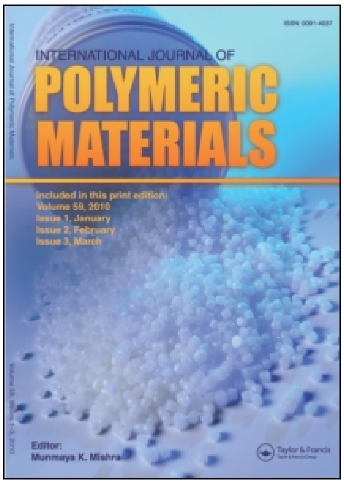

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Fibrillation of Crystallizable Polymers in Flow Exemplified by Melts of Mixtures of Polyoxymethylene and Copolyamides

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Fibrillation of Crystallizable Polymers in Flow Exemplified by Melts of Mixtures of Polyoxymethylene and Copolyamides

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In extrusion (or in extension) of melts of mixtures of a number of polymers, which differ essentially in the rate of crystallization, degree of crystallinity or melting temperature, the rapidly crystallizable component of a mixture forms tens and hundreds of thousands of very thin fibres of practically infinite length, whose diameter depends on the composition of the mixture and the extrusion conditions. This also refers to mixtures of crystallizable and amorphous polymers.

After the polymer forming the matrix is extracted with a solvent (from the solidified extrudate) the high-crystalline dispersed component is in the form of a bundle of extremely thin fibres with a diameter less than one micron.

INTRODUCTION

Considerable attention has recently been paid to the phenomenon of fibrillation in homopolymers. One may cite, for example, very interesting publications by R. S. Porter and coworkers,[1,2] who observed the easy splitting into fibres of extremely high-oriented films of linear polyethylene. The method of fibrillation of oriented films of polypropylene has found industrial application. In the case

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of block copolymers such as, for example, block copolymers of butadiene and styrene, there are obtained, at definite ratios of the components, ordered cylindrical formations of hexagonal structure, arranged in the form of domains.[3,4] Other examples might also be cited as to the formation of highly ordered supramolecular structures, accompanied by the fibrillation or building of unidimensional and two-dimensional formations.[5] Attention should also be paid to the specificity of the crystallization of polymers from their solutions during mixing.[6]

Of considerable interest is the study of the formation of fibres of small diameter and films of small thickness in the extrusion of mixtures of polymers, one of which has a higher melting point and is more rapidly crystallizable, while the other must be amorphous or crystallizable at lower temperatures. The formation of fibres and films must take place under the conditions favourable for the sterically directed process of crystallization of one of the components. This is actually confirmed in experiments on mixtures of polymers of different nature, such as polypropylene–polystyrene and polypropylene–polyethylene mixtures and mixtures of polyoxymethylene with various polyamides and copolyamides. The most significant results have been obtained with mixtures of polyoxymethylene (POM) and copolyamides (CPA) readily soluble in alcohols (for example, in ethyl alcohol). This facilitates on the one hand, the mixing of powdered POM with a copolyamide in an alcoholic solution, and, on the other, the extraction, with alcohol, of the polyamide matrix and isolation of the POM fibres. An extrudate with a diameter of the order of 1 mm may contain tens and hundreds of thousands of POM fibres of practically unlimited length. Analogous results can be obtained in the extension of molten mixtures of POM and polyamides. In this study, we discuss the results obtained in the extrusion of molten mixtures of polyoxymethylene and copolyamide through capillaries at rather small pressure drops.

EXPERIMENTAL

We have studied mixtures of a formaldehyde copolymer containing 2% of 1,3-dioxolane (POM) and mixed copolyamide (CPA), which is a copolymer of caprolactam (44 percent), hexamethyleneadipate (37 percent), and hexamethylenesebacate (19 percent). The characteristics of the polymers used are listed in Table I.

The polymers were mixed as follows. Granules of polyamide together with stabilizing agents for POM were dissolved in ethanol at 60°C. To the solution was added a weighed portion of powdered POM and the resulting suspension was thoroughly mixed. When the alcohol evaporated, the mixture was dried to constant weight in a vacuum at 60°C.

TABLE I

The characteristics of starting polymers

Polymer	External appearance	Intrinsic viscosity in dimethylformamide at 150°C	Melting temperature according to DTA data, °C	Stabilizing agents, percent by weight
POM	Highly dispersed	0.56	171	0.5 of dicyanodiamide and 0.5 of 2,2′-methylene-bis-(4-methyl-6-tert-butylphenol)
CPA	Granules	0.270	165	—

The rheological properties of the molten mixtures were investigated at a temperature of 190°C on a capillary constant-pressure viscometer[7] over the range of shear stresses (τ) from 1.94×10^4 to 4.0×10^5 dynes/cm^2. The root-mean-square error (a confidence of 0.95) in the determination of the viscosity of the melt ranged from 2 to 5 percent, and the reproducibility of experiments was not less than 97 percent.

