

Rheology and Morphology of Polymer Blends Containing Liquid-Crystalline Component in Melt and Solid State

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SYNOPSIS

The rheological properties of polymer blends containing polysulfone and LC polyester have been investigated in terms of the morphology and physical-mechanical characteristics of the extrudates. The peculiarities of rheological behavior are connected with the morphology of stream, the latter being maintained also in solid extrudates. The reinforcement of an isotropic matrix by LC polymers as well as formation of an anisotropic surface layer leads to a specific change in the strength properties of compositions. A maximal increase in the strength and initial modulus was observed for blends containing not more than 10% LC polymer.

INTRODUCTION

At the present time, special attention is devoted to the reinforcement of thermoplastic materials by using their mixtures containing liquid-crystalline (LC) polymers.¹ Such an approach renders it possible to modify commercial thermoplastics properties so as to create essentially new engineering materials by mixing available polymers in diverse compositions. The preparation of thermotropic LC polymers proved to be the decisive moment with respect to this question, for it is the appearance and utilization of LC melts, as opposed to solutions, that made it possible to solve the problem of the increase in stiffness of commercial thermoplastics of a variety of classes: polyamides,²⁻⁴ polyesters,^{2,3,5-7} polystyrene,⁸ chlorinated poly(vinyl chloride),⁹ etc.

So far, precise scientifically grounded principles for choosing the appropriate pairs do not exist, either for ordinary polymers or for LC polymers. Unfortunately, we have not gotten developed ways and rules of blending; we have only general consideration about the direction of the total effect under combining rigid (soft) matrices with soft (rigid) disperse

phases, about the rule of additivity, and about necessity of controlling the interphase interaction^{10,11} in order to achieve high physical-mechanical characteristics of final products.

Besides, extremely important in the sense of formulation is the method itself for producing polymer mixture products. In extrusion of incompatible polymer blends, the presence of a convergent stream in the zone of the constriction of the flow-line section gives rise to a peculiar reinforcement of materials (fibers, films, rods, tubes, etc.) due to extension drops of the disperse phase in the anisometric (in the extremal case, "threadlike") formations.¹² At the same time, even if injection molding leads to the formation of threads of one polymer in the matrix of another, their orientation may not coincide with the main axis of the molded product. Finally, the stamping (molding) method could not, in general, cause a reinforcement effect.

It is possible to assume that in the latter case the properties of the mixture will vary practically additively. In the case of injection molding, the formation of irregular fiber bundles of one polymer in the matrix of another can give rise to an additional change in the properties in comparison with the additive scheme. But the most pronounced reinforcement effect should appear under extrusion conditions when the long axes of the forming fibers of the disperse phase coincide with the extrusion direction.

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In the present work, we shall deal namely with the extrusion scheme.

The utilization of LC polymers as one of the blend components is of specific character. First, the LC and mesophase polymers fibrillize, as a rule, under deformation.^{13,14} This is due to the high molecular orientation which is achieved by flow through the narrow channels and due to the instability of the superhigh oriented system probably during crystallization. Secondly, the LC polymers possess unusual rheological properties, in particular, viscosity and elasticity anisotropies and low absolute viscosity values. The manner in which these features will influence the rheological properties of the blends, stream morphology, and solidified extrudates is still not known enough. The answer to this question is the main aim of this work and this paper tends to generalize certain initial premises regarding the "blending ideology."

EXPERIMENTAL

The objects under investigation were LC copolyester (PES) "Ultrax-4002" (BASF, F.R.G.), as well as the typical thermoplast polysulfone (PSPH), P-3500 (Amoco, U.S.A.), prepared from diphenylolpropane and dichlorodiphenylsulfone. PES at room temperature (T) contains two phases—crystalline and frozen liquid-crystalline. At $T \sim 200^\circ\text{C}$ PES forms a wholly LC melt, which undergoes the transition into isotropic liquid at $T > 340^\circ\text{C}$. PSPH is a practically amorphous polymer with softening temperature, 200°C .

The flow curves of the initial polymers and their blends were obtained on a capillary viscometer of the "melt-indexer" type¹⁵ in the shear stress range $\tau = 10^3$ – 10^5 Pa at 240, 260, and 280°C . The L/D capillary ratio was 8 at $D = 1.25$ mm. Blending was first carried out in solid state followed by a fourfold run of the composition through the capillary viscometer at 240°C . In doing so, the composition viscosity became stabilized. The PES contents in the compositions were 3, 10, 30, 50, 70, and 90% (weight).

