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Rheological Properties of Aqueous Suspensions of Swollen Starch Granules

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ABSTRACT

Rheological measurements have been made on aqueous starch systems in which swollen granules are the dominant structural feature. An interesting cross-over phenomenon was observed. Low swelling starches have a lower viscosity than high swelling starches at low concentration; however, at high concentration this situation is reversed. This behaviour could be explained by a model which takes into account the existence of two concentration regimes. In the dilute regime the viscosity is governed by the volume fraction of swollen granules; in the concentrated regime it is governed by particle rigidity. Moreover, the dynamic loss angle and the shear thinning index were found to level off in the concentrated regime. Suspensions of swollen starch granules differ from starch solutions in a fundamental way. These differences are believed to have their origin in the static and motional characteristics of both kinds of system.

INTRODUCTION

Rheological measurements are frequently used to test the performance of starches and starch products as a thickening agent (Schutz, 1974; de Willigen, 1976). Generally, the purpose of these measurements is to predict the behaviour of aqueous starch systems in a practical situation as accurately as possible (Evans & Haisman, 1979). On the other hand, little is known about the mechanism of thickening action (Hofstee & de Willigen, 1953; Hofstee, 1962; Launay *et al.*, 1986).

The literature on starch rheology is vast and confusing. A reason for this lack of clarity is the use of widely different measuring equipments and conditions. Perhaps more important is that an aqueous starch system

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changes its appearance, and its rheological properties, fundamentally as temperature and shear are increased – a fact which has been emphasised repeatedly (Hofstee & de Willigen, 1953; Hofstee, 1962; Doublier, 1981; Doublier *et al.*, 1987). At room temperature an aqueous starch system can be considered as a suspension of rigid spherical granules, the rheological properties of which are governed only by concentration (de Willigen, 1976). Above the gelatinisation temperature the starch granules lose their semi-crystalline structure and are able to swell by adsorbing considerable amounts of water.

A swelling capacity (q) may be defined as the volume occupied by 1 g of dry starch after swelling to equilibrium in excess solvent. As temperature is raised further, increasing amounts of starch material go into solution, but remnants of the granular structure remain, even at temperatures above 120°C. It is only above 140°C that a true macromolecular (though unstable) starch solution is obtained. However, in many practical situations swollen starch particles are the dominant structural feature.

Hofstee and de Willigen were among the first to suggest that the rheological properties of aqueous starch systems are due to the mutual friction of highly swollen gel particles (Hofstee & de Willigen, 1953; Hofstee, 1962). This view was challenged by Miller *et al.* (1973), who argued mainly on electron microscopic evidence that dissolved macromolecular material leached out from the swollen granules is responsible for the high viscosity. However, rheological measurements do indeed point to a gel-like nature of aqueous starch systems prepared under mild conditions of temperature and shear. A zero-shear viscosity characteristic for polymer solutions is not observed, not even at very low shear rates (Evans & Haisman, 1979; Steeneken, unpublished). In a dynamic experiment the storage modulus (G') is rather insensitive to frequency and always higher than the loss modulus (G'') (Evans & Haisman, 1979; Wong & Lelievre, 1981). Finally, many starch systems exhibit a yield stress (Evans & Haisman, 1979; Bagley & Christianson, 1983).

In view of the prominent influence of particulate material, theories developed for polymer solutions and melts (Graessley, 1974; Doi & Edwards, 1978, 1979; Ferry, 1980) are likely to be of little use to the description of aqueous starch systems. Ten years ago Taylor and Bagley provided an equally elegant and simple explanation for the rheology of suspensions of swellable particles (Taylor & Bagley, 1974, 1977; Taylor, 1979). This model was successfully applied to starch-grafted copolymers and cross-linked carboxymethylstarch. Although elements of the Taylor–Bagley concept have been used to describe aqueous dispersions of native starches as well, the potential of their model does not seem to have been fully exploited.

In the present study we have measured some rheological properties of aqueous systems of native and modified starches prepared under relatively mild conditions of temperature and shear, at which the particulate structure was largely preserved, with the aim of identifying the structural features responsible for the rheological behaviour. The results are discussed in the light of the Taylor–Bagley model. Apart from its scientific interest, insight into the thickening action of starch is important for the development of new products with controlled rheological behaviour.

MATERIALS AND METHODS

Starches

Native, lightly cross-linked and highly cross-linked potato starch were supplied by Avebe BA (Veendam, The Netherlands), native maize starch and native and highly cross-linked waxy maize starch were from CPC Benelux BV (Sas van Gent, The Netherlands), and native prime wheat starch from Latenstein BV (Nijmegen, The Netherlands).

Equilibrium swelling volume and solubility

The swelling volume (q) is defined as the equilibrium volume of 1 g of dry starch after swelling under specified conditions in an excess amount of water.

The starches were gelatinised by rotating mixtures of starch and water on a water bath at 92°C (potato starches) or 97°C (cereal starches) at 180 rpm in round-bottom flasks for 30 min. After settling under gravity for 24 h the volume of the swollen granules was measured by a dye exclusion method with Blue Dextran (Dengate *et al.*, 1978) as described by Evans & Haisman (1979, variant A). Swelling volumes were not corrected for solubilised material. Solubility was calculated from the carbohydrate content of a known amount of the supernatant solution, as measured with the anthrone method, after centrifugation at 15 000 **g**, taking into account that dissolved material occupies only a part of the volume of the system. Solubility (s) is expressed as a weight fraction on a dry basis.

