Journal of Engineering Physics and Thermophysics, Vol. 76, No. 3, 2003

INFLUENCE OF THE DEGREE OF COMPATIBILITY OF POLYMERS ON THE RHEOLOGICAL PROPERTIES OF A MIXTURE MELT AND THE PROCESSES OF STRUCTURE FORMATION

M. V. Tsebrenko, V. G. Rezanova, and
I. A. Tsebrenko

UDC 541.64:532.135

A study has been made of the rheological properties of the melts and the processes of structure formation of polypropylene/copolyamide mixtures containing additions of individual compatibilizers and their mixtures: ethylene copolymer with vinyl acetate, sodium oleate, and siloxane liquids. The compatibilizing effect manifests itself as a decrease in the interfacial tension, which improves the fiberization of polypropylene in the copolyamide matrix. It is shown that the introduction of these additives makes it possible to realize the phenomenon of specific fiberization in the region of a phase change in the polypropylene/copolyamide mixtures of composition 40/60, 50/50, and 60/40. The introduction of binary mixtures of compatibilizers is more efficient than the introduction of individual substances. The melts of such mixtures are characterized by a higher elasticity and a pronounced capacity for being longitudinally deformed.

Mixtures of polymers represent a special class of colloidal systems of the "polymer in polymer" type. Their peculiarity is that an interphase (transition, boundary) layer of certain extent is formed between two incompatible polymers in a melt or in a solution. The developed boundary layer is a specific phenomenon characteristic of only polymer mixtures, which determines to a large measure the physicochemical and mechanical properties of polymer mixtures and products of them. The transition layer plays an especially important role in the case of realization of the so-called phenomenon of specific fiberization implying that one of the components (dispersed-phase polymer) of a polymer-mixture melt flowing through a molding hole forms, under the influence of rheological forces, a set of ultrafine fibers (microfibers) oriented strictly in the extrusion direction in the mass of the other (matrix) polymer [1]. These microfibers can be isolated from the composite extrudate by extraction of the matrix polymer with the use of a corresponding solvent. This phenomenon has been investigated in detail in [1–3] and has made it possible to develop a number of fundamentally new technologies of production of fine-fiber materials, for example, filters of precision cleaning.

According to the Taylor theory [4], a flowing dispersion medium acts on a drop dispersed in it with a force T_η proportional to the gradient of the rate of shear dV_x/dy and the viscosity of the medium, which is a function of the viscosity ratio of the components:

$$T_\eta = C\,(dV_x/dy)\,\eta_2\,f(\eta_2/\eta_1)\,. \tag{1}$$

The force T_η cannot be transferred to a drop and cannot extend it unless there is a bond between the two polymers of the mixture, namely, the transition layer of a certain extent and a sufficient degree of interaction between the components in it. A polymer drop of the dispersed phase resists deformation with a force

$$T_\gamma = 2\gamma_{\alpha\beta}/r\,. \tag{2}$$

When T_η is equal to T_γ, the radius of the drop and hence the radius of the microfibers is determined by the expression

---

Kiev National University of Technologies and Design, Kiev, Ukraine; email:vlasenko@ekma.Kiev.ua. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 76, No. 3, pp. 68–75, May–June, 2003. Original article submitted December 2, 2002.

$$r = [C\gamma_{\alpha\beta}]/[(dV_x/dy)\,\eta_2\,f(\eta_2/\eta_1)]\,. \tag{3}$$

It follows from Eq. (3) that the larger the viscosity of the matrix polymer and the gradient of the rate of shear and the smaller the viscosity of the fiberizing polymer and the interfacial tension, the finer the microfibers. The value of the interfacial tension can serve as an indirect characteristic of the degree of compatibility of polymers.

It is known that because of the negligible entropy of mixing, the majority of polymers in mixtures are thermodynamically incompatible. Weak intermolecular interactions in the interphase layer decrease the adhesion at the interphase boundary in both the molten and solid states. For example, the interphase viscosity has been estimated in the works of Utracki [5]; it turned out to be 100 times lower than the viscosity of the entire mixture melt. It is because of this the property–composition dependences for polymer mixtures usually have a negative deviation from additivity. The foregoing shows that it is necessary to improve the compatibility of the components of a polymer mixture. This is especially important for realization of the phenomenon of specific fiberization when it is necessary to extend a drop into a jet. The problem of compatibility becomes pressing in the case where polypropylene (PP)/copolyamide (CPA) mixtures are used for production of polypropylene fibers. Polypropylene and copolyamide strongly differ in chemical structure; therefore, they are incompatible. The degree of their compatibility [5] can be improved in several ways: (1) introduction of block- and grafted copolymers, (2) realization of specific interactions between the macromolecules of the mixture components, and (3) introduction of low-molecular-weight, oligomeric, and polymeric additives capable of participating in specific interactions with one or both polymers of the mixture. The specific interactions imply the formation of hydrogen, dipole–dipole, and ion–dipole bonds, the donor–acceptor interaction, and the formation of stereocomplexes between the macromolecules of the mixed polymers. The term "specific interactions" was introduced into polymeric science by A. A. Tager. The substances which improve the compatibility of polymers and the compatibilization itself are considered as a phenomenon of modification of the interphase surface and morphology. Three-component incompatible but compatibilized mixtures with a modified interphase boundary and morphology are called polymeric alloys. In our investigations, the second and third ways were used for improving compatibility. We have shown [6–8] that the specific interactions are realized between the macromolecules of the following pairs of polymers: polyoxymethylene (POM)/copolyamide, polyoxymethylene/ethylene copolymer with vinyl acetate (ECVA), and copolyamide/ECVA. The method of infrared spectroscopy provided support for the view that hydrogen bonds are formed between the macromolecules of the indicated polymers at the interphase boundary. This leads to the formation of an interphase layer of a fairly large extent and allows transfer of stresses from the matrix to the dispersed-phase regions of the polymer. As a result, the kinetic stability of the polymeric dispersion and the degree of dispersion increase and the realization of specific fiberization is pronounced. Of particular interest is the third method of improving the compatibility of polymers, namely, the introduction of the third component serving as a compatibilizer into a binary mixture.

