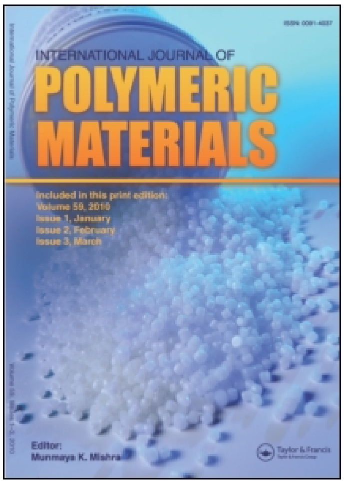

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Fibrillation of the Mixtures of Crystallizable, Amorphous and Poorly Crystalline Polymers†

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The paper gives a brief review of investigations devoted to the formation of ultrathin fibres in the flow of melt of mixtures of thermodynamically incompatible polymers through forming ducts (fibrillation phenomenon). It considers the mechanism of the process, the role of rheological factors in the initiation of fibrillation, and the peculiarities of viscoelastic properties of melts of polymer mixtures for which this phenomenon is clearly observed. The paper shows the possibility to control the fibrillation process by varying the deformation conditions, rheological properties of mixture components, the introduction of plasticizer, surface-active substance, and varying the degree of dispersion of fibre-forming component. It also points out a number of characteristic properties and structural features of ultrathin synthetic fibres in comparison with the fibres formed using ordinary technology.

INTRODUCTION

In recent years the production of ultrathin synthetic fibres (microfibres) is being progressively developed due to the extension of the range of their application in the production of synthetic paper,

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artificial leather, nonwoven materials, reinforced fibres and films, sound-proof and heat-insulated materials, and so on. There are various methods of obtaining microfibres: the bulging of melt sprays or a polymer solution at the spinneret outlet, stretching of fibres with a high drawing ratio, high-spead spinning, grinding of fibres, fibrillation of films, and forming from the dispersions (to be more exact, emulsions) of polymer melts.[1–7] The last method is very interesting and is extensively studied,[8–16] since it produces the fibres with specific properties and structure. The essence of this method is that in the melt flow of the mixture of incompatible polymers (usually in the form of dispersion of a highly crystalline component in the amorphous or slightly crystalline polymer) through forming ducts the polymer of the disperse phase (the fibre-forming polymer) forms in the bulk of the other (matrix) polymer multitude of fibres strictly oriented in the direction of extrusion. These fibres have the diameter from several microns to tenths of micron and can be separated by the extraction of the matrix component with a solvent inert with respect to the fibre-forming polymer. This fibrillation in polymer mixtures is a rather typical process and is observed for many polymer pairs possessing a number of definite properties and extruded at definite conditions.[17]

It should be noted, however, that at present fibrillation is studied insufficiently. There still remain some problems associated with the mechanism of the process, specific properties of mixture melts, necessary and sufficient conditions of realization of the process, structure and properties of microfibres, etc. To create the theory of the processing the polymer mixtures, these and other problems should be solved.

This paper presents a brief review of investigations carried out by the author and her colleagues into fibrillation in the flow of the mixtures of highly crystalline, amorphous, and slightly crystalline polymers. It considers the influence of the nature of matrix polymer, the peculiarities of viscoelastic properties of melts of incompatible polymer mixtures, the possibilities to control the phenomenon by varying the deformation conditions, varying the ratio of viscoelastic properties of mixture components, degree of dispersion, by introduction of plasticizers, surface-active substances (SAS), and the peculiarities of properties and structure of ultrathin synthetic fibres.

EXPERIMENTAL

The objects of investigation were the mixtures of polyoxymethylene (POM) with various (soluble in ethyl alcohol) copolyamides (CPA), POM with ethylene and vinyl acetate copolymer (EVAC), POM with atactic polystyrene (PS), low-pressure polyethylene (LPPE) with CPA, and POM with polycaproamide (PCA). The characteristics of polymers and mixing technique are given in[11, 18–21]. LPPE had intrinsic viscosity in decaline (100°C) of 1.99, which corresponds to the molecular mass of 300 000. The information on viscous properties of melts was obtained using constant-pressure capillary viscometers at temperatures 170–210°C, at shear stresses (τ) 2.7×10^3–3.2×10^5 Pa · s and at shear rate gradients ($\dot{\gamma}$) 1.2–5.0×10^3 s^{-1}. The microscopic structure of mixture extrudates was estimated qualitatively using photomicrographs of cuts and fracture of frozen extrudates and quantitatively using a specially elaborated procedure.[18] Copolyamides were extracted from extrudates by ethyl alcohol, PS and EVAC by benzene, and PCA by μ-crezol. The degree of dispersion of a fibre-forming polymer in a mixture was varied both by using POM powders of various dispersities and by the repeated extrusions of the mixture melt through a viscometer capillary. The variation of the ratio of viscosities of matrix and fibre-forming polymers was realized using various EVAC samples.[18] Triethylene glycol[22] and polyethylene glycols with molecular masses 300, 400, 600, 1000, 2000, and 15 000 in amounts of 0.5, 5, 10, and 30% of POM mass were used as selective plasticizers. Ethylene glycols are effective plasticizers of POM,[23] slightly affecting the properties of CPA melt; for this reason they can be considered as selective when they are added to the POM–CPA mixture. The effect of SAS on fibrillation in the flow was studied using the product of the reaction between ethylene oxide and higher aliphatic alcohols.[24]

The composite and complex threads consisting of ultrathin polyoxymethylene fibres were formed in a laboratory spinning setup[25] and in an experimental industrial arrangement.[21,26] To estimate the peculiarities of fine and supermolecular structure of microfibres was used of differential thermal analysis (DTA),[23,27] infrared spectroscopy and X-ray analysis,[27,28] isometric heating,[29] and electron microscopy.

RESULTS AND DISCUSSION

1. Mechanism of fibrillation

The formation of ultrathin fibres was observed also during the extension of melts of polymer mixtures.[11] This made it possible to put forward a working hypothesis on the mechanism of fibrillation in the flow of the mixture melt through forming ducts, according to which fibres are formed in the flow not behind the capillary outlet but in the entrance zone under the effect of tensile stresses.[12,17] This is a specific feature of such a fibre formation. To confirm the working hypothesis special experiments were carried out on freezing the flow by liquid nitrogen. For this purpose dismountable capillary consisting of semi-cylinders was used.[30] The viscometric tank (loaded with a mixture) and capillary were thermostated, the pre-set pressure was applied, and when the steady-state flow conditions had been established, the tank with the capillary were rapidly immersed in liquid nitrogen. The system was dismounted at room temperature and the samples were extracted from the tank and dismountable capillary. Rapid cooling made it possible to fix the character of the distribution and the shape of POM formation in the bulk of copolyamide in all regions of the flow. Photomicrographs of the longitudinal section of the frozen sample from entrance zone area in convincingly confirm that fibre formation occurs in the entrance zone

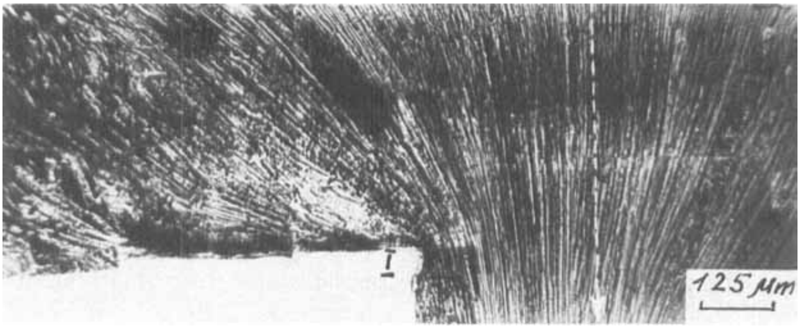

FIGURE 1. Photomicrograph of a longitudinal section of a frozen sample from the capillary entrance zone area at a distance ~200 μm from the flow axis: I—entrance to capillary, the arrow indicates the capillary axis and the direction of the flow.

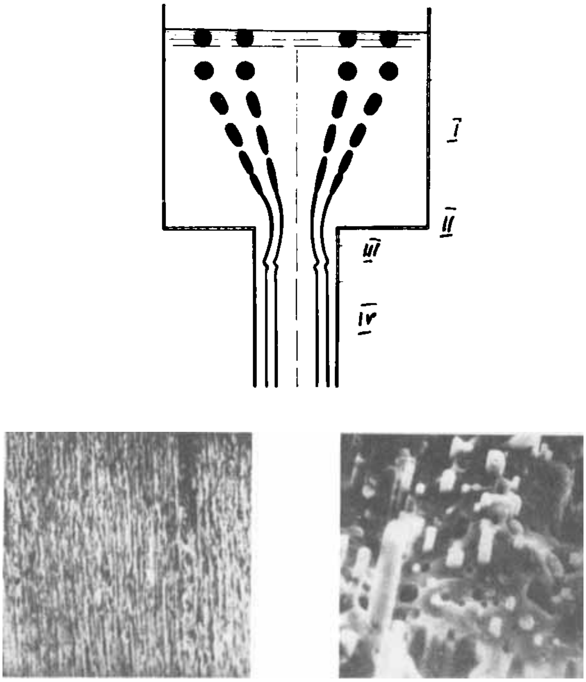

FIGURE 2. Schematic representation of the fibrillation process in the polymer mixture flow in the entrance zone and in the channels of forming ducts; I—zone of tension and fibre formation; II—flow narrowing; III—relaxation zone; and IV—orientation in the shear field.

(Figure 1). The fibrillation process in the flow of polymer mixture melts through the forming ducts is schematically shown in Figure 2. In the zone of the viscometer tank adjoining the capillary entrance the drops of fibre-forming component are stretched and coalesced in the direction of flow. Close to the entrance to the capillary the stream sharply narrows. At a definite distance from the capillary entrance the influence of its walls becomes manifest, leading to the intensive development of shear and retardation of the stream. This is the region of the velocity profile formation, flow development and tensile stresses relaxation. As a result of action of the above-mentioned factors the shrinkage of fibres and the loss of parallelism in their mutual arrangement are observed. Under the effect of shear forces the fibres again acquire ordered mutual arrangement and become oriented along the flow. The coalescence of deformed drops in the longitudinal direction is a prerequisite for the formation of continuous fibres.

The presented idea on the mechanism of the processes in the flow of polymer mixture melts in the entrance zone of the forming duct agrees well with the results of the known papers by Han and Drexler[31–33] and Vinogradov *et al.*,[34–36] where the stress and velocity distributions in the tank zone adjoining the slit channel region are quantitatively investigated for the melts of individual polymers. For example,[35,36] the effects of the growth and relaxation of tensile stresses along the flow axis were investigated for polybutadienes and polyisoprenes using the optical polarization method. It was shown that in the transient region of viscoelastic systems from the tank to the channel, near the channel mouth the maximum of tensile stresses was reached. The position of the point inside the tank corresponding to the maximum is at a distance from the mouth of two-three tenths of the channel width. The channel length where the tensile stresses are relaxed to zero depends on the shear stress.

