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Swelling of the thermoplastically extruded potato starch–soybean protein mixtures — relation to extrudate structure

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The relation between the structure of mixed starch–soybean protein extrudate and properties such as solubility and degree of kinetics of swelling has been studied. The state of water in the extrudates at starch levels ranging from 0 up to 100% on dry matter has been investigated by pulsed NMR. It has been shown that the multiphase nature of the swollen thermoplastically extruded products affect the content and distribution of water inside them. A relation between the fibrous structure of the extrudates and swelling properties has been found. In this case, quantitative information as to the water distribution between various fractions, i.e. water within microcapillaries and/or gel network and capillary water has been attained.

INTRODUCTION

From the beginning of the 1970s there has been an increase in the range of thermoplastically extruded products available (Van Zuilichem & Stolp, 1986). Extrudates are used in food, chemical and other industries (Smith, 1976; Colonna *et al.*, 1987). Mixtures of biopolymers are used in many extrusion processes; however, the factors determining the extrusion behavior and extrudate structure remain in many respects unclear (Ledward & Mitchell, 1988). It has been shown that extrudates based on biopolymer mixtures have a multiphase structure (Guy & Horne, 1988; Zasypkin *et al.*, 1990). A hypothesis for the mechanism of structure formation in these extrudates has been suggested (Tolstoguzov, 1988; Yuriev *et al.*, 1989). The formation of multiphase biopolymer melts undergoing fibrillization during extrusion by shear forces lies at the foundation of the hypothesis.

The multiphase nature of the extrudates based on biopolymer mixtures affects extrudate properties. Some mechanical properties of the soybean protein isolate-potato starch extrudates over the full range of starch content were investigated by Zasypkin *et al.* (1990). The extrudates were made by employing a cooling nozzle to decrease the product temperature below 110°C and to avoid explosion-like water evaporation at the nozzle outlet. The discontinuity in extrudate properties as the starch content increased from 0 to 100% (on a dry weight basis) testified to phase inversion, i.e. a transition from a continious matrix of one polymer to that of the other one. The second polymer formed disperse particles as a filler.

In view of the important role of water in the course of the formation of the extrudate functional properties, swelling and water state in the extrudates were studied relative to the composition, properties and structure of the product.

MATERIALS AND METHODS

Extrusion

Soluble soybean isolate proteins (30%), Purina 500E (product code Pp 500E, Ralston Purina (St. Louis, USA) (protein (dry basis) 95%; fat 1·2%; ash 3·8%), referred to as protein and potato starch (Scientific-Industrial Corp. (Korenyovo, Russia) 'Starch Products') (amylose/amylopectin ratio 1:4) were used without additional purification. Powder-like protein and starch were mixed at various weight fractions (on a dry basis) by means of a blade mixer. In the course of mixing, small portions of water were added, up to 30% moisture,

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in the blend (in g water/g moistened mixture × 100%), depending on the initial moisture of the powders. The wet materials were sealed hermetically and stored for 24 h at 5°C prior to extrusion.

A Brabender (Duisburg, FRG) laboratory extruder (model DN, L/D 20:1) powered by a Do-corder drive was used for the thermoplastic extrusion experiments. The compression ratio of the screw was 4:1 and the screw speed was kept at 20 rpm; the maximum torque was 40 Nm. The following temperatures were employed: feed zone 60°C; heating, metering zones and extruder die 160°C. The temperature (T) was maintained automatically in the range of 155°C < T < 170°C. The extruder was equipped with a cooled metal nozzle of the following dimensions: length 250 mm, height 90 mm, and width 90 mm. The channel in the nozzle through which the extrudate flowed had a rectangular cross-section of 20 mm × 2 mm. An additional nozzle cooled the melt down to 110°C to avoid an explosion-like water evaporation at the nozzle end. Flow rate (defined as the volume of nonexpanded mass at the nozzle outlet per unit time) was maintained approximately constant.

Extrudates were sealed hermetically and stored at 25°C for up to 7 months under sterile conditions in the presence of a small quantity of ethanol.

Swelling

Extrudate swelling was carried out in distilled water at 25 ± 1°C while the samples approached a state close to equilibrium. Sodium azide was used at weight concentration of 0·005% to suppress bacteriological activity.