The aim of the present work is to investigate the rheological properties of melts and the processes of structure formation in compatibilized polypropylene/copolyamide mixtures.

Objects and Methods of Investigation. The objects of investigation were polypropylene/copolyamide mixtures of composition 20/80, 30/70, 40/60, 50/50, and 60/40 wt.%. The characteristics of the polymers studied are presented in [9, 10]. Copolyamide represents a copolymer of caprolactam and hexamethylene adipate in a 50:50 ratio. It has a melting temperature close to that of polypropylene and, in heating, is dissolved in ethyl alcohol, which was used for extraction of copolyamide from the composite extrudates for the purpose of isolation of polypropylene microfibers. The production of polypropylene microfibers is currently a pressing problem because of the widespread use of polypropylene fibers and filaments obtained according to the usual technology of melting. The valuable properties of polypropylene become an order of magnitude better in polypropylene microfibers obtained by processing of melts of polymer mixtures. As the compatibilizers we used ECVA, sodium oleate, PES-5 and PMS-100 polyethyl siloxane liquids, and binary mixtures of the indicated compatibilizers. The ethylene copolymer with vinyl acetate was introduced in amounts of 5, 10, 20, and 25% of the polypropylene mass. The amount of introduced salt (sodium oleate) was 0.5 and 3.7% of the polypropylene mass. The siloxane liquids were added in amounts of 0.1, 0.3, 0.5, and 1.0% of the polypropylene mass. We used the following binary mixtures of compatibilizers: 5% of ECVA/3% of sodium oleate of the polypropylene mass, 5% of ECVA/0.5% of PES-5 of the polypropylene mass, and 3% of sodium oleate/0.5% of PES-5 of the polypropylene mass. Mixing of the polymers and introduction of the additives were carried out with the

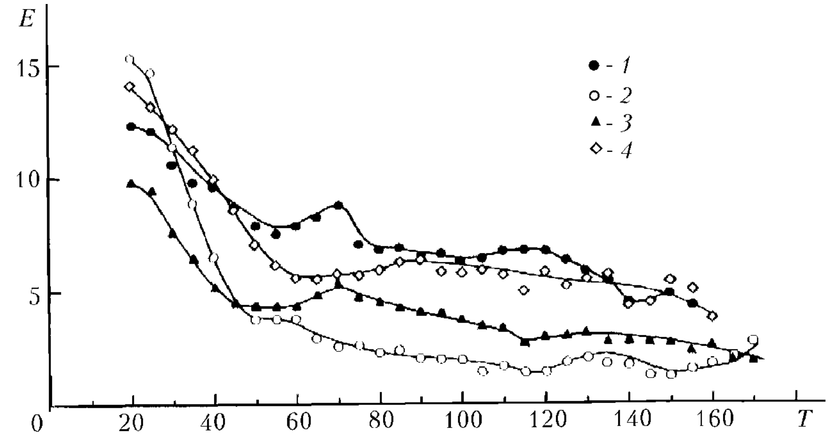


Fig. 1. Dependence of the loss modulus on the temperature: 1–4) correspond to the samples of PP, CPA, the PP/CPA mixture of composition 50/50, and the PP/CPA/ECVA mixture of composition 45/50/5 respectively.

use of a combined screw-disk extruder. The ethylene copolymer with vinyl acetate was introduced by three methods: simultaneous mixing of all three components (method 1), mixing of ECVA first with polypropylene and then, on the second extrusion, with copolyamide (method 2), and mixing of ECVA first with copolyamide and then, on the second extrusion, with polypropylene (method 3). The other mixtures were prepared by method 1. It is precisely in the disk zone, in the gap between the mobile and immobile disks, that a fine mixing of polymers and the distribution of an additive in the mixture melt are realized. The viscous properties of the melts were investigated by the method of capillary viscosimetry. The elasticity of the melts was judged by the swelling of the extrudates of the mixtures subjected to annealing by the special procedure [11] for complete relaxation of the accumulated highly elastic deformations. The capability of a mixture melt of being longitudinally deformed was judged by the maximum possible spinneret stretching Φ_m, which was determined as the ratio of the velocity of inflow of a jet to the velocity of its outflow from the capillary opening at a constant shear stress τ and a constant temperature. The processes of structure formation in the extrudates of the mixtures were investigated quantitatively and qualitatively by the method of light microscopy. The types of specific interactions were determined by the method of infrared spectroscopy. As a result of the investigations carried out, we have revealed new phenomena and established new regularities.