Mixtures of POM and CPA were prepared in all the cases (except where otherwise specified) by using a 20-percent solution of copolyamide in ethanol.

To investigate the phenomenon of fibre formation from molten mixtures of the polymers indicated, extrudates were obtained (on a viscometer MB-2[7]) with a length of 100 mm under the following conditions (unless otherwise specified): the extrudate was cut off at a distance of 20 mm from the exit of the capillary. The diameter of the capillary was 0.8011; the capillary length, 8.00 mm; $t = 190$°C; $\tau = 3.9 \times 10^5$ dynes/cm^2; the duration of melting and tempering in the chamber of the viscometer was 12 min; the polymer flows freely into the air atmosphere at a temperature of 20°C. The diameter of the successive portions of extrudate along its length was as follows: 0.98, 1.02, 1.05, 1.08, 1.11, 1.14, 1.17, 1.21, 1.26, 1.32, 1.38 mm. These data and all those discussed below are related to the extrudate of a mixture of 40 percent of POM and 60 percent of CPA.

The nature of the extrudate structure formed was examined in thin lateral or longitudinal sections by means of an interference-polarizing microscope. The cuts were obtained on a portion of the extrudate having a length of 10 mm, the upper edge of which was at a distance of 20 mm from the exit of the melt from the capillary. To prepare sections, a portion of extrudate having a length of 10 mm was covered with epoxy resin in a gelatin capsule and placed in a thermostat ($t = 50$°C) for 48 hours to be solidified. Sections 10–15 microns thick were made with the aid of a piezoelectric ultramicrotome. Since the copolyamide was partially crumpled during the cutting, lateral sections were, as a rule, elliptical in form. The sections were examined under a microscope (magnification 100-1270) and photographed. The copolyamide was found to be completely dark in the vision field of the microscope and structural formations of polyoxymethylene were seen against its background.

The present work is devoted to a study into the effect of the conditions in which the polymers are mixed and the extrusion conditions (melt temperature, shear stress, capillary diameter, the number of successive extrusions of the mixture through the capillary) on the process of fibre formation (the number of fibres formed, their mean diameter, diameter distribution, the form of the cross-section).

To obtain information on the distribution of diameters of the polyoxymethylene fibres cross sections of the extrudate were examined under the microscope at a magnification of 900. The fibre diameters were measured in a section strip 15 microns wide. The arrangement of the strips is shown in Figure 1. The number of strips in one section was 6. The diameter distribution was calculated on the basis of the data for 10 sections. The total number of fibres (N), for which the diameters were measured, was about 2000. The numerical fraction of fibres of a given diameter was found as $\Delta N/N \times 100$ percent, where ΔN is the number of fibres of a given diameter d_i. Knowing the diameter distribution, we calculated the mean diameter ($\bar{d}$):

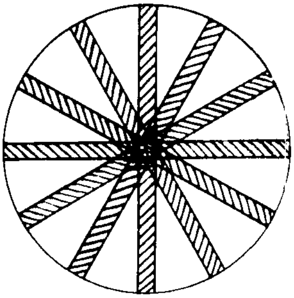

FIGURE 1 The arrangement of strips for which the calculation was carried out and the diameters of polyoxymethylene fibres were determined.

$$\bar{d} = \sum_{i=1}^{n} d_i \, \Delta N/n$$

and the mean surface area, $\bar{S} = \pi \bar{d}/4$, of one fibre.

The mean number (Z) of fibres in the extrudate of known diameter and composition was determined from the relation

$$Z = S/S$$

where S is the total surface area occupied by all the polyformaldehyde fibres in the cross-sectional area of the extrudate of known diameter and composition.

The total number of fibres z was also found by the gravimetric method:

$$Z = m/\bar{m}$$

where m is the weight of all the fibres in the extrudate (having a length of 10 mm) of known diameter and composition. Here m is the mean weight of one polyoxymethylene fibre

$$m = (\pi \bar{d}^2/4)l\gamma$$

where l is the length of fibre, equal to 10 mm, and γ is the specific gravity of fibre, equal to 1.418 g/cm^3. The specific gravity was determined by the gradient-tube method[8] in a mixture of CCl_4 and $C_6H_5CH_3$.

The washout of copolyamide from the fibre was accomplished in a Soxhlet apparatus with ethanol at 75°C. The time required to remove CPA depends on the size of the extrudate and the conditions of its extrusion. As a result, a bundle of very thin polyoxymethylene fibres was obtained. The mean diameter, the diameter distribution and the number of fibres in a bundle were determined in the same way as for an unextracted extrudate.

The relative error in the determination of $\bar{d}$ and Z (0.95 confidence) was ± 10 percent.

