Carbohydrate Polymers 32 (1997) 131–139
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0144-8617/97/$17.00 + .00

ELSEVIER PII: S0144-8617(96)00160-9

The gelation of dialdehyde starch

S. Veelaert,[a]* D. de Wit,[a] K.F. Gotlieb[b] & R. Verhé[c]

[a]ATO-DLO, Agrotechnological Research Institute, PO Box 17, 6700 AA Wageningen, The Netherlands
[b]Wildervankstraat 12, 9648 LC Wildervank, The Netherlands
[c]University of Ghent, Faculty of Agricultural and Applied Biological Sciences, Coupure links 653, 9000 Ghent, Belgium

(Received 8 March 1996; revised version received 9 July 1996; accepted 14 July 1996)

The rheological behaviour of periodate oxidized potato starches has been investigated in both dilute and concentrated aqueous dispersions. On heating, low viscosity solutions were obtained at low concentrations and viscoelastic gels at high concentrations. During the gelation process, two types of gel structure were distinguished. First a particle gel is formed, and on continued heating and shearing, deformation and disruption of the granules is observed, resulting in the formation of a polymer network. The increasing stability of the particle gels with increasing degree of oxidation has been attributed to an increase in particle rigidity. The aldehyde groups in dialdehyde starch are supposed to reinforce the granular structures, as a result of intragranular hemiacetalization. The gel stability could be improved by adding native potato starch to the premix. © 1997 Elsevier Science Ltd

INTRODUCTION

Dialdehyde starch, obtained after periodate oxidative cleavage of the C2–C3 bonds in the anhydroglucose units of starch, is an interesting product with several viable industrial applications (Tegge, 1960; Beduneau, 1961; Borchert, 1961; Mehltretter, 1966; Mehltretter, 1967; Radley, 1976; Tegge and Mayer, 1984). In particular, in the paper industry dialdehyde starch has been proven to be very effective as a wet-strength improver (Hofreiter *et al.*, 1960; Hofreiter *et al.*, 1974; Laleg and Pikulik, 1993). In the 1950s research had already started into the properties of the oxidized product (Sloan *et al.*, 1956; Mellies *et al.*, 1958; Levine *et al.*, 1959). It was stated by Sloan *et al.* (1956) that at higher levels of oxidation corn starch does not gelatinize in the manner characteristic of starch. The granules have to be heated for a certain time at 90°C, depending on the degree of oxidation, to exhibit some swelling. Light-scattering, sedimentation, and viscosity measurements have shown that the average particle weight in solution generally decreases with increased level of oxidation and time of heating (Levine *et al.*, 1959). The depressed viscosity of dialdehyde starch dispersions was attributed to the degree of swelling and fragmentation of the granules (Mellies *et al.*, 1958).

Although much research has been performed on dispersion properties of dialdehyde starch, actual knowledge on this subject is too limited for further applications. Most of the applications of dialdehyde starch are based on a crosslinking reaction with, e.g. cellulose in paper, cotton in textiles or proteins in pharmaceuticals or leather. To make use of the complete potential of dialdehyde starch, i.e. its chain length and functionality, the polyaldehyde macromolecules have to be dispersed in water with minimal depolymerization.

The 'gelatinization' of dialdehyde starch was investigated in our laboratory to elucidate its actual behaviour during heating in an attempt to reevaluate dialdehyde starch as a macromolecular crosslinking agent. Both polymeric degradation and physical transitions were of interest. The results reported in this paper cover the influence of concentration, degree of oxidation, shearing forces and the addition of native potato starch on the rheological and mechanical properties of oxidized potato starches. A following paper will cover the polymeric degradation during heating of dialdehyde starch suspensions at different pH values. Upon heating at 90°C and below pH 4 degradation occurs but to a very low extent. Under neutral conditions, on the other hand, the average molecular weight decreases very rapidly (Veelaert *et al.*, 1996).

MATERIALS AND METHODS

Materials

Dialdehyde starches with different degrees of oxidation, have been synthesized by periodate oxidation of potato

---

*To whom correspondence should be addressed.

starch (PS) as described earlier (Veelaert *et al.*, 1995). Potato starch was supplied by Avebe (Foxhol, The Netherlands) and analytical grade sodium periodate was purchased from Merck. The oxidation was performed in a 10 wt% aqueous suspension at pH 3 and 25°C in the dark. After filtration and washing, the products were freeze-dried. Consequently, the dried products were sieved and the granular fraction smaller than 150 μm was applied for rheology measurements. The degree of oxidation (DO) of the oxidized starches was determined chromatographically after reduction and hydrolysis and represents the percentage of oxidized anhydroglucose units (Veelaert *et al.*, 1995). A dialdehyde starch with a DO equal to a percentage X, will be called DAS-X. X refers to the percentage of anhydroglucose units oxidized to a dialdehyde. Beyond a degree of oxidation of 30% the materials did not show any significant X-ray diffraction. Oxidation occurred in a random way, without any preference for either amylose or amylopectin at least at degrees of oxidation above 5% (Veelaert *et al.*, 1995). The moisture content of each type of starch was determined by measuring the decrease in weight while heating the powder at 95°C in a Sartorius moisture analyser (MA 40).

