REVIEWS

PREPARATION OF ULTRA-THIN FIBRES FROM POLYMER MIXTURES

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The problem of replacing natural leather for shoe uppers and clothing can be solved by organizing the manufacture of high-quality synthetic leather-like materials which are close to natural leather in their properties.

The synthetic leather which is produced at present in the USSR from polyester fibres of low linear density (0.12 tex), based on nonwoven, needle-punched materials, satisfies the requirements imposed on materials for shoe uppers in its basic properties, but has a number of important defects: an increased stiffness, and insufficient mobility of its "structural" elements, which shows up adversely in its comfort. The reason for these indicated defects is insufficient fineness of the elementary filaments which form the structure of the nonwoven base of the leather.

Natural leather is a unique natural composite material, the base of which is very thin collagen fibres, consisting of protein molecules. The transverse dimensions of the collagen fibres are 1-4 μ. Consequently, the decisive factor in the preparation of artificial leather which approaches natural leather in its properties is the preparation of ultra-thin fibres with cross-sectional dimensions of less than 10 μ from fibre-forming polymers.

The technological and apparatus design of processes for the manufacture of man-made fibres which exists at present does not permit one to spin elementary filaments of such fineness from polymers, since the "noise-sensitivity" of the spinning process rises abruptly on reducing the diameter of the elementary filament below 10 μ [2]. This is especially true of the melt-spinning method, by which the polyester, polyamide, and polyolefin fibres are produced which are most widely used in making artificial leather. This leads to an increase in breakage and nonuniformity in the linear density of the fibres obtained.

At present, a number of specific methods of spinning ultra-thin fibres have been developed, which, in principle, can be used in the manufacture of a high-quality artificial leather. These are: deformation of fibres with a high degree of stretch (unoriented stretch) [3], spinning from an emulsion [4], electrostatic spinning [5], and others. However, its own set of difficulties arises in each of these methods. Contemporary textile technology equipment (needle punching, combing, or roving machines) which is used in the manufacture of nonwoven materials is practically unfit for processing such thin fibres. Therefore a compromise should be accepted between fibre (i.e., raw material) fineness and the conditions of textile processing. In this connection, exceptional interest is being displayed at present in developments in the region of preparing ultrathin fibres via the stage of spinning them from polymer mixtures with a two-phase structure of the "fibrils in a matrix" structure (Fig. 1b) or "island in the sea" type (Fig. 1a). The "fibrils in a matrix" structure is characterized by a multiplicity of very thin fibrils of one polymer, disposed in an unordered fashion in a matrix of the other polymer. By an "island in the sea" type of struc-
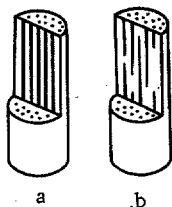

a   b

Fig. 1. Schematic depiction of the "island in the sea" (a) and "fibrils in a matrix" (b) structures.
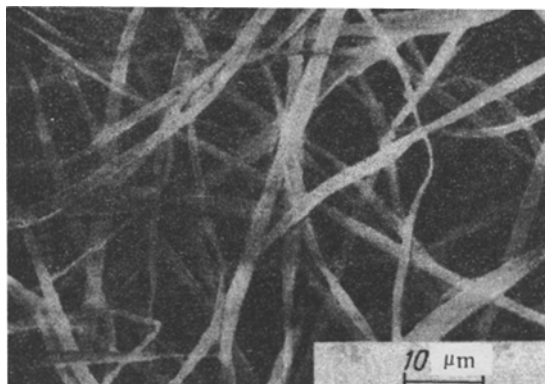
Fig. 2. Electron microscope photographs of ultra-
thin polyester fibres isolated from a mixed fibre
which had been drawn 4-fold.

ture we usually understand a structure analogous to the "fibrils in a matrix" structure, but differing from the latter by an assigned disposition of the fibrillar component in the matrix.