Results and Their Discussion. *Specific interactions in ternary mixtures polypropylene/copolyamide/additive.* The results of the infrared spectroscopy have directly confirmed the fact that in the investigated three-component systems polypropylene/copolyamide/compatibilizer there arise specific interactions at the level of dipole–dipole bonds. For example, the interaction between the –NH– group of the copolyamide macromolecules and the C═O group of copolyamide or sodium oleate manifest themselves as a shift of the frequencies of the –NH– (3300 cm^{-1}) and C═O (1640 cm^{-1}) bands to the high-frequency region and as a broadening of the bands [12]. The appearance of absorption in the region of 1715 cm^{-1} at the low-frequency edge of the C═O band of ECVA (γ = 1740 cm^{-1}) is additional evidence of the participation of ECVA macromolecules in dipole–dipole interaction of the type of hydrogen bonds with copolyamide macromolecules. In this case, the effect of ECVA or sodium oleate is similar to the effect of a polar solvent on the intermolecular interactions in copolyamide, namely, the carbonyl groups of ECVA and of sodium oleate break the hydrogen bonds NH...C═O of polyamide and form NH...C═O bonds with the ester group of ECVA or the salt. Sodium oleate also enters into ion–dipole interactions of the type of C═O (amide) ... Na$^+$ (salt). Introduction of siloxane liquids into the binary mixture polypropylene/copolyamide causes the same changes in the stretching vibrations of the –NH– and C═O groups as in the case of addition of ECVA and sodium oleate.

The content of vinyl-acetate groups in the ECVA macromolecule is low (12%); the other part of the macromolecule has a hydrocarbon structure, which provides the affinity of ECVA to polypropylene. Sodium oleate also has a long hydrocarbon radical ($C_{17}H_{33}$), which allows the salt to act as a compatibilizer between polypropylene and copolyamide. When a compatibilizer is introduced, the degree of compatibility of polypropylene with copolyamide improves as a result of the specific interactions. Indirect estimation of the degree of compatibility of polymers was performed by the method of dynamic mechanical analysis with the use of a modified model of a frequency relaxometer

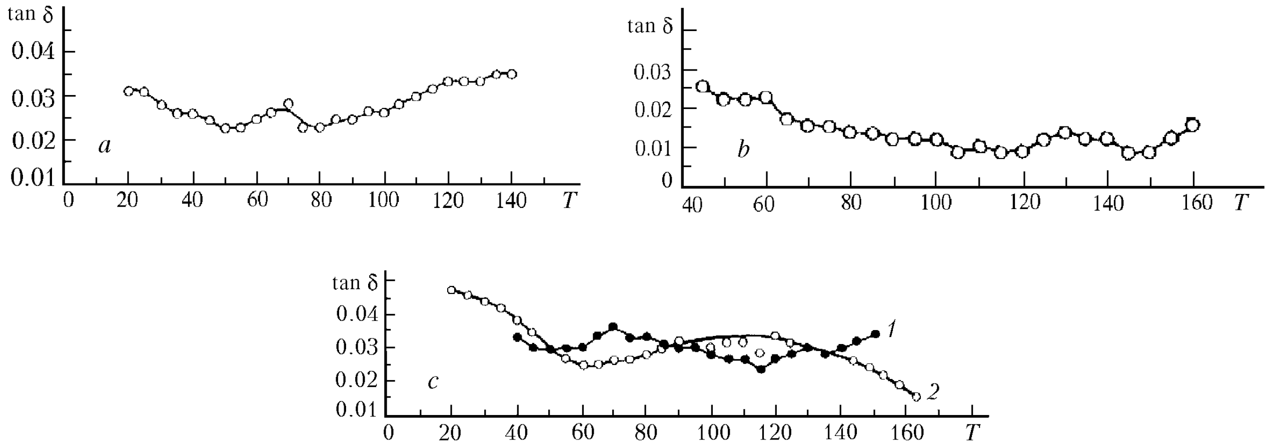
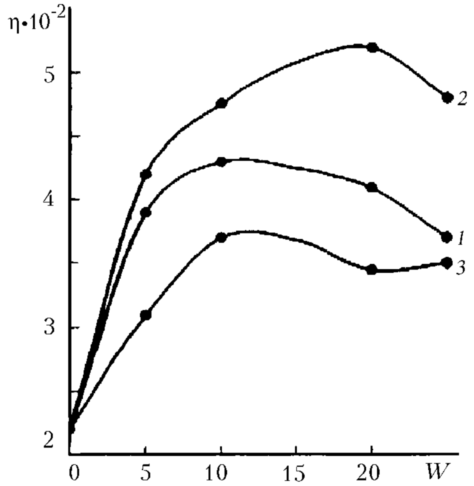


Fig. 2. Dependence of the tangent of the mechanical loss angle on the temperature: a) PP, b) CPA, and c) the PP/CPA mixture of composition 50/50 (1) and the PP/CPA/ECVA mixture of composition 45/50/5 (2).