In the papers by Chin and Han[37–39] are given the results of experimental and theoretical treatment of the deformation in the entrance zone of a cylindrical channel of a viscoelastic drop suspended in a viscoelastic medium. Filming and direct observations proved that strong deformation of the drop in the direction of the flow took place in the entrance zone of the cylindrical channel. Viscoelastic drops were less deformed than the Newtonian drops, and the medium with higher viscosity facilitated stronger deformation of the drops. The deformability of drops is determined by the flow conditions, initial size of the drop, and rheological properties of the disperse phase and dispersion medium. Chin and Han's investigations were carried out using polymer mixtures in solutions: 0.6–4% solutions of polyacrylamide-dispersion medium and 0.6–10% solutions of polyisobutylene-viscoelastic drops. Melts of polymer mixtures are much more complex systems for the experimental and theoretical studies.

When considering the mechanism of fibrillation for polymer mixture melts it is necessary to take into account the possible effects of shear and especially tensile stresses on the phase state of the crystallizable component. It is known[40,41] that shear and tension in certain conditions initiate polymer crystallization, for example, in the form of plastic crystals.[42] This also should facilitate the formation of continuous fibres.

As will be shown below, the process of fibrillation is determined by many factors: the nature of fibre-forming and matrix polymers, mixture composition, shear stress, temperature, geometry of forming ducts, rheological properties of mixed components, the degree of dispersion, and the presence of additives.

2. Peculiarities of viscoelastic properties of polymer mixture melts for which fibrillation is realized

The melts of the mixtures of incompatible polymers are characterized, from the rheological viewpoint, by a number of specific features which are difficult to predict and explain theoretically proceeding from the present notions. The specific viscoelastic properties of melts are as follows: as a rule, sharp difference in viscosity and elasticity of the mixture melt from those of individual components; the presence of extrema in the viscosity vs. composition and elasticity vs. composition curves; the viscosity of the mixture melt can be lower than that of the lowest-viscosity component; clearly non-newtonian nature of the flow; high sensitivity of rheological properties to mixing conditions, mixture composition, shear stress and other deformation parameters, and to the type of the disperse structure of the mixture.[43–54]

These specific features are especially well pronounced in the rheological properties of mixture melts in which microfibres are formed in the flow.

Figures 3–7 give the dependences of viscosity vs. composition for the studied mixtures. Their common features are a nonmonotonic dependence of the melt viscosity on the mixture composition, the presence of extremal points, and sharp dependence of the shape of the curves on the shear stress. None of the known dependences of the type $\eta = f$ (composition) given by Taylor,[55] Takayanagi,[56] Kuleznev,[53] Heitmiller *et al.*,[57] and Horio *et al.*[58] can be used to describe the presented experimental data.

The comparison of the curves in Figures 3–6 shows that though the same POM sample was used everywhere, the properties of mixture melts sharply vary depending on the nature of the second

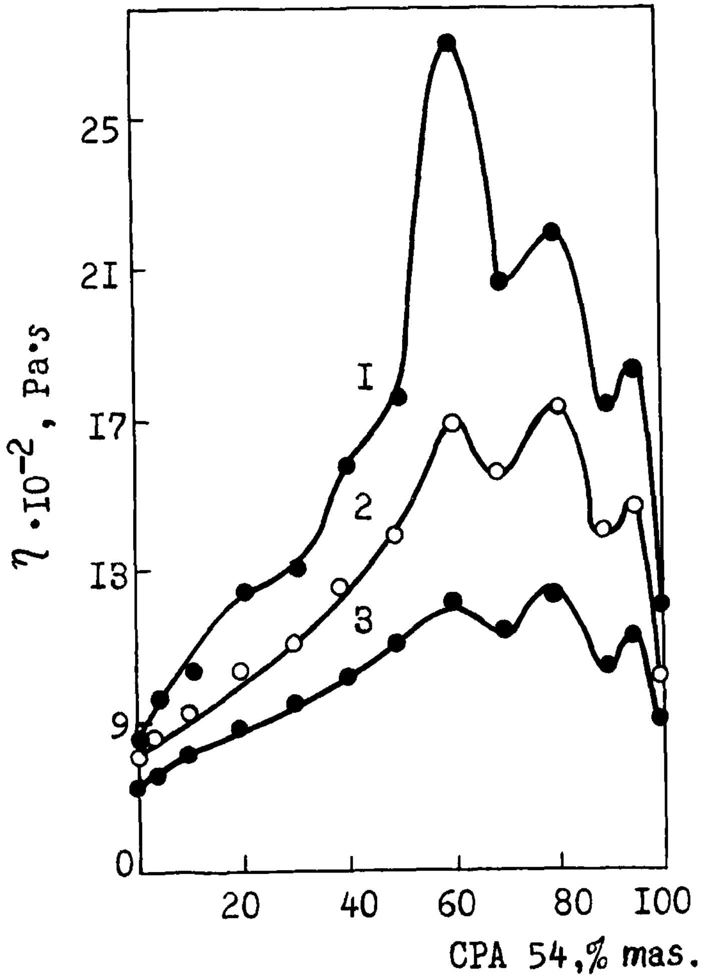

FIGURE 3. Viscosity vs. composition curve for POM–CPA 54 mixture at $\tau\cdot10^{-4}$ Pa: 0.64 (1); 2.26 (2); 4.13 (3).

(matrix) polymer. For the POM–CPA mixture the $\eta = f$ (composition) curves lie above the values of viscosities of the initial components, while for POM–EVAC, POM–PS, and LPPE–CPA mixtures they are, as a rule, below the viscosity of the polymers being mixed. The number and the positions of extrema are also different. The

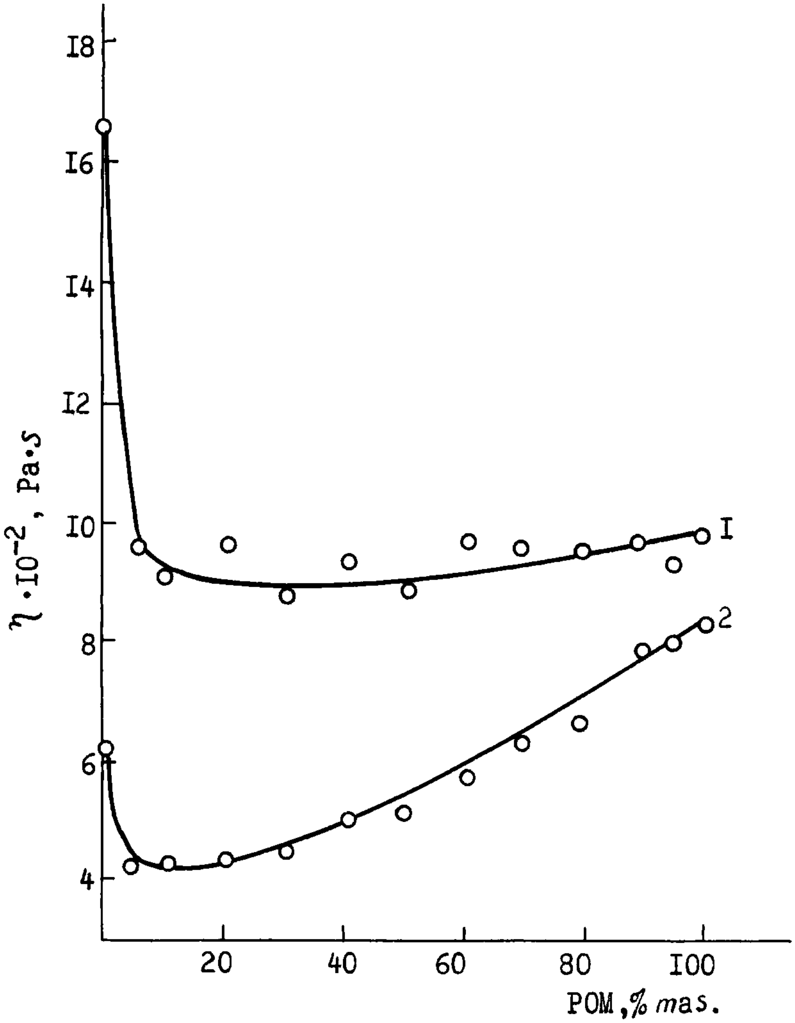

FIGURE 4. Viscosity vs. composition curve for POM–EVAC mixture at $\tau \cdot 10^{-4}$ Pa: 1.6 (1); 5.7 (2).

method of IR spectroscopy was used to demonstrate that for POM–CPA mixtures there is the possibility of the local formation of methylene bridges between CPA macromolecules due to chemical reaction between formaldehyde (released during partial destruction of POM) and NH-group of copolyamide.[27] In[59] it was shown that in

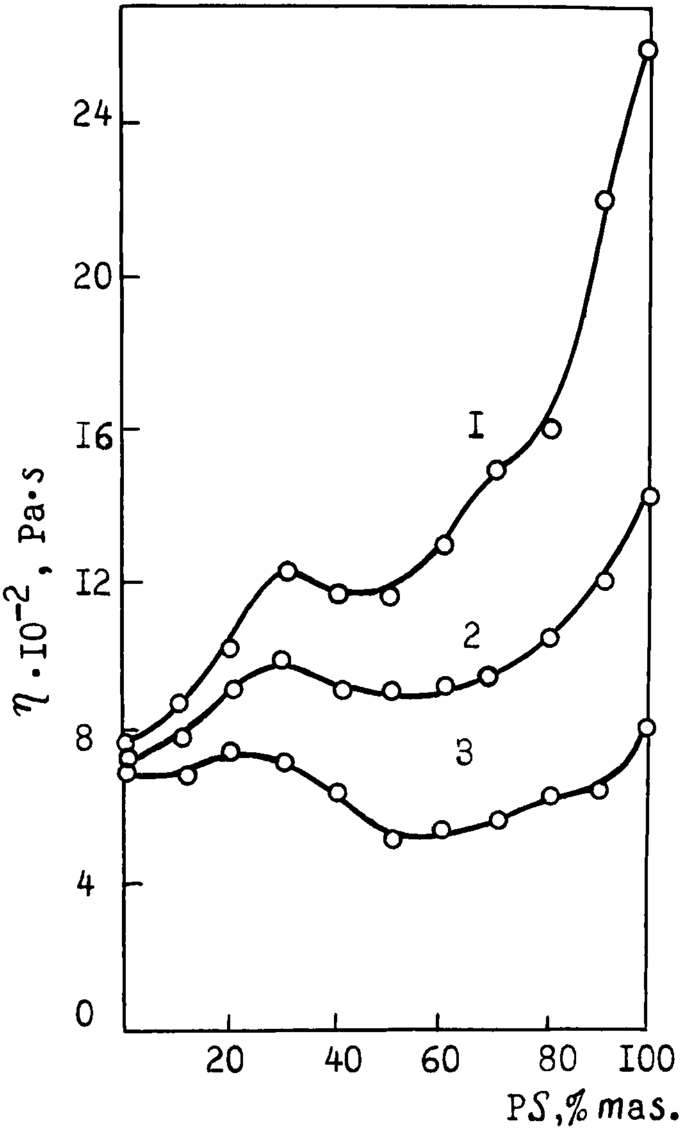

FIGURE 5. Viscosity vs. composition curve for POM–PS mixture at $\tau \cdot 10^{-4}$ Pa: 2.2 (1); 3.3 (2); 5.3 (3).

