The Rheological Properties of Molten Mixtures of Polyoxymethylene and Copolyamide: Their Fibrillation and Microstructure

T. I. ABLAZOVA, M. B. TSEBRENKO, and A. B. V. YUDIN,
*Kiev Technological Institute of Light Industry, Laboratory of Synthetic Fibres,
Kiev, Ukranian SSR, USSR 252011;* and
G. V. VINOGRADOV and B. V. YARLYKOV,
*Institute of Petrochemical Synthesis of the USSR Academy of Sciences,
Laboratory of Polymer Rheology, Moscow, USSR 117071*

Synopsis

The rheological properties of molten mixtures of polyoxymethylene and copolyamide have been investigated by the methods of capillary viscometry over a wide range of shear stresses. It has been found that at relatively close values of the melt viscosity polyoxymethylene (POM) and copolyamide (CPA) form mixtures which differ markedly in viscosity and elastic properties from the original polymers. Depending on the magnitude of the shear stress, the viscosity of mixtures of definite composition may be either higher or lower than the viscosity of the components. Three- to tenfold swelling of the stream emerging from the capillary is observed for such mixtures, whereas at the same temperatures no swelling of the POM and CPA extrudates is practically observed. The data obtained are accounted for by the fact that the flow of mixtures through the capillary involves the formation of hundreds of thousands of ultrathin fibres of POM in the matrix of CPA, which are oriented along the flow axis.

INTRODUCTION

At present, multicomponent polymer systems have found extensive application.[1] Polymer mixtures are thermodynamically incompatible, as a rule; compatible polymers are an exception.[2] In spite of the incompatibility of polymers, when mixed they, however, exert an effect on the crystallization from melts, which is reflected in a radical change of their supramolecular structure. The mixing of polymers therefore is an effective way of modifying their properties and preparing polymeric systems having new properties.[3,4] Thus, the possibility has been reported in the literature[5,6] of preparing ultrathin fibers and films of low thickness in the extrusion of molten mixtures of thermodynamically incompatible polymers differing in the rate of crystallization, crystallinity, or melting temperature and also of molten mixtures of crystallizable and amorphous polymers.

Of considerable interest in this connection are rheological investigations of molten polymer mixtures,[7–10] especially those which are concerned with the effect of the telescopic layer distribution of one polymer into another.[7,11,12] Mention

must also be made of patents[13,14] in which a suggestion is made of the advantage of formation of specific structures in mixtures of incompatible polymers.

Mixtures of POM and CPA serve as convenient model systems for studying the general relationships of the formation of ultrathin fibers, tubular membranes, and films during the flow of mixtures of incompatible polymers. This may be attributed to the rapid crystallization and high degree of crystallinity of POM and also to the ease of separation of amorphous CPA from it on dissolution. Moreover, the combination of a crystallizable polymer and an amorphous one is convenient for study of extrudates in the polarizing microscope.

The aim of the present work is to study the viscous properties of molten mixtures of POM and CPA over a wide range of stresses (τ) and shear rates ($\dot{\gamma}$) and also the effect of the deformation conditions on the microstructure of the extrudates.

EXPERIMENTAL

The materials for investigation were mixtures of a copolymer of formaldehyde with 2% 1,3-dioxolane (POM) and a mixed copolyamide (CPA) which is a copolymer of caprolactam (44%), hexamethyleneadipinate (37%) and hexamethylenesebacinate (19%). These polymers are briefly characterized in Table I.

The content of CPA in the mixtures changed from 0 to 100% by weight. Particular emphasis was made in our studies on the properties and microstructure of the extrudates with the following weight ratios of POM/CPA: 60/40, 30/70, and 20/80 chosen on the basis of the results reported in the literature,[15] according to which these compositions are characterized by the strongest alteration of the thermodynamic and structural properties of the polymers in a mixture as compared with the properties of the original components. For the other mixtures there have been obtained viscosity–composition relations in the region of shear stresses $\tau = (0.89-5.76) \times 10^5$ dynes/cm².

The polymers were mixed as follows. The granules of copolyamide were dissolved together with stabilizing agents for POM in ethanol at 60°C (20%), a weighed portion of powdered POM was introduced into the solution, and the resulting suspension was thoroughly mixed. After the evaporation of the solvent, the mixtures were dried to constant weight under vacuum at 60°C. The study of the viscous properties of the melts of the systems indicated was carried out on capillary constant-pressure viscometers at temperatures of 170°, 190°,

TABLE I
Characteristics of Original Polymers

Polymer	External appearance	Intrinsic viscosity in dimethyl-formamide at 150°C	Melting temp. according to DTA data, °C	Stabilizing agents added, wt-%
POM	Dispersed powder with an average particle size of 53 microns	0.56	171	0.5% dicyandiamide plus 0.5% 2,2-methylene-bis(4-methyl-6-tert-butylphenol)
CPA	Granules	0.27	165	

TABLE II
Capillary Sizes and Deformation Conditions

No.	Capillary diameter D, mm	Capillary length L, mm	L/D	τ, dynes/cm²	$\dot{\gamma}$, sec⁻¹
1	0.500	11.4	22.8		
2	0.786	7.9	10.0		
3	0.992	5.0	5.0		
4	1.000	22.5	22.5	2.7×10^4 to	1.2–5.0
5ᵃ	1.056	1.1	1.0	3.2×10^6	$\times 10^3$
6	1.118	46.6	41.6		
7	1.800	39.3	21.9		
8	3.000	79.7	26.6		

ᵃ Capillary no. 5 was used to estimate the effect of very small values of L/D on the microstructure of the extrudate.

and 210°C. The capillary sizes and the ranges of shear stresses and rates are presented in Table II. The frontal cross section of the capillaries was 90° to their axis. The viscometric reservoir had a diameter equal to ¹/₂ in.

