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Role of Maltodextrin in Promoting Structure Formation in Extruded Soya Isolate

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ABSTRACT

The structure of maltodextrin soybean protein, and protein maltodextrin extrudates has been studied by optical microscopy, X-ray diffraction and FTIR-spectroscopy. Extrudates were obtained after the cooling viscous biopolymer systems using a long die to avoid vaporisation of water.

X-ray diffraction pictures showed no dominant orientation of the biopolymers in the extrudates. IR-spectroscopy of the extrudate powders revealed no molecular protein–maltodextrin interactions. X-ray structural analysis and optical microscopy showed the texturates were multiphase systems. The composition and structure of extrudates have been observed to influence their equilibrium degree of swelling.

It is concluded that the results cannot be explained by the orientation and cross-linking of biopolymeric molecules to form long aggregates. The results of this work indicate that the disperse particles of a multiphase water-plastified biopolymeric mass orientate in the flow during extrusion.

INTRODUCTION

Nowadays, thermoplastic extrusion is widely employed to obtain fibrous protein structures (Horan, 1977; Kinsella, 1978; Tolstoguzov, 1978; Kazemzadeh *et al.*, 1982; Harper, 1986; Ledward & Mitchell, 1988; Tolstoguzov, 1988).

It is generally accepted (Horan, 1977; Kinsella, 1978; Harper, 1986; Ledward & Mitchell, 1988), that thermoplastic extrusion is accompanied by the denaturation of biomolecules and the transition of the initial mixture of biopolymers to a viscous 'melt' state. When subsequent cooling is accompanied by vaporisation of water, the resulting texturates

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display a non-uniform structure. The average length of the fibres does not exceed their maximum diameter. If cooled without water vaporisation, the texturate sometimes consists of well-oriented fibres of average length many times that of the diameter (Yuryev *et al.*, 1989). The fibrous structure is already formed in the metering zone of the extruder irrespective of the cooling technique used (Kazemzadeh *et al.*, 1982).

A model, incorporating the orientation of macromolecular chains in the flow direction and their subsequent association after cooling to long aggregates, was suggested to account for the mechanism of fibrillation during thermoplastic extrusion (Horan, 1977; Kinsella, 1978; Shen & Morr, 1979; Kazemzadeh *et al.*, 1982; Harper, 1986; Ledward & Mitchell, 1988). Nevertheless, the manufacture of extrudates of a required structure relies mainly on the empirical choice of raw materials and processing parameters, making extrusion something of an 'art' (Ledward & Mitchell, 1988).

In view of the heterogeneity of the extruded mixtures and the incompatibility of many proteins and polysaccharides in aqueous solutions (Antonov *et al.*, 1975, 1987; Polyakov *et al.*, 1986), the authors (Tolstoguzov, 1988, Yuryev *et al.*, 1990) regard fibre formation as due to the deformation of disperse particles of a heterophase liquid system in flow. The more prominent fibrousity of the extrudates, obtained from biopolymer mixtures supports this conclusion. Thus, the mechanism of texture formation is open to controversy and is of much interest.

The objective of the present work was to study the mechanism of fibre formation in systems where vaporisation of water vapour does not occur.

EXPERIMENTAL

Isolates of soybean proteins (Purina 500 E; Ralston Purine Co., USA) (subsequently referred to as 'protein') and maltodextrin, isolated according to the method of Richter *et al.* (1972) were used.

Extruded mixtures, having a water content of 33% (w/wt), were obtained by mixing the materials with subsequent water addition. The feed material was stored for 24 h at 5°C before the extrusion.

Protein, maltodextrin and their mixtures were extruded using a Brabender extruder driven by a Do-corder (E 330, Brabender, FRG). The extruder was equipped with a 4:1 compression correlation for a screw with an L/D ratio of 20:1. The screw speed was 20 r.p.m. The following temperatures were employed: feed zone, 60°C, employed: metering zone, 150°C and extruder die, 150°C. The extruder was

