a slope of approximately -1 (Ross-Murphy, 1994).

Frequency sweeps, recorded following gelatinisation and cooling to 40 °C, for a range of starch concentrations are shown in Fig. 7. The four sweeps in each chart are offset for clarity. The frequency sweeps obtained from dispersions prepared in distilled water (Fig. 7a) show a strong gel response for all starch concentrations. The values of G' and G'' are predominantly frequency independent and η^* decreases across the entire frequency range with a slope approaching -1, which is indicative of true gel-like behaviour (Ross-Murphy, 1994). Similar behaviour is observed for the dispersions prepared in 0.13 M NaOH (Fig. 7b), with gel-like spectra obtained for all starch concentrations. Increasing the concentration of NaOH in the dispersions to 0.24 M results in a change in the spectra at low concentrations (Fig. 7c). The values of G' and G'' are now more frequency dependent and closer together, resulting in higher values of tan δ (tan $\delta = G''/G'$). These spectra indicate that the gel structure is less cohesive and more liquid-like in its nature. In the spectrum shown for 7.3 wt% starch, the values of G' and G'' are almost identical, indicating that the starch is on the point of gelation. The final set of spectra obtained from dispersions prepared in 0.5 M NaOH (Fig. 7d) have frequency dependent values of G' and G'' for all starch concentrations, accompanied by values of tan δ that are close to 1. The high concentration of NaOH therefore

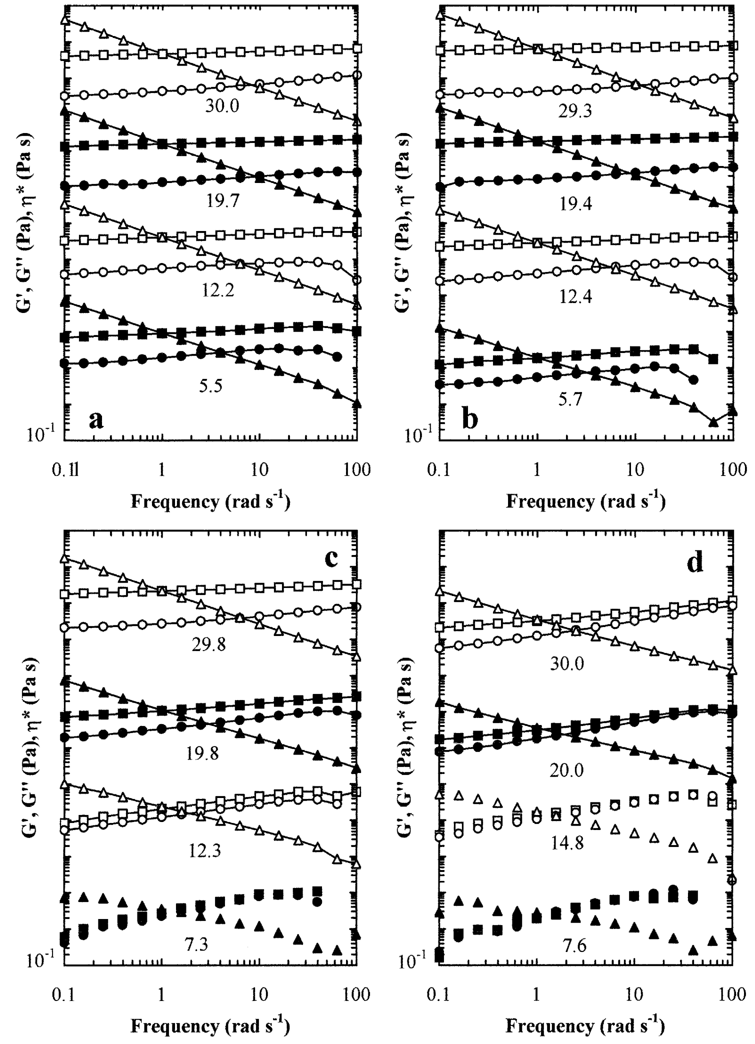

Fig. 7. Frequency dependence (40 °C; 1% strain) of G' (squares), G'' (circles) and η^* (triangles) for starch dispersions after the gelatinisation treatments described in the text, prepared in (a) distilled water, (b) 0.13 M NaOH, (c) 0.24 M NaOH and (d) 0.5 M NaOH. The starch concentration (wt% of the total sample weight) is given below each data set. The y-axis ranges from 10^{-1} to 10^{11}, and the data sets are scaled by factors of 10^0, 10^2, 10^4 and 10^6 as the starch concentration increases.

produces gels that are much less cohesive than those observed in dispersions of distilled water.

