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Phase state of starch gels at different water contents

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Amylose, amylopectin, their mixtures and pea starch gels have been investigated by means of thermomechanical analysis over a wide range of water contents. The phase state of gels obtained from natural and model three component systems (starch–water and amylose–amylopectin–water) depends on water content: at high water contents (>70 wt.% w.w.b.) such gels are biphasic and at low water contents (15–40 wt.%) monophasic. The values of the glass transition temperature obtained by extrapolation to zero water content using the Jurkov equation were similar for amylose and amylopectin. Gelation of high water content systems was determined by the immiscibility of amylose and amylopectin whereas gelation at low water contents was governed mainly by intermolecular interactions.

INTRODUCTION

It is well known (Tolstoguzov, 1978), that from a physicochemical point of view the majority of food products are gels. This is why biopolymer gelation, and the structure and properties of biopolymer gels have been extensively investigated by food scientists. Starch is widely used as a gelling agent in the food industry (Tolstoguzov, 1978). Starch gels are the basis of such products as jellies, fruit and vegetable sauces, baked and extruded food products. These products vary widely in water content but the dependence of the mechanism of starch gelatinization on the water content remains unclear.

Native starch — a polymeric carbohydrate — is a heterogeneous material consisting of two major types of polymers — amylose and amylopectin, with the same backbone structure but with varying side chain structures (Wurzburg, 1986). Amylose is essentially a linear polymer whereas amylopectin is branched. Antonov *et al.* (1987) demonstrated that the miscibility of linear and branched neutral polysaccharides is generally limited. This was confirmed by Ring (Kalichevsky & Ring, 1987) in a study of the amylose–amylopectin–water system and Yuryev (German *et al.*, 1992) in a study of the structure and properties of gels, obtained from this system. Evidently, from these data starch gel formation results from the thermodynamic immiscibility of the starch polysaccharides in the gelatinized state and thus the gels will exist as two-phase systems. However, one could suppose that with decreasing water contents phase separation may be physically inhibited and interactions of amylose and amylopectin macromolecules may be possible. In this case, starch gels with a low water content would have a different phase state, and different preparation methods may result in different mechanisms of structure formation.

The phase state of polymer mixtures may be investigated by thermomechanical analysis (TMA), by determination of their glass transition temperatures (T_g). It is well known (Pal & Newman, 1978), that the two-phase polymer systems, obtained from a mixture of polymers with different glass transition temperatures, are characterized by two T_g values, whereas monophasic polymer mixtures are characterized by only one T_g value. The latter value of the glass transition temperature of such polymer a system is located in the temperature range, confined by the T_g values of the individual components. The present work deals with the investigation of the phase state of starch gels at different water contents in order to determine the mechanism of starch gelation.

MATERIALS AND METHODS

Sample preparations

Amylose (from potato starch) was supplied by Serva Feinbiochemica (Heidelberg/New York; M $\approx$ 150000).

Amylopectin (from maize) was supplied by Fluke AG (CH-9470 Buchs; ash $<0{\cdot}1\%$, $M \approx 6 \times 10^6$). Pea starch was isolated from 'Orlovskii-3' variety, as described elsewhere and contains 24% amylose.

Gels of the investigated substance (at <40 wt.% w.w.b.) were prepared by mixing water and the dispersed powders, pressing to 30 kg/cm^3, then heating to 120°C for 5 min and cooling to ambient temperature as described elsewhere (Yuryev *et al.*, 1992). Gels with water contents greater than 70 wt.% were prepared by intensive mixing of the water dispersions of polymers at 98°C for 30 min and cooling to ambient temperature. The sample moisture contents were determined by drying samples at 105°C to constant weight. The gels obtained had no optical activity.

TMA measurements

Thermomechanical measurements were carried out on fresh samples using a Du Pont TA 990 unit TMA 943. The standard heating rate used was 5°C min^{-1}. The glass transition temperature was determined as described elsewhere (Yuryev *et al.*, 1992).