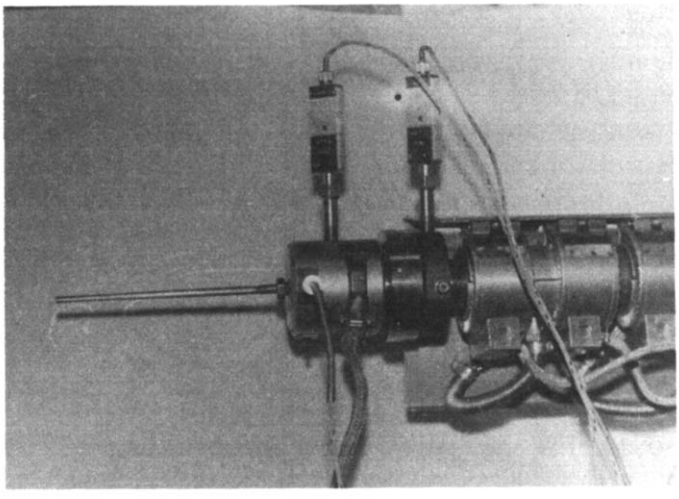

Fig. 1. The extruder die extension.

additionally provided with a metal jet 210 mm long and 6 mm in diameter (Fig. 1) to avoid explosion-like water evaporation as at the end of the long system jet the extrudate had cooled to a temperature below 100°C.

X-ray diffraction was employed to determine the orientation of macromolecules in the extrudates. Samples (1 mm thick) were cut from the extrudates and dried to 3% humidity. X-ray patterns were initially taken with the primary X-ray beam oriented along the symmetry axis of the sample. This axis coincided with the flow direction of the melted biopolymers in the die. Then for the same samples X-ray patterns were taken with the primary X-ray beam perpendicular to the axis of symmetry of the sample.

Compartive estimates of the sample crystallinity were based on the analysis of the number of rings and their relative intensivities and sharpness on X-ray pattersn on flat cassettes, taken with an RKV camera (USSR) using CuK_{α} emission. Scattering rays were recorded in the angular range from 4° to greater than 50°.

Considering the ability of dried maltodextrin gels to crystallise (Reuther *et al.*, 1984), X-ray diffractions patterns were taken 'on reflections' with a Dron 3 diffractometer at 20 ± 1°C using CuK_{α} emission in the angular range from 4° to 43°. In this experiment samples were prepared in the same way as that used for the scattered X-ray beam experiment.

IR-spectroscopy was employed to investigate the protein–polysaccharide interactions predicted by Oates *et al.*, 1987 and Asp, 1986. An IR Fourier 'Bruker'-IRS-113 (FRG) spectrometer was used to obtain IR-absorption spectra for protein, maltodextrin and protein–maltodextrin extrudates and kept for 48 h in a dessicator over $CaCl_2$. The samples were prepared as pills with KBr or suspensions in vaseline oil. The resolution of the IR spectrometer was 2 cm^{-1}.

The texturates were examined microscopically (NU-2 Carl Zeiss Yena, FRG). To stain the maltodextrin, a thin longitudinal slice of an extrudate was first put in a weak aqueous solution of iodine for 24 h at 20°C.

The degree of swelling of the samples was determined on A-gram aliquots by putting them into 50 ml of distilled water at 20°C until equilibrium was achieved; drying them with filter paper and weighing them. Equilibrium values of the degree of swelling were recorded 48 h later, as $(m - m_0)/m_0$ where m is the mass of a swollen sample and m_0 is the mass of this sample, dried at 20°C to equilibrium humidity.

RESULTS AND DISCUSSION

Figure 2 displays a photograph of an extrudate after extrusion processing. The texturate consists of fibrillar elements parallel to the axis of

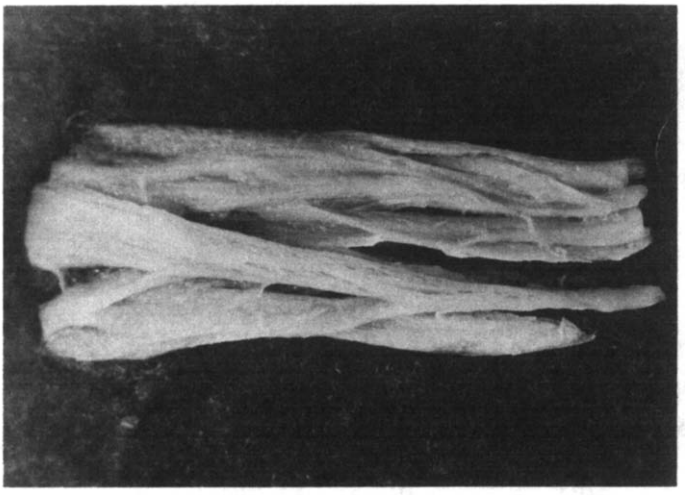

Fig. 2. Extrudate after heating in water at 98°C for 120 minutes. The extrudate contains 90% of isolated soybean protein and 10% of maltodextrin.

