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Expansion ratio of extrudates prepared from potato starch–soybean protein mixtures

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The expansion ratio of extrudates based on potato starch and isolated soybean protein was measured for a range of compositions and die diameters. It was shown that the expansion ratio was influenced by the multiphase nature of the melt as well as its rheology. The composition where the expansion was maximal was found. The conclusion was drawn that the departure of the expansion from that expected from the sum of the expansion of the individual components was affected by the deformation of the dispersed phase. Their deformation was influenced not only by the shear stresses in the flow and the viscosity ratio of the continuous and disperse phases, but probably also by elastic properties.

INTRODUCTION

Thermoplastic extrusion is widely used for the texturization of proteins, polysaccharides and their blends (Smith, 1976). Biopolymer blends can be either natural or prepared. By changing the cooling regime of the biopolymer melt at the die outlet, expanded or nonexpanded extrudates can be prepared (Guy & Horne, 1988). Nonexpanded extrudates can be produced by cooling the die to avoid an explosive flash-off of water vapour as steam (Yuryev *et al.*, 1991). The use of short non-cooled dies leads to water vapour release and formation of extrudates with a porous macrostructure. It was shown that both expanded and nonexpanded extrudates based on biopolymer blends, display, under certain conditions, an anisotropic microstructure (Yuryev *et al.*, 1991; Kazemzadeh *et al.*, 1982). Nonexpanded extrudates can have a fibrous macrostructure (Zasypkin *et al.*, 1992).

To explain fibrous structure formation, it was suggested that the disperse particles of the multiphase melt deform under the action of the shear and extensional stresses in the extruder die. The above concept was advanced in detail for the process when a cooled die was used (Zasypkin *et al.*, 1992). The question of the role of the multiphase nature of the biopolymer melt in the case of structure formation of the expanded extrudates remains open.

According to papers dealing with the extrusion of synthetic polymer blends (Tsebrenko *et al.*, 1985, 1991), deformation and interaction of the dispersed particles of the multiphase melt affect the morphology and properties of nonexpanded extrudates which have an anisotropic microstructure. It was shown that there was a deviation of the expansion ratio (B) from additivity when the blend composition gave a melt with a fibrous microstructure (Tsebrenko *et al.*, 1985). Tsebrenko *et al.* (1991) showed that the deviation occurred due to additional normal stresses appearing when the deformation of the disperse particles was observed. Results obtained in the case of the extrusion of wheat gluten (WG)–potato starch (PS) blends were consistent with the above interpretation (Yuryev *et al.*, 1993). It was found that the deviation of the B values from the additive line was equal within experimental error for both expanded and nonexpanded extrudates with a fibrous microstructure. It can be seen from the literature (Tsebrenko *et al.*, 1985, 1991), that the expansion ratio of the melt is one of the most sensitive characteristics of melt morphology and in particular as regards the deformation of the disperse particles being subjected to shear and extension forces in the flow.

According to Tsebrenko *et al.* (1974, 1991) deformation of the disperse particles of the multiphase melt based on polymer blends is affected by blend composition and the ratio of the viscoelastic properties of the disperse particles and matrix at different shear rates. In

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this context, the behaviour of the expansion ratio of the isolated soybean protein (ISP)–potato starch (PS) blends at different shear rates and blend compositions has been investigated to obtain a clear mechanism for structure formation of the expanded extrudates based on biopolymer blends.

EXPERIMENTAL

Isolated soybean proteins (ISP) Purina 610 (Ralston Purina Co., St. Louis, USA) and potato starch (PS) (NPO Krahmaloprodukty, Korenyovo, RF) were used. ISP and PS powders were mixed to various weight fractions. During mixing, a small portion of water was added to give a total water content of 25 ± 1% (w.w.b.). Calculation of the component weights was made taking into account their initial moisture and required composition of the blends. The wet materials were stored hermetically for 24 h at 5°C prior to extrusion.

