Thermoplastic Extrusion—the Mechanism of the Formation of Extrudate Structure and Properties[1]

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Systems processed by thermoplastic extrusion can be regarded as heterophase polymer melts of incompatible water-plasticized biopolymers. In the process of thermoplastic extrusion, proteins and polysaccharides are melted at high pressure and temperature below the temperature region of their thermal decomposition. Dispersed particles of these systems can be deformed in flow. The mixed-melt anisotropic structure, formed in flow, is fixed by rapid conversion of the melt jet that lets the extruder die from a viscous state to a rubber-like state and then to a glassy state caused by cooling and drying. Incompatibility of proteins and polysaccharides in their water-plasticized melt mixtures impacts on structure formation and texturization during thermoplastic extrusion.

KEY WORDS: Extrusion cooking, extrusion of soybean protein, functions of water, protein denaturation, protein T_g, spinneretless spinning, starch/protein melts, starch/protein/water interactions, thermodynamic incompatibility of biopolymers, thermoplastic extrusion.

The main objective of this paper will be to explain how anisotropic fibrous and lamellar structures of extrudates are formed. The mechanism under discussion is illustrated in Figure 1. This is a general scheme of the processing of two-phase liquid systems into anisotropic materials with fibrous or lamellar structure. This process has been developed recently and is called spinneretless spinning or spinneretless fiber shaping (1–5). With this process two phenomena exist, namely the incompatibility of biopolymers in their mixed aqueous solutions, which gives rise to the formation of water-in-water emulsions, and the presence of emulsion-dispersed particles that deform in flow. A flowing emulsion may acquire an anisotropic structure because of deformation and orientation of liquid-dispersed particles. The shape of liquid filaments can be fixed by converting one or both liquid phases into the solid (gelled or glassy) state. Just like the conventional spinning technique with spinnerets, the spinneretless spinning process makes use of shaping nozzles. The specific feature of the spinneretless spinning process is that each nozzle produces many fibers simultaneously, whereas in spinneret technology each hole yields only a single fiber. In the spinneretless process, the dispersed phase acts as a spinning dope, while the dispersion medium may function as a spinneret and coagulating bath and as a binder for the spun fibers at the same time. The thermoplastic extrusion process can be regarded as a particular version of spinneretless spinning. Food raw materials processed by thermoplastic extrusion are always multicomponent systems containing proteins and polysaccharides. Within the extruder barrel we are dealing with heterophase mixed melts of water-plasticized biopolymers (5). The heterogeneity of extruded systems is due to the immiscibility of biopolymers in a melt. A major contribution to the extrudate structure comes from the deformation and orientation of liquid dispersed particles in flow (1–5). Accordingly, the contents of this paper will cover several subjects related to these assumptions. What is the phenomenon of the incompatibility or limited thermodynamic compatibility of biopolymers? What is spinneretless spinning? We will discuss these questions as well as the causes for which a thermoplastic extrusion process and a wide range of other food technologies can be regarded as versions of spinneretless spinning.

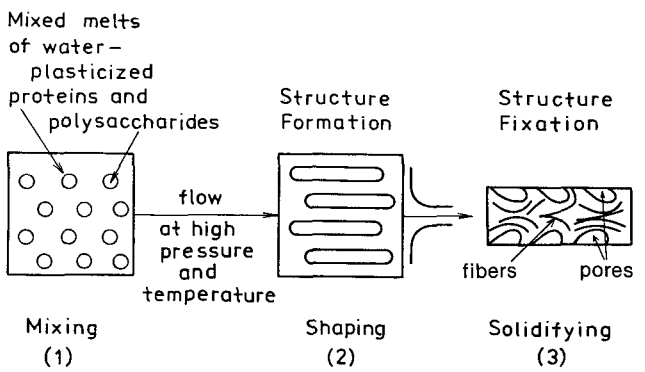

FIG. 1. General scheme of food system processing, including the thermoplastic extrusion process.

Treatment of data will be based on the following assumptions. First, despite the fact that the majority of food systems and processing methods, including thermoplastic extrusion, are of a nonequilibrium nature, our considerations will have a strong thermodynamic component. Thermodynamic approaches can provide valuable information on the possible state and potential behavior of food systems. Thermodynamic approaches are necessary for a deeper understanding of biopolymer behavior in multicomponent systems as well as the kinetic aspects of food processing. Second, in general, proteins and polysaccharides are immiscible in both solutions and melts. Therefore, thermodynamic incompatibility of chemically and structurally dissimilar biopolymers is important, not only because of its role in determining the structure of extrudates but also because it is typical of food systems, which affects the structure and properties of many foods. Finally, the majority of food technologies can be subdivided into three main steps: (i) to produce a multicomponent liquid system of a required composition by mixing of ingredients; (ii) to arrange the structure and shape of this liquid system by its formation; and (iii) to fix the food product structure and shape by its solidification, *e.g.*, by means of heating (cooking), cooling or drying. In the first and second stages, food systems, which are almost always multicomponent and heterophase systems, are usually subjected to shear forces. In the third stage the

[1] Presented at the 20th ISF World Congress and 83rd AOCS Annual Meeting and Expo, May 10–14, 1992, Toronto, Ontario, Canada.