Rheological measurements

Suspensions were prepared by rotating appropriate amounts of starch and water in a round-bottom flask at 180 rpm on a water bath at 92°C (potato starches) or 97°C (cereal starches) for 30 min. Starch concentration was calculated from the sample weight after heating.

Measurements were made at 60°C in a Deer rheometer (G. E. van Bremen BV, Nieuwleusen, The Netherlands), a constant stress apparatus enabling us to measure at the very low strains necessary to remain within the linear viscoelastic region (typically 0·01). Concentric cylinder geometries were used throughout this work. The rheometer, thermostatted at 60°C, was filled with the hot starch suspension which was topped with a thin layer of paraffin oil of low viscosity to prevent loss of moisture.

After temperature conditioning (30 min) the sample was sheared at a shear rate ($\dot{\gamma}$) of 75 s^{-1} for 5 min in order to minimise hysteresis effects. After a definite resting time (5 min for native potato starch, 30 min for other starches) a plot of shear stress vs. shear rate (rheogram) was taken with the use of a programmer. Maximum shear rate depends on the maximum torque applied, but was always less than 75 s^{-1} (typically 30 s^{-1}). Time upwards to maximum torque and downwards to zero torque was 10 min in each direction.

Viscosity (η) at 1 s^{-1} and the shear thinning index (n), defined as

$$\eta(\dot{\gamma}) = \eta(\dot{\gamma} = 1)\dot{\gamma}^n \qquad (1)$$

were calculated from the descending part of the rheogram by means of a double logarithmic plot of the data. In several cases viscosity data were checked by measurements at constant shear stress.

After completion of the rheogram dynamic measurements were made at an angular frequency of 1 rad s^{-1} in the linear viscoelastic region, from which the dynamic storage modulus (G') and the dynamic loss angle (δ) were obtained.

Finally a second rheogram was taken in order to detect any change in the sample.

RESULTS AND DISCUSSION

Equilibrium swelling volume and solubility

Equilibrium swelling and solubility values are given in Table 1. Difficulties were encountered in the measurements on native potato and waxy maize starch. Sediments of the former starch shrink after addition of Blue Dextran, whilst waxy maize starch dispersions contain extremely small gel fragments that do not settle under gravity. Therefore, the values for both starches have to be considered as an approximation.

TABLE 1
Equilibrium Swelling Volume (q), Solubility (s) and Close Packing Concentration (c^*) of Native and Modified Starches

Starch type	q ($ml\,g^{-1}$)	s	c^* ($g\,ml^{-1}$)
Potato, native[a]	(60·0)	(0·412)	(0·017)
Potato, lightly cross-linked	43·3	0·113	0·0231
Potato, highly cross-linked	12·4	0·026	0·0806
Maize, native	14·0	0·116	0·0714
Prime wheat, native	12·6	0·150	0·0794
Waxy maize, native[a]	(18·8)	(0·403)	(0·0532)
Waxy maize, highly cross-linked	10·4	0·026	0·0962

[a] Values for native potato and waxy maize starch were difficult to measure and are set between parentheses.

The amount of dissolved material is small in all cases except for native potato and waxy maize starch. However, it will be shown in a later section of this paper, that in the concentration range of interest here, the contribution of solubilised starch to viscosity and modulus is limited. Hence the data indicate that swollen granules are the dominant structural feature of the dispersions at the conditions applied for gelatinisation. The swelling volume (q) is a measure of the starch concentration (c_i) within the swollen granules.

$$q = 1/c_i$$

It may be remarked that there is an analogy between q and $[\eta]$, the intrinsic viscosity of a polymer in the sense that $1/[\eta]$ is a measure of the concentration of segments within a polymer coil.

Preliminary remarks on rheological measurements

The rheological properties of aqueous starch dispersions are markedly dependent on shear history (Doublier, 1981; Doublier *et al.*, 1987). Therefore the sample preparation was standardised as much as possible. Rheograms were taken twice on each sample, before and following the dynamic measurements, in order to detect any change. A reasonable stability could be attained by a previous shearing of the sample at a rate higher than the maximum value encountered in the subsequent experiment. Nevertheless, in several cases large variations between duplicate experiments (50% or even more) were observed, especially with native maize and wheat starch at high concentrations.

Dispersions of these starches have a short, ointment-like consistency. In this kind of system slip at the wall of the measuring system may become important. This has to be examined in a subsequent investigation. However, in view of the very strong concentration dependence of viscosity and modulus of these starches, this effect does not seem to affect greatly our conclusions.

All measurements were made at 60°C. By means of dynamical measurements as a function of time it was ascertained that no retrogradation occurs at this temperature.

