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Structure formation in systems containing amylose, amylopectin, and their mixtures

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Pulsed-NMR, X-ray-diffraction and rheological measurements were used to study the structure of systems containing amylose, amylopectin, and their mixtures. It is shown that aggregates whose lifetime was compatible with or exceeded the relaxation time of water molecules were formed during the gelatinization of starch and dissolution of maltodextrin. Evidence is presented to show that the aggregates are formed by amylose macromolecules.

INTRODUCTION

In our preceding studies (German *et al.*, 1988; German *et al.*, 1989*a*), we used NMR relaxation to analyse the water distribution in dispersions and gels of starches and solutions and gels of maltodextrin. We have shown that these gels are formed from aggregates that can arise from the gelatinization process of starches and the dissolution of maltodextrin as well as during their cooling. They appear to be capable of interaction with each other to create higher-order aggregates, the so-called 'fringed miscelles' (Flory, 1953; Billmeyer, 1984; Slade & Levin, 1988). Depending on the conditions accompanying gelling, these miscelles may form either condensed or condensed–crystalline structures (Rebinder, 1966). According to Rebinder (1966), the formation of certain structures controls the rheological and other major properties of gels. The development of coagulation structures that proceeds during gel formation can occur in disperse media. Such structures are formed as a result of a coupling between colloid particles due to Van der Vaals interactions. The colloidal particles have thin layers of the liquid-disperse phase between them, which keeps them apart even at the sites of cohesion. Such networks have a relatively low modulus, creep under small shearing stress, and show thixotropy. In contrast, crystalline structures are formed by the coupling between colloidal particles owing to direct contacts between them and display long-range order. Unlike gel networks built from coagulation structures, the networks obtained from crystalline structures are not thixotropic and are irreversibly destroyed by high stresses.

Coagulation–crystalline structures are of the mixed type. The properties of the corresponding networks are a combination of the properties of the above two network types.

The structural elements of starch gels can be built either from macromolecules of single species (amylose or amylopectin) or develop owing to the interaction of different molecules. Several authors have suggested interactions between amylose and amylopectin (Mesters, 1986; Schierbaum *et al.*, 1986; Russel, 1987; Orford *et al.*, 1987), although they were not successful in obtaining direct proof of the existence of these biopolymer complexes. Kalichevsky *et al.* (1987) showed that mixing of amylose with amylopectin in aqueous solution at 80°C for 48 hours led to complete phase separation. The authors interpreted the results obtained in terms of the thermodynamic incompatibility of starch polysaccharides and supposed that this phenomenon plays a significant role in starch gelation. Moreover, on aging, the aqueous solution of amylose forms both polymer-rich and polymer-deficient phases (Miles *et al.*, 1985*a*; Miles *et al.*, 1985*b*; Ring *et al.* 1987; Ring 1987; Orford *et al.*, 1987; Clark *et al.*, 1989).

In our opinion, the introduction of amylopectin in the amylose–water system can be considered as the addition of a polymer facilitating amylose aggregation. Consequently, we focused our interest on the role of amylose and amylopectin in the process of starch structurization.

EXPERIMENTAL

We used the following preparations: maltodextrin, obtained by partial enzymatic hydrolysis of potato starch according to a procedure developed by Richter *et al.* (1972) in the Central Institute of Nutrition (Potsdam-Reinbrucke, Germany), with a degree of polymerization, $\bar{p}_n$, of 23–26, and starches of rye, pea, and field beans isolated by a method described by Richter *et al.* (1969). The amylose content was estimated in the Central Institute of Nutrition (Potsdam-Reinbrucke, Germany), the respective figures being: rye starch —25%, pea — 24%, field beans — 33%. In the present study, we used amylose preparations manufactured by Serva ($\bar{M}_w$ = 152 kDa) and those of amylopectin (Schuchart, $\bar{M}_w$ = 380 kDa). Gelatinization of starches and the dissolution of maltodextrin and amylopectin were carried out by intensive stirring for 30 min at 98°C.

In order to obtain an amylose solution, the required amount of the preparation was dispersed in water, followed by the addition of 2M NaOH with subsequent dilution by water. Finally, the solution obtained was neutralized with 1M HCl on heating.

The spin-spin relaxation time of water molecules (T_2) was determined by using pulse NMR (Minispec, PC-120, Bruker, Germany), the operational frequency being 20 MHz. The values of T_2 were determined by using a Carr-Purcell-Meibom-Gill pulse sequence (Carr & Purcell, 1954; Meibom & Gill, 1958), 15 min after sample preparation. We used PC numerical simulation to decompose the experimentally obtained echo envelope into single exponentials. The experimental error in the estimation of T_2 did not exceed 6%.

