

# Structure/Rheological Properties Relations of Crosslinked Potato Starch Suspensions

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**ABSTRACT:** Some rheological properties of aqueous suspensions of crosslinked hydroxypropylated potato starches were investigated. The crosslinking was performed at a temperature above the gelatinization temperature and the degree of crosslinking varied between 0.05 and 0.75% wt. The samples were characterized by the swelling power  $Q$  and the average particle size  $D$  and observed by light microscopy and low-temperature SEM. The swelling power decreases with the extent of crosslinking, whereas the average particle size increases. From these observations, the starch samples can be described as suspensions of deformable particles suspended in a continuous suspending medium constituted of polymer chains plus water. The rheological properties allow us to define different concentration regimes depending on the close packing of swollen particles at a concentration  $C^*$ , which is close to  $1/Q$ . In dilute conditions, that is, for  $C < C^*$ , the viscosity is little influenced by the degree of crosslinking and, hence, by the particle size. Two domains can be defined: a “true dilute” one for  $C < 0.6C^*$  and a semidilute one for  $C > 0.6C^*$ , in which the viscosity rapidly increases with the concentration. Moreover, an apparent yield stress and elastic properties are observed in the concentrated regime, for  $C > C^*$ . Two domains can be also defined: a first one for  $C < 2C^*$ , in which the rheological characteristics sharply increase with the concentration, and a second one, a quasi-plateau domain, for  $C > 2C^*$ . The variations of these rheological properties suggest that the rigidity of the swollen particles can be considered, contrary to the viscosity in the true dilute regime. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2480–2489, 2001

**Key words:** crosslinked starch; suspensions; microscopy; rheological properties; yield stress

## INTRODUCTION

Starch is a polymeric carbohydrate composed of anhydroglucose units and is extracted in granular

form from tissues of certain plants. Starch is known to be composed of two types of glucose polymers: amylose, a linear polysaccharide, and amylopectin, which has a highly branched structure.<sup>1</sup> The amylose/amylopectin ratio varies with the starch origin and is responsible, to a large extent, for its functional characteristics.

Starch is extensively used in the food industry as a thickening, stabilizing, or gelling agent.

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These applications imply a good understanding of the hydration and rheological properties of these macromolecular systems as shown by an abundance of the literature.<sup>2-6</sup> In its native form, a starch granule is insoluble in cold water and most uses involve a heating treatment in the presence of an excess of water. Below a critical temperature (about 60°C), that is, the so-called gelatinization temperature, starch granules absorb water and undergo swelling to many times their original size. This process is often attributed to the diffusion of linear amylose chains outside the swelled granule. Beyond this critical temperature, the swollen starch granules can undergo a disruption into smaller aggregates or particles. A complete solubilization of all the starch macromolecules may occur when starch is heated at temperatures beyond 100°C. The heating treatment is therefore associated with large changes of the viscosity characteristics. Overall starch suspension properties are strongly influenced by their botanical origin and by the shearing and/or heating conditions under which they are prepared.<sup>7,8</sup>

These peculiar properties can be modulated through chemical modifications. This allows other potential uses in many different industries. Chemical substitution and chemical crosslinking are the main types of modifications that are carried out. Chemical crosslinking is particularly used to inhibit granule disruption. Depending on the extent of crosslinking, granule swelling will be more or less important, leading to a wide range of rheological properties. The properties of crosslinked starch suspensions are nearly similar to those of closely packed microgel dispersions and can be described on a similar basis.<sup>6,9-12</sup>

By an appropriate choice of the native starch source (potato, maize, wheat, etc.) and of the chemical-modification type, derivatized starches with very useful properties can be obtained. The abundance and natural origin of such new starch derivatives could make them relevant candidates for many applications, especially if there is an environmental concern. They can be extensively used in many practical applications, such as in the oil, gas, or paper industry, by taking advantage of their swelling and solubility properties.

The present study was undertaken to investigate the relations between the physicochemical and rheological properties of crosslinked hydroxypropylated potato starch suspensions. The results were interpreted in terms of concentration and particle characteristics.

## EXPERIMENTAL

### Starch Samples

Modified starches were kindly provided by AVEBE (Foxhol, The Netherlands) and originated from native potato starch. They were chemically modified by a crosslinking reaction with epichlorohydrin and then etherified with hydroxypropylene oxide. The substitution degree of hydroxypropylation, DS, was 0.5 for all crosslinked starches (HPC) investigated here.

The addition of the crosslinking agent, that is, epichlorohydrin, was carried out at a temperature beyond the gelatinization temperature so that the crystalline structure was lost before performing the chemical modifications. Different samples were prepared this way. The theoretical extent of crosslinking ranges from 0.05 to 0.75% wt and the samples used in this work were called HPC 0.05, HPC 0.1, HPC 0.25, and HPC 0.75.