The morphological and mechanical investigations were performed on extrudates prepared at $\log \tau = 4.0$ (Pa). In certain cases, the PSPH was washed out of compositions with a selective solvent (methylene chloride, 20°C). The electron-microscopic observations were carried out on a scanning microscope (Tesla BS 301, C.S.F.R.); the optical observations of the extrudates cross sections were made using an

Interphako microscope (D.D.R.). The samples were prepared by conventional methods.

The tenacity characteristics of the extrudates were obtained using an Instron 1122 tensile testing machine (extension rate 10 mm/min).

The molecular orientation in the extrudates was recorded by the wide-angle X-ray scattering method (IRIS-3.0 apparatus, CuK_α -irradiation, Ni-filter, flat film).

RESULTS AND DISCUSSION

Rheology

In the applied range of shear stresses, the melts of individual polymers exhibit a non-Newtonian behavior, the degree of viscosity anomaly being substantially higher for PES (Fig. 1). The addition of the second component leads to a decrease of viscosity and to a change in the degree of deviation from the linear viscoelastic behavior. Thus, the viscosity anomaly for blends with 3 and 10% PES at 240°C increases (in comparison with PSPH), while that for 30, 50, and 70% blends decreases as compared

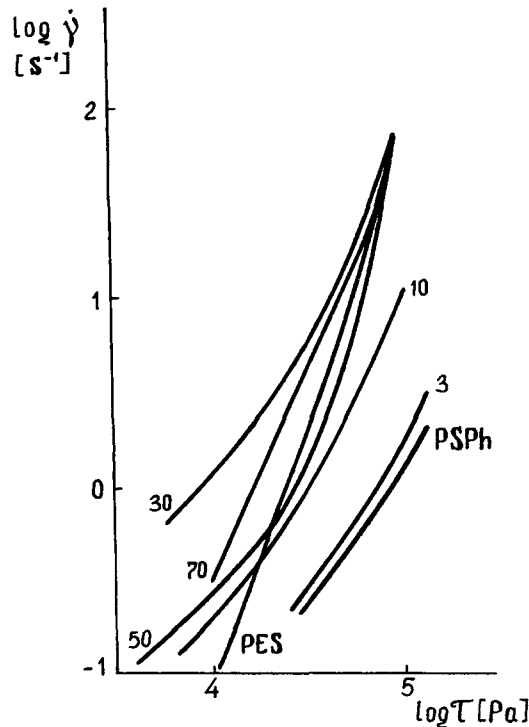


Figure 1 Flow curves of different compositions of PSPH/PES blend melts at 240°C (PES content indicated on the curves).

with PES. The 3% mixture has viscosity especially at low shear rates close to PSPH viscosity, whereas the other compositions are comparable in viscosity at high shear rates with that of PES. In other words, at small PES contents, the flow in the linear region is affected according to PSPH and only at elevated rates does the PES-phase make a contribution to the dissipative losses of blends. At the same time for compositions with $C_{\text{PES}} \geq 30\%$ at high shear rates, the flow proceeds according to PES, whereas at low shear rates the blend viscosity is essentially lower. The 10% mixture occupies an intermediate position. Such unusual flow curves of blend melts are undoubtedly related to the stream morphology. This is confirmed by the fact that, depending on the temperature, the order of the curves' positions for different compositions varies substantially.

The above-mentioned consideration is illustrated in Figure 2, in which the concentration dependencies of the viscosity at 240, 260, and 280°C and constant shear stress ($\tau = 10^4$ Pa) are given. At 240°C the viscosity-composition dependence consists of two arches crossing at $C_{\text{PES}} \sim 50\%$. At 260°C, it represents one smooth curve with a minimum in the $C_{\text{PES}} \sim 50\%$ region. At 280°C, the viscosity-composition dependence becomes practically additive.

The temperature coefficients of PES and PSPH viscosities are essentially different. As mentioned above, the disperse phase polymer forms anisometric particles in the polymer matrix medium when the extrusion of noncompatible polymers is carried out.¹² One of the necessary conditions for the thin fiber formation is a proximity of the mixture components viscosities.¹⁶ Thus, at 240°C, we may expect a more homogeneous extrudates structure from the viewpoint of diameters and uniformity of the fiber distribution of one polymer in the matrix of another. However, the homogeneity of the structure depends also on the mixture content.

