Colloid Polym Sci 275:378–389 (1997)

ORIGINAL CONTRIBUTION

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Structure of starch–bentonite gels

Received: 29 May 1996
Accepted: 1 November 1996

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Abstract Mixed gels of starch and bentonite are investigated in the interval 0.056–0.089 of total solids/water ratio and 0–100% starch in the solids. The bentonite was a sodium calcium bentonite with a Na/Ca ratio of 1.76. In water it forms gels consisting of a network of band-type structures. Starch forms gels through hydrogen bonds between granules and/or amylose and amylopectin present on the external surfaces of granules and/or in fully stretched form.

Mixed gels of bentonite and starch were obtained by adding corn starch granules to the already formed bentonite gels and heating the mixture above the Kofler gelatinization temperature. Amylose and amylopectin were adsorbed on strands of band-type structures of montmorillonite lamellae. Starch gellation, e.g. diffusion of amylose out of the granule, was facilitated in the presence of bentonite. On the other hand, the presence of starch favored delamination of the montmorillonite particle into thinner lamellae. Maximum gelatinization and polymer adsorption were observed for gels with 20% starch and 80% bentonite. Montmorillonite networks formed the continuous phase for 0–80% starch. At higher starch concentrations, montmorillonite flakes were dispersed within the polymer network. Increase in the water content of the gels caused segregation of the bentonite and starch.

Key words Mixed gels – starch – bentonite – band-type structures – polymer adsorption

Introduction

Facial masks used in cosmetic applications are in essence a mixture of clay and starch gels together with emulsifiers and polyalcohols used as moisturizing agents. Clays are also used as suspension agents and stabilizers together with natural or synthetic hydrocolloids in cosmetic emulsions, paints and other products of industrial importance.

Starch occurs as ellipsoidal, semi-crystalline granules of glucose polymers in plants as a source of reserve energy, analogous to glycogen in animals. Glucose polymers can be in the form of linear (amylose) or branched chains (amylopectin) (Fig. 1). The ratio of amylose to amylopectin varies between 1/5 and 1/3 in normal cereal grains. Though still a controversial issue, the starch granules are accepted to possess radial symmetry with the concentration of amylose increasing toward the center [1]. Amylopectin has long branches repeating in every 16–25 glucose residues. The linear polymer amylose, is responsible for crystallite formation within the granule [1, 2]. When the hydrogen bonds between an amylose molecule and the adjoining polymers of the crystal lattice within the granule are broken, amylose assumes the form of a helical