Viscosity changes during gelatinization

The desired amount of dialdehyde starch (dry weight) was suspended in 400 ml of demineralized water and stirred for 5 min. The resulting suspension was added to the measuring unit of the Brabender Viscograph-E. While stirring at 75 rpm the temperature was increased from 30° to 90°C at a rate of 1.5°C/min, and kept at 90°C for at least 15 min. The dialdehyde starch concentration was varied in a range between 5 and 20 wt%. For some purposes, which will be explained later, the volumes of the suspensions were reduced to 250 ml.

Viscoelastic measurements during gelation

A dialdehyde starch suspension was preheated in the Brabender Viscograph to 75°C for DAS-50 and 85°C for DAS-100. In a different series of experiments the total dry weight concentration varied from 5 to 18 wt%. The storage modulus G' and loss modulus G'' were recorded in a Bohlin VOR Rheometer. Gelation was followed on heating the suspension in concentric cylinder geometry (C14). The rheometer was fitted with a 293.2 g cm torsion bar. The starting temperature was 60°C for DAS-50 and 75°C for DAS-100. During oscillation, the temperature was increased to 90°C with a heating rate of 2°C/min and held at 90°C for about 1 h. Every 30 s the moduli were recorded at a strain of 0.01 and a frequency of oscillation of 5 or 0.1 Hz. At the applied strain all samples showed linear viscoelastic behaviour, which means that the amplitude of stress and strain were proportional to each other. To avoid evaporation of water during heating, the samples were covered with a thin film of paraffin oil, which was easy to perform in the concentric cylinder geometry. In comparison with other configurations, the one described appeared to give the best results with respect to the reproducibility of the measurements.

RESULTS AND DISCUSSION

'Gelatinization' of dialdehyde starch

The Brabender Viscograph was employed to measure the 'gelatinization' process of dialdehyde starches at continuous deformation. The term gelatinization is not exactly appropriate to describe the changes that occur during heating of dialdehyde starch in excess water, for gelatinization is generally supposed to correspond to an order–disorder transition accompanied by high swelling and amylose leakage. In earlier research any granular or crystalline ordering was demonstrated to be absent in dialdehyde starches with degrees of oxidation above 30% (Veelaert *et al.*, 1995). Furthermore, the high integrity of dialdehyde starch granules is responsible for low degrees of swelling.

In a first series of experiments the gelatinization of 4.5 wt% suspensions has been studied for several dialdehyde starches with varying degree of oxidation (DO). From the resulting viscosity profiles, shown in Fig. 1, it can be concluded that with rising degree of oxidation the viscosity response decreases, while onset and peak temperatures shift to higher values. Values of onset temperature, peak temperature and peak viscosity are listed in Table 1.

As expected, the behaviour of starch is significantly influenced by the introduction of aldehyde groups upon oxidation. Besides effecting a decrease in crystallinity and hydrophilicity, the C2 and C3 aldehydes are prone

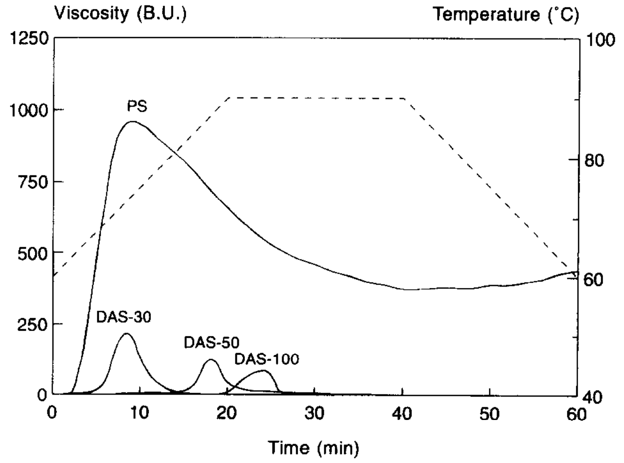


Fig. 1. The Brabender curves for 4.5 wt% suspensions (sample volume 400 ml) of native potato starch (PS), DAS-30, DAS-50 and DAS-100. ——— Viscosities; - - - - temperature.

Table 1. Onset temperature (T_{onset}), peak temperature (T_{peak}) and peak viscosity in Brabender Units (B.U.) for 4.5 wt% suspensions of dialdehyde starches with different degrees of oxidations, recorded during heating in a Brabender Viscograph

	T_{onset} (°C)	T_{peak} (°C)	B.U
PS	61	74	3840
DAS-30	65	71	865
DAS-50	80	86	392
DAS-100	90	90	360

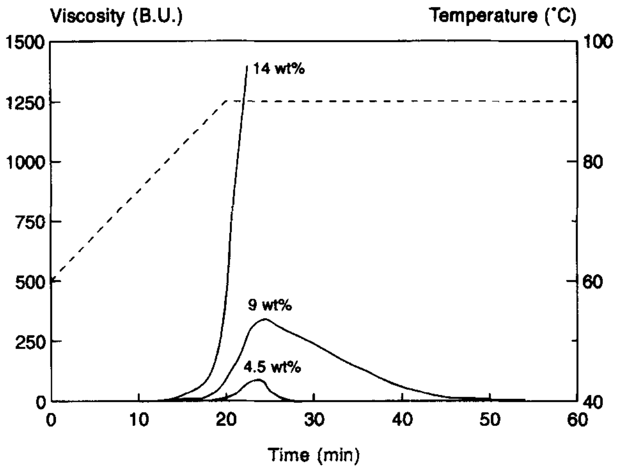


Fig. 2. The Brabender curves for DAS-100 suspensions at different concentrations: 4.5, 9 and 14 wt% (sample volume 400 ml).

to form several inter- and intramolecular hemiacetal and acetal linkages. These linkages can be considered as intragranular crosslinks, inducing a reinforcement of the granules. Consequently, in spite of the amorphous character, the tendency to interact with water at elevated temperatures becomes lower upon oxidation, and this results in retarded swelling and a lower viscosity response. Since no chemical analysis method is known to determine the amount of crosslinks in this complex dialdehyde starch structure, physical observations are used to characterize the granular composition.

