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ORIGINAL CONTRIBUTION

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Shear-dependent rheological properties of starch/bentonite composite gels

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Abstract Rheological properties of starch/bentonite gels (5.3–8.2% solids, 0–100% starch) were investigated at shear rates 0.0083–0.33 s^{-1} (Brookfield viscometer). Prior to these measurements the strain introduced during preparation of the gel was kept as low as possible. Under these conditions six different types of structural units could be identified in the gel: bentonite particles associated in a band-type structure; bands coated with starch polymers; bundles of bands interlaced and enveloped by starch polymers (strands); individual bentonite platelets dispersed in a polymer matrix; starch polymer networks; and swollen granules. A power-law model was fitted to the experimental viscosity data: $\mu_{app} = K\dot{\gamma}^{n-1}$. In all cases n was found to be less than 0.5. Its value decreased with the ability of the structural components to reorient under applied shear. K was found to be proportional to the compaction and/or entanglement of the structural units. These trends in K and n were further confirmed by the index of thixotropy (IT) and complex modulus of shear elasticity (G^*) measurements.

Key words Bentonite – starch – rheology – viscosity – thixotropy – amylogram

Introduction

The rheological behavior of bentonite/polymer gels is of special interest in cosmetics and surface coatings. Structure of these gels was reported in a previous paper [1]. The bentonite has a Na/Ca ratio of 1.046 in the pristine state and 1.76 after purification by sedimentation. The corn starch used contained 25% (w/w) amylose and 75% amylopectin. In the absence of starch, bentonite forms predominantly band-type structures. The framework of the starch gels is formed of fully swollen granules linked by hydrogen bonds. Crystalline domains within the granules are relatively stable: the granules are difficult to disperse into random polymer coils. Amylose forms helical structures even in the gel phase outside of the granules. At low solids/water and starch/bentonite ratios the granules are completely disintegrated. It was found that the presence of bentonite promoted leaching of polymers from the granules (gellation). On the other hand, the presence of the starch polymers favored lamination of the montmorillonite bands. The different structures are shown in Fig. 1. Increasing water contents decrease the compactness of these structures, promotes gellation of granules and makes the montmorillonite bands as well as the remnants of the starch granules more fragile.

The behavior of these gels under applied shear stresses and strains are of particular interest in cosmetic and surface coating applications. In the literature, rheological properties of starches are investigated in relation with the structural transformations brought about by heat transfer during cooking [2–5]. Therefore, special instruments

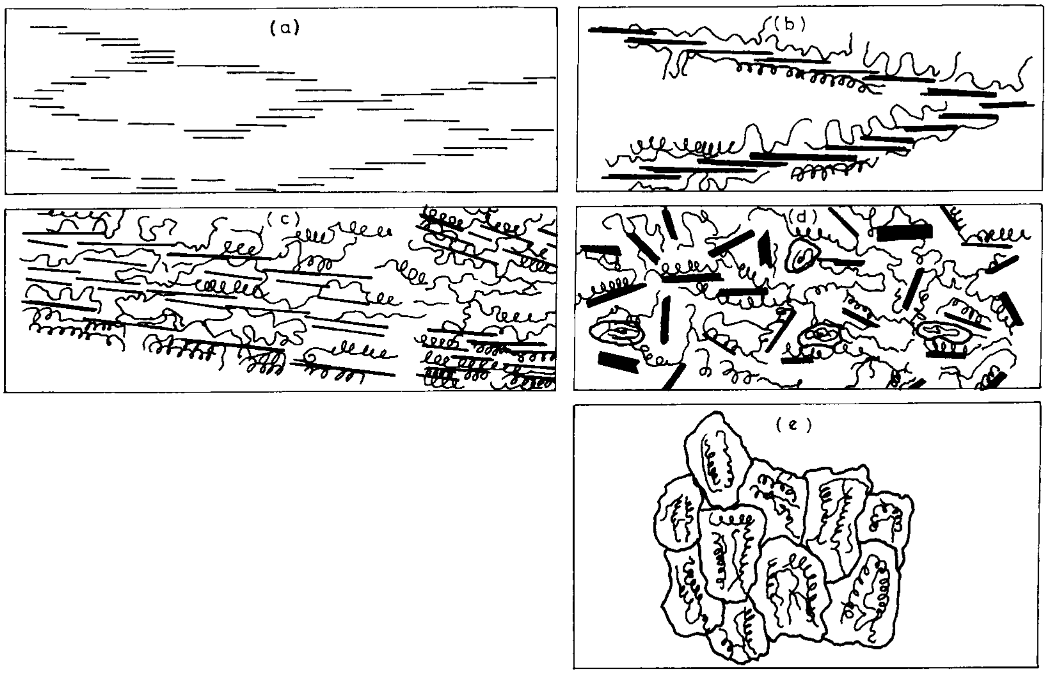


Fig. 1 Possible structures of bentonite/starch gels: (a) pure bentonite gel; (b) montmorillonite bands coated with starch polymers (at 10–20% starch); (c) montmorillonite bands forming strands with starch polymers (50%); (d) montmorillonite platelets dispersed in starch polymers and granules (80%); (e) granular structure of pure starch gels

adapted to conditions during cooking are used for the measurement of viscosity. One of these, the "viscoamylograph", is universally used to measure the viscosity during the gelatinization of starch. It is a modified form of rotaviscosimeter with a sensor/stirrer consisting of seven pins instead of a cylinder. Because of the complex geometry of the sensor, the measured viscosity in terms of Brabender Units (BU) cannot be correlated with the viscosity measured in a rotational viscometer with a well-defined cylindrical sensor, especially with power-law fluids. The stirrer rotates with 75 rpm. Generally, 6.6% (w/w) starch solutions in water are used in the tests. The content of the bowl is heated at a rate of 1.5 °C/min, so the viscosity is recorded simultaneously as a function of time and temperature. A typical Brabender amylograph [6] is given in Fig. 2.

O: Heating of the mixture is started at a rate of 1.5 °C/min with stirring at 75 rpm.
A: Gelatinization by swelling of granules has advanced to a considerable extent to cause a measurable increase in viscosity.
B: Maximum viscosity is reached when the granules are fully swollen.
C–D: Disintegration of granules and leaching out of amylose and amylopectin cause a decrease in viscosity. If these polymers are cross-linked, as in modified starches, the viscosity rises above that of fully swollen state at point B.
D–E: Setting of a stable gel (retrogradation) on cooling to 50 °C. Natural starches show a greater viscosity increase than cross-linked starches.
F: The final viscosity indicates the stability of the fully gelatinized starch.

In the fully swollen state natural corn starch (6.6% in water) shows a maximum viscosity of 400–500 BU at 62–72 °C. Its viscosity decreases slightly during digestion at 95 °C due to the disintegration of the granules.

Bentonites have long been known to exhibit Bingham plastic behavior [7], showing at high shear rates the behavior of a Newtonian fluid. So the rheological behavior of bentonite dispersions was investigated after homogenization [8]–[10]. Bingham yield stress values τ_B were found by extrapolating the linear section of the flow curve to $\dot{\gamma} = 0$.