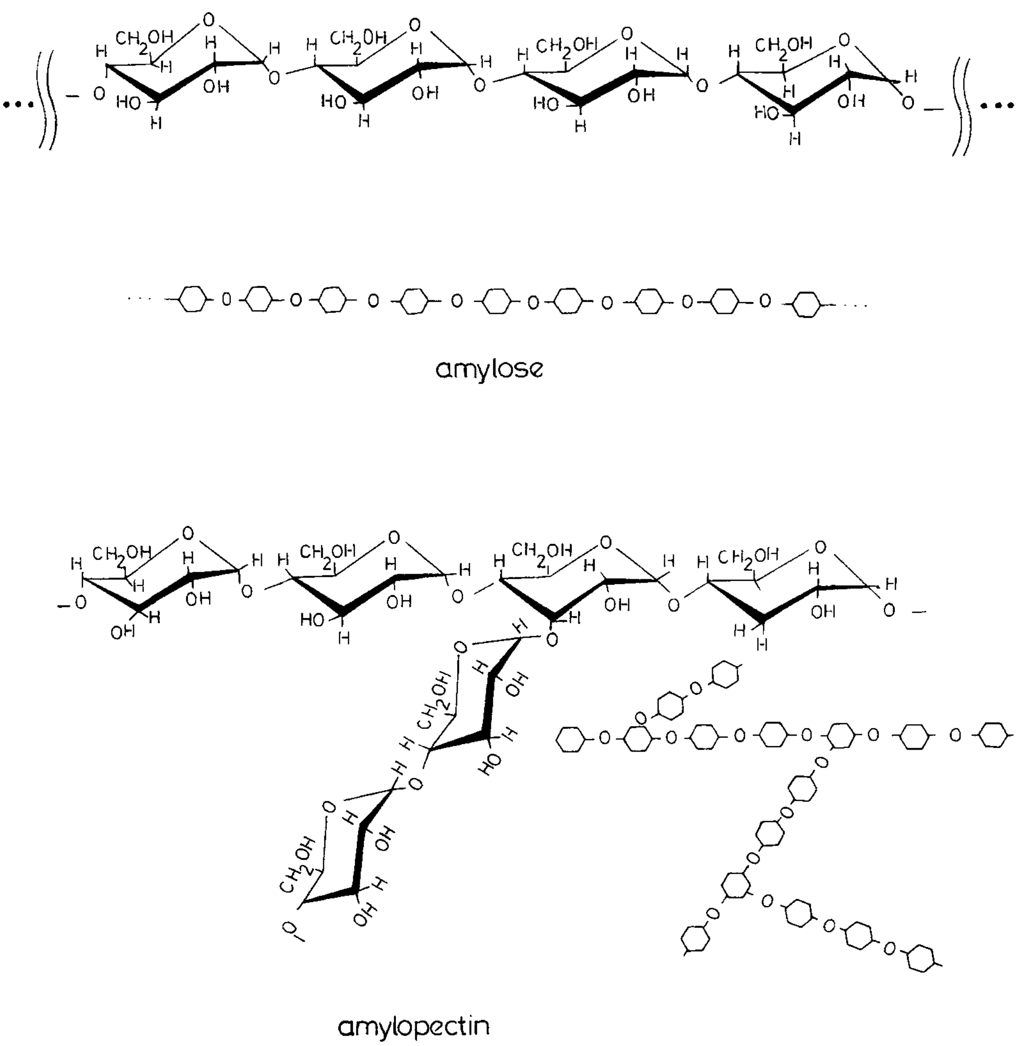


Fig. 1 Chemical structure of amylose and amylopectin

coil with six glucose units per turn. It forms complexes with iodine, lipids and primary alcohols by including these molecules within the helix. Iodine, present in the form of I_5 species within the helix is used the identify amylose [3], since the ability of amylopectin to form inclusion complexes is very limited [2]. Iodine, in the form of I_5 chains [3] is sorbed into helices formed by amylose within a repeat distance of 15.5 Å, approximately equal to twice the repeat distance of the amylose helix. Amylose adsorbs 25% of its own weight of iodine from gaseous iodine. Since amylopectin branches hardly form helices of this length, its iodine uptake is negligible, e.g. less than 0.7%. Thus, extent of iodine sorption is actually a measure of the quantity of amylose in helical conformation.

Granules have no external membranes. Due to the highly hydrophylic character of the polymers, water is sorbed into the ultramicropores of the granules. About 43 g water/100 g starch, on the average, are adsorbed by corn starch. As the water content of the starch suspension increases beyond this value, the water adsorbed on the crystallite surfaces disrupts the hydrogen bonds between –OH groups of the polymers. These free –OH groups are immediately surrounded by water molecules and the granules swell. Water adsorption and swelling continues until a critical concentration is reached. This is defined as the concentration of starch required so that the swollen granules occupy virtually the entire volume leaving no free water between them [4] in the paste obtained at 95 °C. For corn starch, it is 0.24 kg starch/L water. At concentrations equal or below the critical concentrations, gels form on cooling by the formation of hydrogen bonds between the granules (Fig. 2a). Amylose is soluble in water. During the swelling of the granule, amylose diffuses into the surrounding water. The molecules in solution form hydrogen bonds with the polymers in the granules [1]. In this way a continuous three-dimensional network of amylose polymers

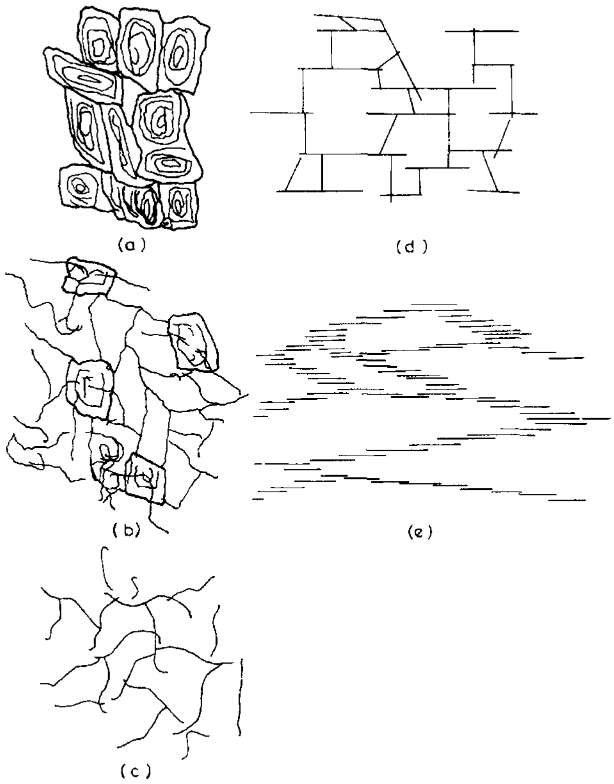


Fig. 2 Starch and montmorillonite gel structure

and swollen granules is formed (Fig. 2b). Provided there is sufficient water present to leach-out the amylose from the granules, enough thermal energy available to break the hydrogen bonds, and ample time for the completion of the diffusion controlled processes, only amylopectin molecules will remain of the original granule. The gel formed on cooling will be a network of glucose polymers held together by hydrogen bonds (Fig. 2c).

Montmorillonites, the basic mineral of bentonitic clays, consists of silicate layers [5]. Exchangeable cations are present in the interlayer spaces to neutralize the negative charge on the layers. When sodium or lithium are interlayer cations, the particles dispersed in water delaminate into the single silicate layers, thus forming a colloidal dispersion (see e.g. Fig. 8 in [8]). If the medium is acidic, the edges of the layers attain a positive charge and edge (+)/face (−) contacts lead to card-house-type gel structures (Fig. 2d) [6]. When pH increases above 5, the edges are recharged. The card-house structure is no longer stable and breaks down. Band-like structures then become the preferential structure of the gels [7, 8] (Fig. 2e).

While formation and structure of starch and montmorillonite gels are well defined, knowledge on mixed gels is still empirical [9] and literature on this subject is very meager: The adsorption of uncharged polymers, such as polysaccharides on montmorillonite is largely an entropy-driven process [10]. Solvent water molecules have to be desorbed from the surface before the –OH groups of the flexible chain of the polysaccharide can be adsorbed, which increases the enthalpy of the system. If the functional groups, such as –OH, along the polymer chain occur frequently, then the initially coiled polymer will be forced to lie flatly in extended form on the surface. Since the probability of simultaneous desorption of all the –OH groups from the surface is very low, the adsorption of polysaccharide is kinetically irreversible. If the interlayer cations are mainly sodium in aqueous media, the uncharged polymers can enter into the interlayer spaces. Entry of the polymers is severely restricted in Ca-montmorillonites.

The aim of this research is the investigation of the gel structure of mixed bentonite–starch system as a function of bentonite/starch ratio.