Besides a lower peak viscosity, the graphs presented in Fig. 1 also show very low final viscosity for the dialdehyde starch dispersions. In fact, upon prolonged heating the dispersions turned into yellow coloured aqueous solutions, accompanied by a slight decrease in pH from ±4.5 to ±4.

The results concerning the poor swelling of dialdehyde starch and its low viscosity development on continued heating are in agreement with previous results (Sloan *et al.*, 1956; Mellies *et al.*, 1958; Levine *et al.*, 1959). The low viscosity, however, cannot be attributed to polymeric degradation alone. Any relation, arbitrarily or not, between the viscosity of a native starch paste and its molecular weight is not applicable for dialdehyde starch due to its deviating conformation, functionality and hydrophilicity.

Gelation of macromolecules is in general only possible above a critical concentration which is dependent on the physicochemical structure and the degree of polymerization of the polymer. A concentration of 4.5 wt% is too low to form a dialdehyde starch gel. Consequently, heating results in dissolution or at least complete dispersion without the occurrence of abundant intermolecular interactions and eventually depolymerization.

Another set of experiments was performed, increasing the concentration of dialdehyde starch gradually. The resulting viscosity profiles are depicted in Fig. 2. Although peak viscosity was higher at 9 wt%, at least compared to the 4.5 wt% suspension, the viscosity still dropped very rapidly during measurement. At 14 wt%, however, the total mass formed a gel, which could yet not be stirred by the Brabender apparatus. Because of blocking of the spindles, i.e. the stirring part of the Brabender Viscograph, any further thermal or mechanical degradation of the gel on prolonged heating could not be detected with this procedure. From these experiments a 'critical concentration for gelation' is assumed to be between 9 and 14 wt%. Below this concentration the material dissolves to give a low viscosity solution and above it the material forms a gel. In this respect it is notable that gelation also occurred during thickening of a dilute dialdehyde starch solution on evaporation of water.

In order to characterize the formation and stability of the highly viscoelastic dialdehyde starch gels and to detect a more precise 'critical concentration for gelation', the volume of the dialdehyde starch suspension in the viscograph was reduced from 400 to 250 ml. The torque effected by the gel was thus prevented from exceeding the limit of the apparatus and an extended gelation profile was recorded, for both DAS-100 and DAS-50. Some viscosity profiles, recorded at concentrations in a range from 11 to 18 wt%, are depicted in Fig. 3(a and b) to illustrate the influence of concentration and degree of oxidation. Besides the already mentioned effects of oxidation, i.e. the increase of onset temperature and the decrease of peak viscosity, some other interesting phenomena were observed. The most notable feature was the appearance of two peaks at a concentration of 13 wt% or more, irrespective of the degree of oxidation. The measured decrease in viscosity found half-way through the gelatinization process might be explained by slippage. Microscopic analysis, however, revealed that significant structural changes take place during this viscosity decrease.

The extent of oxidation had a strong influence on the gel stability. This was demonstrated by the relatively high final viscosity for the 18 wt% DAS-100 gel; the DAS-50 gel was characterized by a very rapid viscosity drop, although its peak viscosity was higher. Both the appearance of two peaks and the gel stability will be referred to in further discussions.

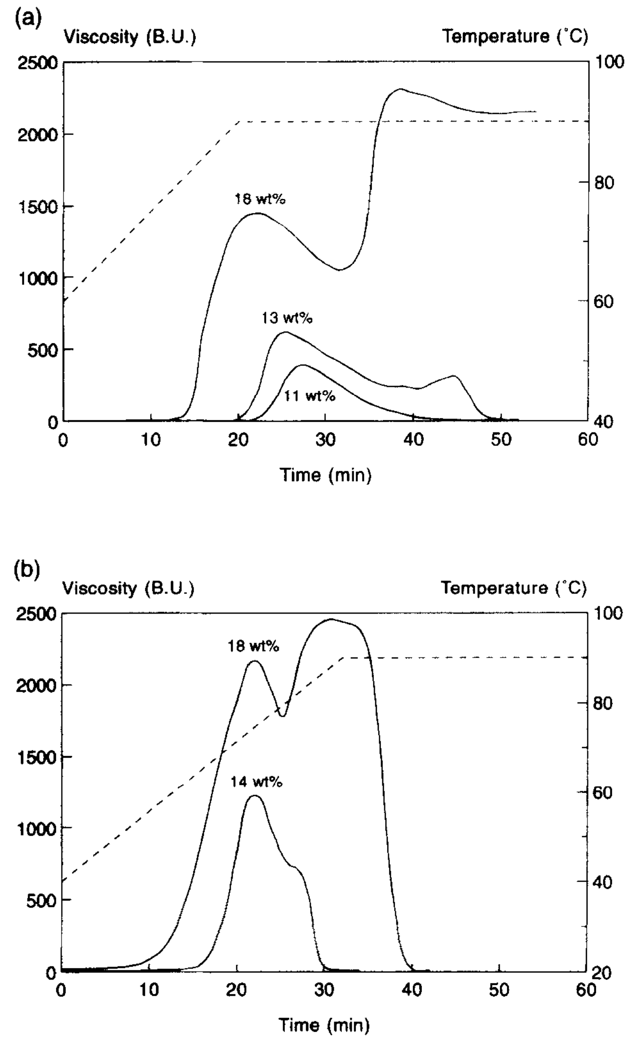


Fig. 3. The Brabender curves for DAS suspensions at reduced sample volume (250 ml): (a) DAS-100; 11, 13 and 18 wt% concentration; (b) DAS-50; 14 and 18 wt% concentration.

