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Mechanical properties of the products obtained by the thermoplastic extrusion of potato starch – soybean protein mixtures

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The mechanical properties of extrudates produced by thermoplastic extrusion of potato starch–soybean protein isolate mixtures have been studied over the full range of starch contents. Extrudates were obtained through a water cooled nozzle in order to avoid explosion-like water evaporation. It was shown that the mechanical properties of the extrudates were affected by their multiphase nature. The authors conclude that phase inversion occurs in the extrudates over the starch content range 60–80% (on dry weight basis). This conclusion is drawn from an analysis of the dependence on starch content of the extrudate expansion ratio at the nozzle outlet, its apparent density, initial elastic modulus, real tensile strength, failure strain and apparent cutting stress. It was shown that the extrudates have maximum anisotropy at starch contents of 10–30%.

INTRODUCTION

A wide range of extruded products based on protein and polysaccharides are produced by the food industry (Horan, 1977; Tolstoguzov, 1978; Kazemzadeh *et al.*, 1982; Harper, 1986). As a rule, multicomponent systems such as moistened powder-like mixtures of biopolymers are processed by extrusion cooking (Horan, 1977; Tolstoguzov, 1978; Kazemzadeh *et al.*, 1982; Ledward & Mitchell, 1988). However, up to now the choice of recipes in extruded systems is to a significant extent a technological art (Ledward & Mitchell, 1988).

Taking into account (1) the thermodynamic incompatibility of proteins and polysaccharides in solution under certain conditions, and (2) the incompatibility of some synthetic polymers in solutions and melts, a mechanism of structure formation in the extrudates on the base of biopolymer mixtures was suggested. This mechanism can be regarded as a particular case of spinneretless spinning (Tolstoguzov, 1988; Yuryev *et al.*, 1989). It assumes the formation of a multiphase biopolymer melt in the course of extrusion cooking. The multiphase nature of extrudates prepared from biopolymer mixture has been reported previously (Kazemzadeh *et al.*, 1982; Yuryev *et al.*, 1990). The purpose of the work reported in the present paper is to show the interrelation between the multiphase nature of extrudates and their mechanical properties.

MATERIALS AND METHODS

Thirty per cent soluble isolated soybean proteins Purina 500E (Ralston Purina Co. St. Louis, USA) subsequently referred to as protein and potato starch (Biochimreactiv, Olaine, Lithuania) were used. Protein and starch powders were mixed to various weight fractions. During mixing, a small portion of water was added to give a total water content of 30%. Calculation of the component weights was made taking into account their initial moisture and required composition of the blends. The starch weight fraction as a percentage (dry weight basis) will be denoted S. 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 mixtures. The compression ratio of the screw was 4 : 1 and the screw speed was kept at 20 rpm; the torque reached 40 N m. The following temperatures were employed: feed zone, 60°C; metering and extruder die, 160°C. The extruder was equipped

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with a cooled metal nozzle 250 mm long × 90 mm × 90 mm and a channel section 20 mm × 20 mm. An additional nozzle cooled the melt down to 110°C to avoid an explosion-like water evaporation at the end of the nozzle.

The expansion ratio (E) of the extrudates was computed as: $E = (H - H_0)/H_0$, where H is the extrudate thickness at equilibrium after leaving the nozzle, and H_0 is the nozzle channel height (2 mm).

The apparent density ρ of the extrudates was determined by means of volumetric flasks (capacity 50 ml), water being used as the liquid being displaced. The standard deviation of the extrudate density did not exceed 0·005 g/cm^3.

Extrudates were tested by extension and cutting using an Instron TM-SM-L universal testing machine with a crosshead speed of 5 mm/min. The moisture of the samples before testing was 25%. To obtain samples with equal moistures, all extrudates were stored together hermetically for seven days. When conditioned, the extrudates with appropriate sizes for testing were cut with a special knife. In the course of the tests the moisture of the extrudates decreased less than 0·5%.