In 1989, Cameron [11] showed that for power-law fluids with a low viscosity index such as clay suspensions and polymer gels, the observation of apparent slip may result from a change of fluid properties under high shear. When large shear stress gradients are applied, the fluids are assumed to flow in layers, the index of viscosity n decreasing with an increase in the shear stress. Based on this

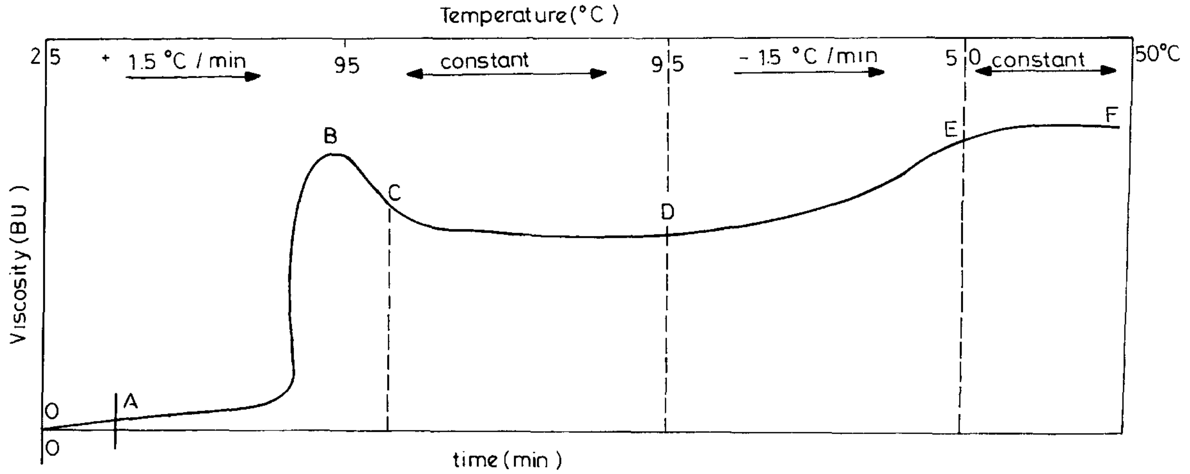


Fig. 2 A typical viscosity curve for starch gels obtained in a Brabender amylograph

model Barnes and Carnali [12] showed for Veegum PRO clay suspensions that what has hitherto been considered as a yield stress is actually a decrease in viscosity by an order of magnitude in a very narrow range of applied stress. This sudden change in viscosity was attributed to thixotropic structural variations taking place within the fluid under stress and was identified with the yield stress.

The rheological behavior of bentonite/starch gels with such structural variations as discussed in the previous paper could not be expected to be fitted by a single model. Nevertheless, to monitor the effect of the structural changes, the most versatile model, the Oswald–de Waele or power law was tested:

$$\tau = \mu_e \dot{\gamma} , \qquad (1)$$

$$\mu_e = K \dot{\gamma}^{n-1} . \qquad (2)$$

Experimental

Materials

Bentonite with a Na/Ca ratio of 1.06 was obtained from SAMAS A.S. The bentonite was purified from silica and hematite by sedimentation [1]. The Na/Ca ratio in the purified bentonite was 1.76. Edible corn starch consisting of 25% amylose and 75% amylopectin was bought from Piyale A.S.

Experimental design

Employment of high shear rates to maintain experimental reproducibility would destroy the characteristic conformation and resultant shear behavior. On the other hand, unavoidable experimental errors could be introduced by inhomogenieties in the gel structure, when low strains only are applied during the preparation of the gels. To differentiate between both effects, experimental design methods [13] were used and the central composite rotatable design method of Box and Hunter [14] was chosen as the most suitable.

In the central composite design method, the two variables are designated on the x- and y-axes (Fig. 3). The z-axis normal to this plane represents the response obtained in the experiments. The following procedure is used in making the design:

1) The limits of the variables on the x (% starch in the solids) and y (% solids in the gel) axes are determined.

2) A central point in the plane of the variables is chosen.

3) These variables are converted into dimensionless forms ($x = X_1$, $y = X_2$) by suitable mathematical rearrangements:

X_1 = {(% starch)-(% starch at center)}/{Half of the total variation in % starch},

X_1 = {(% starch)-50}/50, (3)

X_2 = {(ml water in the gel)-(ml. water used in center point)}/(Half of the total difference between the water contents)

= {(ml water in the gel)-700}/140 . (4)

X_2 actually represents the percentage of the solids. But the total amount of solids was fixed at 50 g in the preparation of the gels during the experiments. So the solids content was expressed in terms of the dilution of the gel in the

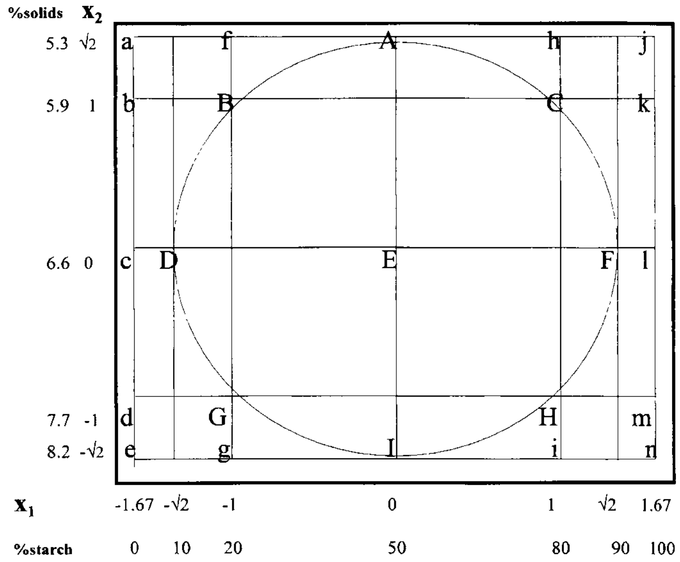


Fig. 3 Layout of the experimental design

non-dimensional form, X_2. Zero level of solids content ($X_2 = y$) was set at the level employed in the viscoamylograph (6.6% solids or 700 ml water). The upper limit was set at 5.3% (840 ml water), below which bentonite gels show Newtonian behavior. Once the radius of the circle was determined with these limits, the lower level was automatically set at 8.2% (560 ml water). The natural midpoint of starch is 50% on the $x = X_1$ axis.

4) Eight experimental points at a distance of $\sqrt{2}$ (in dimensionless terms) are located at the points (1, 1), (− 1, 1), (− 1, − 1), (1, − 1), (2, 0), (0, 2), (− 2, 0) and (0, − 2) on a circle with center at (0, 0). The final design form is given in Fig. 3 as the dotted circle.

5) Experiments are performed at these eight points and at the central point (0, 0) to determine experimental errors. In addition to this basic design format, extra experimental points were added on a square in which the design circle was inscribed to be able to treat the data parametrically on conventional graphs.

Amylograph measurements

Standard procedures were followed in the experiments with the amylograph (6): 35 g (dry basis) of corn starch or starch/bentonite mixture were dispersed in 500 ml of water. With cooling or heating coils the initial temperature of the dispersion in the amylograph is adjusted to 25 °C. The dispersion is stirred with 75 rpm while being heated to 50 °C. The viscosity, in terms of Brabender Units (BU), is still zero. After equilibration at 50 °C the dispersion is heated with 1.5 °C/min under stirring and the viscosity is recorded continuously. The dispersion is held at 95 °C for 30 min, then is cooled with 1.5 °C/min down to 50 °C where it is held constant for another 30 min for completion of gellation.