RESULTS AND DISCUSSION

The viscous properties of molten mixture of POM and CPA

The results of measurements of the viscosity of molten mixtures of POM and CPA over the entire range of compositions at various shear stresses are presented in Figure 2. As seen from this figure, the viscosity-composition curves lie at all the shear stresses above the values of viscosity of the melt of the starting components and are characterized at $\tau < 2.5 \times 10^5$ dynes/cm^2 by the presence of maxima in the region of ≈ 60 and 90 percent content of copolyamide. At the extreme points the viscosity of the melt increases by a factor of 2 or 2.5 as compared with the viscosity of the melt of starting components. The process of fibre formation was studied mainly for a mixture corresponding to 60 percent content of copolyamide.

Effect of the concentration of a solution of copolyamide

The concentration of the solution (in ethanol), from which the polymers were mixed, varied within the range of 5 to 30 percent. The experiments

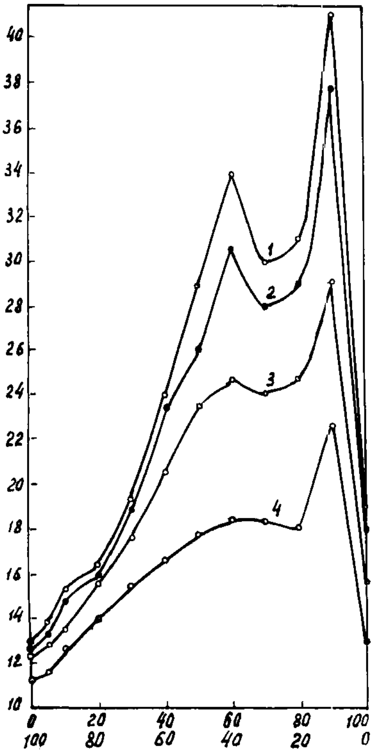

FIGURE 2 The composition dependence of the viscosity of a molten mixture of POM and CPA after the first extrusion through a capillary at t = 190°C. The curves 1–4 correspond, respectively, to the following shear stresses: 0.6, 0.9, 1.8, and 3.5 dynes/cm^2.

carried out have shown that when the concentration of CPA in alcohol exceeds 20 percent, the solutions become extremely viscous and inconvenient for mixing. On the other hand, if the solution concentration decreases, this leads to the increase of the number of large particles of POM, unevenly distributed in the copolyamide matrix. This is illustrated by the photomicrographs (in polarized light) of the sections of extrudates of a mixture of 40 percent of POM and 60 percent of CPA, obtained from a 20 percent solution of polyamide (Figure 3) and also from a 10 percent solution (Figure 4). Thus, as the concentration of the polyamide solution decreases (below 20 percent), the process of fibre formation of POM is noticeably impaired. Probably, the distribution of the POM particles in the copolyamide solution become less uniform with dilution. In all further experiments, a 20 percent solution of CPA was used to prepare mixtures of POM and CPA.

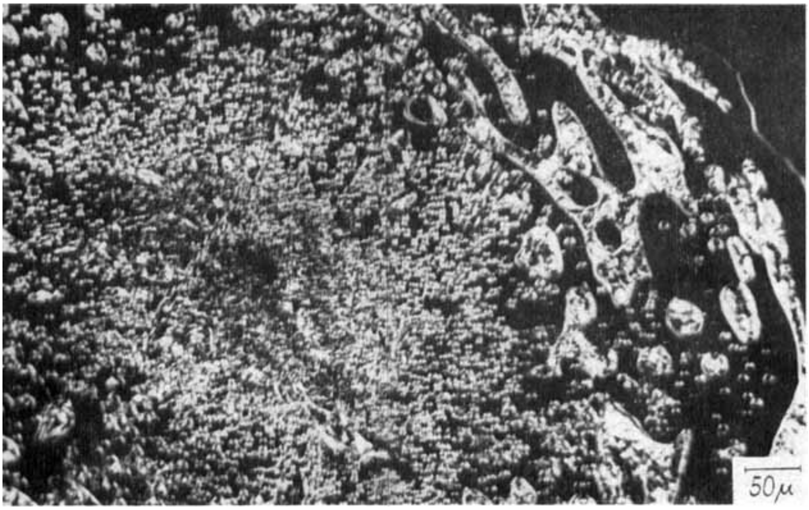

FIGURE 3 Photomicrograph of a cross section of an extrudate of a mixture of POM and CPA. The mixing was carried out from a 20 percent solution of CPA in ethanol.

FIGURE 4 Photomicrograph of a cross section of an extrudate of a mixture of POM and CPA. The mixing was carried out from a 10 per cent solution of CPA in ethannol.