When tested in extension, the stretched part of the samples had the following dimensions: length 30 mm, width 5 mm, and thickness varying from 2 to 5 mm, depending on extrudate composition (Fig. 1(a)). Initial elastic modulus (M), tensile strength (σ) and failure strain (ε_F) were determined from the stress–strain curve. Taking into account the homogeneous deformation of the extrudates and the closeness of the strain corresponding to the tensile strength to the failure strain, the real tensile strength (σ_r) was determined as: $\sigma_r = \sigma(1 + \varepsilon_F)$. Critical stress ($\sigma_c$) was determined as the ordinate of the intersecting point of the asymptotes to the two linear regions of the stress–strain curve (Fig. 2(a)) (Askadsky, 1973).

When tested by cutting, the sample size was 20 mm × 20 mm. The thickness of the extrudates varied from 2 to 5 mm, depending on extrudate composition. The knife edge was sharpened at an angle of 6° and was positioned in the direction coinciding with the symmetry axis of the samples in the first series of tests and in the perpendicular direction in the second series. The symmetry axis of the samples coincided with the flow direction of the melt during extrusion. Cut stress was obtained by dividing the value of the loading force by the sample section area. A typical cut load–deformation curve is shown in Fig. 3, (insert). We can recognize three regions in the curve. The first one corresponds to the elastic deformation of the surface layer. The second is related to the cutting of the material. As a rule the stress–strain curve is linear at this stage. It is the slope of the linear region that we take as a characteristic of the sample strength (Gul, 1978). The last region corresponds to sample rupture.

The average values of the measured characteristics were obtained by averaging at least five experimental values. The confidence interval was computed from the normal distribution of the sample mean value according to the t-criterion with a confidence limit of 95%.

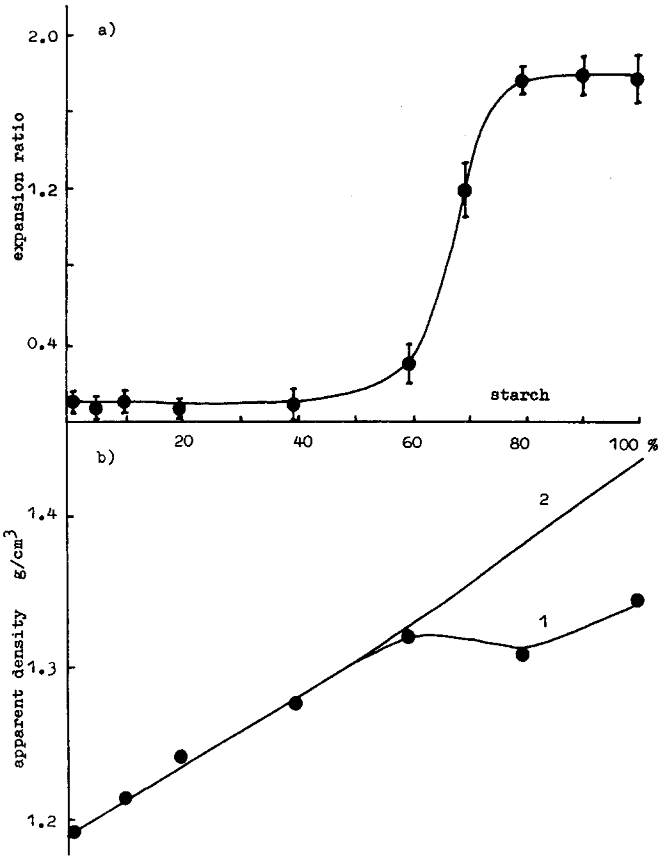

Fig. 1. (a) Expansion ratio of the extrudates at the nozzle outlet versus starch content (% wt on dry basis). (b) Dependence of the extrudates apparent density on starch content (%wt on d.b.): 1, experimental curve; 2, calculated curve.

