

Morphology and Rheology of Polysulfone/Vectra-A950 Blends

P. L. MAGAGNINI,^{1,*} M. PACI,¹ F. P. LA MANTIA,² I. N. SURKOVA,³ and V. A. VASNEV³

¹C.N.R., Centro Studi dei Processi Ionici di Polimerizzazione, Dipartimento di Ingegneria Chimica, via Diotisalvi 2, 56126 Pisa, Italy; ²Dipartimento di Ingegneria Chimica, viale delle Scienze, 90128 Palermo, Italy; and ³Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov st. 28, Moscow, Russia

SYNOPSIS

Blends of polysulfone (PSu) with a liquid crystalline copolyester (Vectra-A950; VA) have been prepared by melt mixing. Their morphology has been studied by scanning electron microscopy (SEM). Either blend specimens as obtained from the melt mixing or fibers drawn from the melt were used for the SEM analysis. Further information on the morphology of the blends was gained by extraction of the PSu phase with methylene chloride. Preliminary rheological characterization of the blends was made by measuring the viscosity curves at 290 and 300°C, with a capillary viscometer having a die of 1 mm diameter and L/D = 40. Finally, an attempt at improving the phase compatibility was made by synthesizing a copolyester, having the same structure of commercial VA, in the presence of preformed PSu and using the product as a possible compatibilizer.

It was demonstrated that the blends are composed of two immiscible phases showing poor adhesion. The LCP droplets could, nevertheless, be deformed into oriented fibrils under elongational flow conditions. The LCP particles were shown to coalesce into large domains, and to migrate toward the outer layer of, e.g., extruded rods, under the influence of appropriate flow conditions, thus showing that there is a strong mutual influence between morphology and rheology of these materials. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Thermotropic liquid crystalline polymers (LCPs) have been actively studied during the last decade as blend components for commercial thermoplastics.¹ One of the interesting aspects of these blends is that they may provide, under appropriate processing conditions, self-reinforcing materials, where the LCP fibrils produced *in situ* reinforce the thermoplastic matrix. Because the properties of the finished articles depend largely on morphology, and this is, in turn, determined by the flow field involved by processing, a number of researchers have focused their attention on the study of the rheology-morphology-property relationships in blends of LCPs with different thermoplastic polymers, with or without compatibilizers.²⁻⁸

The rheological and morphological characteristics of blends of bisphenol-A polysulfone (PSu) with a

liquid crystalline polymer (LCP) were first described by Kulichikhin et al.⁹ These authors demonstrated that a reinforcing effect is played by the fibrillar LCP particles in blend extrudates, the effect being more pronounced at low LCP contents (< 10%). Moreover, the rheological characterization showed that, under appropriate measurement conditions, the presence of minima in the viscosity-composition curves could be observed. This was thought as being due to peculiarities of the morphology of the blends in the molten state. The formation of a LCP layer at the wall of the capillary, as well as of a conical LCP envelope at the die inlet, was also ingeniously demonstrated.

Subsequent studies by Skovby et al.,¹⁰ Hong et al.,¹¹ Golovoy et al.,¹² and Kozlowski¹³ confirmed that the rheological behavior of the PSu/LCP blends is strongly morphology dependent. The addition of LCP into PSu was always found to improve the processability of the latter polymer.⁹⁻¹³ In injection-molded blend specimens, a pronounced skin-core morphology, with the LCP particles oriented

* To whom correspondence should be addressed.

in the skin and globular in the core, was observed.¹² In extruded specimens and drawn fibers, appreciable reinforcing of PSu, due to the fibrillar LCP dispersed phase, was obtained,⁹⁻¹¹ although the interfacial adhesion between the PSu and the LCP phases was always found to be poor.⁹⁻¹³

In this article, we describe the results of a morphological and rheological characterization of blends of PSu (Udel P-1700, by Amoco) with a commercial LC copolyester (Vectra-A950, by Höchst-Celanese). An attempt at improving the PSu/LCP interphase adhesion has also been made by carrying out the LCP synthesis in the presence of PSu, and using the product as a possible compatibilizer.

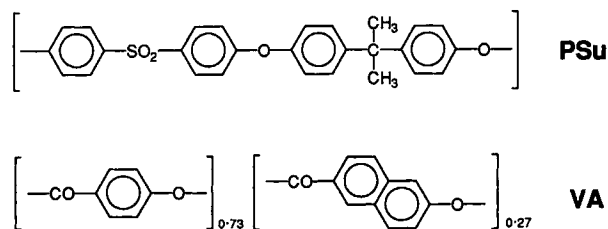
EXPERIMENTAL

Materials

PSu was a commercial bisphenol-A polysulfone (Udel P-1700 NT 11) generously supplied by Amoco Chemical Belgium N.V. The MFI, measured at 343°C using a die with 2.1 mm diameter and 8.0 mm length (L/D = 3.8) and a pressure of 300 kPa, was 8.1 g/(10 min).

The LCP, referred to as VA, was a commercial product (Vectra-A950) sold by Höchst-Celanese. This is a wholly aromatic copolyester having a molar composition of 73% 4-hydroxybenzoic acid and 27% 2-hydroxy-6-naphthoic acid units. According to the producer, the melting point of this LCP is 280°C. We measured a $T_m = 286.4^\circ\text{C}$, for our sample, by differential scanning calorimetry (cf. Fig. 1). At temperatures higher than T_m , VA gives rise to a nematic mesophase that is stable up to above the temperature of initial degradation.

The structures of PSu and VA are the following.



4-Hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid of commercial source were acetylated with acetic anhydride in 5% aqueous sodium hydroxide solution, at 0°C. The acetoxyacids were recrystallized twice from ethanol. Their melting points were 196°C and 230°C, respectively.

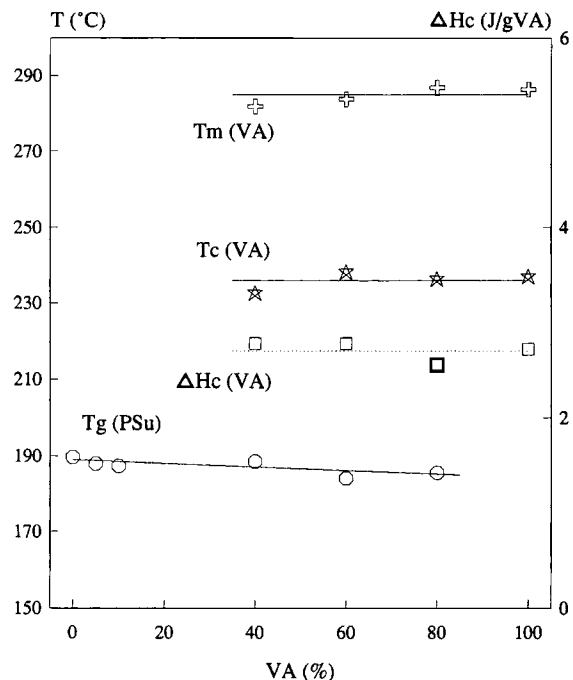


Figure 1 Thermal properties of the PSu/VA blends determined calorimetrically.

Blends

PSu and VA were dried under vacuum at 120°C for at least 24 h, before use. The blends were prepared in a laboratory Brabender mixer at 290°C and 100 rpm, for 3–4 min.