The first of the examined structures (Fig. 1b) can be prepared by extruding a preliminarily prepared mixture of melts from two incompatible polymers through the hole of a common spinneret. Thereupon, the very fine particles of the disperse phase, which, in making up the polymer mixture usually have a form which is close to spherical, are converted into fibrils whose length is determined by the initial size of the disperse phase particles and their degree of deformation during the process of spinning and orientation stretch.

Spinning of the second structure (Fig. 1a) requires the use of special spinnerets with separate delivery of two polymer melts. It is clear that these two structures (in addition to the difference in regularity of fibril disposition) differ in the geometrical characteristics of the fibrillar phase. Because of the specifics of formation of a structure of the "fibrils in a matrix" structure, the fibrils in this structure have a definite, more or less broad distribution in size. This is true of both the crosswise and lengthwise dimensions of the fibrils, since both the first and the second are determined by the dimensions of the particles of the disperse phase in the mixture of polymers from which the structure of the mixed fibre is formed. It is obvious that the particles of disperse phase in the polymer mixture differ from one another in size, which also brings about nonidentity of the fibril dimensions.

In a structure of the "island in sea" type, the cross-sectional dimensions of the fibrils are basically determined by the geometric features of construction of the special spinneret which is used to prepare fibres with this type of structure. Therefore, at a sufficient spinning process stability, the fibrils in a structure of the "island in sea" type have a constant diameter over the whole fibre length. It is understood that in this case the fibril length is practically unlimited.

Spinning fibres with a structure of the "fibrils in a matrix" or "island in a sea" structure makes it possible to overcome the difficulties indicated above, associated with the preparation of ultra-thin fibres and using them in the manufacture of new generation artificial leather. On one hand, since fibres from a mixture of polymers having the indicated structures have the usual thickness, problems of nonuniformity in linear density and elevated fibre breakage in spinning vanish. The removal of the matrix component from such fibres leads to obtaining a whole bundle of ultra-thin elementary filaments (fibrils) (linear density down to 0.001 tex).

On the other hand, removal of the matrix component can be carried out after the stage of preparing the fibre lap on traditional technological equipment in the manufacture of artificial leathers [6]. At present, methods of splitting the matrix-fibrillar structure into elementary filaments have been worked out up to industrial application [7, 8]. To do this, there are used either mechanical methods of acting on a fibre from a mixture of polymers, or temperature methods, or the method of selective solution of one of the components of the mixed fibre. It is interesting that in the latter case, depending on which of the components is dissolved (the matrix polymer or the fibril polymer), one can obtain either a
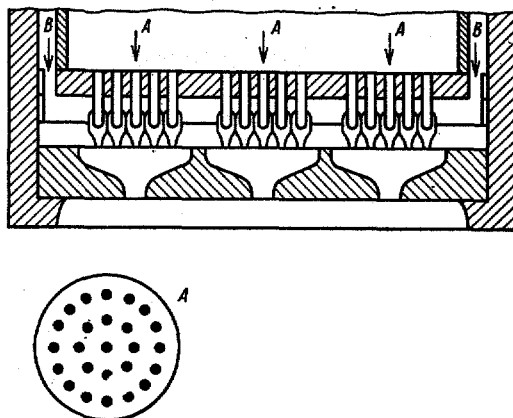
Fig. 3. Spinneret of the Toray Co.
and cross-section of mixed fibre [10].

bundle of ultra-thin fibres (solution of the matrix polymer) or a multiporous fibre (solution of the fibril part of the fibre) [1]. Thus, this solves not only the problem of obtaining ultra-thin fibres, but also the problem of creating a fibrous lap from them. In Fig. 2 we show a microphotograph of a bundle of ultra-thin fibres, which were obtained on dissolving out the matrix component of a fibre based on a polyamide (matrix) — polyethylene terephthalate (fibril) mixture.

Use of the technology of spinning fibres from polymer mixtures to obtain ultra-thin fibres made it possible for the Japanese "Toray" and "Kuraray" companies to set up industrial manufacture of synthetic leather-like materials at the start of the seventies; the base of these consists of fibres having a linear density of 0.1-0.001 dtex [1, 10].