Effect of the capillary diameter

At constant shear stress (3.9 × 10^5 dynes/cm^2) we obtained extrudates on capillaries of the following diameters: 0.42; 0.80; 1.17; 2.16; 3.23 mm. The examination of the photomicrographs of the cross sections has shown (Figures 3 and 5) that the diameter distribution of polyformaldehyde fibres is most uniform in extrudates obtained from a capillary of diameter 0.8 mm (about 70 percent of all the fibres have a diameter of less than 2 microns). The uniformity of the diameter distribution for all the other capillaries used is worse. With increasing capillary diameter the number of layered structures (of the film type) along the extrudate surface, the number of relatively thick fibres (with a diameter of up to 60 microns) and also the number of large formations with an irregular cross-section increase. Extrudates from capillaries of 2.16 and 3.23 mm have a concentric structure: regions with thin fibres alternate with films (Figure 5). Because of this, the extraction of copolyamide becomes very difficult (the process takes more than 14 hours).

Effect of shear stress

For the shear stress changing even within a relatively narrow range (6.2 × 10^4 to 3.9 × 10^5 dynes/cm^2) it has been found that with decreasing τ the ability of POM to form ultrathin fibres in the matrix of copolyamide becomes worse: the number of thin fibres decreases and the fraction of amorphous formations increases (Figures 3 and 6). Thus the magnitude of shear stress is one of the determining factors in the process of fibrillation.

Effect of the number of repeated extrusions through the capillary

The extrudate obtained from a capillary of 0.8 mm diameter at $\tau = 3.9 \times 10^5$ dynes/cm^2 and 190° was ground by cutting and then pressed into tablets and again forced through the capillary under the same conditions. The extrudate was again cut, pressed into tablets and again forced through the capillary. The examination of the photomicrographs (Figures 3, 7 and 8) has shown that none of the factors considered above affects the ability of POM to crystallize in the form of very thin fibres as the repeated extrusions. After two extrusions the shell of the extrudate surface and amorphous formations practically disappear; but films and fibres with a diameter of about 30 microns are still encountered. After a third extrusion the picture changes qualitatively, polyoxymethylene forms thin fibres uniformly over the entire section. What has been said above is illustrated by the data presented in Table II.

The three successive extrusions result in an almost twofold decrease of the fraction of large-diameter fibres. It should be specially stressed that though

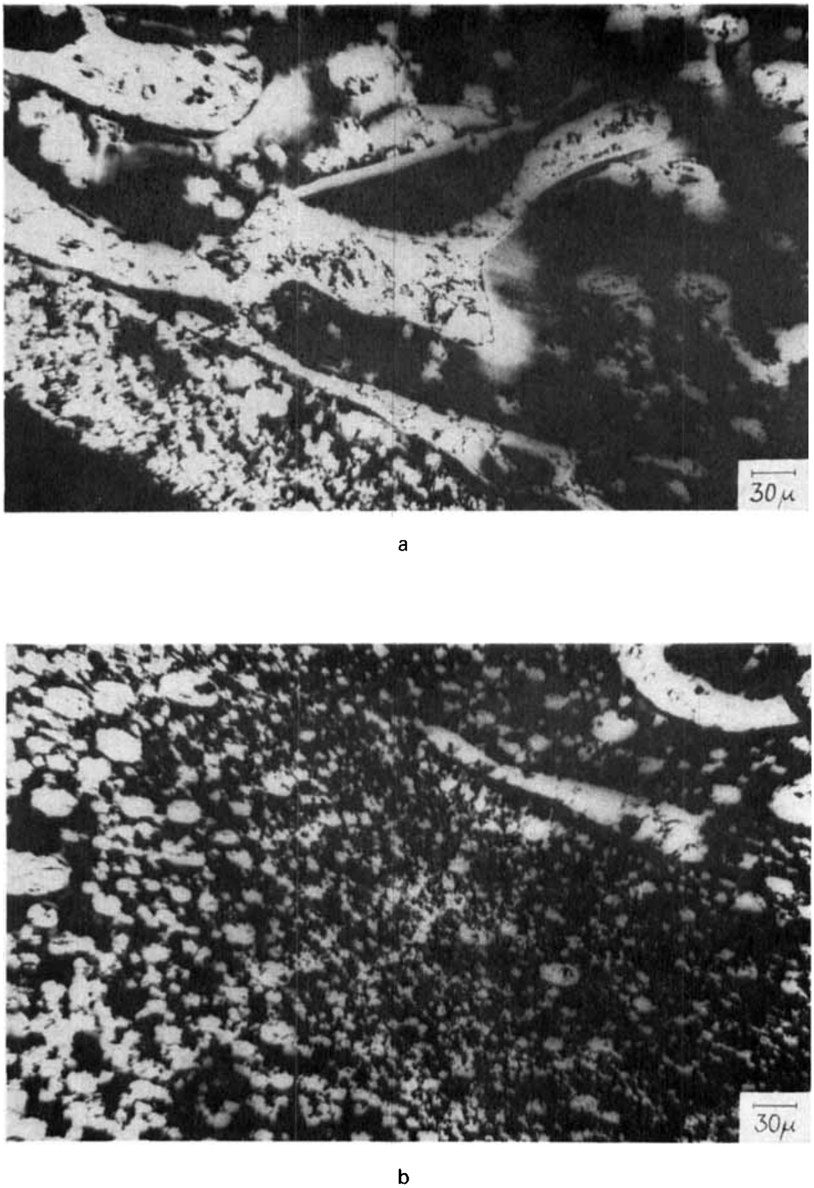

FIGURE 5 Photomicrograph of a cross section of the extrudate obtained from a capillary of 3.23 mm diameter: a—surface layer of extrudate; b—centre of extrudate.