Microscopic studies

The gel structure corresponding to the first peak appeared to consist of a granular aggregate; therefore it can be termed a particle gel (Fig. 4). The granules were swollen but still regularly oval shaped. Upon continued heating, the granules lost their shape (Fig. 5), corresponding to the decrease in viscosity. At the second peak most granules had disappeared. The gel was almost homogeneous, transparent and had a faint yellow colour (Fig. 6).

The complete gelation mechanism can thus be considered as the combination of several processes. First, the dialdehyde starch granules swell until a particle gel is formed by touching granules. This gel is disrupted due to shearing and heating in the apparatus. This gel destruction is mainly attributed to a weakening and deformation of the granules until these are completely disrupted and corresponds with the measured viscosity decrease. Of course, slippage occurred simultaneously. Once disrupted, the polymeric molecules released from the granules might aggregate, at least if present in a sufficient concentration, and form a highly elastic network (second peak). This network, formed by physical entanglements and chemical crosslinks, is capable for absorbing a relatively high volume of water (up to 8 times its own weight under these conditions), and might be considered as a weak hydrogel. In its turn, this type of gel is destructured upon further heating and stirring until finally a low viscosity solution is obtained. The low viscosity, is only partly attributable to a decrease of the molecular weight (Veelaert *et al.*, 1996), since cooling and then ageing this solution for one day at room temperature results in gel formation.

Fig. 4. DAS-100 particle gel at the first viscosity peak (10×).

Fig. 5. DAS-100 particle gel between the two viscosity peaks (10×).

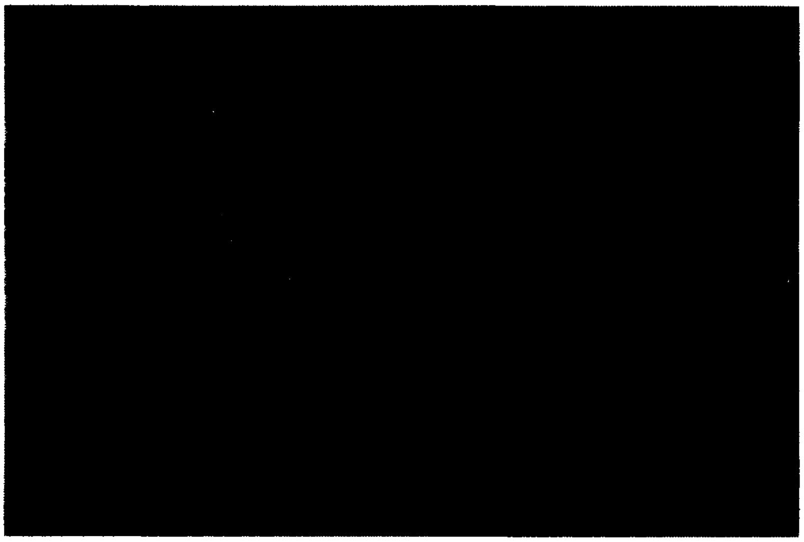


Fig. 6. DAS-100 gel at the second viscosity peak (10×).

Viscoelastic measurements

Gelation was followed in the Bohlin VOR Rheometer at small oscillatory deformations. The measured viscoelasticity was characterized by the storage modulus G' and the loss modulus G''. The ratio G''/G' ($=\tan\delta$) is used to evaluate the elasticity of the gel. A decrease in the phase lag δ corresponds to a transition from a more fluid-like to a more solid-like material or, in other terms, from a viscous to an elastic response. The 'gel-point' can be characterized by a $\tan\delta$ value equal to one, but this is often influenced by the frequency of oscillation; a maximum G'' value is an alternative criterion (Doublier *et al.*, 1992).

Prior to gelation in the Bohlin Rheometer, DAS-100 and DAS-50 samples were preheated to 85° and 75°C, respectively. The swelling process was thus allowed to start outside the measuring unit in order to obtain stable suspensions of slightly swollen particles which did not sediment during oscillation. The influence of concentration and degree of oxidation will be discussed successively.

Influence of concentration

Some viscoelastic data, recorded at a frequency of 5 Hz, are depicted vs time in Fig. 7(a–c) for 10, 14 and 18 wt% DAS-100 suspensions, respectively. From the development of $\tan\delta$ vs time, a transition from a viscous material ($\tan\delta > 1$) to an elastic one ($\tan\delta < 0.1$) is obvious after short heating for 30–45 min at 90°C. The elastic character rose with increasing concentration. Between the 10 and the 14 wt% gels only slight differences were observed, except for the appearance of a second G' peak after 45 min for the latter gel. The 18 wt% gel was characterized by relatively strong elastic and viscous

