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PHENOMENON OF SPECIFIC FIBER FORMATION IN POLYPROPYLENE/COPOLYAMIDE MIXTURES CONTAINING POLYETHYLENEGLYCOL

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We have investigated the influence of a polyethyleneglycol additive and a binary mixture of compatibilizers ethylene copolymer with vinylacetate/polyethyleneglycol on the flow behavior and the processes of structure formation in 30/70 polypropylene/copolyamide mixtures. It has been shown that polyethyleneglycol decreases the viscosity and increases the elasticity of the polymer mixture melt. From the point of view of fiber formation, polyethyleneglycol is an effective compatibilizer for the polypropylene/copolyamide mixture. The introduction of binary mixtures of compatibilizers is more effective than the introduction of individual substances. It has been established that individual compatibilizers and their mixtures stabilize liquid polypropylene jets in the copolyamide matrix, which permits obtaining microfibers of smaller diameters.

In recent years, multiphase mixtures of polymers have been increasingly attracting the attention of researchers. This is primarily due to the possibility of further widening of the complex of properties of materials while preserving the existing industrial base of their production. Moreover, processing of melts of polymer mixtures provides wide possibilities for obtaining modified fibers which exhibit the best qualities of the mixture components or acquire special properties.

It is known that the fiber formation of one polymer in the mass of another in the mixture melt flow is based on such microrheological processes as extension of droplets and confluence of liquid jets of the dispersed-phase polymer in the flow direction, disintegration of the liquid jets formed in the inlet zone of the forming hole into drops by virtue of the hydrodynamic instability, and migration of the dispersed-phase polymer to the walls of the forming-hole channel. Among other factors, the decisive effect on the above microrheological processes in the melts of polymer mixtures is produced by the degree of compatibility of the mixture components. However, because of the negligibly small mixing entropy, most polymers in mixtures are incompatible. The weak intermolecular interaction in the interphase area leads to a low adhesion at the interface in both the melt and the solid state. From the foregoing it follows that compatibilization [1], i.e., improvement of the compatibility of the mixture components is needed. The latter is of particular importance for realizing the specific fiber formation where it is necessary to deform a drop to a jet.

There are several ways of increasing the degree of compatibility of mixture components [2]. However, of interest for us is the method of compatibilization by introducing low-molecular, oligomeric, polymer additives capable of entering into specific interactions with one or both polymers of the mixture. By such interactions is meant the formation of hydrogen, dipole–dipole, and ion–dipole bonds, the donor–acceptor interaction, and the formation of stereo complexes between the macromolecules of the polymers being mixed.

The compatibility problem is most topical for polypropylene/copolyamide (PP/CPA) mixtures because of their sharp difference in chemical structure. In the previous work, as compatibilizers for these mixtures, the ethylene copolymer with vinyl acetate (ECVA), sodium oleate, PÉS-5 and PMS-100 polyethylsilicon liquids, as well as binary mixtures of the above compatibilizers were used [2–4]. At the present time, however, the search for other compatibilizers not only improving the compatibility, but also imparting new properties to the obtained microfibers is still topical.

The aim of the present work is to investigate the influence of the polyethyleneglycol (PEG) additive on the flow behavior and the processes of structure formation in PP/CPA mixtures.

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TABLE 1. Rheological Properties of Melts of PP and CPA, and Their Mixtures with Additives of Compatibilizers

Mixture of polymers	Mixture composition, mass %	η^*, Pa·sec	n	B	Φ_m, %
PP	—	420	2.0	1.6	10 700
CPA	—	635	1.7	1.5	48 600
PP/CPA	30/70	230	1.6	5.3	5500
PP/CPA/PEG	30/70/0.5	230	1.5	6.1	5600
PP/CPA/PEG	30/70/3.0	220	1.5	6.9	6100
PP/CPA/PEG	30/70/5.0	210	1.5	5.5	5700
PP/CPA/ECVA/PEG	30/70/0.5/0.5	350	1.8	7.4	13 100
PP/CPA/ECVA/PEG	30/70/1.0/1.0	320	1.8	7.3	10 200
PP/CPA/ECVA/PEG	30/70/5.0/5.0	213	1.7	5.5	6000
PP/CPA/ECVA/PEG	30/70/10.0/3.0	250	1.8	6.1	8000

$^*\tau = 5.75 \cdot 10^4$ Pa.