Two schemes of preparing the mixed fibre were used in the manufacture of such leather-like materials. In one of these, special spinnerets of complex construction (Fig. 3) were used, in which several jets of a melt which had the "core-skin" form are brought into a common stream (Fig. 3). By the other scheme, a fibre is spun from a preliminarily prepared mixture of polymer melts, through an ordinary spinneret. As the matrix polymer, the Japanese companies used polystyrene; as the fibrillar component, polyester or polyamide [11]. After the stage of forming the nonwoven lap and impregnating it with a polyurethane binder, the polystyrene matrix is subjected to treatment with an organic solvent (trichloroethylene), as a result of which extraction of the polystyrene takes place, with formation of bundles of ultra-thin polyester or polyamide fibres, which confer on the material a high elasticity and a unique complex of mechanical and physico-hygienic properties. By subjecting the lap of ultra-thin fibres to abrasion, one obtains an artificial chamois (Exane), or by laminating it with a porous polyurethane film, a synthetic leather (Clarino L-26). In external appearance and organoleptic properties, such leather-like materials essentially do not differ from high-quality elastic natural leathers.

The foregoing demonstrates the viability of both schemes of preparing fibre from polymer mixtures for the manufacture of a second generation artificial leather. At first glance, it may seem that the preparation of ultra-thin fibres by the scheme using an ordinary spinneret via the stage of forming a "fibrils in matrix" structure is preferable as compared with spinning a fibre with the "island in sea" structure, since it does not require the use of special spinnerets. Nevertheless, spinning fibres from a melt of a mixture of polymers admits a whole series of scientific and engineering problems.

The process of spinning fibres from polymer mixtures includes the following stages: preparation of a mixture of melts of two polymers; spinning a fibre from the mixture of melts; and orientation stretching.

A number of articles of a review character [12-15] have been devoted to a study of questions associated with spinning fibres having as structure of the "fibril in matrix" type. In these reviews the thermodynamic aspects of the formation of mixtures of incompatible polymers are examined in detail; and also questions of the formation of a disperse structure in the stage of mixing melts of polymers. A knowledge of the principles which determine the qualitative and quantitative characteristics of the disperse structure of a mixture of incompatible polymers undoubtedly has first-degree practical importance, since it is precisely at
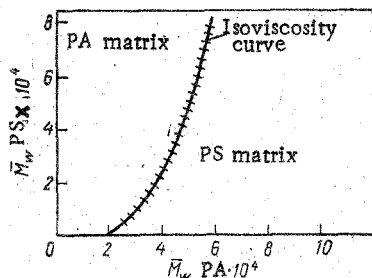
Fig. 4   Fig. 5

Fig. 4. "Phase diagram" of PS — PA system, which de-
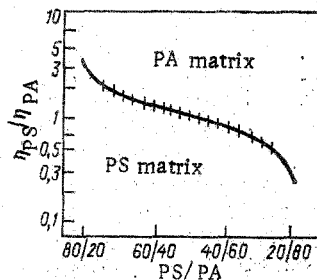termines the structure of the polymer mixture; t =
240°C, $\dot{\gamma} = 10^2$ sec^{-1} [1].

Fig. 5. Dependence between proportions in mixture,
relative viscosity, and matrix-fibrillar phases; t =
240°C, $\dot{\gamma} = 10^2$ sec^{-1} [1].

the stage of preparation of the polymer mixture that such valuable parameters of the final
structure of the mixed polymer as physico-chemical properties and geometric features of the
fibrillar phase are built in.

The degree of dispersity which is attained in the mixing stage depends on the character
and intensity of melt mixing, the rheological characteristics of the two phases, and the sur-
face tension at the interface [12].

It is generally accepted that, on mixing melt of two polymers, if the viscosity and
elasticity of the component which is present in the mixture in smaller amount is higher than
the viscosity of the matrix, then, on mixing, a coarse dispersion of the component present
in the smaller amount in the second component is formed. In the opposite relationship of
viscoelastic characteristics, the component having the lower concentration is dispersed to a
finely-disperse state. If both phases have approximately identical properties, the smaller
component also gives a fine dispersion.

