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FORMATION OF A PHASE STRUCTURE OF THE "FIBRILS IN MATRIX" TYPE IN A COMPOSITE FIBRE BASED ON HIGH-DENSITY POLYETHYLENE AND POLYETHYLENE TEREPHTHALATE

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Composite fibres of the "fibrils in matrix" type are promising for the development of a new generation of artificial leathers. When the matrix material is removed by a selectively acting solvent, ultrathin fibres remain which imitate the bundles of collagen fibres in natural leather [1]. The possibility of forming structures of this type on passage of a mixture of polymers through the capillary of a viscometer has been established for various systems. It depends on a number of factors, such as the ratio of the effective viscosities of the polymer pair, the surface tension at the interface, the elastic properties of the components of the mixture, the geometric characteristics of the capillary, and the rate of forcing the melt through the capillary [2]. In [3], the rheological and fibre-forming properties of melts of mixtures of high-density polyethylene (HDPE) and polyethylene terephthalate (PET) were investigated and the possibility was demonstrated of preparing composite fibres with a structure of the "fibrils in matrix" type. In the present work the conditions for forming such a structure in fibre spinning are examined.

The materials for the study were HDPE-1, extrusion type 210-01, HDPE-2, from the Union Carbide Corporation (USA), type 6147, and PET having an intrinsic viscosity, η, of 0.28×10^2 cm^3/g in o-chlorophenol at 298 K. The polymers were mixed in a Brabender (West Germany) plastograph extruder in the molten state at 553°K (rate of rotor rotation, 8 rpm; capillary diameter, 1 mm).

Viscosity properties of the mixture melts were determined using a "Rheoscope-1000" constant speed capillary viscometer from the "Ceast" Company (Italy) which was equipped with a device for taking up fibre, in the temperature range 543-563 K and in the shear rate ($\dot{\gamma}$) range of 10-10^6 sec^{-1} (capillary diameter, 0.82 mm) by the procedure of [4].

The phase structure of the mixtures was characterized by etching monofilaments with a selectively acting solvent (xylene or dichromate mixture), and also by studying lengthwise and transverse sections of the monofilaments under an MIN-8 microscope in reflected polarized light.

Microstructure was studied by the x-ray method under wide diffraction angles in an IRIS-3.0 set-up (CuK_α-radiation, Ni filter in the primary beam, planar photocassette). Diffractograms were obtained on a DRON-3.0 x-ray diffractometer [5]. Specimens were characterized by the differential scanning calorimetry method on a DSK-2 instrument from the Perkin-Elmer Company.

From the dependences of the effective viscosity, η_{eff}, of the HDPE-1—PET and HDPE-2—PET mixtures on shear stress, τ (Fig. 1), it is plain that in the region of τ values from 10^2 to 10^4 Pa the PET melt is a typical Newtonian liquid, but the HDPE-1 and HDPE-2 are typical non-Newtonian viscoelastic liquids. Mixtures of these occupy an intermediate position, the deviation from Newtonian behavior increasing with increase in the HDPE content of the mixture. When $\tau > 10^4$ Pa, the PET also begins to display viscoelastic properties. Thus, depending on shear stress, flow of a Newtonian liquid in a non-Newtonian or two non-Newtonian liquids is realized. At a τ 12.5×10^4 Pa, all the flow curves intersect at a single point (Fig. 1a), where isoviscous flow of the melts of the two polymers is realized; however the elasticity of the two polymers is different thereupon.

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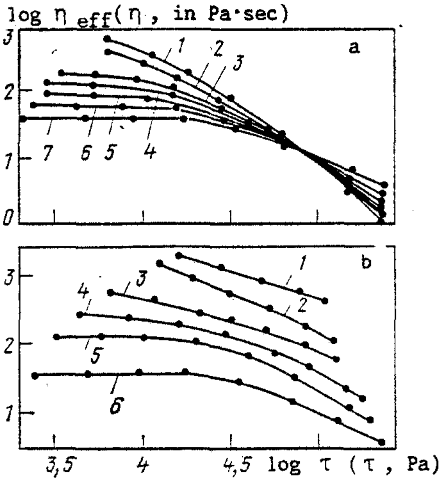