The experimental data were treated by the generally accepted procedure: τ and $\dot{\gamma}$ were determined on the capillary wall. The root-mean-square error of the arithmetic mean in measurements of viscosity (η) and $\dot{\gamma}$ was ±5% (with 0.95 confidence).

The nature of the resultant structure of the extrudates (produced by extrusion of the mixtures through capillaries) was observed in thin cross and longitudinal sections with the aid of the polarizing microscope. To prepare these sections, a 1-cm length of extrudate was covered by epoxide resin in a gelatin capsule and placed into a thermostat for 48 hr to be solidified. Sections 10 to 15 microns thick were obtained with the aid of a piezoelectric ultramicrotome. The sections were studied (in polarized light) in the microscope (magnification ×57 to ×420) and photographed. The copolyamide was found to be completely dark in the visual field of the microscope in all the cases. The structural formations of polyoxymethylene were clearly seen in its background. The bundles of fibers resulting from the washing-off of the copolyamide from the extrudate and distributed in the immersion liquid were also visually studied under the microscope. The extraction of copolyamide was carried out with ethanol in Soxhlet apparatus at 75°C. The duration of removal of CPA depends on the size of the extrudate and the conditions of its preparation.

RESULTS

The Viscous Properties of the Melt

The treatment of the experimental data (with account taken of the entry corrections) showed that the flow curves for original polymers (Fig. 1) as well as for their mixtures (Figs. 2–4) are invariant with respect to capillary size and that their separate portions are satisfactorily approximated by the well-known power equation $\dot{\gamma} = k\tau^n$. The values of n are listed in Table III.

A sharp change in the conditions of flow of the molten mixtures of POM and CPA as compared with the original components in the region of high shear stresses attracts attention.
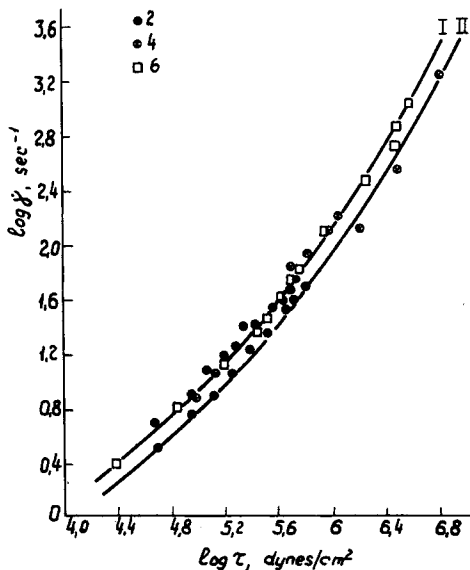
Fig. 1. Flow curves for a molten POM (I) and CPA (II) at 190°C. Points 2, 4, and 6 correspond to the capillary sizes listed in Table II.
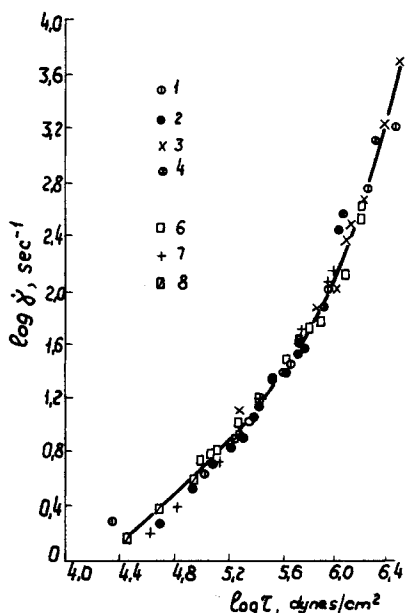

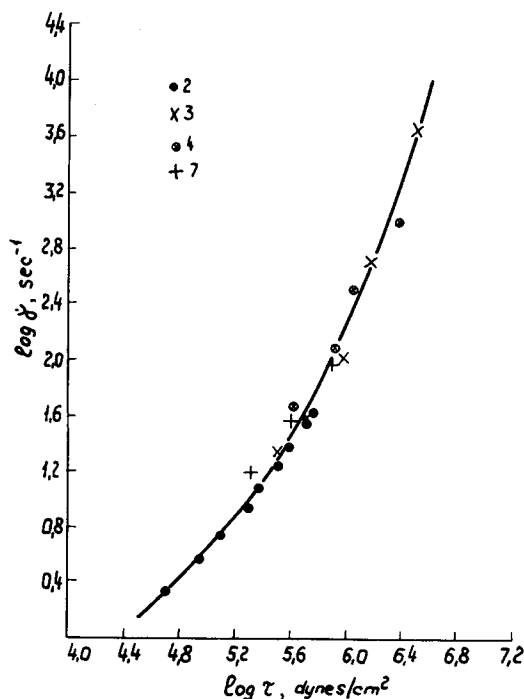Fig. 2. Flow curve for a molten mixture of POM + 70% CPA, 190°C. Points 1-4, 6-8 correspond to the capillary sizes listed in Table II.

A number of investigators[7]−[10] point to the specificity of the properties of molten mixtures which are difficult to predict if the viscosity and elastic properties of the original components are known.   What has been said refers also to the POM–CPA mixtures studied in the present work: with relatively close values of the viscosity of the melt, POM and CPA when mixed over the entire range of compositions

TABLE III
Flow Conditions for Melts of Original POM and CPA and Their Mixtures

$\tau \times 10^5$, dynes/cm^2	Values of n for mixture compositions given, wt-%				
	100% POM	100% CPA	POM + 40% CPA	POM + 70% CPA	POM + 80% CPA
0.16–2.5	1.0	1.0	1.1	1.0	1.0
2.5–12.6	1.3	1.3	1.8	1.7	1.8
12.6–40	1.7	1.7	2.7	4.0	3.0

Fig. 3. Flow curve of a molten mixture of POM + 80% CPA, 190°C. Points 2, 3, 4, and 7 correspond to the capillary sizes listed in Table II.