The relative elongation plot ($(L - L_0)/L_0$) of the samples versus temperature was obtained by means of a DuPont TMA-973 thermal analyzer used at a heating rate of 5°C/min. The initial sample length (L_0) was 8 mm.

RESULTS

Figure 1(a) displays the expansion ratio (E) of the extrudates at the nozzle outlet as a function of composition. The expansion ratio of the extrudates containing up to 50% starch is insignificant (about 0·1). However, it increases sharply (more than 18 times) when S increases from 50% up to 80% and becomes constant at the higher starch contents. Spherical air voids with an average diameter of 0·1 mm were observed in extrudates containing over 40% of starch. There is no visible air phase in the extrudates at starch contents up to 40%.

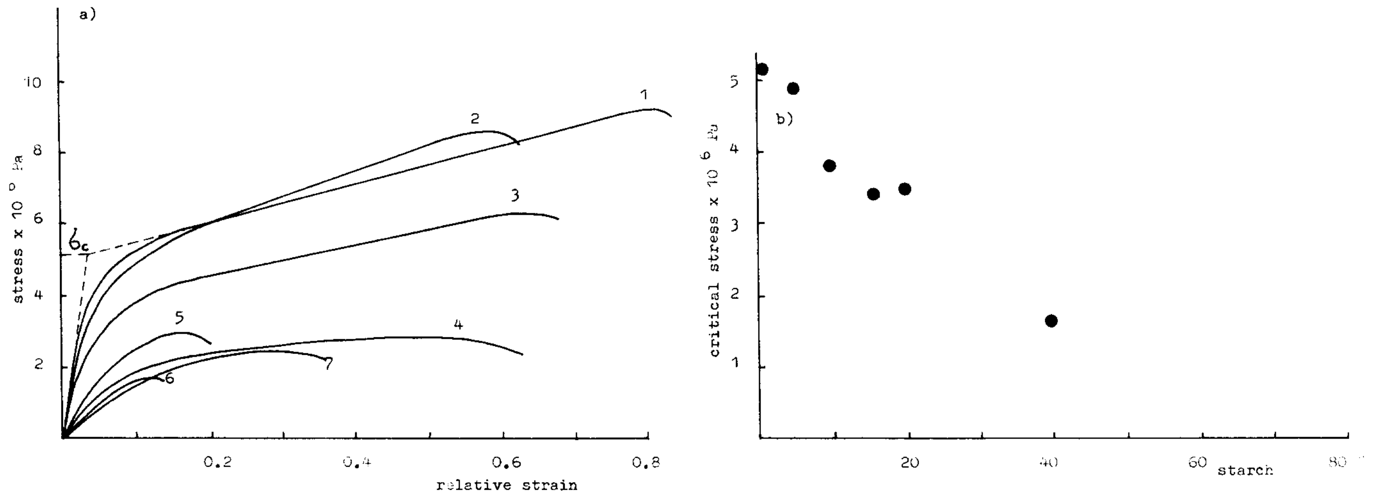

Fig. 2. (a) Stress–strain curves for extrudates in the strain testing mode at various starch contents (%wt on d.b.): 1, 0%; 2, 5%; 3, 10%; 4, 40%; 5, 60%; 6, 80%; 7, 100%. Method of determining σ_c is shown using curve 1 as an example. (b) Critical stress σ_c for extrudates in the strain testing mode versus starch content (%wt on d.b.).