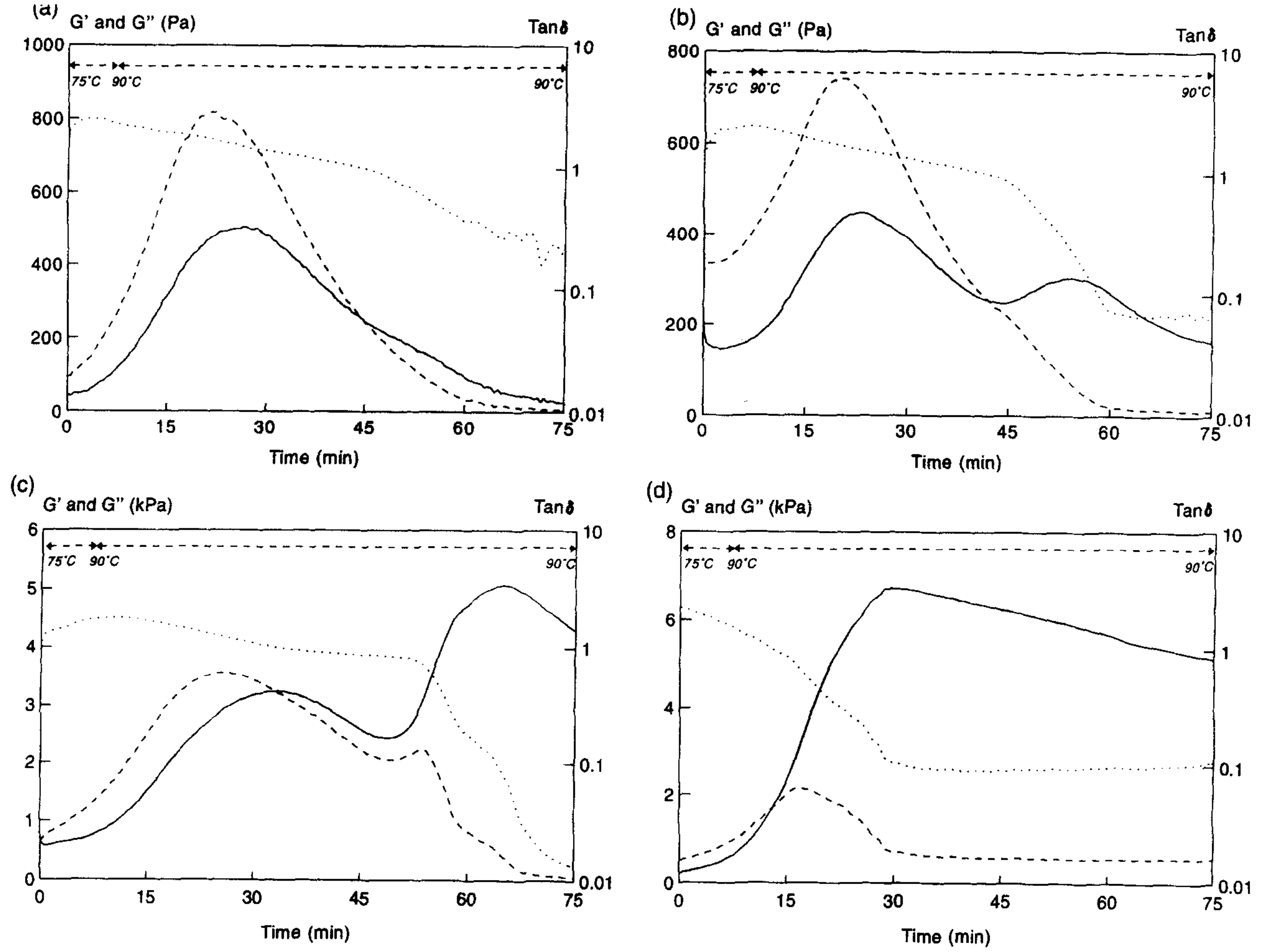


Fig. 7. The storage modulus G′, the less modulus G″ and tan δ while heating DAS-100 suspensions at varying concentrations and frequencies of oscillation: — G′; - - - - G″; · · · · tan δ. a) 10 wt% DAS-100 and 5 Hz; b) 14 wt% DAS-100 and 5 Hz; c) 18 wt% DAS-100 and 5Hz; d) 18 wt% DAS-100 and 0.1 Hz.

responses, both the *G*′ and *G*″ profiles showing two peaks. Basically, these results are in agreement with those from the viscosity measurements: i.e. a depressed 'end-viscosity' at the lowest concentrations and the appearance of two distinctive peaks at higher concentrations. The peaks are supposed to originate from two different gelation mechanisms as previously discussed. The first peak corresponds with a particle gel, the second results after disruption of the granules as shown by optical microscopy. The results of several strain and frequeny sweeps performed at different moments during the heating process of the gel revealed that no slippage occurred under the applied conditions.

Viscoelastic measurements during heating have also been performed at a lower frequency of oscillation, i.e. at 0.1 Hz. In contrast with the measurements at 5 Hz no second peak arose, while the *G*′ peak value was higher (Fig. 7d). At the peak value the gel structure consisted of particles, which were gradually disrupted during continued heating as observed by optical microscopy. To characterize the concentration dependency of the *G*′ response of the particle gels, several gelation processes have been performed for DAS-100 as well as for DAS-50 and PS at different concentrations. From the course of the elastic response as function of the gel concentration it is possible to get some information with respect to the granular rigidity and swelling (Doublier, 1987; Steeneken, 1989).