Fig. 1

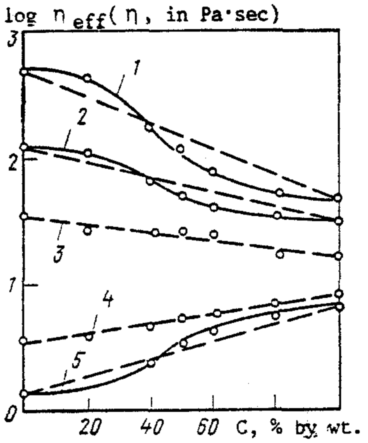

Fig. 2

Fig. 1. Dependence of effective viscosity, η_{eff}, of melts of HDPE-1—PET (a) and HDPE-2—PET (b) mixtures on shear stress, τ, at 553 K: a) 1) 100:0; 2) 80:20; 3) 60:40; 4) 50:50; 5) 40:60; 6) 20:80; 7) 0:100; b) 1) 100:0; 2) 90:10; 3) 75:25; 4) 50:50; 5) 25:75; 6) 0:100.

Fig. 2. Dependence of effective viscosity, η_{eff}, on PET content for HDPE-1—PET mixture at 553 K: 1) $\tau = 6.3$, $k = 11$; 2) $\tau = 25.1$, $k = 4$; 3) $\tau = 63.1$, $k = 1.7$; 4) $\tau = 160$, $k = 1.9$; 5) $\tau = 250$, $k = 5$.

Microscopic study of phase structure was carried out on monofilament specimens, for which, with the objective of reducing the influence of the jet swelling effect on change in the structure of the mixture melt after exit from the capillary, the take-up rate of the fibre was so chosen that the diameter of the spun extrudate was equal to the diameter of the capillary. Thereupon, apparently, changes in fibre structure are less significant than in extrudates taken with abrupt cooling but without appropriate tension in fibre take-up [6], or an annealing of specimens to complete restoration of elastic residual deformations [7].

Analysis of microphotographs of transverse and lengthwise sections of extrudates of the mixtures (Table 1) shows that, practically, at a ratio $k = \eta$ of matrix/η of dispersed component, k, which is equal to or greater than 1, ultrathin fibres of the dispersed component predominate in the system, or at a 60:40 ratio of the components, structures of the type of "interpenetrating networks" which are strongly deformed in the direction of flow. When k is less than 1, the composition consists of spherical inclusions of the component which is contained in smaller amount in the mixture, dispersed in a matrix of the main component.

Data from washing the mixtures with a selectively acting solvent agree with the microscopy evidence. After washing a mixture of 80:20 composition with xylene, ultrathin fibres of PET remain, the linear density of these increasing with increase in τ, as well as the amount of them. After washing a composition of 60:40 composition with xylene or dichromate mixture, a porous fibre remains in each case. This indicates the presence of a structure of the "interpenetrating networks" type in the original fibre; that is, apparently an interchange of phases is taking place at this ratio of the components. On washing a mixture of 50:50 or 40:60 composition at $k \geqslant 1$ fine HDPE fibres remain; but when $k < 1$, the residue consists of particles of spherical form. A comparison of the linear density of the HDPE and PET fibres from the residue after washing a fibre prepared at isoviscous flow shows that the PET fibres are thinner than the HDPE fibres. This is probably caused by the greater elasticity of the HDPE phase. Thus, for stable specific fibre-formation in the preparation of a composite fibre of the "fibrils in matrix" type from HDPE—PET, apparently not only is predominance of the content of the matrix masterial having $k \geqslant 1$, required, but also large shear stresses (at which k is still equal to or greater than 1), and, so far as possible, a low elasticity of the fibril material.

In Fig. 2 we give concentration dependences of the effective viscosity of polymer mixtures at a fixed shear stress. When k is greater or less than unity, the form of the curves

TABLE 1. Effect of Ratio of Effective Viscosities of Components, k, and of Shear Stress, τ, on Phase Structure of Composite Fibre Based on HDPE-1—PET

k	log τ (τ, Pa)	HDPE-1:PET, %			
		80:20	60:40	50:50	40:60
30	3,1	Fib.	IPN	Sph.	Sph.
20	3,5	»	»	»	»
10	3,9	»	»	»	»
5	4,3	»	»	»	»
1,5	4,7	»	»	»	»
1	5,0	»	»	Fib.	Fib.
1,9	5,2	Sph.	»	»	»
5	5,4	»	»	»	»

Notation. Fib. indicates fibres of the dispersed component; Sph. indicates particles of the dispersed component having a spherical form; IPN indicates interpenetrating networks.

has an S-shaped character, the S-shaped form becoming more definitely expressed with the deviation of k from unity. The intersection of the curve for concentration dependence with the line obtained by the rule of logarithmic additivity occurs at a component ratio of 60:40 in the region of phase inversion.