Experimental

Materials used

Edible corn starch was bought from Piyale A.Ş with the composition given in Table 1. The bentonite was obtained from SAMAŞ, A.Ş. It was purified of its quartz and hematite content by sedimentation. Initially, 6% bentonite dispersions in distilled water were prepared in 1 L flasks of 20 cm height. These were left to settle for three days. At the end of this period a hematite-rich section was observed at the lower section of the dispersion. The upper portion containing mainly the montmorillonite gel was transferred to another flask and made up to 1 L by addition of distilled water. At the end of three days the upper portion of the dispersion was collected again down to the pink-colored zone. The height of the pink-colored zone decreased at

Table 1 Composition and properties of corn starch

Protein	0.83%
Fat	0.3%
Ash	0.1%
Acid-insoluble ash	0.04%
Acidity	1
Moisture	10.2%
pH	5.9
SO_2	24.3 ppm
Particle size (d_p)	< 150 μm
$d_p > 150$ μm	0.13%
Amylose	25%
Amylopectin	75%
Molecular weight of amylose	10000–60000
Molecular weight of	50000–100000
Gelation temperature (°C)	92

each cycle. The sedimentation process was repeated until only a bentonite gel with no apparent sediment layer at the bottom of the flask was observed at the end of three days. The initial Na/Ca molar ratio was 1.046 in the pristine bentonite. After sedimentation this ratio increased to 1.76 due to removal of $CaCO_3$ present in the bentonitic clay. The bentonite gels obtained were dried in thin layers at 105 °C and stored in air-tight jars. X-ray diffraction and infrared spectra showed the purified bentonite to be essentially constituted of montmorillonite.

Preparation of the gels

Alternative procedures for the preparation of the gels were tested in a preliminary set of experiments. The most reproduceable results were obtained when, first, the bentonite gel was formed to which a starch suspension was added with stirring. Thus, the following experimental procedure was adopted in the preparation of the mixed gels: Starch and bentonite were weighed separately to obtain the required weight ratio on a dry basis. Starch was soaked in 100 ml of cold water and gently stirred to homogenize the dispersion. The bentonite was mixed with a certain amount of water to give the required solids/water ratio after mixing with the starch solution. The bentonite dispersion was heated to 100 °C for 10 min at a constant stirring rate of 70 rpm with a six-blade impeller. At the end of 10 min, the cold starch solution was added to the bentonite dispersion. The temperature dropped to about 70–75 °C. The mixture was stirred until the gelation temperature was exceeded. For gelation to be completed, the mixture was set aside for 24 h in tightly covered vessels. The composition of the gels is reported in Table 2.

Methods

The following measurements were made to probe the structure of starch/bentonite gels:

1. X-ray diffraction to determine the basal spacing of the montmorillonite.
2. Fluorimetric measurements to determine the extent of amylose diffusion.
3. Electron microscope investigations to determine the distribution of bentonite and starch in the gel.
4. IR absorption to determine the extent of adsorption of starch.
5. DSC analyses to determine the qualitative variations in enthalpy.

X-ray diffraction analyses

The basal spacing of the montmorillonite in the gels and also the reflections of the starch were determined with Jeol SDX 100S instrument.

Fluorimetric measurements

Starch montmorillonite gels were dried in thin layers to form films of approximately 0.5 mm thickness. These films were placed on the top of 50 ml beakers containing saturated iodine solutions in water. The level of the solutions was kept constant 4 cm below the films. The beakers were placed in a heater held constant at 80 °C. The films were taken out and weighed at half-hour intervals. Adsorption was stopped when the films reached constant weight. The quantity of iodine adsorbed by the samples was determined in Jeol SDX 100S fluorescence spectrometer.

Electron microscopic investigations

The cross sections of the mixed gel films were coated with a carbon film. Aluminum was chosen as the natural indicator for montmorillonite, and iodine included into amylose helices, for starch. Iodine and aluminum distributions were determined with Jeol 733 superprobe. Iodine analysis was made with a reference crystal of $2d = 4.0267$ Å, and aluminum analysis with a reference crystal of $2d = 25.75$ Å. The cross sections of the films were then

Table 2 Composition of the gels

Designation	Water(g)	Starch(g)	Bentonite(g)	% Solids	% Starch in solids	Solid/water
c	93.3	0	6.7	6.7	0	0.071
D	93.3	0.7	6.0	6.7	10	0.071
s	93.3	1.3	5.4	6.7	20	0.071
E	93.3	3.3	3.3	6.7	50	0.071
t	93.3	5.4	1.3	6.7	80	0.071
F	93.3	6.0	0.7	6.7	90	0.071
l	93.3	6.7	0	6.7	100	0.071
A	91.8	4.1	4.1	8.2	50	0.089
I	94.4	2.8	2.8	5.6	50	0.056

coated with gold and scanned in the electron microscope. Typical images were selected and photographed.

IR and DSC analyses

IR analyses were made with an IR-470 Shimadzu spectrometer. SETARAM DSC 92 apparatus was used for DSC measurements. In each case, 5 mg of solid and 18 mg of water were placed in the closed stainless-steel cells. The same amount of distilled water was placed in the reference cell. Temperature was increased by 1 °C/min. The whole system was kept under N_2 atmosphere.

Results

X-ray diffraction

The X-ray powder diagrams of the gels show basal spacings of the montmorillonite to be 11.8 and 12.6 Å and *d*-values of the starch of 5.47 and 6.56 Å (Table 3). The basal spacings of the montmorillonite indicate that the hydration of the montmorillonite comprises only a water monolayer but the lamellae are not uniformly hydrated as two (0 0 1)-reflections are observed. In gels with higher contents of starch (>50%) the (0 0 1)-reflections of montmorillonite are obscured but the *d*-values of starch are recognized. One may assume that $d = 5.47$ corresponds to the starch in the granules and that of 6.56 to crystalline forms outside the granules.