Two processes contribute to the swelling — water adsorption and sample dissolution. To determine the degree of swelling (DES), per unit weight of dry matter, and the solubility of the extrudates, the samples were cut with dimensions: width 20 mm, thickness h from 2 to 5·5 mm, depending on extrudate composition (thickness was equal to that of the extrudates after elastic recovery at the nozzle outlet (Guy & Horne, 1988; Zasypkin *et al.*, 1990). The samples had a length five times greater than their thickness to reduce any errors due to end effects.

To avoid the possibility of hysteresis phenomena in the course of sorption–desorption in the concentrated systems (Lillford *et al.*, 1980), the swelling of the samples was carried out starting with an initial moisture that was 25 ± 2%.

Before weighing, the swollen samples were dried by means of an air flow (at 25 ± 2°C) until the disappearance of luster from the surface water. The DES was calculated as

$$\alpha_F = \frac{m(t) - m_d}{m_d} \quad (1)$$

where $m(t)$ was the sample mass at time t and m_d the mass of the sample swollen up to the equilibrium state and dried at 105°C for 10 h. This way of determining the degree of swelling allowed corrections to be made on extrudate solubility and the weight of water per unit of a dry extrudate mass to be calculated. The solubility S was calculated as

$$S = \frac{m_d(0) - m_d}{m_d(0)} = 1 - \frac{m_d}{m(0)\,(1 - (m'(0) - m'_d)/m'(0))} \quad (2)$$

where $m_d(0)$ and m_d are, respectively, the mass of a dry sample before swelling and after swelling up to an equilibrium state, $m(0)$ is the mass of the sample (at the initial moisture) before swelling, and $m'(0)$ and m'_d are the masses of an additional sample before and after drying. The additional sample was used to determine the initial moisture of the primary sample and to calculate $m_d(0)$. The initial moisture of the primary and additional samples cut from the same extrudate were equal.

The results were averaged for the three samples. The quoted errors were calculated for a confidence level of 95%.

Nuclear magnetic resonance

Part of the sample dried as described in the section on 'swelling' was cut into portions and placed into a glass ampoule (7 mm diameter).

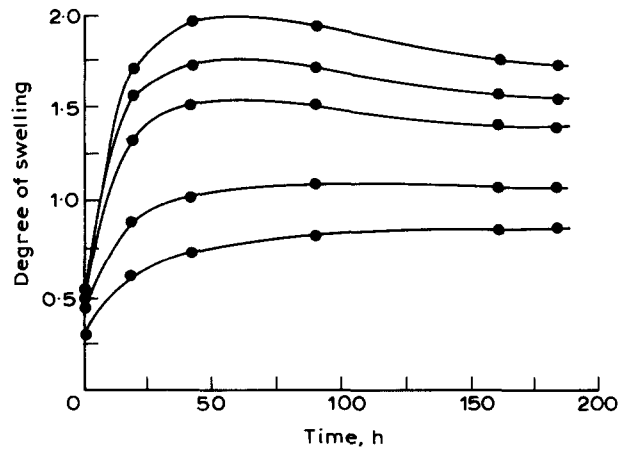
The spin-spin relaxation time (T_2) of the protons in the systems studied was measured at a temperature 25 ± 1°C, using a pulsed NMR spectrometer (Bruker Minispec PC-20; Billeria, MA) at a frequency of 20 MHz, according to Carr & Parcell (1954) and Meiboom & Gill (1958). The delay between the 90° and 180° pulses (tau) was fitted in the range from 20 to 40 μs, depending on the starch content of the measured sample. The magnetization was measured after every 10 of the 180° pulses. Thus, the minimum interval between the 90 pulse and the first sample pulse (when magnetization was measured) was nearly 450 μs. The number of points in the decay was chosen to be in the range from 100 to 160. The value of T_2 was measured for at least 100 scans. The echo envelope was resolved by means of a personal computer Duet-16 (Panafacom, Tokyo, Japan), using the programs developed by the IBM company. Results were averaged for the five to seven samples. The error interval was calculated at a confidence level of 95%.

