Investigation of the Morphology of Polymer Mixtures Depending on Flow Conditions of Melts

Recently, attention has been increasingly concentrated on the problem of formation of fibrillar structures in the flow of polymer melts.[1-9] In this connection, it is important to define the tendency to form fibrillar and stratified structures depending on the basic parameters which determine the conditions of flow of melts of mixtures in ducts. The conditions of freezing or relaxation of the forming structures in the outflow of two-phase polymer mixtures from the ducts are the most important factors here.

EXPERIMENTAL

We investigated mixtures of polypropylene (PP) and polystyrene (PS). Mixtures were prepared from powdered isotactic polypropylene ($M_v = 3 \times 10^5$) and emulsion polystyrene ($M_v = 4.5 \times 10^5$) as the second component. The powdered polymers differed little as to their degree of dispersion (particle size from 5 to 15 μm). The viscosities of the PP and PS melts were also close to each other. The starting mixtures were obtained by mechanical mixing of powders of both polymers. The amount of PP in thg mixture was 30% by weight (or 33% by volume). The flow of melts of the PP + PS mixtures was investigated by means of a constant-pressure capillary viscometer KVPD-2.[10] The melts were kept at 190°C for 20 min and then squeezed at constant pressure through a capillary 1 mm in diameter. The samples thus obtained differed in the flow conditions of their melts; the shear stress τ, the temperature at the outflow of the melt from the capillary, and the capillary length-to-diameter ratio (L/d) were measured.

We attempted to investigate in detail the morphology of PP + PS mixtures depending on the flow conditions of their melts. Table I presents the formation conditions of samples under investigation.

The extruded samples were rods 2 mm in diameter. The morphology of such samples was studied both on slices and fracture surfaces obtained in various directions with respect to the sample axes. Slices for the light microscope, ultrathin slices for the transmission microscope, and fracture surfaces for the scanning electron microscope were prepared in directions parallel and perpendicular to the sample axes. Longitudinal slices at a distance of ~0.5 mm from the sample axis were prepared by moving the knife along the axis (type A slice) and perpendicular to the axis (type B slice). Thin (~3 μm, at 25°C) and ultrathin (~500 Å, at −100°C) slices were obtained by using a cryoultramicrotome (L KB8800 plus Cryo-Kit) from samples previously polymerized in an epoxide resin. The fracture surfaces were prepared by splitting the samples in liquid nitrogen; for examination under the scanning microscope, the fracture surfaces were evaporated with carbon and gold while rotating.

The microscopic investigation of the morphology of the PP + PS mixtures was carried out by means of a Zetopan light microscope (in polarized and unpolarized light), a transmission electron microscope JE M 6A, and a scanning electron microscope JS M 35.

The microphotographs thus obtained were used for identifying the components. The phase distribution in the samples of the mixture was determined by means of stereometric analysis[11] using the "rule of intercepts."

TABLE I
Flow Conditions of PP + PS Melts

Sample no.	L/d	$\tau \times 10^{-5}$, dynes/cm^2	Temperature of outflowing melts, °C
1	8	6.2	0
2	8	6.2	25
3	8	6.2	130
4	10	3.2	25
5	10	5.0	25
6	10	8.4	25
7	21	8.4	25

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RESULTS AND DISCUSSION

Identification of Phases

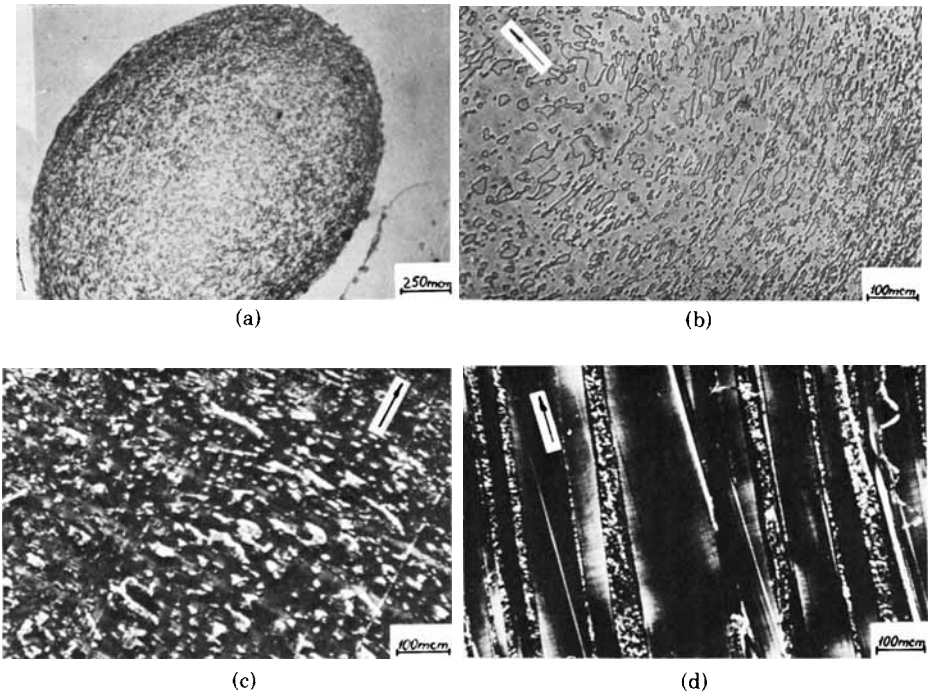
The first task consists in the identification of the mixture components and in the elucidation of the character of their distribution in the extruded samples obtained under various conditions of melt flow. The identification was based on microphotographs (Figs. 1 and 2) and consisted in the determination of the volume fraction of the included phase and of the morphology of components.