### Preparation of Starch Suspensions

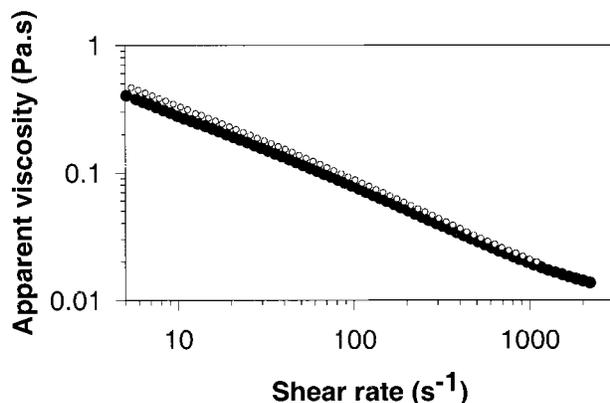
Starch suspensions exhibited swelling at room temperature and, hence, did not need a further heat procedure. Weighted amounts of starch were slurried under mechanical agitation (rotation speed of 125 rpm) in deionized water at 25°C for 2 h. We limited our studies to starch concentrations from 0.3 to 20% w/w

### Swelling Power of Starch Suspensions

Low concentrated starch suspensions (0.3%) were centrifuged (Sigma 2 K 15, 700g, 15°C, 40 min), leading to a separation of a liquid supernatant and a sediment. The swelling power  $Q$  was expressed in milliliters of water per gram of starch by weighing the sediment and, hence, estimating the amount of water absorbed by the nonsoluble materials.<sup>13</sup>

### Particle-size Distribution

The particle-size distribution of starch suspensions was determined from the analysis of the light scattered by particles with a computer-controlled laser diffraction particle-size analyzer (Mastersizer Micro, Malvern, Great Britain). For particles having a diameter much larger than the wavelength of the light, the behavior of scattered light followed the same law as that of the Fraunhofer diffraction theory for solid disks of the same diameter.



**Figure 1** Flow curve of an HPC 0.75 suspension ( $C = 10\%$ ;  $T = 25^\circ\text{C}$ ); comparison of measurements with (●) a double-gap cylinder,  $500\ \mu\text{m}$ , and (○) a cone-plate geometry,  $55\ \mu\text{m}$ .

### Light Microscopy

The structure of starch was assessed by light microscopy using a LEICA microscope. The starch powder was placed on a glass blade. Then, a drop of a lugol solution ( $\text{I}_2 + \text{IK}$  at  $0.02M$ ) was added and the coverslip was placed. The lugol solution in excess was eliminated by rinsing with deionized water. Starch was dyed blue by iodine. The observation was performed under a  $\times 40$  magnification.

### Cryo-preparation and Low Temperature: Scanning Electron Microscopy (SEM)

Low concentrated starch suspensions ( $0.3\%$ ) were prepared and frozen in nitrogen at  $-192^\circ\text{C}$ . The sample was placed in a cryogenic room (HEXLAND-OXFORD CT 1006) and prepared through a cryosection. The examination was performed with a scanning electron microscope (JEOL, JSM 35 CF) after sublimation at about  $-100^\circ\text{C}$ .

### Rheological Measurements

In the dilute regime, the viscosity was determined using a low-shear 30 viscometer (Contraves). All the measurements on concentrated suspensions were performed with a Carrimed CSL 100 controlled-stress rheometer (TA Instruments). Depending on the concentration, the measurements were performed using a double-gap cylinder ( $R_1 = 20\ \text{mm}$ ,  $R_2 = 20.38\ \text{mm}$ ,  $R_3 = 21.96\ \text{mm}$ ,  $R_4 = 22.38\ \text{mm}$ ), a cone-plate ( $4\ \text{cm}^2$ ), and a plate-plate ( $2\ \text{cm}$ ) geometry. These three measuring systems were equipped with a solvent trap

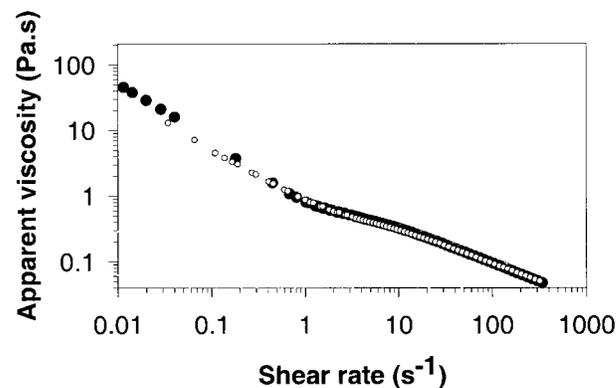
to prevent any solvent evaporation. All the measurements were performed at  $25^\circ\text{C}$ .

Since we are dealing with suspensions of particles with an average diameter larger than  $10\ \mu\text{m}$ , caution has to be taken to fulfill the theoretical requirements of rheological measurements: the system can be considered as continuous, which means that the particle size must be small enough in comparison with the distance between the surfaces of the measuring system and that no slip at the wall must occur. To verify these requirements, measurements with different gaps were performed. This is illustrated in Figures 1 and 2.

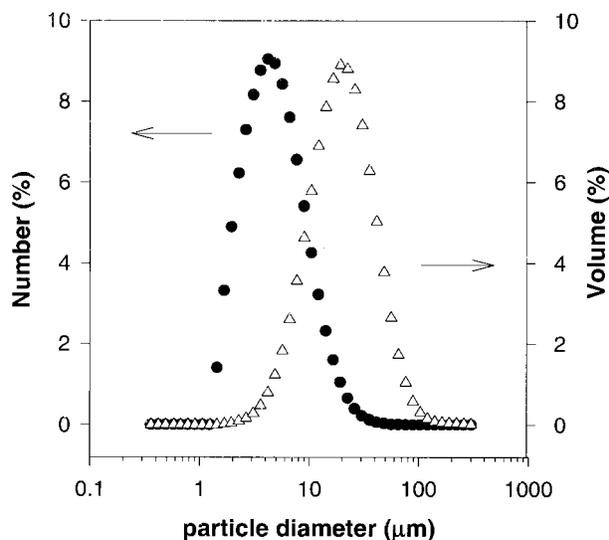
Figure 1 shows a typical flow curve from an HPC 0.75 suspension obtained with a cone-plate geometry (truncature distance =  $55\ \mu\text{m}$ ) and a double-gap cylinder geometry (gap =  $500\ \mu\text{m}$ ). The fact that both curves were the same indicates that the particle size is not detrimental to the rheological measurements. On the other hand, measurements were performed using a rough-surface "sanded" cone, which has been proved to eliminate slippage, and compared to measurements with a smooth one (Fig. 2).