RESULTS AND DISCUSSION

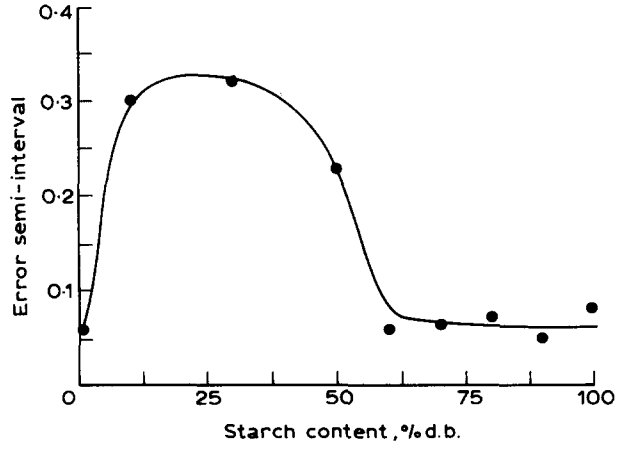
Functional properties of the extrudates such as water binding capacity, water holding, solubility and organ-

oleptic qualities can be expected to be strongly influenced by the water content and state of water in the product. At first, let us regard parameters of the extrudate swelling, characterizing the extrudates in terms of water content.

The rate of swelling as a function of starch content is displayed in Fig. 1. At a starch content up to 60% the DES shows a maximum while the curves corresponding to the extrudates at higher starch contents form a plateau. One can suppose that the qualitative difference is due to a higher solubility of the protein-rich extrudates. This is confirmed by the data in Fig. 2, which shows a sharp transition in extrudate solubility in the range of 60 to 80% starch content. There is also a sharp transition at 60% starch content for the time corresponding to a maximal value of DES (Fig. 3). Previously, Zasypkin *et al.* (1990) have shown similar



(a)



(b)

Fig. 1. (a) Typical curves showing the degree of swelling α_F of the extrudates versus time of swelling. Percentage of starch in the extrudates (on a dry weight basis): (1) 0%; (2) 30%; (3) 50%; (4) 70%; (5) 100%. (b) The mean error (semiinterval, 95% confidence limits) of the extrudate degree of swelling versus starch content in the extrudates.

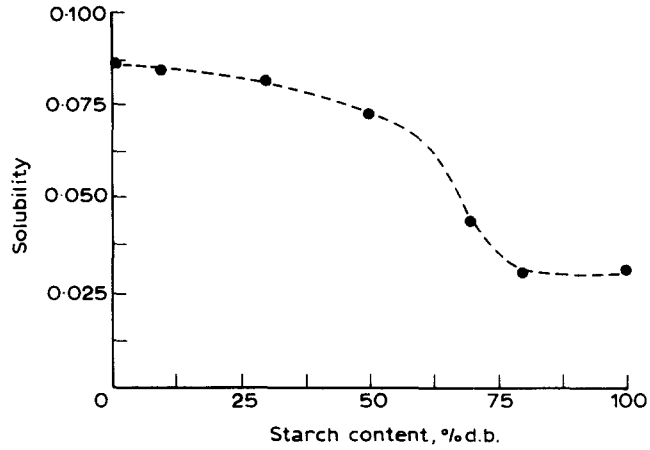


Fig. 2. Dependence of the extrudate solubility on its composition after swelling for 184 h.

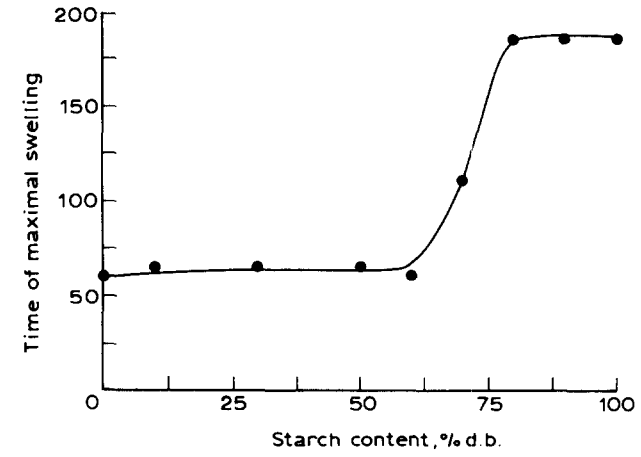


Fig. 3. Time to reach maximum swelling versus extrudate composition.

behavior for a number of extrudate properties such as elastic recovery at the nozzle outlet, breaking strain and real maximal stress. Besides, starch extrudates are dispersed completely when heated at 90°C for 2 h in the presence of excess of water, in contrast to protein extrudates, which just swell. The transition from limited swelling to dispersibility occurs as the starch content in the extrudates exceeds 50%. The most suitable explanation for this behavior is to postulate a phase inversion in the region of 60 to 80% starch content, i.e. a transition from a continuous protein phase with disperse starch particles to that of a starch polymer phase with disperse protein particles. It was also shown that the continuous protein matrix extrudates displayed a fibrous structure, and the starch particles looked like microfibrils. The same approach allows one to explain the data shown in Figs 2 and 3.

