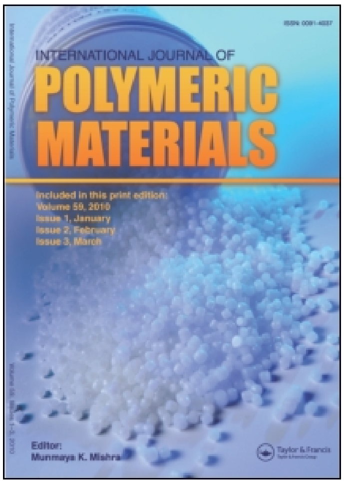

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The Rheology of the Fiber-Forming Process in Melts of Incompatible Polymers at Highly Uniform Shear†

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INTRODUCTION

As was shown in some works,[1–8] the morphology of mixtures of incompatible polymers depends on a number of factors, such as composition of the mixture, viscoelastic properties of the components, conditions of their mixing, and surface tension at the interphase. The rheological properties of the components and, consequently, the conditions of their mixing produce a tangible effect on the phase state of the mixture and its microstructure. The morphology, in turn, determines to a great extent the mechanical properties of the products based on mixtures of incompatible polymers. For example, the anisometry of the dispersed phase particles leads to anisotropy of the mechanical properties.[9,10] In some cases, for instance, when a mixture of polymers is pressed through ducts, the dispersed phase is observed to form a fibrous structure, which results in one polymer being reinforced by the other.[8,11,12]

The two-phase structure of polymer mixtures may represent a continuous phase of one polymer, in which the other one is dispersed, or consist of two continuous mutually penetrating phases.[13,14] The probability of a mixture component forming a continuous phase increases with its concentration and

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as its viscosity decreases as compared to that of the other component. It is not clear, however, what should be the minimum concentration of the low-viscosity component, at which it would form a continuous phase. It is important to point out that most studies into microstructure and viscoelastic properties have been carried out with the mixtures being deformed in a nonuniform shear field at sufficiently high shear rates and stresses when all structural changes are fast and become difficult to observe.[2,5–8,11,15,16] In embarking upon this work, we intended to study the viscoelastic properties of polymer mixtures in a broad range of component concentrations and viscosities in a field of relatively low shear rates ($\dot{\gamma}$) and highly uniform shear stresses (τ).

EXPERIMENTAL

Taken for the experiments were mixtures of polyethylenes (PE) and polystyrenes (PS) with characteristics as listed in Table I.

The PE samples were obtained on a complex catalyst $(C_2H_5)_2\,TiCl_2 + (C_2H_5)_2AlCl$ in the presence of ethyl chloride and were essentially high-density polyethylenes containing less than 0.5 CH_3 groups per 1000 carbon atoms in the chain.[17] The PS-1 sample was a commercial product of emulsion polymerization with a wide molecular weight distribution. The PS-2 sample was synthesized on a butyllithium catalyst.[18] The PE-2/PS-1 and PE-3/PS-1 mixtures were obtained by mechanical stirring of the powdered components in ethyl alcohol with subsequent drying to a constant weight at 80°C. The PE-2/PS-2 mixture was derived from a suspension of polyethylene in a polystyrene-methyl-ethyl ketone solution by evaporating the solvent with subsequent drying at 80°C. The test samples were formed by compressing at 140°C.

To study the viscous properties of the mixtures use was made of a PIRSP-1 rotary viscometer of the cone-plate type,[19] operating at a constant shear rate.

TABLE I

Characteristics of polymers

Polymer	Designation	Molecular weight, $M \cdot 10^{-4}$	M_w/M_n	$\eta \cdot 10^{-4}$ Pa·s at $\dot{\gamma} = 10^{-3}\,s^{-1}$ and 180°C
Polyethylene	PE-2	6.0	2	40
Polyethylene	PE-3	2.9	2	0.8
Polystyrene	PS-1	45.0	2	20
Polystyrene	PS-2	13.8	1.7	1.1

The angle between the cone and plate was 2°. The experiments were conducted in the range of shear rates from 10^{-3} to 1 s^{-1} and at temperatures ranging from 110 to 180°C. The high-elastic behavior was studied by the recoil method using an EVR-2 elastomers of the cone-plate type.[20] The experiments were carried out in an argon atmosphere. The method of selective dissolution of polystyrene with methyl-ethyl ketone was used to determine the phase continuity of the components in the mixture.[21] The results of structural studies are published in a separate publication,[22] therefore, we shall not dwell upon them.