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temperature and pressure may be sharply changed. This means that Figure 1 also represents the general scheme for processing of food systems.

This paper discusses some aspects of the mechanism of the formation of extrudate structure as well as some ideas and experimental results that can be essential to the understanding of the mechanism of thermoplastic extrusion. We will start with the phenomenon of biopolymer incompatibility.

Thermodynamic incompatibility of food macromolecules. Incompatibility of biopolymers in aqueous media means that their sufficiently concentrated solutions can be immiscible. This phenomenon is schematically displayed in Figure 2. This figure also shows a typical phase diagram for a biopolymer$_1$-biopolymer$_2$-water system. The binodal curve separates the regions of single- and two-phase systems. The binodal points do not lie on the phase diagram axes. This reflects the partial co-solubility of biopolymers in the common solvent, water. The region lying under the binodal curve corresponds to single-phase mixtures of biopolymers, while the region lying above the curve represents compositions of two-phase systems. This means that on mixing aqueous solutions of proteins and polysaccharides we may arrive at two different results, namely either a homogeneous stable mixed solution with a low total concentration of different biopolymers (*e.g.*, those whose composition correspond to the line A-B) or a liquid two-phase system. For instance, if point A_1 represents the initial polysaccharide solution and point B_1 is the initial protein solution, their mixture of composition C can be obtained. This latter breaks down into two phases: phase D and phase E, and a water-in-water (W/W) emulsion can be formed. Phases of a W/W emulsion, *e.g.*, E and D, can be separated by a centrifuge. In general, one phase is rich in protein (B_2) whereas the other phase is rich in polysaccharide (A_2). The thin line is the tie-line. It connects the points representing the compositions of the co-existing phases. At the critical point F, the co-existing phases are of the same composition and volume. The phase volume ratio corresponds to the ratio of the tie-line segments EC/CD. The protein concentration (B_2) in phase E is usually higher than that in the initial solution B_1. This means that on phase separation the equilibrium between the phases may set up by means of water transfer. As a result, the protein phase is concentrated ($B_2 > B_1$) and the polysaccharide phase is diluted ($A_2 < A_1$). This is one of the features of W/W emulsions containing biopolymers strongly differing in hydrophilicity and in their ability to self-associate and to form an ordered structure in concentrated solutions. This feature of mixed biopolymer solutions underlies a new method for concentrating protein solutions, which has been given the name of membraneless osmosis (6,7).

Thermodynamic incompatibility of biopolymers has been studied so far for about 200 biopolymer pairs. The main classes of proteins (*i.e.*, albumins, globulins, glutelins and prolamines) as well as the main types of polysaccharides were used in this study. Figure 3 exemplifies several phase diagrams for protein-polysaccharide-water and protein$_1$-protein$_2$-water systems. The main result of this investigation is that biopolymer incompatibility, or more precisely limited compatibility in solutions, is one of the

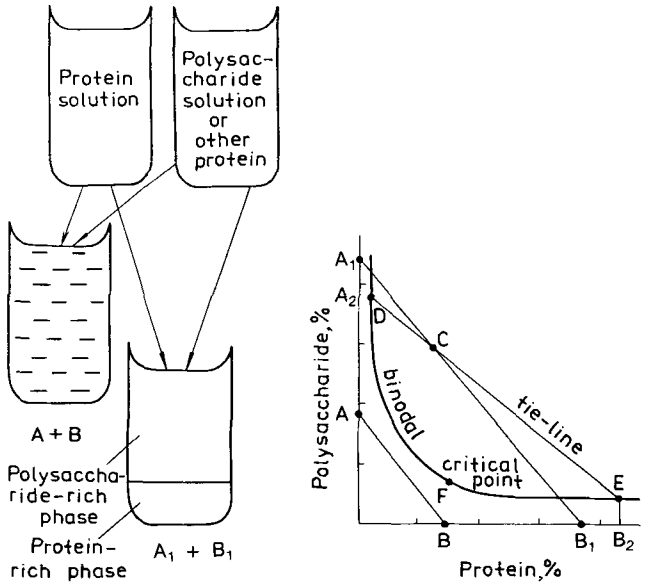

FIG. 2. Schematic representation of the biopolymer incompatibility phenomenon and a typical phase diagram for a biopolymer$_1$-biopolymer$_2$-water system.