form systems which differ in viscosity and elastic properties of the melts from the original components (Figs. 5 and 6). From Figure 5 it is seen that the character of the $\eta = f$ (composition) curve is determined by the shear stress; at $\tau <$ 6.3×10^5 dynes/cm^2, the viscosities of the mixtures are higher than those of the original components and the curves have maxima over the entire range of compositions. In the region of shear stresses exceeding 6.3×10^5 dynes/cm^2, the character of the viscosity–composition relation is radically changed: the viscosities of the molten mixtures are now lower than those of the POM and CPA melts and the curves have a minimum in the region of the 20% concentration of POM. Moreover, at high shear stresses there is observed a sharply pronounced non-Newtonian behavior for the molten mixtures (Fig. 6). Thus, whereas the viscosities of the POM and CPA melts decrease approximately by a factor of 3 in the range of 1.2×10^5 to 6.3×90^6 dynes/cm^2, the viscosity of POM/CPA mixtures (60/40, 30/70, and 20/80) decreases by 17, 57, and 38 times respectively. In
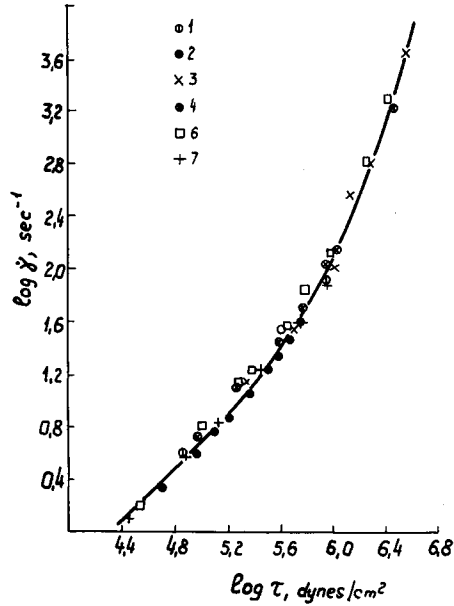
Fig. 4. Flow curve of a molten mixture of POM + 40% CPA, 190°C.   Points 1–4, 6, and 7 correspond to the capillary sizes listed in Table II.
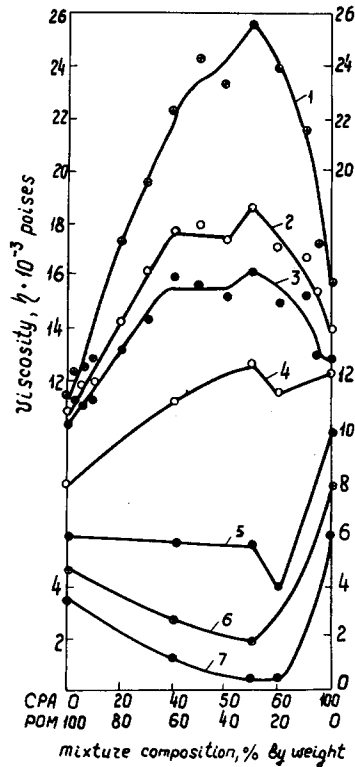

Fig. 5. Viscosity of molten mixtures vs. composition.   Curves 1–7 correspond to shear stresses, respectively (1.27, 3.93, 5.44, 6.30, 12.59, 19.25, 31.62) × 10^{-5} dyne/cm².

TABLE IV
The Values of Entry Corrections for POM Melts and POM–CPA Mixtures

$\dot{\gamma}$, sec^{-1}	Values of m for the mixture composition given, wt-%			
	100% POM	POM + 40% CPA	POM + 70% CPA	POM + 80% CPA
25	1	1	1	1
100	1.2	1	1	0.8
200	1.2	1.4	1.2	2.0
400	1.2	2.2	2.0	2.6
800	1.2	3.2	2.6	3.0
1600	1.2	3.2	2.8	3.0
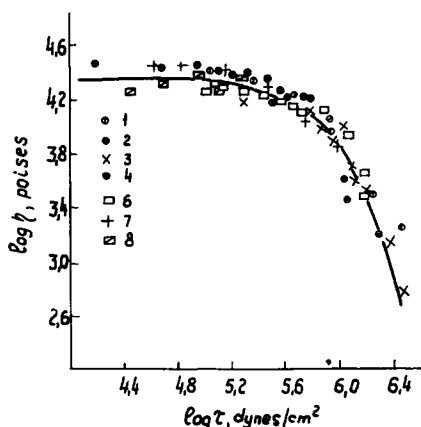
Fig. 6. Effect of shear stress on the viscosity of a molten mixture of POM + 70% CPA at 190°C.   Points 1–4 and 6–8 correspond to the capillary sizes indicated in Table II.

this respect, the behavior of the mixtures in flow is similar to that of certain filled polymers.[18]   Probably, this behavior of molten mixtures of POM and CPA is primarily associated with the change of the phase state, shape, and size of POM particles and with the mode of their distribution in a molten mixture, which, as will be shown below, is supported by the results of investigations of the micro-structure of the extrudates of the mixtures obtained at high shear stresses.

The values of the activation energy of viscous flow (E) of molten mixtures of POM and CPA, as calculated from the temperature–viscosity relation, were found to be 12–15 kcal/mole.   This means that in a temperature range of 190–210°C (when both polymers must be in the fluid state), the fluidity of the mixtures is controlled by copolyamide (E_{CPA} = 12–15 kcal/mole, E_{POM} = 7–9 kcal/mole).

For molten POM/CPA mixtures, the entry loss (m expressed in equivalent radii) is extremely low, which is seen from the data given in Table IV.