A Brabender laboratory extruder (model DN, L/D 20:1) powered by a Do-corder drive was used to process the protein–starch blends. The compression ratio of the screw was 4:1 and the screw speed was kept at 200 rpm, the torque reached 40 Nm. The following temperatures were employed: feed zone 60°C, metering zone and extruder die 180°C. The extruder was equipped with dies ranging in diameter from 2 to 6 mm.

The expansion ratio (B) of the extrudates was calculated as:

$$B = d/d_0, \qquad (1)$$

where d is the extrudate diameter when extrudate was cooled to 20°C; d_0 the diameter of the die. The results were averaged over 30 measurements of B. An approximate shear rate ($\dot{\gamma}$) for the melt at the nozzle wall was evaluated according to the relation:

$$\dot{\gamma} = 32\,Q_{\mathrm{m}}/\pi d^3 \sigma, \qquad (2)$$

where Q_{m} is the flow rate, (g/s); σ the specific gravity of the melt in the nozzle; $\pi = 3{\cdot}142$. The flow rate of the biopolymer melt was calculated as the mass of material extruded through the die per unit time. The specific gravity of the melt was taken as that of the nonexpanded extrudates (Zasypkin *et al.*, 1992). In the latter case it was assumed that the elastic recovery of the flow did not affect the specific gravity of the material since at the die outlet although relaxation of the shape of the macromolecules and disperse particles occurred, the specific volume of the melt did not change.

A melt viscosity of ISP and PS was obtained from:

$$\eta = K\dot{\gamma}^{n-1}, \text{ (Pas)} \qquad (3)$$

using the following for K and n: for ISP: $K = 300\,\mathrm{Pa.s}^n$, $n = 0{\cdot}65$ (Jao *et al.*, 1978); for PS: $K = 21\,880\,\mathrm{Pa.s}^n$, $n = 0{\cdot}36$ (Colonna *et al.*, 1987).

RESULTS AND DISCUSSION

In Fig. 1 the expansion ratio of the extrudates vs composition is given for the various die diameters. The extrudate diameter in all cases exceeded the die diameter, so values of B ranged from 1 to 4. The observed expansion can be due to two phenomena: an elastic recovery of the melt flow and expansion of the extrudates as a result of vapour release. The former is affected by normal stresses occurring when the melt is flowing, and its relaxation when melt flow conditions change at the die outlet. This phenomenon is known in the literature as a Barrus effect. Expansion of the extrudates due to vapour release also occurs at the die outlet and it can be explained through a sharp change in the external pressure acting on the melt.

Figure 1 shows that the values of B are generally higher than expected on the basis of an additive model. Such deviations were previously observed for expanded and non-expanded extrudates prepared from WG–PS blends (Yuryev *et al.*, 1993).

The observation at the lower die diameters of two maxima with a local minimum is similar to the behaviour observed for extrudates prepared from synthetic polymer blends (Tsebrenko *et al.*, 1985). In this case it was shown that maximums in the dependence of B on extrudate composition, correspond to a fibrous or coaxial lamellar structure of the extrudates whereas a local minimum corresponds to an 'entangled' morphology. The latter type of structure generally occurs where there is a transition from the continuous phase based on

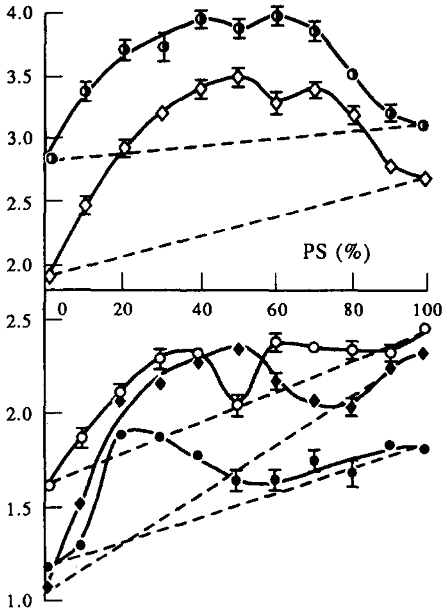

Fig. 1. The expansion ratio (B) of the extrudates of the ISP–PS blends plotted against %PS for the following die diameters (mm): ◑ −2; ◇ −3; ○ −4; ◆ −5; ● −6. The broken lines show the expansion ratios expected on the basis of an additive model.

polymer 1 and a continuous one on the base of polymer 2. In other words, the local minimum in the curve of *B* vs mixture composition should correspond to a phase inversion in the extrudates.