The maximum *G*′ value of the gels is plotted vs the concentration in Fig. 8. The concentration was varied from 5 to 30 wt%. At concentrations above 15 wt% the elastic response increased significantly as function of concentration at least for both dialdehyde starches. Below a concentration of 15 wt% the maximum elastic response of the native potato starch appeared to be higher compared to the dialdehyde starches.

These measurements confirm that gelation of dialdehyde starch is only possible at concentrations above 15 wt%. At this concentration it is supposed that close-packing of the granules is reached. This implies that below this concentration, the rheological properties are determined by the volume fraction of the granules: the dialdehyde starch granules are only slightly swollen due

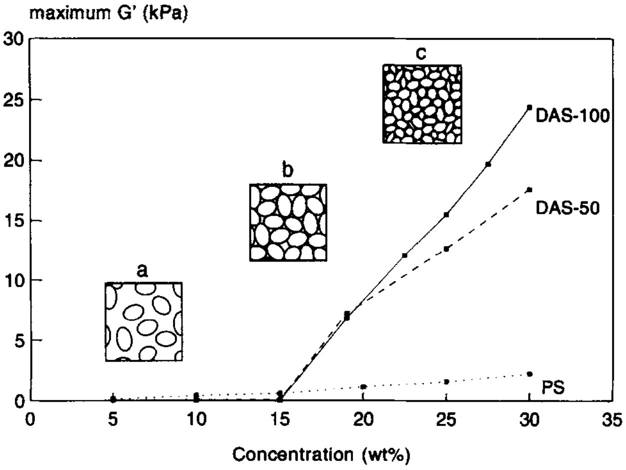


Fig. 8. The maximum G' value measured during gelation at 0.1 Hz for DAS-100, DAS-50 and PS as function of the concentration in the gel. The corresponding gel structures are depicted: (a) dilute regime: swelling to equilibrium; (b) close-packing: swelling to equilibrium; (c) concentrated: swelling to less than equilibrium.

to crosslinking. Native potato starch on the other hand is highly swollen and therefore shows a higher response below 15 wt%. Above this concentration, the rheological properties are determined by the rigidity of the granules, which are then swollen to less than equilibrium. The dialdehyde starch granules are significantly more rigid than the swollen and deformed native potato starch granules.

The effect of crosslinking, which is supposed to be proportional to the degree of oxidation, appears to be very influential since the maximum G' values measured for DAS-100 exceed those for DAS-50 (Fig. 8). A deviating rigidity between DAS-100 and DAS-50 is also shown by the shape of the dialdehyde starch granules in the respective gels at peak elasticity, which is regularly oval for DAS-100 and considerably distorted for DAS-50.

Influence of degree of oxidation

The G′ and G″ responses upon heating of 18 wt% DAS-50 are depicted in Fig. 9(a and b) for oscillatory measurements at 5 and 0.1 Hz. These results can be compared with those for DAS-100 depicted in Fig. 7(c and d). Clearly, DAS-50 gels are formed in an earlier heating stage than DAS-100 gels. For DAS-50, however, the elastic response decreased very rapidly and a second G' maximum did not arise at 5 Hz. In this respect the behaviour of DAS-50 deviates from that of DAS-100.

The decay of the elastic modulus, can be considered as a measure of the thermal instability of the gels and particularly the particles. It is supposed that the stability of the DAS-100 gel is higher due to a difference in particle rigidity as mentioned earlier. The hypothetical difference in granule rigidity is also supported by slightly deviating heating times required to reach gelation. The easier granular disruption of DAS-50 might be responsable for the fact that no two peaks were distinguished. The transition of a particle gel into a homogeneous polymer network is supposed to develop gradually for DAS-50 and more abruptly for DAS-100.

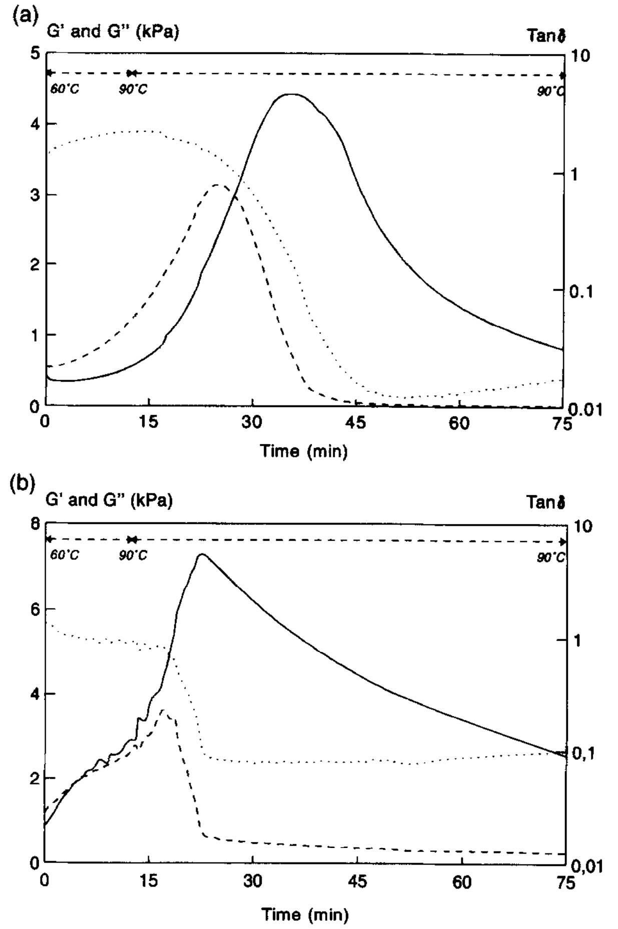


Fig. 9. The elastic modulus G', the viscous modulus G'' and tan δ while heating DAS-50 suspensions at varying concentrations and frequencies of oscillation: ——— G'; - - - - G″; · · · · tan δ. (a) 18 wt% DAS-50 and 5 Hz; (b) 18 wt% DAS-50 and 0.1 Hz.