Once again, both flow curves were the same. This result tends to prove that with smooth surfaces no slip occurs at the suspension-wall interface. So, we estimated that a cone-plate geometry with smooth surfaces could be used for characterizing such suspensions, at least in the range of the used shear rates.

Flow measurements were carried out as follows: the stress was applied continuously to a shear rate of  $1200\ \text{s}^{-1}$ , immediately followed by a decrease of the shear rate to 0. This "up"-and-



**Figure 2** Flow curve of an HPC 0.1 suspension ( $C = 10\%$ ;  $T = 25^\circ\text{C}$ ); comparison between (●) a nonroughened and (○) a roughened cone-plate geometry.



**Figure 3** Volume and number-average size distribution of HPC 0.1 sample (temperature, 25°C).

“down” cycle lasted 10 min. These measurements were completed with the following procedure: stress is then applied during a period of 2 min to reach a steady value of the shear rate.

Oscillatory shear measurements were performed within a frequency range between 0.01 and 10 Hz. This allowed us to measure the viscoelastic moduli ( $G'$ , storage modulus, and  $G''$ , loss modulus) as a function of the frequency. The strain amplitude was lower than 0.02 and it was checked that the measurements were carried out within the linear viscoelastic region.

## RESULTS AND DISCUSSION

### Characterization of the Starch Samples

Figure 3 shows that the particle-size distributions are rather broad and that the polydispersity, defined as the ratio of the volume-average diameter to the number-average diameter, is relatively important. All the samples exhibit a similar distribution and are compared on the basis of their volume-average diameter. These values are reported in Table I along with the swelling power values. We can note that the average particle size increases with the extent of crosslinking, whereas the swelling power decreases.

Microscopic observations are shown in Figures 4 and 5. In the case of HPC 0.1 [Fig. 4(a)] and HPC 0.25 [Fig. 4(b)], a blue coloration is observed all over the medium. So, the particles, shown by

these photographs, do not correspond to starch granules. They probably arise from the breakdown of the granules during the process. It may also be assumed that the particles swell when iodine is added. The result would be that they appear more diffuse.

For samples with higher degrees of crosslinking, HPC 0.5 [Fig. 4(c)] and HPC 0.75 [Fig. 4(d)], individual particles were clearly displayed. In the case of HPC 0.5, some of them are apparently more swollen than in the case of HPC 0.75. However, some particles of lower size are also observed. The fact that in these latter samples (HPC 0.5 and HPC 0.75) a large part of starch particles apparently keep their initial structure, whereas the lowest crosslinked samples (HPC 0.05, HPC 0.1, and HPC 0.25) are broken down, is quite surprising since all these samples experienced the same thermal treatment. It is generally believed that the heating of native potato starch above the gelatinization temperature results in the loss of the crystalline structure as well as in the rupture of starch granules. It may be assumed that the chemical modification (crosslinking plus derivatization) is performed on swollen integral granules and that their rupture could take place during the derivatization. Another hypothesis is that the chemical modification was carried out on fragmented particles arising from the gelatinization process. Nevertheless, a higher degree of crosslinking probably makes the starch granules more resistant to rupture than does a lower degree of crosslinking (HPC 0.05–HPC 0.25). This hypothesis is consistent with the thermal stability results and will be discussed in a future article.<sup>14</sup>

Figure 5 shows photographs of the two starch suspensions, obtained by low-temperature SEM. We can observe two phases: some particles and a continuous suspending medium. The particles are not spherical and their size increases with the degree of crosslinking. The average particle size was about 20  $\mu\text{m}$  for HPC 0.1 and 60  $\mu\text{m}$  for HPC 0.5. An important size distribution is evidenced. These results are consistent with the previous data reported in Table I. Moreover, it could be assumed from the molecular weight determination that the continuous suspending medium (between 10 and 30 wt %) is composed of water and polymer chains ( $\bar{M}_w = 3.5 \times 10^4$  g/mol), which are more solubilized than are the particles.

From all these observations, the starch samples can be described as suspensions of deform-