Polycondensation

The polycondensation of 4-acetoxybenzoic acid and 2-acetoxy-6-naphthoic acid, either alone or in the presence of PSu, was carried out under dry argon, in a pyrex tube heated in a thermostated metal block, with the following temperature–time profile: 220°C—0.5 h; 260°C—0.5 h; 280°C—2.5 h; 300°C—0.5 h. No catalyst was used. During the last 3-h period, vacuum was gradually applied to the system, and the polycondensation was completed, maintaining the residual pressure below 130 Pa during the last 2 h. When the synthesis of the LCP was made in the presence of PSu, the latter was ground, dried as described before, and added to the acetylated monomers; the amount of PSu was calculated to obtain a 20/80 PSu/VA blend, assuming a stoichiometric yield of LCP. The actual content of PSu in the obtained product was, in fact, only slightly higher, as estimated by IR analysis.

Techniques

The thermal properties of neat polymers and blends were determined by differential scanning calorimetry, with a Perkin Elmer DSC-4 apparatus. The measurements were made under nitrogen, using a scanning rate of 20 deg/min.

The rheological measurements were made with a CEAST Rheoscope-1000, using a capillary with 1 mm diameter and $L/D = 40$.

The morphology of the samples was studied with a Jeol T300 scanning electron microscope. The specimens were normally prepared by fracturing at the liquid nitrogen temperature either small blocks of material as received from the melt mixer, or strands prepared by extrusion at 290–300°C in a melt index apparatus equipped with a die of 1 mm diameter and $L/D = 1$, under a pressure of ca 3.5 MPa, or fibers drawn from the molten material with a pair of tweezers. The fracture surfaces were coated with gold. In some instances, the blend specimens were extracted with methylene chloride before SEM examination. The extraction experiments were made with the following technique. A small piece of material (ca. 40 mg) was cut out of the blend, weighed, introduced in a preweighed test tube with ca. 5 ml methylene chloride, and left at room temperature for 24 h, with occasional shaking. Then, ca. 2 ml benzene were added to reduce the specific weight of the solution and the test tube was centrifuged at 2000 rpm for 5 min. The clear solution was carefully separated and another portion of 5 ml methylene chloride was added to the residual solid. This procedure was repeated four times. The undissolved material was finally dried and weighed in the tube. The combined solutions were poured into excess hexane under stirring, and the precipitated PSu was dried and weighed. The percent amount of PSu extracted from the blends was calculated from the weights of both the undissolved material and the precipitated PSu. The residue was mounted and gold coated for SEM examination.

The separation of the VA particles obtained by extraction into coarse and fine ones, was made by stirring into a new portion of methylene chloride the insoluble residue of the previous extraction, and by filtering the suspension through a wire netting (mesh size, ca. 1 mm). The flocky residue on the sieve was repeatedly washed, dried, and weighed. The combined percolated suspensions of small VA particles were centrifuged after benzene addition, and the decanted solid was also dried and weighed.

Optical microscopic observations were made with a Leitz Ortholux-Pol equipped with a hot stage and polarizers.

RESULTS AND DISCUSSION

Calorimetry

The DSC analysis of the blends proved that PSu and VA give rise to immiscible phases. A similar conclusion had already been reached by others for the same PSu/VA system,^{11–13} as well as for other PSu/LCP blends.^{9,10} As it is shown in Figure 1, the T_g of the PSu phase decreases slightly on increasing the VA content of the blends. This is in agreement with the data of Hong et al.,¹¹ and with those found by Skovby et al.¹⁰ for blends of PSu with a different LCP. However, the extent of the observed T_g lowering did not exceed 4°, and this is not far from the limit of the experimental errors. On the other hand, the temperatures of melting (T_m) and crystallization (T_c) of the VA phase, as well as the associated enthalpies (calculated per gram of VA), remained practically constant over the composition range between 40 and 100% VA (cf. Fig. 1). Due to the comparatively low fusion and crystallization enthalpy of VA, a reliable measurement of T_m and H_m of the VA phase in blends with less than 40% VA was not possible.

Morphology

The viscosity curves for neat PSu and VA, measured with a capillary viscometer at 290 and 300°C, are shown in Figure 2. At these temperatures, VA is in the nematic mesophase. Both polymers are seen to deviate from the Newtonian behavior and to shear thin over the whole shear rate range investigated. As expected, the shear thinning behavior is more pronounced for VA. It may also be observed that the viscosity of the LCP is lower than that of PSu by approximately an order of magnitude. The viscosities of VA and PSu, measured at low (ca. 8 s⁻¹) and high (ca. 300 s⁻¹) shear rates, are given in Table I, and the relevant viscosity ratios η_{VA}/η_{PSu} are calculated. It is apparent that, on increasing the shear rate and the temperature, the viscosity ratio η_{VA}/η_{PSu} decreases. On the basis of the empirical relation:¹⁴

$$\Phi_{VA}/\Phi_{PSu} = \eta_{VA}/\eta_{PSu} \quad (1)$$

the concentration of VA (Φ_{VA}) at which the phase inversion is expected to occur in PSu/VA blends can be calculated. The Φ_{VA} values thus calculated, which are also included in Table I, indicate that the phase inversion is expected to take place over a range of VA concentrations around 12%, at low shear rate, and around 6%, at high shear rate.

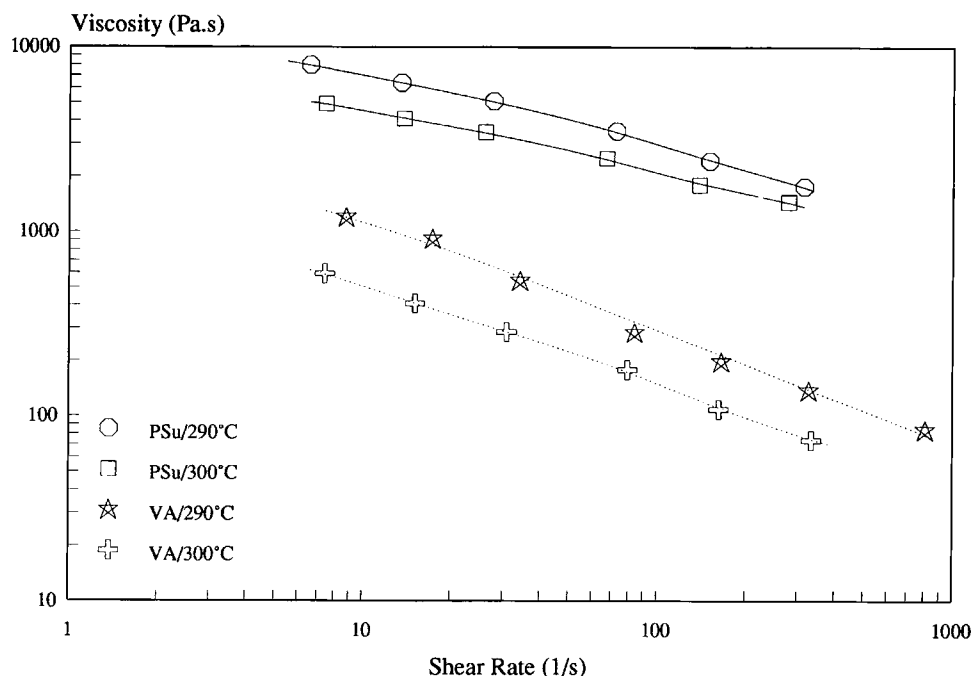


Figure 2 Viscosity curves of neat PSu and VA, measured at 290 and 300°C.