Microphotographs of the extrudate cross sections with different C_{PES} obtained at 240°C are presented in Figure 3. It is seen in the figure that at 3% PES content, more or less homogeneous elongated particles penetrating the PSPH section are formed. At 10% PES, the particles look like threads and tend to form layer structures. At 30% PES, one can observe PES layers in the PSPH matrix, whereas, at 50%, it is already impossible to detect the polymer matrix and the polymer phase. At 70% PES content is no longer a matrix; at $C_{\text{PES}} = 90\%$ the PSPH anisometric particles are distributed in the PES matrix. At 260°C the situation as a whole is analogous to the preceding one, but at 280°C, it is much more chaotic, starting from small PES contents. The lat-

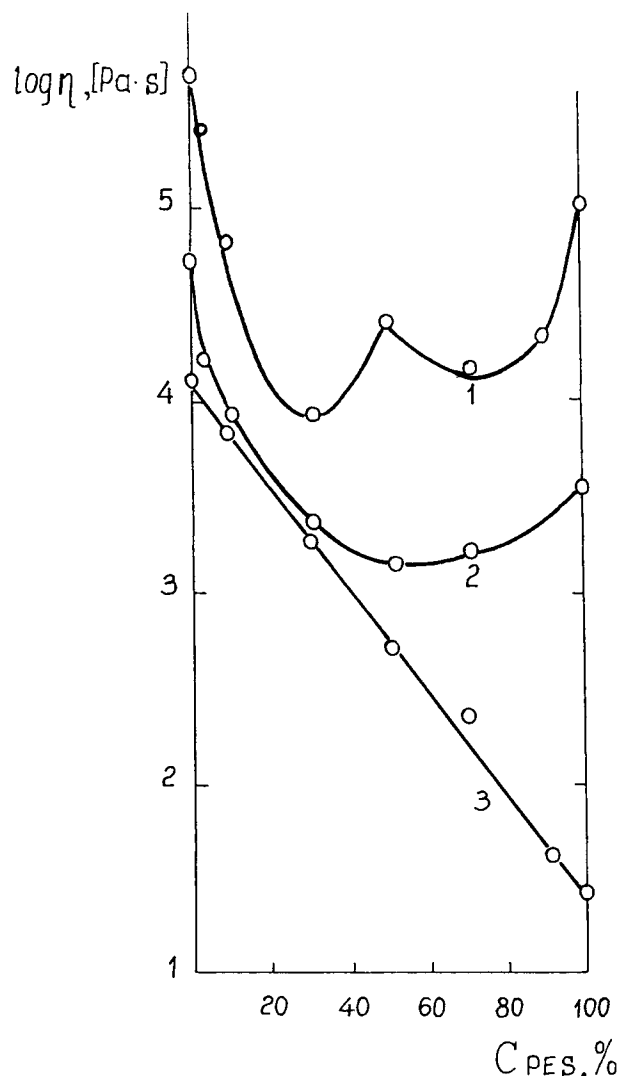


Figure 2 Viscosity vs. composition for PSPH/PES blends at temperatures of 240°C (1), 260°C (2), and 280°C (3).

ter is due to instability of the emulsion under this temperature.

Thus, the morphology of the stream proved to be complicated enough and, naturally, the mixture viscosity will be determined not only by the fraction of one or another component in the stream section, but also by the way one component is distributed in another. From this point of view, the most interesting compositions proved to be 3, 10, and 90% PES content for which the specific fiber formation is typical. However, the viscosity minima are displayed for other compositions: $C_{\text{PES}} = 30$ and 70% at 240°C and $C_{\text{PES}} \sim 50\%$ at 260°C. The viscosity minima are probably due to the formation of thin surface layers of the disperse phase polymer on the polymer matrix by which the flow takes place.