TABLE 2. Influence of Additives on the Structure Formation in 30/70 PP/CPA Mixtures

Additive	Content of additive, mass %	Long fibers		Short fibers		Particles		Portion of films, %
		d, μm	portion, %	d, μm	portion, %	d, μm	portion, %	
Without additive	0	2.6	47.6	2.0	18.8	2.5	15.4	18.2
PEG	0.5	2.8	40.2	2.1	23.2	2.3	24.0	12.6
PEG	1.0	2.1	63.8	1.8	15.0	1.7	10.2	11.0
PEG	3.0	2.5	54.2	1.9	15.4	2.6	21.6	8.8
PEG	5.0	3.0	33.6	2.6	12.4	2.8	28.0	26.0
ECVA/PEG	0.5/0.5	2.9	48.4	2.1	21.4	2.3	24.0	6.2
ECVA/PEG	1.0/1.0	2.7	46.2	2.0	21.2	2.3	17.0	15.6
ECVA/PEG	5.0/5.0	2.9	22.6	2.3	32.6	2.0	24.0	20.8
ECVA/PEG	10.0/3.0	2.7	29.0	2.0	28.6	2.1	22.0	20.4

Objects and Methods of Investigations. The objects of the investigation were 30/70 PP/CPA mixtures with PEG additives in the amount of 0.5, 1.0, 3.0, and 5.0% of the PP mass. Since it is known from the literature [5] that a mixture of compatibilizers is more effective than substances taken separately, we used in our work a binary ECVA/PEG additive in ratios 0.5:0.5, 1.0:1.0, 5.0:5.0, and 10.0:3.0% of the PP mass.

Mixing of the polymers and introduction of additives were carried out with the use of a commercial combined LGP-25 screw-disc extruder, which permitted fine dispersion of one polymer in the other and uniform distribution of the additive in the mixture melt. The viscous properties of the melts were investigated by the capillary viscosimetry method. The elasticity of the melts was evaluated by the degree of swelling B of extrudates of mixtures subjected to annealing by special methods [6]. The longitudinal deformability of the mixture melt was judged by the largest possible spinneret extract Φ_m under the condition of a smooth increase in the take-up rate. The microstructure of extrudates was investigated qualitatively by the microphotographs of the cross and longitudinal sections and quantitatively by the results of the analyses of the PP microfiber residues upon extraction of the matrix polymer CPA [6]. The data of the microscopic studies were processed by the methods of mathematical statistics: the mean diameter d of continuous-length fibers, short fibers, and particles, and the sizes of the films and the fibrous outer coating were calculated. The results obtained are presented in Tables 1–4.

Results and Discussion. It has been established that the viscous properties of melts of mixtures with additives are determined, on the one hand, by the processes of structure formation and, on the other hand, by the possible structurization of the mixture melt due to the specific interactions between the PEG hydroxyl groups, ECVA carbonyl, and the NH-group of CPA [7]. Moreover, PEG additives can produce a plasticizing effect on the PP melt.

TABLE 3. Influence of Additives on the Parameters of the Process of Ultrathin PP Fiber Decay in the CPA Matrix

Mixture composition, %				R, μm	a_0, μm	a_0/R	λ_m, μm	$2\pi R/\lambda_m$	t_{life}, sec	t_{life}/R
PP	CPA	ECVA	PEG							
30	70	—	—	1.78	3.36	1.89	16.06	0.69	90	51.0
30	70	—	3.0	1.39	2.78	2.00	14.98	0.58	90	60.2
30	70	0.5	0.5	1.99	3.53	1.77	14.70	0.85	120	65.0

TABLE 4. Influence of Compatibilizers on the Interphase Tension in the PP/CPA Melt

Mixture composition, %				d_0, μm	λ_m, μm	q	$2\pi R/\lambda_m$	σ, mN/m
PP	CPA	ECVA	PEG					
30	70	—	—	4.42	16.06	0.040	0.86	2.36
30	70	—	3.0	4.11	14.98	0.029	0.86	1.96
30	70	0.5	0.5	3.79	14.70	0.031	0.81	1.31