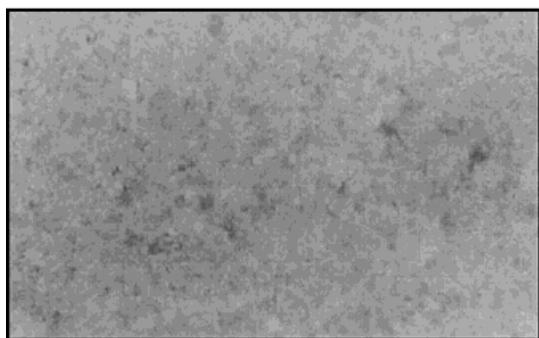


Fig. 4a

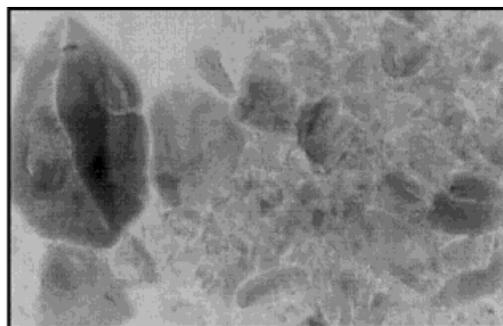


Fig. 4c

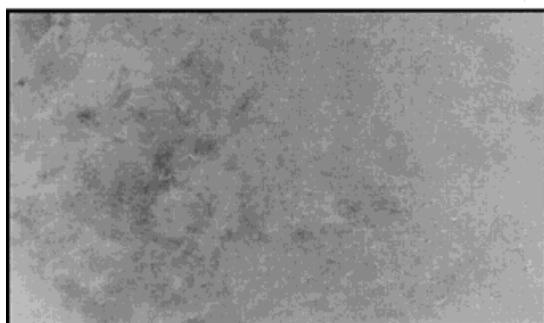


Fig. 4b

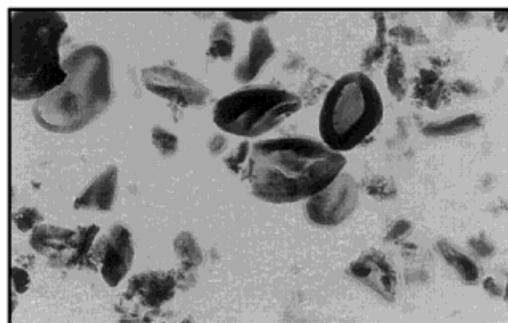


Fig. 4d

**Figure 4** Light microscopic observations of crosslinked starch samples: (a) HPC 0.1; (b) HPC 0.25; (c) HPC 0.5; (d) HPC 0.75 (scale: 0.9 cm for 100  $\mu\text{m}$ ).

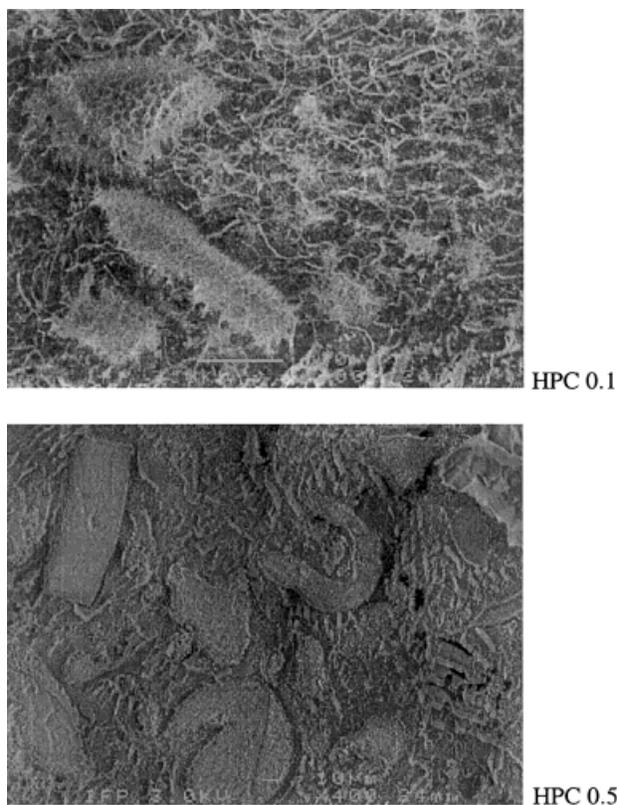
able particles suspended in a continuous suspending medium constituted of polymer chains plus water. Depending on the amount of solvent available, the particles swell in water at room temperature and their size increases with the degree of crosslinking. It is usually possible to define a critical concentration  $C^*$  for suspensions which corresponds to the “space-filling concentration,” that is, the concentration at which the system appears homogeneous. It has been demonstrated that this critical concentration is close to the inverse of the swelling power, in the case of starch suspensions.<sup>6,7</sup> So, two concentration regimes can be defined: a dilute regime for  $C < C^*$  and a concentrated one for  $C > C^*$ . The values of this critical concentration  $C^* = 1/Q$  for the different samples are reported in Table I. Indeed, the higher the extent of crosslinking, the lower the swelling power and, hence, the higher is the space-filling concentration.

#### Rheological Properties: Flow Properties

The study in the dilute domain was limited to the lightly crosslinked samples (0.05–0.1–0.25%) for which no sedimentation was observed in the time scale of the measurements. Indeed, the highly crosslinked samples (HPC 0.5 and HPC 0.75) settle down in a few minutes. This is due to their poor swelling ability (about 16 mL/g) and, hence, to the high density of the swollen particles.

In Figure 6, the apparent viscosity is plotted as a function of the shear rate for the HPC 0.1 sample. A Newtonian behavior is observed for concentrations below 30 g/L. Above this concentration, flow curves show a shear-thinning behavior in the range of the shear rates tested. This characteristic concentration is close to the critical concentration  $C^*$  (here, 33 g/L; see Table I).