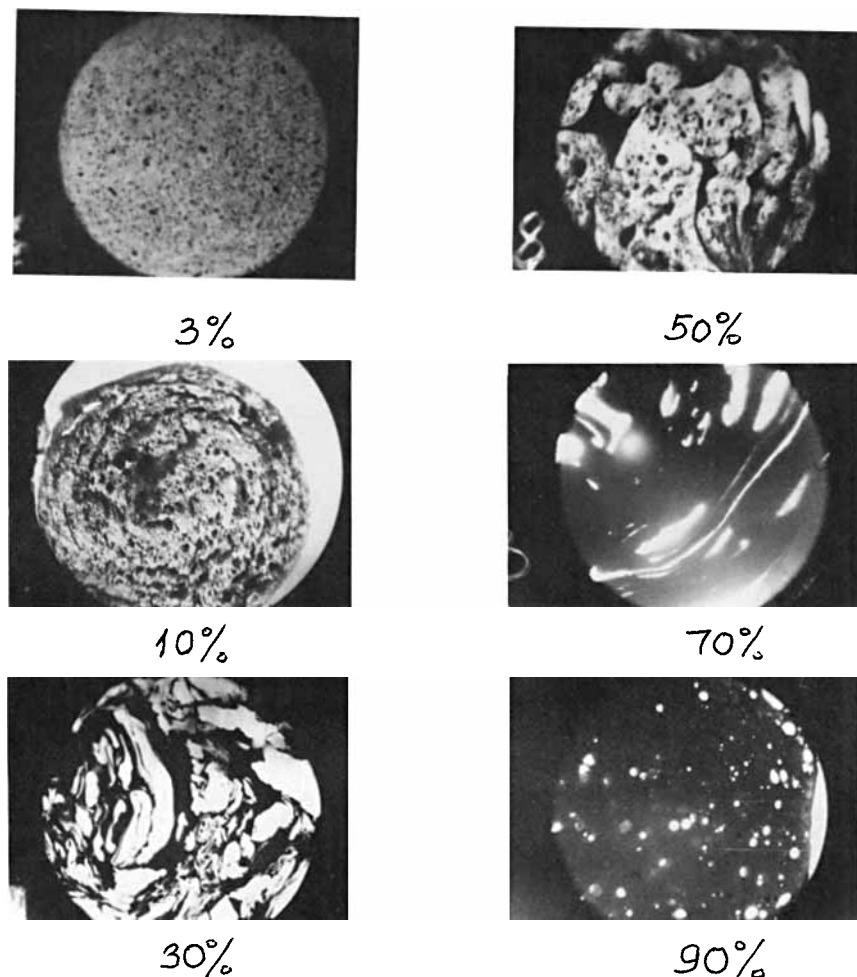


Figure 3 Photomicrographs (35 \times) of cross sections of blend extrudates with different concentration of PES (indicated on the figure).

Tendency to the formation of the surface layers is principally known also for polymer pairs which do not contain the LC component,¹⁷ but for LC polymer this process is more sharp, though the reason for this phenomenon is not yet clear. We suppose that the formation of such a fibrous envelope takes place at the channel entrance zone when the elongated drops of the disperse phase under the action of the extension stresses in entrance cone come in contact with the hypothetic cone surface separating the regions of the primary and secondary flows. By the secondary stream we mean moving of the microvolumes of the substance along a closed trajectories in the stagnant zones. It can be predicted that the deceleration of the primary liquid fibers will lead to a loss of their kinetic energy and spilling along the conical surface which in the channel transforms into a cylindrical shape envelope. Another reason for cone LC-surface forming could be the local increase of thin fiber concentration on the interzonal

boundary as a consequence of the low viscosity component migration onto the periphery of the stream.

The supposition about location of the envelope occurrence was proved by direct experiments using sectional capillaries with entrance angles of 180 and 120°. The flow ceases after developed stationary stream and the reservoir capillary system is cooled. After dismounting the capillary, washing the PSpH, and electron-microscopic study of the morphological PES skeleton, the formation of a PES fibrillized envelope at the entrance zone to the channel only for capillary with an entrance angle of 180° was confirmed (Fig. 4). For another capillary we did not observe the formation of the continuous LC envelope.

Such a complicated stream morphology sets serious problems before rheologists: for example, concerning the parabolicity of the velocity profile and linearity of the stress profile in the stationary Poiseuille flow. Speculatively, we can presuppose two



Figure 4 The appearance of sample obtained with using a sectional capillary (entrance angle 180°) after washing out PSPh and removing a PES from stagnant zones. Magnification $15\times$.

variants of local velocity profiles along the cylindrical channel diameter.

Both are based on the experimental evidence regarding the formation of thin LC-polymer threads and the conelike envelope at the transition zone from the entrance to the cylindrical part of the channel. In the first variant, thanks to the stability of the LC threads, they are not destroyed in the region of the change in the velocity profile and move without shear deformation at the interphase boundaries. The flow is affected over the surface layer. This is the so-called plug flow with a planar velocity profile in the flow core and the sharp change velocity in the surface layer [Fig. 5(a)].

The second one concerns the polyparabolic velocity profile [Fig. 5(b)], taking into account the shear of the materials along the interphase boundaries. In this case it is possible to expect a higher degree of molecular orientation of the LC polymer in the extrudate than in the first version. Therefore, an indirect confirmation of the flow mechanism of the polymer mixture can be the X-ray data which indicate the fact that the LC PES orientation in the blend is substantially lower than in a 100% PES.

Thus, we may assume that no additional orientating strain along the interphase surfaces takes place and therefore the plug flow can be regarded as being more probable.

It should be noted that when we obtained the extrudates of the blends, we used in all the cases the same shear strain conditions without allowing practical extension deformation besides occurring at the capillary entrance. The extension of the extrudates would undoubtedly lead to a more pronounced orientation effect depending on the mixture composition. This question will be analyzed separately.