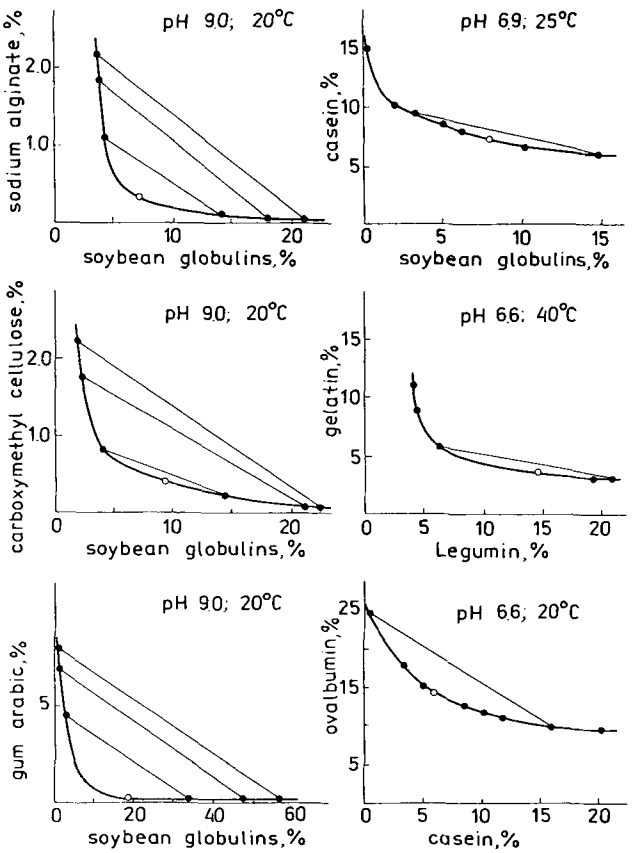

FIG. 3. Phase diagrams for systems: soybean globulins-sodium alginate-water (pH 9.0; 20°C); soybean globulins-carboxymethyl cellulose-water (pH 9.0; 20°C); soybean globulins-gum arabic-water (pH 9.0; 20°C); soybean globulins-casein-water (pH 6.9; 25°C); legumin-gelatin-water (pH 6.6; 0.5M NaCl; 40°C); ovalbumin-casein-water (pH 6.6; 20°C).

most characteristic properties of biopolymer mixtures. Incompatibility is observed in mixed solutions of proteins belonging to different classes within the Osborne classification, in mixed solutions of proteins and polysaccharides, as well as in solutions of structurally unlike polysaccharides. This phenomenon takes place at certain ionic strengths and pH values when the bulk concentration of the biopolymers exceeds 3–4% for mixtures of polysaccharides, or of proteins and polysaccharides, and when it exceeds 12–15% for mixtures of globular proteins. The incompatibility of proteins with polysaccharides usually increases with salt concentration, temperature and polysaccharide molecular weight. The incompatibility increases as the protein molecules are denatured and aggregated. This results from an increased hydrophobic accessible surface and excluded volume of denatured protein molecules compared to those of an initial native protein. Normally, under the conditions for incompatibility, any attractive interactions between dissimilar biopolymers should be inhibited. In view of the unfavorable interactions between segments of dissimilar biopolymers, each macromolecule shows preference for a surrounding of its own type. The interaction of incompatible biopolymers is mainly due to the excluded volume of their molecules. With the investigation of the affinity of biopolymers for each other and for the solvent, water in dilute solutions enables the phase behavior of concentrated mixed biopolymer solutions to be predicted (6–9).

The spinneretless spinning process. Next we will look at the behavior of W/W emulsions in flow. Emulsions of the W/W type are notable for low interfacial tension and for relatively easy deformability of the dispersed particles. The low interfacial tension is presumably the direct consequence of the relatively similar compositions of the phases in W/W emulsions. Their specific feature is the common solvent, water and the significant co-solubility of biopolymers in co-existing phases. Figure 4 shows that in a shear field, spherical dispersed particles of a W/W emulsion may easily deform into liquid filaments. These are not stable. They break down into smaller spherical droplets and may coalesce to form larger drops. As a result, in a flowing emulsion, a dynamic equilibrium may set up between the process of drop deformation, break down and drop coalescence. The shift in equilibrium to the breakdown of liquid filaments leads to the formation of a W/W emulsion with tiny droplets. In contrast, an increase in the stability or lifetime of liquid filaments favors the formation of a fibrous structure in a given system. The shape of liquid filaments and an anisotropic structure of a W/W emulsion can be fixed by gelation of any phase when the gelation time does not exceed the lifetime of liquid filaments. Low interfacial tension and high viscosity of the system phases are contributory factors to the lifetime of liquid filaments. Figure 4 also shows that the degree of asymmetry of dispersed particles increases with the shear rate and as the viscosities of the dispersed phase and of the dispersion medium approach each other. Three main types of products of the spinneretless spinning process are given. Both short and infinite fibers can be produced by deformation, coalescence and gelation of liquid dispersed particles in flow. Coalescence is greatly increased in a concentrated emulsion in a shear field. If the dispersion medium is gelled in flow, gels filled with oriented liquid filaments may be formed. Gels filled with