The DES of the extrudates after 184 h versus starch content is displayed in Fig. 4. The degree of swelling of protein-rich extrudates is higher than that of starch-rich ones. A maximal value of α_F corresponds to a 30%

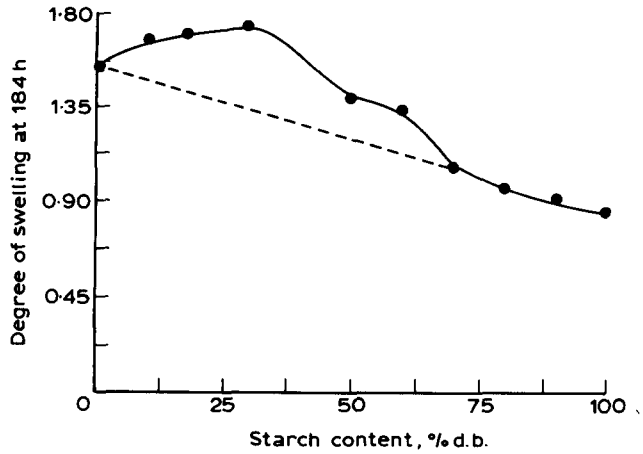


Fig. 4. Dependence of the extrudate degree of swelling at 184 h of swelling on the extrudate composition.

starch content, but a deviation of swelling degree from the additive line is observed for all compositions up to the phase inversion area. Maximal deviation from the straight line occurs at 30% starch content. Thus, DES and solubility are maximal for the protein-rich extrudates. It is worthwhile paying attention to the fact that the area of maximal deviation of α_F from the additive line (10–50% starch content) coincides with a region corresponding to pronounced fibrosity of the extrudates, and to their anisotropy measured as a difference between slopes of the cut stress–strain curves at the different (parallel and perpendicular) orientations of the knife relative to the extrudate flow direction (Zasypkin *et al.*, 1990).

Figure 5 shows photographs of a cross-section of the extrudates. The extrudates display a capillary structure at starch contents from 10 to 60%. The largest capillaries are observed at 30, 50 and 60% of starch content. The data obtained suggest it is the capillary structure developed that is the reason for the deviation of the DES from the additive line (Fig. 4). Besides, in the same area a maximal sample inhomogeneity can be noted. This is the reason for a larger error interval shown for the DES at that starch content (Fig. 1(b)).

To analyze the effects of composition and structure of the extrudates on their properties, the data on the state of the water and its distribution in the swollen extrudates are of interest. The evidence was obtained using a pulsed NMR method. The graphs in Fig. 6 (a–c) show typical magnetization decays of the protons included in the extrudates. Curves for the extrudates based on the single components and the mixture at 30% starch are taken as examples. In all cases, two-component relaxation decays are observed. Relaxation times lie in the range 2–150 ms and for the systems under consideration correspond to water protons not bound in the hydration monolayer (Leung *et al.*, 1979; Lillford *et al.*, 1980; Brosio *et al.*, 1983; Lillford (1988)). The state of the water will be discussed in terms of the observable components, with the shorter and longer relaxation times, T_{2B} and T_{2F}, respectively.

Relaxation times T_{2B} and T_{2F} versus extrudate content are shown in the Fig. 7(a). The relaxation time T_{2F} corresponding to the less bound component of water sharply increases with the development of capillary and fibre structure in the extrudates at starch levels of 15 to 70%. In this case, values of T_{2F} even exceed 100 ms, suggesting a water fraction within large capillaries of 0·01 to 0·1 mm diameter. The T_{2B} time change from 2 to 15 ms seems to be related to the water included in a gel network or in microcapillaries (Lillford *et al.*, 1980).