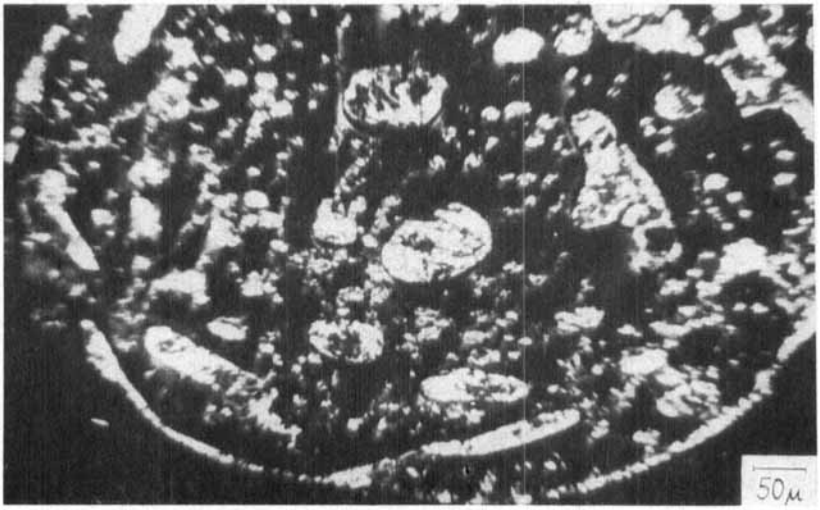

FIGURE 6 Photomicrograph of a cross section of the extrudate obtained at a shear stress of 6.2 × 10^4 dynes/cm^2.

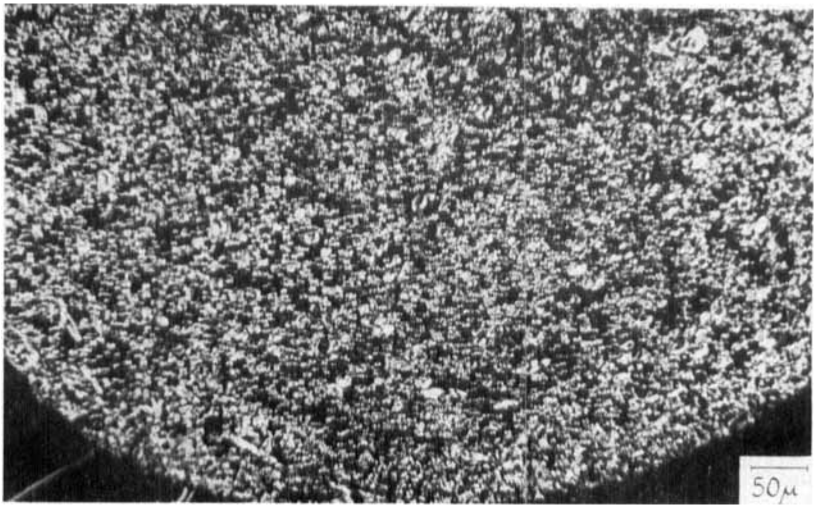

FIGURE 7 Photomicrograph of a cross section of the extrudate obtained after the threefold extrusion of a mixture of POM and CPA through a capillary.