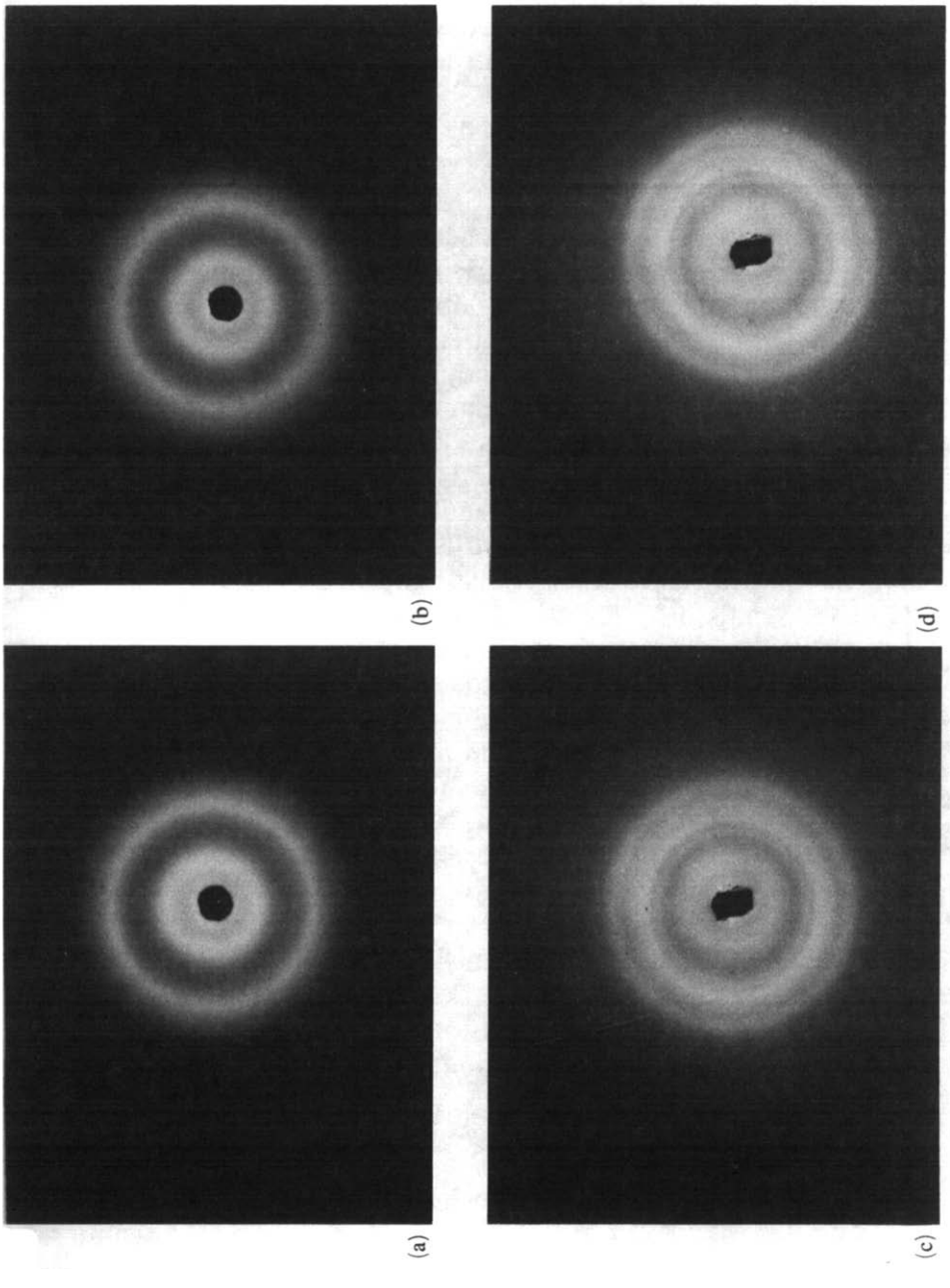

Fig. 3. X-ray diffraction patterns of extrudates. Figure 3a and 3b, soya isolate alone. X-ray bean parallel (a) and perpendicular (b) to direction of flow of extrudate. Figure 3c and 3d, isolate: maltodextrin ratio 70:30 X-ray beam parallel (c) and perpendicular (d) to direction of flow.