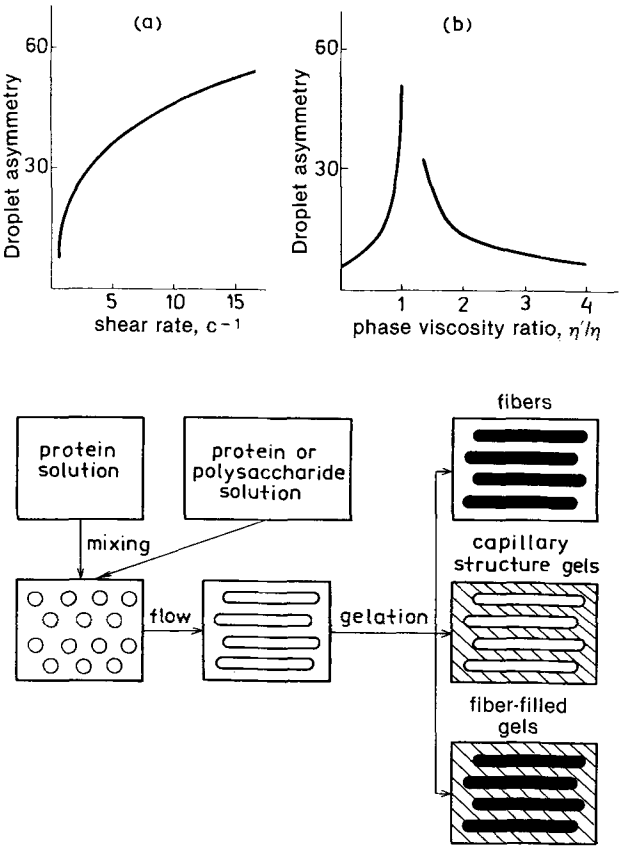

FIG. 4. General scheme of the spinneretless spinning process. The degree of asymmetry (axial ratio, R) of the dispersed particles of W/W emulsions *vs.* (a) shear rate and (b) phase viscosity ratio (the viscosity of the dispersed phase/the viscosity of the dispersion medium).

oriented gel-like fibers are formed by converting the two phases of W/W emulsion into the gelled state in flow. Thus, spinneretless spinning is the process of shaping an anisotropic (fibrous or lamellar) structure of heterophase liquid systems in flow and fixing this structure through rapid solidification (such as a gelation) of one or both phases of a system. Because the phenomena of biopolymer incompatibility and deformation of liquid dispersed particles in a W/W emulsion in flow are of a general nature, both phenomena may play a key role in the formation of structure and properties of many foods (5). Presumably, thermoplastic extrusion is one of these processes.

Thermoplastic extrusion: (i) process features. Figure 5 shows structural changes of a food system during thermoplastic extrusion. Thermoplastic extrusion is the process in which a low-water, powder-like raw material is pressed and heated simultaneously in a shear field, converted into a plastic mass, forced through a shaping die and rapidly hardened by cooling. In view of the low-water content (about 10–35%), the initial systems usually look like either dry or moistened powders. Within the extruder barrel, a mass of solid moistened particles is melted (at temperatures of about 140–200°C and pressure of up to 100 atm) and produce a continuous liquid phase of one biopolymer filled with liquid dispersed particles of the other biopolymer. In the last section of the extruder barrel, the formation of fibrous and lamellar structures has

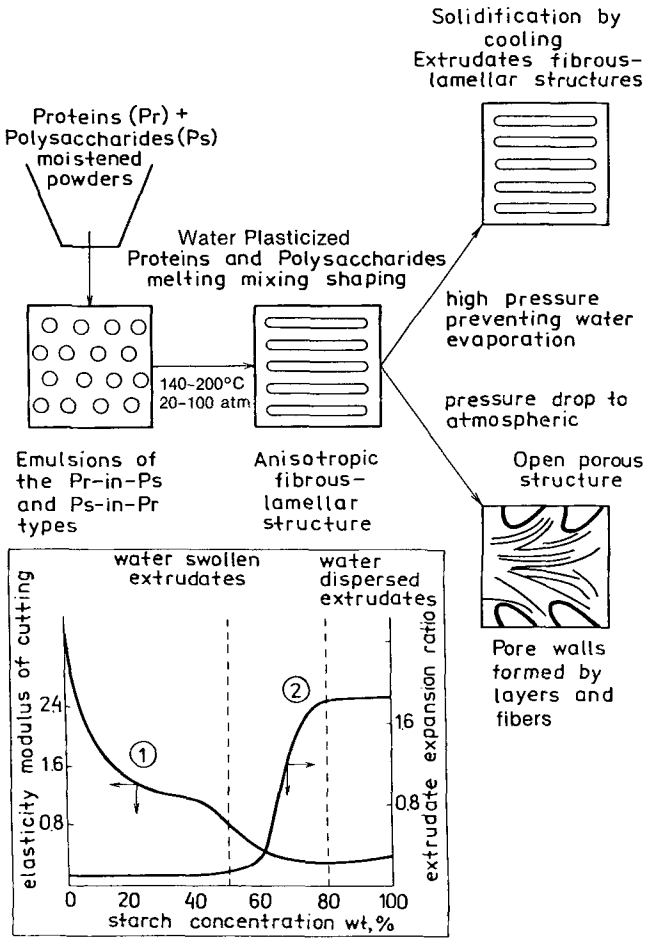

FIG. 5. Food system structural changes during extrusion. Thermoplastic extrusion of soybean protein isolate-starch mixtures: Curve 1—apparent elasticity moduli of extrudates under cutting and Curve 2-elastic expansion of an extruded jet *vs.* starch content. Extrusion conditions: Extruder Brabender DN (L/D 20:1); 4:1 compression screw; 20 rpm; zones: conveying, heating, forming die at 160°C, cooled die (2 × 30 × ×100 mm) at 110°C. Initial water content = 30%.

been observed (10). Figure 5 shows two main versions of the process: (i) a sharp pressure drop at the exit from the extruder die is accompanied with system foaming, and (ii) the extruded mass is forced through a cooled die, which prevents explosive water evaporation and foaming. On leaving the extruder, the liquid system cools and changes to a solid state, either under higher pressure in a cooled die or at atmospheric pressure by flashing off water.