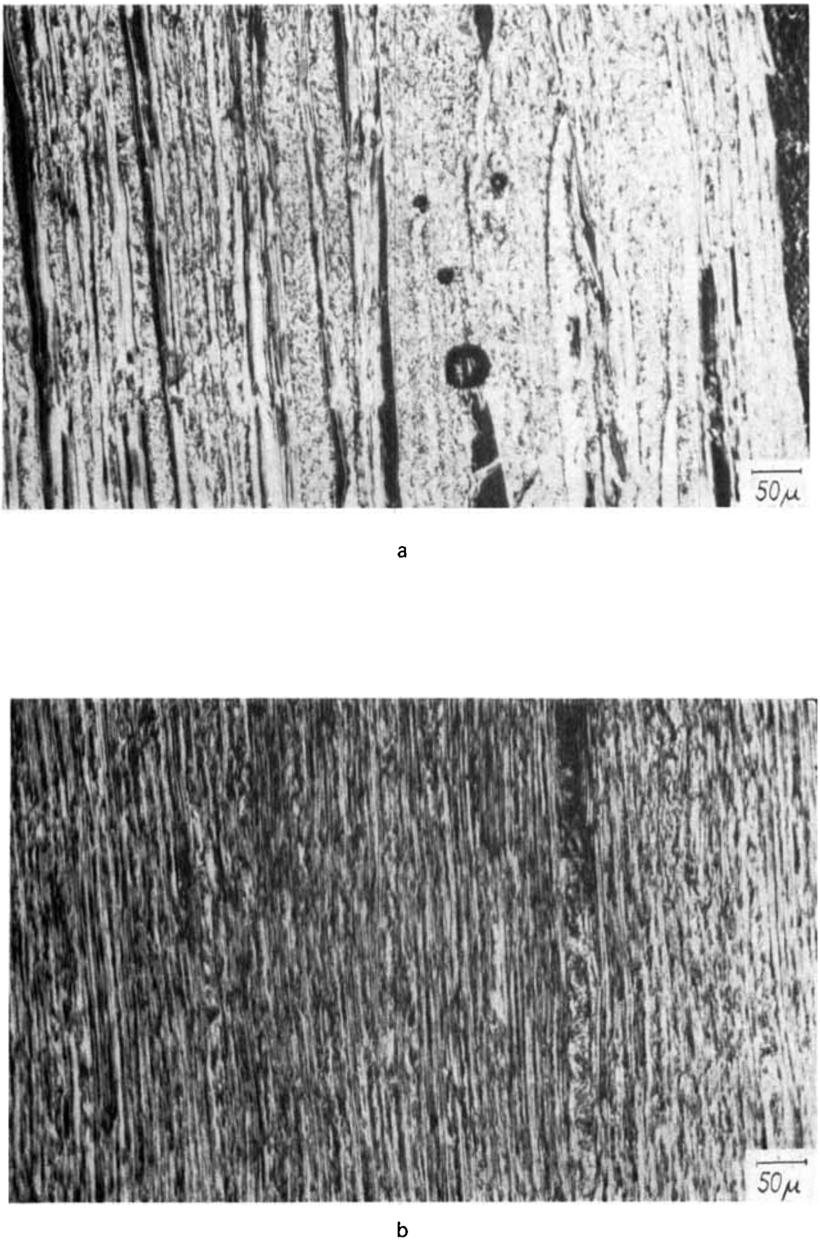

FIGURE 8 Photomicrograph of longitudinal sections of extrudates: a—after the first extrusion; b—after the third extrusion through a capillary.

TABLE II

Distribution of fibres in extrudates and in bundles of fibres washed off from CPA as a function of the number of extrusions through capillary

Sample and extrusion no.		Percentage fraction of fibres of definite diameter											Mean diameter $\bar{d}$, microns
	Fibre diameter	0.9	1.9	2.8	3.7	4.7	5.6	6.5	7.4	8.4	9.3	> 10	
First extrusion	Extrudate	50.7	18.4	9.0	6.2	5.4	3.0	2.1	1.7	0.9	0.6	2.1	2.53
	Bundles of fibres after washout of CPA	7.3	12.5	14.6	14.9	11.2	6.8	5.7	5.2	3.9	2.1	15.7	6.03
Third extrusion	Extrudate	46.6	23.6	10.6	6.5	4.9	2.3	2.1	1.2	1.1	0.3	1.1	2.28
	Bundle of fibres after washout of CPA	20.2	29.7	17.8	11.5	8.7	3.7	1.9	1.5	1.3	0.9	2.8	3.13

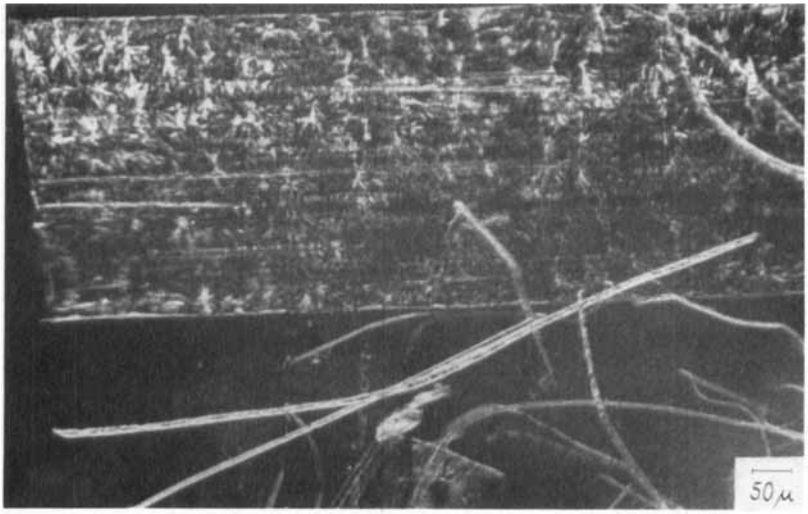

FIGURE 9 The appearance of a polyoxymethylene film contained in a bundle of fibres obtained after the washout of CPA from extrudate. The extrudate is the one obtained after the first extrusion.

there are layered structures of the film type (Figure 9) in the extrudate after one extrusion (and in a bundle of fibres after the washout of CPA), they disappear completely as a result of three-fold extrusion.