In contrast to ordinary polymeric systems, however, in spite of the absence of considerable entry effects there is observed a very strong (three- and fourfold and sometimes even tenfold) swelling of the stream leaving the capillary.   With increasing degree of dispersity of the original powdered POM, the swelling is increased.   Thus, for example, if the average diameter of the particles of powdered POM is 2 microns, the emerging stream of the mixture of POM + 70% of CPA swells approximately by ten times.

The above-described specificity of the viscoelastic properties of molten POM/CPA mixtures is determined in the first place by the ability of POM to form hundreds of thousands of streamlets and fibers in the CPA matrix on extrusion of molten mixtures through the capillary,[5] which is verified by the results of investigations into the microstructure of the extrudates.

The Microstructure of Extrudates

At a temperature of 170°C (i.e., at a temperature lower than the melting temperature of POM), POM/CPA mixtures of composition 60/40, 30/70, and 20/80 are capable of flowing, but no fibers of POM are formed. The degree of swelling of the extrudate emerging from the capillary is too low to be recorded. After the extraction of CPA from the extrudate, polyoxymethylene remains in powder form. Ultrathin polyoxymethylene fibers are obtained only at temperatures exceeding the melting temperature of POM (Fig. 7). The analysis of sections and bundles of fibers washed off from CPA showed (Fig. 8) that as the temperature of the melt becomes higher than the melting temperature of POM, its dispersity in the extrudate increases (in the sense that the diameter of the fibers is decreased and their number increased) and there is obtained a bundle of fibers more uniform as to the diameter distribution of fibers and the decrease of the number of spheres, short fibers, and films. The principal factor responsible for this is the decrease of the viscosity of the mixture with rise of the temperature of the melt, which facilitates the coalescence of particles of polyoxymethylene in the


(a)

(b)

Fig. 7 (continued)

(c)

Fig. 7. Microphotographs of longitudinal sections of extrudates of original POM (a) (arrow indicates the direction of flow) and mixtures of POM + 70% CPA (b) and POM + 80% CPA (c) after they have flown out of capillary no. 5 at 190°C. Shear stresses are as follows: (a) 6.0×10^6; (b) 1.41×10^6; (c) 1.20×10^7 dynes/cm².

stream flow. What attracts attention here is the distinctly pronounced difference in the dispersity of POM in the central part of the extrudate as compared with the regions lying nearer to the edge, which, as will be shown below, is typical of all the samples obtained at relatively high τ values. In the region of low τ values, the rise of temperature enhances especially strongly the coalescence of particles and contributes to the aggregation of polyoxymethylene particles in the molten mixture.[6]

The capillary size and the ratio of the diameter of the capillary to that of the viscometric reservoir are important. When large-diameter capillaries are used and the ratio of the diameter of the viscometric reservoir to that of the capillary is considerably reduced, the effect of fiber formation may not be observed at all. The best effect with respect to the formation of ultrathin fibers is attained when very short capillaries those of the die type are used.
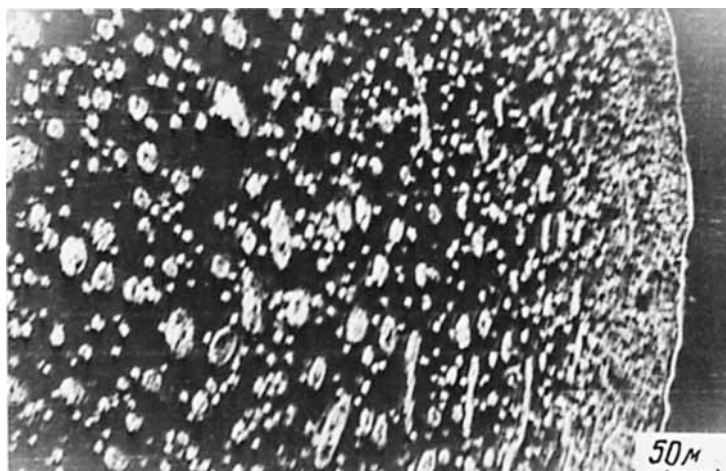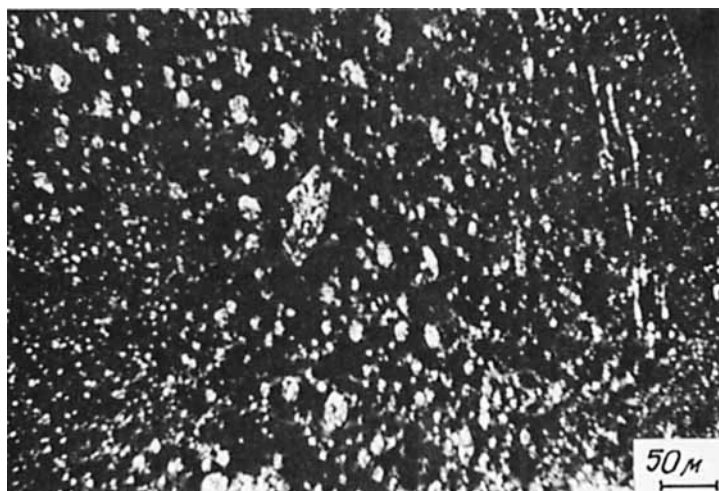

(a)

Fig. 8 (continued)
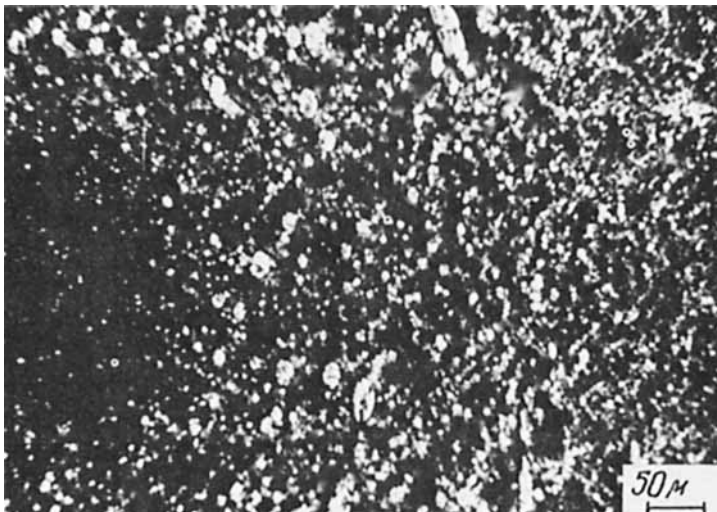
(b)

Fig. 8. Effect of temperature of the melt on the microstructure of the extrudate of a mixture of POM + 70% CPA.(cross section). Capillary no. 4: (a) 190°C, $\tau = 5.37 \times 10^5$ dynes/cm²; (b) 210°C, $\tau = 6.92 \times 10^5$ dynes/cm².