Previously, it has been shown (Zasypkin *et al.*, 1991) that a fibrous structure for nonexpanded extrudates based on ISP–PS blends was observed in the composition range of 5–50% of PS, and phase inversion was detected at 60–80% of PS. It is to be expected that the melt multiphase nature results in a microfibrous structure of the extrudates irrespective of the method of cooling. The phase inversion region for the expanded extrudates based on ISP–PS blends are given in the Fig. 2 as a function of die diameter. The evaluation was carried out by measuring two independent parameters. The composition at which the extrudates are able to disperse in water and the point of the local minimum in the dependences of *B* vs extrudate composition. The idea behind the first method is the fact that extrudates with a starch continuous phase are able to disperse when boiled but protein-enriched extrudates are only able to swell. From the data obtained it can be assumed that phase inversion in the extrudates occurs at the 50–70% starch level. The position of this region is not dependent on the diameter of dies used. Thus, the results confirm the concept that the melt formed from the biopolymer blend has a multiphase character. In this case one polymer gives a continuous phase and the second one forms disperse particles. Under stress by shear and extension forces in flow the particles disperse under certain conditions and coalesce, forming microfibrils or lamellar structures. Deformation of the disperse particles can also result in additional normal stresses appearing. These stresses affect the melt expansion ratio and hence may explain the dependence of *B* on blend composition.

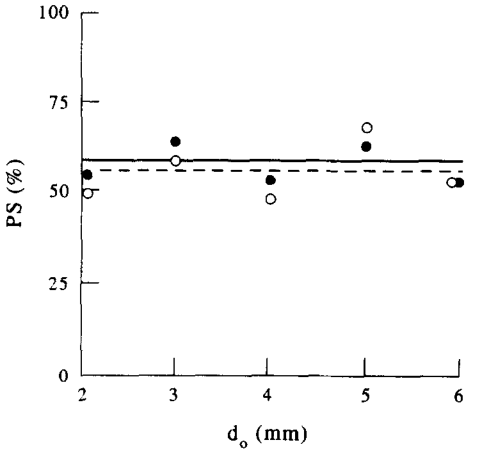

Fig. 2. The extrudate compositions corresponding to the 'local' minimum values of the expansion ratio (○) (Fig. 1) and the transition from swelling of the extrudates to dispersibility in hot water (2 h at 98°C) (●), vs die diameter. Broken and thin lines show an average PS level for the empty and filled circles, respectively. The average value was calculated using a least mean square criterium assuming PS is constant.

The degree of deformation of the disperse particles in the multiphase melt is influenced by the type of biopolymers forming the melt and the melt rheology (Tolstoguzov, 1988; Yuryev *et al.*, 1993). Let us consider how the degree of deformation of the disperse particles and hence, *B* depend on the shear rate ($\dot{\gamma}$).

The shear rate in the melt varies with the die diameter used. The values of $\dot{\gamma}$ for melts containing different PS levels and different die diameters (d_0) are given in Table 1. For each value of d_0, there is a tendency for $\dot{\gamma}$ to increase with increasing PS level. There is no correlation between $\dot{\gamma}$ and *B* at constant d_0. Shear rate increases over the whole PS range with decreasing die diameter. In this case the *B* values increase with $\dot{\gamma}$.

The regions of extrudate compositions where the deviation of *B* from the additive values occurs are influenced by d_0 and the corresponding range of $\dot{\gamma}$ values. An examination of Fig. 1 shows that at low shear rates (d_0 = 5 mm and 6 mm), *B* only departs from the additive values where ISP is the continuous phase. At d_0 = 4 mm ($\dot{\gamma}$ = 170–300 s^{-1}) departure is observed for blends containing 5–45% of PS and 55–80% of PS. In the phase inversion area located between these two regions, departure from additivity is not seen. At high shear rates d_0 = 3 and 2 mm deviation occurs for all blend compositions. In these cases the relationship between *B* and %PS becomes more symmetrical. We interpret these results as follows. At low shear rates corresponding to die diameters of 6 and 5 mm, deformation of the starch disperse particles only occurs in the continuous ISP phase. At low values of d_0 (4, 3 and 2 mm) when $\dot{\gamma}$ values exceed 170 s^{-1}, the deformation of the disperse particles of starch in a protein matrix as well as protein particles in a starch continuous phase is likely to be occurring.