Figure 7 shows the viscosity at a constant shear rate for the lightly crosslinked samples as a function of the concentration. Two zones are dis-



**Figure 5** Low SEM observations (scale bar: HPC 0.1: 1.5 cm for 10  $\mu\text{m}$ ; HPC 0.5: 1.5 cm for 10  $\mu\text{m}$ ).

played as the concentration increases: First, the apparent viscosity of the starch suspension proportionally increases with the concentration up to a concentration  $C_1$ ; afterward, it sharply increases until a concentration  $C_2$ . This variation is more and more pronounced with the extent of crosslinking. Also, these concentrations,  $C_1$  and  $C_2$ , increase with the degree of crosslinking. This can be explained by a decrease of the swelling power and an increase of the particle size. The concentration  $C_1$  is about 14, 18, and 28 g/L, respectively, for HPC 0.05, HPC 0.1, and HPC 0.25 and limits the “true dilute domain.” In this domain, the viscosity is little influenced by the degree of crosslinking and, hence, by the size of particles as expected for dilute suspensions.

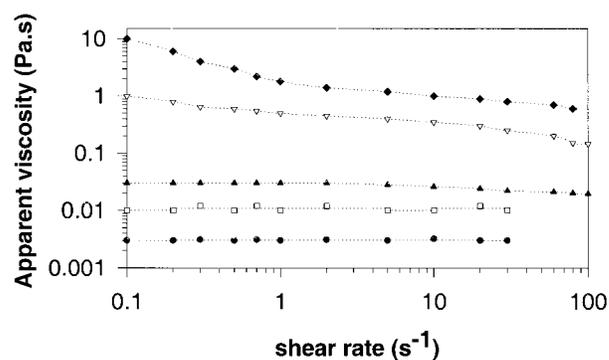
A semidilute regime can be defined between  $C_1$  and  $C_2$ . The large increase of viscosity in this regime, which depends on the extent of crosslinking, can be explained by the decrease of the distances between particles, leading to an increase of interactions between them. The concentration  $C_2$  is about 26 g/L for HPC 0.05, 30 g/L for HPC 0.1, and 40 g/L for HPC 0.25. These values are approx-

imately equal to the critical concentration  $C^*$  calculated previously (see Table I) and  $C/C^*$  seems, thus, to be a determining parameter. So, the viscosity data of Figure 7 are reported in Figure 8 as a function of this parameter. We can see that all the data, whatever the crosslinking degree ( $<0.5\%$ ), collapse reasonably well to a single master curve. Figure 8 also shows that the apparent viscosity slowly increases with the parameter  $CQ$  to 0.6, corresponding to  $C = C_1$ , and reaches an asymptote at  $CQ = 1$ .

In Figure 9, the apparent viscosity is plotted as a function of shear stress, for different samples in the concentrated regime, at a value of  $CQ = C/C^*$  equal to 2.75. Obviously, this parameter does not have a real physical meaning when it is above unity. However, it can provide, as in the dilute regime, a convenient scaling of concentration in terms of a potential phase volume as suggested by Evans and Lips.<sup>12</sup>

Flow curves show a shear-thinning behavior, which is more and more pronounced when the degree of crosslinking increases. This probably reflects a change in the organization of the system. A comparison of the “down” and the “up” curve allows one to show the thixotropic behavior of the system. In the case of HPC 0.05 and HPC 0.1, the “down” and “up” curves are surimposed, reflecting the nonthixotropic character of the system. The two other suspensions (HPC 0.25 and HPC 0.75) exhibit a hysteresis loop. These results may be explained by the high rigidity of the particles. It should also be mentioned that when these suspensions are left at rest for 1 min they recover their initial state, showing, therefore, a thixotropic behavior.

On the other hand, the upward curvature of the curves toward the low shear stress suggests



**Figure 6** Flow curves of HPC 0.1: (●) 0.8%; (□) 1.4%; (▲) 2%; (▽) 3%; (◆) 4%.

**Table I Granule Size ( $D$ ), Swelling Power ( $Q$ ), and Critical Concentration ( $C^*$ ) of Crosslinked Starch Derivatives**

Measurement	Sample				
	HPC 0.05	HPC 0.1	HPC 0.25	HPC 0.5	HPC 0.75
$D$ ( $\mu\text{m}$ ) <sup>a</sup>	20	22	45	60	60
$Q$ (mL/g)	41	30	24	17	15
$C^* = 1/Q$ (g/L)	24	33	42	58	66

<sup>a</sup>  $D$ : volume-average diameter.

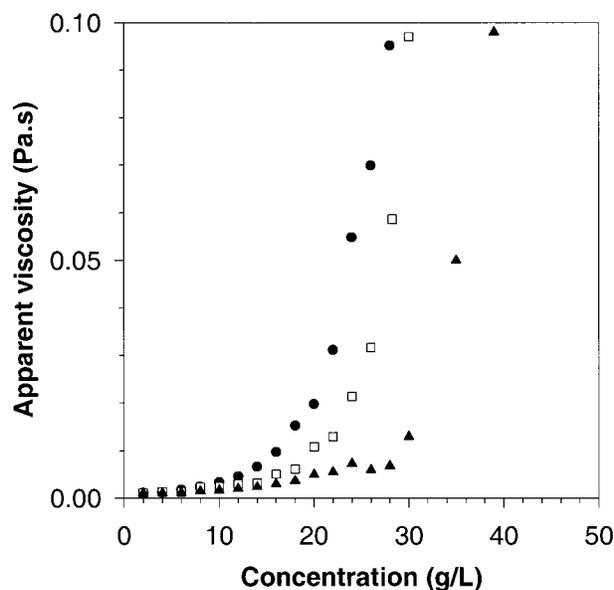
that the systems exhibit an apparent yield stress, classically defined as the critical stress below which no flow is recorded.<sup>15</sup> Therefore, this can be approximately evaluated from the asymptote obtained from the viscosity–shear stress curve toward low shear stress. The value of the apparent yield stress deduced from Figure 9 are the following: 1, 10, 20–30, and 100–200 Pa, respectively, for HPC 0.05, HPC 0.1, HPC 0.25, and HPC 0.75.