The microstructure of extrudates of the mixtures is greatly affected by the shear stress (Fig. 9). With increasing τ, the mean diameter of polyoxymethylene fibers decreases (from 3 microns at $\tau = 3.9 \times 10^5$ dynes/cm² to dimensions that go beyond the resolving power of optical microscopes at $\tau > 10^6$ dynes/cm²); the layer arrangement of polyoxymethylene fibers is observed (Figs. 9c and 9d); these layers are found to be shifted to the capillary walls, and in the axial zone the fibers are invisible under the optical microscope (Fig. 10a). After the removal of CPA from such an extrudate, a set of concentric fibrous tubes is obtained, be-
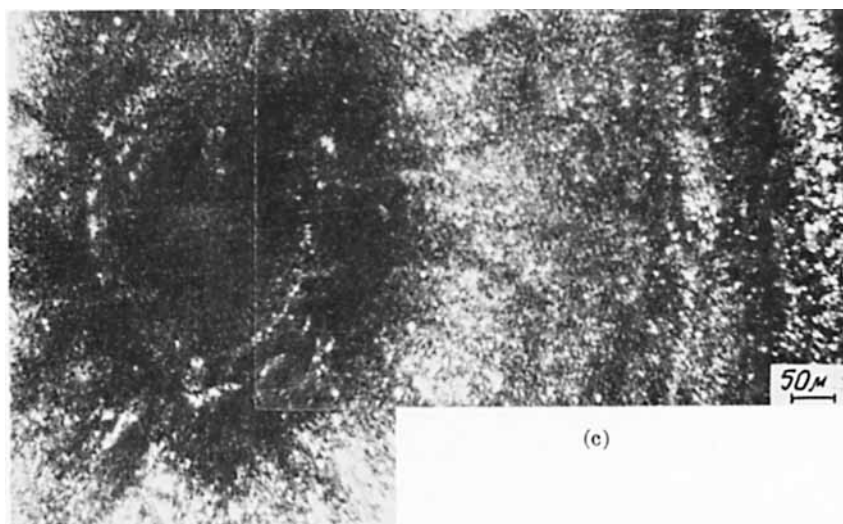

(a)

Fig. 9 (continued)

(b)

(c)

Fig. 9. Effect of shear stress on the microstructure of the extrudates of a mixture of POM + 70% CPA (cross section). Capillary no. 4, 190°C. Shear stresses are: (a) 5.4×10^5; (b) 8.5×10^5; (c) 2.1×10^6 dynes/cm².

tween which there are found a small number of fibers. A microphotograph of such a tube is presented in Figure 10b, from which it is seen that the tube probably consists of fibers, but, in distinction to a spherulite tube (Fig. 10c) it has numerous pores, owing to which such a fibrous tube does not interfere with the extraction of CPA even from the central part of the extrudate. But if a spherulite film is formed (at low τ values), the process of extraction is practically impossible.
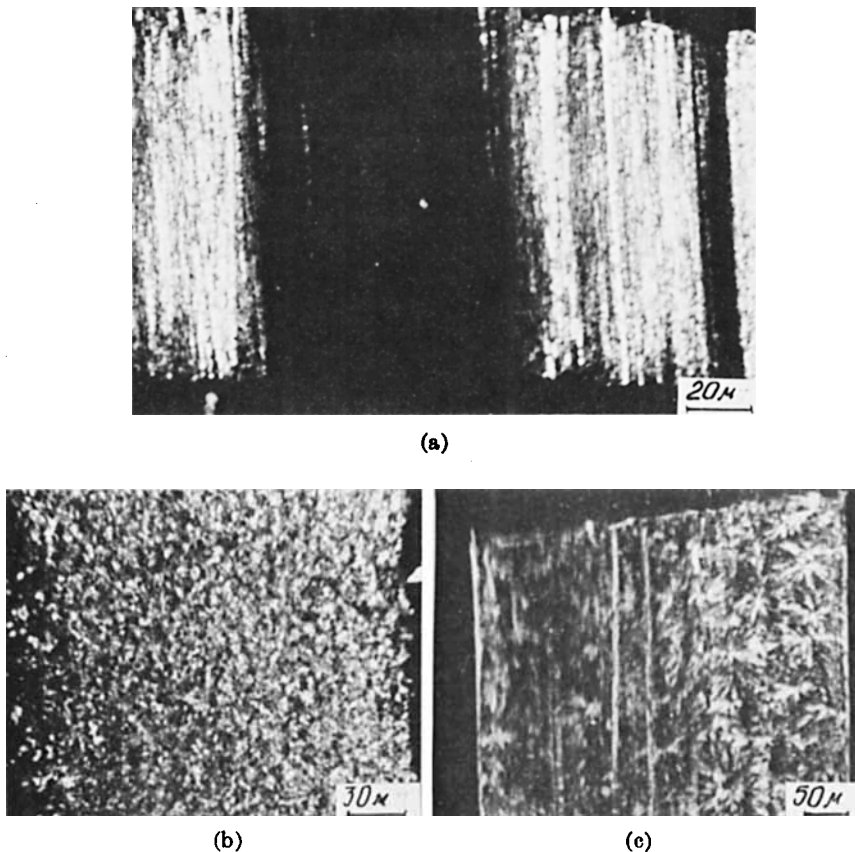
Fig. 10. Microphotographs of longitudinal section of the extrudate of a mixture of POM + 70% CPA (a) and a fragment of a fibrous tube (b); capillary no. 4, 190°C; $\tau = 2.1 \times 10^6$ dynes/cm²; (c) a fragment of spherulite film formed at $\tau < 10^5$ dynes/cm². Capillary no. 4, 190°C.