Metelkin and Blekht,¹⁵ on the basis of theoretical considerations on the formation of phase structures in heterogeneous polymer mixtures, derived an expression for predicting the continuity of the phases that also takes into account, besides the rheological parameters, the surface tension of the components. They showed that, in a fairly wide composition range around that corresponding to the phase inversion as predicted by Eq. (1) for a binary mixture, the flow induced formation of two cocontinuous phases is possible.

The SEM micrographs of PSu/VA blends, as obtained from the Brabender mixer, are shown in Figure 3. In the 95/5 blend [Fig. 3(a)], the LCP phase appears in the form of small (0.2–2 μm) spherical particles. As the VA concentration increases, not only does the average dimension of the particles in-

crease, but their size distribution grows as well, and larger, more or less elongated domains, partially coalesced into laminar aggregates, appear (cf. Fig. 3(b–d)). The blends with a VA concentration of 60% or more (cf. Fig. 3(e, f)) have the LCP as the matrix, and the PSu phase is in the form of elongated droplets that, as it is shown in Figure 3(e), are accompanied by larger domains.

In Figure 4, similar micrographs of the fracture surfaces of blend fibers obtained by drawing the melt are shown. In both as-mixed materials (Fig. 3) and fibers (Fig. 4), the biphasic character of the blends is clearly demonstrated for all compositions, and the interphase adhesion appears to be distinctly poor. Despite this, the dispersed phase displays a considerable tendency to fibrillate when the specimen is produced under elongational flow conditions (cf. Fig.

Table I Viscosities and Viscosity Ratios of VA and PSu at Two Shear Rates and at Two Temperatures

Shear Rate	$T = 290^\circ\text{C}$				$T = 300^\circ\text{C}$			
	η_{VA}	η_{PSu}	$\eta_{\text{VA}}/\eta_{\text{PSu}}$	$\Phi_{\text{VA}} (\%)$	η_{VA}	η_{PSu}	$\eta_{\text{VA}}/\eta_{\text{PSu}}$	$\Phi_{\text{VA}} (\%)$
$\dot{\gamma} \approx 8 \text{ s}^{-1}$	~ 1200	~ 8000	0.15	13	594	~ 5000	0.12	11
$\dot{\gamma} \approx 300 \text{ s}^{-1}$	136	~ 1760	0.077	7	75	1450	0.052	5

VA concentrations corresponding to the phase inversion, calculated according to equation (1).

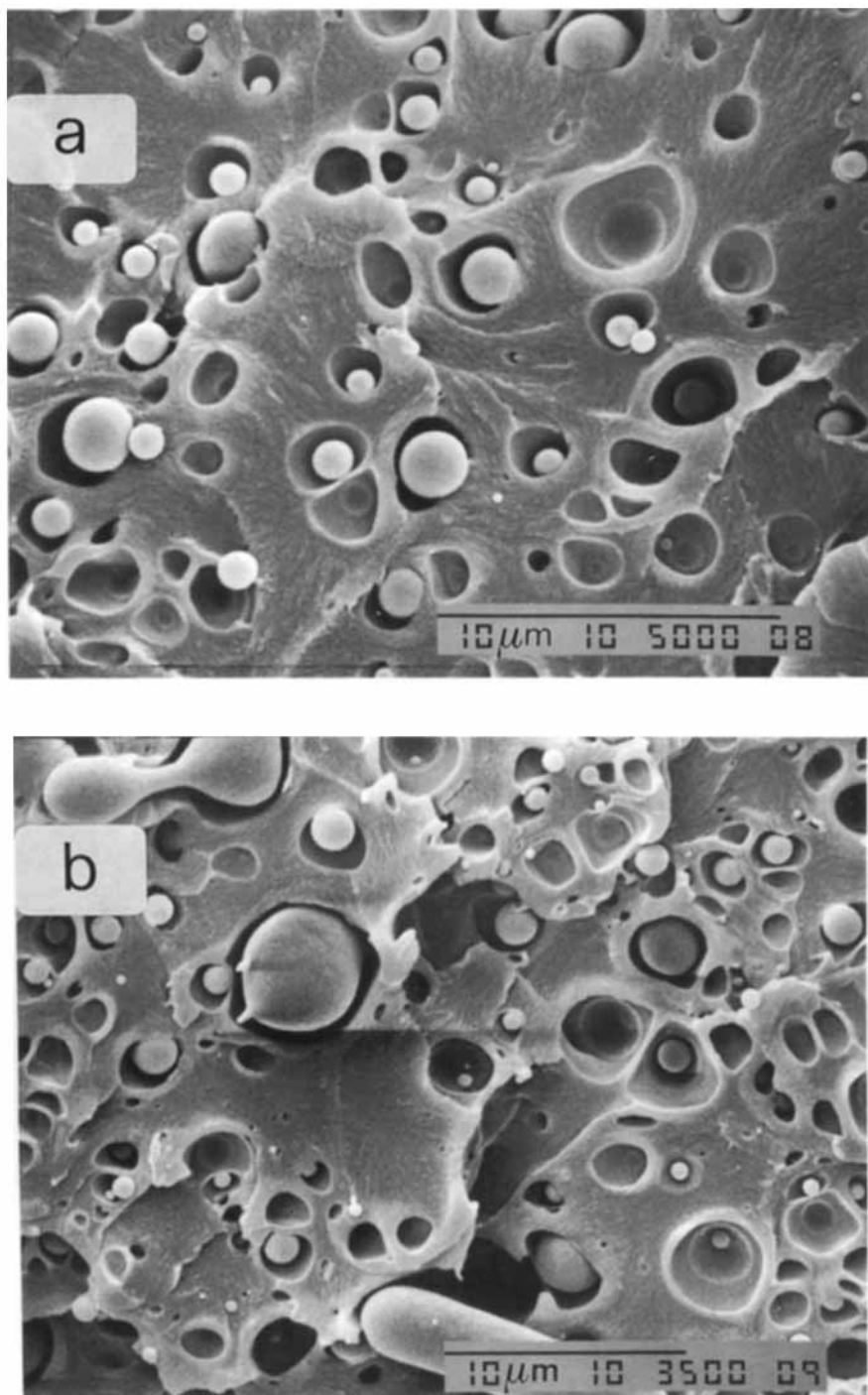


Figure 3 SEM micrographs of the fracture surfaces of PSu/VA blends specimens of different composition, as received from the melt mixing operation. (a) 95/5; (b) 90/10; (c) 80/20; (d) 60/40; (e) 40/60; (f) 20/80.