Moreover, the viscoelastic characteristics of the phases, together with the concentra-
tion of the components in the mixture, determine which of the components in the mixture will
play the role of disperse phase, and which that of the matrix phase. In [1], results are
given from a study of the effect of the viscosity characteristics of the polymers being
mixed on the structure of the mixture obtained for the system polystyrene (PS)—polyamide (PA).
In Fig. 4 we show the unique "phase diagram" of the PS—PA-6 system in coordinates of $\bar{M}_{wPS}$ vs
$\bar{M}_{wPA}$, in which, depending on the molecular weight which determines viscosity properties, re-
gions are established in which the disperse phase is either PS or PA. In Fig. 5 we show the
dependence of the ratio of apparent viscosities of the PA and PS at which inversion of
phases takes place on the composition of the mixture. This dependence divides the coordi-
nate plane into two regions, in one of which the matrix component is PA, and in the other is
PS. In Figs. 4 and 5, in the cross-hatched region the difference between the matrix and dis-
perse phases is not discernible.

Knowledge of the dependences examined above makes it possible to prepare a matrix-fi-
brillar fibre with various fibril diameters by selecting appropriate combinations of poly-
mers and mixing conditions [16].

The effect of the surface tension at the interface on the dispersability of one polymer
in the other is rather trivial: the less the surface energy at the interface, the higher
(under otherwise equal conditions) the degree of dispersity of one polymer in the other. In
the theory of emulsion flow, the counteraction of surface tension deformation forces in
spherical drops is taken into account under conditions of shear flow by the use of the dimen-
sionless parameter of [17], $K = \sigma/\dot{\gamma}\eta_0 \, r$, where σ is the value of the interfacial tension, $\bar{\gamma}$
is the shear rate, η_0 is the viscosity of the dispersion medium, and r is the drop radius.
When $K > 10$, a spherical drop is essentially not deformed. Therefore a decrease in surface
tension leads to an increase in the deformability of the disperse phase particles, which fa-
cilitates dispersion of one polymer in the other.

The questions examined relate to the first stage of preparing fibres from polymer mix-
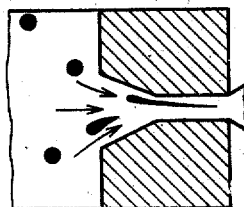
Fig. 6. Conversion of a spherical particle into
a fibrillar formation on elongation of the
stream at the inlet to the spinneret hole [12].

tures with a structure of the "fibrils in matrix" type, specifically, to the stage of prepar-
ing a mixture of melts of the two polymers. The stage of extruding the mixture obtained
through the spinneret hole has no less importance in spinning the disperse structure of the
mixed fibre. In the research indicated above, attention is hardly paid to this stage in
the preparation of fibres from polymer mixtures, although it is very complex in the prepara-
tion of mixed fibres with a matrix-fibrillar structure.

Before going over to an analysis of research pertaining to the stage of fibre spinning
from polymer mixtures, it is necessary to dwell on one small, but very important problem
which arises in the preparation of fibres from polymer mixtures. A polymer mixture which
has been prepared in a mixing device at large shear stresses should be delivered along the
melt line under the action of comparatively low shear stress to the spinneret. Thereupon,
coagulation of disperse phase particles takes place. One of the ways to eliminate this phe-
nomenon is to include elements in the melt line construction which create additional mixing
of the polymer mixture; as these, one can use the recently developed "immobile" homogenizer-
mixers [18-20].