The average diameter ($\bar{D}$) of the maltodextrin aggregates was determined by laser-correlation spectroscopy (Coulter-4N, France) at a scattering angle of 90°. The wavelength of the helium-neon laser was 6328 Å. The spectra were recorded 15 min after sample preparation.

To study the phase behavior of the aqueous system amylose-amylopectin (C_{am} = 1·5%; C_{amp} = 1·9%), it was kept for 48 h at 85°C, resulting in spontaneous decomposition into two coexisting phases. The lower phase was then dried to constant weight at 105°C to yield the polysaccharide concentrations.

We also used spectrophotometric analysis for a qualitative estimation of the composition of the lower phase according to the position of the absorption maximum of polysaccharide dissolved in (KI + I_2) solution.

The crystallinity of aqueous amylose-amylopectin and amylose gels was measured at 25°C by using a Dron-1 diffractometer (USSR), 48 h after the gel preparation.

The rheological characteristics of the three component gels of aqueous systems consisting of amylose and amylopectin were examined by using creep experiments in uniaxial compression. The measurements were taken at 25°C, 2 and 48 h after preparation of the samples.

RESULTS AND DISCUSSION

Table 1 reports the values of the spin-spin proton-relaxation times in systems studied after gelatinization of starches and dissolution of maltodextrin. By comparing the values of T_2 obtained with the published data (Ablett *et al.*, 1978; German *et al.*, 1988), it can be deduced that the values of the spin-spin relaxation time (Table 1) reflect the mobility of water molecules.

As the table shows, the spin-spin relaxation of water molecules is characterized by two relaxation times, T_{2a} and T_{2b}. These two components indicate that there are two types of water molecules, differing in their mobility (Abragam, 1961; Ablett *et al.*, 1978). One could have assumed that the time T_{2b} might characterize the mobility of molecules in swollen or destroyed starch granules. However, this contradicts results obtained during studies on the mobility of water molecules in a maltodextrin–water system free from starch granules (Table 1).

According to the current ideas (Lillford *et al.*, 1980), the complex relaxation of water molecules was observed in case of an unhomogeneous distribution of water throughout the system's volume maintained over the time compatible with, or exceeding, the relaxation time of water molecules. An unhomogeneous structural distribution of this type may arise from the formation of structural elements of gels (aggregates) during

Table 1. The values of the spin-spin relaxation times of water molecules (T_2) and fraction of protons of water molecules bound with aggregates (P_b) at 85°C in starch-water systems after gelatinization of starches and of maltodextrin

Starch	C(%)	T_{2a}(ms)	T_{2b}(ms)	P_b(%)
Rye	11·0	631·4	39·1	9·1
Field beans	8·9	672	49·3	4·0
Pea	9·1	671·9	50·0	5·5
Maltodextrin (Potato)	15·0	986·5	75·5	4·6

gelatinization of starch and dissolution of maltodextrin. Consequently, this implies that times T_{2a} and T_{2b} characterize the relaxation of 'free' water and water bound to the structural elements, respectively. The fraction of water molecules exhibiting relaxation time T_{2b} (P_b) is given in Table 1. Taking into account the fact that the formation of such aggregates precedes the creation of a 3-dimensional network of starch gels (German *et al.*, 1988; German *et al.*, 1989*a*; German *et al.*, 1989*b*) it can be assumed that these aggregates are nucleation centers of a 3-dimensional starch-gel network.

The results of studies on the relaxation properties of water molecules as a function of the maltodextrin concentration are given in Fig. 1. The independence of T_{2b} on maltodextrin concentration with a simultaneous increase in the fraction of fast-relaxing water molecules (P_b) is indicative of a microheterogeneous system (German *et al.*, 1989*b*). This means that increasing the content of maltodextrin in the system should not modify the structure of the aggregates, and it affects only a proportion of the latter (Grinberg *et al.*, 1985).