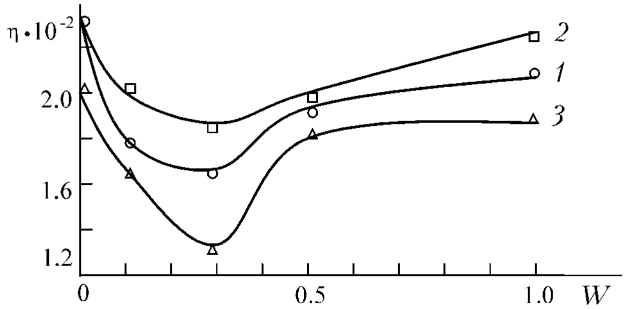


Fig. 3. Dependence of the viscosity of the melt of the mixtures PP/CPA/ECVA on the ECVA content at T = 185°C, the composition of PP/CPA is 40/60: 1–3) methods of mixing 1, 2, and 3, respectively.

Fig. 4. Influence of the siloxane additives on the viscosity of the melts of PP/CPA mixtures of composition 50/50/PES-5 (1), 50/50/PMS-100 (2), and 40/60/PES-5 (3).

with automatic measurement of the phase angle [13]. Figures 1 and 2 give the temperature dependences of the loss modulus and tan δ for the initial polymers, the binary mixture polypropylene/copolyamide of composition 50/50 wt.%, and the ternary mixture polypropylene/copolyamide/ECVA of composition 45/50/5 wt.%. It is clearly seen that in the case of the binary mixture there appear reflections of the initial components (polypropylene and copolyamide), which are only slightly shifted in temperature. The compatibilized mixture is characterized by a single broad reflection located between the reflections of polypropylene and copolyamide. The regularity found confirmed to the fact that the degree of compatibility of polypropylene and copolyamide increases on introduction of ECVA.

Influence of additions of individual compatibilizers on the rheological properties of polypropylene/copolyamide melts. The viscosity of the melt of compatibilized polypropylene/copolyamide mixtures is determined by two factors. The considered dipole–dipole interactions between the macromolecules of ECVA (or salt molecules) and copolyamide structurize the copolyamide melt and the entire mixture, which increases the viscosity of the latter. The viscosity decreases due to the formation of liquid jets of the dispersed-phase polymer (subsequently microfibers) in the

TABLE 1. Values of Φ_m for the Melts of PP, CPA, and Binary and Ternary Mixtures

Polymer, polymer mixture	Φ_m, %	Polymer mixture	Φ_m, %
PP	20 000	PP/CPA/0.5% of salt	23 000
CPA	25 400	PP/CPA/3% of salt	20 000
PP/CPA	7630	PP/CPA/7% of salt	7400

Note. At T = 180^{o}C; the PP/CPA ratio is 30/70.

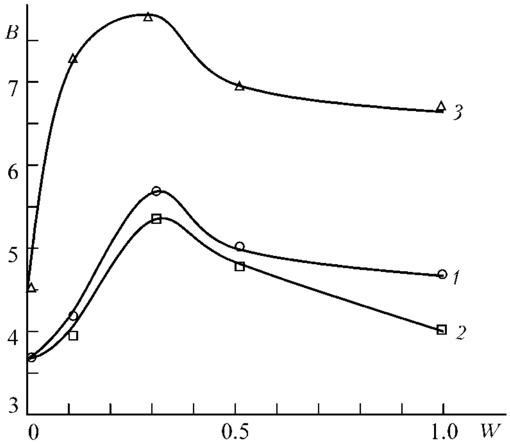


Fig. 5. Influence of the siloxane additives on the swelling of the extrudates of the PP/CPA mixtures of composition 50/50/PES-5 (1), 50/50/PMS-100 (2) and 40/60/PES-5 (3).

copolyamide matrix. The resulting action of these two antipodal factors determines η of the mixture melt. The experiments have shown that for mixtures with additions of sodium oleate or ECVA the structurizing action of the additive prevails and the viscosity of the mixture melt increases (Fig. 3). It is also clearly seen that the viscosity of the melt of the ternary mixture depends on the method of mixing of the components. The mixtures obtained by the third method have the lowest viscosity, which, as will be shown below, is due to the pronounced realization of specific fiberization. The siloxane liquid is introduced into the binary mixture in small amounts; therefore, the degree of structurization of the melt is smaller than in the case where two other additives are used. As a result, the viscosity of the melt of the ternary mixtures decreases (Fig. 4), passes through a minimum, and then (at 1.0 wt.% of the additive) increases, remaining lower than η of the binary mixtures.