Measurements of rheological properties

The gels were kept at 25 °C for 24 h before any measurements were made. They were directly poured into 600 ml beakers where the viscosity was measured with the Brookfield spindle. In this way strains and stresses introduced into the gel before measurements were minimized, and the viscosities reflected the true structure of the gel. For this reason, Brookfield viscometer was preferred over other types of rotaviscometers because of the small dimensions of the spindles which did not cause excessive strains during placement into position.

The viscosities were measured at 0.5, 1, 2.5, 5, 10 and 20 rpm. Measurement at a given stirring rate was continued until viscosity was constant. The stirring rate was then increased to a larger value. After reaching 20 rpm it was decreased in steps to 0.5 rpm to complete one cycle. $\mu^0_{0.5}$ denotes the viscosity at the beginning of the measurement at 0.5 rpm. Generally, viscosity decreased with time, thus $\mu^{eq}_{0.5}$ denotes the equilibrium value of the viscosity at 0.5 rpm. The value of the viscosity, at the end of one cycle was denoted as $\mu^f_{0.5}$.

Results

The viscosity measurements in the Brabender viscoamylograph are given in Fig. 4. The original coordinate system on the recorder paper was transferred to rectangular coordinate system used in Fig. 4, by coinciding with respect to time, the first peaks giving the maximum viscosity in gellation regardless of the temperature at which it occurred. The main points in these plots are summarized in Table 1.

According to the literature (6), gelatinization (swelling) temperature ranges from 62 °C to 72 °C and the maximum viscosity is given as 400–500 BU. The maximum viscosity is related to the extent of amylose leached. The swelling temperature is related to the amylose/amylopectin ratio. Since amylose forms crystalline domaines and amylopectin does not, the greater the amylose fraction the higher is the swelling temperature. Our data (in Table 1 of the previous paper) show that the amylose molecules used in this work have larger average molecular weights than given in the literature. A consequence is that the granules cannot swell (expand) considerably and amylose cannot

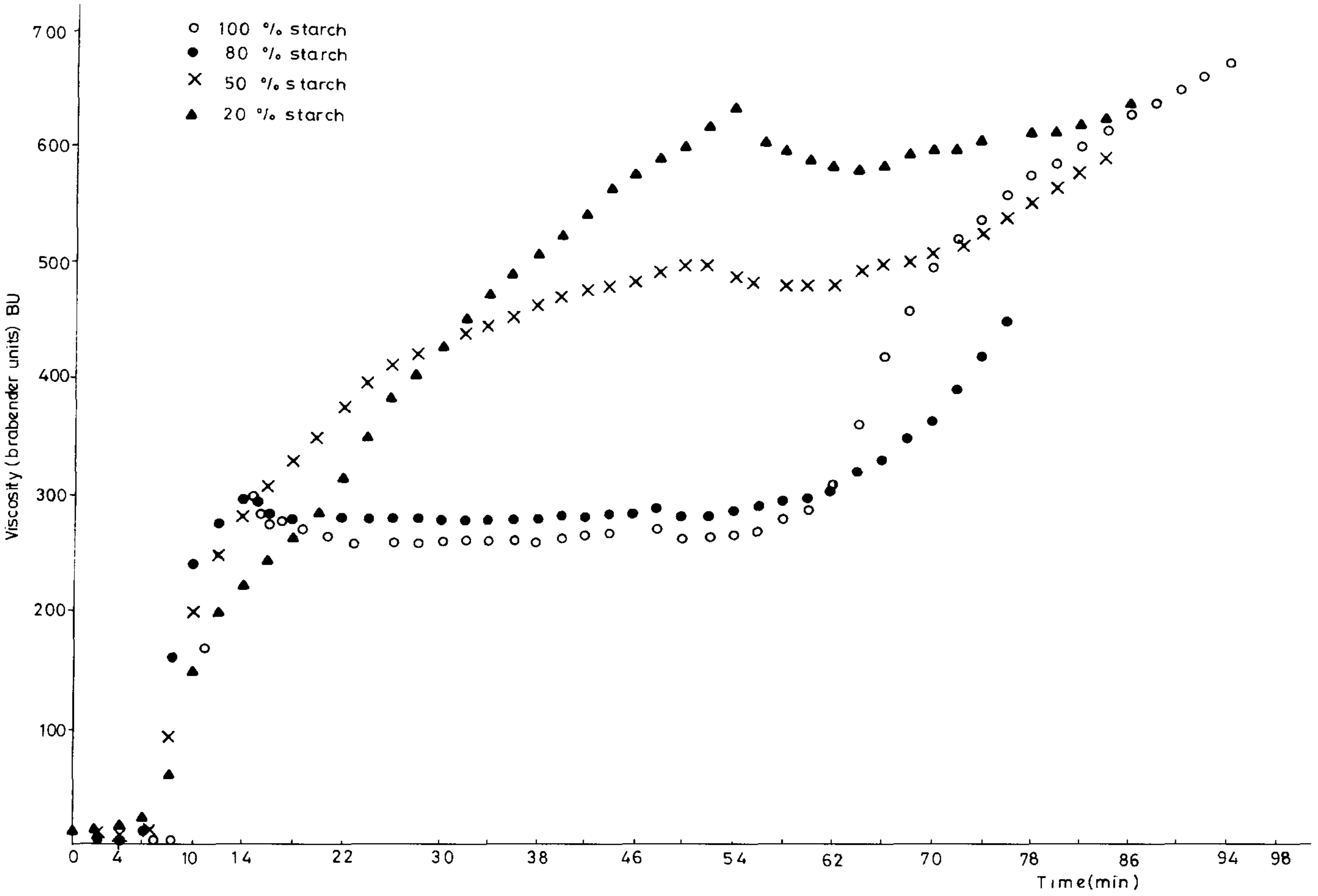


Fig. 4 Viscosity of bentonite/starch gels obtained with a Brabender Viscoamylograph

easily diffuse out of them. One should distinguish between swelling and gelatinization temperature: Swelling temperature is the lowest temperature at which the viscosity increases. Gellation temperature is the temperature where the viscosity reaches the maximum value. The values of both temperatures are given in Table 1.

From the amylograph measurements, the following conclusions are drawn:

1) The swelling temperature decreases with a decrease in the starch content because the bentonite bands facilitate the leaching out of the polymers; in addition, they support the starch granules (see previous paper) (1).

2) The maximum viscosity decreases with the starch content because the concentration of the polymers in the gel decreases.

3) The gellation temperature decreases with an increase in the bentonite content because montmorillonite facilitate swelling and disintegration of the granules.

4) The viscosity decrease during gellation in pure starch indicates the fragility of the granules. In the presence of 20% bentonite the fragility is reduced, and there is

Table 1 Results of viscoamylograph measurements

% starch in the solids	20	50	80	100
Swelling temperature T (°C)	53	66.5	69.5	83
Max. viscosity μ_{max} (BU)	130	140	285	300
Gellation temperature T (°C)	59	73.5	81	92
Variation in viscosity during gellation ($\Delta\mu$)	490	360	−5*	−18**

*Constant at 280 BU.
**Constant at 265 BU.

less variation in the viscosity during gellation. The viscosity increases as the starch content decreases because the disintegration of the granules is facilitated and an amorphous polymer network is formed. Delamination of montmorillonite is favored by the polymers, increasing the number of particles and the viscosity. In modified starches, the increase in the viscosity during gellation indicates the cross bonding between the polymers (3, 6). In our case, the viscosity increase indicates formation of bonds between delaminated montmorillonite and the polymers, e.g., montmorillonite particles act as cross-binding agents.