4). This holds true even for the VA-rich blends, where the dispersed phase is represented by PSu, i.e., by the more viscous of the two polymers. An-

other important conclusion that can be drawn from the observation of the micrographs is that the phase inversion appears to take place in a range of VA

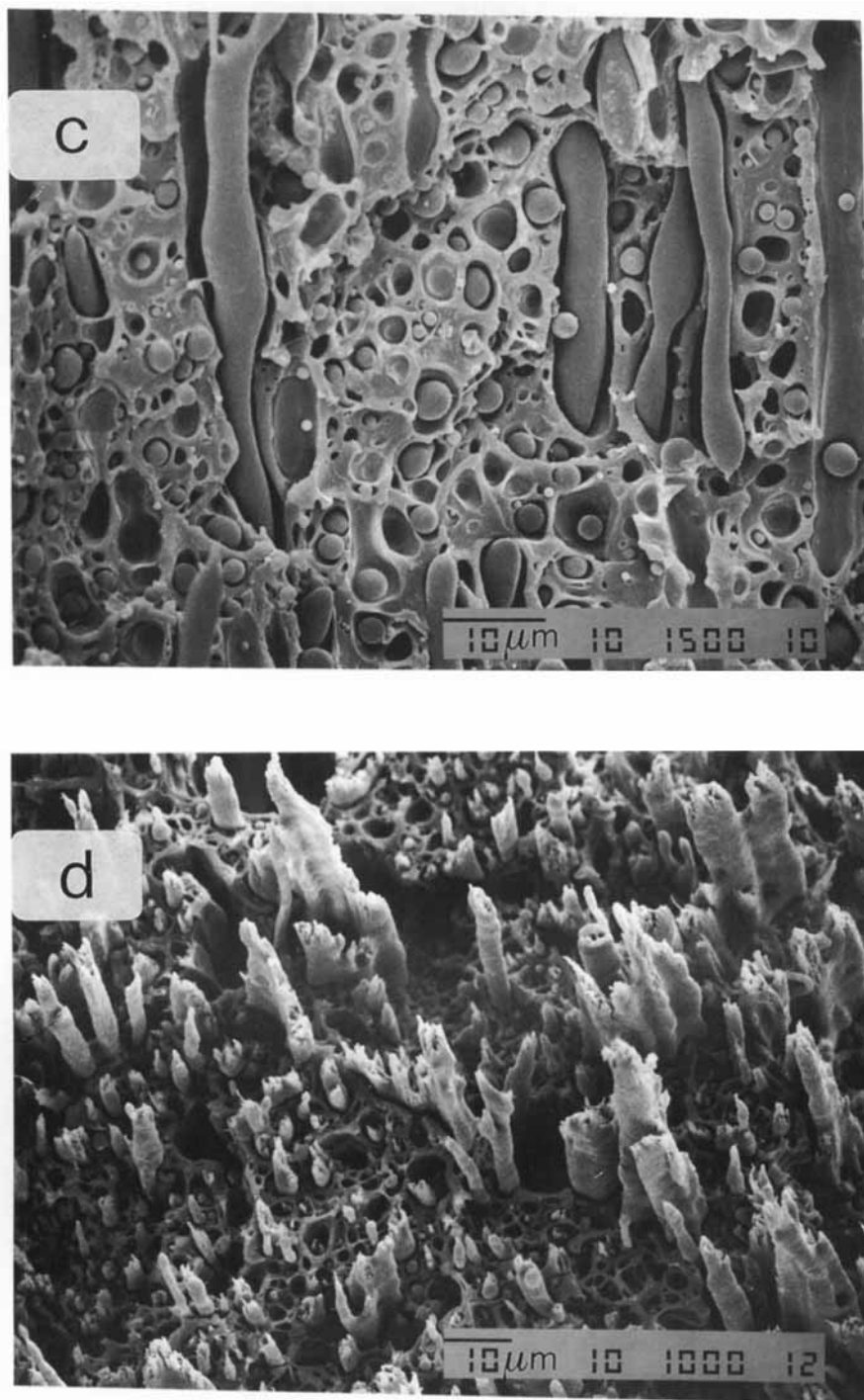


Figure 3 (Continued from the previous page)

concentration between 40 and 60%, which is much higher than that expected on the basis of Eq. (1) (cf. Table I). In this respect, however, it must be emphasized that the micrographs of PSu/VA blends with intermediate composition demonstrate that the

dispersed phase is made up of both small droplets and larger aggregates, thus indicating that there is a tendency of the minor component to form a "semicontinuous" phase.

Further insight into the morphology of these

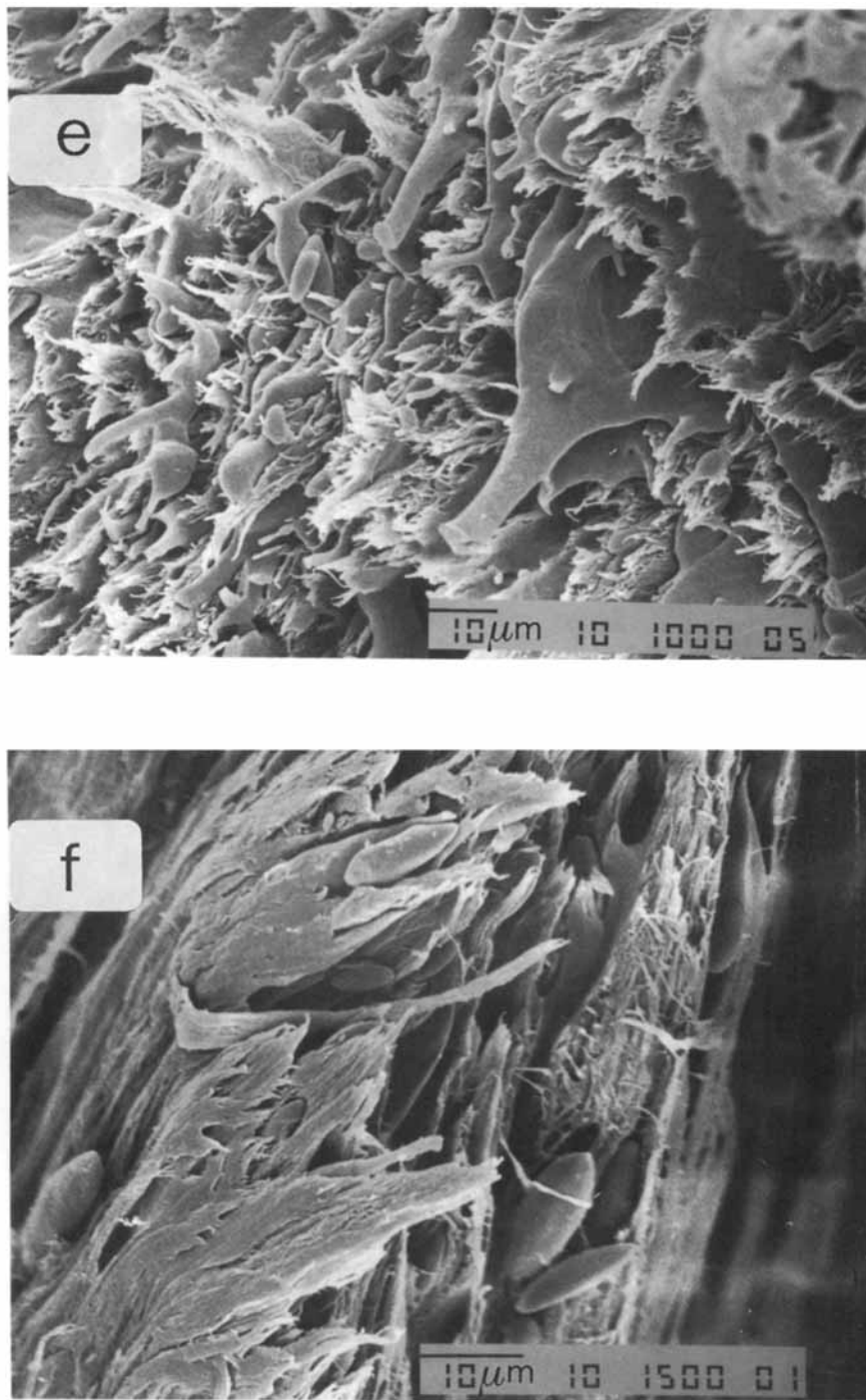


Figure 3 (Continued from the previous page)

blends has been gained through extraction experiments. The latter are based on the principle that the treatment of a blend specimen with methylene chloride, a good solvent for PSu, followed by separation of the insoluble VA phase, is expected to grant an almost complete separation of PSu only if this

represents the continuous phase. The extraction was done as described in the experimental section. The percent amounts of PSu extracted from PSu/VA blends are shown in Table II. They demonstrate that the conclusions drawn from the SEM analysis of the blends, i.e., that PSu represents the continuous