Figure 7(b) shows the proportion of the water with longer relaxation times versus extrudate composition. This is a minimum for the intermediate starch level extrudates. To analyze the dependence it is necessary to pay attention to qualitative changes in the state of water with a longer relaxation time T_{2F}. It is reasonble to argue that the values of T_{2F} for the extrudates at 20 to 60% starch content belong to capillary water, while T_{2F} for other compositions is relevant to the gel network or microcapillary water. It is a reason why points in Fig. 7(a, b) are connected by the broken lines.

Another feature of the dependences shown in Fig. 7(a, b) is the similarity between the NMR parameters in the case of single componment extrudates and an abrupt difference as the content of the second component exceeds 20% (on a dry weight basis). The relaxation time T_{2F} for the single component extrudates is close to 20 ms, T_{2B} is a few milliseconds, and the proportion of protons with a longer relaxation time T_{2F} approaches 90%. Typical values of T_{2F} and T_{2B}, as well as the lack of dependence of the water distribution on the nature of the macromolecules forming the extrudate, testify that all the water contributing to the visible magnetization decay is included in the gel network or microcapillaries and is not relevant to hydration water that seems to be more sensitive to the nature of the macromolecules (Kuntz, 1971; White *et al.*, 1972; Leung *et al.*, 1979).

As to the two-component extrudates, especially in the range of 30 to 60% starch content, it can be concluded that the water in the swollen extrudates can be divided into hydration water inside the gel networks or microcapillaries and capillary water, which is closest in NMR terms to biopolymer solution water.

Considering that the deviation of the DES from the additive line is relevant to the appearence of capillary water, we can calculate the masses of all the water fractions in the swollen extrudates. In view of possible fast proton and/or spin energy exchange between water fractions it is possible to do this most accurately for the fibrous extrudates where the relaxation times differ by a factor of 10. Figure 8 shows the values of DES for the single component extrudates as well as for the most fibrous ones swollen for 135 h. Let us determine the