Concentration dependence of viscosity

Viscosity data at 1 s^{-1} are shown in Fig. 1. Not all data are included in order to avoid crowding in the figures. The most striking feature is a 'cross-over' in viscosity behaviour between low and high swelling starches as concentration increases. At low concentrations the high swelling starches have a higher viscosity than the low swelling starches; at high concentrations this situation is reversed. The concentration

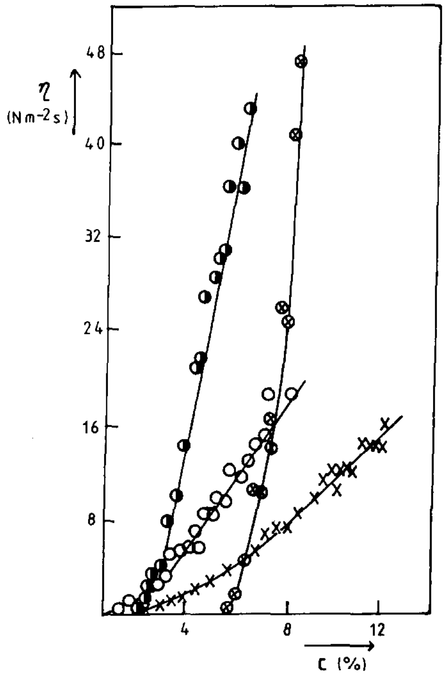

Fig. 1. Viscosity (η) vs. concentration (c) of native and modified starches. ○ Potato starch, native; ◑ potato starch, lightly cross-linked; × waxy maize starch, native; ⊗ waxy maize starch, highly cross-linked.

dependence of the storage modulus mimics the viscosity behaviour (Fig. 2). Furthermore viscosity and modulus show a linear dependence on concentration at high concentrations. This remarkable 'cross-over' can be explained by taking into account the different concentration regimes that are encountered in suspensions of swellable gel particles as pointed out by Taylor & Bagley (1974, 1977) and Taylor (1979). These different regions are depicted in Fig. 3.

At low concentrations the gel particles are completely swollen. These systems are not homogeneous in the sense that the internal starch concentration $c_i = 1/q$ is higher than the external concentration $c_0 = sc$, with s and c being solubility and nominal starch concentration respectively. We can assign a rigidity G^* to the fully swollen granules which will be defined later (Table 2).

Increasing the starch concentration eventually leads to a situation where the fully swollen granules just fill up the available space. At this space-filling concentration (Table 1) the system becomes homogeneous.

$$c = c^* = 1/q$$

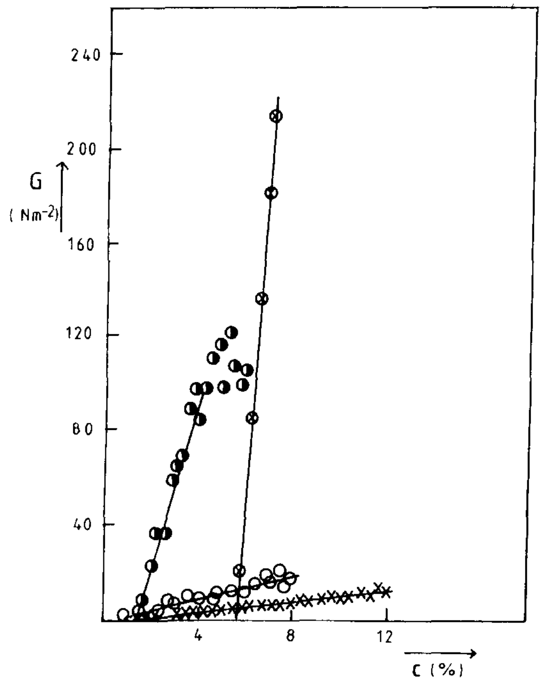

Fig. 2. Storage modulus (G) vs. concentration (c) of native and modified starches. Symbols as in Fig. 1.

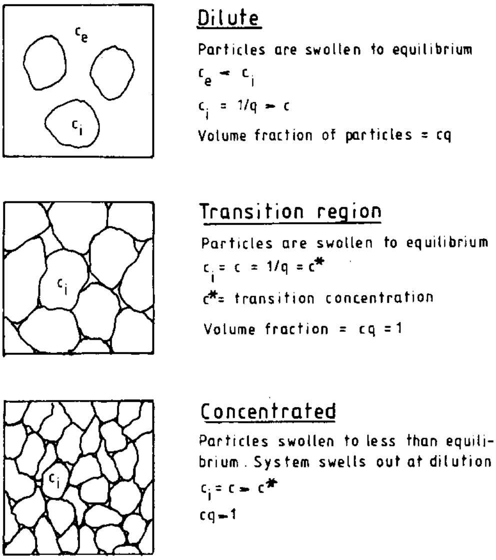

Fig. 3. Concentration regimes in suspensions of gelatinised starch granules. c, Nominal starch concentration; c_e, c_i, concentration outside and inside swollen granules respectively; c^*, space-filling concentration; q, equilibrium swelling volume.