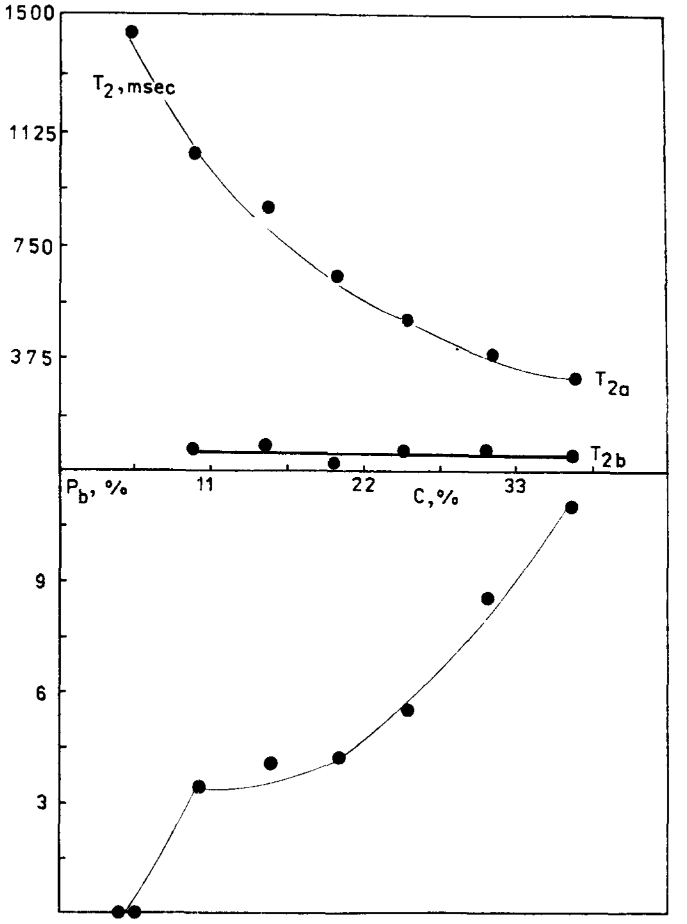

Fig. 1. The dependence of the spin-spin relaxation times of water molecules (T_2) and fraction of water molecules incorporated into aggregates (P_b) as a function of maltodextrin content in maltodextrin-water systems (T = 85°C).

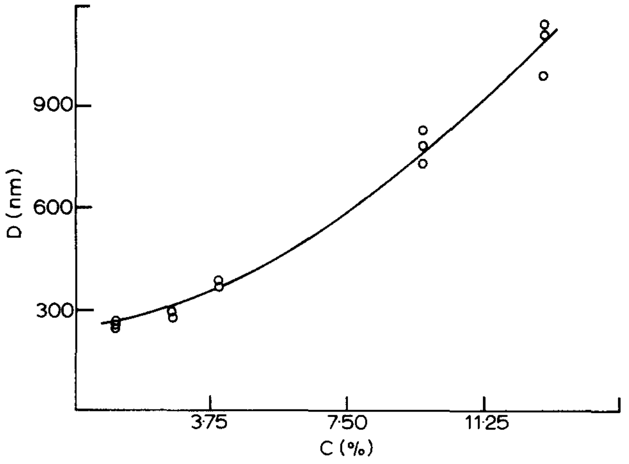

Fig. 2. The dependence of the average diameter ($\bar{D}$) of aggregates in the maltodextrin-water systems as a function of concentration of maltodextrin (T = 85°C).

It is clear from Fig. 1 that, at concentrations of maltodextrin of less than 12%, the spin-spin relaxation of water molecules is single exponential. The absence of T_{2b} is due to the small amount of aggregates. However, such aggregates can be detected when D_2O is used as a solvent (German *et al.*, 1989*b*).

Figure 2 displays the concentration-dependence of the average diameter of maltodextrin aggregates. As can be clearly seen from the figure, the average diameter increases with concentration.

It is apparent that the gelatinization of starches and dissolution of maltodextrin results in the formation of aggregates with a lifetime comparable with the relaxation time of water molecules (or even higher). The mobility of water inside and outside these aggregates is different, whereas their amount is dependent on the polymer concentration. Such aggregates may interact with each other and give rise to structures of higher order.

Table 2 shows the distribution of relaxation times of water molecules in binary systems. These results are obtained in aqueous systems consisting of either amylopectin or amylose. It should be noted that, even at high polysaccharide concentrations (considerably higher than those in starch-water and maltodextrin-

Table 2. The spin-spin relaxation time of water molecules (T_2) and fraction of 'free' water (P_a) at 85°C in amylopectin-water, and amylose-water systems

C(%)	T_{2a}(ms)	T_{2b}(ms)	P_a(%)
	Amylopectin - Water		
8·4	581·9	—	100
13·6	355·0	—	100
18·8	249·9	—	100
	Amylose (P = 938)-Water		
4·5	467·3	—	100

water systems), there is only one relaxation time for the water molecules. Consequently, one can conclude that the complex relaxation of water molecules observed in aqueous starch systems (see Table 1) stems from the presence of amylose and amylopectin in the common solvent.

We can also suggest that the transition from the binary (polysaccharide 1-water) to the ternary (polysaccharide 1-polysaccharide 2-water) system may decrease the thermodynamic quality of the solvent for polysaccharide 1 owing to exclusion-volume effects, thereby facilitating aggregation of amylose macromolecules. It should also be noted that the aggregation of amylose in a binary system may occur owing to a decrease in the thermodynamic quality of the solvent with respect to polysaccharide 1 as the temperature decreases.