RESULTS AND DISCUSSION

Figure 1a,b,c shows TMA scans of amylose, amylopectin and starch gels at different water contents. Analysis of the curves permits the determination of the gels, glass transition and ice–water phase transition temperatures. The existence of the latter shows the presence of freezable water in amylose, amylopectin and pea starch gels at water contents greater than 20 wt.% (Yuryev *et al.*, 1992). Similar results were obtained in studies of water mobility in the starch gels from different biological sources at high water contents (German *et al.*, 1992; Yuryev *et al.*, 1992). The observed T_gs (Table 1) correspond to the results of other authors (Kalichevsky *et al.*, 1992; Zeleznak & Hoseney, 1987; Liu & Lelievre, 1991). Some of the variations between observed T_g values and literature data may be due to different biological sources of the polymers and/or differences in methods of T_g measurement and experimental conditions.

As shown by Table 1, pea starch gels with a water content greater than 70 wt.% manifesting two glass transition temperatures corresponding to those of amylose and amylopectin. Polymer mixtures which show two glass transition temperatures, equal to the values of the glass transition temperatures of the components, are generally two-phase systems (Pal & Newman, 1978). Hence, if one considers starch as a natural mixture of two biopolymers — amylose and amylopectin (Wurzburg, 1986), then pea starch gels are two-phase. It is necessary to point out that in starch gels (Blanshard, 1987) a three-dimensional network is built from amylose macromolecules, whereas amylopectin plays the role of the filler. As starch gels are prepared by cooling of the starch–water dispersions, in the gelatinized state, one may suppose that the amylose and amylopectin macromolecules are immiscible in the gelatinized state. This result corresponds to that of Ring (Kalichevsky & Ring, 1987).

Table 1. The glass transition temperatures of amylose, amylopectin and pea starch gels

Biopolymer gel	Water content in biopolymer gel, wt.% (w.w.b)	T_g (°C)
Amylose	80–95	−45±10
Amylopectin	70–80	−20±10
Pea starch	70–95	−20±15 −45±15

The typical TMA curves of the gels of amylose, amylopectin and their mixtures, and pea starch, at water contents less than 40 wt.%, are presented in Fig. 1a,b. In contrast to the gels with water contents greater than 70 wt.% (Fig. 1c, Table 1), the gels obtained from the mixtures of amylose and amylopectin, and pea starch gels show only one glass transition temperature. It should be pointed out that starch gels, obtained from other biological sources, with water contents less than 25 wt.% reveal one glass transition temperature (Kalichevsky *et al.*, 1992; Zeleznak & Hoseney, 1987; Liu & Lelievre, 1991).

Figure 2 shows that in the water content range investigated the glass transition temperatures of pea starch gels obtained from amylose and amylopectin mixtures are always higher than that of the amylose gels, but lower than that of the amylopectin gels at the same water content i.e.:

$$T_g \text{ (amylose gels)} < T_g \text{ (pea starch gels, amylose + amylopectin gels)} < T_g \text{ (amylopectin gels)}.$$

Consequently, the gels, obtained both from the model three-component system (amylose–amylopectin–water mixtures) and from the natural three-component system (starch–water), are homophase at water content 15–40 wt.%. Possibly, at low water contents in the gelatinized starch–water system, amylose and amylopectin macromolecules are miscible and interactions between them are possible.

Thus, our investigation shows, that the phase state of the starch gels depends upon the water content. It may be assumed that at higher water contents the starch polysaccharides are immiscible in the gelatinized system, whereas at lower water contents interactions of the amylose and amylopectin macromolecules become possible. The latter assumption follows from the proposition of Antonov (Antonov *et al.*, 1987), de Gennes (de Gennes, 1982) and Khokhlov (Grosberg & Khokhlov, 1989).