Fluorimetric measurements

Iodine sorptions of starch–montmorillonite mixtures determined by fluorescence spectroscopy are given in Table 4. Since the quantity of starch is not equal in all the samples, the relative heights of the peaks (second row of Table 4) were corrected for the mass fraction of starch. The third row gives the ratio of the corrected peak height for the mixture to peak height of pure starch. As the exterior of the starch granules predominantly consist of amylopectin, this ratio also gives the extent of leaching of amylose from the granules, e.g. extent of gelation. The low value of pure starch shows that the exterior surfaces of the granules are essentially composed of amylopectin, and sorption of iodine occurs only by physical adsorption on these polymers.

Observations in the electron microscope

The distribution of montmorillonite platelets and starch polymers were assessed by the images of the cross sections of the dried gel films obtained in the electron microscope. These images were related to the two-dimensional distribution of Al and I_5, the indicator elements for montmorillonite and amylose, respectively, to identify the structural components. Micrographs are given in Fig. 3 for solid compositions with a total solids/water ratio of 0.071 (6.7% solids) for gels of 0, 10, 20, 50, 80, 90 and 100% starch, respectively.

The continuity of the laminates observed in pure montmorillonite and 10% starch gel (Figs. 3a and b) suggest the band-type structure to be dominant. The thickness of the layers is less than 0.2 μm [8]. The starch in the 10% gel is completely dispersed and evenly distributed on and between the montmorillonite lamellae. In 20–50% starch gels the montmorillonite lamellae are enveloped by the amylose and amylopectin molecules to form strands of 1–20 μm thickness. The thickness of the polymer film on the montmorillonite strands is proportional to the starch content. In a 90% starch gel, some amylose is extracted into the continuous phase to form a gel network. But granules are still visible (Fig. 3f). The swollen granules of

Table 3 *d*-values of starch/bentonite gels (solid to water ratio = 0.071)

Composition (%starch)	0	10	20	50	80	90	100
Spacing of the diffraction planes [Å]	11.78 12.11	12.27 12.63	12.9 —	11.78 12.11	5.47 6.56	5.47 6.56	5.47 —

Table 4 I_5 sorption by starch/bentonite mixtures determined by fluorescence spectroscopy

%starch	0	10	20	50	80	90	100
Relative height of peak, L [mm]	2.1	6.5	13	8.5	9	8.5	2.2
Equivalent height per unit weight of starch, L_{mix}	—	65	65	17	11.3	9.4	2.2
L_{mix}/L_{starch}	—	29.5	29.5	7.7	5.1	4.3	1.0

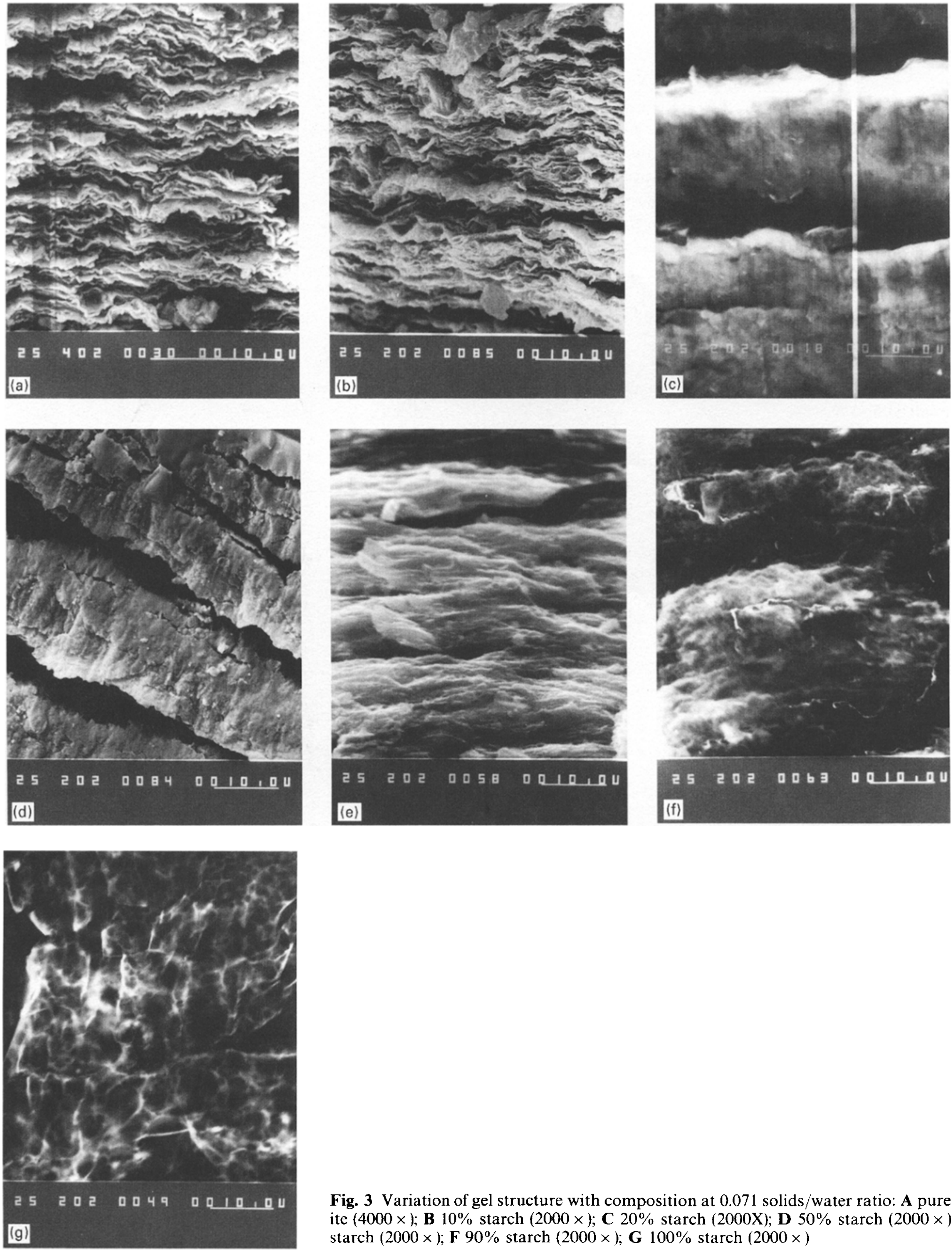


Fig. 3 Variation of gel structure with composition at 0.071 solids/water ratio: **A** pure bentonite (4000 ×); **B** 10% starch (2000 ×); **C** 20% starch (2000X); **D** 50% starch (2000 ×); **E** 80% starch (2000 ×); **F** 90% starch (2000 ×); **G** 100% starch (2000 ×)

starch attached to each other along the peripheries are clearly visible in Fig. 3g.