Since the processing of the melts of polymers and their mixtures leads not only to shear deformation but also to longitudinal deformation, the spinnability of the melts was estimated by the maximum possible spinneret stretching Φ_m of a melt jet flowing from the capillary. When the melts of three-component mixtures are flowing, polypropylene is predominantly deformed into thin liquid jets which, after solidification, transform into microfibers. From the works of Kuleznev [14] it is known that the formation of anisotropic structures increases the deformability of the entire polymeric mixture. Indeed, the data obtained (Table 1) have shown that the existence of thin liquid polypropylene jets in the copolyamide mass improves the deformability of the mixture melt in the extension field.

The data presented in Table 1 indicate that the copolyamide melt has a maximum capacity for processing, and Φ_m for the binary mixture polypropylene/copolyamide decreases sharply. This is explained by the fact that this mixture is two-phase and has a transition layer with a weakened interaction of the components in it. Introduction of a (0.5–3.0)% salt sharply improves the fiberization properties of the polypropylene/copolyamide-mixture melt, which is explained by the above-mentioned influence of sodium oleate. The quantity Φ_m of the melt of the polypropylene/copolyamide/salt mixture of composition 30/70/0.5 is close to Φ_m of the copolyamide. We were the first to establish this regularity. This is not only a scientific but also an important practical result.

An indirect characteristic of the elasticity of the melt of a polymer or a polymer mixture is the swelling B of the extrudate. In our works [3], it has been shown that B serves as an indirect characteristic of specific fiberization:

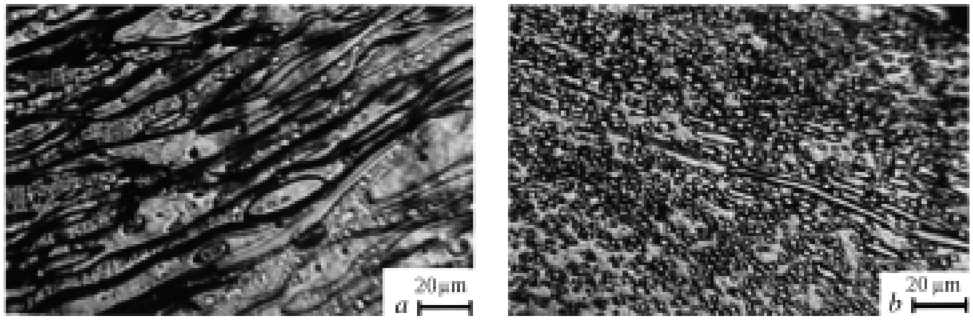


Fig. 6. Microphotographs of the cross sections of the extrudates of the PP/CPA mixture of composition 50/50 (a) and the PP/CPA/ECVA mixture of composition 45/50/5 (b).

the larger the number of microfibers formed in flow of a mixture melt and the thinner they are, the larger the values of *B*. It is seen from Fig. 5 that on introduction of the siloxane liquid into the polypropylene/copolyamide mixture, *B* increases and the curve passes through the maximum when the additive accounts for 0.3% and the swelling reaches 7.6 as opposed to 3.8 for the binary mixture. This is indirect evidence of the pronounced fiberization of polypropylene in the copolyamide matrix. The latter is confirmed by direct macroscopic investigations.

Influence of compatibilizers on the processes of structure formation. In any colloidal system, including mixtures of polymers, a change in the component ratio leads to a phase reversal. This is one of the most interesting but, at the same time, most complex and least theoretically understood phenomena. Essentially, the problem is as follows: the dispersion medium and the dispersed phase exchange places under the action of external factors. Such external factors can be variation of the composition of the mixture, introduction of a new substance, change in the temperature, and others. In low-molecular-weight emulsions, a phase reversal occurs spasmodically at a component ratio close to unity. In polymeric mixtures the phase-change region covers a wide range of compositions when two phases are continuous (matrix structures). For polypropylene/copolyamid mixtures, the phase-change region covers the component ratios 40/60, 50/50, and 60/40 wt.%. The investigations carried out previously [3] have shown that the phenomenon of specific fiberization is best realized at a dispersed-phase content of 20–30 wt.%. Fiberization is absent in the phase-change region.

We were the first to establish that introduction of a compatibilizer into a polypropylene/copolyamide mixture provides fiberization of polypropylene for compositions corresponding to the phase-change region (polypropylene/copolyamide ratios 40/60–60/40 wt.%). The extrudates of polypropylene/copolyamide mixtures of composition 50/50 wt.% have a layer morphology (Fig. 6a). Polypropylene microfibers are not formed in the copolyamide matrix. Introduction of 5 wt.% of ECVA qualitatively changes the microstructure of the extrudate: polypropylene microfibers of continuous length become its predominant type (Fig. 6b). Additions of sodium oleate and siloxane liquids act in the same direction. We particularly emphasize that the diameter of the microfibers in compatibilized mixtures is much smaller than that in binary mixtures (3.2–4.2 μm as opposed to 5.6–7.2 μm). This is explained by the fact that the lifetime of a liquid jet increases in the presence of a compatibilizer. For example, it is known that a liquid cylinder (jet) is thermodynamically unstable because of the disadvantageous ratio between the surface and the volume, and with time such a jet decomposes into a chain of drops. To a first approximation, the lifetime of the liquid jet (decomposition time) is determined from the expression