Since it was shown elsewhere[6,11,20] that the optimal conditions of fiber formation are attained at concentrations close to 30% by weight of the dispersed phase, we took PE in the consentrations for the main experiments. However, both lower and higher concentrations also received due attention.

Experimental results and their discussion

The specific rheological behavior of mixtures of incompatible polymers is determined by the ratios of both viscous and elastic properties of the components.[2,4,21] This is why it is important, in studying the effect of the viscosity of polymers on the properties of their mixtures, that the difference in the high-elastic properties of the components be minimal. As can be inferred from Figure 1, the high-elasticity moduli of the polyethylenes, polystyrenes, and PS-PE mixtures used in the experiments are close at various temperatures and shear stresses. Therefore, one can ignore the effect of different high-elastic properties of the components on the rheological properties of the mixtures as a whole.

Structural studies of the mixtures by the selective dissolution method have

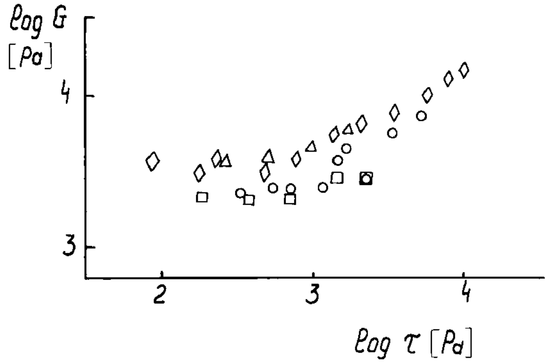

FIGURE 1 Steady-state high-elasticity modulus *vs.* shear stress: △ – PS-1; ◇ – PE-2; □ – PE-3; ○ – PE-2/PS-1; △, ◇ – 180°C; □, ○ 150°.

shown that after their compression all samples containing 30% of polyethylene retain their shape after removal of PS, which is indicative of the fact that the PE phase is continuous.[21]

Thus, it may be assumed that irrespective of the components viscosity ratio the phase structure of the initial samples with a 30% content of polyethylene, prepared by hot pressing at 140°C, is the continuous PE phase in the PS matrix, or so-called matrix structure with both phases being continuous. A similar study of mixtures containing 5% of PE has shown that they are characterized by a structure in which PS is the continuous phase and PE is the dispersed phase.

Consider now the effect of the ratio of viscosities of polyethylene and polystyrene on the rheological behavior of their mixtures in a uniform shear field. Figure 2 represents flow curves of the PE-2/PS-2 mixture containing 30% of polyethylene by weight at three temperatures: 140, 160 and 180°C. The energy of activation of viscous flow of the mixture, calculated at constant shear stresses, was found to equal to $1.34 \cdot 10^5$ J/mole in the temperature range of 160 to 180°C, that is the same as the flow activation energy of polystyrene. This indicates that in this case the dispersing medium (continuous phase) is the less viscous component, polystyrene, which is also present in a greater amount. Thus, deformation of the mixture having a matrix structure brings about, in accordance with the ratio of viscosities and contents of the components a phase reversal and polyethylene as the more viscous component changes from the continuous to dispersed phase. This is vividly illustrated by Figure 3 which

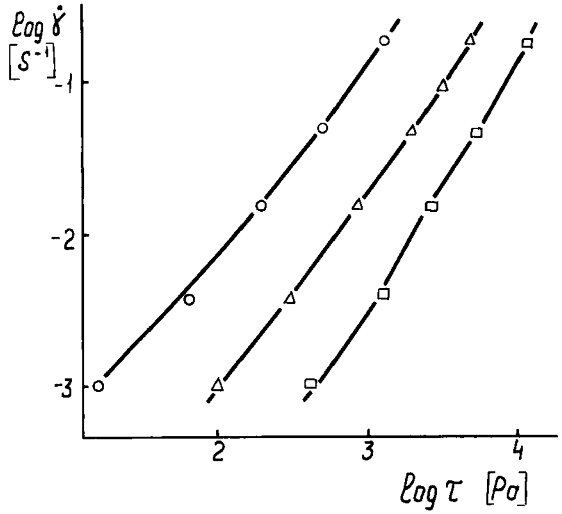

FIGURE 2 Flow curves of PE-2/PS-2 mixtures with 30% PE-2 at 140° (□), 160° (△) and 180° (○).