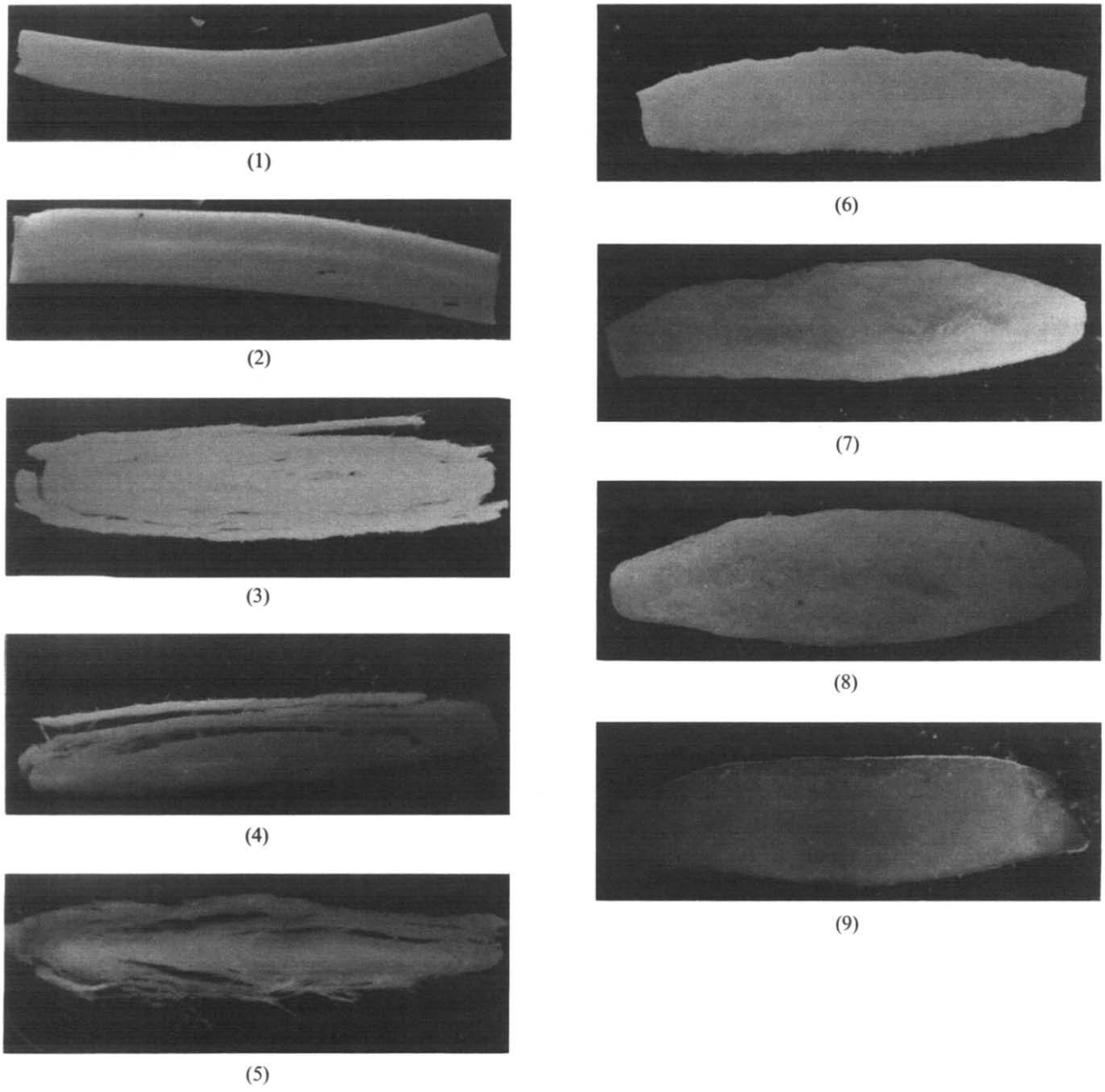


Fig. 5. Photographs of cross-sectional slices of the extrudates at their starch content (% on a dry weight basis): (1) 0%; (2) 10%; (3) 30%; (4) 50%; (5) 60%; (6) 70%; (7) 80%; (8) 90%; (9) 100%. Magnified about five times.

amount of water in the extrudates at 30 and 50% starch content, which relaxes faster than 1 ms and therefore does not contribute to the magnetization decays of protons (Fig. 6(a–c)). The majority of this water is likely to be relevant to the hydration layer, possessing the shortest relaxation times. Considering that we observe in the decays all fractions of water, the part P_F of a capillary one is given as

$$P_F = \frac{m_c}{m_w} \tag{3}$$

where m_c is capillary water mass, and m_w is whole water mass in the swollen extrudates. However, as was mentioned above, a certain fraction of water does not contribute to the visible relaxation processes, which means a decrease in the total mass of water measured by NMR. P_F is then expressed as

$$P_F = \frac{m_c}{m_w - m_d w} \tag{4}$$

where the part of 'invisible' water is given as a sample mass dried after swelling during 135 h multiplied by a