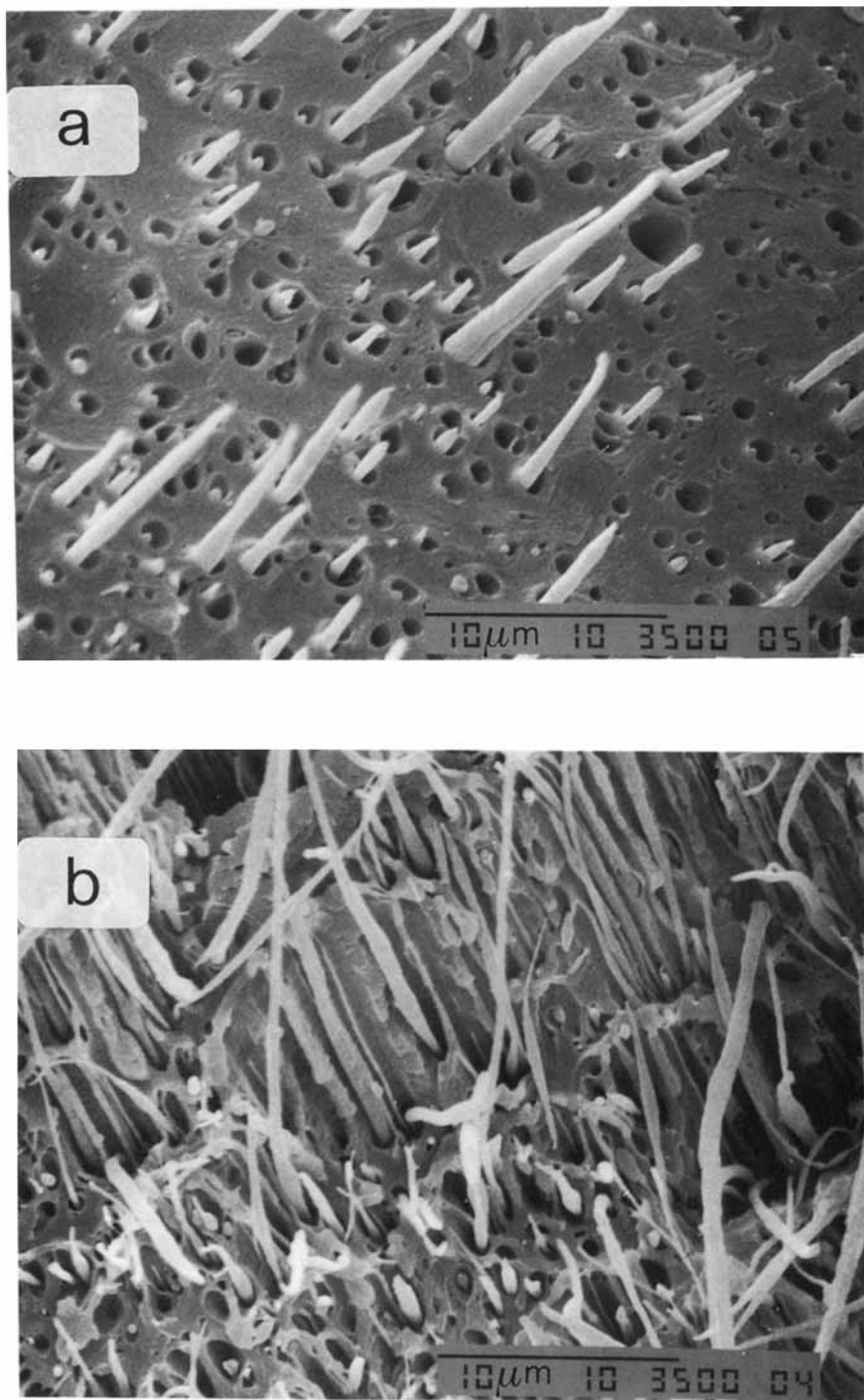


Figure 4 SEM micrographs of the fracture surfaces of PSu/VA blends specimens of different composition, prepared by pulling a fiber from the melt with a pair of tweezers. (a) 95/5; (b) 90/10; (c) 60/40; (d) 40/60.

phase as long as the concentration of VA remains lower than ca. 60%, is basically correct. On the other hand, this conclusion is supported by the observation

of the macroscopic behavior of the blends during the solvent extraction: in fact, the blend specimens with a VA content below 60% did collapse upon ad-