It has already been mentioned above that the telescopic mode of distribution of one polymer in a melt of another (on condition that the components are incompatible) was observed by Walczak[11] for PP to which poly(ethyleneoxy-benzoate) was added, and by White and coauthors[12] and Han and Yu[7] for polyolefin–polystyrene mixtures. In the case of short capillaries, the concentricity of the extrudate structure is less pronounced (and at $L/D = 1$ it is practically absent) due probably to the short residence time in the capillary. The values of τ at which the extrudate has a telescopic structure correspond to the region of the sharply pronounced non-Newtonian part of the flow curves.

If the extrudates of mixtures are taken not into the air medium at 20°C but into a mixture of Dry Ice and acetone (−40°C), one can suppress the swelling of the extrudate and fix the structure formed during the flow in the capillary. The examination of the sections (and washed-off fibers) showed that the conditions of cooling (and hence swelling) exert a great effect on the microstructure and diameter of the extrudate and on the mode of distribution of polyoxymethylene fibers (Fig. 11). When the stream is cooled, fiber formation is observed in the axial zone so that the samples washed off from CPA are found to be bundles of con-

tinuous fibers enclosed in a thin fibrous film.   An intensive swelling of the stream leaving the capillary enhances the formation of concentrically arranged tubular membranes, which in the long run leads, at high values of τ, to the telescopic structure of the extrudate.   Microscopic studies of the fiber bundles obtained from the extrudates showed that the swelling leads to the increase of the fraction of short fibers and spheres, and the samples obtained at high shear stresses are sets of concentric tubes.
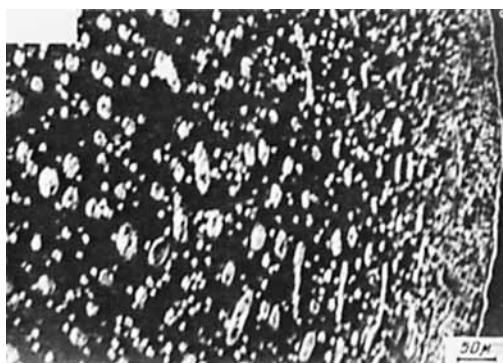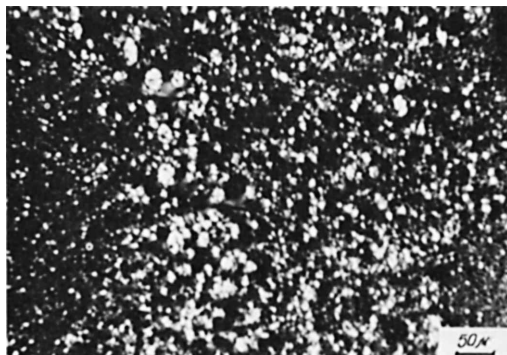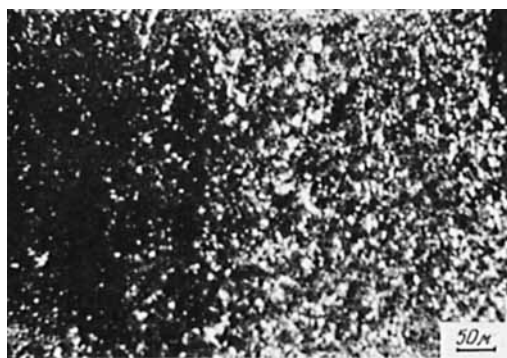

(a)

(b)
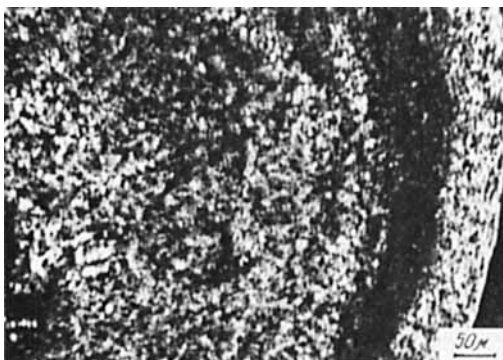
(c)

(I)

Fig. 11 (*continued*)

(a)

(b)

(c)

(II)

Fig. 11. Effect of cooling conditions on the microstructure of the extrudates of a mixture of POM + 70% CPA (cross section). Capillary no. 4, 190°C; (I) extrudates were taken into the air, 20°C; (II) extrudates were taken into a mixture of Dry Ice and acetone (−40°C); shear stresses: (a, b, c) 3.16×10^5, 1.0×10^6, 2.51×10^6 dynes/cm², respectively.