symmetry of the sample. Texturates containing from 0 to 40% of maltodextrin develop similar structures.

Figure 3 represents X-ray pictures of longitudinal and transverse slices of protein (Fig. 3(a) and (b)) and protein–maltodextrin (weight ratio is 70% to 30%) extrudates (Fig. 3(c) and (d)). The X-ray pictures taken in two basic directions display only De Bay's rings in all cases. Other protein–polysaccharide ratios in extrudates gave similar results. The identity of these X-ray pictures (Fig. 3) points to the lack of a dominant direction of macromolecular chain orientation in the samples. Therefore, a model incorporating the orientation of macromolecules in flow under thermoplastic extrusion of globular proteins (Horan, 1977; Kinsella, 1978; Shen & Morr, 1979; Kazemzadeh *et al.*, 1982; Harper, 1986; Ledward & Mitchell, 1988) does not reflect the actual process.

Figure 4 displays, IR absorption spectra of powders prepared from protein, maltodextrin and protein–maltodextrin extrudates as well as simple mixtures of powders of protein and maltodextrin extrudates. The IR spectra of the extruded mixture is identical to that of the protein and polysaccharide mixed subsequent to extrusion and can be obtained by combining the spectra of the two individual materials.

No frequency shifts or changes in the intensity of absorption bands, which would point to chemical interactions of the components, were observed for the mixtures. Protein-maltodextrin ratios of 85% to 15%; 60% to 40%; 10% to 90% gave similar results.

Figure 5 displays an X-ray diffraction picture of a sample of a protein–maltodextrin (weight ratio is 70% to 30%) extrudate. Crystal reflections are distinguishable against the amorphous halo.

The values for the interplane distances (Table 1) d are in good agreement with the X-ray data for amylose powder (Whu & Sarko, 1978*a*,*b*) and maltodextrin gels (Reuther *et al.*, 1983). However, it is difficult to distinguish between A and B types of amylose as the extrudates have a low crystallinity. Protein–maltodextrin texturates are believed to be hetero-phase systems since the fragments of amylose and amylopectin in maltodextrin are capable of crystallisation even in the presence of the soybean proteins.

The hetero-phase picture is also backed by the results of microscopic investigations of their longitudinal slices. For example, Fig. 6 displays a micrograph of a longitudinal slice of a texturate with protein–maltodextrin weight ratio of 70% to 30%. The dark oblong areas in the picture are the structural elements containing mainly maltodextrin which turns blue when stained with a weak iodine solution. Investigation of protein–maltodextrin texturates with weight ratios of, respectively, 90% to 10% and 30% to 70%, produced the same results.