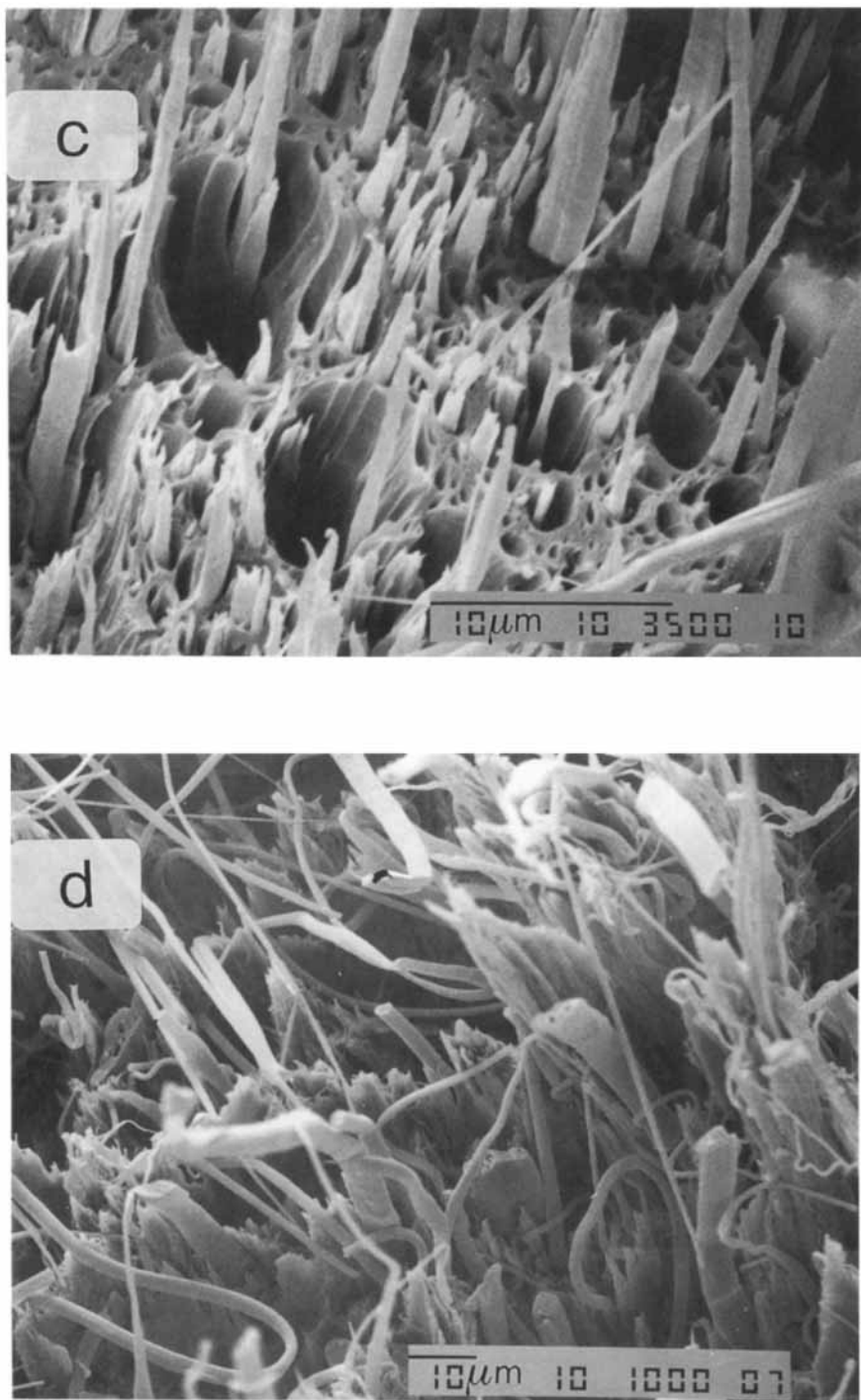


Figure 4 (Continued from the previous page)

dition of methylene chloride, whereas the geometry of the specimens was not altered by the solvent when the VA content was 60% or higher.

However, because the micrographs in Figure 3 show that the dispersed LCP particles tend to give

rise to large aggregates when the concentration of the LCP exceeds the Φ_{VA} values calculated according to Eq. (1), it seemed interesting to attempt a separation of the small VA particles from the large aggregates and to measure the relative amounts of the

Table II Percentages of PSu Extracted with Methylene Chloride at Room Temperature, from PSu/VA Blends

PSu/VA	% Extracted PSu (From Undissolved Material)	% Extracted PSu (From PSu Precipitation)
100/0	98.8	96.2
97/3	98.9	92.9
95/5	99.8	95.7
90/10	97.5	96.5
85/15	99.5	95.1
80/20	97.7	94.2
60/40	98.8	93.5
40/60	76.2	72.2
20/80	56.2	42.6

two parts. This was done as described in the experimental part. The results of the analysis, shown in Table III, are certainly affected by appreciable error, especially for the blends with a low VA content (such as that with only 5% VA) due to the small amount of insoluble material, and should, therefore, be taken as roughly indicative. Nevertheless, it may be safely concluded that, even for the blends with a small VA content, the LCP phase is formed not only by small particles but, partly, by larger aggregates that may somehow be classified as a "semicontinuous" phase. Thus, if the term "dispersed phase" is restrictively used to indicate that part of the LCP that is present in the form of small particles, and the data are plotted as a function of the blend composition (cf. Fig. 5), there seems to be, for the investigated PSu/VA blends, no abrupt phase inversion at a given Φ_{VA} but, rather, a tendency for dispersed and semicontinuous LCP phases to coexist over almost the whole composition range.

The SEM micrographs of the two types of LCP phases, separated as described from a 90/10 PSu/VA blend, are shown in Figure 6. The VA particles

obtained by centrifugation of the percolated suspension appear as small spheres or fibrils with average dimensions of the order of a few μm [Fig. 6(a)]. On the contrary, the residue on the sieve is made up of fibrils and coalesced aggregates of much larger dimensions [Fig. 6(b)]. The differences in the local flow conditions are probably responsible for the observed size and shape variation of the VA particles.

The effect of the flow conditions on the morphology of the blends has been clearly demonstrated by the following experiment. The 90/10 PSu/VA blend (ca. 5 g) was put in the matrix of a melt index apparatus, equipped with a die of 1 mm diameter and $L/D = 1$, and left there at 300°C for 10 min, to reach thermal equilibrium. Then, a pressure of ca. 4.5 MPa was applied and several specimens of the extruded strand were cut, at time intervals. The melt flow index calculated under these nonstandard conditions was found to increase gradually with extrusion time and to level off at ca. $5.5 \text{ g}/(10 \text{ min})$. Two strand specimens (ca. 40 mg), one obtained at the beginning of the extrusion and the other after stabilization of the melt index, were extracted with methylene chloride as described previously. The former specimen collapsed rapidly and left a milk-like suspension, thus showing a behavior perfectly similar to that of a 90/10 blend specimen as received from the Brabender mixer (cf. a and b in Fig. 7). The second specimen, on the contrary, gave a clearer suspension and left a straw-like, hollow strand with almost unchanged external geometry (cf. c and d in Fig. 7). The tubular residue was washed several times with fresh solvent to remove PSu and the loose LCP small particles completely and was then drawn out of the liquid and dried. By doing so, the thin tube became squashed but, nevertheless, it could be

Table III Classification of the VA Phase Particles in PSu/VA Blends

PSu/VA	Small VA Particles (%)	VA Aggregates (%)
95/5	~ 85	~ 15
90/10	~ 77	~ 23
85/15	75	25
80/20	82	18
60/40	22	78
40/60	5	95
20/80	8	92

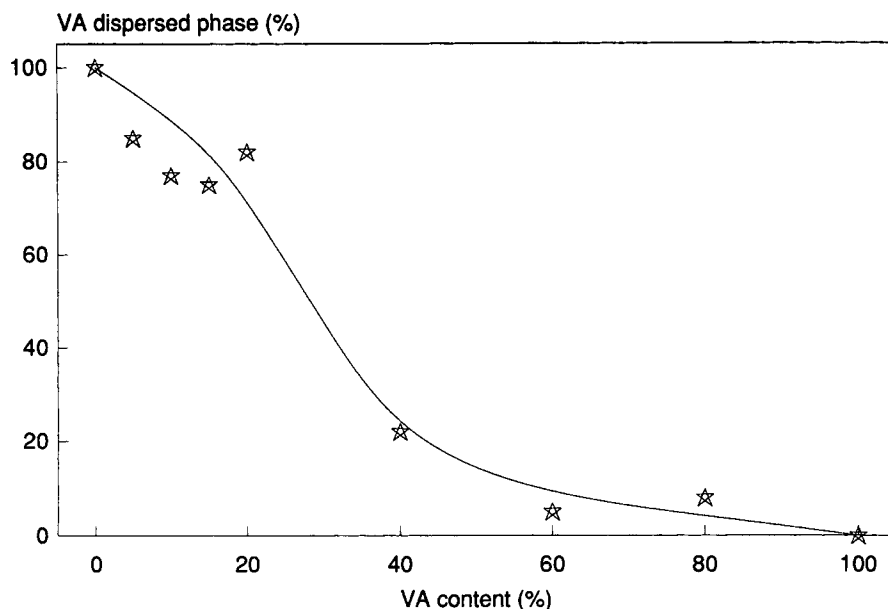


Figure 5 Percentage of the VA phase that is present in the PSu/VA blends in the form of small particles, as a function of the blend composition (cf. Table III, and Fig. 6).

weighed and examined by SEM. A number of experiments of this kind showed that the average weight of this residue amounted to ca. 20% of the overall LCP content of the blend. Thus, the radial migration of LCP taking place upon extrusion in the indicated conditions leads to the concentration of ca. 20% of the LCP phase in a skin layer with a thickness of the order of 10 μm . The micrographs in Figure 8 show that the outer part of the extruded rod, after solvent extraction, appears as a felt of partially coalesced fibers which, in some zones of the skin, are highly elongated and oriented predominantly in the direction of the strand axis, whereas in others, are much shorter, have practically random orientation, and are joined to each other to form an irregular network. Large, flat LCP domains are also present, as it may be seen in the lower magnification micrographs.