$$t_{\text{life}} = \eta R / \gamma_{\alpha\beta} \,. \tag{4}$$

On the one hand, it is seen that, all other things being equal, liquid jets of smaller radius are stabilized as $\gamma_{\alpha\beta}$ decreases, i.e., conditions for obtaining finer fibers are realized. In our opinion, it is precisely to the decrease in $\gamma_{\alpha\beta}$ that we relate the mechanism of action of a introduced additives. On the other hand, the decrease in $\gamma_{\alpha\beta}$ leads to the formation of a transition layer of a fairly large extent, which provides the transfer of the deforming forces of the matrix to the drops of the dispersed-phase polymer. The indicated two factors provide fiberization in the phase-change region.

TABLE 2. Influence of Compatibilizers on the Rheological Properties of the Melts of PP, CPA, and the PP/CPA Mixture of Composition 50/50 wt.%

Composition of a mixture, wt.%	η, Pa·sec	n	B	Φ_m, %
PP Melt				
PP	480	1.9	1.6	15,110
PP/5% of ECVA	440	2.1	1.7	27,070
PP/0.5% of PES-5	400	2.1	1.7	27,500
PP/3% of sodium oleate	390	1.9	1.7	29,330
PP/5% of ECVA/0.5% of PES-5	420	2.1	1.8	38,630
PP/3% of sodium oleate/5% of ECVA	370	1.9	1.9	40,820
PP/3% of sodium oleate/0.5% of PES-5	370	2.1	1.8	36,000
CPA Melt				
CPA	960	1.2	1.7	92,500
CPA/5% of ECVA	1630	1.3	1.9	149,800
CPA/0.5% of PES-5	1520	1.3	1.6	141,170
CPA/3% of sodium oleate	1220	1.2	1.5	130,000
CPA/5% of ECVA/0.5% of PES-5	1950	1.3	2.0	153,880
CPA/3% of sodium oleate/5% of ECVA	1500	1.2	1.7	132,500
CPA/3% of sodium oleate/0.5% of PES-5	1360	1.3	1.5	145,900
PP/CPA Melt				
PP/CPA	230	2.0	3.6	3700
PP/CPA/5% of ECVA	300	2.1	5.0	8780
PP/CPA/0.5% of PES-5	190	2.0	5.0	4100
PP/CPA/3% of sodium oleate	160	2.0	4.6	3900
PP/CPA/5% of ECVA/0.5% of PES-5	390	2.1	5.1	21,600
PP/CPA/3% of sodium oleate/5% of ECVA	300	2.1	5.4	27,400
PP/CPA/3% of sodium oleate/0.5% of PES-5	200	2.1	5.1	6800

Note. $T = 190^{o}$C and $\tau = 5.69 \cdot 10^4$ Pa.

Influence of binary mixtures of compatibilizers on the rheological properties of a melt and the processes of structure formation. It is known from the literature [15] that mixtures of compatibilizers are more efficient than individual substances. Therefore, we used mixtures of different copolymers to improve the compatibility of polyethylene with polyethylene terephthalate [15]. The most pronounced effects are observed for mixtures of diblock- and comb-shaped copolymers, when $\gamma_{\alpha\beta}$ decreases to zero. Each individual compatibilizer does not provide this effect. At a very low value of $\gamma_{\alpha\beta}$, there are no large energy barriers to the formation of the interface, and the dispersed-phase polymer, in mixing, can be dispersed to very small dimensions, which sharply increases the interphase adhesion. Lyatskaya and Balazs [15] explain the revealed unusual effects by the segregation of one-type blocks in the interphase layer and the formation of two sublayers — inner and outer. This double interphase layer is more packed than that in the case where individual copolymers are used. As a result, $\gamma_{\alpha\beta}$ decreases to zero.

The above-described phenomenon is very important in the case of realization of specific fiberization where it is necessary to deform a drop into a jet. Therefore, we used binary compositions of the compatibilizers ECVA, sodium oleate, and siloxane liquids in processing of polypropylene/copolyamide mixtures of composition 50/50 wt.%. The compositions of the mixtures are given in the methodological part. It was of interest to estimate the influence of individual additives and their mixtures on the rheological properties of the initial polymers (polypropylene and copolyamide). The results are presented in Table 2 and point to the fact that additives have a different influence on the properties of polypropylene and copolyamide melts.