5) The rise in viscosity during the last part of the experiment is due to solidification of the gel structure on cooling to 50 °C. The decrease in slope of the viscosity against time with a decrease in starch ratio shows that bentonite/polymer gel is affected by temperature to a lesser extent than the polymer gels. Especially, the low slope at 20% and 50% starch gels show that the bentonite band structure determines the overall gel compactness.

An example of Brookfield measurements is given in Fig. 5 for the variation of viscosity with time and shear rate

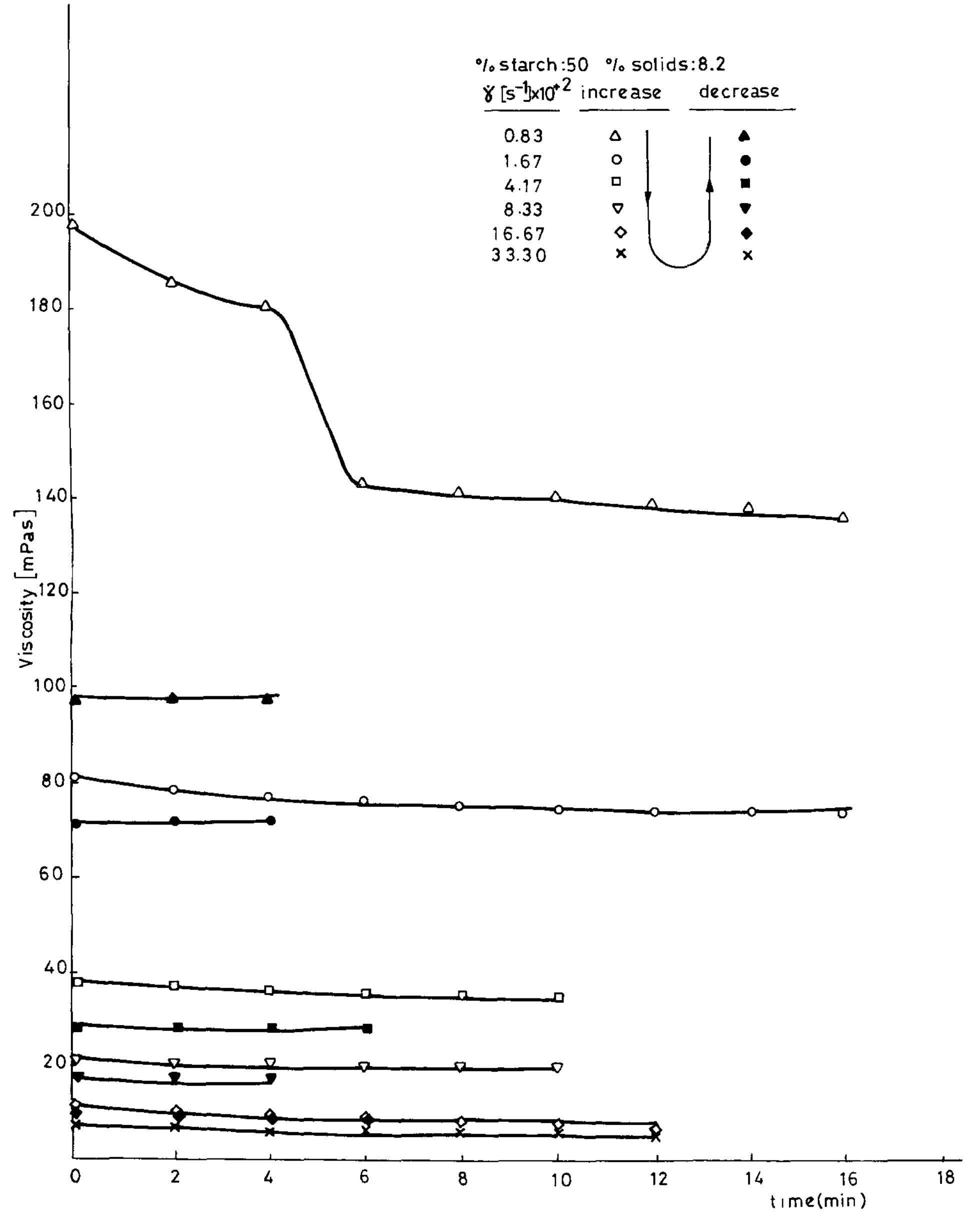


Fig. 5 Change of viscosity with time and shear rate (Brookfield)

over one cycle for the gel denoted as (I) in Fig. 3. The viscosity initially decreases with time at the lowest stirring rates of 0.0083 s^{-1} (0.5 rpm) and 0.0166 s^{-1} (1 rpm) and then remains constant at higher stirring rates. The difference between the viscosities in the increasing and decreasing shear rate parts of the curves is greatest at the lowest shear rate of 0.0083 s^{-1}. The different viscosities which will be used later in this paper can be identified here numerically: $\mu^{0}_{0.5} = 198$ mPas, $\mu^{eq}_{0.5} = 136$ mPas and $\mu^{f}_{0.5} = 98$ mPas, as the initial viscosity at zero time, equilibrium viscosity value attained (after 16 min in this case) and the viscosity at 0.5 rpm obtained at the end of the cycle, respectively.

The sudden decrease in viscosity in the upper curve in Fig. 5 at 0.5 rpm is probably related to slip. A similar curve was obtained by Barnes and Carnali (14) at considerably lower shear strain rates for Veegum PRO clay suspension, and was interpreted as a thixotropic reorientation in the fluid boundary layer. Shearing at constant rate for about 4 min in our experiments probably caused such