Figure 1 shows microphotographs of the transverse (a–c) and longitudinal (d) type A slices typical of all extruded samples of the PP + PS mixture. By means of stereometric analysis (using Fig. 1b), the volume of inclusions was found to be 34.6%, close to the total content of PP in the mixture (33% by vol). Microphotographs taken in unpolarized light [Figs. 1(a) and (b)] show inclusions which in polarized light [FIGS/ [(c) and (d)] are of light color.

The electron microscope reveals the spherolitic structure of inclusions [Fig. 2(a)]. These data indicate that the inclusions consist of PP dispersed in the polystyrene matrix. It should be noted that the matrix possesses bands situated perpendicular to the direction of the moving knife [which is particularly clear in Figs. 1(d) and 2(a)]. These bands are due to the compression of the samples under the knife during slicing. Direct measurement showed that at 25°C, the compression is ~30%.

DISTRIBUTION OF COMPONENTS IN THE MIXTURE ACCORDING TO FORMATION CONDITIONS OF SAMPLES

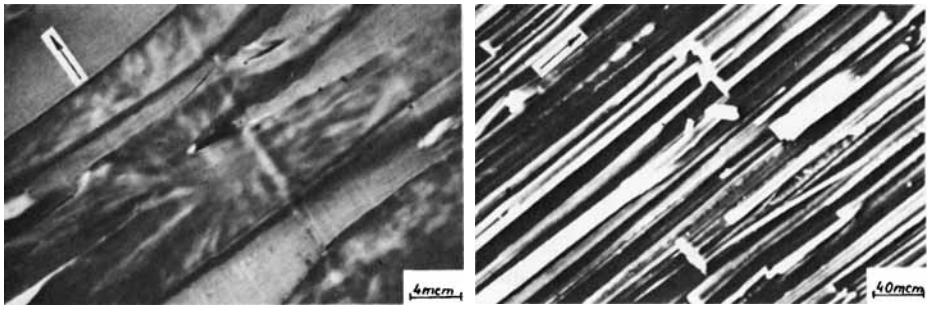
The extruded samples of the PP + PS mixtures consist of thin PP fibrils distributed in the PS matrix. After removal of PS from the extruded sample by extracting it with toluene, the samples had the form of a bundle of long, thin fibrillar formations. As demonstrated by the microphotographs, the fibrils are well orientated in the direction of the melt flow [Fig. 2(b)] and possess a spherulitic structure [Figs. 1(d) and 2(a)]. The character of distribution of fibrils in the extruded samples and the shape of their transverse cross sections are distinctly seen in Figures 1(a) and (b). Stereometric analysis showed that on passing from the center to the margin of the sample, the volume content of the disperse phase, the number of the PP fibrils, and the asymmetry of their cross section increased.



(a) (b)

(c) (d)

Fig. 1. Microphotographs under light microscope of the transverse (a,b,c) and longitudinal type A (d) slices in unpolarized (a,b) and polarized (c,d) light (sample no. 6).



(a) (b)

Fig. 2. Microphotographs of the longitudinal type B slice under transmission electron microscope (a) and of the fracture surface along the axis under the scanning electron microscope (b) (sample no. 2).

(a) (b) (c)

Fig. 3. Effect of ambient temperature at the outflow of the melt from the capillary on sample morphology: (a) sample no. 3, 130°C; (b), (c) sample no. 1, 0°C; (a,b) unpolarized light; (c) polarized light.

(a) (b)

Fig. 4. Effect of capillary length on sample morphology. Longitudinal type A slices, polarized light: (a) sample no. 7, $L/d = 21$; (b) sample no. 6, $L/d = 10$.

Morphology of PP + PS Mixtures

The morphology of the PP + PS mixtures was investigated depending on the temperature of the medium at the outflow of the melt from the capillary, on the shear stress, and on the length of the capillary. When comparing the structures of samples whose melts on leaving the capillary were kept at 130° [Fig. 3(a)] and 0°C [Figs. 3(b) and (c)] for 20 min, we found that squeezing of the melt into water at 0°C gave rise to thinner fibrils packed in concentric layers of different density, which can be well observed in both unpolarized [Fig. 3(b)] and polarized [Fig. 3(c)] light. The nonuniform distribution of fibrils in the cross section is related to the inhomogeneity of the melt which becomes fixed if the melt is extruded into water at 0°C. A decrease in the length of the capillary also leads to the formation of thinner PP fibrils and of layers in their arrangement. This can be seen by

comparing microphotographs of the longitudinal type A slices shown in Figure 4 for a long L/d = 21 [Fig. 4(a)] and a short L/d = 10 [Fig. 4(b)] capillary. Similar results were found if the shear strain was increased during the melt flow. In this case, too, the extruded sample contains thinner fibrils arranged in layers.

CONCLUSIONS

A conclusion drawn from the study of the morphology of the PP + PS mixtures is that the formation of samples under conditions providing fewer possibilities of relaxation (low ambient temperature at the outflow of the melt from the capillary, decrease in the capillary length, increase in the shear strain) gives rise to thinner PP fibrils arranged in layers in the PS matrix.

The results obtained are in accord with those in reference 12, in which it was shown that the formation of structures in the melt flow proceeds in the inlet zone of the capillary.

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