A series of researches by Yudin et al. [21-24] and by Dietrich [25, 26] has been de-
voted to a study of the laws governing the spinning of fibres from polymer mixtures in the
stage of flow of the melt through the spinneret hole. In these, the phenomenon of "specific
fibre-formation" in the flow of a mixture of melts from two polymers through the channel of
a spinneret hole is examined. In distinction from melts of the individual polymers, in
which extension of the melt jet which determines the diameter of the elementary filaments
takes place after exit from the spinneret channel, stretching of the disperse phase parti-
cles in spinning a fibre with the "fibril in matrix" structure takes place both after exit
from the spinneret hole (jet stretch), and also on entry of the polymer mixture melt into
the spinneret channel (Fig. 6). The stretching of the disperse phase particles in the entry
to the spinneret hole is caused by the generation of a lengthwise flow velocity gradient due
to the sharp change in stream cross-section [21, 22, 26]. By analogy with jet stretch, this
process has been called "pre-jet stretch." The magnitude of the "pre-jet stretch" is obvi-
ously determined by the ratio of the flow rates of the melt in the spinneret channel and in
the pre-jet zone.

On exit from the spinneret channel, the particles of the disperse phase which have been
subjected to stretching deformation on entry into the spinneret hole tend toward restoration
of their initial form under the action of elastic forces and surface tension forces [27].
This leads to an anomalously large (as compared with spinning fibres from melts of the indi-
vidual polymers) expansion of the melt jet on exit from the spinneret channel. In [23] it
was noted that the concentration dependences of the degree of expansion of jets leaving the
spinneret hole for the polyoxymethylene—polyethylene and polyoxymethylene—isotactic polypro-
pylene and the ability of the corresponding melts to be spun are similar.

The larger the jet expansion, the less stable is the spinning process. Consequently,
relaxation of the deformation of disperse phase particles on exit from the spinneret channel
is a significantly adverse feature in the process of spinning fibres from polymer mixtures.
Therefore one of the basic problems in preparing fibres with the "fibril in matrix" is sup-
pression of the process of deformation relaxation of the disperse phase particles on exit of
the jet of melt from the spinneret.

Dietrich and coworkers [26] have obtained dependence of the maximum jet expansion on
shear rate and on the length of the capillary. It was shown that the critical value of
shear rate, below which jet expansion ceases to be observed, is very small, while the criti-
cal value of capillary length is very large. Consequently, to avoid jet expansion, it is ne-

cessary either to carry out the process at a very low rate or to greatly increase the length of the capillary channel. Both of these are inapplicable from the technological point of view. What is more, although the structure of the fibre obtained under conditions of an absence of jet expansion was not analyzed, to all appearances in this case we have to do with undeformed disperse phase particles in the spun fibre. Therefore, probably, one of the very real ways of keeping the disperse phase particles in the form of fibrils and ensuring spinning stability is to cool the jets of melt as fast as possible upon exit from the spinneret channel.

There are practically no data in the literature on the effect of the orientation stretching stage on the physico-chemical properties and geometric characteristics of the disperse phase fibres. We do indicate the work of Romankevich et al. [9], in which it was shown that, as a result of orientation stretching of a fibre spun from a polymer mixture, the character of fibril distribution by size changes. The fact that, in addition to the decrease in mean cross-sectional dimensions of the disperse phase, a transition to a narrower size distribution of the disperse phase particles is observed, is interesting. Further studies in this direction may present extremely great interest.

The material examined above does not give an unequivocal answer to the question of which of the ways of preparing ultra-thin fibres (using a complex special spinneret or using an ordinary spinneret) is more promising. However, from our point of view, at an appropriate level of scientific and technological developments, much success in developing ultra-thin fibres can be had by spinning fibres from polymer mixtures. Thereupon, probably, for each system which has practical interest from the point of view of preparing a mixed fibre with the "fibrils in matrix" structure, a thorough search for the technological parameters which ensure development of the required product and stability of the spinning process is necessary.

In favor of this conclusion is the development of mixed fibres for the preparation of synthetic leather-like materials using ordinary spinnerets; the nonwoven based of these consists of still finer elementary filaments (as compared with the leather-like materials developed at the start of the seventies), having a linear density of 0.001 dtex [28]. The preparation of ultra-thin fibres from various polymers will make it possible to considerably enlarge the assortment of materials for the manufacture of outer clothing and shoes, and also for other branches of the national economy.

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