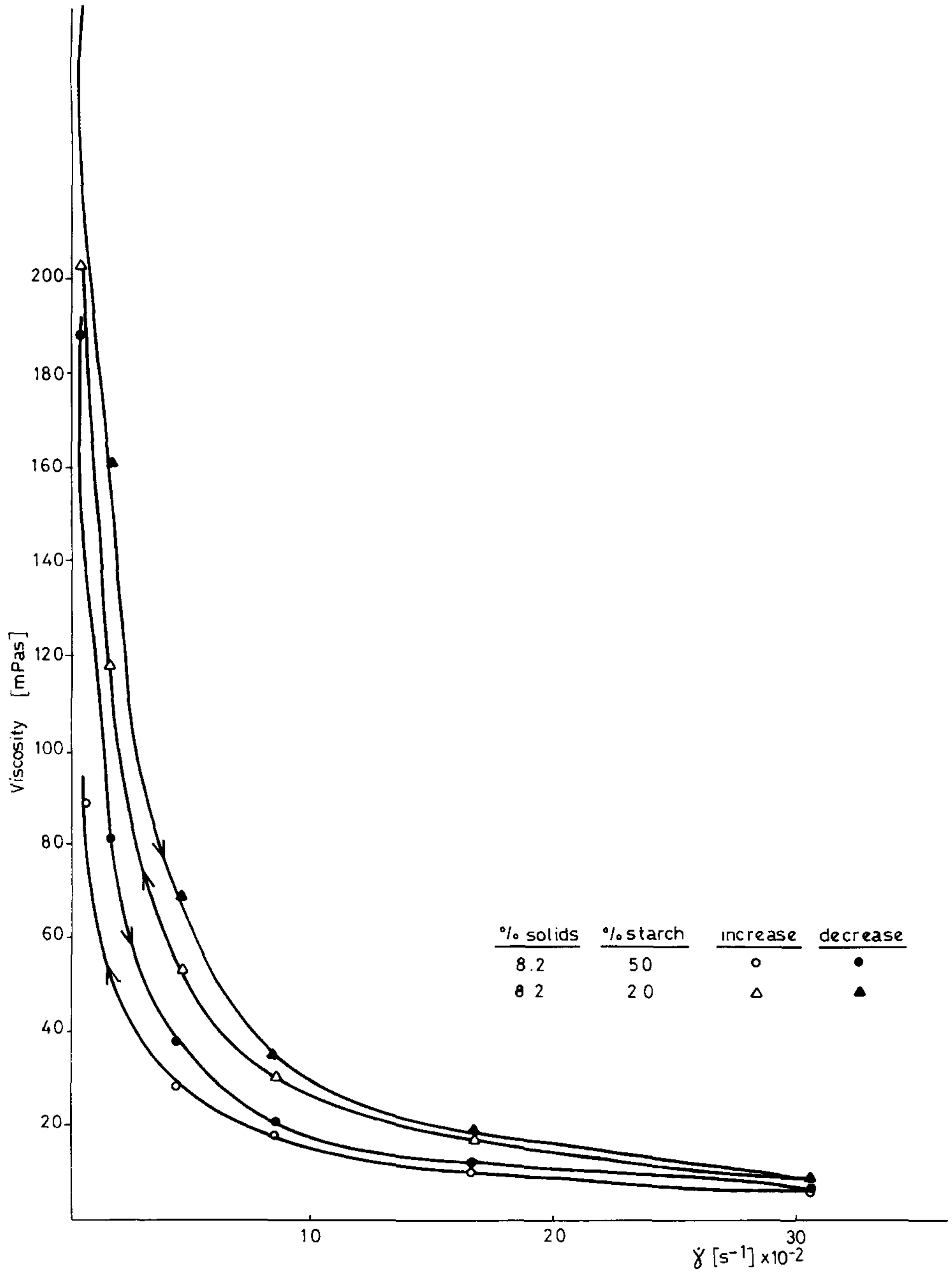


Fig. 6 Hysteresis loops of viscosity

a reorientation to take place within the boundary layer adjacent to the spindle.

Such a viscosity decrease with time was not observed with all gels (such as the case of B in Fig. 3). For example, in 20% starch gels delamination of the montmorillonite was maximum, and the viscosity increased with time of shearing. Such a result is expected, since amylose and amylopectin preferably formed bonds to the montmorillonite surfaces instead of cross linking which breaks the bentonite bands into a larger number of particles. This increase in viscosity was observed only during the initial measurement at 0.5 rpm (0.0083 s^{-1}). At higher shearing rates, the viscosities decreased or remained constant with time. Examples for the hysteresis loops are shown in Fig. 6 for gels, with 20% and 50% starch.

The variation of the viscosities $\mu^0_{0.5}$ and $\mu^f_{0.5}$ as a function of starch ratio at different solid contents are given in Fig. 7a and b. The general shape of the curves are similar, but the viscosities are lower and not so different when the structure is broken (Fig. 7b). The following conclusions are drawn:

1) The viscosity of the gels increase steeply at starch contents greater than 80% due to cohesive forces between the particles.

2) The viscosity of pure starch gels is determined by the concentration of amylose and amylopectin polymers and the stability and integrity of the swollen granules. At solid contents 5.9–6.6%, the viscosity remains constant with shearing ($\mu^0_{0.5} = \mu^f_{0.5}$). At greater solid contents viscosity decreases due to disintegration of the granule network, and at lower solid contents due to the ease in the disentanglement of the polymers.

3) Viscosity minima are observed around 50% starch. The number of particles decrease as a consequence of formation of strands and of reduced entanglements of the

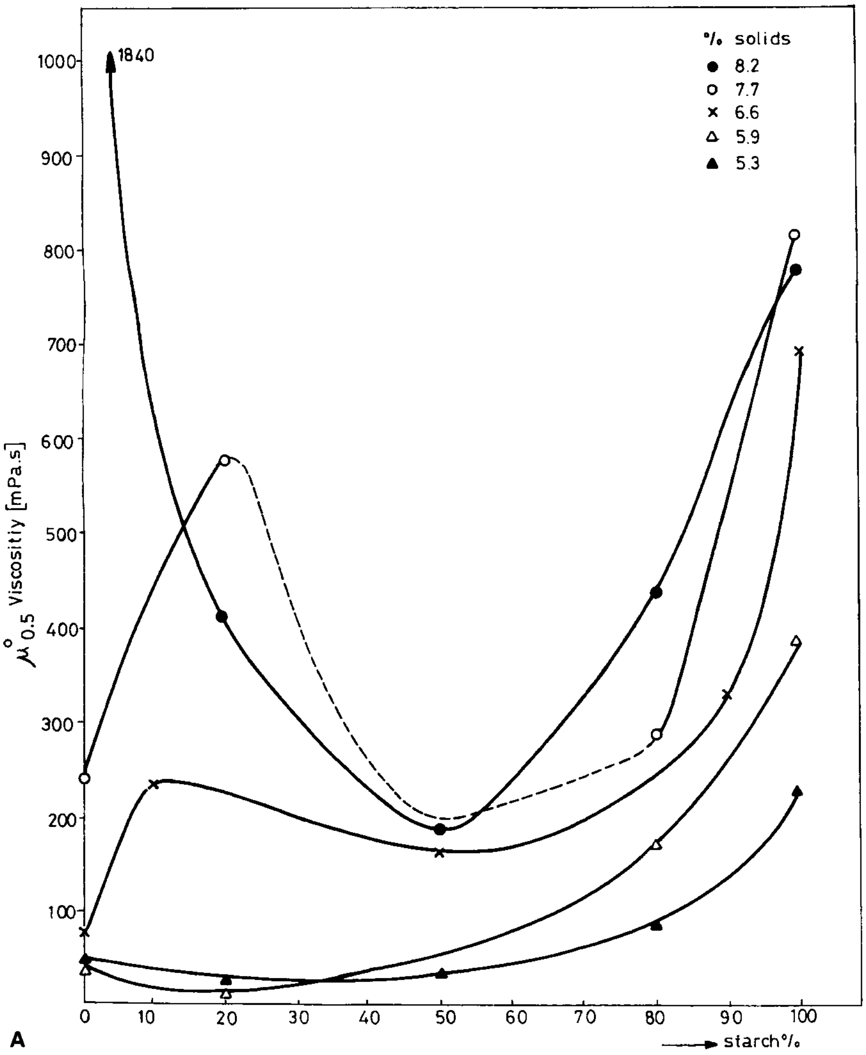
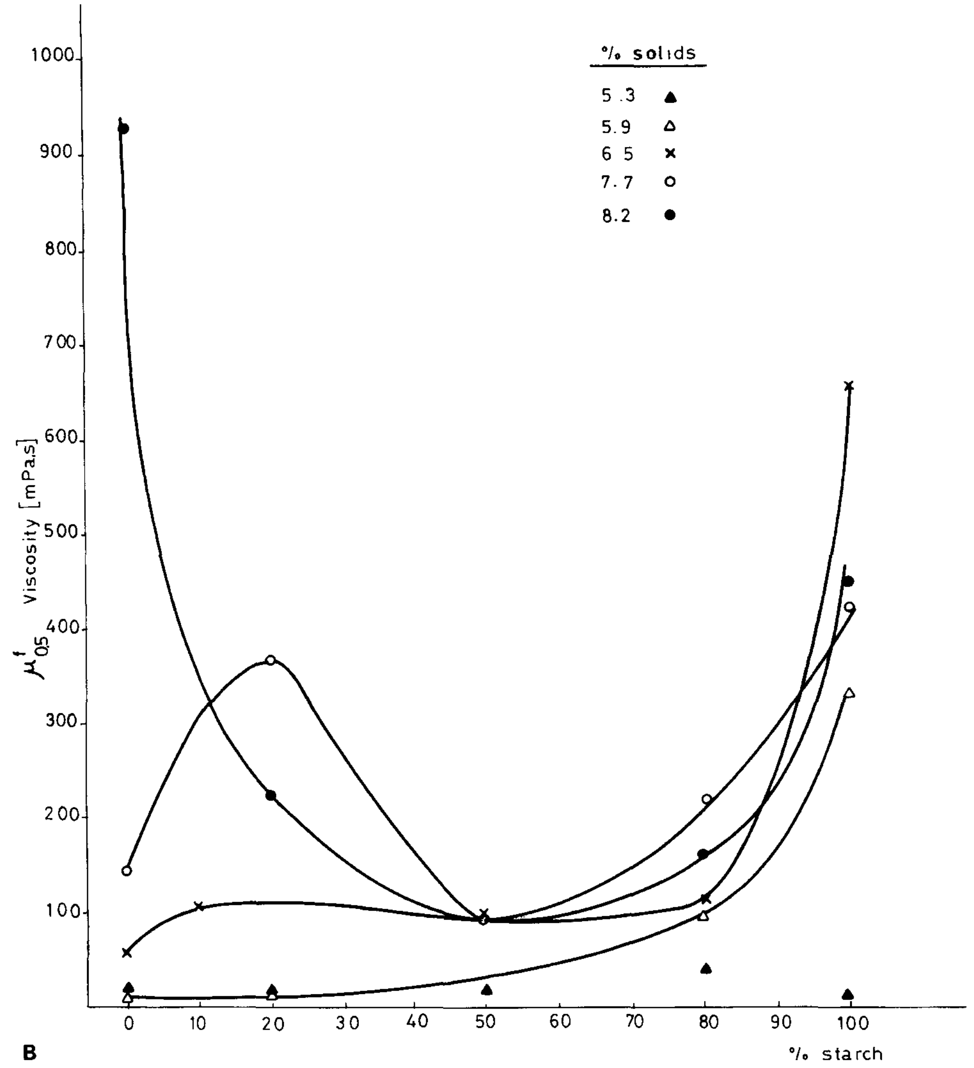