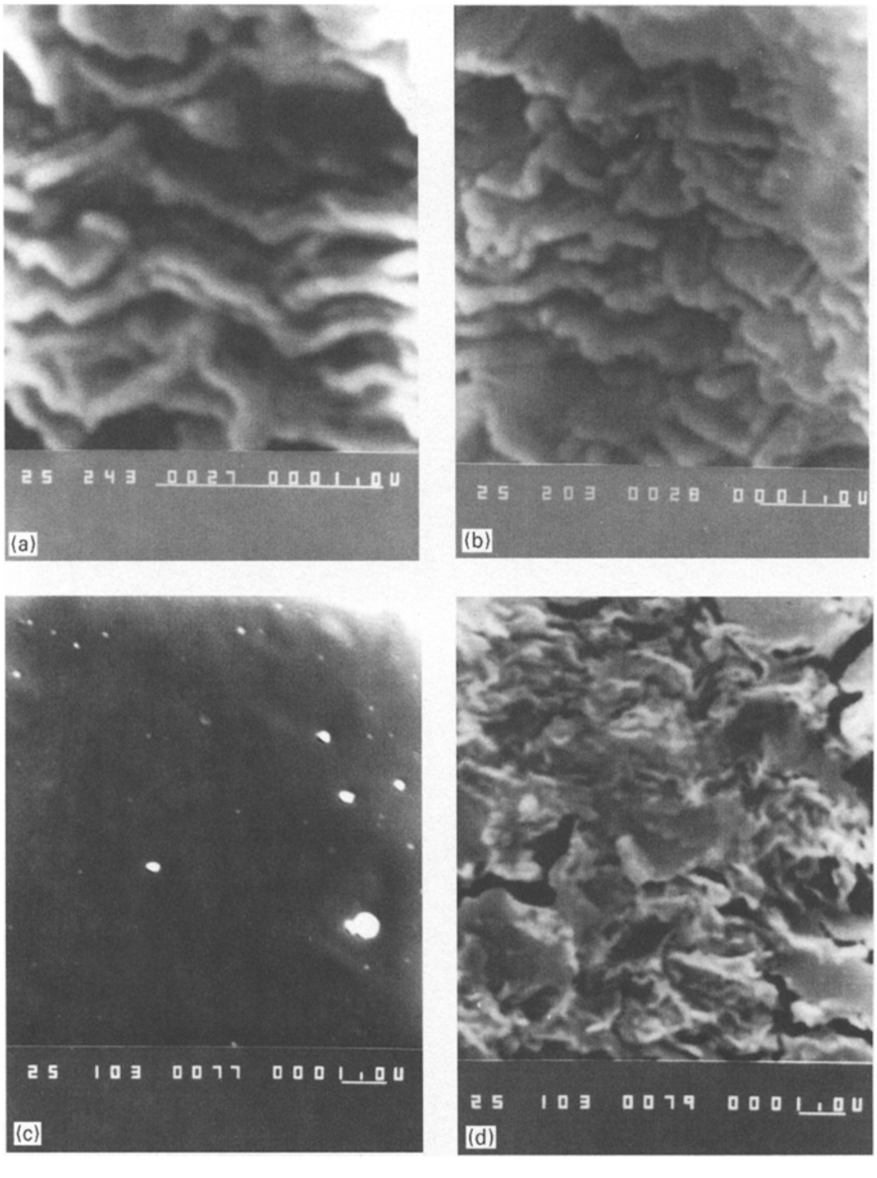
The details of the gel structure can be seen in the highly enlarged images given in Fig. 4. The continuity of the lamellar pattern shown with a magnification of 24 000 in Fig. 4a is the dominant structure of pure montmorillonite gels. However, regionally chaotic configurations reminiscent of collapsed card-house structures are also observed (Fig. 4b). The smoothness of texture of the amylose and amylopectin films covering the montmorillonite strands is readily visible in the 10 000 times enlarged photograph of 20% starch gels in Fig. 4c. The dispersion of montmorillonite flakes within the continuous starch polymer network can be observed in Fig. 4d (80% starch, magnification 10 000).

The effect of total solids/water ratio on the gel configuration is investigated for 50% starch gels and solids/water ratios $X_2 = 0.089, 0.071$ and 0.056 (Figs. 5a, c and e), respectively. The Al and I_5 concentration distributions were determined on the white bands on the photographs (Figs. 5b, d and f).