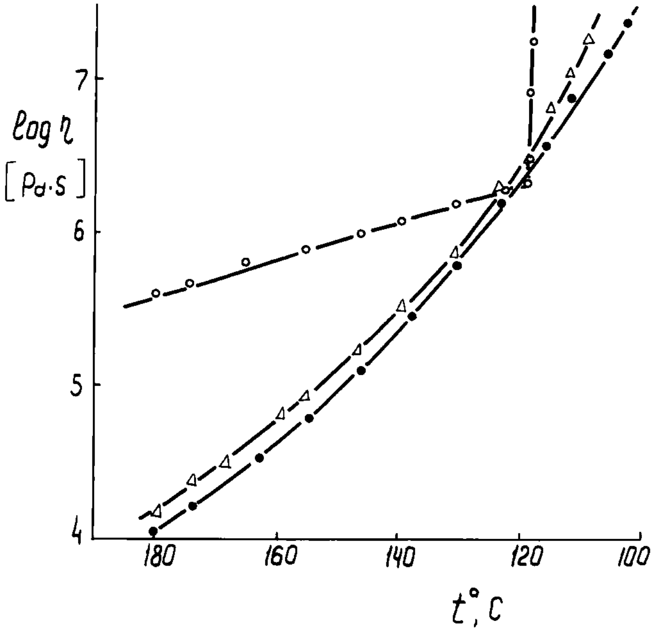

FIGURE 3 Viscosity *vs.* temperature at a shear rate $\dot{\gamma} = 10^{-3}\ s^{-1}$ for PE-2 (○), PS-2 (●) and a mixture with 30% PE-2 (△).

represents the temperature dependences of the viscosity of the PE-2/PS-2 mixture and its components, derived when the melt was cooled down from 180°C at a rate of 1 deg/min with continuous deformation at a shear rate of $10^{-3}\ s^{-1}$. The state of equilibrium of the cooling curves was verified by the stepped cooling method when corresponding to each fixed temperature was an equilibrium value of the polymer system viscosity. In this case, the obtained viscosity values were equal to those for the same temperatures, both on the cooling and flow curves.

The trend of the log $\eta - t^{\circ}$ curves for polyethylene and polystyrene is substantially different, as is shown in Figure 3. Besides, while the polymers are being cooled, the viscosity of polyethylene, unlike polystyrene, sharply increases at 120°C, which is due to the PE crystallization process in view of the fact that the PE crystallization temperature determined by differential thermal analysis was found to approach the abovementioned value (115°C). The viscous flow activation energy determined from the cooling curve using expression similar to the Arrhenius formula is in fact equal to that calculated from the flow curves at $\dot{\gamma} = 10^{-3}\ s^{-1}$. In the case of systems whose behavior is close to the Newtonian one, this energy is equal to the true viscous flow activation energy. In the case of PE-2 which is a high viscous non-Newtonian system the activation energy determined from the log $\eta - t^\circ$ curve was found to equal to $4.19 \cdot 10^4$ J/mole, whereas the viscous flow activation energy calculated from the initial Newtonian viscosities is $5.45 \cdot 10^4$ J/mole. The slight difference between these two values permits the viscous flow activation energy to be evaluated, in the first approximation, from the log $\eta - t^\circ$ curves.

As can be seen from Figure 3, the viscosity of the PE-2/PS-2 mixture changes, during cooling, in the same manner as that of pure polystyrene, while the flow activation energies calculated from these curves in the temperature range of 180 to 150°C were found to equal $1.34 \cdot 10^5$ J/mole, that is equal to the flow activation energy of PS-2 and its mixtures with PE-2, determined from the flow curves. In addition, when the mixture is cooled, no sharp increase in viscosity is observed near the polyethylenes, crystallization temperature. Thus, analysis of the cooling curves clearly shows that when a mixture in which the viscosity of PE is much greater than that of PS is deformed its behavior in a uniform shear field is determined by the properties of polystyrene as the continuous phase.