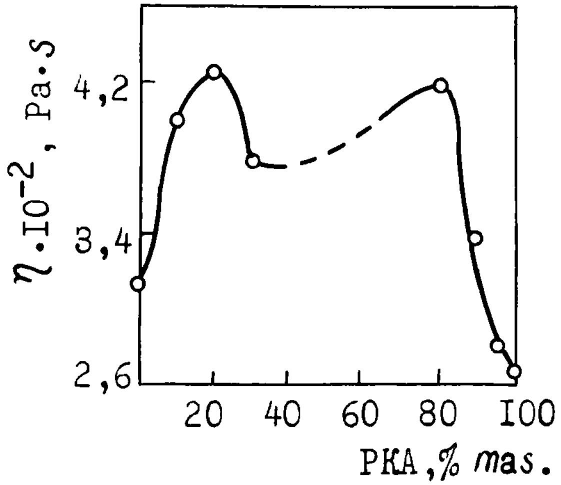

FIGURE 6. Viscosity vs. composition curve for POM–PCA mixture at $\tau = 5.7 \times 10^4$ Pa.

the mixture hydrogen bonds appear between POM and CPA macromolecules. These two causes are apparently responsible for a considerable increase in viscosity of POM–CPA mixture melts. It was established,[60] however, that with intense deformation ($\tau > 6.3 \times 10^4$ Pa · s) the course of the viscosity vs. composition dependence for POM–CPA mixtures sharply varies: the viscosities of melts become lower than those of POM and CPA. Below we shall show that this is due to specific feature of structure formation processes at high τ and also due to possible destruction of hydrogen bonds in these conditions. If in the mixture with POM practically amorphous copolyamides (CPA 548, CPA 54, ultramid 1-C[20] under investigation) are replaced by a crystallizable polyamide (polycaproamide), the resulting viscosity vs. composition curves (Figure 6) are similar to the respective dependences with a copolyamide matrix (see Figure 3). This is an indication of the general nature of the processes in the polyoxymethylene-polyamide mixtures.

Thus, on the basis of the cited experimental data we may conclude that the viscosity vs. composition dependence for polymer mixture melts is in general of a complex nature since it is determined by many factors and processes. For this reason at the

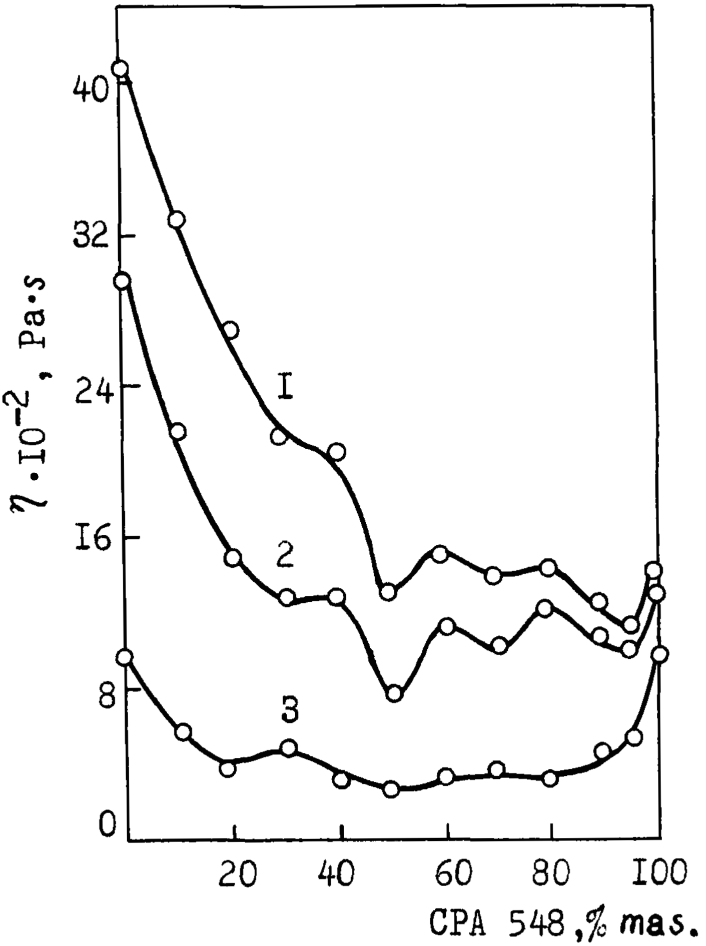

FIGURE 7. Viscosity vs. composition curve for LPPE-CPA 548 mixture at $\tau \cdot 10^{-4}$ Pa: 1.4 (1); 2.2 (2), and 6.0 (3).

moment our knowledge on the properties of polymer systems hardly makes it possible to describe the variation of the viscosity of mixture in the entire composition range by a single equation.

An important specific feature of the melts of mixtures of incompatible polymers is a high degree of swelling (*B*) of the melt spray at the capillary exit and during subsequent annealing, which is an indication of the accumulation of considerably greater deformations and normal stresses of the mixture melt in the flow in comparison with the melts of the components (Figures 8–11). Most of researchers at present consider swelling as a vivid manifestation of high elasticity of polymer systems and their memory of deformation at the channel entrance and inside the channel.[34,61] Han explains the elevated elasticity of mixture melts in comparison with that of individual components by the fact that elastic deformations stored by the disperse phase at the entrance relax in the flow through the

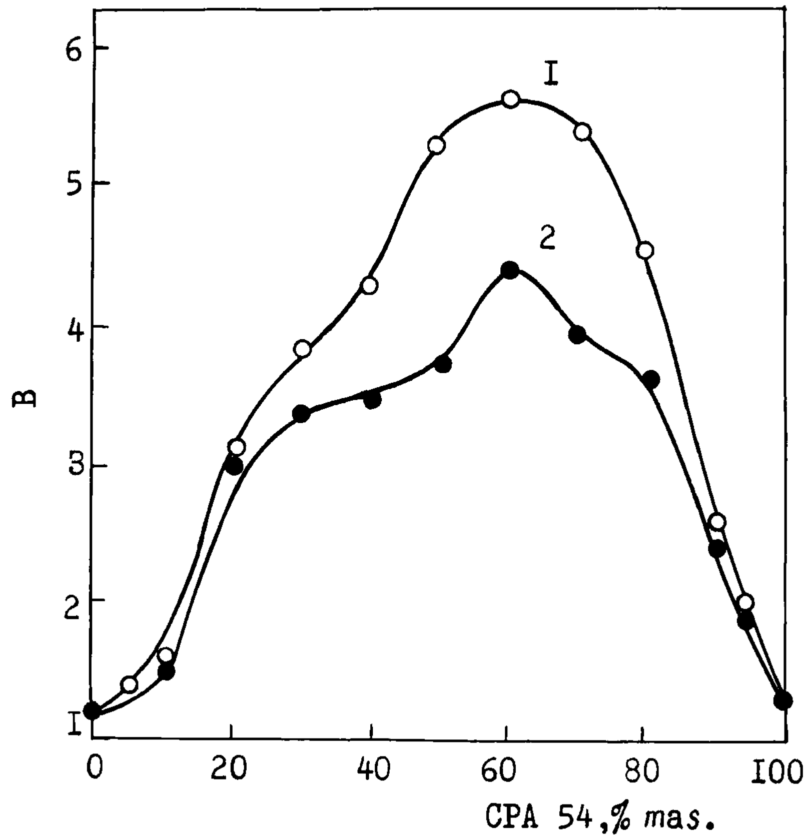

FIGURE 8. Degree of swelling of extrudate as a function of the composition of POM-CPA 54 mixture at $\tau \cdot 10^{-4}$ Pa: 4.1 (1); 1.6 (2).

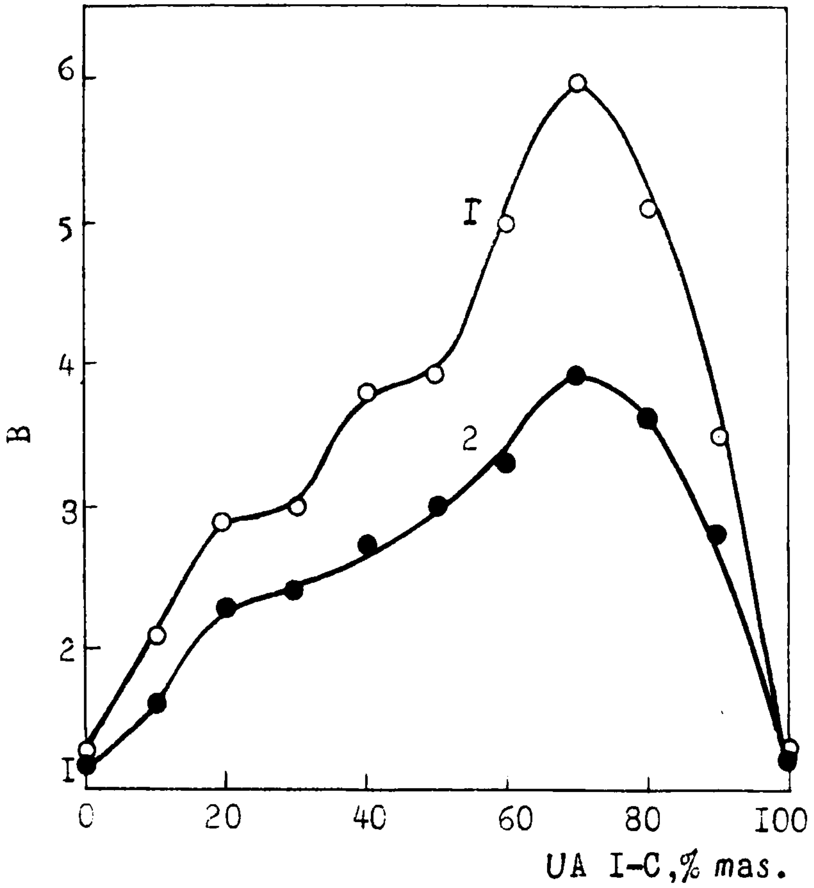

FIGURE 9. Degree of swelling of extrudate as a function of the composition of POM-ultramid I-C at $\tau \cdot 10^{-4}$ Pa: 4.1 (1); 1.6 (2).

capillary to a lesser extent than the deformations of the dispersion medium.[47] In Kuleznev's opinion the increase in elasticity of polymer mixtures is associated with the orientation and deformation along the flow of not only segments of macromolecules in each phase but also of the particles of the disperse phase, which are new relaxing elements characteristic only of a two-phase system.[62] In the case of fibrillation the anisotropy of the disperse phase drops reaches its maximum, and for this reason "*B*" also increases several times