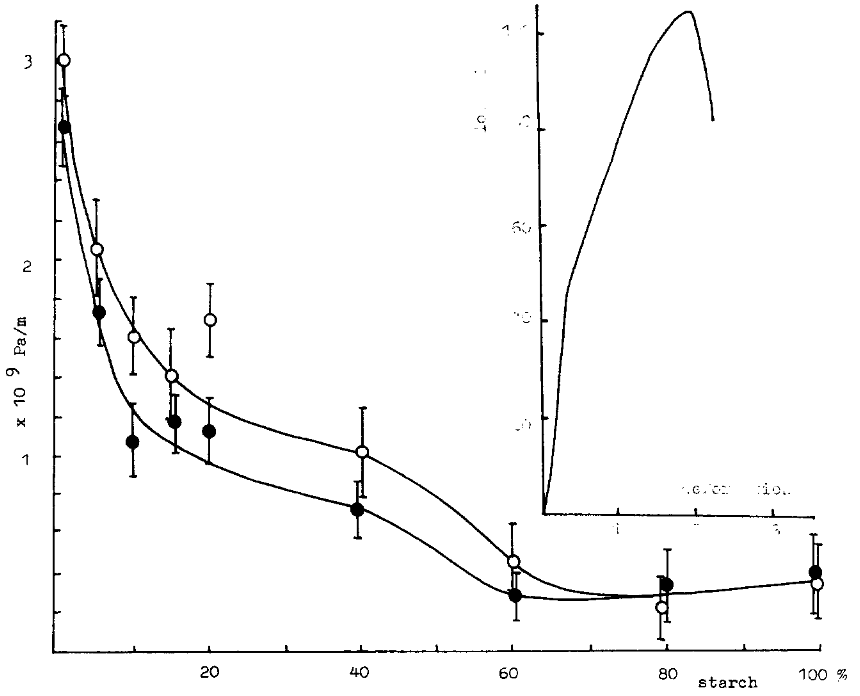

Fig. 3. The slope of the linear region for extrudates from cut testing versus starch content (%wt on d.b.). The knife edge was positioned in the direction relative to the extrudate symmetry axis: O, perpendicular; ●, parallel. Insert: typical cut load-deformation curve (10% starch, 90% soybean protein isolate, on dry weight basis).

The extrudate density versus its composition is given in Fig. 1(b). When *S* increases up to 60%, the density rises and becomes constant at starch constants in the range 60–80%. When the starch content is higher than 80%, the density increases slightly.

Figure 2(a) displays a family of stress–strain curves obtained in extension testing. The curves show two linear regions at *S* less than 60%. The magnitudes of σ_c for these extrudates are given in Fig. 2(b). The values of σ_c falls as the starch content increases. As *S* exceeds 60% it becomes impossible to determine σ_c since, because of sample inhomogeneity and rupture, we cannot obtain the second part of the stress–strain curve, corresponding to the region of rubber-like elasticity for the extrudates. The relative elongations of the starch and protein extrudates versus temperature are represented in Fig. 4. For both curves one can observe two linear regions with a transition area at a temperature of about −10°C.

The failure strain (ε_F), real tensile strength (σ_r) and initial elastic modulus in extension testing mode versus extrudate composition are given in Fig. 5. At extrudate