What are the features of thermoplastic extrusion or the extrusion cooking process? The most important feature of this process is specific time-temperature-pressure-shear conditions within the extruder barrel. During thermoplastic extrusion, in the shear field many structural elements of raw materials can be disrupted and destroyed, pressure can rise up to several hundred atmospheres, temperature may reach 140–200°C and the residence time can be from several seconds to a few minutes. Under these conditions, the time required for cooking of any food system ingredients is so strongly reduced that any differences in the cooking time of different raw materials can completely disappear. As a result, this process is universal and really versatile. It is especially suitable for development of new food product formulations. The conditions used in this continuous process are quite sufficient to cook and process highly concentrated food raw materials at a high rate. Furthermore, as mentioned above, three main steps of many food technologies, *i.e.,* mixing of food system components, shaping of a food system and fixing the form and structure of a given food product, can be successively and continuously accomplished within the extruder barrel and at the exit from the extruder die at controllable conditions. Therefore, this is a highly efficient continuous method for rapid cooking, processing, sterilizing and drying a wide variety of food raw materials with reduced food ingredient deterioration and losses. This method is valuable for producing an edible product with good nutritional qualities, storage stability and safety. This process is also energy-efficient. A significant part of the heat required for materials processing arises from the screw mechanical work in highly viscous media. Therefore, this process is especially technologically, nutritionally and economically efficient.

(ii) Formation and fixation of the structure. The mechanism responsible for the formation of an anisotropic fibrous or fibrous-lamellar microstructure of liquid extruded systems and extrudate is important. Normally, starting raw materials for the thermoplastic extrusion of foods contain different proteins and/or polysaccharides, primarily starch. Incompatibility of biopolymers in a solution generally suggests their incompatibility in the absence of a solvent (11), *i.e.,* in a mixed melt of water-plasticized biopolymers. This means that in the thermoplastic extrusion process we are dealing with heterophase mixtures of melted, water-plasticized biopolymers. Therefore, a major contribution to the formation of anisotropic fibrous and lamellar structures of extrudate comes from the deformation and coalescence of dispersed particles in flow. This assumption means that the mechanism of the formation of extrudate structure and properties is a particular version of the spinneretless spinning process. The latter process seems to dictate a fibrous microstructure of pore walls of porous extrudates with an open-celled macrostructure. This assumption has been confirmed by some experimental results (6,9,12,13).

Extrusion of highly purified single-chain globular proteins, such as serum albumin or ovalbumin, results in isotropic extrudates. Under conditions excluding incompatibility effects, extrudates show neither heterogeneity nor fibrous structure.

Relatively small (about 5% wt) additives of proteins (such as gelatin, casein, serum albumin or ovalbumin) or starches to soybean protein isolate provide similar influences on the structure of extrudates, namely the anisotropic fibrous microstructure of extrudates becomes more clearly expressed. Here, the heterogeneity arises from the incompatibility of the added biopolymers with the processed protein. Both thermodynamic and kinetic (diffusion) factors may be the cause of the more pronounced heterogeneity induced by the additives. Kinetic factors seem to be less infuential here because they usually are more dependent on the nature and properties of the additives, such as their relative viscosity and hydrophilicity. However, due to a nonequilibrium nature of the process and its products, kinetic factors are obviously important for the formation properties of extrudates. Figure 5 shows

the effect of starch content on some properties of extrudates produced from mixtures of soybean protein isolate with either partially hydrolyzed starch (dispersible in water) or potato starch. Vegetable proteins, mainly seed storage proteins, and starch are major components of many extruded foods. Therefore, they deserve special attention as model systems. Mixtures of soybean protein isolate with starch have been extruded through a cooled die under conditions preventing explosive water evaporation. Extruded mixtures were moistened to 30% dry-weight basis. Extrusion was performed with a Brabender extruder DN(L/D 20:1) (Duisburg, Germany) at the screw speed of 20 rpm and a 4:1 compression ratio, with temperature zones for conveying, heating and forming die of 160°C, and for the cooled die (channel 2 × 30 × 100 mm) of 100°C.

Figure 5 shows the changes in the elasticity modulus (curve 1) and the swelling behavior of the extrudate as well as the expansion of a viscoelastic jet at the exit of the shaping die (curve 2) *vs.* system composition. The degree of swelling of the extrudate increases with the content of partially hydrolyzed starch in the processed system. When this polysaccharide concentration exceeds 80%, the extrudates become dispersible in hot water. Both this transition from water-swollen extrudates to water-dispersed extrudates and specific changes in the expansion of a viscoelastic jet of the extruded system at the exit of the shaping die correspond to the phase-inversion phenomenon in the mixtures of the melts of water-plasticized proteins and polysaccharides. This experimental result is in agreement with the assumption that biopolymers are incompatible in melts.