Figures 4 and 5 represent data for mixtures of PE-2 and PS-1 when the viscosities of the components at 160° to 180°C are closely similar. The viscous flow activation energies of the 30% mixtures, calculated from the flow (Figure 4) and cooling (Figure 5) curves were equal $1.05 \cdot 10^5$ J/mole and $9.22 \cdot 10^4$ J/mole, respectively, that is values intermediate between the flow activation energies of PE-2 and PS-1 ($5.45 \cdot 10^4$ and $1.34 \cdot 10^5$ J/mole, respectively).

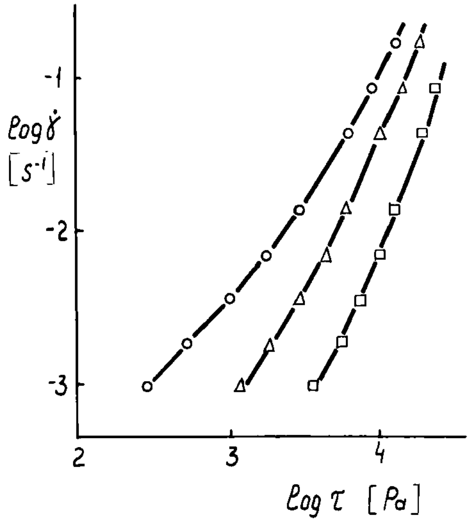

FIGURE 4 Flow curves of PE-2/PS-1 mixtures with 30% PE-2 at 140° (□), 160° (△) and 180° (○).

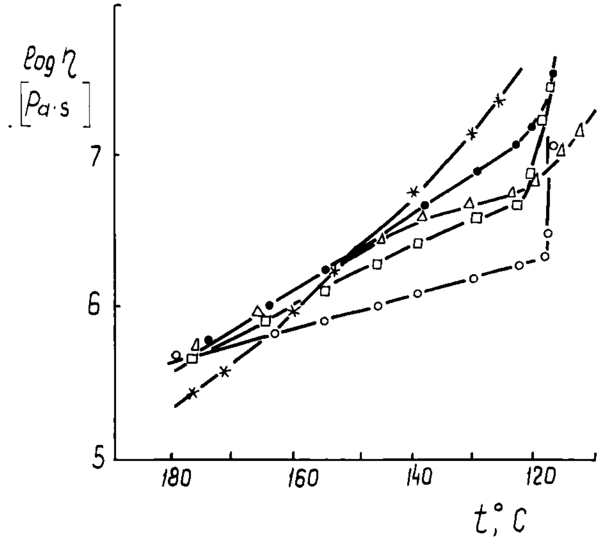

FIGURE 5 Viscosity *vs.* temperature at a shear rate $\dot{\gamma} = 10^{-3}\ s^{-1}$ for PE-2 (○), PS-1 (✻), and their mixture containing PE-2 in an amount of: △—10%, ●—30% and □—50%.

Mixtures of different compositions produce a bundle of cooling curves with different slopes, hence, different flow activation energies depending on the ratio between the components. In the temperature range of 118 to 122°C all mixtures except for the one containing 10% of PE-2 exhibit a marked increase in viscosity, during cooling of the melts, which seems to be due to crystallization of polyethylene in the mixture. Such a behavior of the mixtures when the viscosity sharply increases and the melt loses its fluidity as the PE crystallization temperature, can be explained only assuming the existence of a three-dimensional structure (continuity of the PE phase). On the other hand, the dependence of the activation energy on the composition and the "vagueness" of the PE crystallization process in the mixture indicate that in the case of mixtures with relatively close component viscosities we are dealing with a matrix structure when both phases are continuous and each component makes its contribution to the properties of the two-phase system as a whole.

In the case where the viscosity of the crystallizing component, that is polyethylene, is much lower than that of polystyrene, the rheological behavior of the mixtures is entirely different. The log $\dot{\gamma}$ – log τ curves of Figure 6 have been derived for the 30% PE-3/PS-1 mixture by deformation of the initial sample with increasing shear rate (right branches) which then decreases (left branches).