The transition from true gel-like behaviour towards a more fluid system (Fig. 7), coupled with the deviations observed in the concentration dependence of G' (Fig. 6), indicate that there is a change in the final structure of the gels obtained as the amount of NaOH is increased. The microscopy experiments revealed that there were remnants of granule structure present in the gelatinised starch following the combined action of NaOH and heating (Fig. 3d). They were however smaller and fewer structures than those observed in distilled water after heating (Fig. 2c). Smaller, less structured filler particles would account for the lower values of modulus observed (Fig. 6), and the changes in the frequency dependencies of G', G'' and η^* (Fig. 7). The deviation in the concentration dependence of G' towards higher values, at high concentrations of starch (Fig. 6), may then be due to the presence of larger, more structured granule remnants which are disrupted to a lesser degree by the action of the NaOH because of the lower amount of NaOH per starch molecule. The presence of filler particles such as these would strengthen the gel structure, resulting in the observed changes in the frequency sweeps, and the increase in the concentration dependence of G'.

Addition of NaOH to the starch dispersions also introduces small ions to the system, affecting the polyelectrolyte properties of the polymer. Hydroxyl groups may promote charge screening of the junction zones on the starch chains, disrupting the hydrogen bonding which causes the formation of a gel. This would weaken the starch network and produce the more fluid-like gels observed in the frequency sweeps. The effect of ions within the solvent on the gelatinisation process and the properties of the resulting gel is complex and depends on the nature and concentration of the ions present. The gel modulus may be raised or lowered depending on the exact conditions used. This has been

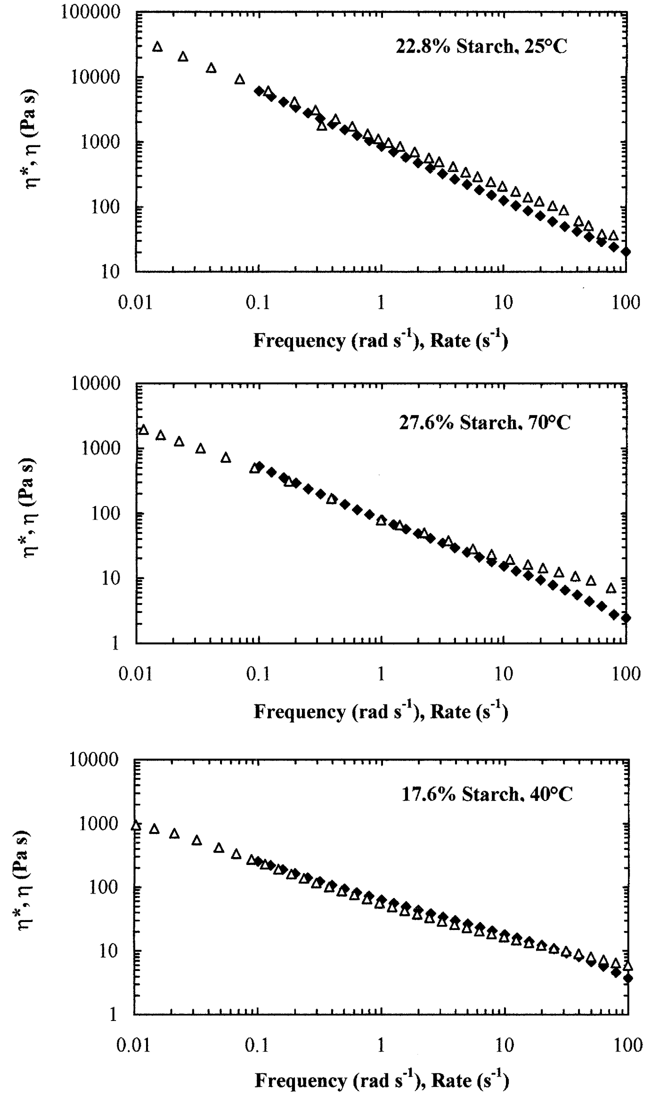

Fig. 8. Shear rate dependence of η (△) and frequency dependence of η^* (◆) at equivalent numerical values of shear rate and frequency, illustrating compliance with the Cox–Merz rule, for samples observed at 25 °C (before gelatinisation) and at 70 and 40 °C (after gelatinisation) as described in the text, at a fixed NaOH/starch ratio of 5:95.

studied in neutral solution by Ahmad and Williams (1999) and Jane (1993). However, the effect of neutral salts on gel strength is generally smaller in magnitude than those seen here, and is unlikely to fully explain the changes observed.