In a recent article,¹⁶ Kenig and co-workers have shown that the extrusion of PC/VA blends makes the LCP droplets migrate radially to the wall of the rod, and to form there long fibrils, partially coalesced and well oriented in the flow direction. This phenomenon is more pronounced the higher is the applied shear, and the longer is the capillary. Our data may perhaps be reconciled with this conclusion. In effect, we carried out the extrusion with a die having very low aspect ratio ($L/D = 1$), but we applied a fairly high pressure to the melt, and these conditions

may probably account for the observed migration of VA toward the periphery and for the limited coalescence of the fibers and their poor orientation along the axis. If the similarity of our data with those of Kenig et al.¹⁶ is to be considered, it may be expected that the extrusion through a capillary having higher L/D would lead to the formation of a more coherent LCP skin layer, similar to that observed by Kulichikhin and co-workers.⁹ Experiments in this direction are being carried out in our laboratory, and the results will be published in a forthcoming article. At any rate, what we want to stress here is that the morphology of the PSu/VA blends can be profoundly altered by changing the flow conditions.

Rheology

A preliminary rheological characterization of the PSu/VA blends was made by measuring the viscosities at two temperatures, 290 and 300°C, with a Rheoscope-1000 equipped with a capillary of 1 mm diameter and $L/D = 40$. The relevant viscosity curves are shown in Figures 9 and 10.

At 300°C, the viscosity of the blends is intermediate between those of the pure components. The behavior observed at 290°C, a temperature that is very close to the melting point of the LCP measured calorimetrically ($T_m = 286.4^\circ\text{C}$), is more complicated: the viscosity of some of the blends is lower

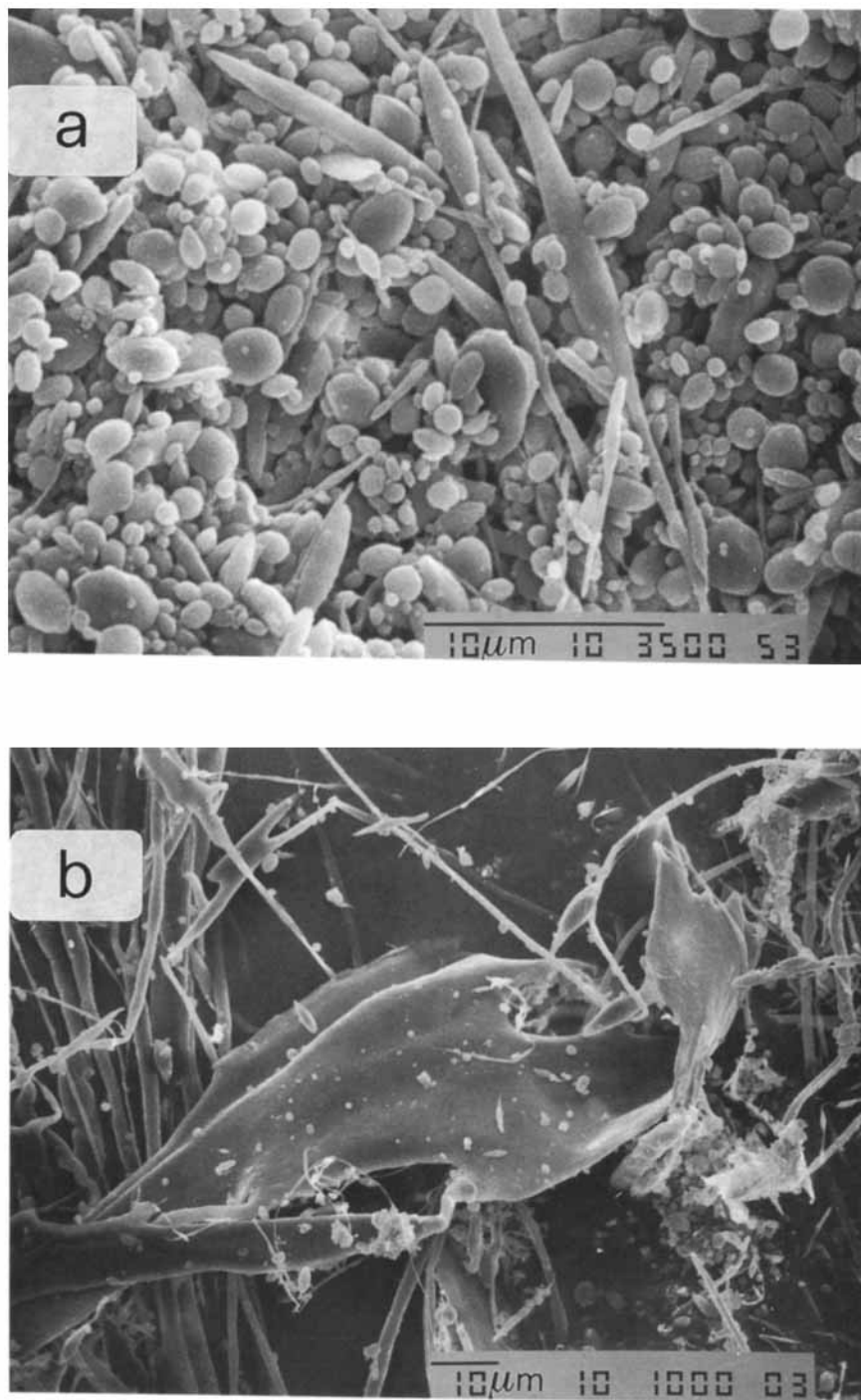


Figure 6 SEM micrographs of the solvent-separated VA phase, initially present in a 90/10 PSu/VA blend as received from the mixer. The small particles (a) and the larger domains (b) were separated by filtration through a wire net (see text).

than that of both pure components. Actually, as it is shown in Figure 11, the viscosities measured at two shear rates (7 and 300 s^{-1}) display a marked

negative deviation from the additivity rule, at both temperatures. For the case of the data measured at 290°C , this deviation gives rise to a minimum in the