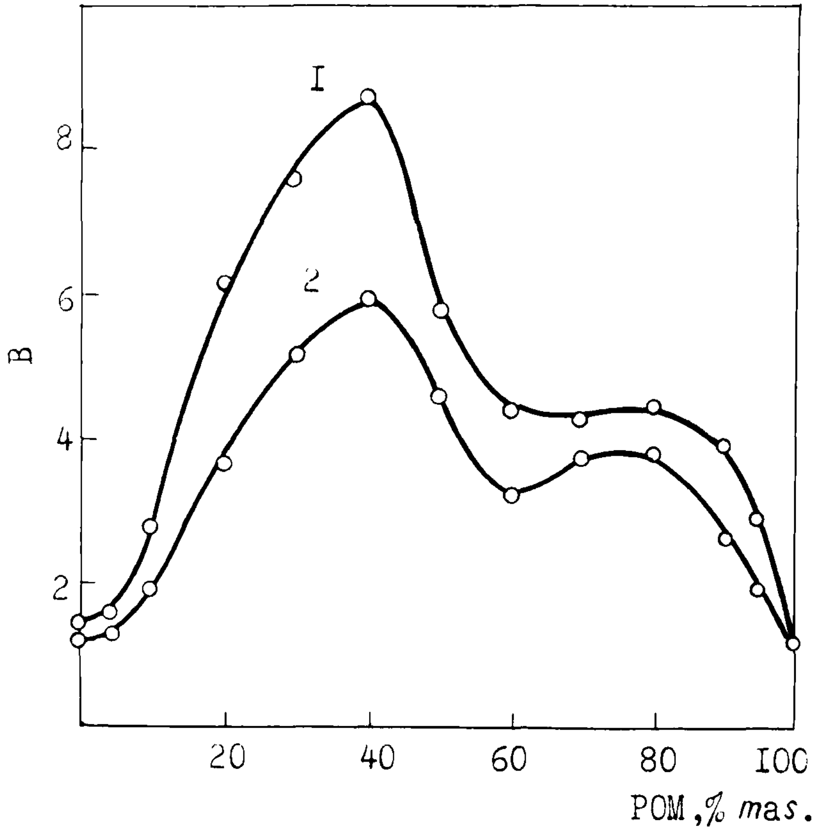

FIGURE 10. Degree of swelling of extrudate as function of the composition of POM–EVAC mixture at $\tau \cdot 10^{-4}$ Pa: 5.7 (1); 1.6 (2).

(Figures 8–11). As will be shown below, "*B*" is always correlated with fibre formation and can serve its indirect measure.

In the number of papers[6,63] swelling is regarded as the relaxation of the shape of deformed drops of the disperse phase, which takes place at the capillary exit under the effect of surface tension. As the result of this relaxation the deformed drops of the disperse phase should return to the spherical shape characterized by the minimum free surface energy.

Many researchers derived various relationships between "*B*" and

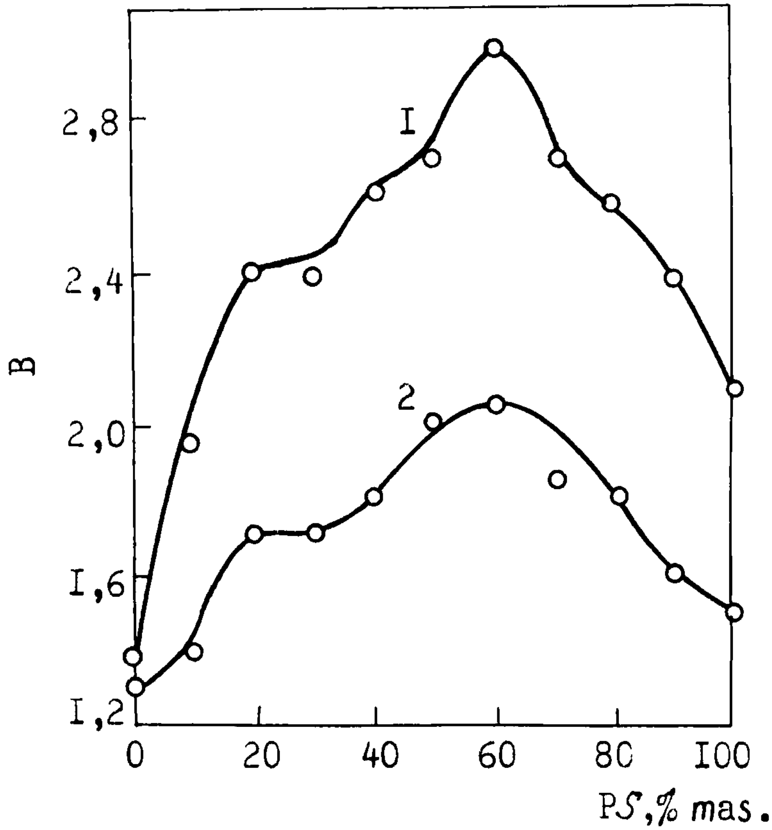

FIGURE 11. Degree of swelling of extrudate as a function of the composition of POM–PS mixture at $\tau \cdot 10^{-4}$ Pa: 6.0 (1); 1.8 (2).

such direct characteristics of high elasticity of polymer melt as highly elastic deformation, difference of normal stresses, shear modulus. The appropriate literature is generalized in.[34,64]

Direct experiments on the analysis of swelling of polymer mixture extrudates containing microfibres showed that disintegration of fibres into drops is the determining process in swelling.[65] Equilibrium swelling accompanied by the disintegration of all microfibres occurs at temperatures close to the melting point of the disperse phase polymer. For example, microscopic observations of the longitudinal section of the extrudate of a POM–CPA mixture during gradual increase of temperature showed that up to 150°C there are no visible changes in POM fibres. At 155° the disintegration of the finest microfibres was observed. In the temperature interval from 150 to 160° the share of disintegrated fibres reached 15%, and the average diameter of formed particles ($\bar{d}$) was the same as that of fibrilles in extrudate. At 165°C the share of non-disintegrated fibres amounted to 8%, some of them showing the tendency to division. These were, as a rule, the most coarse fibres. The complete disintegration of fibres into drops was observed at 170°C—instantaneously in the cut and taking 3 min, in extrudate. The disintegration was accompanied by a sharp contraction of the section or extrudate.

Thus, these and other factors (e.g., increase in "B" when SAS is introduced into the mixture) testify to the consideration of swelling as the relaxation of deformations and stresses stored during the formation of microfibres. Elasticity of dispersion medium makes a considerably less contribution.

A characteristic feature of the melts of mixture of incompatible polymers is the increase in activation energy (E) with increasing τ in a definite narrow temperature range. For example, for POM–CPA mixtures in the τ range $(0.5–31.63) \times 10^5$ Pa, E increases from 79.8 to 218.4 kJ/mol. This phenomenon has analogy with concentrated polymer solutions in "poor" solvents[66] and is associated with anisometric nature of particles in the disperse phase, with orientation and reinforcement (and at large τ also with a partial distruction of its structural elements, e.g., fibres) in the flow.

3. Microstructure of extrudates of polymer mixtures

It is known[47,67] that when the melt of the mixture of two incompatible polymers flows through a forming duct, two types of dispersions can be formed: stratification or droplet-fibre formation. The first type is a lamellar flow in which the two components form continuous phases with a continuous interface. The second type is the flow in which one of the components exists as a dispersed phase (droplets, fibres) in the other component forming a continuous phase. For commensurable component concentrations the resulting structure is of the form of interlaced networks. Eventually this type of dispersion also produces droplets, but in this case many "composite" droplets are formed (droplet inside drop). The type of dispersion itself is stable with respect to shear. Even when the flow becomes turbulent, the strata tend to follow vortex motion without destruction into droplets. Hence Van Oene[67] attributes the fibre formation of one polymer in the bulk of the other to the second type of disperse systems.

Van Oene theoretically analysed the mechanism of structure formation processes in the melt of the mixture of two incompatible viscoelastic liquids from the morphological point of view. He formulated the criterion of the dispersion type. The parameters responsible for the dispersion type are the dimension of particles, the composition, interfacial tension and the difference in visco-elastic properties of the two phases. For the dynamic interfacial tension ($\gamma_{\alpha\beta}$) of dispersion (droplets of polymer α in the matrix of polymer β or droplets β in matrix α) the following relations were derived:

$$\gamma_{\alpha\beta} = \gamma^0_{\alpha\beta} + \tfrac{1}{6} a[(T_{\langle ZZ\rangle} - T_{\langle\theta\theta\rangle})_\alpha - (T_{\langle ZZ\rangle} - T_{\langle\theta\theta\rangle})_\beta]$$

$$\gamma_{\beta\alpha} = \gamma^0_{\alpha\beta} - \tfrac{1}{6} b[(T_{\langle ZZ\rangle} - T_{\langle\theta\theta\rangle})_\alpha - (T_{\langle ZZ\rangle} - T_{\langle\theta\theta\rangle})_\beta]$$

where $\gamma^0_{\alpha\beta}$ is the static interfacial tension, "*a*", "*b*" are the dimensions of droplets, and in the brackets are the differences of normal stresses.

It follows from these equations that the phase with higher elasticity will always form droplets in the phase with lower elasticity. Phase β which has lower difference of normal stresses will stratify on phase α. Formation of droplets of phase β in α is possible only for submicron initial dimensions of particles.

In the studied polymer mixtures we observed all described types of structures. Polyoxymethylene (or LPPE) formed ultrathin fibres in the mixture with the second polymer content $\geqslant 50\%$ (Figures 1 and 2). Then according to the Van Oene theory in complementary mixtures the matrix component (CPA, PA, PS, or EVAC) should stratify in the phase of POM or LPPE. However, we observed stratification only for the POM:PCA mixture with component ratio 80:20 (Figure 12). Other polymers (PS, EVAC, and CPA), according to photomicrographs, are dispersed in the form of rough formations in POM. It is known that the lamellar (as well as any other) structure is stable only in the flow and is retained behind the

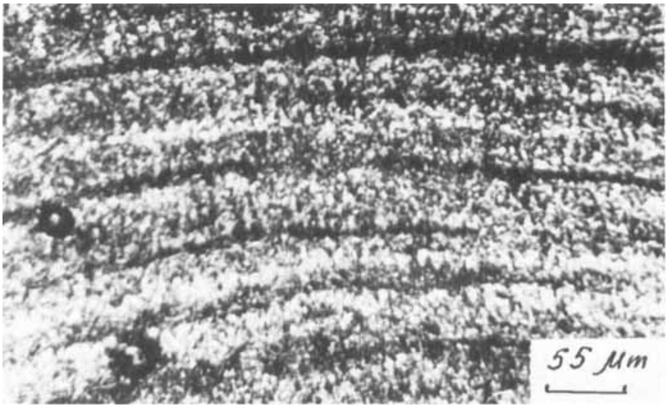

FIGURE 12. Photomicrograph of the cross section of the extrudate of PCA/POM 20:80 mixture. Dark regions—PCA, bright regions—POM.

capillary exit only at rapid cooling or polymer crystallization. We were extruding the studied mixtures into atmosphere at room temperature. Probably this was why we observed (on the photomicrographs of cuts) the stratification of PCA as a polymer crystallizing behind the capillary exit.