The temperature-dependence of the spin-spin relaxation time of molecules of water (T_2) along with the fraction of water bound with aggregates (P_b) in the amylose-water system (the polymer concentration being 5·4%) are given in Fig. 3. It can be seen that, in the high-temperature domain, the spin-spin relaxation time of water molecules is characterized by one time, whereas, at 58°C, i.e. near the critical temperature of gel formation and below it, one observes two relaxation times T_{2a} and T_{2b}. In other words, decreasing the thermodynamic quality of the solvent favors the formation of the structural elements of the gel (aggregates).

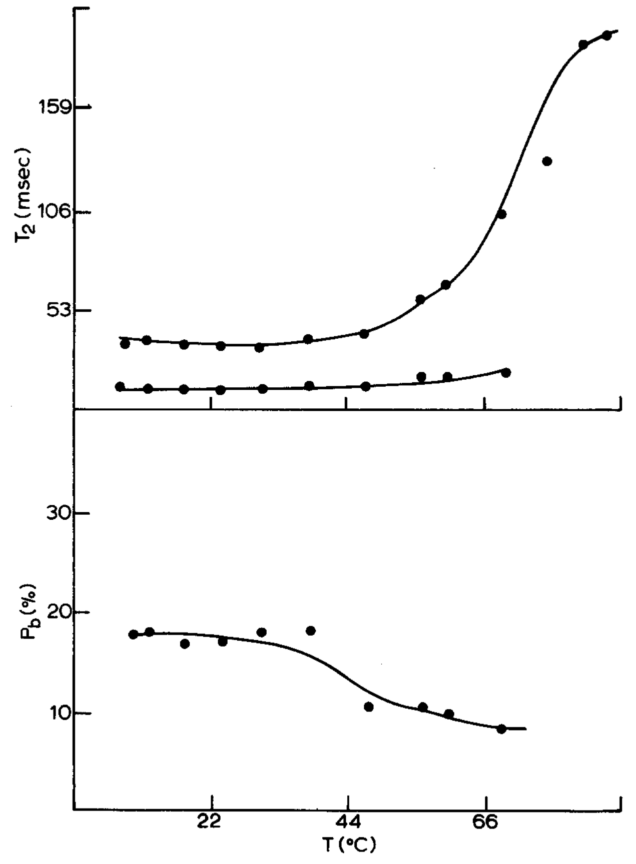

Fig. 3. The temperature-dependence of the spin-spin relaxation time of water molecules (T_{2a}, T_{2b}) and their fraction in aggregates as a function of temperature in amylose-water systems. The degree of polymerization of amylose P_n = 938; the concentration of the polymer, C_{am} = 5·4%.

The lowering of the concentration of amylose in the system (to 1·5%) results in separation of the solution into polymer-rich and polymer-poor phases. The former is a precipitate, whereas the latter is a weakly opalescent solution. As was shown by Clark *et al.* (1989), the interaction of particles in the polymer-rich phase leads to the formation of a 3-dimensional gel network. The spin-spin relaxation of water molecules in both phases at 25°C exhibits two times: T_{2a} = 165 ms, T_{2b} = 40 ms, In the polymer-rich phase, P_b = 23% (the polymer concentration in the phase being 15·0%); T_{2a} = 2080 ms, T_{2b} = 110 ms, P_b = 9% in the polymer-poor phase (polymer concentration 0·4%). At the same time, we should point out that the spin-spin relaxation of water molecules in the binary amylopectin-water system is characterized by one relaxation time, similar to the situation observed both at high temperatures (Table 2) and at 25°C 24 h after preparation (German *et al.*, 1989*b*). The studies of binary systems thus revealed that the temperature decrease leads to a decrease in the thermodynamic quality of the solvent, resulting in the creation of amylose aggregates.

Figure 4 shows the variation in the spin-spin relaxation time of water molecules in the amylose-amylopectin-water system as a function of the amylopectin content. In the absence of amylopectin, the relaxation properties of water molecules are characterized by one relaxation time, T_2. However, when the content of amylose exceeds 0·7%, the complex relaxation phenomenon of the water molecules is observed in the above ternary system.

Our studies revealed that there is complete phase separation of the three-component system (C_{am} = 1·5%; C_{amp} = 1·9%) (see Fig. 5), the lower phase being the precipitate of amylose macromolecules. It should be mentioned that the mobility of water molecules in both phases is mirrored by two relaxation times, T_{2a} and T_{2b}. Consequently, the transition from the binary amylose-water system to the ternary one (amylose-amylopectin-water) is always accompanied by the aggregation of amylose, i.e. the introduction of amylopectin reduces the thermodynamic quality of the solvent. In other words, amylopectin can be considered as a precipitator, whose introduction in the binary system increases the effective concentration of macromolecules of amylose.