The process of fiber formation in POM/CPA mixtures greatly depends on the content of the high-crystalline component. When its content is decreased, the fiber diameter is reduced, their diameter distribution is narrowed, and the length homogeneity is increased. This is in good agreement with the results available in the literature,[19] according to which for most mixtures of incompatible polymers
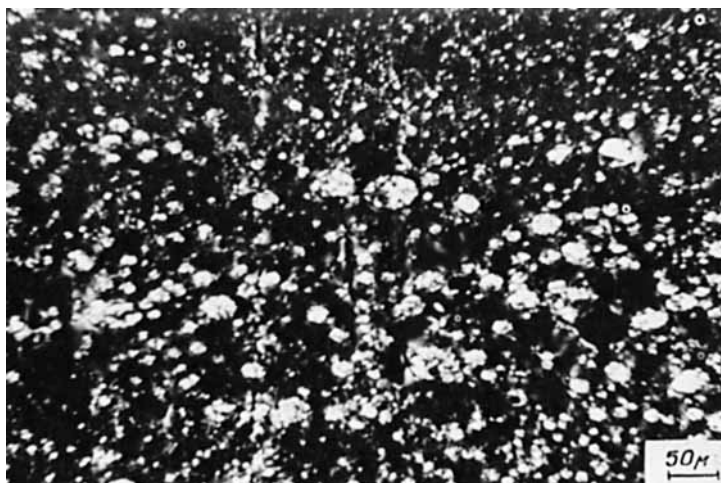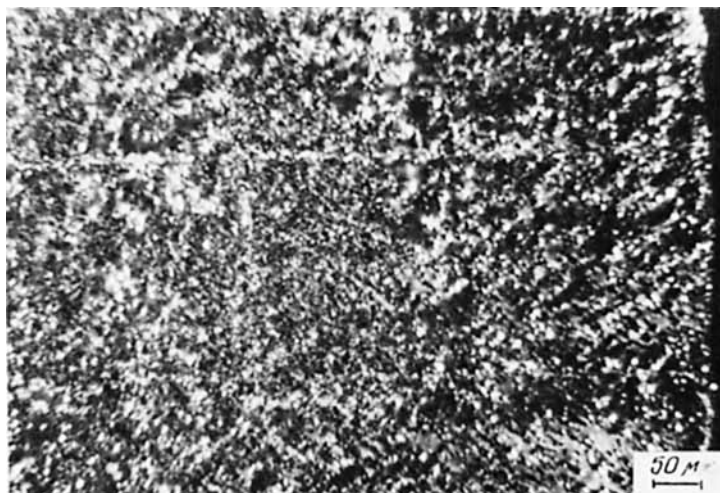
Fig. 12. Effect of mixture composition on the microstructure of extrudates (cross section). (a) POM + 70% CPA; (b) POM + 80% CPA. Capillary no. 4, 210°C; $\tau = 2.34 \times 10^5$ dynes/cm²; (b) $\tau = 2.56 \times 10^5$ dynes/cm².

as the content of the more crystalline component in the mixture decreases there is observed a gradual increase of its dispersity and a narrowing of particle size distribution.

Thus, the microstructure of extrudates is controlled by the composition of the mixture, capillary size, and deformation conditions.

DISCUSSION

A mixture of molten POM dispersed in molten CPA is an emulsion in which the coalescence of dispersed particles is hindered by the high viscosity of the dispersion medium when the mixture is at rest.

When the mixture is flowing, particles of POM are elongated at the entrance into the capillary under the action of a longitudinal velocity gradient (the effect known for forty years[20]). Since the stream in this zone is narrowed, this facilitates the encounter and coalescence of particles. As a result of this, ultrathin, long thread-like streamlets are formed. For the coalescence of the particles to be intensive, the stream at the entrance into the capillary must be considerably narrowed. This may probably account for the low effectiveness of the process of formation of ultrathin fibers when large-diameter capillaries are employed. Since the process under consideration is localized in the entrance zone, ultrathin fibers can be produced in very short capillaries ($L/D = 1$). Moreover, in such cases fibers are formed which are more uniform with respect to diameter and length.

The extremely high mobility of very thin thread-like streamlets and crystallizable fibers and also the slowed-down flow of the medium near the perimeter of the capillary opening and at its wall are responsible for the formation at the stream periphery of ultrathin tubular membranes (tubes). In the zone adjacent to the tube at the capillary wall, the concentration of POM is found to be decreased. Therefore, the next tube concentric relative to the extreme one is formed in the zone of the stream where there is a rather high concentration of thread-like streamlets or crystallizable fibers. In this way, the layered structure of the extrudate is formed. With decreasing velocity of the stream (shear stress), the processes of coalescence of streamlets and sticking of crystallizable fibers are facilitated—the tubes become thicker and their cylindricity may be disturbed. The conditions of tube formation are the least favorable at the stream axis where the linear velocity of the medium is the highest, and, what is particularly important, the stream does not change its direction at the entrance into the capillary. Therefore, the presence of the thinnest fibers is observed in the central zone of the stream.

It is important to note that the layered structures oriented in the direction of the stream are observed not only in POM/CPA mixtures but in the original POM as well, especially at high shear stresses (Fig. 7a). A layered structure like those described above has been observed very clearly by Kovriga and coauthors[20] in POM samples produced by molding.

In the light of what has been said above, it becomes clear that the presence of ultrathin POM fibers in the flowing matrix is responsible for the exceptionally strong effect of extrudate swelling. Of interest in this connection is the work of Busse,[22] in which a 2.5-fold increase of the swelling of the extrudate of polyethylene and polystyrene was observed after the introduction of small amounts (fractions of a per cent) of long and thin Teflon fibers. Mention should also be made of the work reported in the literature.[23] It has been shown in this work that the beginning of crystallization of polyethylene on extrusion through the capillary is accompanied by the considerable swelling of the extrudate. Of importance are the experiments described above and concerned with the rapid freezing of the extrudate emerging into the Dry Ice–acetone mixture. The sections of the extrudate after being heated to room temperature do not practically change in their dimensions (are indefinitely long). But on heating the extrudate to 150–170°, its diameter increases and attains the size typical of unfreezed extrudates.

The swelling of the extrudate causes a sharp change in the stream profile—a change in their direction of movement of fibers and tubes, which may lead to

their breakdown.   This agrees with data reported in the literature,[7] which show that in the course of the cooling of extrudates of polyolefin–polystyrene mixtures emerging from the capillary, there is observed a change in the microstructure of the system accompanied by the breakdown of the dispersed phase domains elongated in the flow direction and by the formation of droplets.