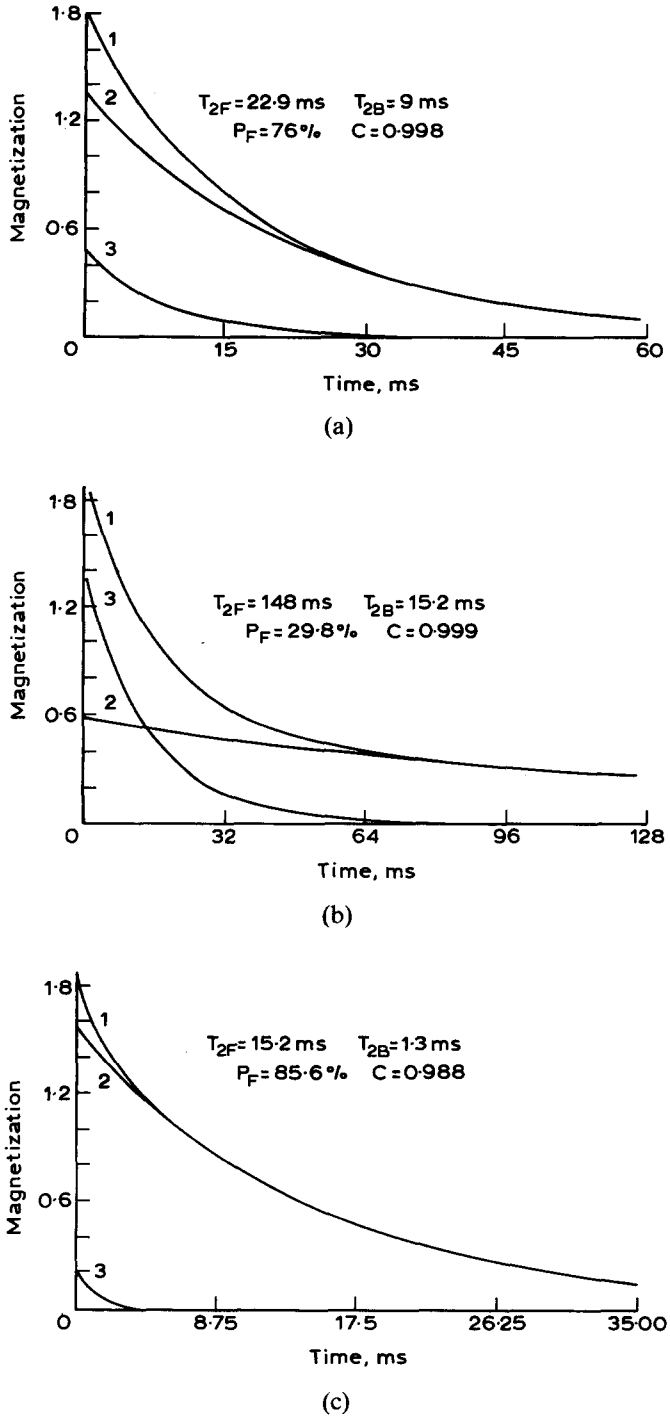


Fig. 6. ^{1}H magnetization decay (in relative units) of the extrudates at a starch content (on a dry weight basis): (a) 0%; (b) 30%; (c) 100%. It is noted by digits: (1) decay observed; (2) and (3) decays of the exponential components characterized by longer (T_{2F}) and shorter (T_{2B}) relaxation times, respectively; P_F — proportion of the protons with longer relaxation time; C-correlation coefficient.

coefficient w equal to the quantity of the 'invisible' water per unit of dry extrudate mass. m_w can be derived from eqn (1):

$$m_w = m(135) - m_d = \alpha_F \cdot m_d \quad (5)$$

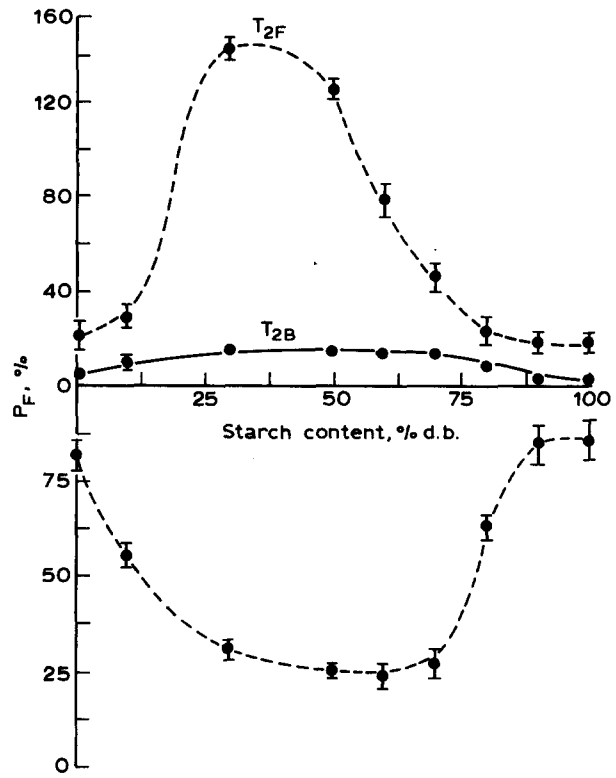


Fig. 7. Dependences on extrudate composition of: (a) the spin-spin relaxation times T_{2F} and T_{2B} of the two relaxational processes; (b) proportion P_F or protons characterized by T_{2F} relaxation time in relation to all protons observed (see text). Time of swelling is 135 h.

From eqns (4) and (5) the value of w can be obtained as

$$w = \alpha_F - \frac{m_c}{P_F \cdot m_d} \quad (6)$$

The unknown value m_c can be also expressed as

$$m_c = (\alpha_F/\alpha'_F) \cdot m_d \quad (7)$$

where α'_F is extrudate swelling degree, corresponding to the values in the additive line (Fig. 8). In view of eqn (7), w becomes

$$w = \alpha_F - \frac{\alpha_F - \alpha'_F}{P_F} \quad (8)$$

Calculated values of w, capillary water content (α_c) and water fraction (α_n) within the gel network or microcapillaries, per unit of dry extrudate mass after swelling, are given in the Fig. 9. Within error intervals, the w values for the extrudates at 30 and 50% starch content are equal to 0·45 g water/g dry matter and are close to the upper limit of typical hydration level intervals of the biopolymer macromolecules in solution, i.e. 0·3 to 0·5 g water/g dry matter (Kuntz, 1971; White *et al.*, 1972).