The difference between the first and the third extrusion becomes more sharply pronounced on washed-off fibres (Table II).

It might be supposed that such a strong effect of the number of extrusions through the capillary is associated with the increase of the total time of residence of the molten mixture in the chamber of the viscometer. The experiments however have shown that increasing the residence time (from 12 to 36 minutes) prior to extrusion impairs the fibre formation (Figures 3 and 10): POM is found to aggregate into large formations. The same effect is caused by a rise of temperature.

As is known, conditions of laminar flow in extrusion improve the homogenization of polymer mixtures. Evidently, this circumstance is largely responsible for the effect of repeated extrusions of mixtures through the capillary on the process of specific crystallization of POM in the form of fibres.

The investigations carried out have shown that repeated extrusion substantially alters the viscoelastic properties of a molten mixture of POM and CPA. With each further extrusion the viscosity of the melt increases regularly (Figure 11) and higher and higher elastic deformations accumulate, which is evidenced by the swelling of the molten polymer forced out of the capillary of 0.8 diameter and 8 mm length (Table III).

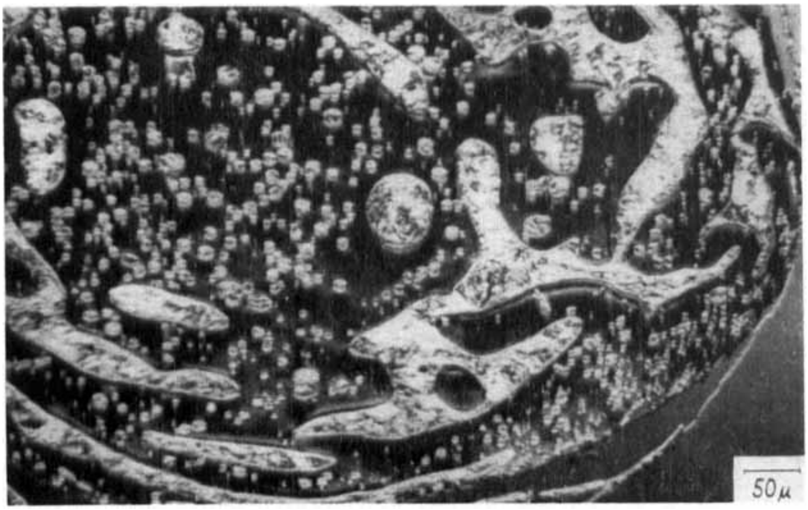

FIGURE 10 Photomicrograph of a lateral section of the extrudate obtained when the time of melting and tempering of a mixture prior to extrusion was 36 min.

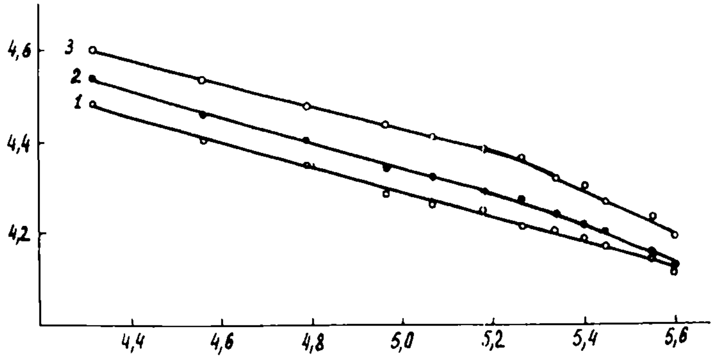

FIGURE 11 Dependence of the viscosity of a molten mixture of POM and CPA on the shear stress at 190°C. The curves 1–3 correspond to the first, second, and third extrusions, respectively. The logarithmic scales—for the viscosity in poises and the shear stress in dyne/cm^2.

TABLE III

The effect of repeated extrusions through the capillary on the swelling of an extrudate of a molten mixture of 40 percent POM and 60 percent of CPA (t = 190°C)

	Diameter of extrudate in mm at a distance of 120 mm from exit from the capillary		
$\tau \times 10^5$ dynes/cm^2	1st extrusion	2nd extrusion	3rd extrusion
3.9	1.38	1.59	1.95
1.8	1.24	1.54	1.92
0.62	1.11	1.45	—

Effect of the extraction of copolyamide

The data presented in Table II show that the process of extraction of copolyamide with alcohol (the temperature is 75°C and the duration of extraction in a packet of tight filter paper is about 3 hours) has a substantial effect on the diameter distribution of fibres; for example, the fraction of thin fibres decreases as compared with their fraction in the extrudate. An examination under the microscope of a bundle of fibres from the extrudate extracted in a packet of tight filter paper has shown that in the course of extraction a large number of thin polyoxymethylene fibres are ruptured, forming short fibres and spherical particles (Figure 12), which in the case of extraction in a packet remain in the bundle. Table IV gives the numerical fractions of fibres of

FIGURE 12 The appearance of short fibres and "spherical" particles of POM (resulting from the washout of CPA) in a bundle of continuous fibres.