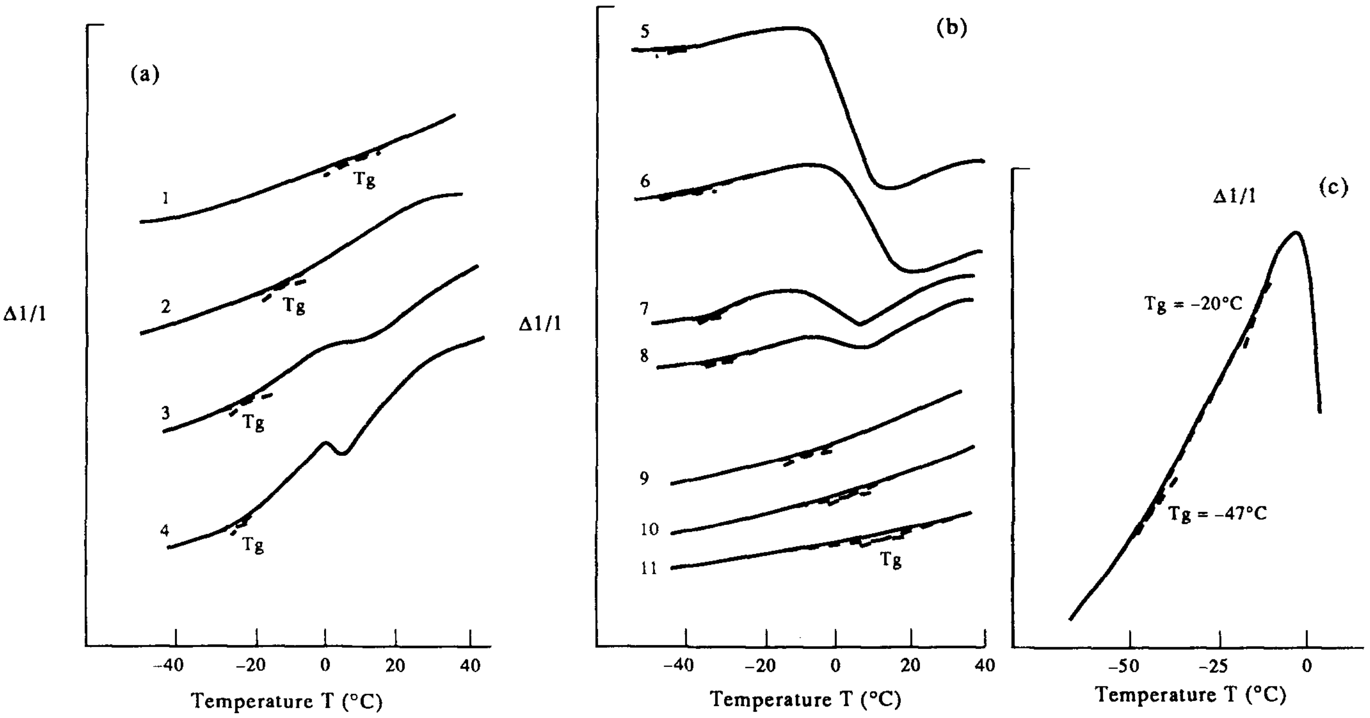

Fig. 1. Typical TMA scans for gels of the pea starch–water system (water contents (% w.w.b.) are a, 1–11·4; 2, 2–17·4; 3–24; 4–25·7% wt.% and c, 80) amylose–water system (b, 5–43; 6–34; 7–26·9; 8–25) and amylopectin–water system (b, 9–20; 10–15·2; 11–11·4 wt.%) at heating rate 5°C min^{-1}.