TABLE 2

Rigidity of Fully Swollen Granules (G^*), Rigidity Index ($(G/c)_c$) and Thickening Power ($(\eta/c)_c$) of Native and Modified Starches

Starch type	G^* *($N m^{-2}$)*	$(G/c)_c$ *($N m^{-2} ml g^{-1}$)*	$(\eta/c)_c$ *($N m^{-2} s ml g^{-1}$)*
Potato, native	2·3[a]	238	295
Potato, lightly cross-linked	32	2 300	1 130
Potato, highly cross-linked	875	27 000	1 860
Maize, native	78	6 080	691
Prime wheat, native	60	10 200	1 240
Waxy maize, native	5·3[a]	113	196
Waxy maize, highly cross-linked	790	19 400	2 760

[a] Approximate values.

This space-filling state can be realised because the gel particles are highly deformable. Of course each starch has its own space-filling concentration, defined by the value of q. In a thermodynamic sense a microgel suspension at c^* is formally equivalent to a fully swollen macroscopic gel; the only obvious difference is that the microgel particles are not linked together. Hence we define the rigidity of fully swollen granules (G^*) as the storage modulus of the suspension at c^*.

Finally, at high concentrations the amount of water becomes the limiting factor. Therefore the gel particles cannot swell to their equilibrium volume. In fact, beyond c^* the swelling volume of all starches is the same and equal to $1/c$, irrespective of q. This situation is equivalent to a macroscopic gel swollen with a limited amount of diluent, of course without linkages between granules.

Dilute regime

Introduction of the volume fraction of swollen gel particles $c/c^* = cq$ as the concentration variable as proposed by Taylor & Bagley (1974) greatly improves our understanding of the concentration dependence of the viscosity. In Fig. 4 the viscosity of several starches in the dilute regime is shown as a function of c/c^*. At small values of c/c^* the viscosity is uniquely determined by the particle volume fraction. In this region starches with the highest swelling capacity are the most viscous at a given concentration.

At higher values, when particle interactions become important, the curves diverge, showing the greatest increase for starches with the greatest particle rigidity (G^*). This can be explained by taking into account that at a given volume fraction particles flow more easily past each other as they are more deformable. As c/c^* approaches unity, viscosity is determined by volume fraction and by particle rigidity as well.

Concentrated regime

Beyond c^* the system is completely filled by starch particles. So c/c^* is not a measure of the particle volume fraction anymore. In fact, at a given concentration, the degree of swelling is the same for different starches and equal to $1/c$. For that reason we switch over to c as the concentration variable in this regime. A linear relationship between η and c was found with a characteristic slope for each starch type (Fig. 5). This slope may be used as a measure of the thickening power of a particular starch.

Hence we define

$$(\eta/c)_c = \frac{\eta - \eta^*}{c - c^*}$$

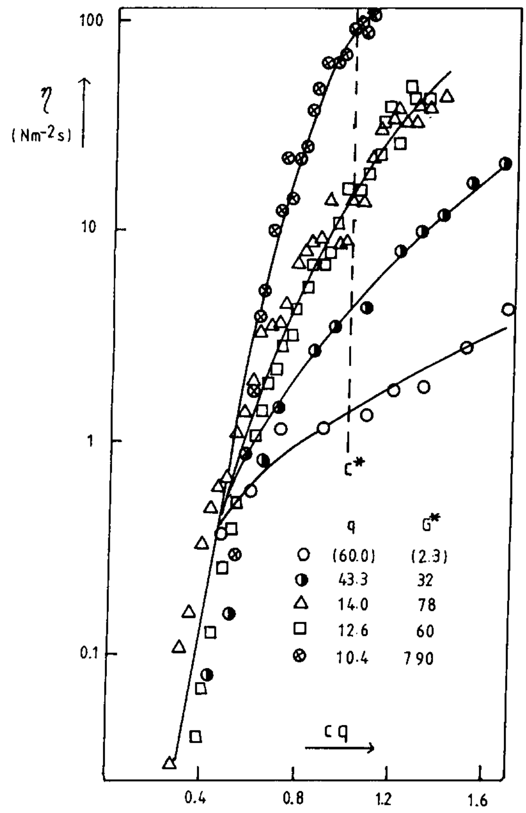

Fig. 4. Viscosity (η) vs. particle volume fraction (cq ($=c/c^*$)) of native and modified starches in the dilute regime. q, Equilibrium swelling volume; G^*, rigidity of fully swollen particles. ○ Potato starch, native; ◑ potato starch, lightly cross-linked; △ maize starch, native; □ prime wheat starch, native; ⊗ waxy maize starch, highly cross-linked.

The asterisk stands for the limit of complete filling, the subscript c for the concentrated regime.

A linear concentration dependence of viscosity was also observed by Taylor & Bagley (1974, 1977) who instead defined $(\eta/cq)_c$ as a measure of thickening power. Unlike the dilute regime, where the particle rigidity is constant and defined by G^*, this property becomes concentration dependent. Rather than a dependence of G on $c^{1/3}$, as predicted by the classical theory of elasticity for an entropic network swollen with a limited amount of diluent (Treloar, 1958), a linear relationship between G and c was observed.

We define

$$(G/c)_c = \frac{G - G^*}{c - c^*}$$

as a characteristic index of the particle rigidity of a particular starch in a space-filled system.