Base hydrolysis of the starch chains may also be occurring in the presence of NaOH (Ragheb, Adb El-Thalouth, & Tawfik 1996). This would shorten the starch chains and higher starch concentrations would be required to form a continuous starch network, raising c_0, the critical gelling concentration. The observed differences in behaviour for the starch gels prepared in distilled water, 0.13, 0.24 and 0.5 M NaOH are therefore probably the result of a combination of the size and strength of the filler particles, the influence of ionic strength on solvent quality and charge screening, and the hydrolytic effect of NaOH on the starch chains. Each of these factors may lower the modulus at higher concentrations of NaOH, although it is not possible to gauge their relative importance.

The abrupt change in slope of the concentration dependence of G' occurred at starch concentrations of approximately 8, 20 and 24 wt% for 0.13, 0.24 and 0.5 M NaOH, respectively. The ratio of NaOH/starch at these points is 6:94, 4:96 and 6:94, that is, it is approximately constant at about 5:95. The three points are highlighted in Fig. 1c to show where they lie in relation to the series of experiments that were carried out with a fixed NaOH/starch ratio of 5:95. The dispersions prepared at this ratio of NaOH/starch are therefore at the limit of the regions with a c^2-dependence of G'. If the amount of NaOH falls below this critical ratio, the modulus of the gel increases sharply.

It seems reasonable to conclude that the ratio of NaOH/starch of 5:95 represents the critical ratio at which the starch will be fully chemically gelatinised by the NaOH. This is equivalent to one mole of NaOH for every 5 mol of starch monomer. This critical NaOH/starch ratio is rather lower than that reported by Ragheb et al. (1995), in their study of the gelatinisation of maize starch in the presence of NaOH. However, these authors were observing the visual appearance of the pastes rather than the rheological properties. It is interesting to note that although the ratio of water/starch affects the overall value of the modulus, it would appear that the ratio of NaOH/starch is critical in determining whether complete chemical gelatinisation occurs.

3.3. *Rheological observation of starch gelatinised at a fixed NaOH/starch ratio*

From the above analysis it is apparent that a ratio of NaOH to starch of 5:95 provides a convenient maximum value for the starch component in processing since increasing the amount of starch further gives a sharp rise in gel modulus, whatever the ratio of water/starch. We therefore present a full rheological characterisation of starch gelatinised at a fixed NaOH/starch ratio of 5:95, with varying water content.

The flow properties of the starch dispersions containing a NaOH/starch ratio of 5:95 were recorded after initial preparation at 25 °C, after heating to 70 °C and following cooling to 40 °C. Measurements of both the steady shear viscosity (η) and the complex viscosity (η^*) were recorded at each temperature, and then compared for numerically equivalent values of shear and frequency. At each temperature the viscosity values increased with increasing starch concentration, and decreased linearly across the range of experimental shear rates and frequencies. Fig. 8 shows a typical set of results for each temperature. These plots reveal that the values of η and η^* are almost identical for the range of shear rate and frequency examined. Behaviour of this type has been observed in a number of polymer systems in which the frequency dependence of η^* and the shear rate dependence of η are closely superposable at