IR absorption

IR absorption analyses at certain frequencies could be used to identify montmorillonite and starch (Table 5). The absorbance at 3350 and 3200 cm^{-1} indicate bound and free -OH groups, on starch polymers [11] and montmorillonite. The peak at 1625 cm^{-1} (C–C streching vibration)

Fig. 4 Details of the microstructure of the gels (solids/water = 0.071): **A** pure bentonite (24 000 ×); **B** pure bentonite (20 000 ×); **C** 20% starch (10 000 ×); **D** 80% starch (10 000 ×)



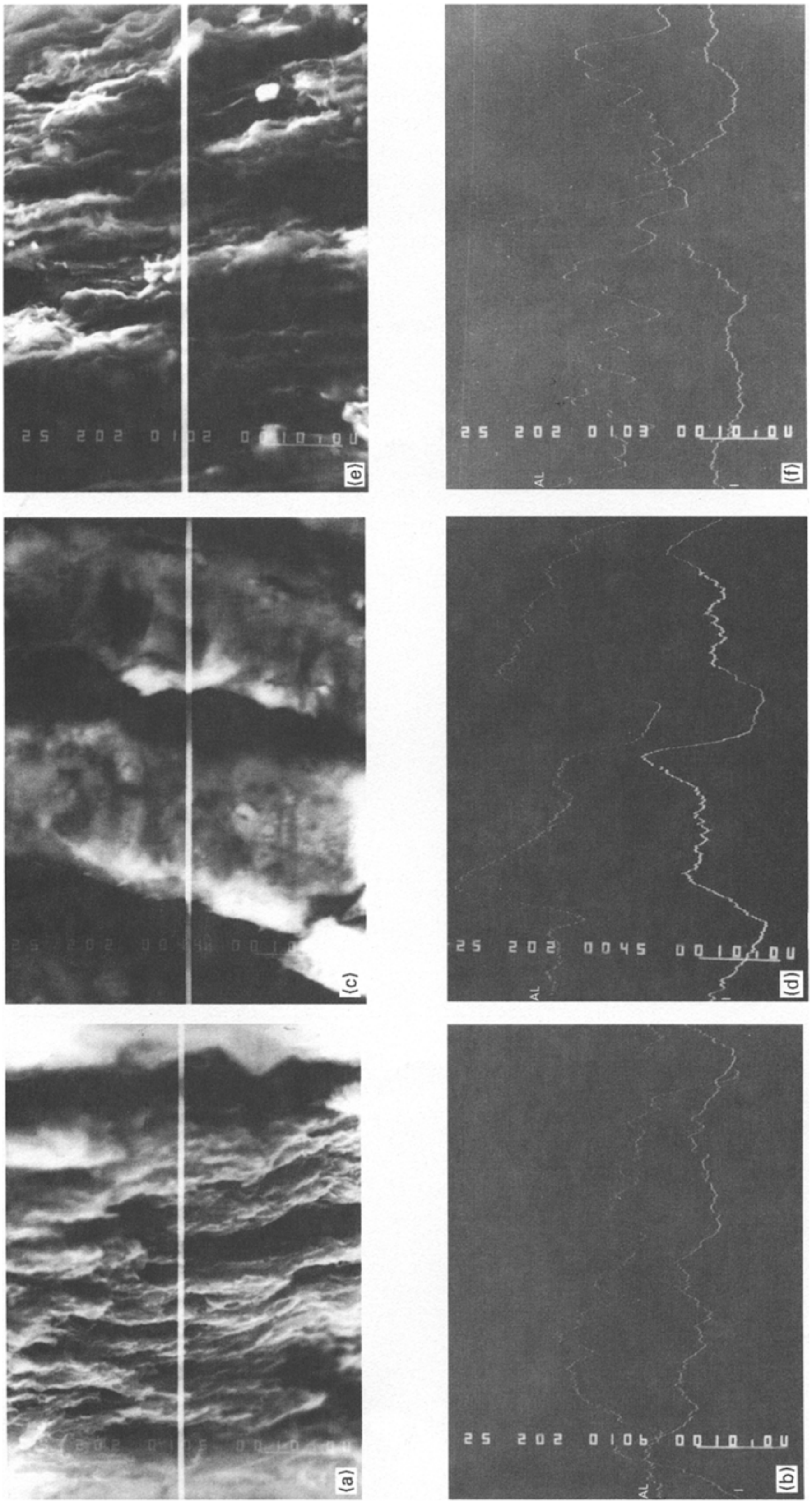


Fig. 5 Effect of solids/water ratio on the microstructure of starch/bentonite gels: **A,B** $X = 0.089$; **C,D** $X = 0.071$; **E,F** $X = 0.056$

indicates the extent of gelation, e.g. decomposition of the granule into its components. In pure montmorillonite, absorption at 1630–1660 cm^{-1} is related to the deformation of bound water. The results of IR spectra are given in Table 5.

DSC analyses

Only exothermic peaks are observed in the DSC profiles for montmorillonite (Fig. 6) and starch (Fig. 7). Exothermic processes involve the formation of hydrogen bonds between water and –OH groups of starch in the case of swelling of starch granules and between –OH groups and –O– groups of montmorillonite in the case of water adsorption. Mainly endothermic peaks are observed in the DSC profiles of starch/bentonite mixtures (Fig. 8). These endothermic processes involve the breaking of hydrogen bonds between –OH groups in starch and desorption of water from the surfaces of montmorillonite. The enthalpy changes are reported in Table 6.

Table 5 IR absorption of starch/bentonite mixtures

%starch in mixture	0	10	20	50	80	90	100
A_{3350}	0.26	0.48	0.72	0.49	0.50	0.58	0.26
A_{3200}	—	0.04	0.08	0.08	0.11	0.12	0.02
A_{1625}	0.09	0.14	0.22	0.14	0.13	0.17	0.07
A_{3350}/A_{3200}	—	12.0	9.0	6.1	4.5	4.8	13.0

Discussion

A model for the formation of starch/bentonite gels

In the experiments, a montmorillonite gel was initially formed to which a starch solution was added. Gelation of starch in the added solution was negligible as the time interval was short, e.g. less than an hour, and the ambient