Values of $(\eta/c)_c$ and $(G/c)_c$ are collected in Table 2. As c is expressed as a weight fraction of starch (neglecting for the moment the density of the system which is close to unity), $(\eta/c)_c$ and $(G/c)_c$ in fact represent the viscosity and the modulus of the system when the amount of solvent approaches zero. At a given concentration above c^* the most important difference between aqueous starch systems must be the network structure (rigidity) of the swollen granules as the degree of swelling is the same. Indeed we find that the steepness of the slope of the η vs. c curve depends on $(G/c)_c$ (Fig. 5).

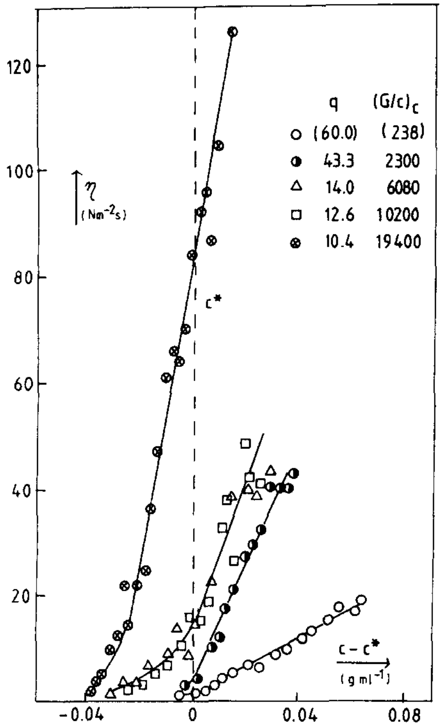

Fig. 5. Viscosity (η) vs. normalised concentration $(c-c^*)$ of native and modified starches in the concentrated regime. q, Equilibrium swelling volume; $(G/c)_c$, rigidity index of swollen particles in the concentrated regime. Symbols as in Fig. 4.

To explore this relationship further, values of $(\eta/c)_c$ for different starches were plotted against $(G/c)_c$ on a double logarithmic scale (Fig. 6). The data for ten phosphorylated potato and maize starches were found to fall on the same curve. A plot of $(\eta/cq)_c$ vs. $(G/c)_c$ according to Taylor and Bagley did not fit the results. It may be concluded that thickening power in the concentrated regime is mainly, if not uniquely, determined by the particle rigidity of the swollen granules.

On the other hand it remains to be established whether the observed relationship is universal as there is no theoretical basis for it at the moment. Obviously some theoretical studies on gel particle systems would be most welcome.

Explanation of the 'cross-over' behaviour

The observed cross-over in viscosity of aqueous starch systems can now be explained if one takes into account the different behaviour of these systems in the dilute and concentrated regime. In dilute systems the viscosity is proportional to the volume fraction of the swollen particles, which depends on the swelling capacity (q). In concentrated systems the viscosity is determined by particle rigidity.

According to Flory (1953) the swelling capacity depends on the network density (or degree of cross-linking) and the polymer-solvent interaction. This latter factor is determined by the detailed interaction

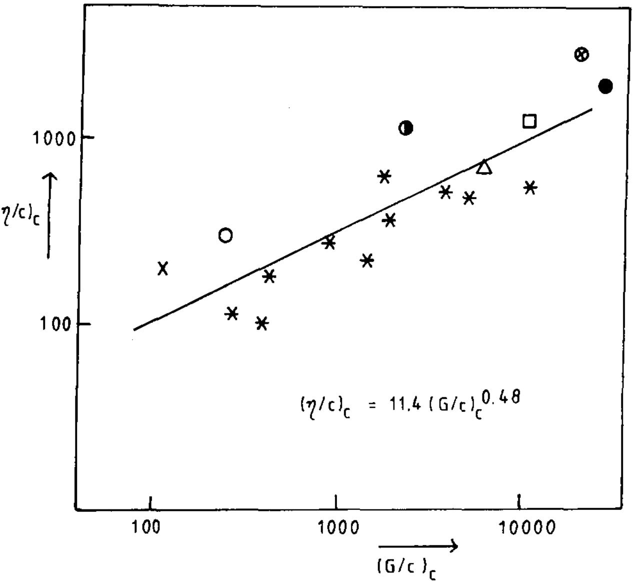

Fig. 6. Thickening power ($(\eta/c)_c$) vs. particle rigidity index ($(G/c)_c$) of native and modified starches in the concentrated regime. ○ Potato starch, native; ◑ potato starch, lightly cross-linked; ● potato starch, highly cross-linked; △ maize starch, native; □ prime wheat starch, native; × waxy maize starch, native; ⊗ waxy maize starch, highly cross-linked; ✱ phosphorylated starches.

between the chemical units of the polymer and the solvent and is likely to be the same for all the native and slightly modified starches studied here. Network density and gel rigidity are linearly related. Following Flory there is an inverse relationship between the network density (and the particle rigidity) and the swelling capacity. (Native waxy maize starch is an exception; both q and $(G/c)_c$ are rather low for this starch). So, in general, in the dilute regime the higher swelling starches are the more viscous, whereas in the concentrated regime the lower swelling starches are more viscous.

The model outlined above may serve as a guideline for the development of highly viscous starch-based thickeners. Assuming for the moment that the relationship of Fig. 6 is universal, it may be judged that a high thickening power requires a high particle rigidity. The most interesting are those products that exhibit a high viscosity at a low concentration. To meet this requirement both $(G/c)_c$ and q have to be as high as possible, because a high value of q ensures a transition to the concentrated regime at low c. This seems to be a conflicting demand because in most cases $(G/c)_c$ and q are inversely related, as discussed before.