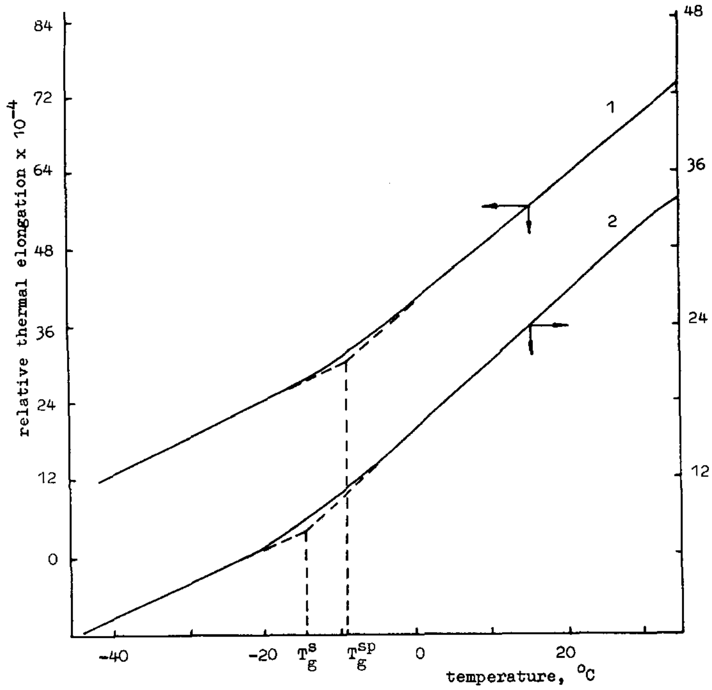

Fig. 4. Relative thermal elongation of the extrudates versus temperature: 1, protein extrudate; 2, starch extrudate. (T_g^s and T_g^{sp} = glass transition temperature for starch and protein extrudates, respectively.

starch contents up to 40%, ε_F, σ_r and the initial elastic modulus show a similar behaviour; that is, they diminish and approach a plateau. The values of σ_r and ε_F drop sharply as S increases from 40% to 60%. In the 60–80% starch content range, σ_r and ε_r and ε_F have minimal values. The initial elastic modulus decreases when $S > 60\%$.

In Fig. 3 the slope of the linear region of the cut stress-deformation versus the extrudate composition is plotted with the knife edge oriented parallel ($M_\parallel$) and perpendicular ($M_|$) to the symmetry axes of the sample. $M_\parallel$ and $M_|$ diminish as the starch content of the extrudates increases, approaching minimal values for values of S in the range 50–80%.

DISCUSSION

The dependence of the extrudates mechanical properties on the extrudates composition (Figs 1, 2(b), 3 and 5), shows several characteristic regions: region 1, $S < 50\%$; region 2, $50\% < S < 80\%$; region 3, $S > 80\%$. The character of the composition dependence for most mechanical properties of the extrudates changes in region 2. A number of facts show that region 2 corresponds to the phase inversion region. It has been shown that extrudates consisting of polysaccharide-protein mixtures have a multiphase structure (Yuryev *et al.*, 1991). Protein extrudate is practically insoluble in water at temperatures below 100°C while maltodextrin and starch extrudates can be dispersed in water at 20 and 100°C, respectively. Extrudates containing maltodextrin-protein or starch-protein mixtures are dispersed at the same temperatures when polysaccharide content exceed respectively about 50% and 70% on a dry weight basis. It is reasonable to suppose that the transition from a continuous protein matrix filled with disperse starch particles to a continuous starch matrix filled with protein particles occurs as the starch content reaches 50–80%.