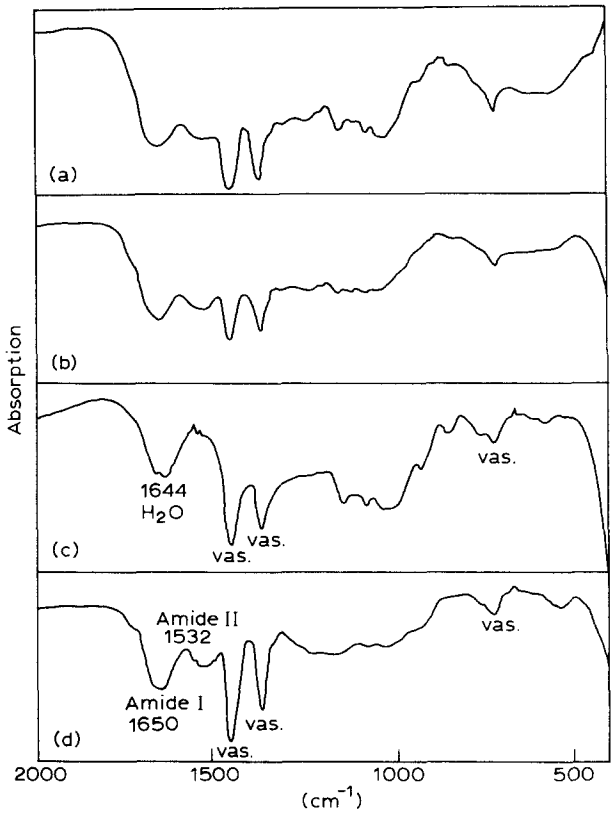

Fig. 4. IR absorption spectra for: (a) protein extrudate; (b) maltodextrin extrudate; (c) a protein-maltodextrin extrudate (protein, 70%, maltodextrin, 30%); (d) a mixture of powders, containing 70% of the protein extrudate powder and 30% of maltodextrin powder.

Table 2 displays the relation between crystallinity of extrudates and their composition. Crystallinity is highest at a protein–maltodextrin weight ratio of 70% to 30%.

The mobility of macromolecules with stereoregular sections determines their crystallisation and the maximal crystallinity is found at the optimal mobility level. The texturate containing 30% of maltodextrin seems to be well-adjusted to this requirement.

The properties of extrudates may be expected to depend on their hetero-phase structure. Figure 7 shows the dependence of the equilibrium swelling degree of extrudates on their composition. The maximal crystallinity of samples (maltodextrin content is 30–40%) coincides with a minimum in the degree of swelling, thus correlating with the lowest degree of water–maltodextrin interaction. The maximum

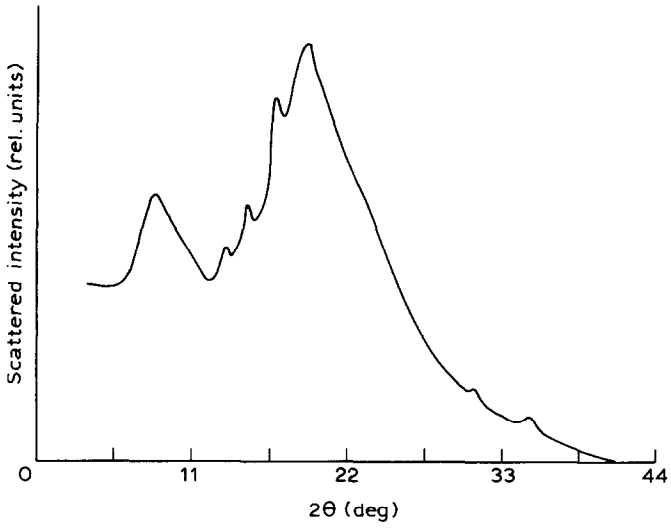

Fig. 5. An X-ray diffraction pattern of a protein–maltodextrin texturate (protein–maltodextrin ratio is 70% to 30%).

TABLE 1
The Inter-Plane Distances (d) and the Intensity of Reflections in Protein–Maltodextrin Texturates with Weight Ratio of Components 70–30%

d, Å	*Intensity of reflections*
6·58	Medium
5·90	Strong
5·18	Strong
2·88	Weak
2·56	Weak

crystallinity of samples occurs at a maldodextrin content of 30% and there is a steady increase in the equilibrium degree of swelling above this point until complete dissolution of pure maltodextrin samples occurs.

CONCLUSION

It is considered that the data show that the fibrous structure of protein and protein–maltodextrin extrudates does not result from the orientation of macromolecular chains in the flow direction (Fig. 3). This suggests