To confirm the existence of an apparent yield stress, equilibrium measurements were carried out. Taking into account the time-dependent behavior of the systems, this is a more appropriate method to obtain a steady state, especially in the low shear-rate region. This experiment corresponds to a succession of creep measurements within the whole shear-rate range. Increasing

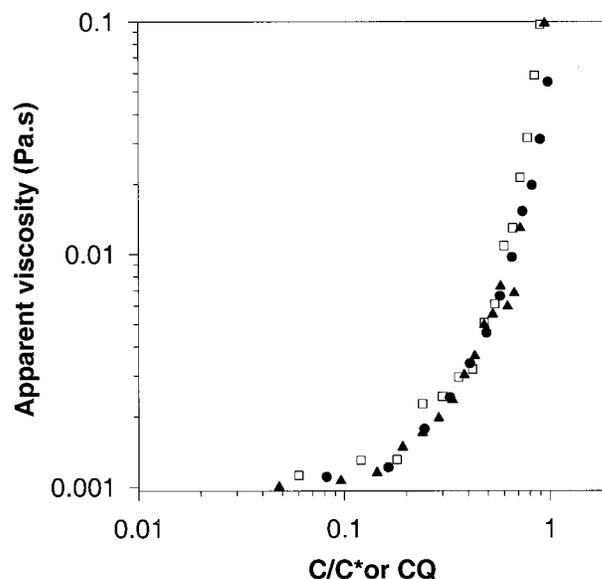
stresses are applied stepwise; each measurement lasts 2 min and the time between two measurements is 1 min. An example is given in Figure 10, where the shear stress is plotted as a function of shear rate for HPC 0.25 at 10% ( $CQ = 2.4$ ).

This procedure allows one to determine the apparent yield stress of the HPC samples; for example, the data of Figure 10 lead to a value of 30 Pa. Figure 11 shows the variation of the apparent yield stress with the concentration, for different degrees of crosslinking.

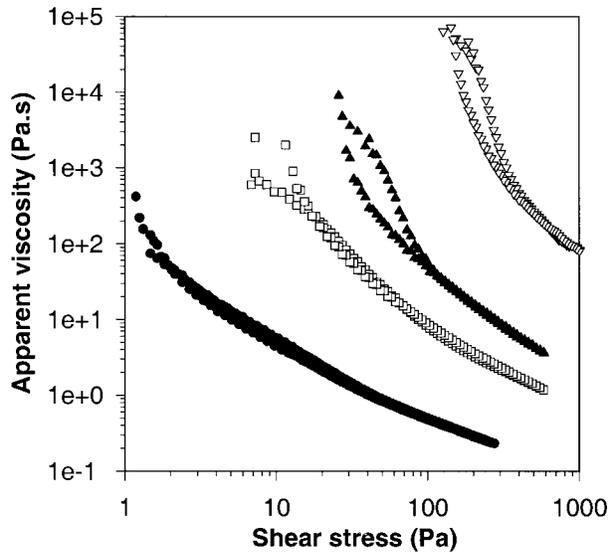
For the three lowest crosslinked starches (HPC 0.05, HPC 0.1, and HPC 0.25), the same type of variation is exhibited. The apparent yield stress increases progressively with the concentration but reaches a quasi-plateau at a high concentration. The level of this plateau increases with the



**Figure 7** Variations of the apparent viscosity at  $1 \text{ s}^{-1}$  as a function of the concentration ( $T = 25^\circ\text{C}$ ): (●) HPC 0.05; (□) HPC 0.1; (▲) HPC 0.25.

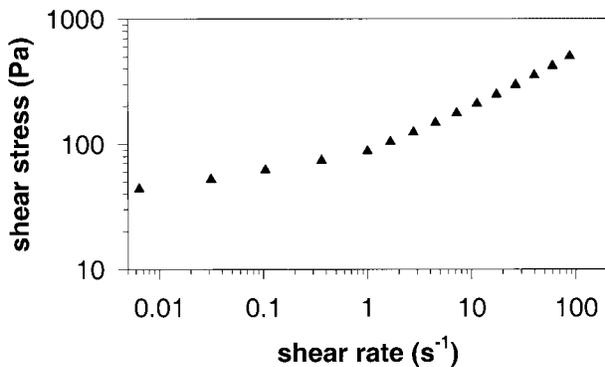


**Figure 8** Variations of the apparent viscosity at  $1 \text{ s}^{-1}$  as a function as the nondimensional parameter  $CQ$  ( $T = 25^\circ\text{C}$ ): (●) HPC 0.05; (□) HPC 0.1; (▲) HPC 0.25.