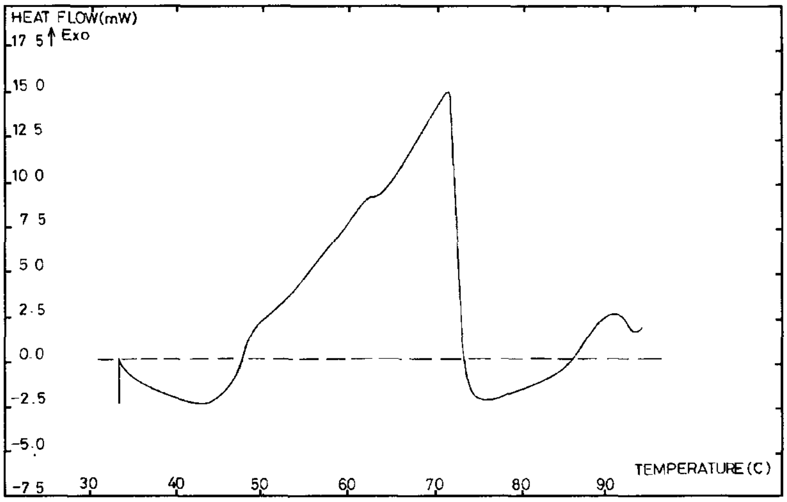


Fig. 6 DSC diagram for pure bentonite (bentonite/water ratio = 0.28)

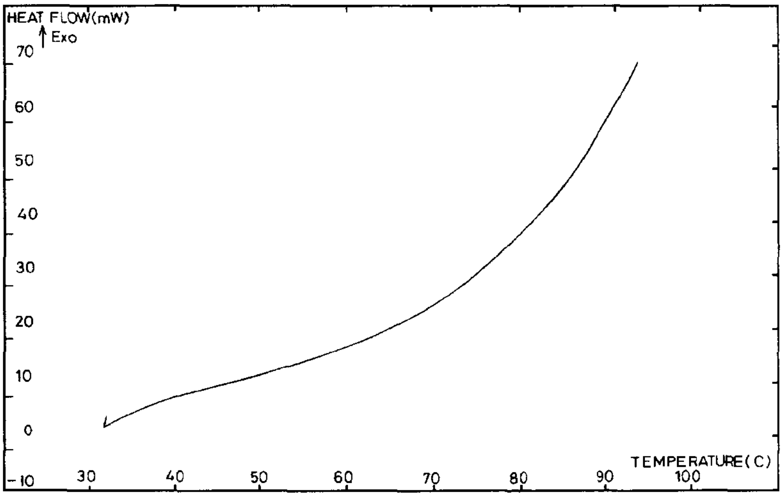


Fig. 7 DSC diagram for pure starch (starch/water ratio = 0.28)

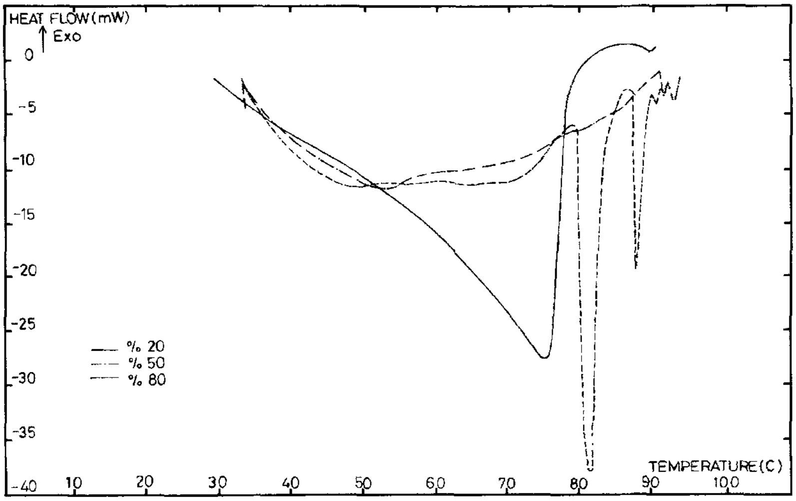


Fig. 8 DSC diagram for mixed gels (solids/water ratio = 0.28)

Table 6 Enthalpies related with the gelation of bentonite/starch mixtures at a solid/water ratio of 5/17

	Enthalpy of adsorption(+)/ desorption (−) of water on bentonite (J/g bentonite)	[J/g water adsorbed]	Enthalpy of formation of H-bonds(swelling) of starch(+) [J/g starch]	Enthalpy of breaking down of crystallites in starch (−) [J/g starch]
100% bentonite	1796	5165	—	—
20% starch, 80% bentonite	− 6017	1416	—	− 25.1
50% starch, 50% bentonite	− 5636	805	—	− 16.4
80% starch, 20% bentonite	− 9456	556	—	− 31.64 − 3432 − 824.6
100% starch	—	—	15527.5	—

temperature was well below the Kofler gelatinization temperature. So essentially starch granules were added to the already formed montmorillonite gel. The gels are generally alkaline, except for pure starch (Table 7). Under these conditions, band-type aggregation of montmorillonite laminates is the dominant structure; card-house arrangements may occur only locally.

Initially, water is adsorbed on the surfaces of montmorillonite evidenced by the exothermic peak of Fig. 6. When starch is added to the system hydrogen bonds are formed between water and the hydroxyl groups present in the external surfaces of the granules and water (DSC analyses in Fig. 7). When a starch granule comes into contact with the surface of a montmorillonite lamella, it attracts the adsorbed water molecules. In addition, it forms hydrogen bonds with the oxygen atoms on the clay mineral surface. Heating during the gel formation favors both the desorption of water from the clay mineral surface and the breaking of the hydrogen bonds in the crystallites within the granules. As a result endothermic peaks are obtained in DSC analyses (Fig. 8).