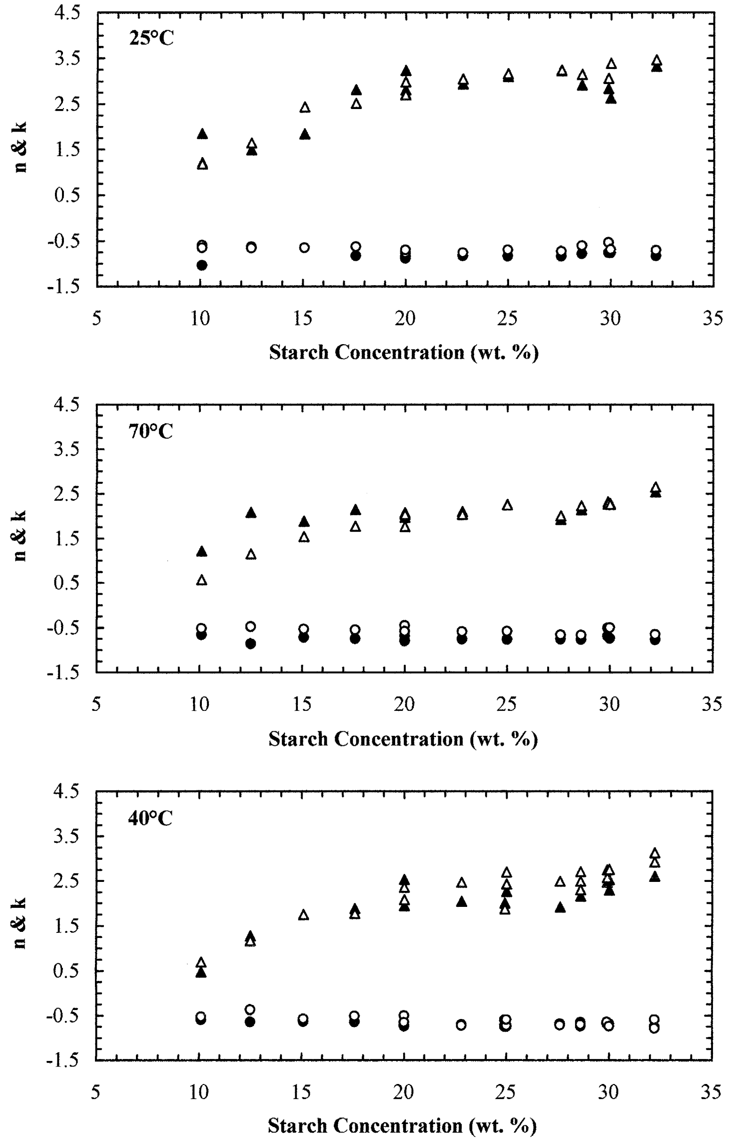

Fig. 9. Concentration dependence of the fitting parameters n (circles) and k (triangles) derived from log–log plots of η versus $\dot{\gamma}$ (open symbols) and η^* versus ω (filled symbols), for samples observed at 25 °C (before gelatinisation) and at 70 and 40 °C (after gelatinisation) as described in the text, at a fixed NaOH/starch ratio of 5:95. The concentration of starch is given as a wt% of the total weight of the sample.

numerically equivalent values of frequency and shear rate (Cox & Merz, 1958).

Log–log plots of η and η^* show a linear decrease with increasing shear rate ($\dot{\gamma}$) and frequency (ω). These linear dependencies were fitted to power law equations of the following type.

$$\eta = K\dot{\gamma}^n \tag{1}$$

$$\eta^* = K\omega^n \tag{2}$$

Taking logs of these equations we obtained the following equations, from which we extracted the fitting parameters n and k (where $k = \log K$)

$$\log(\eta) = n\log(\dot{\gamma}) + k \tag{3}$$

$$\log(\eta^*) = n\log(\omega) + k \tag{4}$$

Plots of log(η or η^*) versus log($\dot{\gamma}$ or ω) were then used to obtain values of n (gradient) and k (the intercept) for each of the starch dispersions analysed.

The values of n and k obtained were then plotted versus starch concentration for each temperature. The results are shown in Fig. 9. The value of n remains virtually constant across the entire concentration range and is also unaffected by the changes in temperature. Thus, the shear thinning behaviour of the starch gels is independent of starch concentration and temperature in the range studied. The values of k increase with increasing starch concentration, tending towards a linear increase at higher concentrations. The values of k at 25 °C are higher than those observed at 70 °C, reflecting the weakening of the gel structure due to rupturing of the starch granules. On cooling to 40 °C the gels stiffen slightly, but the change is very small and the values of k are almost identical.

4. Conclusions

Microscopy revealed that addition of NaOH to a dispersion of starch granules causes them to swell instantaneously. Heating the NaOH treated starch dispersion caused further swelling, leading to rupturing of the granules. The swelling observed in NaOH treated dispersions were greater than that observed in distilled water, and the granule remnants were smaller and more homogeneous than those observed in distilled water.

Rheological observation of dispersions with different fixed NaOH/water ratios revealed that gelatinisation in the presence of NaOH involved both chemical and physical mechanisms. If the amount of NaOH is greater than in a ratio of NaOH/starch of 5:95, gelatinisation was predominantly brought about by the action of the NaOH, which resulted in a c^2-dependence of G'. As the amount of starch was increased, the ratio of NaOH/starch decreased, and the values of G' rose sharply to values closer to those of starch gelatinised in pure water. In these cases, gelatinisation resulted from a combination of the effects of NaOH and heating. The values of modulus are probably the result of a combination of the effects of size and strength of the filler particles, the influence of ionic strength on solvent quality and charge screening, and the hydrolytic effect of NaOH on the starch chains. Each of these effects tend to produce a lower modulus at higher NaOH concentrations.

The NaOH/starch ratio was then fixed at 5:95 (i.e. 5 wt% NaOH based on the dry weight of starch), which allowed the rheological properties of NaOH gelatinisation to be studied. The flow properties were modelled using power law type equations. Extraction of the fitting parameters n and k at different temperatures enables us to be able to predict the viscosity of starch dispersions at concentrations between 10 and 30 wt%. This ratio of NaOH to starch gives a convenient maximum starch content for processing since it represents the value above which a sharp rise in gel modulus occurs.

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