At every given shear rate the stress tends to decrease and eventually reaches

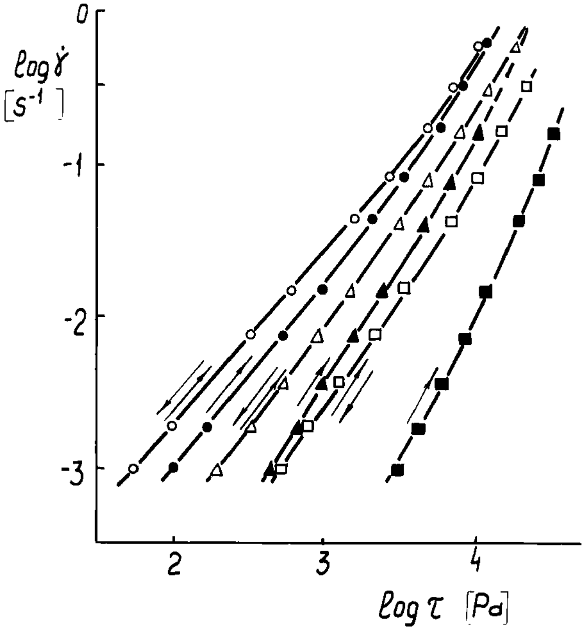

FIGURE 6 Shear rate *vs.* shear stress for PE-3/PS-1 mixtures with 30% PE-3 at 180° (○, ●), 160° (△, ▲), and 140° (□, ■).

a constant level corresponding to steady-state deformation conditions. But in accordance with the experimental procedure the shear rate was increased so that the decrease in the shear stress could be ignored, which corresponds to the black symbols presented in Figure 6. The left branches at 180° and 160°C resulted from a gradual decrease in the shear rate so that all points on this branch corresponded to the steady-state condition. As far as the flow curves at 140°C are concerned, we could not achieve such maximal shear rates that would correspond to the most pronounced change of the system at these temperatures, therefore, the left branch of the flow curve at 140°C was derived after preliminary deformation of the sample at 180°C and $\dot{\gamma} = 3 \cdot 10^{-1}\ s^{-1}$ by gradually decreasing the shear rate. Interestingly, the time of transition from the right to left branches depends on the shear rate, while the amount of deformation remains constant and equal to 40 relative units for the mixture with 30% PE in PS and 130 relative units for the mixture with 10% PE in PS.

Calculation of the temperature dependence of viscosity using the left branches of the $\log\dot{\gamma} - \log\tau$ curve gives the value of the viscous flow activation energy for the PE-3/PS-1 mixture equal to $7.12 \cdot 10^4$ J/mole, that is close to the flow activation energy of PE-3 ($6.70 \cdot 10^4$ J/mole). The viscous flow activation energy corresponding to the right branches was found to equal $1.26 \cdot 10^5$ J/mole, which approaches the activation energy of polystyrene.

The results of selective dissolution of polystyrene from PE-3/PS-1 samples after their deformation at $\dot{\gamma} = 10^{-3}\ \mathrm{s}^{-1}$ corresponding to the left and right branches of the $\log \dot{\gamma} - \log \tau$ curve have shown that in the former case, as distinct from the latter, the washed off samples cleave along the melt flow lines (circumferentially). In view of this and the derived values of the flow activation energy it may be assumed that corresponding to the right branches is the matrix structure of the melt, while the left branches correspond to such a state of the melt when the dispersion medium is the less viscous component, polyethylene despite its relatively low content in the mixture. The transition from the right branch to the left one is associated with ordering and orientation of the initial matrix structure of the melt, accompanied by phase reversal as a result of which the more viscous component, polystyrene, becomes the disperse phase.

Two-phase systems are characterized by an S-shaped viscosity *vs.* composition curve whose inflexion region corresponds to phase reversal.[21] On the curve representing viscosity *vs.* component ratio for the PE-3/PS-1 mixture at 180°C, derived from the left branches of the flow curves (Figure 7), the portion corresponding to phase reversal is practically undetectable. As a result, the entire viscosity-composition curve is arched toward the abscissa, which indicates that the less viscous component, polyethylene, is the dispersing medium practically in the entire range of compositions. The effect of the concentration of the low-viscosity component on the phase state of the melt is