Additions of individual compatibilizers and their mixtures decrease only slightly the viscosity of a polypropylene melt without significantly changing the regime of flow *n* (slope of the tangent to the given point of the flow curve) and the elasticity of the melts. Noteworthy is a sharp improvement in the spinnability of a polypropylene melt with introduction of ECVA, sodium oleate, and PES-5 (Φ_m increases by almost a factor of two). The binary mix-

TABLE 3. Characteristics of the Microstructure of the Extrudates of Compatibilized PP/CPA Mixtures

Composition of the mixture, wt.%	Fibers of continuous length			Content, %		
	mean diameter *d*, μm	content *W*, %	dispersion σ^2, μm^2	short fibers	particles	films
PP/CPA	film structure cannot be dispersed					
PP/CPA/5% of ECVA	4.0	70.0	3.3	13.1	10.1	6.8
PP/CPA/0.5% of PES-5	4.1	72.0	5.0	12.6	9.3	6.1
PP/CPA/3% of sodium oleate	5.8	72.0	3.0	11.3	10.7	6.0
PP/CPA/5% of ECVA/0.5% of PES-5	2.8	78.0	2.2	11.3	6.0	4.7
PP/CPA/3% of oleate/5% of ECVA	2.6	80.0	1.8	7.9	7.3	4.8
PP/CPA/3% of oleate/0.5% of PES-5	3.2	73.0	2.5	11.4	12.2	3.4

ture of compatibilizers improves the spinnability of a polypropylene melt to an even greater extent. For example, whereas Φ_m of the initial polypropylene melt is 15,110%, the introduction of the binary mixture 3% of sodium oleate/5% of ECVA increases the maximum spinneret stretching to 40,820%. The revealed regularity can be explained by the plasticizing action of the additives on the polypropylene melt.

If the viscosity of a polypropylene melt decreases on introduction of additives, the viscosity of a copolyamide melt significantly increases. This effect can be explained by the structuring influence of the compatibilizers on the copolyamide melt due to the specific interactions. The regime of flow and the elasticity of copolyamide melts change insignificantly under the action of the additives. Special attention must be given to the fact that even though η of the copolyamide melt increases, its spinnability increases too. Thus, it may be concludede that the additions of the compatibilizers studied have a positive effect on the polypropylene and copolyamide melts.

We also evaluated the influence of the above additives and their mixtures on the properties of the melt and the processes of structure formation of polypropylene/copolyamide mixtures of composition 50/50 wt.% (Table 1). Addition of 5 wt.% of ECVA increases the viscosity of the melt of the binary mixture polypropylene/copolyamide, which is explained by the formation of hydrogen bonds between the carbonyl of the ECVA and the amide group of the copolyamide. Addition of 0.5 wt.% of PES-5 or 3 wt.% of sodium oleate decreases the viscosity of the melt of the binary mixture polypropylene/copolyamide. This is due to the competing influence of the structurization of the melt due to the specific interactions between the additive and copolyamide and the realization of specific fiberization. The first factor increases the viscosity, while the second factor decreases it. Binary mixtures of additives variously affect the viscosity of the melt of a polypropylene/copolyamide mixture: introduction of the mixture 3 wt.% of solid oleate/0.5 wt.% of PES-5 or 3 wt.% of sodium oleate/5 wt.% of ECVA decreases η of the polypropylene/copolyamide mixture melt; the viscosity of the melt of a polypropylene/copolyamide mixture containing 5 wt.% of ECVA/0.5 wt.% of PES-5 increases. The revealed dependence is also determined by the competing influence of fiberization and structurization.

As has already been noted, there is a significant correlation between the swelling of the extrudate *B* and the degree of realization of specific fiberization. From this viewpoint, individual additives and their mixtures improve the fiberization of polypropylene in the copolyamide mass. The melt of the binary mixture polypropylene/copolyamide is characterized by the lowest value of Φ_m, which is explained by the fact that this mixture is two-phase and has interphase boundaries with a weakened interaction between the components in it (low compatibility of polypropylene and copolyamide). Addition of compatibilizers improves the spinnability of the polypropylene/copolyamide-mixture melt. The following binary mixtures are the most efficient from this viewpoint: 5 wt.% of ECVA/0.5 wt.% of PES-5 and 3 wt.% of sodium oleate/5 wt.% of ECVA.

The characteristics of the microstructure of the extrudates of three- and four-component mixtures are presented in Table 3, from which it follows that in the case of a binary mixture of compatibilizers, the mean diameter of the microfibers decreases and their number and homogeneity increase (the dispersion decreases from 5.0 to 1.8). It must be also noted that the microstructure was analyzed by the method of light microscopy; therefore, very fine fibers (tenths of a fraction of a micrometer in diameter) were invisible and cannot be taken into account in analysis. To refine the data obtained, we will analyze the microstructure with the use of electron microscopy.

TABLE 4. Characteristics of the Decomposition of PP Microfibers in the CPA Matrix (d = 3.4 μm)

Composition of the mixture, wt.%					λ_m, μm	q	$2\pi R/\lambda_m$	$\gamma_{\alpha\beta}$, mN/m
PP	CPA	ECVA	PES-5	sodium oleate				
20	80	–	–	–	20.0	0.0618	0.54	2.60
50	50	5	–	–	31.7	0.0362	0.37	1.85
50	50	–	–	3	13.9	0.0364	0.78	1.92
50	50	–	0.5	–	27.6	0.0362	0.39	1.90
50	50	5	–	3	18.6	0.0327	0.58	1.30
50	50	5	0.5	–	20.8	0.0139	0.52	1.35

Estimation of the interfacial tension. Since all the above-described phenomena in the compatibilized mixtures polypropylene/copolyamide are related in one way or another to the interfacial tension $\gamma_{\alpha\beta}$, we calculated this parameter on the basis of the Tomotika theory [16]. To obtain initial data, we placed thin sections of mixture extrudates on the heating microscope stage. We increased the temperature and photographed different stages of the decomposition process. The data obtained were processed in accordance with the above theory; we determined the wavelength of the decomposing disturbance λ_m, the instability coefficient q, the wave number $2\pi R/\lambda_m$, and the interfacial tension $\gamma_{\alpha\beta}$ (Table 4).