Table 7 pH values of starch–bentonite mixtures (solid to water ratio = 0.071)

Starch [%]	pH
0 (pure bentonite)	9.8
10	9.4
20	8.7
50	8.8
80	8.6
90	8.8
100	6.5

The experimental results reported above indicate facilitation of starch gelation by the presence of montmorillonite lamellae. Also the amylose and amylopectin molecules promote delamination of the montmorillonite particles (Figs. 3 and 4). In the light of the experimental evidence obtained, a possible mechanism could be the following: Amylose molecules are too large to enter the interlayer spaces of montmorillonite (Table 3). Adsorption takes place on the external surfaces of the montmorillonite particles. If one end of an amylose molecule becomes adsorbed on the surface of a montmorillonite particle, it will be carried away with it under the action of turbulent convection created by the impeller. Since at high temperatures, hydrogen bonds within the crystallites are broken more easily, montmorillonite particles carrying away one or more amylose and amylopectin molecules will help to unwind the polymer coil within the granule structure. This model is further supported by the lowering of gelation temperature as will be explained in a following paper. Amylose with a molecular weight of 10 000–60 000 and amylopectin of 50 000–100 000 are very large and long molecules. With some ends attached to the montmorillonite surfaces and others to the granule, they will move randomly under the action of turbulent convection. When the attractive forces exerted by the polymers are greater than the attractive forces between montmorillonite lamellae, the particles will partially delaminate.

Another aspect of the gels is the smooth coating of polymer on the surfaces of montmorillonite (Fig. 4c) [7]. If an amylose molecule becomes adsorbed near one end of a band of particles, it will be very easy for the rest of the molecule to spread over the surface when the bands move along with the convection current. The prerequisite is the availability of sufficient surface area and interparticle space for the polymer to elongate.

Effect of starch/bentonite ratio on the gel structure

Under the same conditions of heating and stirring, when there is no bentonite in the starch, the granules keep their identity in the swollen state (Fig. 3g). If the amylose molecules are not pulled away from the granule, gelation by diffusion alone is too slow a process even for the shortest amylose chains of mol/masses of 10 000. Within the 30 min time period allowed for gelation in this study, virtually no diffusion of amylose could take place and gel network is formed solely by the hydrogen bonds between the amylopectin molecules at the external surfaces of the granules. Further evidence of this type of gel structure comes from the low level of I_5 sorption (Table 3) and the reduced IR absorption at 1625 cm^{-1} (Table 5).

The presence of montmorillonite in a 90% starch gel greatly promotes the diffusion of amylose to the exterior of the granule. As the surface area of the montmorillonite is not sufficient, many oval or polyhedral granules remain (Fig. 3f). Fluorescence has increased only four times with respect to starch, while IR absorption at 1625 and 3200 cm^{-1} have increased much more, indicating the diffusion of amylopectin along with the amylose. Little improvement in the extent of polymer diffusion is observed with 80% starch gels in terms of fluorescence and IR absorption, since starch remains to be the continuous phase in the gel (Figs. 3e and 4d).

With equal amounts of starch and bentonite (of Fig. 3c), the IR absorbance at 3350 and 1625 cm^{-1} is similar to the 80% gel, which simply shows that the diffusion of polymers outside of the granule has increased, again demonstrating the dissolving power of montmorillonite. It is not clear from the electron micrographs, which component is the continuous phase, but formation of the strands indicate that more than monolayers of starch are adsorbed on the montmorillonite surfaces. Thin layers of amylose–amylopectin are formed between the montmorillonite bands. When broken at the weakest planes due to shrinkage of the starch polymer network during drying of the specimen, band-like formations appeared in the electron micrographs. Delamination of the particles is so high that amylose and amylopectin can spread smoothly over all the surfaces (Figs. 3d and 4c). The increase in IR absorbances at 3350 and 1625 cm^{-1} frequencies even when the starch fraction has decreased to 0.20 in the solid mixture shows that all the diffused polymers (1625 cm^{-1}) are adsorbed on the montmorillonite surfaces or cross-linked to other polymers in the gel network (3350 cm^{-1}). The increase in fluorescence peaks also confirms that all the amylose has moved outside of the granule and is in helical conformation.

When there is only 10% starch in the mixture, amylose and amylopectin molecules can spread only as a monolayer over the montmorillonite surfaces. Evidence for this condition comes from the similarity of the electron micrographs (Figs. 3a and b). Extent of delamination of montmorillonite is visible in the images.

Effect of solids/water ratio on the gel structure

An even distribution of starch polymers on bentonite is characteristic of concentrated gels (Figs. 5a and b). The thickness of the montmorillonite strands, e.g. the width of the Al peaks, varies between 1 and 10 μm. Starch polymers cover the surfaces and fill the interstices of the strands.

The thickness of the montmorillonite strands are readily visible in 0.071 solids/water gels (Figs. 5c and d). There is a correlation between the variation of montmorillonite and amylose peaks. Within a single-strand Al concentration decreases as amylose concentration increases suggesting an accumulation of starch polymers between the montmorillonite strands.

When the solids/water ratio decreases to 0.056, the montmorillonite strands decrease in thickness, as can be observed from the width of the peaks on the Al distribution profile at the left-hand side of the photograph. This is to be expected from the lower viscosity of the initial bentonite suspension in the preparation of the gels and the greater turbulence shear stresses exerted on the particles. In this region starch is also fully gelatinized showing no prominent peaks due to granules.

Conclusions

The following generalizations can be made:

1. The extent to which the granules are disintegrated into their polymers determine the structure of the gel. It is a function of starch/bentonite, total solids/water ratios, as well as temperature, shear stresses involved and time.

2. Affinity of hydrophylic starch polymers to bentonite surfaces is extremely high. Entropy increases in the process as a result of desorption of hydration water from montmorillonite and the amorphous state of adsorbed amylose.

3. The presence of bentonites within the gels promotes leaching of the amylose from the granules (gelation).

4. The formation of an amylose network favors the delamination of the montmorillonite particles into thinner lamellae.

5. Montmorillonite lamellae are arranged in band-type structures.

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