It should be noted that in general the processes of structure formation in mixture extrudates proceed nonuniformly-along with the predominent type of structure there are also some others. For example, in the conditions corresponding to the formation of ultrathin fibres the extrudate may contain continuous microfibres, particles (often of micron and submicron dimensions), short fibres, and rough and thin films (as stratification elements). To achieve the predominant formation of microfibres in the flow of polymer mixture melts it is necessary to establish the relationship of this phenomenon with deformation conditions, the properties of polymers being mixed, the degree of dispersion, the presence of a plasticizer and surface-active substances.

4. Effect of viscosity of mixture components on fibrillation

Using POM–EVAC mixtures, we studied the influence of the ratio of viscosities of melt components ($\eta_{\mathrm{POM}}/\eta_{\mathrm{EVAC}}$) on the processes of fibre formation in extrudates.[18] The indicated ratio was within the limits from 0.35 to 27.7 and was varied using POM of various molecular mass (Table I) and using EVAC of varying melt viscosity (Table II). It follows from the obtained results that ultrathin fibres distributed in the bulk of EVAC are the sole type of structure when the viscosity ratio of components is close to unity. The elastic properties of POM and EVAC melts, according to swelling of the extrudates, are the same. If $\eta_{\mathrm{POM}}/\eta_{\mathrm{EVAC}}$ greatly exceeds unity, the extrudate contains short fibres, high-dispersity powder, and defective fibres consisting of the multitude of incompletely coalesced POM particles (Figure 13). The content of such fibres amounts to ~50% at $\eta_{\mathrm{POM}}/\eta_{\mathrm{EVAC}} = 4.1$.

If the ratio of viscosity of fibre-forming polymer melt to the viscosity of matrix polymer exceeds 10 (Table II), the extrudate contains POM in the form of particles of initial size ($\bar{d} = 53\ \mu\mathrm{m}$). If $\eta_{\mathrm{POM}}/\eta_{\mathrm{EVAC}}$ is lower than 1, films are formed along with the fibres (Tables I and II).

The degrees of extrudate swelling for the blends are several times higher than that of POM and EVAC. The analysis of the obtained results revealed that fibrillation correlates with swelling: the thinner the fibres and the large is their number, the higher is degree of swelling. The maximum swelling was observed for extrudates containing only microfibres (Tables I and II). The presence of films suppresses "*B*" more than does the presence of short fibres.

As early as 1934 Taylor[55] showed that the behaviour of newtonian droplets in the newtonian liquid medium during deformation substantially depends on the ratio of viscosities of phases. According to the theory of hydrodynamic stability of viscous droplets,[68] the deformability of a newtonian viscous droplet is determined by two parameters: the ratio (λ) of the viscosity of emulsified liquid to the viscosity of the medium and by the ratio (K) of interfacial tension (γ) to the product of the shear stress by the particle's radius (a): $K = \gamma/(\tau \cdot a)$.

The typical realizable shear stresses in polymer melts are from 10^4 to 10^5 Pa and $\gamma = 5 \times 10^{-3}$ N/m. Then for submicron droplets value of $K \gg 1$, which means that surface phenomena will play a substantial role in deformation. For the droplets larger than a micron the determining factor will be the viscosity ratio of the melts of phases. The results of our research are in good qualitative agreement with the Cox theory.[68] For example, POM and EVAC

TABLE I

Effect of the ratio η_{POM}/η_{EVAC} on distribution characteristics of POM microfibres in blend extrudate[a]

N	η_{POM}, Pa · s	$\frac{\eta_{POM}}{\eta_{EVAC}}$	η of mixture, Pa · s	B	Mean diameter $\bar{d}$ of fibres, μm	Distribution, dispersion δ^2, μm^2	Roat-mean-square deviation δ, μm	Total number of fibres in extrudate by $\bar{d}$ calculated	Remarks
1	280	0.35	380	5.9	5.3	6.48	2.54	6150	Extrudate contains 17% by mass of films, no powder present
2	720	0.91	430	6.8	4.2	3.42	1.85	13 200	100% of continuous-length fibres in extrudate
3	830	1.05	440	6.1	5.5	12.87[b]	3.59	6800	100% of continuous-length fibres in extrudate
4	1320	1.67	510	5.8	6.2	12.60	3.55	4300	Extrudate contains 20% by mass of films, no powder present
5	3270	4.14	560	4.7	7.3	34.08	5.84	4400	About 50% by mass of imperfect fibres, 1.5% by mass of films

[a] POM was mixed with EVAC with melt viscosity 790 pa · s ($t = 190°C$, $\tau = 5.7 \times 10^4$ Pa).

[b] The distribution dispersion δ^2 for the third sample of POM was greater than that for the second sample since the mean diameter of the initial powder of POM sample 3 was 53 μm and for POM sample 2 it was 36 μm.

TABLE II

Effect of ratio η_{POM}/η_{EVAC} on the rheological properties of molten blends and on the characteristics of the distribution of POM microfibres in extrudates

N	η_{EVAC}, Pa · s	$\frac{\eta_{POM}}{\eta_{EVAC}}$	η[a] of blend, Pa · s	B[a] of blend extrudate	$\bar{d}$, μm	δ^2, μm^2	δ, μm	Total number of fibres in extrudate	Remarks
1	1270	0.65	870	3.4	6.9	14.04	3.34	3980	11% by mass of films
2	980	0.85	690	4.0	4.9	7.2	2.68	6850	22% by mass of films
3.	790	1.05	440	6.1	5.5	12.87	3.59	6800	No films
4	630	1.32	330	6.3	4.8	7.02	2.65	10 270	No films
5[b]	96	8.64	92	4.9	8.5	20.34	4.51	—	Short fibres, 24.8% by mass; long fibres, 75.1% by mass; particles with $\bar{d} = 5.0$ μm 0.1%
6[b]	77	10.77	77	4.6	10.2	21.60	4.65	—	Short fibres, 52.3% by mass; long fibres, 47.1% by mass; particles with $\bar{d} = 5.0$ μm, 0.6%
7	300	27.7	34	2.5	Extrudate contains 95% by mass of the powder with diameter of 53 μm, the rest being rough fibres				

[a] At temperature of 190°C and $\tau = 5.7 \times 10^4$ Pa; POM with $\eta = 830$ Pa · s was used for mixing.

[b] The data for long fibres, number fraction is to 38.5% for EVAC-15 and to 11% for EVAC-19.8.

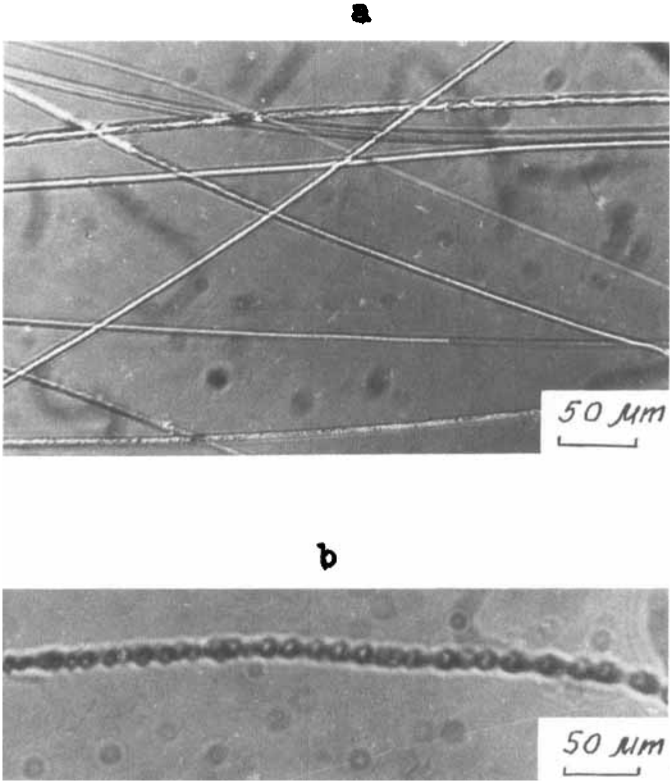

FIGURE 13. Photomicrographs of ordinary POM microfibres (a) and defective ones (b).

have similar degrees of swelling and hence, their melts have similar elasticities. The degree of dispersion of POM in EVAC is such that the dimensions of particles (fibres) of the disperse phase exceed a micron. As a result, it may be presumed that the main factor that governs structure-formation must be the ratio of the melt viscosities of the components. Then according to the Cox theory for large λ the deformation of the drop in the flow will be insignificant, that is fibre formation should be absent, that is just observed in experiment (Table II). Fibre formation is the most clearly pronounced at the melt viscosity ratio close to unity.

Van Oene has noted that the transition from a droplet to a fibre in the polyethylene-polystyrene blend was observed when the viscosities of the disperse phase and dispersion medium were equal, that is when the phases differ little hydrodynamically.[67] Starita[69] has found qualitatively, using polyethylene-polystyrene blends, that the less is the difference in viscosities and elasticities of blend components, the finer dispersion is achieved. The same conclusions have been made by Kuleznev and coworkers[70] and Porter *et al.*[71] But the quantitative estimation of fibre formation during the flow of polymer blends depending on the ratio of the viscosities of the molten components was made for the first time and reported by the author and her colleagues.[18]

5. Effect of shear stress

Shear stress at which extrusion of blends occurs is an important factor determining fibrillation during the flow of the molten polymer blends. There are optimal shear stresses for which the greatest amount of ultrathin fibres are formed and the formations of other types of the structure are absent.

We have carried out the quantitative analysis of fibre formation in extrudates of POM–EVAC blend at $\tau = 5.7 \times 10^4$ Pa and 5.3×10^4 Pa. At the indicated values of τ, the ratio η_{POM}/η_{EVAC} is near unity. The results show (Table III) that even such a slight variation of the shear stress (towards lower values) leads to an increase in the average diameter of fibres, the formation of films, and to a decrease of the total number of fibres (by a factor of 1, 8).

TABLE III

Effect of shear stress on the characteristics of POM microfibres

$\tau \cdot 10^{-4}$ Pa	$\frac{\eta_{POM}}{\eta_{EVAC}}$	$\bar{d}$, μm	Total number of fibres in extrudate	Remarks
5.7	1.05	5.5	6800	No films, no powder
5.3	1.0	6.9	3860	Films 4.3% by mass, no powder

For large $\tau(\geqslant 10^5$ Pa) the nonuniformity of the extrudate microstructure in the section increases. It begins at the entrance due to the nonuniformity of the tension field. Tension is maximum in the inlet funnels,[35–39] and correspondingly the degree of dispersion is maximum at the centre. With increasing distance from the inlet funnels the diameter of the formed fibres grows. When the melt enters the channel of a forming duct, tensile stresses start to relax and the velocity profile is formed. The radial nonuniformity of the shear stress field also contributes to the nonuniformity of microstructure in the extrudate section.