It can easily be seen from Fig. 4 that the time T_{2b} does not depend on the content of amylopectin. As has been already suggested, such behavior is indicative of microheterogeneous systems. In contrast to the relation T_{2b} = f(C_{am}) the function T_{2a} = f(C_{amp}) has a more

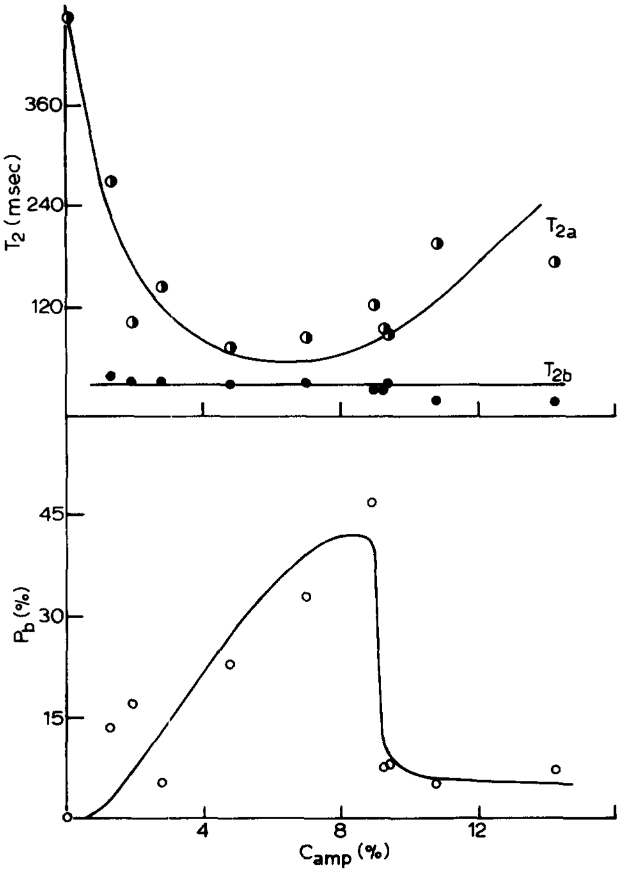

Fig. 4. The dependence of the spin-spin relaxation time of water molecules (T_{2a}, T_{2b}) and their fraction in the aggregates (P_b) as a function of the concentration of amylopectin (C_{amp}) in the amylose-amylopectin-water systems at 85°C; the concentration of amylose, C_{am} = 5·9%.

complex character. It can also be seen that increasing the concentration of amylopectin to 6% results in a decrease in $T_{2a} = f(C_{amp})$, which is presumably caused by the decreasing mobility of 'free' water with an increase in the concentration of the polymer in the system (Abragam, 1961). The further increase in the concentration of amylopectin in the system increases T_{2a}, which may be caused by diminishing amounts of water 'bound' to the biopolymer owing to variation of the interactions between the amylose aggregates. It may be suggested that, in the above situation, there is a transition from coagulation to coagulation-crystalline structures of amylose aggregates. Such a transition should be accompanied by increasing density of aggregates and a decrease in the fraction of water molecules incorporated into the structural elements. In this case, the mobility of water molecules in structural elements may decrease sharply. Since the instrument we used could register only spin-spin relaxation times above 1 ms, it was quite natural that the variation of relaxation features could not be detected in our case.

The character of the function $P_b = f(C_{amp})$ (Fig. 4) can be easily explained by taking into account the proportionality of the value P_b to the amount of aggregates in the system (German *et al.*, 1989), and the fact that amylopectin can be considered as a precipitator of amylose aggregates. An increase in P_b over the concentration range 0–9% of amylopectin can be caused by increasing the effective concentration of amylose aggregates in the system as a result of the introduction of the precipitating component, whereas a sharp decrease in P values may stem from packing of aggregates due to a variation in the interaction mechanisms.

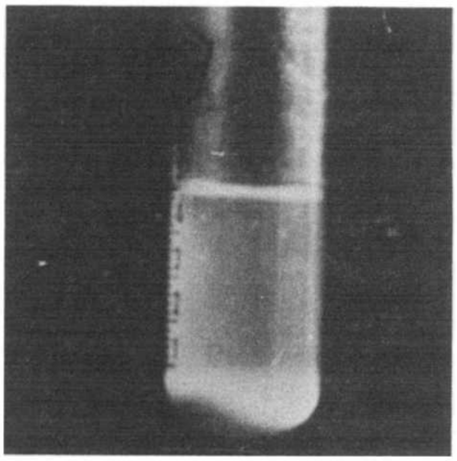

Fig. 5. Photograph of the amylose-amylopectin-water systems after spontaneous decomposition at 85°C taken 48 h after preparation. Initial concentrations: amylose, C_{am} = 1·5%; amylopectin, C_{amp} = 1·9%. Concentration of precipitate = 17% w/v, concentration of supernatant = 2·4% w/v.