The experimental curves (in Fig. 5) can be subdivided into three segments corresponding to the three specific regions of system compositions. In the first region with a starch content of up to 40%, we are dealing with extrudates in which the dispersed phase is formed by starch and the dispersion medium is made up by a protein. In the second region, with 40 to 80% starch content, the system has two continuous phases. In the third region, corresponding to extrudates containing more than 80% starch, the dispersion medium or single continuous phase of the system is made up by the starch. Transition from extrudates with compositions corresponding to the first to those corresponding to the third is likely to reflect the system phase inversion. The effect of protein (or starch) additives on extrudate properties (curve 1 and 2) is more pronounced within the second region of compositions. The moduli of elasticity and tensile strength of fibers produced by spinning two-phase protein-polysaccharide mixed solutions with two continuous phases were linear functions of dispersed-phase volume fraction, *i.e.,* they obey the additivity law (5,6). A similar situation is likely to take place in the intermediate second region of extrudate composition. As the phase volume ratio varies, the properties of extruded systems (curve 2) changes from one virtually constant level to another. The elastic expansion of an extruded jet is determined primarily by the continuous or matrix phase and is independent of the phase volume ratio within the first and third regions. This result is similar to that related to fiber formation by spinneretless spinning. The spinnability of W/W emulsions (*i.e.,* two-phase mixed solutions of proteins and polysaccharides) varies from one level to another at the phase inversion of the sytems studied. It is determined by the spinnability of the dispersion medium and is independent of the phase volume ratio and of the spinneret hole diameter (5).

A significant decrease in the modulus of elasticity of extrudates (curve 1) results from a small amount of starch added to the protein. This is much like the behavior of gels filled with dispersed particles of the other incompatible biopolymer (1,6,8). The thermodynamic incompatibility of biopolymers may be the cause of low adhesion between the phases of a composite extrudate. This means that we are dealing with a complete immiscibility of biopolymers in mixed melts, rather than their limited cosolubility. The latter is typical of mixed solutions of biopolymers. Similar to the most stable emulsions of O/W and W/O types, the extruded systems undergo phase inversion at a volume fraction of dispersed phase exceeding 80–85%. This latter value seems to correspond to the maximum density packing of spherical dispersed particles in a system volume.

Unlike the W/W type of emulsions, extruded systems with a low-water content can be regarded as emulsions of a protein melt in a polysaccharide melt, *i.e.,* "protein-in-polysaccharide" (Pr/Ps), or its converse, "polysaccharide-in-protein" (Ps/Pr) types. Since we are dealing with the incompatibility of biopolymers in mixed solutions and melts, and with some new emulsions of W/W, Pr/Ps and Ps/Pr types, it may be of interest to clarify what kind of surfactants can be used for these emulsions. Surface-active agents for W/W, Pr/Ps and Ps/Pr emulsions containing proteins and polysaccharides could obviously be compounds that consist of the protein and carbohydrate parts covalently linked together. This means that protein-carbohydrate hybrids, which can be formed by Maillard reaction during thermoplastic extrusion, may be able to affect the adhesion between structural protein and polysaccharide elements in composite extrudates. However, two factors may be mainly responsible for the adhesion between the extrudate phases, namely (i) the adsorption of surface-active components, such as lipids and protein-carbohydrate hybrid compounds, and (ii) the diffuse interfacial layer that results from the incomplete separation of highly viscous system phases.

Because of the ever-widening use of thermoplastic extrusion in processing of a large variety of starch-based raw materials and their mixtures, incompatibility in mixtures of different polysaccharides is also important for the structure formation processes in extrudates. It has been shown by Kalichevsky and Ring (14,15) that amylose and amylopectin are limitedly compatible in a mixed solution. This result is in agreement with the findings (6,16,17) that incompatibility is typical of mixed aqueous solutions of structurally unlike polysaccharides. Chinnaswamy and Hanna (18) found that the ratio of amylose and amylopectin in starch determines the jet expansion ratio during thermoplastic extrusion of starches. A 50% amylose starch gave the highest expansion ratio. Presumably, this can be related to the incompatibility of amylose and amylopectin in melts.

(iii) The role of water. Water serves several essential functions in the thermoplastic extrusion process. Its most important functions are to reduce the glass transition temperature, to ensure melting and to reduce the viscosity of an extruding mass. Dry proteins and polysaccharides cannot be melted because their melting temperatures

exceed the temperatures of their thermal decomposition. The glass transition temperature, at which the segmental motion of macromolecular chains is reactivated when a biopolymer is heated, corresponds to a system change from a brittle, solid (glassy) state to a rubber-like or a viscous liquid state. This transition is a kinetic phenomenon that results in a discontinuous change in various physical properties (such as the coefficient of thermal expansion and density) of biopolymers within a specific temperature range characterized by the glass transition temperature.

Typical results of differential scanning microcalorimetric studies on the glass transition and denaturation of a protein are presented in Figure 6. This figure shows the temperature dependence of specific heat capacity of the 11*S* globulin from broad beans *(Vicia faba)* and the effect of water content (varying from 10 to 95%) on its denaturation and glass transition temperatures. The glass transition is accompanied by a remarkable change in specific heat capacity in a relatively wide temperature range, which is dependent on the test conditions. The denaturation temperature is independent of the water content within a wide range of protein concentration until the water level required for primary hydration of the protein is reached. At lower water contents, both the glass transition and denaturation temperatures are increased with decreasing water content. The glass transition temperature of the denatured protein has been determined by repeated heating of the specimen. It coincides with that for the native protein. Water, as an effective plasticizer for biopolymers, is able to lower the glass transition and melting temperatures and the melt viscosity. The glass transition temperature depends on both the flexibility of a biopolymer chain and the interchain interactions. Lowering of the glass transition temperature due to shielding of intra- and interchain interactions, especially between charged and polar groups of biopolymers, may be achieved not only by a low quantity of added water but also by means of some other plasticizers such as glycerol, lipids and salts. It appears that neutral salt ions shield the interaction between charged groups of macro-ions and simultaneously can be competitive for water with macro-ions.