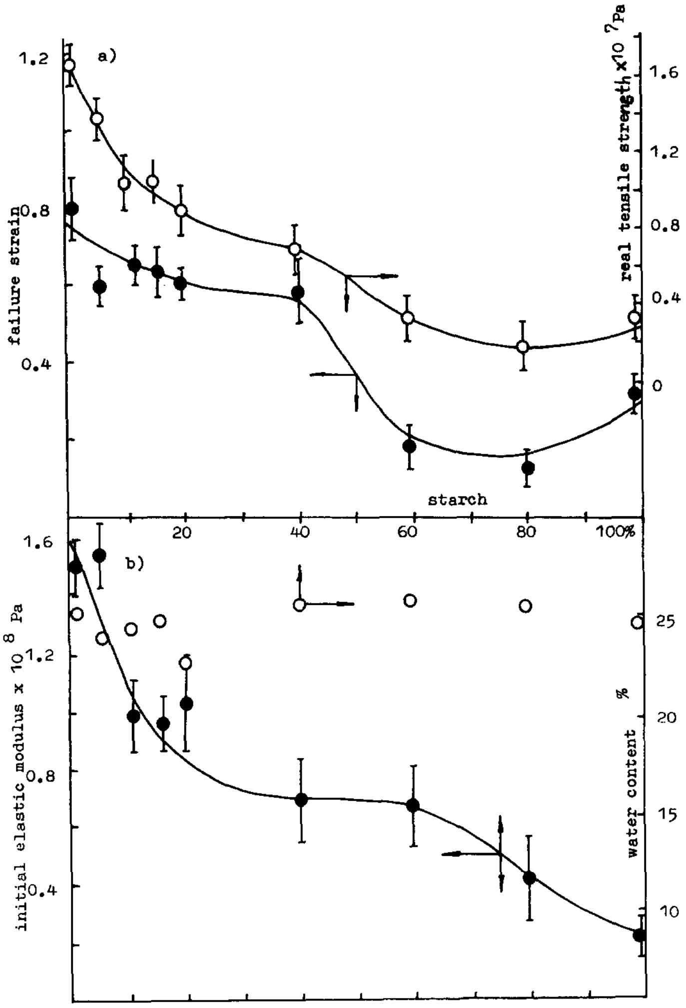

Fig. 5. (a) Failure strain and real tensile strength for extrudates in the extension testing mode versus starch content (%wt on d.b.). (b) Initial elastic modulus and water content (%wt) of the extrudates versus starch content (%wt on d.b.).

Expansion will be determined by elastic recovery of the polymer flow at the nozzle outlet and expansion of the air phase as the pressure drops to atmospheric. The phenomenon of elastic recovery of the polymer melt flow at the extruder nozzle outlet is due first of all to the normal stresses and secondly to the changes in flow boundary conditions at the nozzle outlet (Middleman, 1968). When the mixture of the powder-like biopolymers plasticated by water is extruded, the expansion ratio and density of the extrudates seems to be determined by the properties of three phases: protein, starch and air. In view of (1) the small and constant value of the expansion ratio (5%) of the extrudates at $S < 50\%$ (2) the significant value of the expansion ratio (125%) of the starch extrudates and (3) no apparent air phase in region 1, one can suppose that in this region during the elastic recovery of the extrudates the continuous protein phase prevents change of shape of the starch phase, and the air phase has no effect on the specific volume of the protein and starch phases. If these assumptions are true then the densities of the protein and starch phases should be constant in region 1 and the density of the extrudates should change additively as the starch volume fraction increases. Taking into account the fact that the extrudates represent a two-phase system in region 1, the densities of the protein and starch phase can be designated ρ_1 and ρ_2, respectively. In this case, the dependence of the extrudate density (ρ) on the starch weight fraction p_2, in the extrudates will be given by:

$$\rho = \frac{\rho_1 \rho_2}{\rho_1 + (1 - p_2)(\rho_2 - \rho_1)} \tag{1}$$

We can approximate the experimental dependence of the extrudates density on its composition by this function and determine the magnitude of the phase densities of the extrudates at $S < 60\%$. For this purpose, one can write eqn (1) in the form:

$$Y = A + BX \tag{2}$$

where $Y = 1/\rho$; $X = 1 - p_2$; $A = 1/\rho'_2$; $B = 1/\rho'_1 - 1/\rho'_2$. ρ'_1 and ρ'_2 are the calculated phase densities of the protein and starch extrudates, respectively. Equation (2) describes the experimental dependence of the extrudate density on their composition at $S < 50\%$ with a corresponding coefficient of 0·995. Calculated magnitudes of protein ρ'_1 and starch ρ'_2 phase densities equal 1·193 and 1·435 g/cm^3 (for comparison, see Guy and Horne (1988) and Haine *et al.* (1985)). The calculated value of the protein phase density agreed closely with the experimental value $\rho_1 = 1{\cdot}192$ g/cm^3. The results obtained support the assumption that the protein phase does restrict elastic recovery of the starch phase at $S < 50\%$ and that the air phase does not change the phase densities in the extrudates with starch contents below 50%.

In regions 2 and 3 the density values calculated according to eqn (1) deviate from the experimental values which is accompanied by a sharp rise in the extrudate expansion ratio (Fig. 1).