One possibility is to modify the polymer–solvent interaction or the introduction of charged groups. An example is hydrolysed starch-grafted polyacrylonitrile which, apart from its potential as a 'superadsorbent' (Weaver *et al.*, 1974), was found to be an excellent thickener (Taylor & Bagley, 1977).

Other rheological properties

Dynamic experiments not only probe the resistance to deformation but also establish whether this deformation is solid-like or liquid-like. The relevant parameter in this respect is the dynamic loss angle (δ) which reflects the phase lag between stress and strain. On deformation of a Hookean solid stress and strain are in phase, whereas in a Newtonian liquid they are 90° out of phase (Ferry, 1980).

In Fig. 7 the loss angle of some starches is plotted as a function of c/c^* at a time scale of 1 s (frequency of 1 rad s^{-1}). It was observed that δ decreases at increasing volume fraction of swollen granules. This behaviour can be explained by the increasing contribution of viscoelastic particles to the rheology of the system. However, once the system is completely filled, δ levels off to a constant value (δ_c). This means that the nature of the deformation is invariant with the amount of solvent.

As we have stated previously, a closely packed gel-particle suspension is formally equivalent to a macroscopic gel swollen with a limited

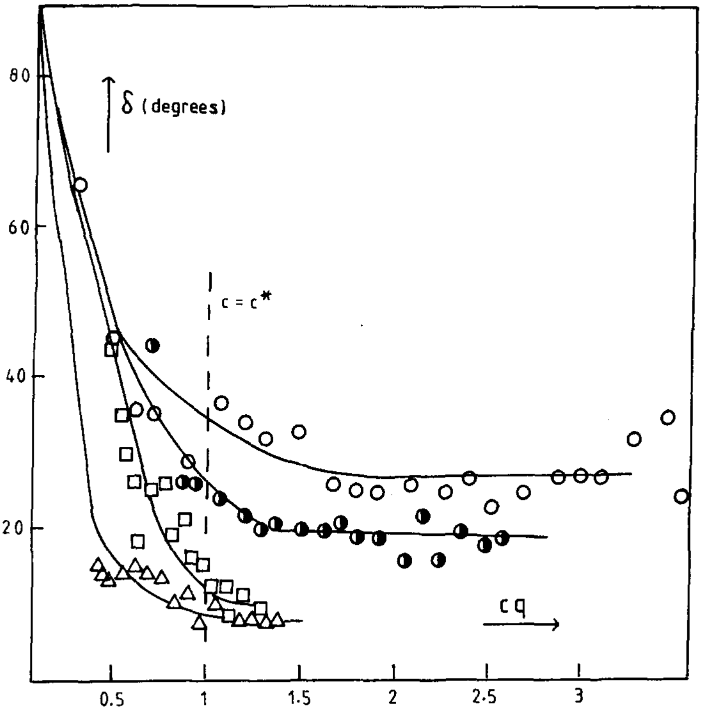

Fig. 7. Dynamic loss angle (δ) vs. reduced concentration ($cq(=c/c^*)$) of native and modified starches. Symbols as in Fig. 4.

amount of diluent. Dynamic experiments reveal that concentrated starch dispersions exhibit a rubbery plateau at the time scales of interest here (Evans & Haisman, 1979; Wong & Lelievre, 1981). This plateau zone is characterised by a storage modulus G' which is largely independent of frequency, whereas the loss modulus G'' and hence tan δ goes through a minimum. This minimum may be quite broad, spanning several decades of frequency. The effect of diluent on a network is to shift all viscoelastic processes to shorter times (or higher frequencies) and to diminish the minimum in tan δ (Ferry, 1980). Hence a decrease of δ_c would be expected at increasing starch concentration. However, if the minimum is very shallow there will hardly be any influence of concentration on δ_c, which is likely to be the case here.

It was observed that the value of δ_c is characteristic for each type of starch (Table 3). Generally δ_c diminishes with increasing degrees of cross-linking, but this cannot be the only factor involved. So, at an equal rigidity index $(G/c)_c$ potato starches are found to be more fluid-like and

TABLE 3
Limiting Values of Dynamic Loss Angle (δ_c) and Shear Thinning Index (n_c) of Native and Modified Starches

Starch type	δ_c *(degrees)*	n_c
Potato, native	28	−0·55
Potato, lightly cross-linked	20	−0·54
Potato, highly cross-linked	15	−0·43
Maize, native	8·9	−0·66
Prime wheat, native	11	−0·60
Waxy maize, native	27	−0·52
Waxy maize, highly cross-linked	11	−0·70

cereal starches more elastic. This difference in behaviour presumably has its origin in a different organisation of physical cross-links in both types of starch but this hypothesis remains to be proven.