The melt of the initial PP/CPA mixture has a viscosity several times lower than the viscosity of the initial polymers, which is typical of melts of polymer mixtures because of their two-phase character, the weak interaction of components in the interphase layer, and the deformation of dispersed-phase droplets in the flow direction, i.e., the fiber formation of one polymer in the matrix of the other. The introduction of a PEG additive in amounts from 0.5 to 5.0% practically does not change the PP/CPA mixture melt viscosity. From Table 1 it follows that the use of the binary mixture of compatibilizers ECVA/PEG in amounts from 0.5 to 5.0% leads to an increase in the mixture melt viscosity, which can be explained by the intensification of the interactions between the compatibilizers and CPA. Moreover, the second ECVA additive has a polymer nature and a higher viscosity, and the previous investigations revealed an increase in the PP/CPA mixture melt viscosity upon introduction of the above additive.

The melts of all investigated mixtures show a typical Newtonian flow, which is confirmed by the 1.5–1.8 range of changes in the n values.

As is known [6], the degree of swelling B of the extrudate is an indirect characteristic of the specific fiber formation: the more fibers are formed and the thinner they are, the higher the value of B. In accordance with this, the results of Table 1 confirm the improvement of the PP fiber formation in the CPA matrix upon introduction of the PEG additive: B increases from 5.5 to 6.9 and some increase in Φ_m is observed.

The data of Table 1 confirm the existing theory that a mixture of compatibilizers is more effective than individual additives [5]. This shows up as a maximum spinnability of PP/CPA melts with ECVA/PEG additives: 13,100% as against 5500% for the PP/CPA mixture melt. The improvement of the process of fiber formation for PP/CPA//ECVA/PEG mixtures is confirmed by the increase in the degree of swelling of the extrudate from 5.3 for the initial binary mixture to 7.4 for the four-component one.

Table 2 presents the data of the microstructure analysis of the PP/CPA mixtures with additives. It follows from Table 2 that, from the point of view of the processes of structure formation, the optimum content of PEG is 1%. As the content of the PEG additive in the mixture is increased to 5%, the fiber formation worsens: the mean diameter of fibers increases and their percentage in the mixture decreases, which can be explained by the plasticizing effect on the PP melt.

We have performed special experiments to investigate the dependences of the disintegration of liquid PP jets in the CPA matrix. To this end, we placed thin shears of mixture extrudates on the microscope heating table and, while increasing the temperature, photographed different stages of disintegration. The data obtained (Table 3) were processed by the known Tomotiki theory. We determined the size of the droplets formed a_0, the wavelength of the breaking perturbation λ_m, the wave number $2\pi R/\lambda_m$, the disintegration time t_{life}, and its reduced value t_{life}/R.

The results indicate that PEG additives promote stabilization of liquid PP jets. This shows up as an increase in the value of t_{life}/R from 51.0 to 65.0 sec/μm. From this it follows that a mixture of compatibilizers is more effective.

The calculation of the interphase tension by the Tomotiki theory (Table 4) has shown that upon introduction of compatibilizers it decreases. The data of Table 4 also confirm the higher efficiency of binary mixtures of compatibilizers as compared to individual additives.

Thus, it has been shown that PEG is an effective compatibilizer for the PP/CPA mixture. A practical application of the results of the present work is the obtaining of PP microfibers by processing melts of PP/CPA mixtures with a PEG additive and an ECVA/PEG binary mixture of compatibilizers, as well as the obtaining of filtering materials from PP microfibers.

NOTATION

a_0, initial perturbation amplitude, μm; B, degree of swelling of extrudate; d_0, fiber diameter, μm; d, mean diameter of microfibers, μm; n, flow conditions (slope of the tangent to a given point of the flow point); q, instability coefficient; R, radius of the initial liquid jet, μm; t_{life}, lifetime of the liquid jet, sec; η, viscosity, Pa·sec; λ_{m}, breaking perturbation wavelength, μm; $2\pi R/\lambda_{\text{m}}$, wave number; σ, interphase tension, mN/m; τ, shear stress, Pa; Φ_{m}, maximum spinneret extract, %. Subscripts: m, maximum; 0, initial; life, life.

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