TABLE IV
Numerical distribution of fibres and spheres in a bundle of polyoxymethylene fibres after extraction of polyamide

	Particles		
	Percentage fraction of		
Number of extrusion	Fibres 0.1 mm in length	Fibres less than 0.1 mm in length	Spheres
First extrusion	10.4	14.7	74.9
Third extrusion	8.6	9.8	81.6

different length and spherical particles in a bundle after the extraction of polyamide. It turned out that the numerical fraction of fibres less than 0.1 mm in length and spheres totals about 90 percent, and the fraction of fibres more than 0.1 mm in length is only 10 percent. The calculations however have shown that spherical particles and short fibres constitute about 0.2 percent by weight as compared with the fraction of continuous fibres.

Since the diameter of "spherical" particles does not exceed 4 microns (Table V), they cannot be regarded as being the original powdered polyoxymethylene that has not participated in the process of fibre formation (the average size of the particles in the POM powder being around 53 microns). A thorough analysis of lateral sections of extrudates has also confirmed that polyoxymethylene fibres are continuous in length and that there are no spherical formations of POM in the extrudate. Evidently, the above-mentioned short fibres and "spherical" particles of POM result mainly from the rupture of the thinnest POM fibres during the extraction of copolyamide in alcohol.

TABLE V

Diameter distribution of "spherical" particles

	Diameter, microns			
	Percentage fraction			
Number of extrusion	0.9	1.9	2.8	3.7
First extrusion	31	45	18	6
Third extrusion	46.5	40.7	12.8	—

The preliminary results of X-ray structure analysis enable one to suppose that the process of extraction of copolyamide with alcohol at 75°C is accompanied by a radical change of the crystal structure of polyoxymethylene, which, however, is the subject of a special investigation.

The treatment of quantitative data on the distribution of polyoxymethylene fibres obtained from a molten mixture of 40 percent of POM and 60 percent of CPA have shown that the mean diameter of fibres in the extrudate is equal to 2 microns, that of the fibres in the bundle washed off from CPA is 3 microns, and the number of fibres is 107,000 and 56,000, respectively (Table VI).

The mean diameter and number of polyoxymethylene fibres obtained from a molten mixture of POM and CPA are determined, apart from the factors discussed in the present work, by the composition of the mixture. With increasing content of copolyamide (above 60 percent) the mean diameter of fibres decreases substantially and may reach tenths and hundredths of a micron.

The observed phenomenon of specific crystallization (in polymer mixtures)

TABLE VI

The characteristics of polyoxymethylene fibres produced from molten mixtures of 40 percent of POM and 60 percent of CPA

Sample	d, microns	S,	m, mg	S,	m^b	Z
Extrudate[a]	2.28	4.08	57.8×10^{-6}	438,000	6.22	$Z = m/m = 107{,}000$ $Z = S/S = 107{,}000$
Bundle of fibres washed off from CPA	3.13	7.68	109×10^{-6}	438,000	6.05	$Z = m/m = 56{,}000$ $Z = S/S = 57{,}000$

[a] This is an extrudate of 1.274 mm diameter obtained at 190°C, $\tau = 3.9 \times 10^5$ dynes/cm^2 in a capillary of 0.8 mm diameter after three extrusions.

[b] This is the weight of all the polyformaldehyde fibres in an extrudate of 1.274 mm diameter, 10 mm length or the weight of a bundle of fibres 10 mm long, obtained after the washout of CPA from an extrudate of diameter 1.274 mm. This weight was calculated for the extrudate and determined by direct weighing for the bundle of fibres.

in the form of extremely thin fibres of the rapidly crystallizable component and the relationships given above are general and are observed not only in the case of the system in question (POM + CPA) but also for many other pairs of polymers: polyethylene–copolyamide, polypropylene–copolyamide, polyoxymethylene–polyester, polyoxymethylene–polystyrene, and others.

CONCLUSION

It has been shown in the present work that in extrusion (or in extension) of molten mixtures of a number of polymers, which differ markedly in the rate of crystallization and in degree of crystallinity or melting temperature, there is observed a specific crystallization of the rapidly crystallizable component of the mixture in the form of a multitude of extremely thin fibres of practically unlimited length. After the extraction (from the solidified extrudate), with a suitable solvent, of the polymer forming the matrix the highly crystalline component remains in the form of hundreds of thousands of parallelly arranged extremely thin fibres (having a diameter ranging from several microns to tenths and hundreds of a micron) of unlimited length.

It has been established that the process of fibre formation and the properties of the resulting fibres are substantially affected by the conditions of mixing of polymers and also by the conditions of extrusion of the molten mixture (shear stress, temperature, time, capillary diameter, repeated extrusion, the uniformity of distribution of the components in the mixture).

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