Fig. 7A Variation of $\mu^0_{0.5}$ as a function of starch content at different solid contents.

Fig. 7B Variation of $\mu^{f}_{0.5}$ as a function of starch ratio at different solid contents



polymers which become fixed on the montmorillonite bands and envelope the strands.

The relative maxima observed in 10% and 20% starch gels around 6–7% solids are due to the excessive delamination of the montmorillonite bands by the polymers (see previous paper). The variation of $\mu^{0}_{0.5}$ and $\mu^{f}_{0.5}$ (values of $\mu^{f}_{0.5}$ in parentheses) over the experimental design layout is seen in Fig. 8a. Similar values of $\mu^{0}_{0.5}$ and $\mu^{f}_{0.5}$ are indicative of stable gel structures. In the case of pure starch, the most stable gels are obtained around 6–7% solids content. In dilute gels with lower solid content the polymers tend to arrange parallel under applied shear stress and the ratio μ^{0}/μ^{f} is highest. In concentrated starch gels, at around 8–9% solids, the granules are not fully swollen and the amylose is not completely leached out. Therefore, the bonds between granules are rather weak and break easily under shear. The stability of bentonite/starch gels is caused by the ease with which the montmorillonite bands can reorient. Maximum stability, e.g., minimum ratio of μ^{0}/μ^{f}, is observed at 6.6% solids where swelling and delamination are optimal. In general, the viscosity is determined by an interplay of attractive forces between the montmorillonite layers, the extent of delamination, degree of packing into strands and extent of swelling of the starch granules and degree of entanglement between the polymer molecules.

The ratio of the viscosities measured as a function of time to their initial value, $(\mu/\mu^{0})_{0.5}$ are reported in Fig. 9a and b for 0.5 rpm. The variation of this ratio is explained by the interplay of the above-mentioned forces. For example, when excessive delamination of montmorillonite

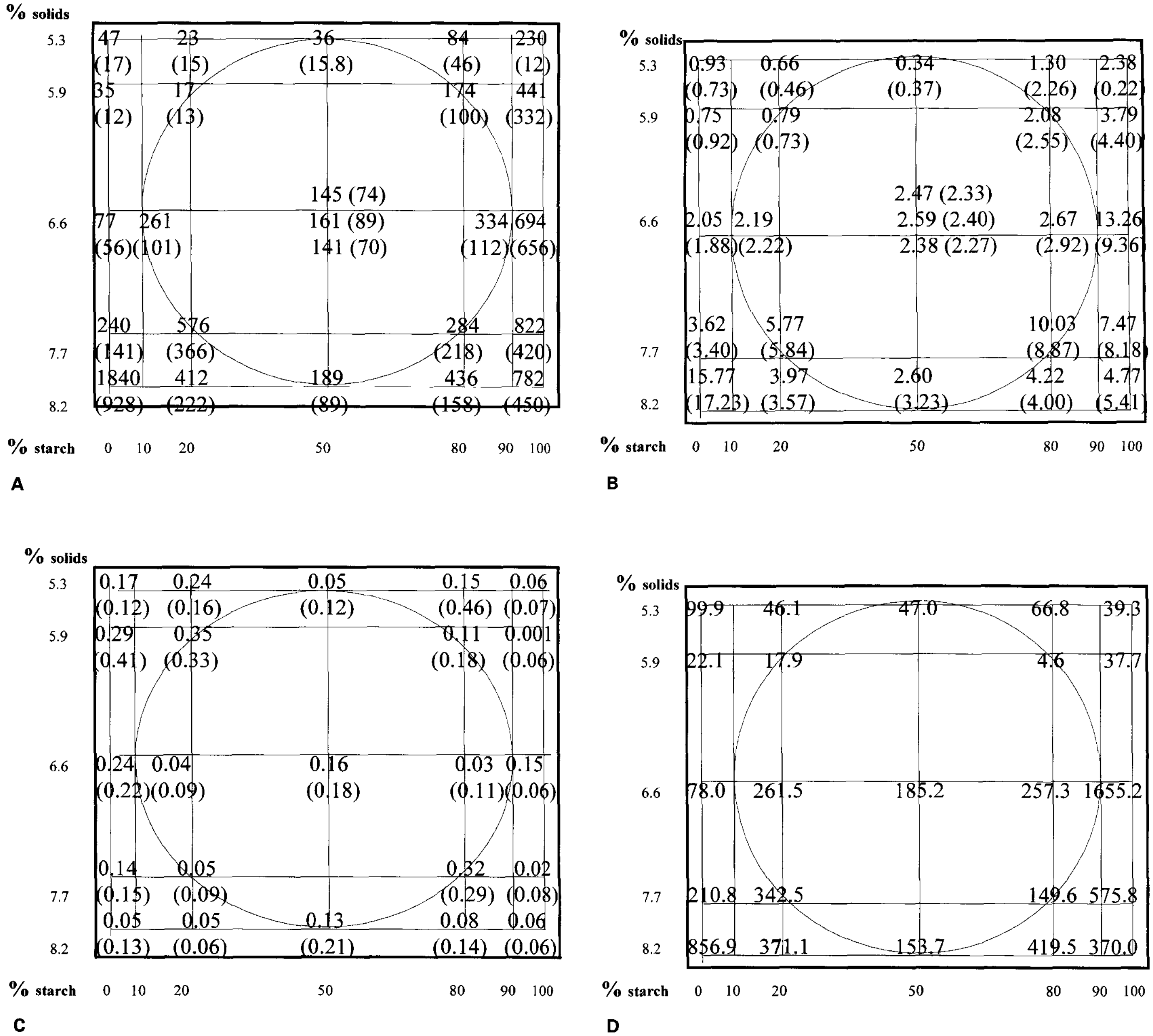


Fig. 8A Variation of $\mu^0_{0.5}$ and $\mu^f_{0.5}$ over the experimental design layout. **B** Variation of consistency K with the composition of the gels. **C** Variation of flow index n with the composition of the gels. **D** Variation of index of thixotropy (IT) with the composition of the gel