Another feature of aqueous starch systems is that they are shear thinning. The shear thinning index defined by eqn (1) is plotted as a function of c/c^* for various starches in Fig. 8. We observe a behaviour similar to that of δ: a decrease in the dilute regime, followed by a leveling off to a constant value n_c as soon as the suspension is filled. Shear thinning behaviour of polymer melts or concentrated solutions is believed to be caused by an enhanced disentanglement (or constraint release) of polymer chains as the shear rate is increased. If the disengagement time at rest greatly exceeds the characteristic time of deformation ($\dot{\gamma}^{-1}$) a limiting value of $n \simeq -0{\cdot}8$ is attained (Graessley, 1974). The shear thinning of gelatinised starch suspensions may have an analogous origin. Although the number of interparticle contacts does not change on deformation, the mutual obstruction to flow is likely to be relieved. Qualitative differences between polymer solutions and gel suspensions will be discussed in the next section.

Like δ_c the value of n_c appears to be characteristic for the type of starch (Table 3). However, a reasonable physical explanation is not yet available. Apparently there is a relationship between n_c and δ_c (Fig. 9), but the scattering of the data leads one to suppose that more factors are involved. Finally it must be remarked that it is by no means sure that n_c represents a true limiting value in view of the limited range of shear rates investigated.

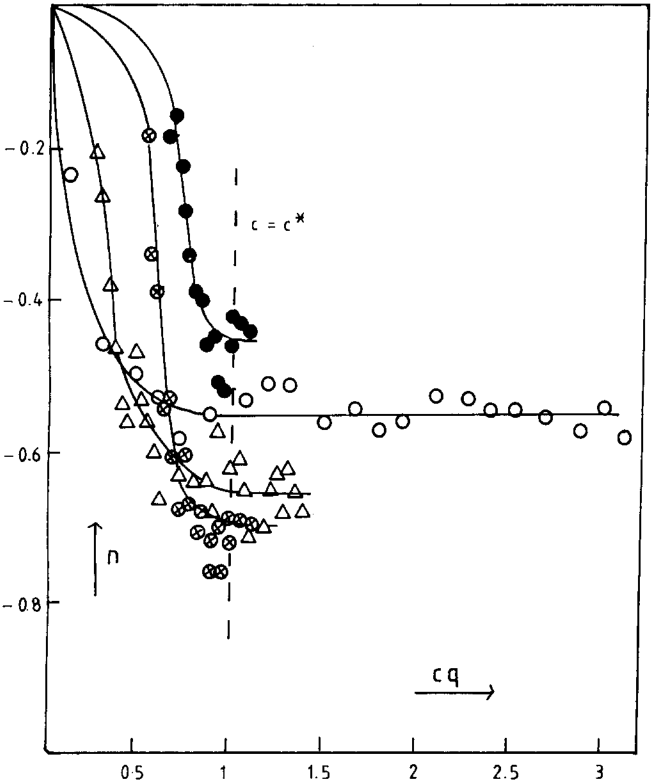

Fig. 8. Shear thinning index (n) vs. reduced concentration ($cq(=c/c^*)$) of native and modified starches. ○ Potato starch, native; ● potato starch, highly cross-linked; △ maize starch, native; ⊗ waxy maize starch, highly cross-linked.

Starch suspensions and starch solutions

As we have pointed out before, the rheology of aqueous starch systems is strongly dependent on the preparation method. To illustrate this point further, we have compared suspensions of gelatinised granules and molecular solutions of waxy maize starch. It is not easy, if not impossible, to prepare true molecular starch solutions. Native waxy maize starch was first defatted by refluxing three times with five volumes of aqueous methanol (85% v/v) for 2 h (Schoch, 1942). The defatted starch was subsequently dissolved in 1M sodium hydroxide solution, neutralised, dialysed and precipitated with acetone. Aqueous solutions of the pretreated starch were prepared by pressure cooking at 140°C. Even after this rigorous treatment the final solutions showed a slight haze which was removed by centrifugation in some cases. Suspensions of gelatinised starch were prepared as described in Materials and Methods. Solutions were measured at 37°C, suspensions at 60°C.

Viscosity vs. concentration curves are shown in Fig. 10. Apart from being much less viscous than suspensions of swollen granules, aqueous solutions exhibit a break in the curve, the slope being steeper at high concentrations. This behaviour is typical for polymer solutions, the location of the break being an indication for the onset of chain overlap (Graessley, 1974; Ferry, 1980; Morris *et al.*, 1981). On the other hand, for suspensions of gelatinised starch granules the slope of the curve declines at high concentrations. According to our previous discussion, a limiting slope of 1 on a double logarithmic representation is to be expected at the upper end of the concentration scale. Other features of molecular starch solutions which are lacking in suspensions are the existence of a zero shear viscosity and the absence of a detectable dynamic storage modulus even at a concentration of 20%. So, in contrast with starch suspensions which are solid-like, starch solutions are fluid-like.

These fundamental differences between solutions and suspensions must have their origin in the static and dynamic (motional) properties of both kinds of systems. For the present discussion let us restrict ourselves to the concentrated regime. As for the static properties, of prime importance is that polymer coils are able to invade each other's domain whereas swollen particles are not.