For DAS-100, a steady minimum of G' was only reached after 5 h. Then, the gel had become a yellow solution. Although the material looked completely depolymerized, the gel structure was steadily being recovered upon ageing (Fig. 10). Both for DAS-100 and DAS-50, the destruction during heating is therefore assumed to be partly physical in nature and not just due to chemical degradation.

Influence of native potato starch

The influence of native potato starch (PS) on the gelation of dialdehyde starch is depicted by the G' responses in Fig. 11. These curves represent the gelation of respectively pure DAS-100, pure PS and a 1:1 mixture

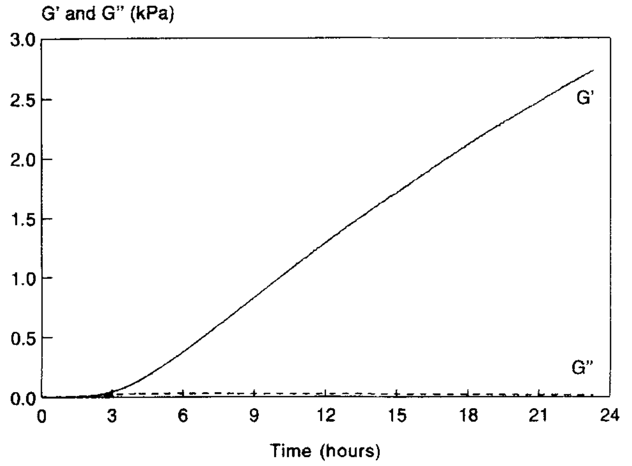


Fig. 10. Increase of the elastic modulus G' and the viscous modulus G'' upon ageing at room temperature; 18 wt% DAS-100.

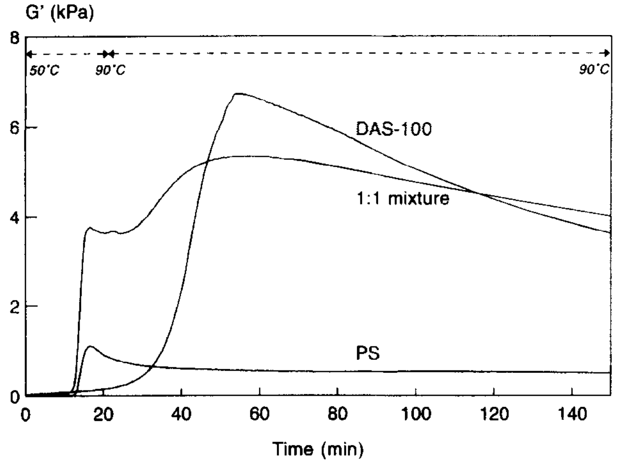


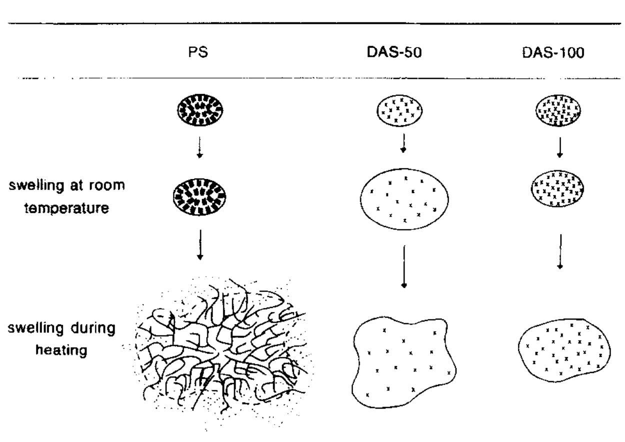
Fig. 11. The elastic modulus while heating 18 wt% DAS-100, 18 wt% PS and a 1:1 mixture of both compounds at the same total concentration (frequency of oscillation 0.1 Hz).

of DAS-100 and PS, each at a total concentration of 18 wt%. The difference in gelation between native potato starch and oxidized starch is clearly illustrated: the elastic response as measured for DAS-100 is more than 6 times higher compared to PS. For the mixture of the two starches, two stages were observed in the gelation profile which is attributed to the difference in gelation temperature. The most interesting aspect of the mixed gel is its improved stability; upon continued heating the decay in G' was relatively slow. Hence, after heating for more than 2 h the elastic response of the mixed gel surpasses that of the pure dialdehyde starch gel. The higher stability of the mixed gel is ascribed to the occurrence of crosslinking between starch and dialdehyde starch. Upon continued heating the texture of the mixed gel is supposed to convert steadily from a composite into a blend which is analogous to the conversion of a particle gel into a homogeneous polymer network.