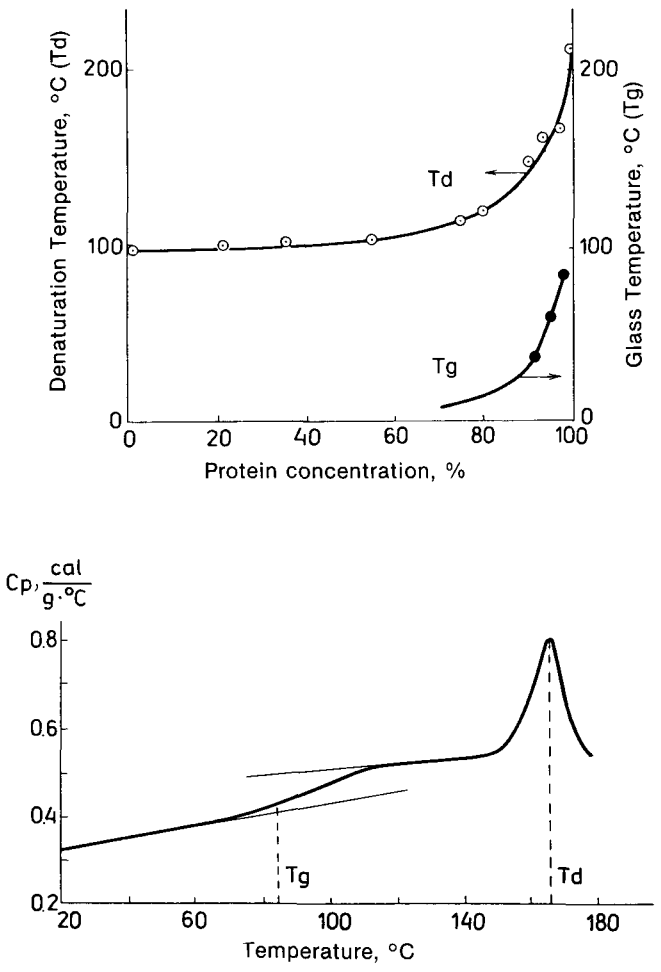

FIG. 6. The glass transition (Tg) and denaturation (Td) temperatures of the 11*S* broad bean globulin.

Because the glass transition temperature reflects the start and development of the motion of disordered structural segments in a protein molecule, it appears to be below the protein denaturation temperature, corresponding to the cooperative melting of structural domains. Proteins may have two (low and upper) glass transition temperatures, corresponding to two (cold and hot) denaturation temperatures, and reflect changes in water-protein interactions at low and high temperatures. The low glass transition temperature and its change as a function of water content for many proteins and carbohydrates have been studied in many laboratories (19,20). The results presented in Figure 6 relate to the upper glass transition temperature.

The incompatibility of biopolymer ingredients of an extrudate may significantly affect its glass transition temperature. The glass transition temperature of a mixture of co-soluble (compatible) biopolymers (within the volume of a system or of its phases) must be between those for the individual biopolymers. Heterophase extruded systems, containing two or more phases formed by thermodynamically incompatible biopolymers, may have two or more glass transition temperatures.

The structure, properties and stability (including shape stability) of an extrudate strongly depend on the shaping and hardening conditions (such as the relationship between the rate of shaping and the relaxation time of extrudate phases, the rate of temperature and pressure drops, the rate of drying and cooling) of an extrudate and its phases, which can widely differ in their glass transition and melting temperatures and their rheological and, in particular, relaxation properties. For instance, it appears that the protein studied in Figure 5 can form a more rigid rubber-like or glassy phase faster than the starch. Therefore, protein addition to an extruded starchy system can depress the extrudate expansion (Fig. 5). In a brittle glassy matrix phase (*e.g.*, protein in the first region of composition in Fig. 5), thermal stresses may lead to microcracking, and cracks may propagate easily along surfaces parallel to the fibers in the anisotropic extrudates. Below the glass transition temperature, extremely low mobility of molecular chains is favored, and products can be stored without structural changes, crystallization and intermacromolecular occurrence of chemical interactions. At a temperature below the glass transition temperature and at a load beyond the elastic limit, large elastic

deformation can occur. Further loading results in increased deformation and fracture of the material. Brittleness (crispness) temperature is likely to correspond to the intersection point of two curves, as shown in Figure 7. The first of those is the temperature dependence of the (elastic limit) critical stress required to produce large deformation of a material at a temperature below the glass transition temperature, and the second is the temperature dependence of the material strength. As the temperature decreases, the strength of a glassy material usually increases but, at the same time, the critical value of stress needed for its large deformation rises more rapidly. The material will obviously fail when the elastic limit exceeds the strength of this material. At a temperature below the glass transition temperature, the large deformation of materials can be achieved only under conditions of very slow loading. This means that the crispness and glass transition temperatures coincide under sufficiently rapid loading conditions and may differ from each other when loading is slow enough. Therefore, this phenomenon might be of interest only when considering storage problems of food products, *e.g.*, shape stability of extrudates. The effect of additives such as water, oil, sugars, salts and glycerol as plasticizers, as well as macromolecular plasticizers (co-soluble with the macromolecular components of a system) on both specific temperature characteristics, *i.e.*, the temperatures of glass transition and brittleness (or two specific water contents) may be of great practical importance.