According to Antonov *et al.* (1987), the immiscibility of neutral polysaccharides in the system polysaccharide 1–polysaccharide 2–water, is caused by the differences in the structure of the macromolecular chains. The results of Ring (Kalichevsky & Ring, 1987) show the immiscibility of the linear amylose and branched amylopectin in systems with a higher water content, i.e. the conditions when the realization of the full range of macromolecular conformations is possible. However, a decrease in the water content in the biopolymer–water system results in a decrease in the range of conformations accessable to the macromolecules (Tahger, 1963). In this case, according to Gennes (de Gennes, 1982) and Khokhlov (Grosberg & Khoklov, 1989), in concentrated solutions or melts, the polymers' macromolecular chains occur as ideal (theta) coils, for which the possibility of the intra- or inter-molecular interactions would be equal. Hence, the possibility of the interaction between macromolecules of the same and different type and, in particular, between amylose and amylopectin is practically the same. This could be one of the reasons for the miscibility of amylose and amylopectin in the concentrated systems.

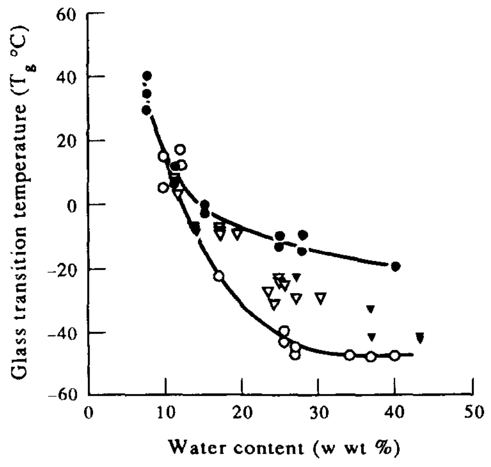

Fig. 2. Effect of water content (w) on the glass transition temperature T_g in amylose (○), amylopectin (●), their mixture (amylose, 60%; amylopectin, 40%) (▽) and pea starch (▼) gels.

This argument is supported by the decrease in the difference between the amylose and amylopectin T_gs with decreasing water content. The T_g at zero water content can be obtained by fitting the data to the classical Jurkov equation (Tinius, 1964):

$$T_g(w+p) = kn + T_g(p), \tag{1}$$

where k is the proportionality coefficient; n, the plasticizer mole fraction (mol.%); $T_g(p)r$ the glass transition temperature of the dry polymer (°C).

The fitting of the experimental data of T_g values of amylose and amylopectin gels to equation (1) are shown in Fig. 3. The experimental results, both in the case of amylose and amylopectin, are well described by equation (1), and the T_g values of the absolutely dry gels of amylose and amylopectin, are close to each other (T_g amylose = 97±15°C, T_g amylopectin = 83±7°C). The decrease in T_g with increasing water content results

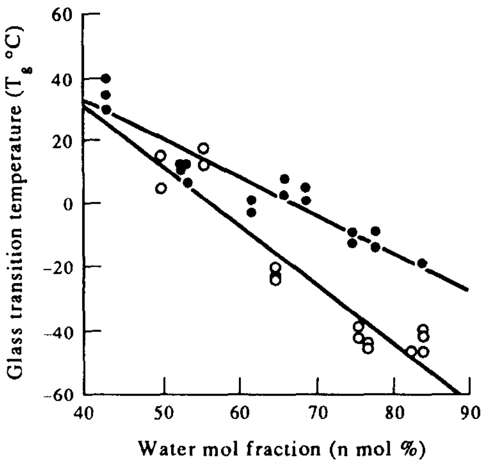

Fig. 3. Graph of glass transition temperature T_g vs mole fraction of water, predicted by an equation (1) (solid lines) and experimentally obtained for amylose (○) and amylopectin (●) gels.

from the interactions of the polar groups of the starch polysaccharides with water and an increase in the conformational mobility of the macromolecular chains of the starch polysaccharides. In absolutely dry gels the conformational mobility of the amylose and amylopectin chains become practically equal at any given temperature.

CONCLUSIONS

The T_g values of amylose and amylopectin obtained experimentally at less than 40 wt.% water (Fig. 3) suggests that a decrease in the water content of amylose and amylopectin gels results in an elimination of the differences in the conformational mobility of the amylose and amylopectin macromolecules. Hence, at low water contents in the model and natural three-component systems, phase separation does not occur. This contrasts to high water content systems where phase separation is clearly seen.

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