It is quite obvious that at high temperature (85°C) the starch-water system is amorphous. Consequently, it is reasonable to suggest that, at higher temperatures, the macromolecules constituting the aggregates will already be positioned in a manner facilitating the crystallization of biopolymers. If the supposition concerning the creation of condensation-crystalline structures of macromolecular amylose aggregates is true, one can expect that, at a concentration of amylopectin above 9% (Fig. 4), the system would sharply increase its crystallinity after cooling and aging. Indeed, as can be seen from Fig. 6, increasing the amylopectin concentration in the system results in the growth of gel crystallinity. The discrepancy between the concentration of amylopectin in the system at which one observes an increase in gel crystallinity (Fig. 6a) and that of amylopectin resulting in a variation of relaxation properties of water molecules (Fig. 4) presumably reflects the inadequacy of the experimental conditions. Taking into account the fact that amylopectin gives rise to the effective concentration of amylose, which is evidenced by the calibration curves of amylose gel crystallinity plotted against polymer concentration (Fig. 6b), one can calculate the effective concentration of amylose in a three-component system. As Table 3

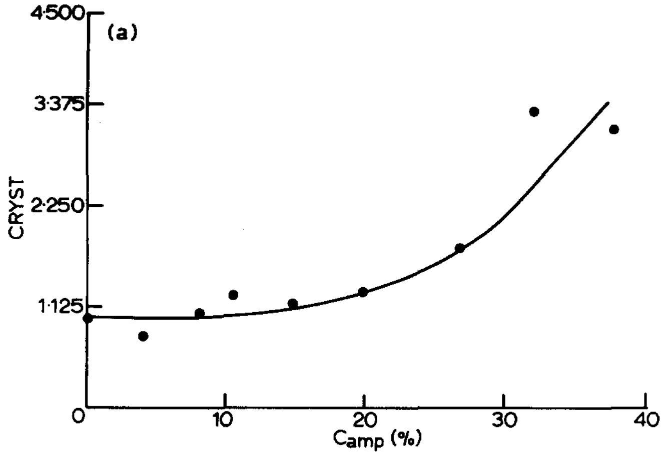

Fig. 6a. The dependence of the crystallinity of gels (Cryst) in the amylose–amylopectin–water systems as a function of the concentration of amylopectin, C_{amp}. Aging time 48 h.

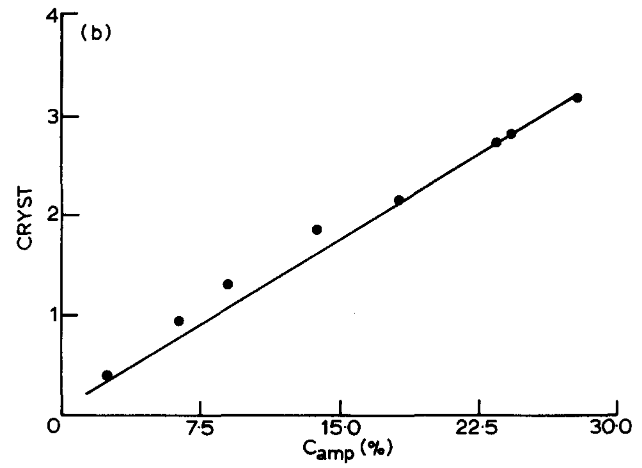

Fig. 6b. The dependence of crystallinity of gels in amylose–water systems (Cryst) as a function of amylose content. Aging time 48 h.

Table 3. The degree of crystallinity (Cryst) calculated effective concentration of amylose (C^{ef}_{am}) in gels of the three-component amylose–amylopectin–water system obtained from x-ray diffraction data 48 hours after preparation of gels*

C_{amp}(%)	Cryst	(C^{ef}_{am})(%)
0	1	6·30
8·6	1·1	8·60
12·0	1·26	10·3
16·9	1·17	9·46
22·1	1·36	11·16
30·3	1·76	14·75
35·0	4·07	35·0
36·4	3·31	28·3
42·5	2·9	24·7

*The concentration of amylose, C_{am} = 6·2%.