Completing the discussion on the rheological properties of the PES-PSPh mixture melts, we can now go over to another aspect, future analysis of which may be fruitful. We have in mind the stabilization of the PSPh flow by means of PES additives. The thing is that the PSPh melts especially in the region of low shear stresses show an unstable flow which is accompanied by defects on the extrudate surface. The adding of 3% LC polyester to PSPh promotes stabilization of the flow and improvement of the extrudate quality (Fig. 6).

Possibly, there occurs suppression of elastic turbulence of the PSPh melt through regulating its high-elastic properties. It is known¹⁸ that small additives of high-disperse fillers such as carbon black promotes widening the shear range of the defectless polymer extrusion. The mechanism for exerting an influence of the thin LC PES jets on the effect of

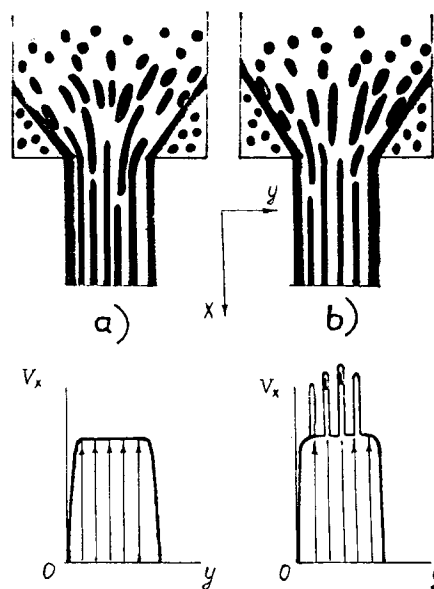


Figure 5 A scheme explaining the appearance of the conical fibrillized envelope at the channel entrance and variants of velocity profiles (see the text).

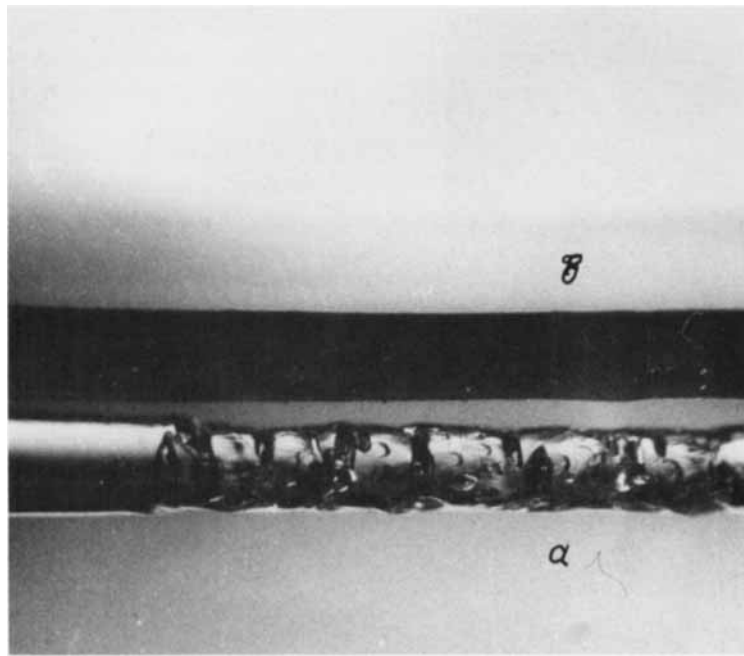


Figure 6 The extrudates of PStPh (a) and blend PStPh/PES 97/3 (b) obtained at $\log \tau = 4.0$. Magnification 8 \times .