According to the data obtained for a number of blends of synthetic polymers (Tsebrenko, 1991; Tsebrenko *et al.*, 1974) an essential condition of the effective fibrous and lamellar structure formation occurs in the vicinity of viscoelastic properties of the disperse and dispersed phases. These properties and, primarily the ratio of phase viscosities depends on the shear rate of the melt flow.

To understand the rheological conditions for the

Table 1. Shear rate (s^{-1}) of the melts based on PS–ISP blends vs its composition and nozzle diameter (d_0)

PS, % d_0, mm	0	20	40	60	80	100
2	1628	2422	2280	1971	2901	2551
3	428	432	665	707	575	765
4	170	308	270	280	290	300
5	124	136	161	211	210	218
6	87·5	68	59	98	99	73

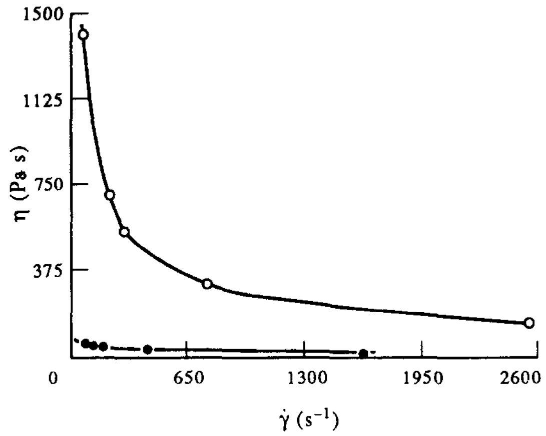

Fig. 3. The apparent viscosity (η) of the melts of PS (○) and ISP (●) vs shear rate ($\dot{\gamma}$).

effective deformation of the disperse particles at different shear rates let us evaluate the ratio of protein and starch viscosities. As a first approximation it can be assumed that the rheological properties of melts are based on individual components. The results of calculation η vs $\dot{\gamma}$ for the ISP and PS melts are shown in Fig. 3. At the $\dot{\gamma}$ values corresponding to die diameters of 3 and 2 mm the viscosities of the ISP and PS melts are closest. This could result in deformation of the disperse particles of PS in the OSP matrix as well as ISP particles in the starch continuous phase. The deviation of B values from the additive model for high PS levels at low die diameters (Fig. 1) supports this idea.

When d_0 increases, the difference between viscosities of the ISP and PS melts grows. Simultaneously, the deviation of B values from the additive model for the extrudates with a continuous PS phase disappears. For the extrudates with an ISP continuous phase the deviation is maintained (Fig. 1). $d_0 = 5$ and 6 mm and the viscosity of the PS phase is significantly higher than the viscosity of the ISP phase. In this case deformation of the ISP disperse particles in the PS matrix would be expected to occur. Since under these conditions departure from additivity is not observed it seems possible that the elastic properties of the ISP reduce the capability of the ISP phase to deform in flow in comparison with the PS phase. This is supported by the high storage modulus of the ISP extrudates and data on the bonds stabilizing the extrudate structure (Zasypkin *et al.*, 1992).

Thus, the expansion ratio of the extrudates based on biopolymer blends forming a multiphase melt is affected not only by the phase viscosities but also by the elastic properties of the phases.

CONCLUSION

The dependence of the expansion of ISP–PS extrudates on composition and shear rate reflect the multiphase behaviour of the melt. The concept of the deformation of the disperse particles in the melt during flow which has previously been put forward to account for fibre formation in nonexpanded extrudates has been extended to describe the process of structure formation in expanded extrudates based on biopolymer blends.

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