Temperature–time effect of granule swelling

In a previous paper a swelling–structure relationship was developed by comparing the swelling of different dialdehyde starches at ambient temperature (Veelaert *et al.*, 1995). The maximum in swelling at intermediate degrees of oxidation (i.e. between DAS-40 and DAS-60), was explained by two counteracting effects: (i) the decrease in crystallinity and ordering at low degrees of oxidation, and (ii) the introduction of hydrophobic aldehydes and inherent hemiacetal and acetal formation. The loss of crystallinity is supposed to be mainly responsible for the high swelling capacity of DAS-50 at ambient temperature. The amorphous dialdehyde starch granules at higher degrees of oxidation, however, exhibited limited swelling due to considerable hemiacetalization. The present results on viscosity development during heating can be explained in a similar way.

For native potato starch, swelling at ambient temperature is hindered by the presence of crystallites. Upon heating, however, these crystallites melt, resulting in enhancing swelling and water absorption. For the oxidized starches at elevated temperatures, swelling capacity is principally determined by dialdehyde content and decreases with degree of oxidation. The aldehyde induced intragranular crosslinks are responsable for the higher rigidity of the granules. Besides the decrease of swelling and hence the decrease in viscosity response, an increase in the energy needed to reach the gelation stage ensues. In particular from the viscosity profiles recorded following the Brabender procedures, it has been seen that peak viscosity drastically falls from DO 0 to DO 50. At higher degrees of oxidation, the temperature of swelling is highly influenced. The combined effect of crystallinity and degree of oxidation on swelling at either room temperature or during heating is illustrated in Scheme 1.



Scheme 1. Comparison of PS, DAS-50, and DAS-100 with respect to granular swelling at ambient temperature and during heating. Influence of crystallinity (///) and crosslinking (X).

CONCLUSIONS

Present investigations on the 'gelatinization' of dialdehyde starch envisaged that the poor gelation capacity of dialdehyde starch can be attributed to limited swelling at concentrations below the critical gel concentration. Concentrated suspensions of dialdehyde starch, i.e. above the critical concentration of 15 wt%, give much stiffer gels than for native potato starch. Microscopic investigations of gel samples were performed to elucidate the gelation mechanism. As a result two types of gel structures have been distinguished: i.e. at first instance a particle gel and subsequently a more homogeneous macromolecular network on continued heating and shearing. Apparently, at lower concentrations the macromolecules dissolved.

At different degrees of oxidation the modified starches behave differently: swelling, onset time of gelation and gel-stability are influenced by the amount of aldehyde groups present. DAS-100 gels are characterized by a higher stability. DAS-50 induce gels earlier. The stability of the gels was improved by adding native potato starch.

Comparing the swelling of native and partially oxidized starch at room temperature the difference in crystallinity has to be taken into account, for the crystallites hinder swelling. Upon heating, the hindrance of crystalline structures on swelling turns out to be less important. Hence the aldehyde content becomes the decisive factor for swelling capacity and viscosity development.

The apparent degradation at longer heating times, does not prevent the material from gelation upon ageing at room temperature. Apparently, the low viscosity development cannot be attributed solely to the effect of polymeric degradation. The described gelation mechanism enables to the behaviour of dialdehyde starch in water to be interpreted in relation to its chemical and physical composition.

ACKNOWLEDGEMENTS

This work was financially supported by the DWT-programme of the Dutch ministry of Agriculture, Nature Management and Fisheries.

REFERENCES

Beduneau, H. (1961) *Rev. Prod. Chim.*, 593–600.

Borchert, P. J. (1961). *Kunststoffe*, **51**, 137–144.

Doublier, J. L., Llamas, G. & Le Meur, M. (1987). *Carbohydrate Polymers*, **7**, 251–275.

Doublier, J. L., Launay, B. and Cuvelier, G. (1992) *Viscoelastic Properties of Foods*, Chap. 14, ed. M. A. Rao and J.F. Steffe, pp. 371–432. Elsevier, Amsterdam.

Hofreiter, B. T., Heath, H. D., Ernst, A. J. & Russel, C. R. (1974). *Tappi*, **57**, 81–83.

Hofreiter, B. T., Hamerstrand, G. E., Mehltretter, C. L., Schulze, W. E. & Ernst, E. J. (1960). *Tappi*, **43**, 639–643.

Laleg, M. & Pikulik, I. I. (1993). *Journal of Pulp and Paper Science*, **19**, J248–J255.

Levine, S., Griffin, H. L. & Senti, F. R. (1959). *Journal of Polymer Science*, **35**, 31–42.

Mehltretter, C. L. (1966). *Starch*, **18**, 208–213.

Mehltretter, C.L. (1967) in *Starch Chemistry and Technology 2*, Chap. 18, pp.433–444. Academic Press, New York.

Mellies, R. L., Mehltretter, C. L. & Wolff, I. A. (1958). *Industrial and Engineering Chemistry*, **50**, 1311–1314.

Radley, J.A. (ed.) (1976) in *Starch Production and Technology*, Chap. 19, pp. 423–448. Applied Science, London.

Sloan, J. W., Hofreiter, B. T., Mellies, R. L. & Wolff, I. A. (1956). *Industrial and Engineering Chemistry*, **48**, 1165–1172.

Steeneken, P. A. M. (1989). *Carbohydrate Polymers*, **11**, 23–42.

Tegge, G. (1960). *Starch*, **12**, 321–327.

Tegge, G. & Mayer, H. (1984). *Getreide Mehl Brot*, **38**, 86–89.

Veelaert, S., Polling, M. & de Wit, D. (1995). *Starch*, **47**, 263–268.

Veelaert, S., de Wit, D., Gotlieb. K. F. and Verhé, R. (1997). *Carbohydrate Polymers*, (submitted).