A vivid manifestation of such a nonuniformity is the formation in the wall region of a fibrous continuous-length jacket (skin) filled with ultrathin fibres. (Figure 14). Experiments showed that this structure was observed when the ratio of viscosities of the disperse phase polymer melt and of the dispersion medium polymer were less than unity. In this case the appearance of a skin can be associated with the known radial migration of a low-viscosity polymer to the channel walls in the polymer blend melt flow, as a result of which high-viscosity melt is capsulated by low-viscosity melt.[72,73]

Other conditions being equal, structure formation processes considerably depend on the ratio of the capillary length to its diameter

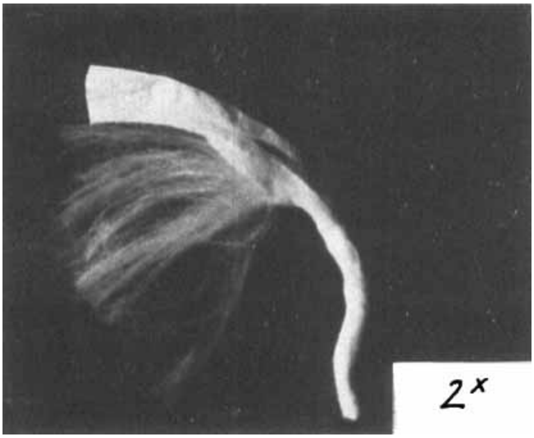

FIGURE 14. Fibrous jacket (skin) filled with ultrathin POM fibres.

(*L*/*D*). For example, for $L/D \geqslant 20$ and $\tau > 2 \times 10^5$ Pa, POM forms in the extrudate not simply an outer skin but thin fibrous films in the form of concentric cylinders.[60] The value of τ at which the extrudate acquires such a telescopic structure corresponds to a sharp decrease in the viscosity of the blend melt in the region where viscosity vs. composition curves lie below the viscosities of POM and EVAC.[60]

6. Effect of the degree of dispersion of fibre-forming component

According to what was said above on the mechanism of fibrillation in the polymer blend flow, fibre formation is realized as a result of stretching and coalescence of the deformed droplets of the disperse phase in the direction of the flow. Deformability of particles depends of their size. According to Van Oene,[67] the submicronic droplets in the flow will remain spherical (underformed) owing to the dominating effect of interfacial tension. If the diameter of droplets is large, films will be formed instead of fibres.[30] On the other hand, the stability of formed fibres in the flow also depends on their diameter. It has been already shown that the most unstable are the fibres of small diameter. All this gives grounds to suppose that there exists an optimal degree of dispersion of the disperse phase at which fibre formation in the polymer mixture melt flow is realized the most completely. Since "*B*" is the quantitiative characteristic of this process, the dependence of the degree of swelling of the extrudate on the degree of dispersion of the disperse phase polymer in the initial mixture should be expressed by the curve with a maximum. This dependence was observed for all the mixtures studied by us. Figure 15 gives the dependence of "*B*" on the mean diameter $\bar{d}$ of POM particles in the initial POM–PS mixture. When $\bar{d}$ of POM powder decreases from 53 to 2.12 μm, "*B*" grows, the number of microfibres in the extrudate increases, and their diameter diminishes. The maximum corresponds to the degree of dispersion ~1.5 μm. When the mean diameter of POM powder is below 1.1 μm, many spherical particles and short fibres are observed in the extrudate and fibre bundle (after PS extraction), which causes the drop in "*B*". Thus, clear correlation between swelling and fibrillation is confirmed again.

It should be noted that the limiting diameter of particles ($d_{\min}$) of

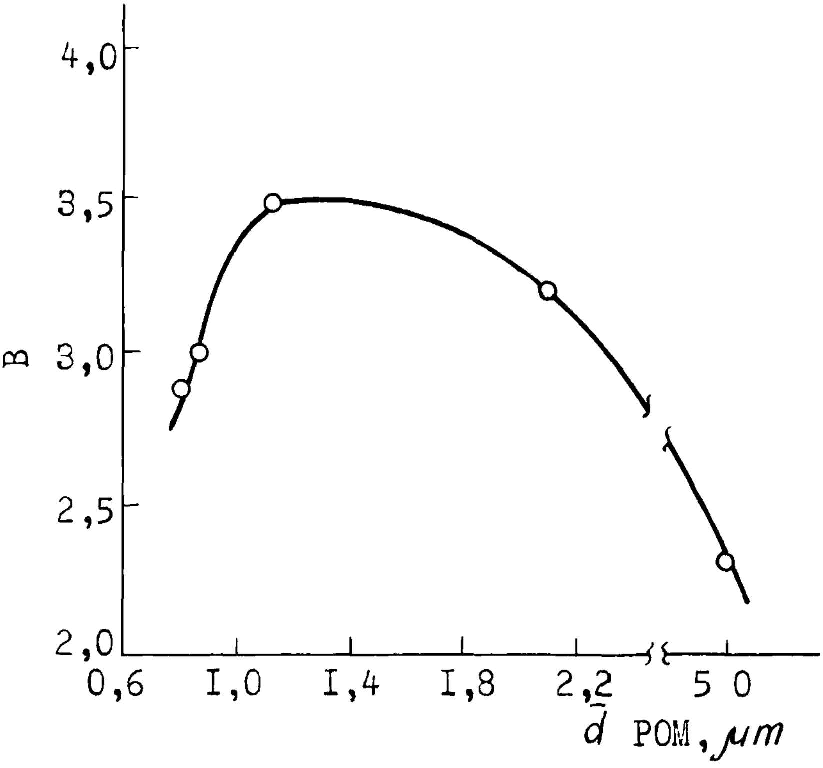

FIGURE 15. Degree of swelling of the extrudate of POM–PS mixture as a function of the mean diameter of particles at $\tau = 6 \times 10^4$ Pa.

the disperse phase for which the formation of ultrathin fibres is the most intense depends on the nature of matrix polymer (Table IV). This is owing to interface phenomena providing the appropriate interaction of polymers and deformation intensity.

It follows from Table IV that the finest fibres are formed with copolyamide matrix. However, the extrudate contains along with long fibres short fibres, particles and films, which affects the degree of swelling. One of the possible reasons for such a nonuniformity of structure formation for POM–CPA extrudate is the small value of the ratio η_{POM}/η_{CPA}. Thus, POM fibre formation is realized the most completely in EVAC matrix.

TABLE IV

Effect of nature of the matrix polymer on POM fibrillation in the blend with 20% POM

Mixture	$\frac{\eta_{POM}}{\eta_{matrix}}$	Characteristics of structure formation for 53 μm mean diameter of POM particles in initial mixture			d_{min}	B_{max}
		$\bar{d}$, μm	B	Presence of other types of structure in addition to long fibres		
POM–PS	0.82	8	2.4	films, 11.4% by mass	~1.5	3.5
POM–EVAC	1.05	5.5	6.1	100% continuous-length fibres	~5	6.0
POM–CPA548	0.70	3.4	2.7	short fibres, particles, films	<1	4.0

7. Effect of selective plasticizer and surface-active substances

The relation between viscoelastic properties of mixed polymers can be controlled not only by varying their molecular masses but also by introducing a selective plasticizer, that is a substance predominantly affecting the properties of the melt of one of the components. Investigations carried out using polyoxymethylene-copolyamide-triethylene glycol mixtures[22] showed that this method can be used to control deformability of the disperse phase and fibre formation in the flow. Triethylene glycol (TEG) affects the properties of blend melt via POM for which it is effective plasticizer.[23] However, the plasticizing effect for blend is stronger in comparison with the effect on POM melt. This can be due to the presence of sufficiently developed interface layer and the variation of interaction between polymers in the interphase layer in the presence of a plasticizer. Using the concept of the mean capillary residence time of melt (ta)[74] the dependences "B" = $f(\log ta)$ were obtained for plasticized and nonplasticized systems (Figure 16), which showed that "B" is almost independent of shear stress and of L/D of the capillary, and that elastic properties of melt depend not on the value of deforming

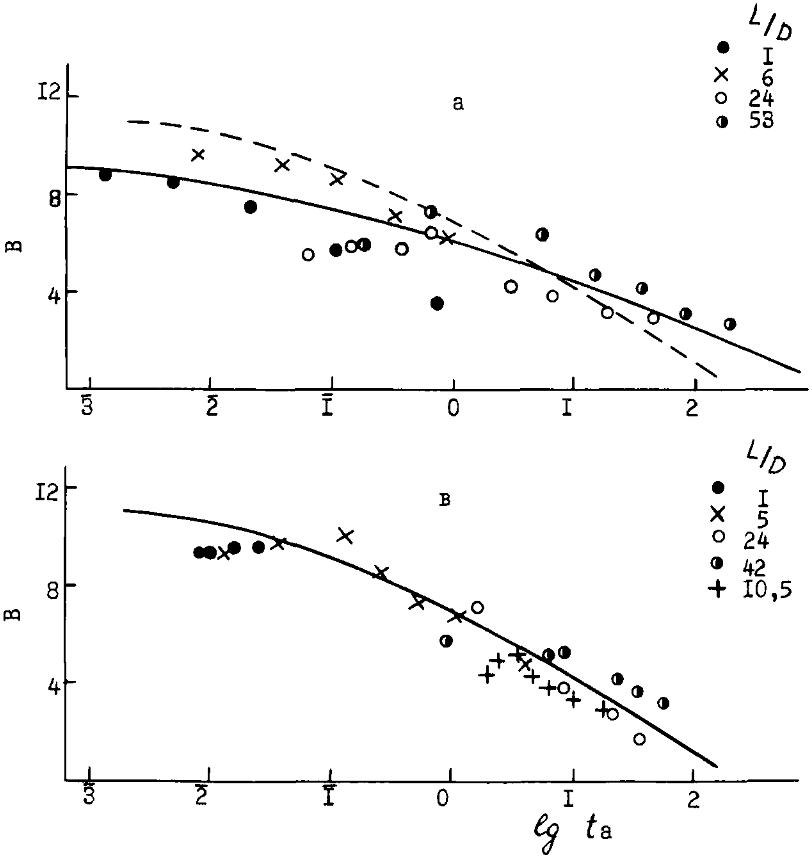

FIGURE 16. Degree of swelling of extrudate as a function of mean capillary residence time of the melt for POM–CPA–TEG (a) and POM–CPA mixtures (b). Dashed line corresponds to POM–CPA mixture.

force but on the duration of its action. By extrapolating these dependences it is possible to determine such characteristics of blends as the limiting value of the degree of swelling (B'_{max}), capillary length L_1 on which the complete relaxation (destruction) of microfibres formed at the entrance will occur, and "B" will be determined by the elasticity of melt of the components, and also the capillary length L_2 for which extrudates can be formed without swelling. The obtained results are given in Table V.

TABLE V

Comparison of characteristics of POM–CPA and POM–CPA–TEG blends

Blend	$B'_{\max}$	L_1, [a]m	L_2, [a]m
POM–CPA	12	0.16	0.40
POM–CPA–TEG	9	0.65	1.78

[a] For $\dot{\gamma} = 36.31\ \mathrm{s}^{-1}$ and $d_c = 990\ \mu\mathrm{m}$.