Analysis of the effect of temperature in spinning a composite fibre on the process of specific fibre formation showed that on varying the temperature the viscosity properties of the components of the mixture change to differing extents. Thereupon the conditions for obtaining fibres with the "fibrils in matrix" structure change correspondingly. Thus, an increase in temperature from 553 to 563 K for an HDPE-1—PET mixture changes the ratio of effective viscosities of the starting components and makes it impossible to obtain fibres in which the fibrils are HDPE minifibres, but, at the same time, expands the range of shear stress in which a structure with fibrils of PET is realized.

Investigation of the microphase structure of the fibre by the x-ray method showed that, both in all mixture compositions, and also in the "pure" fibre, the PET is completely amorphous and unoriented. In the HDPE component, on a background of crystal reflexes of the isotropic material there is a weakly-expressed a-texture which is apparently typical of extrudates [8]. A reflex of the monoclinic modification is also noticeable, which indicates the presence of appreciable shear stresses in the system during the extrusion process [9].

Calorimetric studies also confirm that the PET in the mixture is amorphous. However, as a result of warming at 413 K, the PET crystallizes and at 533 K it melts. In the composite fibre, the HDPE melts at 403 K like the starting homopolymer (its degree of crystallinity is 63%, regardless of the composition of the composite).

CONCLUSIONS

Regions of component ratio and conditions for obtaining a composite fibre of the "fibrils in matrix" type have been determined for the HDPE—PET system.

At an HDPE—PET ratio of 60:40, phase inversion takes place and a structure of the "interpenetration networks" type is realized.

Under identical fibre spinning conditions, the formation of a phase structure of the "fibrils in matrix" type can be regulated by varying the temperature.

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PROPERTIES OF POLYQUINOLINES AND OF FIBRES BASED ON THEM

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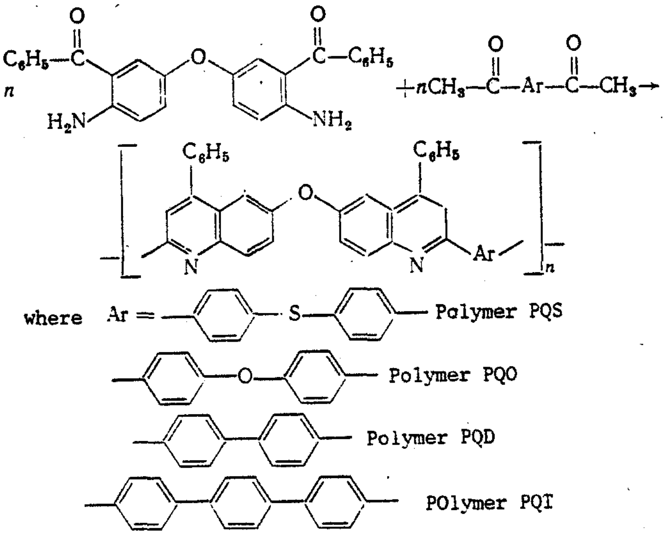
Polyquinolines (PQ) are known as polymers which have elevated resistance to oxidation, and good mechanical and electrical insulating properties. Polyquinolines are prepared by high-temperature polycondensation of o-aminoketones with ketomethylene compounds. The use of catalysts of "acid" character in this reaction, plus the introduction of rigid fragments into the composition of the polymer macromolecules has made it possible to synthesize PQ having high molecular weights and to prepare fibres based on them [1-3].

In the present article, the properties of PQ* of various chemical structures and the conditions for preparing fibres from them are examined. Synthesis of the PQ was carried out in a mixture of m-cresol and phosphorus pentoxide at 140°C by polycondensation of 3,3'-dibenzoyl-4,4'-diaminodiphenyl ether with a series of diacetyl compounds by a previously described procedure [4]:



The polymers were isolated from the polycondensation solutions by precipitation into a mixture of ethanol and triethylamine; they were extracted with boiling ethanol, and were dried to constant weight under vacuum.

The inherent viscosity of the PQ, as measured for reaction solutions diluted with m-cresol which contained 0.50 g of polymer in 100 ml of solvent, were 1.20-4.20 dl/g, and depended on the chemical structure of the repeating unit in the polymer.

Polyquinolines which contain "hinge" groups — the PQS and PQO — are soluble at room temperature in m-cresol, chloroform, or sulfuric acid. The introduction of "rigid" fragments

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