layers occur at high water content the viscosities tend to increase due to disintegration and delamination. At high solid contents the incompletely swollen starch granules and unswollen bentonite layers reorient under shear, resulting in the large drop of viscosity. Formation of strands offsets the effect of solids/water ratio, the viscosity of 80% starch gels, where individual montmorillonite particles are dispersed in a polymer matrix, is more sensitive to the solids/water ratio.

Discussion

If the individual structural units, e.g., montmorillonite particles, bands, polymers, and oval-shaped granules, are free to reorient to reduce the effect of the externally applied shear stresses and strains, the Bingham model with the viscosity being unaffected by the magnitude of strain cannot be valid. Therefore, the values of $\mu^0_{0.5}$ and $\mu^f_{0.5}$ were fitted by the two-parameter power-law equation,

$$\mu_{\text{apparent}} = K\dot{\gamma}^{n-1}\,, \tag{5}$$

where K is the consistency and n the flow index (17). The variation of K (obtained from μ^{f}) with the composition of the gel is given in Fig. 8b, with K^0 (obtained from $\mu^0_{0.5}$ data) in large lettering and $K^{\mathrm{f}}_{0.5}$ in parentheses. The general variation in K is similar to that of $\mu_{0.5}$ except in point H (80% starch, 7.7% solids) where the entanglement of the polymers and montmorillonite bands with rather strong attractions produce a compact gel with high consistency. The following generalizations can be made: The existence of montmorillonite particles disrupts the continuity of the polymer gel structure and reduces the consistency which remains approximately constant at 6.6% solids. K values show a minimum at 50% starch at high and low solid contents due to the formation of strands, where neither the montmorillonite bands nor the starch polymer network can be continuous. At solid concentrations greater than 6.6%, the consistency of the starch gel decreases due to limited swelling of the granules whereas the consistency of the bentonite gels increases due to cohesive forces between the more densely packed particles. If reorientation of the particles under applied shear increase the compactness of the gel, $K^{\mathrm{f}}_{0.5}$ becomes greater than K^0. If, on the contrary, the applied shear breaks the fragile

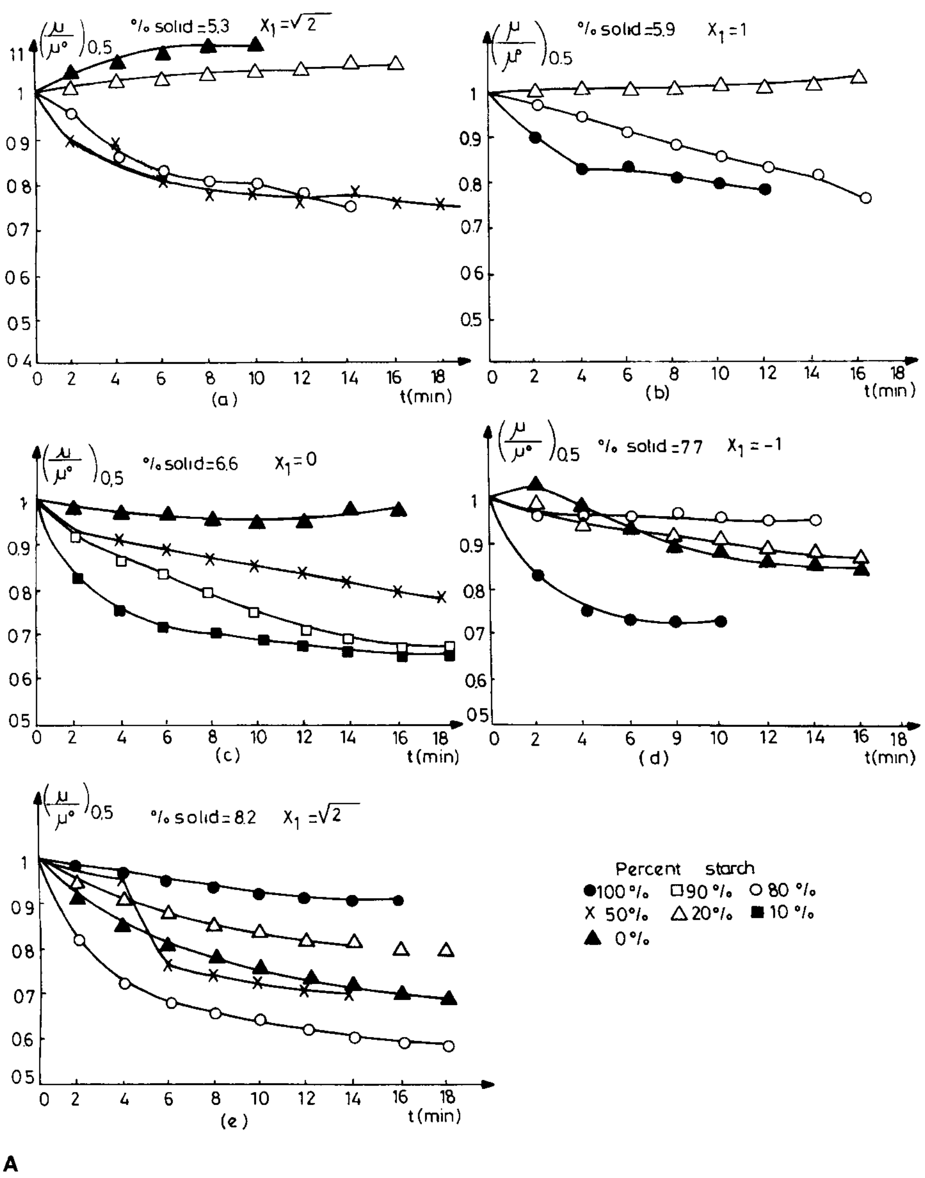


Fig 9A Variation of $(\mu/\mu^0)_{0.05}$ with time at different solid contents.