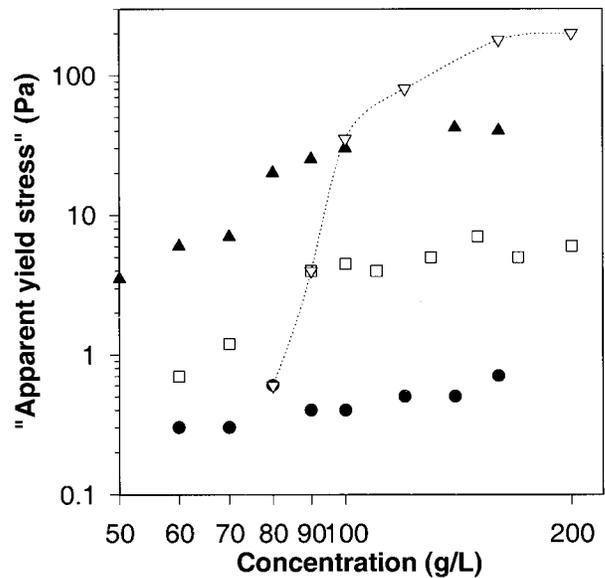


**Figure 9** Flow curves of HPC samples ( $CQ = 2.75$ ): (●) HPC 0.05; (□) HPC 0.1; (▲) HPC 0.25; (▽) HPC 0.75.

degree of crosslinking. Clearly, the apparent yield stress increases with the concentration and is a function of the extent of crosslinking at a given concentration. The higher the extent of crosslinking, the higher is the apparent yield stress. A rather different behavior is observed for HPC 0.75: A sharp increase is observed within the concentration domain of 80–100 g/L, that is, in a zone between  $C^*$  and  $2C^*$ . For  $C > 2C^*$ , the variation parallels that of the other samples. In fact, an examination of the values of  $C^*$ , reported in Table I, indicates that, whatever the degree of crosslinking, the quasi-plateau in the yield stress occurs at a concentration close to  $2C^*$ , which increases with the extent of crosslinking. This concentra-



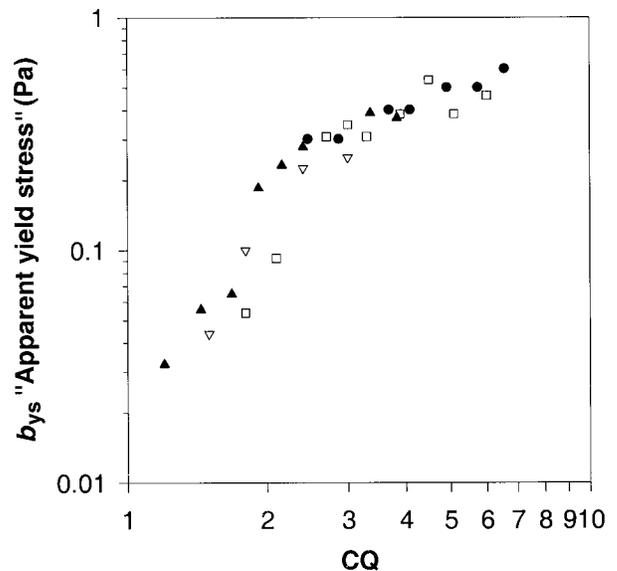
**Figure 10** Flow curve of HPC 0.25 ( $C = 10\%$ ;  $T = 25^\circ\text{C}$ ); equilibrium measurements: applied stress (2 min); rest time between two stresses (1 min).



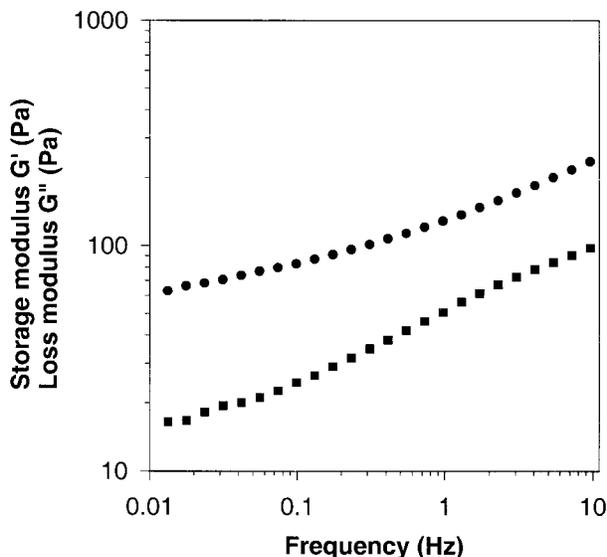
**Figure 11** Variation of the "apparent yield stress" as a function of starch concentration: (●) HPC 0.05; (□) HPC 0.1; (▲) HPC 0.25; (▽) HPC 0.75.

tion dependence seems consistent with the data reported by Evans and Lips<sup>12</sup> for other crosslinked starches.

The data of Figure 11 are plotted in Figure 12 versus the  $CQ$  parameter. Contrary to the viscosity curves in the dilute regime, the normalization



**Figure 12** Normalization of plots shown in Figure 11. X-axis and Y-axis translation factor are respectively  $1/Q$  and  $b_{ys}$ . (Reference curve: HPC 0.05) (●) HPC 0.05, (□) HPC 0.1, (▲) HPC 0.25, (▽) HPC 0.75.