Since the extrudates of the binary mixture polypropylene/copolyamide of composition 50/50 have a layer microstructure and fiberization is not realized, for the sake of comparison we measured the interfacial tension for the polypropylene/copolyamide mixture of composition 20/80. The results of the experiments (Table 4) confirmed the fact that $\gamma_{\alpha\beta}$ decreases for the compatibilized mixtures and that the introduction of a mixture of compatibilizers is more efficient than the introduction of individual substances.

As a result of the investigations carried out, we proposed the following compatibilizers: ethylene copolymer with vinyl acetate, sodium oleate, and polysiloxane liquids. It has been shown that the use of their binary mixtures gives the greatest effect.

NOTATION

T_η, force of action of the dispersion medium on a dispersed-phase drop; T_γ, force of resistance of a drop to deformation; η, viscosity; C, constant; dV/dy, gradient of the rate of shear; η_1 and η_1, viscosity of the melts of the dispersed phase and the dispersion medium, Pa·sec; $\gamma_{\alpha\beta}$, interfacial tension, mN/m; r, radius of the dispersed-phase-polymer drop; λ_m, wavelength of the decomposing disturbance, μm; q, instability coefficient; R, radius of the fiber, μm; Φ_m, maximum spinneret stretching; B, swelling of an extrudate; t_{life}, lifetime of a liquid jet; n, regime of flow, representing the slope of the tangent to a given point of the flow curve; d, mean diameter of microfibers, μm; σ^2, dispersion of the diameter distribution of microfibers; W, amount of siloxane, %; T, temperature, $^{\circ}$C; tan δ, tangent of the phase-shift angle between the stress arising in the sample and its deformation; E, dynamic loss modulus, MPa; x, y, coordinate axes. Subscripts: γ, surface tension; α and β, polymers of the dispersed phase and the dispersion medium; m, maximum; life, life.

REFERENCES

1. M. V. Tsebrenko, A. V. Yudin, T. I. Ablazova, and G. V. Vinogradov, *Polymer*, **17**, 831–834 (1976).
2. M. V. Tsebrenko, *Int. J. Polym. Mater.*, **10**, 83–87 (1983).
3. M. V. Tsebrenko, *Ultrathin Synthetic Fibers* [in Russian], Moscow (1991).
4. G. L. Taylor, *Proc. Roy. Soc. London*, **A146**, 501–526 (1934).
5. L. A. Utracki and M. M. Dumoulin, in: *Polypropylene: Structure, Blends, and Composites*, London (1994), pp. 52–96.
6. T. I. Sizevich, *Study of the Properties of Polyoxymethylene-Copolyamide-Mixture Melts with the Phenomenon of Specific Fiber Formation*, Candidate’s Dissertation (in Engineering), Kiev (1976).

7. N. M. Rezanova, *Influence of the Conditions of Deformation of the Melt of a Polyoxymethylene–Ethylene Copolymer with Vinyl Acetate Mixture and the Viscosity Ratios of the Initial Polymers on the Phenomenon of Specific Fiber Formation*, Candidate's Dissertation (in Engineering), Kiev (1982).
8. M. V. Tsebrenko, N. M. Rezanova, T. I. Sizevich, and I. O. Tsebrenko, *Funktsional'ni Materiali* [in Ukrainian], **2**, No. 3, 362–371 (1995).
9. M. V. Tsebrenko, N. M. Rezanova, and I. A. Tsebrenko, *Polym. Eng. Sci.*, **39**, No. 6, 1014–1021 (1999).
10. M. V. Tsebrenko, N. M. Rezanova, and I. A. Tsebrenko, *Polym. Eng. Sci.*, **39**, No. 12, 2395–2402 (1999).
11. M. V. Tsebrenko, *Khim. Volokna*, No. 3, 21–23 (1983).
12. M. V. Tsebrenko, N. M. Rezanova, and I. A. Tsebrenko, in: *Proc. Int. Symp. on Polymer Composites Science and Technology "Polymer Composites–99,"* Quebec, Canada (1999), (1999), pp. 451–460.
13. V. F. Rosovitskii and V. V. Shifrin, in: *Physical Methods of Studying Polymers* [in Russian], Kiev (1981), pp. 85–93.
14. V. N. Kuleznev, Yu. V. Evreinov, V. D. Klykova, and M. I. Shaposhnikova, *Kolloid. Zh.*, **35**, No. 2, 281–285 (1973).
15. Y. Lyatskaya and A. Balazs, *Macromolecules*, **29**, 7581–7587 (1996).
16. S. Tomotika, *Proc. Roy. Soc. London*, **A150**, 322–337 (1935).