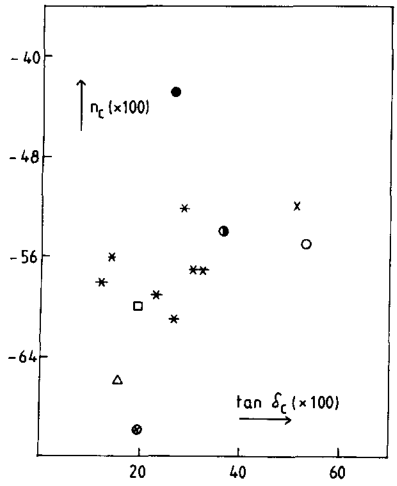

Fig. 9. Relationship between limiting values of shear thinning index (n_c) and dynamic loss angle (tan δ_c) of native and modified starches. Symbols as in Fig. 6.

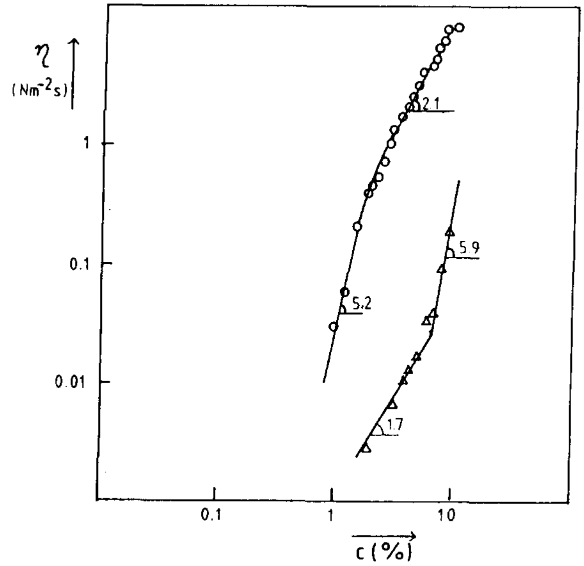

Fig. 10. Viscosity (η) vs. concentration (c) of suspensions of swollen granules and of solutions of native waxy maize starch. ○ Suspensions of swollen granules measured at 60°C; △ solutions measured at 37°C.

As a result, polymer molecules hardly change their dimensions with increasing concentration. In non-interacting solvents (the so-called theta solvents) the molecular dimensions do not change at all. In good solvents a modest decrease with $c^{-0.25}$ is observed, as a consequence of screening of polymer–solvent interaction (de Gennes, 1979). Consequently a dependence of the dynamic storage modulus on c to a power of about 2 is found (Ferry, 1980). In contrast, swellable particles in a suspension with a limited amount of solvent compete for the available solvent and their dimensions decrease with c^{-1}. As these suspensions are formally equivalent to macroscopic gels swollen with a limited amount of diluent, the modulus is expected to change with $c^{1/3}$ (Treloar, 1958). Actually a linear dependence on c has been established.

As for the dynamics, individual polymer molecules in concentrated solutions are able to displace themselves with respect to neighbouring molecules in the absence of external forces. The characteristic diffusion time is intimately related to the zero shear viscosity (de Gennes, 1979). On the other hand individual gel particles are locked in by discrete physical boundaries with other particles. They cannot displace themselves except by cooperative motions brought about by external forces (Antonietti & Sillescu, 1986). This should be the reason why closely packed gel particle systems have no zero shear viscosity, not even at shear rates as low as 10^{-4} s^{-1} (Evans & Haisman, 1979; Steeneken, unpublished), exhibit a yield stress (Evans & Haisman, 1979; Bagley & Christianson, 1983) and behave like a gel in dynamic mechanical experiments (Evans & Haisman, 1979; Wong & Lelievre, 1981).

CONCLUSIONS

Taylor and Bagley have put forward a simple and elegant model to explain the behaviour of suspensions of swellable gel particles. The essential feature of this model is that two concentration regimes are invoked, which are defined by the criterion as to whether or not the suspension is closely packed. The model was found to give a fairly good description of the behaviour of starch-grafted copolymers (Taylor & Bagley, 1974, 1977) and carboxymethylstarch gel suspensions (Taylor, 1979).

In this paper we have demonstrated that their theory (with some minor adjustments) applies equally well to native and the more common types of modified starches provided that swollen granules are the prominent structural feature of the system. In dilute suspensions the viscosity is governed by the volume fraction of the swollen granules (cq), whereas in closely packed systems the rigidity of the particles is the decisive factor. It is interesting to note that the work of Doublier *et al.* (1987), though based on different arguments, points to the same conclusion. It should be considered, however, that between those limiting behaviours a broad transition region exists where the viscosity is determined by both particle volume fraction and rigidity. Most interesting, the model is successful in explaining the 'cross-over' in the viscosity–concentration dependence when comparing a high and a low swelling starch in both concentration regimes.

Furthermore, we have demonstrated that the close packing concentration (c^*) also marks a transition in the behaviour of other rheological properties. So the dynamic loss angle (δ) and the shear thinning index (n) become concentration independent if c exceeds c^*. The fundamental difference in rheological behaviour between suspensions of swollen starch granules and molecular starch solutions is believed to have its origin in the different static and dynamic properties of these two kinds of systems. Finally it must be emphasised that, although many features of aqueous starch systems can be explained by the Taylor and Bagley model, this model is essentially empirical and has as yet no theoretical basis.

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