It is clear that $B'_{\max}$ are reasonable values practically obtained already for capillaries with $L/D = 1$. The values of L_1 and L_2 for both systems are large and cannot be realized in practice. Figure 16 shows that in plasticized blends the relaxation of stored stresses proceeds slower and fibres should retain their stability for longer time. This is due to the fact that TEG increases the elasticity of POM melt which forms ultrathin fibres in the flow. It is known[75,76] that an increase in elasticity rises the stability of liquid cylinder to disintegration due to slowing of growth of the destructive wave. At 2.9% TEG content in the blend fibre formation is deteriorated as a result of the decrease in the ratio $\eta_{\mathrm{POM}}/\eta_{\mathrm{CPA}}$ by a factor of 2 and the increase in elasticity of POM melt. A number of specific features in structure formation are observed: the appearance of concentric formations in extrudates at much lower τ and smaller L/D of capillaries than for two-component blends and the appearance of thin radially arranged films. The formation of unclosed circular layers is associated with a general deterioration in the degree of dispersion of POM in plasticized blends. This can be explained within the framework of the Van Oene theory according to which, when the size of particles is large, the dynamic interfacial tension is small, and the formation of very large surfaces (lamellar structure) becomes possible.

Fibrillation in POM–CPA blends is improved when olygomeric polyethyleneglycols are introduced, which decrease the viscosity of the mixture melt to a lesser extent.

Interfacial regions in polymer blends can be affected by the introduction of SAS. We succeeded to show that SAS produce a dispersing effect on the fibre-forming component of the blend, as a result of which the mean diameter of fibres and the diameter distribution width decrease and rough fibres are absent.[24] The mechanism of action of SAS is connected with a decrease in the work of formation of a new surface when the particles are transformed into fibres in the flow.

8. Peculiarities of properties and specific features of structure of ultrathin synthetic fibres

Fibrillation can be used to obtain not simply ultrathin fibres but at certain conditions a complex thread consisting of hundreds of thousands of microfibres formed through a single duct.[25] The main specific properties of the thread of, for example, POM microfibers are high strength and density, high initial modulus and elasticity, exceptional softness, pleasant feel, and woollilike without special textural procedures. Specific features of fibres always ensue from peculiarities of their micro- and macrostructure. The microfibre formation in the entrance region under the effect of intense tension leads to appearance a new reflex in the X-ray ogram, a sharp inversion of infrared dichroism of the number of bands, and an increase in long period and density of amorphous phase in comparison with those for POM fibres formed using ordinary methods.[28]

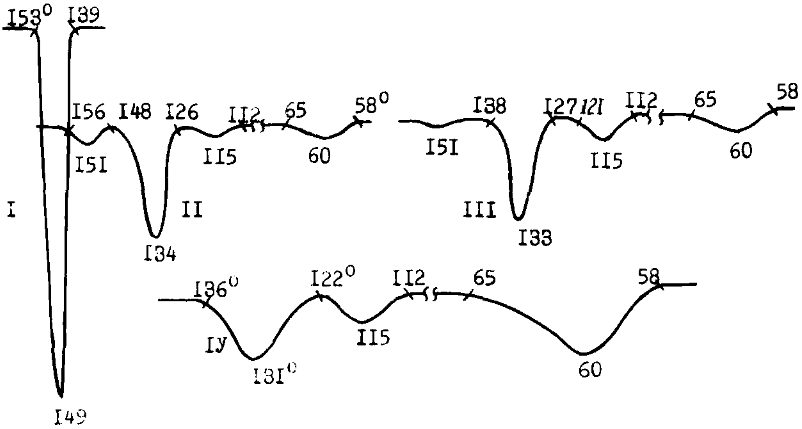

FIGURE 17. Thermograms of crystallization of extrudates of initial POM (1) and POM–EVAC mixtures with component ratio 30:70 (2); 20:80 (3), and 10:90 (4). POM content in weights of the samples was 2 × 10^{-5} kg. Conditions of obtaining extrudates were the same.

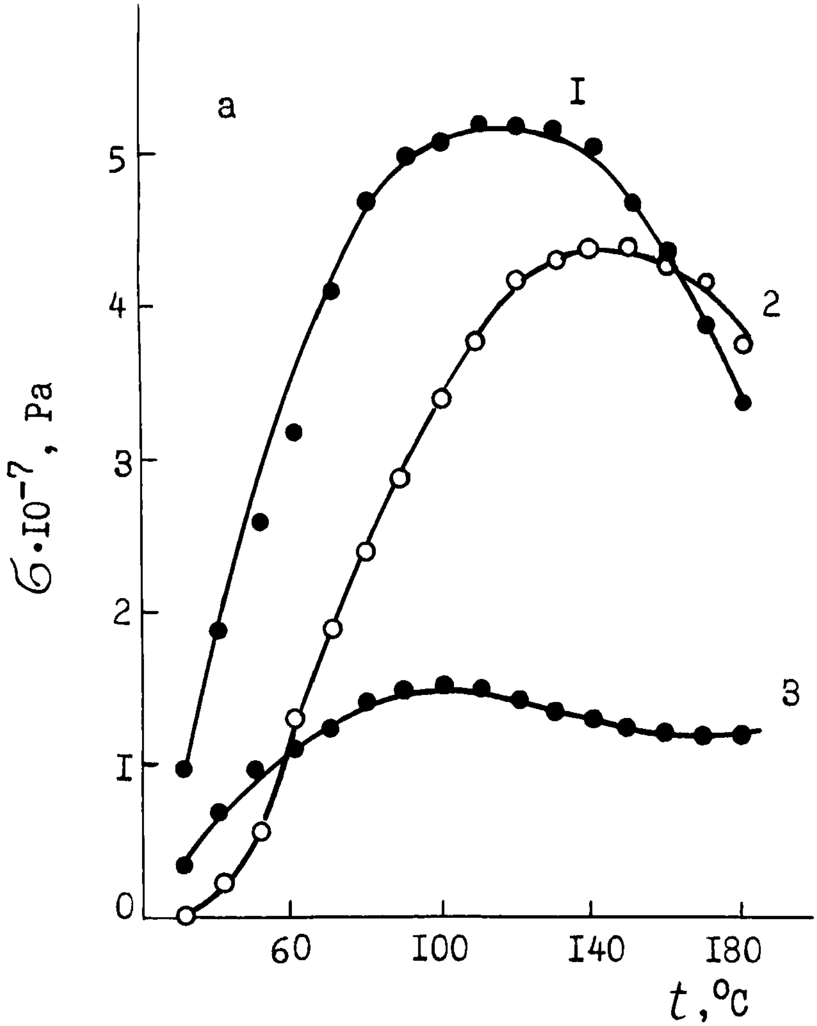

FIGURE 18. Isometric heating curves (a): POM microfibres with elongation factor of 8 (1); ordinary POM fibre with elongation factor of 8 (2); POM microfibre with elongation factor of 6 (3)—elongation occurred in a matrix (EVAC); (b) composite fibre of the POM/EVAC mixture with elongation factor of 6.

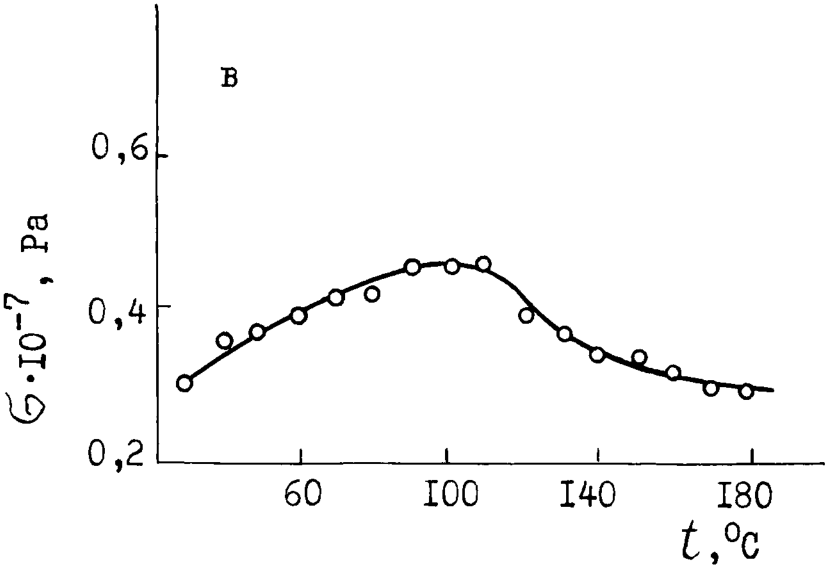

FIGURE 18(b)

Electron-microscopic studies confirmed the unique structure of the surface of microfibres formed from the polymer blend melts: every fibre is covered by a multitude of superthin fibrilles branching from the main fibre.[77] This structure of microfibre surface was mentioned for the first time in patent.[78] Such a peculiarity in the structure of the surface of ultrathin fibres can be refered to the formation of transient layer in the blend of incompatible polymers, which is confirmed by the results of DTA. Figure 17 gives thermograms of crystallization of POM and POM–EVAC extrudate melts. A sharp decrease in temperature and heat of crystallization of POM in the blend is observed; the appeared additional peaks are apparently associated with crystallization of POM in the transient layer.

The results of isometric heating (Figure 18) confirmed the above-mentioned peculiarities of POM microfibres' structure (for example, their improved orientation as compared with ordinary fibres). The most important conclusion, however, ensueing from the results of isometric heating consists in the following. The shapes of the curves and absolute loads for a composite monothread of POM–EVAC mixture (Figure 18b) and for the thread made of POM microfibres (Figure 18a, curve 3) are practically identical. The difference in stresses is due to the difference in cross sections of the extracted from matrix polymer and composite threads. It means that the main stresses are concentrated in microfibres contained in the monothread.

CONCLUSION

The presented brief review of the results of investigations into fibrillation of crystallizable polymers in mixtures with amorphous or slightly crystallizable polymers in the flow through forming ducts, carried out by the author and her colleagues, shows that the study of this phenomenon is interesting from the point of view of creating the theory of the processing of polymer mixtures, determining the role of entrance processes which in the number of cases are of decisive importance and in processing of solutions and melts of individual polymers. For example, entrance phenomena may considerably affect the fibrillizability of formed fibres, and in the processing of rigid-chain polymer solutions, the ability of macromolecules and their associates to orientation. This is confirmed in practice and requires the scientific substantiation for the purposeful control and regulation of these processes. In this connection it is necessary, first of all, to set up investigations in order to obtain quantitative data on stress distribution at the entrance of forming channels (for mixture melts) and the relationships between stresses and appearing deformations.

As to the phenomena of polymer mixture melts flow, the interconnection of deformation conditions, processes of structure formation and the properties of products obtained from them, at present these questions are on the level of empirical understanding and require further thorough and systematic study. The task, apparently, consists not so much in deriving the equations that would describe property vs. composition curves as in elucidating the causes and mechanisms of a peculiar behaviour of mixture melts in various composition ranges and in various conditions.

For the mixtures with clearly pronounced fibrillation in the flow such problems as stability of fibres in the flow, the role of interfacial phenomena and specific features of transient layer formation have not been investigated at all.