At present we cannot state where the thread-like streamlets of molten POM begin to be converted on extrusion into crystallizable fibers.   But the possibility of change of the phase state of POM under the influence of intensive deformation should be taken into consideration.   Indeed, it is known from the literature[24] that POM differs by the extremely high rate of crystallization and the absence of the induction period of crystallization.   This is due to the relatively high ordering of the melt structure.   Therefore, shear and extension may initiate the crystallization of POM in the same way as known for other polymers.[25,26] Attention should also be given to the work by Mikhailov and Nedkov,[27] in which it has been shown that at temperatures higher than 160°C there are formed "plastic" crystals of POM.

The cause of a considerable decrease in the viscosity of mixtures as compared to the viscosity of the original components still remains obscure.

In conclusion, it is necessary to point out that most of the effects described in this work are typical of a wide range of crystallizable and amorphous polymers of different composition, including mixtures of crystallizable polymers and elastomers.   In such cases, fiber formation is observed not only when a crystallizable polymer has been previously distributed in an amorphous one in the form of finely dispersed powder.   The components of the mixture may be in the form of granules or elastomer-in-block and powdered or granulated crystalline polymer. In such cases, fiber formation is observed on repeated extrusion of molten mixtures.   The first extrusion of the melt provides homogenization of the mixture, and only after the second and third forcings through the capillary is there observed intensive fiber formation.   Even in the case of mixtures containing highly dispersed powders of a crystalline polymer, the repeated extrusion of the molten mixture leads to the formation of a more highly dispersed system—the fibers become thinner and the number of large-size compact formations is reduced.[6]   Thus, the structrue of the crystalline phase of the extrudate is governed by the following factors: the initial state of the dispersed phase of the crystallizable polymer; the conditions under which thread-like and film streamlets are formed in the entry zone of the duct, through which the extrusion is effected; the conditions of flow of the molten mixture in it; crystallization; and the effect of extrudate swelling.   This is a complex set of rheological and crystallization processes taking place at all the stage of the movement of the mixture from the entry zone up to the moment of swelling and solidification of the extrudate.

References

1. W. Berger and J. Mellentin, *Faserforsch. Textiltechnnol.*, **21**, 288 (1970).

2. K. Friese, *Plaste Kautschuk*, **15**, 646 (1968).

3. J. M. Starita, *Trans. Soc. Rheol.*, **16**, 339 (1972).

4. M. A. Natov and E. Khr. Jagarova, *Vysokomol. Soedin.*, **A8**, 1835 (1966).

5. M. V. Tsebrenko, A. V. Yudin, M. Yu. Kuchinka, G. V. Vinogradov, and K. A. Zubovich, *Vysokomol. Soedin.*, **B15**, 566 (1973).

6. M. V. Tsebrenko, M. Jakob, M. Yu. Kuchinka, A. V. Yudin, and G. V. Vinogradov, *Polym. Mater.*, **3**, 99 (1974).

7. C. D. Han and T. C. Yu, *J. Appl. Polym. Sci.*, **15**, 1163 (1971).

8. C. D. Han and R. R. Lamonte, *Polym. Eng. Sci.*, **12**, 77 (1972).

9. C. D. Han and T. C. Yu, *Polym. Eng. Sci.*, **12**, 81 (1972).

10. N. Minoshita, S. Kobayashi, M. Shimura, and Y. Kinoshita, *Kobunshi Kagaku*, **28**, 953 (1971).

11. Z. K. Walczak, *J. Appl. Polym. Sci.*, **17**, 169 (1973).

12. J. L. White, R. C. Ufford, K. R. Dharod, and R. L. Price, *J. Appl. Polym. Sci.*, **16**, 1313 (1973).

13. Brit. Pat. 1,280,676 (1972).

14. BRD Pat. 1,931,822 (1971).

15. M. V. Tsebrenko, G. V. Vinogradov, A. V. Yudin, A. Sh. Goikhman, and A. I. Benzar, *Vysokomol. Soedin.*, **A15**, 1719 (1973).

16. M. V. Tsebrenko, G. V. Vinogradov, A. V. Yudin, M. Yu. Kuchinka, and V. E. Vishnevsky, *Plast. Massy*, **No. 8**, 43 (1973).

17. M. V. Tsebrenko, G. V. Vinogradov, and A. V. Yudin, *Khimicheskie Volokna*, **No. 5**, 70 (1970).

18. G. V. Vinogradov, A. Ya. Malkin, E. P. Plotnikova, O. Yu. Sabsai, and N. E. Nikolaeva, *Polym. Mater.*, **2**, 1 (1972).

19. N. F. Bakeev, Z. Ya. Berestneva, Z. V. Zharikova, and M. V. Kazhdan, *Vysokomol. Soedin.*, **A15**, 2128 (1973).

20. J. Taylor, *Proc. Roy. Soc.*, **A146**, 501 (1934).

21. V. V. Kovriga, E. A. Saakayan, and R. G. Gumen, *Plast. Massy*, **No. 3**, 60 (1967).

22. W. F. Busse, *J. Polym. Sci.*, **A2**, 1249 (1967).

23. J. H. Southern, N. Weeks, R. S. Porter, and R. Y. Crystal, *Soc. Plast. Eng., Techn. Pap.*, **17**, 232 (1971).

24. V. P. Roshchupkin, N. S. Andreev, and G. K. Goncharov, *Vysokomol. Soedin.*, **A14**, 477 (1972).

25. R. Y. Crystal and J. H. Southern, *J. Polym. Sci.*, **A2**, 1641 (1971).

26. A. Keller and M. J. Machin, *J. Macromol. Sci., Phys.*, **B1**, 41 (1967).

27. M. Mihajlov and E. Nedkov, *J. Polym. Sci. C*, **No. 38**, 33 (1972).