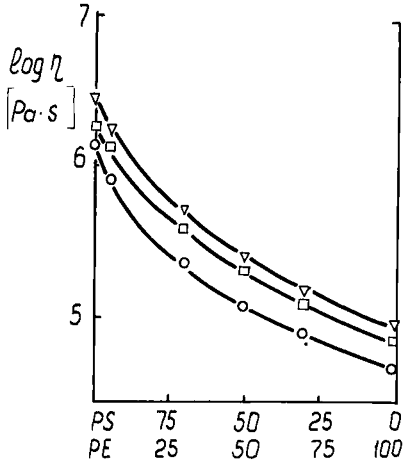

FIGURE 7 Viscosity *vs.* PE-3 content in the PE-3/PS-1 mixture at shear stresses, Pa: ▽—$2 \cdot 10^2$, □—$1 \cdot 10^3$, ○—$5 \cdot 10^3$, 180°C.

well illustrated by the cooling curves for the PE-3/PS-1 mixtures, represented in Figure 8. In the mixtures containing 30 and 50% of polyethylene the latter serves as the dispersing medium which follows from the parallelism of the cooling curves and equality of their flow activation energy to that of pure polyethylene ($6.70 \cdot 10^4$ J/mole). At 5 and 10% concentrations of polyethylene, the flow activation energy of the mixture melts is intermediate between those of the components, which is typical of a matrix structure. This is corroborated by the fact that the complete loss of fluidity by the melt at the PE crystallyzation temperature occurs in mixtures of all examined compositions, which is indicative of continuity of the polyethylene phase when it is present already in a concentration of at least 5%. These results show that, being less viscous, polyethylene may be a continuous phase already at low concentrations in the mixture, becoming a dispersing medium as its concentration increases.

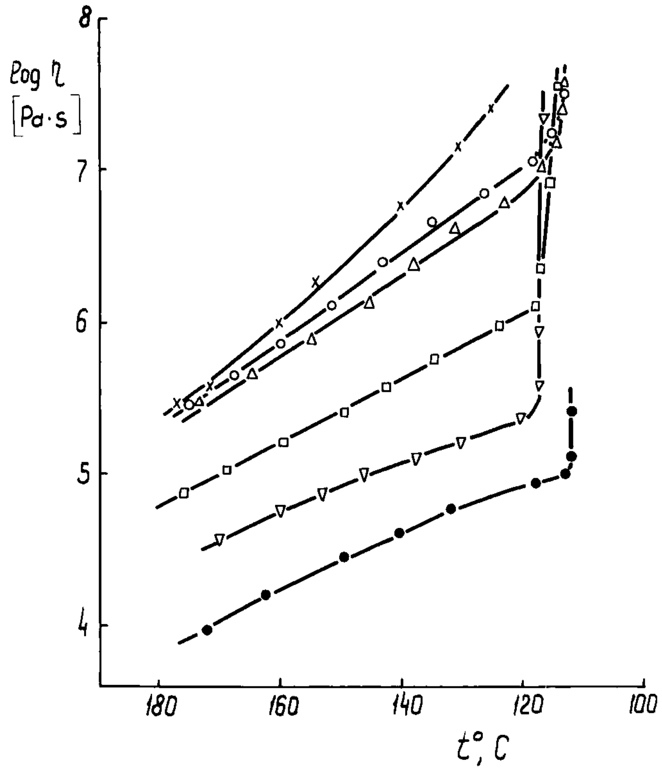

FIGURE 8 Viscosity *vs.* temperature at a shear rate of 10^{-3} s^{-1}: ● PE-3; × PS-1; mixtures with different PE-3 contents %: ○—5, △—10, □—30, ▽—50.

CONCLUSION

For the first time it is shown that under uniform shear field conditions the fibrillation in incompatible polymer melts may occur. Studies of mixtures of linear polyethylene with polystyrene at different viscosity ratios have shown that PE whose viscosity is much higher as compared to PS, forms a continuous fibrous phase at extremely low shear rates. At the same time it was found that PE of a very low viscosity (the viscosity ratio of PE and PS being lower by one order of magnitude) may perform the function of a dispersing medium even when present in an amount of 5%. Transition from one structural state of the system to another due to the polymer melt deformation in uniform shear field has been established. The results of structural—morphological studies are published in a separate paper.

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