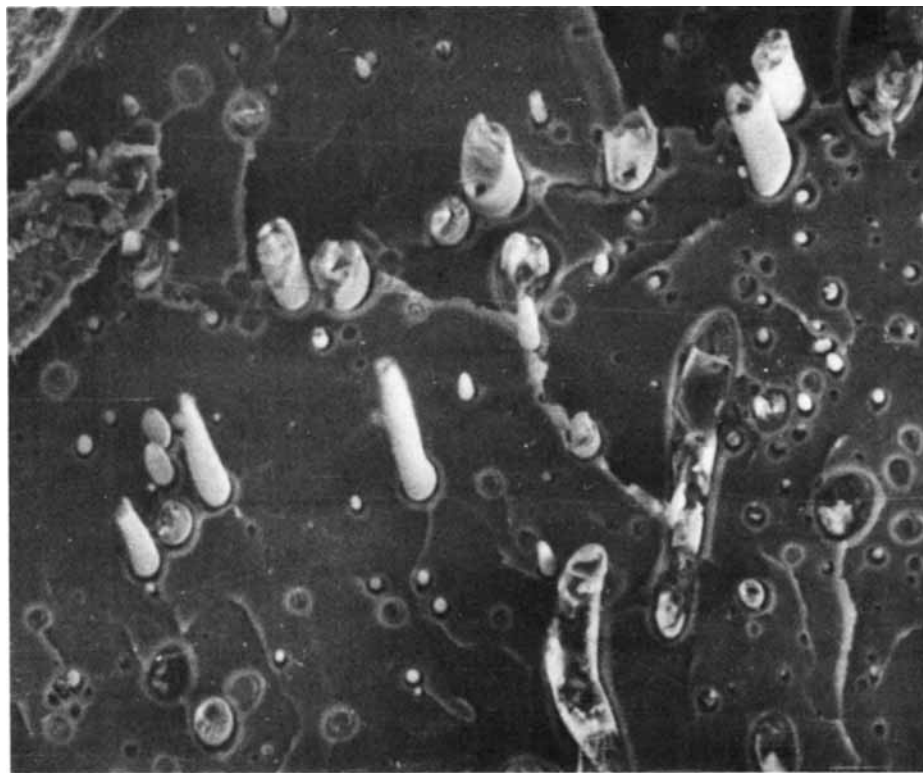


Figure 7 SEM photomicrographs of blend extrudate PStPh/PES 70/30 fracture (2000 \times).

the elastic turbulence is probably similar to the mechanism for disperse fillers in the rubberlike matrix. In both cases it is concerned with the suppression of the high elasticity of the system.

Morphology

From the previous section of this paper we can certainly realize the richness of the morphological aspect of extrudate blends containing LC-component. Let us study this aspect in more detail.

By simple forcing the mixture melt through the capillary, we are able to obtain an arming system (composite in situ). Naturally, the blend under flow preserves its continuity, i.e., even in the case of complete incompatible polymers there is no question as to their spalling along the interphase surface in a fluid state. However, such a monolithic fluid state can become destroyed on cooling and crystallization

of jets. One of the advantages of the linear LC polymers is the low thermal expansion coefficient ($\sim 10^{-5}$ 1/deg), leading to the fact that when the LC phase is cooled, it shrinks to a lesser degree than the thermoplastic isotropic phase. Hence it follows that if the LC polymer represents a disperse phase, then on cooling the matrix PSpH will squeeze the solid PES threads. However, in the opposite region of the compositions ($C_{\text{PES}} \geq 70\%$), the PSpH threads will shrink to a greater extent than the LC matrix, on cooling. In this case the phases may stratify along the interphase boundaries. Figure 7 illustrates the cross-section fracture of the composite extrudate from which it is seen that PES fibers are densely situated in the PSpH matrix. However, these data say nothing with respect to the specificity of the interaction between the phases.

Nevertheless, due to the presence of the phenyl groups in either polymer, we may apparently expect