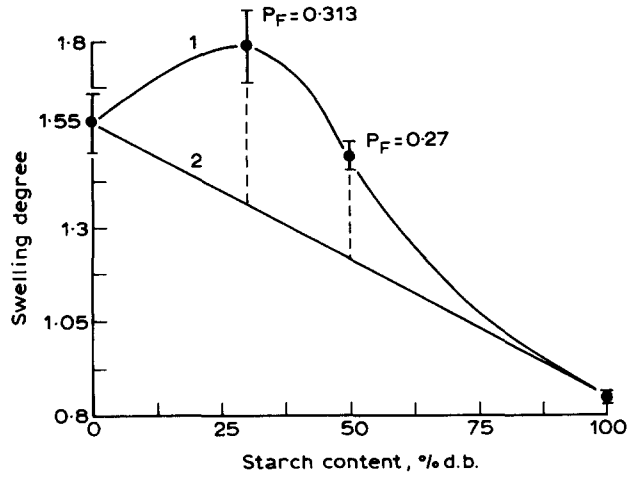


Fig. 8. Curve 1 — degree of swelling at 135 h for the single component extrudates and that for the extrudate with the most developed capillary structure. The calculation of quantity of the different water fractions in the extrudates, using NMR data. Curve 2 — line of additive changing of the extrudate degree swelling.

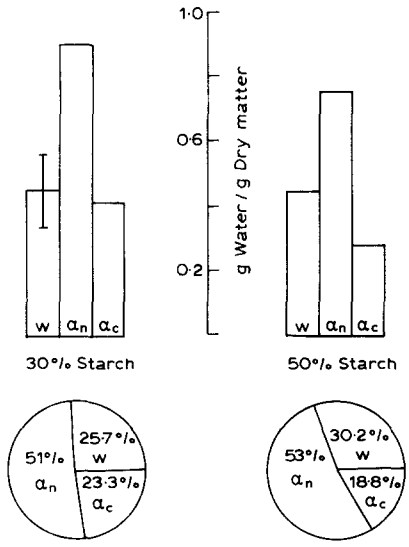


Fig. 9. Quantity of 'invisible' water w, water in the gel network of microcapillaries α_n and capillary water, α_c per unit of dry extrudate mass at 30 and 50% starch content. The percentage of the water fractions is shown in the circle diagrams.

CONCLUSIONS

The data obtained on extrudate swelling are in good agreement with a previously proposed concept of multiphase structure of mixed biopolymer extrudates (Tolstoguzov, 1988; Yuriev *et al.*, 1989). It allows one to conclude that the multiphase nature of the extrudates, based on soybean protein isolate–potato starch mixtures, affects not only the mechanical properties and dispersibility, but swelling, solubility, water holding and distribution of water in the extrudates.

It is worthwhile paying attention to the fact that some properties of the extrudates depend on the fibrous structure, for example, mechanical anisotropy, degree of swelling, water holding capacity and some others (Zasypkin *et al.*, 1990). A number of other properties, such as expansion ratio of the extrudates at the nozzle outlet, dispersibility, solubility and real tensile strength, depend on the inversion of the structural polymer phases in the extrudates. Both phenomena, capillary formation and phase inversion, are a consequence of the multiphase nature of the blends and are observed at different starch contents. To simplify, the capillary structure appears to be pronounced when the viscosity of the continuous matrix is higher than the disperse phase in the molten biopolymer mixture during extrusion (Vinogradov *et al.*, 1982). Phase inversion may depend on the other factors, particularly the thermodynamic incompatibility (interaction) of polymers and kinetic unmixability of structural polymer phases in the melt and under cooling.

The way suggested to determine water distribution in the fibrous extrudates is likely to be useful in evaluating traditional functional properties of meat-based products as well as meat analogs; such parameters as w, α_c and α_n could be considered as functional properties of fibrous extrudates.

The evidence obtained on water content and the state of water in the extrudates can be used for the selection of extrudates for the production of meat products of their analogs with relevant functional properties.

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