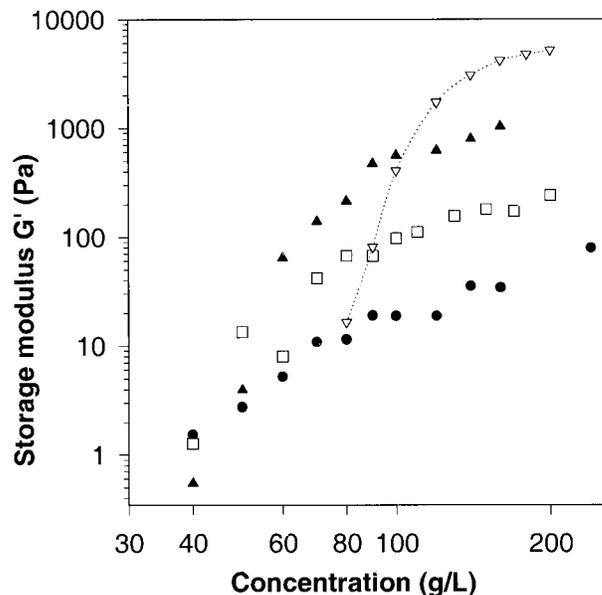
**Figure 13** Storage and loss moduli as a function of frequency for an HPC 0.1 suspension ( $C = 10\%$ ,  $T = 25^\circ\text{C}$ , strain amplitude = 2%): (●)  $G'$ ; (■)  $G''$ .

of the apparent yield stress requires, in addition, the use of the vertical shift parameter  $b_{ys}$ , which strongly increases with the extent of crosslinking. These results also suggest that the properties of the concentrated systems are governed, whatever the degree of crosslinking, by similar mechanisms in which the rigidity of the particle plays a predominant role.

### Viscoelastic Properties

Viscoelastic properties are estimated only for concentrated suspensions, because of the limited sensibility of the rheometer. Figure 13 shows the frequency dependence of storage ( $G'$ ) and loss ( $G''$ ) moduli for HPC 0.1 taken as an example ( $C = 100\text{g/L}$ ;  $CQ = 4.1$ ). Both moduli display a very slight frequency dependence. The storage modulus was much higher than was the loss modulus. These results are typical of all the suspensions investigated, in the linear viscoelastic domain, and suggest a rather solidlike behavior. So, in this concentration domain, the system can be described as a closely packed particle system and the rheology is governed at a given  $CQ$  value by the particle rigidity.

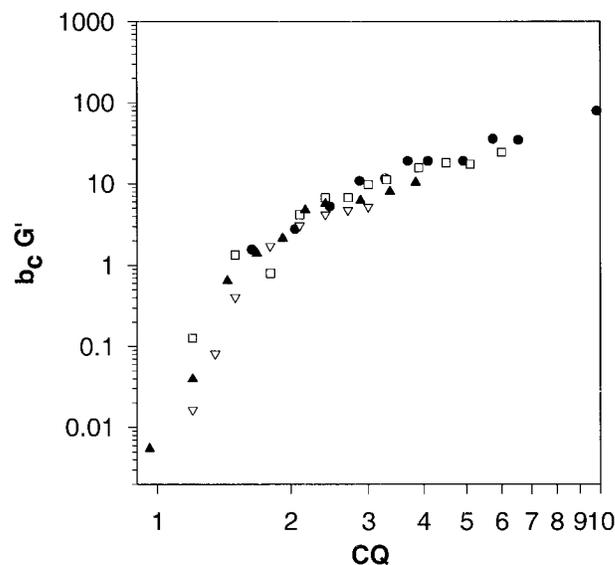
Figure 14 shows the concentration dependence of the storage modulus (measured at 0.1 Hz) for the various systems. The observed results are similar to those obtained for the apparent yield stress measurements. However, a wider range of



**Figure 14** Storage modulus (measured at 0.1 Hz) as a function of starch concentration: (●) HPC 0.05; (□) HPC 0.1; (▲) HPC 0.25; (▽) HPC 0.75.

concentration could be explored. For each system, the lowest measurable concentrations roughly correspond to the critical concentration  $C^*$  (see Table I).

The data from Figure 14 are reported in Figure 15 in which the concentration scale is replaced by



**Figure 15** Normalization of plots shown in figure 14. X-axis and Y-axis translation factor are respectively  $1/Q$  and  $b_{cross}$ . (Reference curve: HPC 0.05) (●) HPC 0.05, (□) HPC 0.1, (▲) HPC 0.25, (▽) HPC 0.75.

the parameter  $CQ$  and the storage modulus is normalized using a shift parameter  $b_c$ , which also strongly increases with the degree of crosslinking as the shift factor  $b_{ys}$  and both factors are equal. All data superimposed quite well on the same curve, and this also suggests that the particle packing and the particle rigidity govern the elastic properties. It is likely that the main parameter implied in these mechanisms is related to the rigidity of the particles.

## CONCLUSIONS

Different modified starches originated from native potato starch were studied. They were characterized in terms of swelling properties, particle-size distribution, light microscopy, low SEM, and rheological properties. The swelling power decreases with the degree of crosslinking, whereas the average particle size increases.

The rheological properties display two concentration regimes below and above a critical concentration  $C^*$  which is approximately equal to the inverse of the swelling power. In the dilute regime  $C < C^*$ , the zero shear-rate viscosity can be described with the lone parameter  $CQ$  whatever the crosslinking degree in the range of 0.05–0.25%. On the other hand, an apparent yield stress and a solidlike behavior were observed in the concentrated regime  $C > C^*$ . The variations of these rheological parameters with the  $CQ$  parameter suggest that, contrary to the viscosity in the dilute regime, the rigidity, which is related to the crosslinking, must be considered. In the future, it will be interesting to relate the macroscopic properties of starch derivatives to the microstructure

of the system, as a function of heat and/or shear treatments that they have been subjected to.

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