Finally, proceeding from the already studied properties of microfibres formed from polymer mixture melts, we can conclude that along with the known fields of their application there can be found some others, for example, the production of consumer goods where their woollilikeness and cottonlikeness can be utilized.

Acknowledgement

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References

1. Okamoto, Miyoshi, Sen-i gakkaishi, *J. Soc. Fiber Sci. and Technol. Jap.*, **32,** 8 (1976).
2. J. H. Southern and R. S. Porter, *J. Macromol. Sci.-Phys.* **B4,** 541 (1970); C. R. Desper, J. H. Southern, R. D. Ulrich, and R. S. Porter, *J. Appl. Phys.*, **41,** 4284 (1970).
3. J. H. Southern and R. S. Porter, *J. Appl. Polymer Sci.*, **14,** 2305 (1970); J. H. Southern and R. S. Porter, *J. Polymer Sci.*, **A2,** 1135 (1972).
4. P. V. Papero, E. Kubu, and L. Roldan, *Textile Research J.*, **37,** 823 (1967).
5. A. L. Breen, pat. USA, 3382305 (1968).
6. B. T. Hayes, *Chem. Eng. Progress.*, **65,** 50 (1969).
7. K. Dietrich and S. Tolsdorf, *Faserforsch. und Textilt.*, **21,** 288 (1970).
8. N. K. Baramboim and V. F. Rakityansky, *Plast. Massy*, **11,** 34 (1971).
9. V. N. Kuleznev, Yu. G. Oganesov, Yu. V. Evreinov, S. S. Voyutsky, L. D. Fillipovich, I. M. Gil'man, *Kolloid. Zhur.*, **34,** 863 (1972).
10. M. V. Tsebrenko, A. V. Yudin, M. Yu. Kuchinka, G. V. Vinogradov, and K. A. Zubovich, *Vysokomol. Soed.*, **B15,** 566 (1973).
11. M. V. Tsebrenko, M. Yakob, M. Yu. Kuchinka, A. V. Yudin, and G. V. Vinogradov, *Intern. J. Polymeric Mater.*, **3,** 99 (1974).
12. A. V. Yudin, M. V. Tsebrenko, M. Yakob, M. Yu. Kuchinka, V. E. Vishnevsky, and G. V. Vinogradov, *Preprints of International Symposium on Chemical Fibres, Kalinin*, **3,** 139 (1974).
13. W. Berger and G. Schmack, *Textiltechnik*, **24,** 36 (1974).
14. Ch. Michels, H. Franz, *Faserforsch. und Textilt.*, **28,** 165 (1977).
15. N. P. Krasnikova, E. V. Kotova, G. V. Vinogradov, and Z. Pelzbauer, *J. Appl. Polymer Sci.*, **22,** 2081 (1978).
16. N. P. Krasnikova, Z. Pelzbauer, E. V. Kotova, and G. V. Vinogradov, *Faserforsch. und Textilt.*, **29,** 92 (1978).
17. A. V. Yudin, M. V. Tsebrenko, M. Yu. Kuchinka, and G. V. Vinogradov,

Abstracts of Completed Research Works in Higher Educational Establishments of Ukraine, **7,** 3 (1974).
18. M. V. Tsebrenko, N. M. Rezanova, and G. V. Vinogradov, *Polymer Eng. and Sci.*, **20,** 1023 (1980).
19. M. V. Tsebrenko, *Vysokovol. Soed.*, **B20,** 600 (1978).
20. M. V. Tsebrenko, A. I. Benzar, A. V. Yudin, and G. V. Vinogradov, *Vysokomol. Soed.*, **A21,** 830 (1979).
21. M. V. Tsebrenko, N. M. Rezanova, V. I. Vislenko, A. V. Yudin, *Khim. Tekhnol.*, **5,** 35 (1980).
22. M. V. Tsebrenko, T. I. Ablazova, A. V. Yudin, and G. V. Vinogradov, *Kolloid. Zhur.*, **38,** 204 (1976).
23. M. V. Tsebrenko, G. V. Vinogradov, T. I. Ablazova, and A. V. Yudin, *Vysokomol. Soed.*, **A17,** 1375 (1975).
24. G. V. Vinogradov, M. V. Tsebrenko, and N. M. Rezanova, *Vysokomol. Soed.*, **B4,** 257 (1981).
25. M. V. Tsebrenko, A. I. Benzar, and A. V. Yudin, *Khim. Volokna*, **4,** 48 (1978).
26. T. I. Sizevich, M. V. Tsebrenko, and A. V. Yudin, *Khim. Volokna*, **5,** 24 (1979).
27. M. V. Tsebrenko, A. V. Yudin, G. V. Vinogradov, A. Sh. Goykhman, and A. I. Benzar, *Vysokomol. Soed.*, **A15,** 1970 (1973).
28. M. V. Tsebrenko, *Vysokomol. Soed.*, **B21,** 836 (1979).
29. L. S. Gerasimova, A. B. Pakshver, *Tekstil. Prom.*, **4,** 59 (1965).
30. M. V. Tsebrenko, A. V. Yudin, T. I. Ablazova, and G. V. Vinogradov, *Polymer*, **17,** 831 (1976).
31. C. D. Han and L. H. Drexler, *J. Appl. Polymer Sci.*, **17,** 2329 (1973).
32. L. H. Drexler and C. D. Han, *J. Appl. Polymer Sci.*, **17,** 2355 (1973).
33. C. D. Han and L. H. Drexler, *J. Appl. Polymer Sci.*, **17,** 2369 (1973).
34. G. V. Vinogradov, A. I. Isaev, V. I. Brizitsky, Yu. Ya. Podolsky, A. Ya. Malkin, and M. P. Zabugina, *Mekhanika Polimerov*, **1,** 116 (1977).
35. Yu. Ya. Podolsky, A. I. Isaev, and V. I. Brizitsky, *Proceedings of VII Congress on Rheology, Ghoeteborg*, 598 (1976).
36. V. I. Brizitsky, G. V. Vinogradov, A. I. Isaev, and Yu. Ya. Podolsky, *Zhur. Prikl. Polimer. Nauki*, **20,** 25 (1976).
37. H. B. Chin and C. D. Han, J. *Rheol.*, **23,** 396 (1979).
38. C. D. Han, Y. K. Pithapurwala, and R. C. King, *J. Rheol.*, **23,** 397 (1979).
39. H. B. Chin and C. D. Han, *J. Rheol.*, **23,** 557 (1979).
40. R. G. Crystal and J. H. Southern, *J. Polymer. Sci.*, **9A2,** 1641 (1971).
41. A. Keller and M. J. Machin, *J. Macromolec. Sci.*, **B1,** 41 (1967).
42. M. Mihaylov and E. Nedkov, J. Polymer. Sci., **C38,** 33 (1972).
43. C. D. Han and T. C. Yu, *Polym. Eng. Sci.*, **12,** 81 (1972).
44. C. D. Han, *J. Appl. Polym. Sci.*, **15,** 2579 (1971).
45. C. D. Han and T. C. Yu, *J. Appl. Polym. Sci.*, **15,** 1163 (1971).
46. C. D. Han, Y. W. Kim, J. Parker, N. Siscovic, and C. R. Huang, *Appl. Polym. Symp.*, **21,** 191 (1973).
47. C. D. Han and Y. W. Kim, *Trans. Soc. Rheol.*, **19,** 245 (1975).
48. H. Van Oene, *J. Rheol.*, **23,** 396 (1979).
49. H. Van Oene, in *Polymer Blends*, (Academic Press, New York, 1978), Vol. 1, p. 295.
50. A. P. Plochocki, in *Polymer Blends*, (Academic Press, New York, 1978), Vol. 2, p. 319.
51. Yu. Lipatov, *J. Appl. Polymer Sci.*, **22,** 1895 (1978).
52. Yu. S. Lipatov, V. F. Shumsky, I. P. Getmanchuk, *Vysokomol. Soed.*, **A21,** 2093 (1979).

53. L. B. Kandyrin and V. N. Kuleznev, *Kolloid. Zhur.*, **36,** 473 (1974).
54. V. N. Kuleznev, O. L. Melnikova, and V. D. Klykova, *Eur. Polym. J.*, **14,** 455 (1978).
55. G. I. Taylor, *Proc. Roy. Soc., London*, **A146,** 501 (1934).
56. S. Uemura and M. Takayanagi, *J. Appl. Polymer Sci.*, **10,** 113 (1966).
57. R. F. Heitmiller, R. Z. Maar, and H. H. Zabusky, *J. Appl. Polymer Sci.*, **8,** 873 (1964).
58. M. Horio, T. Fujii, and S. Onogi, *J. Phys. Chem.*, **68,** 778 (1964).
59. Yu. S. Lipatov, A. E. Fainerman, and O. V. Anokhin, *DAN SSSR*, **231,** 381 (1976).
60. T. I. Ablazova, M. V. Tsebrenko, A. V. Yudin, G. V. Vinogradov, and B. V. Yarlykov, *J. Appl. Polymer Sci.*, **19,** 1781 (1975).
61. L. L. Chapoy and S. Padersen, *Polymer Eng. and Sci.*, **17,** 724 (1977).
62. V. N. Kuleznev, Yu. V. Evreinov, V. D. Klykova, and M. A. Shaposhnikova, *Kolloid. Zhur.*, **35,** 281 (1973).
63. K. Dietrich and H. Versäumer, *Faserforsch. und Textilt.*, **26,** 347 (1975).
64. L. A. Utraski, Z. Bakerdjian, and Musa R. Kamal, *J. Appl. Polymer Sci.*, **19,** 481 (1975).
65. M. V. Tsebrenko, *Vysokomol. Soed.*, **A20,** 93 (1978).
66. V. E. Dreval, A. A. Tager, E. I. Sycheva, and Z. P. Vzvadskaya, *Mekhanika Polimerov*, **5,** 920 (1970).
67. H. Van Oene, *J. Colloid Interface Sci.*, **40,** 448 (1972).
68. R. G. Cox, *J. Fluid Mech.*, **37,** 601 (1969).
69. J. M. Starita, *Trans. Soc. Rheol.*, **16,** 339 (1972).
70. V. N. Kuleznev, A. V. Grachev, and Yu. P. Microshnikov, *Kolloid. Zhur.*, **38,** 265 (1976).
71. Danesi Sergio and R. S. Porter, *Polymer*, **19,** 448 (1978).
72. B. L. Lee, J. L. White, *Trans. Soc. Rheol.*, **19,** 481 (1975).
73. Yu. S. Maloshchuk, V. N. Kuleznev, and S. E. Khanin, *Kolloid. Zhur.*, **35,** 408 (1973).
74. M. C. Rogers, *J. Appl. Polymer Sci.*, **14,** 1679 (1970).
75. M. Gordon, J. Yerushalimi, and R. Shinner, *Trans. Soc. Rheol.*, **17,** 303 (1973).
76. Yu. P. Miroshnikov, M. L. Kaminsky, and V. N. Kuleznev, *Kolloid. Zhur.*, **41,** 1112 (1979).
77. M. V. Tsebrenko, *Khim. Volokna*, **5,** 33 (1980).
78. Pat. USA 3549734 (1970).