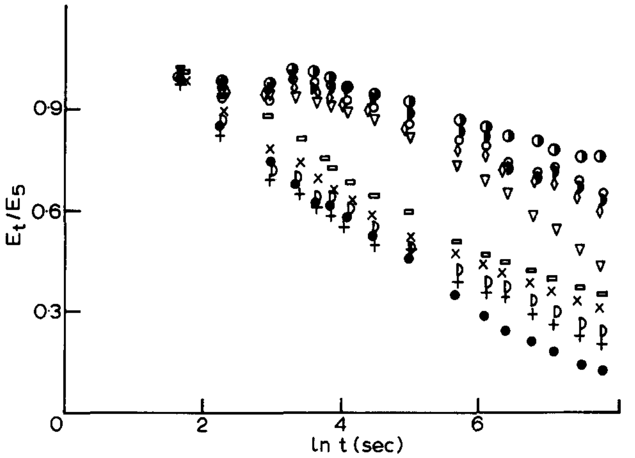

Fig. 7. The generalized creep curves for amylose–amylopectin–water systems (E_t/E_5) where E_5 is the modulus calculated 5 s after the application of the stress and E_t is the modulus calculated after *t* s, as a function of amylopectin content (C_{amp}). Aging time 2 h. Concentration of amylose C_{am} = 5·5%; concentration of amylopectin, C_{amp},%: 0 — D; 2·7 — ●; 3·0 — +; 5·8 — ×; 6·7 — ▭; 12 — ▽; 16 — ◇; 18 — ■; 22 — ◑; 39 — ○.

suggests, the effective concentration of amylose in such systems may attain 35%.

The results of the study of the mechanical relaxation of gels in the three-component systems agree with suggestions concerning the variation in the attraction mechanism in the amylose aggregates. It is well known that the gels of starches are microheterogeneous systems whatever the level of macromolecular structural organization may be (German *et al.*, 1989*a*).

In this case, the variation of relaxation properties may stem from structural variation in relaxation elements (Grinberg *et al.*, 1985). The plots of mechanical-relaxation rates in a three-component amylose–amylopectin–water system are given in Fig. 7 as a function of the amylopectin content. The data were taken 2 h after the preparation of the gels. As the figure shows, at concentrations in the range 0–5·8% and above 12%, there is hardly any concentration-dependence. At the same time as the concentration of amylopectin ranges from 5·8 to 12%, the relaxation rate increases. Similar results were obtained from studies of the mechanical relaxation of gels 48 h after their preparation (Fig. 8). It should be mentioned that in both cases the relaxation behavior of the systems with high amylopectin content is similar to the relaxation behavior of the biopolymers at the beginning of the transition zone from the glassy to the elastic state, although at low concentrations of amylopectin, the relaxation behavior of gels was similar to the relaxation characteristic of the gel systems at the end of the transition zone. This fact also suggests the variation of relaxation elements (Rebinder, 1966), and the transition from coagulation to coagulation–crystalline structures is accompanied by the loss of elastic properties. We should also point out that a variation in the concentration in gels of starch and maltodextrin also

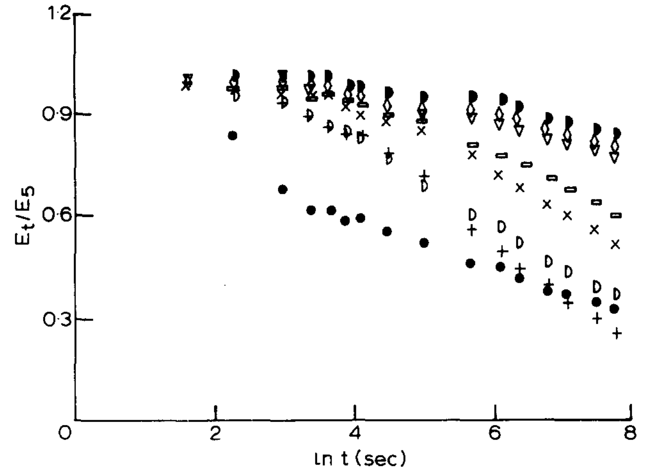

Fig. 8. The generalized creep curves of deformation relaxation (E_t/E_5) for amylose-amylopectin-water systems as a function of amylopectin content, C_{amp}. Aging time 48 h. Concentration of amylose, C_{am} = 5·9%; concentration of amylopectin, C_{amp},%: 0 — ●; 5·4 — +; 9·3 — ▶; 12 — ×; 22 — □; 25 — ▽; 36 — ◇; 39 — D.

increases the rate of the relaxation processes (German *et al.*, 1989*b*).

Figure 9 shows the dependence of the 'initial' elastic modulus of amylose and amylopectin aqueous gels at various aging stages as a function of the amylopectin concentration. These functions are quite complicated. The addition of amylopectin first results in an increase in the 'initial' elastic modulus of the gels. Such behaviour can be caused by an increase in the effective amylose concentration in the presence of amylopectin (see Table 3). It seems that the decrease in the modulus after a further increase in the amylopectin concentration is due to the growth of the network defects during crystallization (Fig. 6a, Table 3). It should be noted that such an effect was observed by Braudo and others (Braudo *et al.*, 1984; Gotlieb *et al.*, 1989; Watase & Nishinari, 1983).