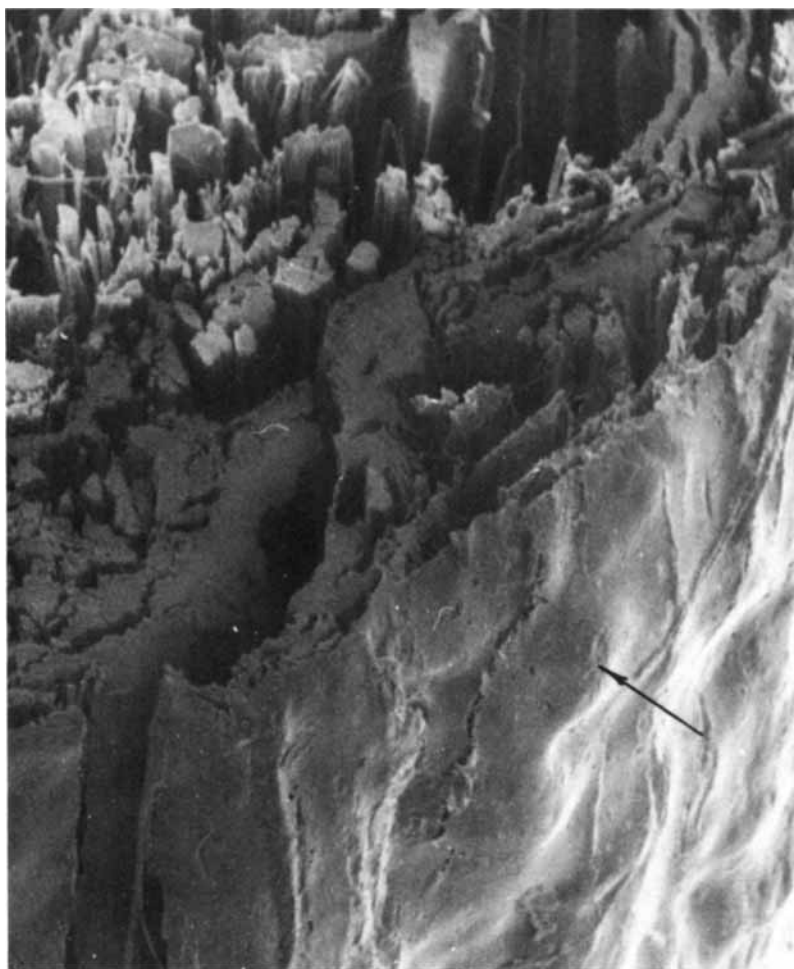


Figure 8 Morphological skeleton of PES (125X) after washing out PSpH from blend extrudate containing 30% PES.

not a zero interphase energy and also a stronger interaction than a frictional one. Monitoring the interaction on the interphase boundary will be the main instrument for modifying the compositions properties.

Because of the not very high molecular orientation in the LC polyester threads, they remain monolithic, i.e., they are not fibrillized. But after testing the materials on the tensile strength machine, one can see the fibrillization effect on the rupture surface. Probably, even the achievement of such an effect will not lead to the destruction of the system in the process of extrudate extension as a result of a thermoplastic matrix presence. Therefore, for compositional extrudates one may expect the maintenance of a definite level of the mechanical properties in the transverse direction.

Figure 8 displays the so-called PES "morphological framework" obtained after removing the polysulfone from the composition PSpH/PES = 70/30. This framework exhibits a strong likeness to that of timber or bamboo fibers. The figure clearly shows the fibrillized PES layers as well as the outer "skin" (shown by the arrow) which are responsible for the unique rheological properties of the melt compositions.

Mechanical Properties

As the names imply, the soft and stiff components are distinctly different by their deformaticity; therefore, in the case of reinforcing fiber continuous lengths, the deformation behavior of the composite will be determined by the stiff component properties, if, of course, we do not take into account sliding along the interphase boundary of the components. In the case of final length fibers, an extension deformation of the soft matrix component can lead to formation of the neck. In both cases the interaction on the interphase boundary of the components play an essential role.

The "stress-strain" dependencies for the initial polymers and a variety of blends are presented in Figure 9. The PSpH deforms through the neck and has a yield point and very high elongation at break. At the same time, PES behaves as a stiff-chain polymer whose strength is twice as high as that of PSpH (in extrudates), the elongation at break being ~ 20%. The stress-strain curves of the composition are located between the appropriate initial components curves, but their location varies nonmonotonically with varying compositions.

The optimal PES content in the compositions

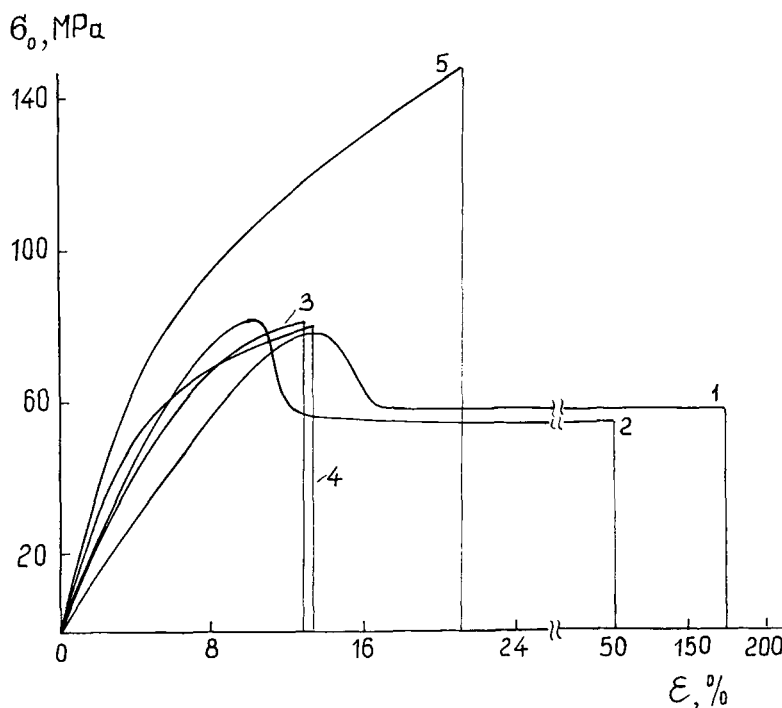


Figure 9 Stress-strain dependencies for blend extrudates containing 100% PSpH (1), 3% (2), 30% (3), 90% (4), and 100% PES (5).

can be revealed from the data on the concentration dependencies of the initial modulus of elasticity, E , tensile strength σ , and elongation at break, ϵ . Since it is difficult to obtain defectless specimens under laboratory conditions, the best model mechanical characteristics can be the initial modulus. The dependencies of E , σ , and ϵ on PES content in extrudates obtained at 240°C are illustrated by Figure 10.