At the same time, one can observe the appearance of an air phase. The question arises, why does the air phase become apparent only after protein–starch phase inversion? The extrudates leave the nozzle when the temperature reaches about 110°C, part of the extrudate water is in the steam-like state and tends to increase the extrudate volume. One can suppose that under these conditions the protein melt viscosity is higher than the viscosity of the starch melt. As soon as the transition from a protein continuous to starch continuous matrix occurs, the steam at 110°C increases the extrudate volume to form the air phase and reduced extrudate density. Explanation of this fact requires further investigation.

One can determine the contribution of the air phase to the expansion ratio. If the deviation of the calculated density for the starch extrudates ($\rho'_2 = 1{\cdot}435$ g/cm^3) from the experimental data is determined completely by changing the specific extrudate volume at the expense of the air phase, one can estimate that the air phase changes the expansion ratio of the starch extrudate by less than 0·07. In the calculations an isotropic volume change of the extrudates was assumed in view of the spherical form of visible air voids. Thus, the air phase has an insiginficant effect on the extrudate expansion ratio in comparison with the elastic recovery of the biopoloymer flow.

In the course of the transition from one continuous phase to another in region 2, a change in the stress–strain curves occurs (Fig. 2). At $S > 60\%$ the shape of the curve is close to that of the elastic state of a polymer (Askadsky, 1973). At the same time, the stress–strain curve (extension testing mode) shows two linear regions and σ_c may correspond to two physical states of the polymer: (1) glass-like state and (2) rubbery state at the temperature (T_g) (Askadsky, 1973). Figure 4 shows relative elongation of the protein–starch extrudates versus temperature. At temperatures of about −10°C an alteration of the linear thermal expansion (elongation) coefficient of the extrudates is observed. In view of the fact that the glass transition temperature for pastes of gelatinized B-type starch is about −5°C at 27% (w/w) water (Slade & Levine, 1988), one can assume that at −10°C the change in the thermal expansion coefficient of the extrudates corresponds to that of the glassy state. Consequently, at 20°C (the temperature of mechanical tests) the extrudates are in the rubbery state regardless of their composition. At the same time, the appearance of σ_c (Fig. 2) for the extrudates shows that their physical state is close to the glassy state.

In the phase inversion area (Figs 1 and 2) a minimum value of σ_r and ε_F (Fig. 5(a)) is observed. Such behaviour appears to be connected with maximal structure inhomogeneity. In contrast to σ_r and ε_F, the elastic modulus does not show a minimum value in the area of phase inversion (Fig. 5(b)).

Differences between $M_{\parallel}$ and $M_{|}$ characterize the extrudate anisotropy. In view of the experimental error the anisotropy of the extrudates is maximum when the starch content is in the range 10–30%. There is no anisotropy for extrudates having a continuous starch phase.

It was shown recently (Yuryev *et al.*, 1989; Yuryev *et al.*, 1991) that in the region of $5\% < S < 20\%$ the extrudates have marked fibrous structure. In this range of starch contents some conditions should be optimal for the appearance of fibres, namely: (1) a higher viscosity of the continuous protein phase relative to the viscosity of the dispersed starch particles (Vinogradov *et al.*, 1982), and/or (2) optimal quantity of disperse particles per unit melt volume for their effective linear coalescence in the flow direction. Hence, the protein phase not only permits starch fibres to be obtained but also fixes their shape at the nozzle outlet.

Thus, the results indicate that the multiphase nature of the extrudates controls their mechanical properties. The values of most mechanical characteristics of the extrudates change sharply in the phase inversion area. In that area the maximum inhomogeneity of their structures is observed. At starch contents of 10–30%, maximum anisotropy is observed corresponding to fibre formation. The data obtained support the authors' hypothesis for the fibre structure formation process in extrudates obtained from biopolymer mixtures (Tolstoguzov, 1988; Yuryev *et al.*, 1991). Deformation and coalescence of disperse particles in the multiphase biopolymer melt occurs in the course of extrusion. Cooling the melt fixes the extrudates structure.

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