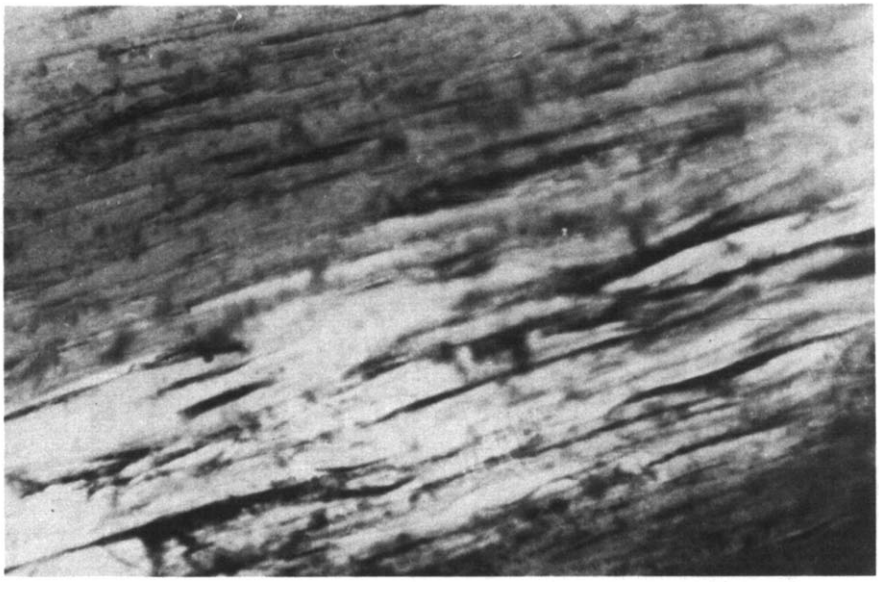

Fig. 6. A photomicrograph of a longitudinal slice of a protein–maltodextrin (70%:30%) texturate. The magnification is 250×. The samples are stained with a weak solution of iodine.

TABLE 2
The Dependence of the Crystallinity of Texturates on the Composition

Protein–maltodextrin weight ratio (%)	*Crystallinity (qualitative estimates)*
100:0	Amorphous
90:10	Amorphous
85:15	Amorphous with occasional regularities
80:20	Slightly regulated
70:30	Crystalline
60:40	Slightly crystalline
30:70	Amorphous
0:100	Amorphous

that the incompatibility of biopolymers determines the formation of extrudate structure. This implies that there are no interactions between the different macromolecular components in the extruded system. This is confirmed by IR absorption spectroscopy of dried texturates which

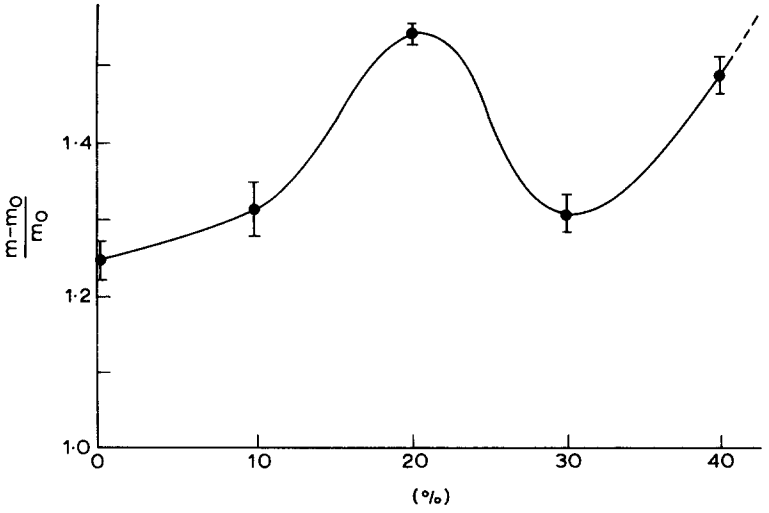

Fig. 7. The relationship between the equilibrium swelling of the extrudate and its maltodextrin content.

show no new bonds between protein and maltodextrin molecules. Studies on the crystallinity of the samples (Fig. 5 and Table 1) indicate that the samples may be regarded as multi-phase systems. Microscopic investigations of extrudates (Fig. 6) confirm the conclusion about the heterogeneity of extrudates in the entire range of protein–maltodextrin ratios under study. Measurements of the equilibrium swelling degree of differently composed texturates point to the inversion of phases when the maltodextrin content is changed from 30% to 70%.

Thus, these studies provide evidence for the formation of the fibrous structures in extrudates which are due to the incompatibility of biopolymers. However, the formation of such structures may result not only from the stratification of the extruded mixture in the melting zone, but also from the non-uniform dispersion of biopolymers in this zone. This problem undoubtedly requires further investigations.

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