The minimal temperature at which thermoplastic extrusion proceeds seems to be universal for all globular native and denatured proteins and is about 130–140°C. This temperature range corresponds to the change of water-plasticized food biopolymers from solid to liquid state as well as to the melting temperature of many protein gels, *e.g.*, of soybean globulins. In this connection, calorimetric studies on the conformational stability of globular proteins show the special importance of this temperature range for the conformational stability of proteins, which led to a new concept of hydrophobic interactions (21,22). The difference between specific heat capacities in the native and denatured states (or the heat capacity increment) is specific for a given protein and is proportional to the number of contacts between its nonpolar groups. The temperature dependencies of the specific heat capacity increment drop to zero at about 140°C for all compact globular proteins studied. Therefore, a heat capacity increase may result from the hydration of nonpolar groups of the unfolded protein molecules; the compact protein structure may be stabilized by van der Waals and hydrogen bonding and destabilized by hydration of nonpolar groups. The destabilizing action of hydration is zero at about 140°C and increases when the temperature decreases. Finally, at this temperature (of about 140°C, which is universal for all nonpolar substances and for all globular proteins studied), water does not hydrate the nonpolar side groups of a protein (22). This may be the basis for the compact structure of denatured protein molecules at the extrusion temperatures. The van der Waals interactions between nonpolar side groups may lead to the formation of densely packed structural domains, which act as physical cross-links that increase molecular rigidity, reduce the glass transition temperature and ensure rapid material conversion from liquid to the rubber-like state at cooling under 130–140°C. Extrudates usually are glassy materials. Presumably, the glass transition temperature is about room temperature at the water content of extrudates after extruding and flashing off water.

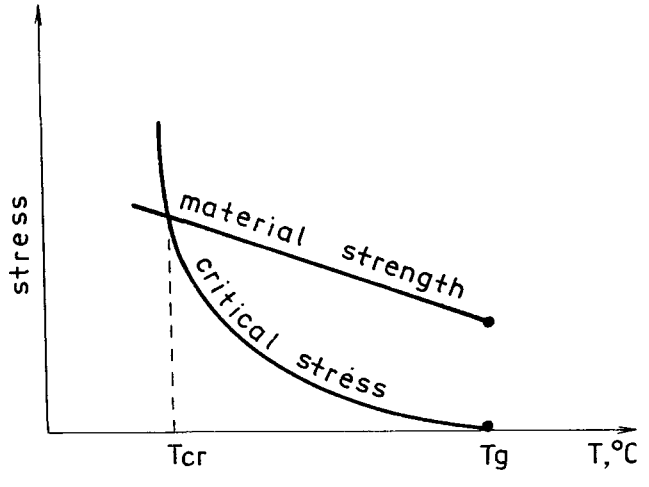

FIG. 7. Schematic presentation of the crispness (Tcr) and glass transition (Tg) temperatures.

Water also acts as a superheated volatile ingredient in an extruded system, ensuring steam distillation of some components, pore formation, system cooling and solidifying. Besides all this, water may act as both a reagent and a product of chemical reactions proceeding during thermoplastic extrusion. The mechanism under consideration may be of interest to develop processes for modified food biopolymers, including duplex compounds or various hybrids by means of thermoplastic extrusion of highly concentrated liquid systems, *i.e.*, to use an extruder as a continuous high-temperature reactor of high efficiency. Because of incompatibility of biopolymers, however, chemical interactions between dissimilar macromolecules are less probable both in solution and in melt.

Thus, water serves several functions in this process. First of all, water acts as a plasticizer. Its plasticizing function is of great importance for both thermoplastic extrusion processes and quality of extruded products. It determines chemical and physical changes in the structure and composition of the processed foods, as well as the conditions of processing and storing of foods.

The physical principles underlying the thermoplastic extrusion process are (i) key functions of water as plasticizer of biopolymers provide melting and viscosity changes in biopolymer melts; (ii) it provides incompatibility of biopolymers in mixed melts; and (iii) it provides the deformation of dispersed particles of heterophase mixed melts.

In conclusion, all man-made food systems may be subdivided into two large groups according to the functions of water, which can act either as a plasticizer and/or a solvent and dispersion medium. Incompatibility of food macromolecular ingredients may occur in both cases, *i.e.*, in all types of food. The general nature of the phenomena of thermodynamic incompatibility of biopolymers and of spinneretless shaping accounts for their important role in dictating the structure and properties of many foods, including those produced by thermoplastic extrusion.

ACKNOWLEDGMENT

The author is indebted to Dr. David Sessa for the invitation to present this paper at the AOCS Annual Meeting and for his help in editing the manuscript.

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[Received May 18, 1992; accepted December 7, 1992]