At small C_{PES} values, the composition modulus rises and then descends, but at 30% PES it again rises. A further dramatic change in the modulus takes place at $C_{\text{PES}} \geq 90\%$. The elongation at break of the extrudates declines to 10% of the PES content in the composition and then stabilizes on the level of 10–15%.

As to the strength dependence on PES content it increases with increasing C_{PES} , passes through maximum at 3.0% PES, and then through a weak minimum at 50% PES and drastically increases in

the narrow range of $C_{\text{PES}} \sim 90\text{--}100\%$. The plot illustrates two strength values: The first is calculated at the initial section (σ_0), and the second is for break deformation (σ_b). The difference between the two values becomes noticeable at $C_{\text{PES}} < 30\%$. In the field of high content of PSPH, the extrudates can principally form the neck under deformation; therefore, the methods of flexible-chain polymer orientation are applicable to them.

The maximal growth of the modulus and strength (taking into consideration the conventionality of the latter characteristics) can be observed at 3% PES. This is in agreement with the electron-microscopic patterns and indicates the greatest uniformity in the PES distribution in the PSPH matrix for this composition. The appearance of layers, especially the PES envelope whose formation is completed at 20–30% PES concentration, influences the mechanical properties of the compositional extrudates. This, in

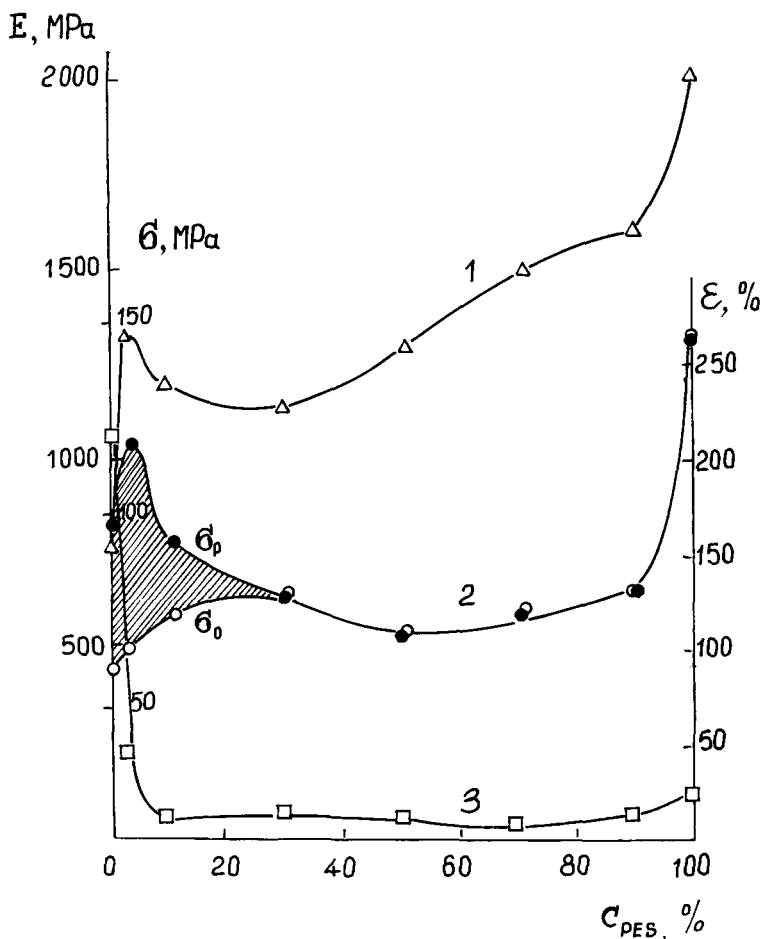


Figure 10 Initial modulus (1), tenacity (2), and elongation at break (3) of blend extrudates vs. composition.

particular, determines the change in the shape of the stress-strain curves, disappearance of the yield point, and sharp decrease in the elongation at break.

At $C_{\text{PES}} > 70\%$, the matrix is already PES. Judging from the morphological investigations, the PSPH also gives rise to anisodiametric formations within the extrudates, and in a number of cases an enriched PSPH surface layer is formed.

CONCLUSIONS

Thus, the addition of LC polymers to ordinary thermoplastic materials can lead to a decrease in the melt viscosity and modification of the physical-mechanical properties of the extrudate. These effects are predetermined by the unique morphology of the extrudated specimens and by the level of the interaction on the interphase boundary.

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