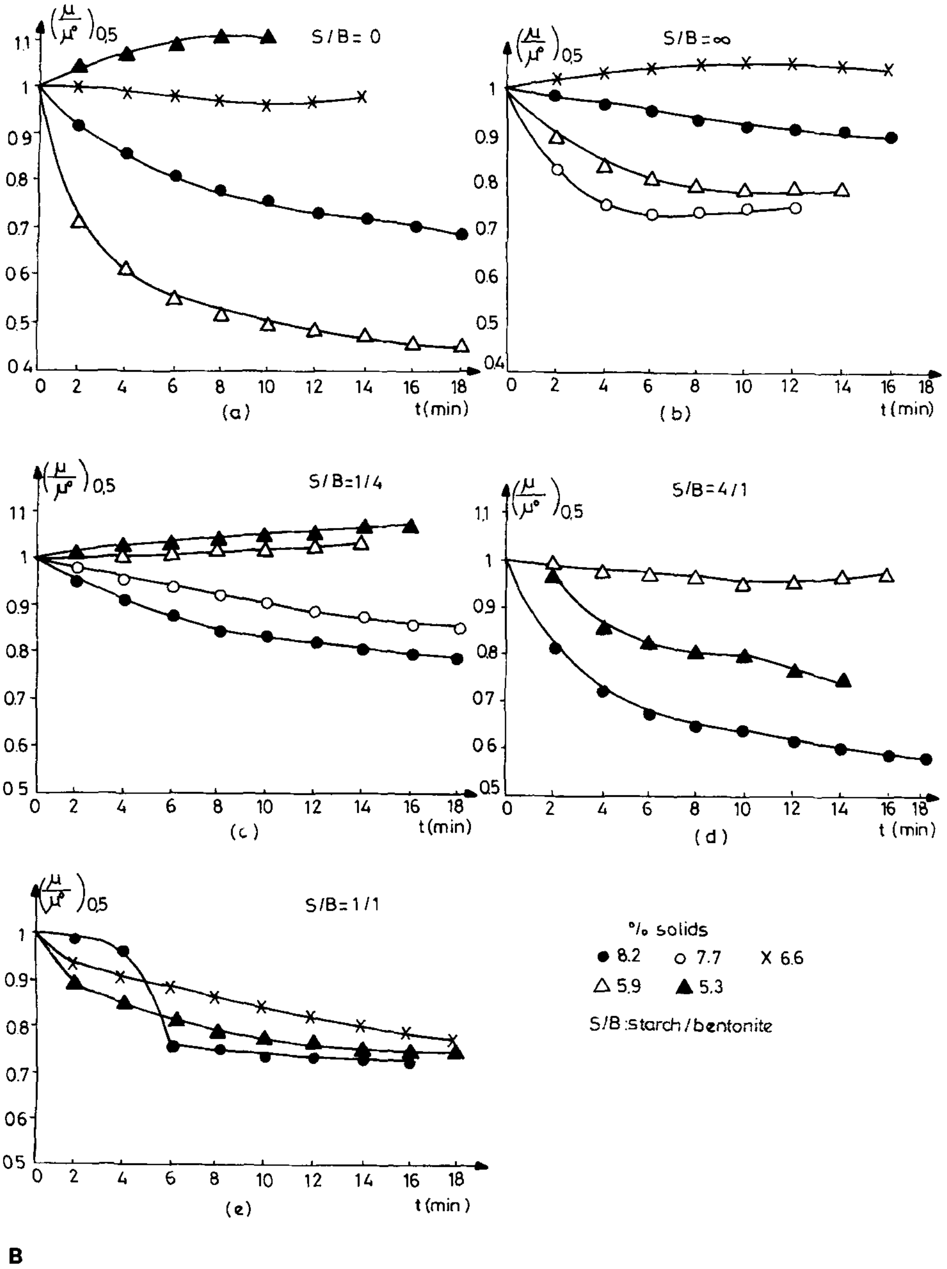


Fig 9B Variation of $(\mu/\mu^0)_{0.5}$ with time at different starch/bentonite ratios

bonds in between the structural units, $K_{0.5}^{\mathrm{f}}$ is smaller than K^0.

Variation of the flow index n^0 with gel composition is seen in Fig. 8c, with n^{f} shown in parantheses. The flow index represent the sensitivity of the gel structure to the applied shear; smaller the n, the more sensitive is the gel structure. Starch and gels with 20% bentonite when the montmorillonite is highly delaminated are most responsive toward applied shear. Once the few hydrogen bonds between the granules are broken, the oval-shaped unswollen granules can easily slide under applied shear. A similar situation applies in the case of highly delaminated montmorillonite.

Index of thixotropy (IT) is defined in this work as the area inscribed by the increasing and decreasing shear rate portions of a thixotropic cycle (Fig. 6) expressed mathematically as

$$\mathrm{IT} = \int \mu(\omega)\,\mathrm{d}\omega \qquad (6)$$

equivalent to energy input per unit volume ($\mathrm{J/m^3} = \mathrm{Pa}$) to bring about the indicated structural change.

Variation of the index of thixotropy IT with gel composition is given in Fig. 8d. Two factors exert opposite effects on thixotropy: decreasing water content reduces the degree of swelling of the granules which decreases all shear-induced rheological properties. On the other hand, decreasing water contents increase the concentration of the polymers and increases the number of hydrogen bonds per unit of the gel volume. The optimum conditions are formed at 6.6% solids with starch as the continuous phase where IT becomes maximum. This is the state of maximum interlinking in the polymers and maximum compaction of the granules.

Conclusion

The complexity of the structural conformations in a bentonite/starch composite gel cannot be described by one rheological model.

The starch polymers and the montmorillonite particles change their orientation under applied stress. The presence of both kinds of structural units in the composite gels does not prevent particle reorientation because most of the polymers cover the montmorillonite bands. Since two dimensions of the montmorillonite particles are much larger than the dimensions of the polymer, reorientation of the particles are not affected by adsorption of starch. The viscosity can be described by a power-law model (Ostwald de Waele).

The consistency index K in the model depends on the compactness of the gel structure. The flow index n depends on the ease with which the particles can change their orientation. The index of thixotropy follows similar trends.

The formation of strands of montmorillonite band and starch polymers increases flow index and reduces the magnitude of the other rheological properties.

References

1. Besün N, Peker S, Köktürk U, Yilmaz H, Colloid Polymer Sci (in press)
2. Leach HW (1973) In: Birch GG, Green LE (eds) Molecular structure and function of food carbohydrates. Applied Science Publishers, London, pp 289–307
3. Collison R (1986) In: Radly JA (ed) Starch and its derivatives Chapman and Hall, London. pp 168–203
4. Biliaderis GG (1992) In: Alexander RJ, Zobel HF (eds) Developments in carbohydrate chemistry. The American Association of Cereal Chemists. St. Paul, pp 87–135
5. Zaslow B (1965) In: Whistler RL, Paschall EF (eds) Starch: Chemistry and technology. Academic Press, New York, pp 279–288
6. Rasper V (1982) In: Shney WC, Tipples KH (eds) The Amylograph Handbook. AACC, pp 1–24
7. Van Olphen H (1959) Clay Colloid Chemistry. John Wiley, New York
8. Brandenburg V, Lagaly G (1988) Appl Clay Sci 3:263–279
9. Permien T, Lagaly G (1994) Appl Clay Sci 9:251–263
10. Permien T, Lagaly G (1994) Clay Miner 29:761–766
11. Cameron JR (1989) J Rheol 33:15–46
12. Barnes HA, Carnali JO (1990) J Rheol 34:841–866
13. Cohran WG, Cox GM (1957) Experimental Designs. Wiley, New York. pp 355–375
14. Box GEP, Hunter JS (1957) Ann Math Stat Vol 28
15. Darby R (1984) In: Lissant KJ (ed) Emulsions and Emulsions and Emulsions Technology. Marcel Dekker, Inc, New York, pp 45–110