The final increase in the modulus is probably caused by the growth of the crystallites within the gel structure that leads to a decrease in the network's defect. Such a possibility has been previously discussed by Braudo *et al.*, (1984) and Gotlieb *et al.*, (1989).

The difference in the rheological behavior between the gels aged for 2 and 48 h after preparation results from the amylose retrogradation during their aging. According to Miles and his co-workers (Miles *et al.*, 1985*a*, Miles *et al.*, 1985*b*), the substantial increase in the crystallinity of the starch gels occurs mainly during the first 48 h after preparation, which leads to the modulus increase. That is why the gel modulus measured 48 h after the preparation at amylopectin concentrations of less than 10% is higher than the modulus measured 2 h after the preparation of the gel. The decrease in the gel modulus due to network defects measured 48 h after gel preparation is more pronounced, since a larger degree of crystallinity is achieved during aging.

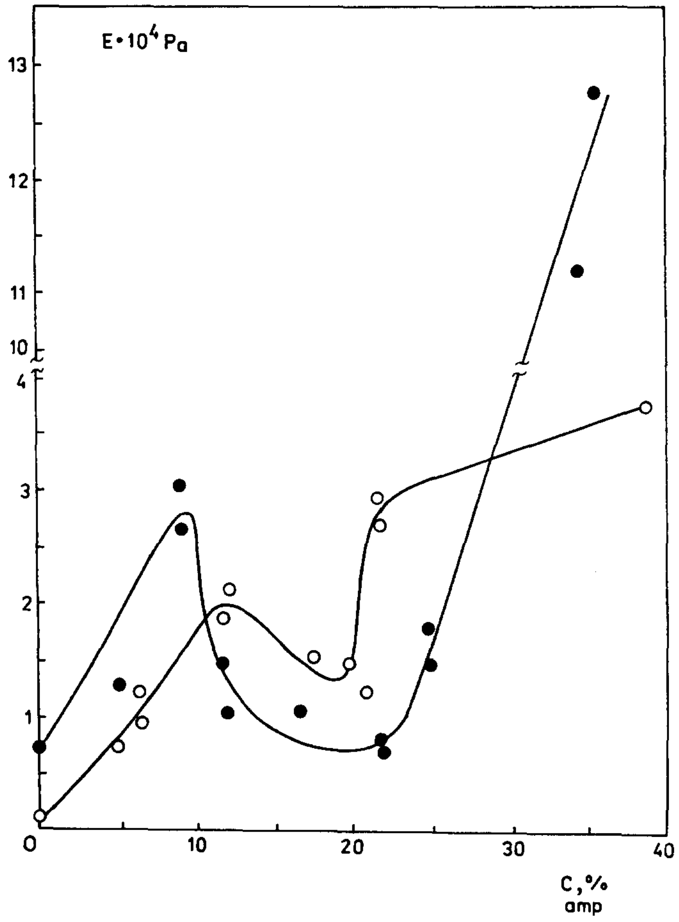

Fig. 9. The dependence of the 'initial' elastic modulus (E_{60}) of gels in the amylose-amylopectin-water system as a concentration function of amylopectin (C_{amp}), C_{am} = 5·8%, gel aging time: 2 h — ○; 48 h — ●.

The problem of correlation between the structure of multicomponent gels with the different crystallization abilities of individual components and their mechanical properties is, of course, rather complex and will have to await additional investigations.

CONCLUSION

The study of starch-water and maltodextrin-water systems and model systems consisting of amylose, amylopectin, and water indicated that during gelatinization of starch and solubilization of maltodextrin, the aggregates (structural elements) composed of amylose macromolecules are being formed. The amylopectin in the amylose-amylopectin-water system can be considered as a precipitating agent facilitating the aggregation of amylose. A decrease in the thermodynamic quality of the solvents in such systems favors the formation of amylose aggregates and separation of the systems into polymer-rich and polymer-poor phases, the latter being free from amylopectin macromolecules. One can suggest that starch and maltodextrin gels belong to gels of the filled type, whose three-dimensional network formed by the polymer-rich phase is filled by amylopectin.

At 85°C, an increase in the content of amylopectin in the amylose-amylopectin-water system results in a variation in the relaxation parameters of water molecules, which in turn leads to changes in the crystallinity of gels and their mechanical-relaxation properties. We believe that such behavior is the result of a variation in the interaction between aggregates, the structural elements of the above systems.

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