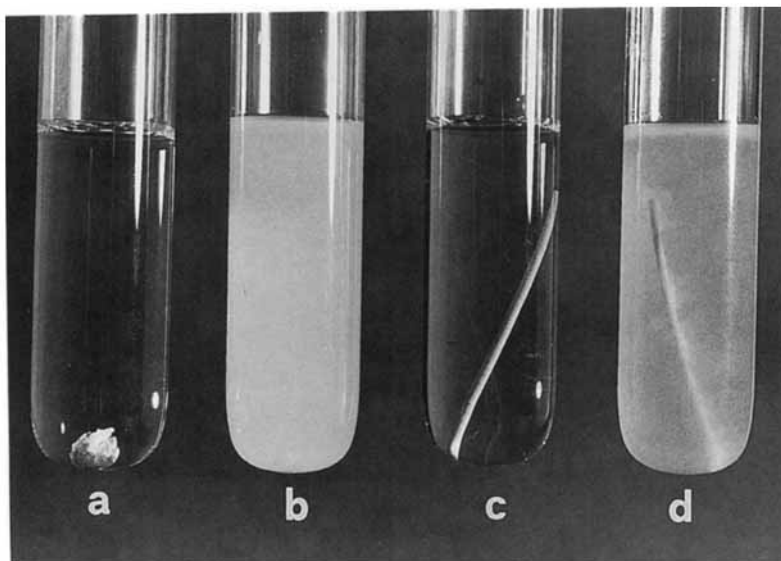


Figure 7 Methylene chloride treatment of two specimens of a 90/10 PSu/VA blend. (a) and (c) Treatment time $t = 0$; (b) and (d) $t = 24$ h. (a) and (b) Specimen as received from the mixer; (c) and (d) Filaments extruded as described in the text.

viscosity–composition curves, and the observed behavior appears to be similar to that described by Kulichikhin et al.⁹ for a different PSu/LCP system. However, also on account of the reproducibility of the measurements that was not very good at 290°C, we believe that a detailed and reliable interpretation of the rheological behavior of these blends cannot be granted by the present data. The rheological behavior is certainly influenced by the morphology of the melt which, as can be argued from the results of the morphological study, is characterized by a layer of VA acting as a lubricant on the capillary wall. The only hypothesis that can be put forward, at this stage, is that the formation of a lubricating layer at the capillary wall, which experiences shear stresses higher than the nominal ones, may be responsible for the negative deviation of the viscosity curves from the additivity rule. We believe that further studies on the rheology–morphology relations will be very useful for a deeper understanding of the behavior of these PSu/LCP blends.

Attempted Phase Compatibilization

From the results of the morphological study described above, it may be concluded that the two phases of these blends are highly incompatible and the interphase adhesion is extremely poor. Thus, despite the good LCP fibrillation obtained in blends

with a small VA content when using processing conditions involving elongational flow, the enhancement of the mechanical properties of PSu that can be expected as a result of the addition of the LCP is probably limited. In order to overcome this difficulty, an attempt has been made to produce a compatibilizer by synthesizing a copolyester having the same composition of VA, in the presence of preformed PSu, as described in the experimental section.

The morphology of some of the products of such polycondensations is shown in the SEM micrographs in Figure 12. From a comparison of these micrographs with those in Figure 3, it seems possible to conclude that the LCP polycondensation carried out in the presence of PSu leads to blends showing improved adhesion between the phases.

Thus, a small amount (4% w/w) of the 20/80 PSu/VA blend prepared *in situ* was fed to the Brabender mixer together with the appropriate amounts of commercial PSu and VA pellets, to produce a 90/10 blend. The micrograph of the fracture surface of the resulting blend is shown in Figure 13. A comparison of this micrograph with that in Figure 3(b) shows that no appreciable improvement of the adhesion between the two phases could be obtained with this technique, although a reduction of the average size of the LCP particles was observed.

Finally, a 90/10 PSu/VA blend was produced by

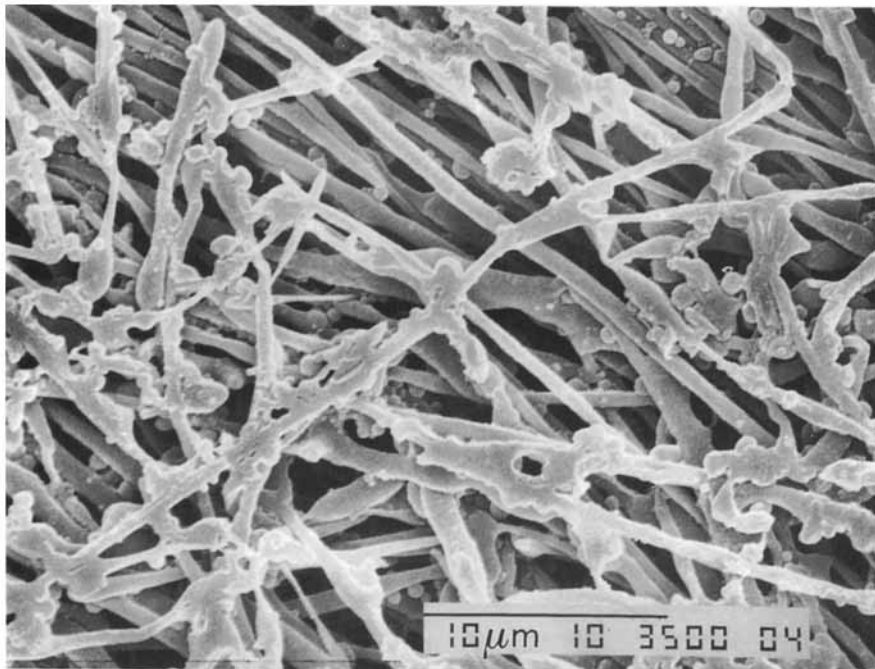
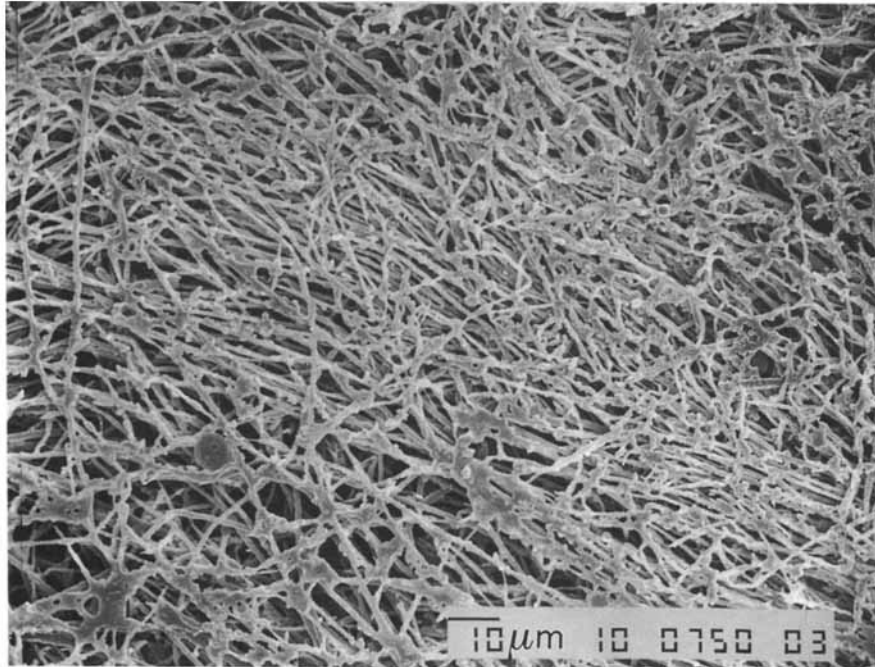


Figure 8 SEM micrographs of the skin layer of an extruded strand of 90/10 PSu/VA blend, separated by extraction with methylene chloride. The micrographs represent different zones of the skin, with different magnification.

the addition, in the mixer, of an appropriate amount of commercial PSu to the 20/80 blend prepared *in situ*. The micrograph of the fracture surface of such

blend is shown in Figure 14. This shows that the average size of the dispersed LCP droplets is drastically reduced with respect to the 90/10 blend pro-

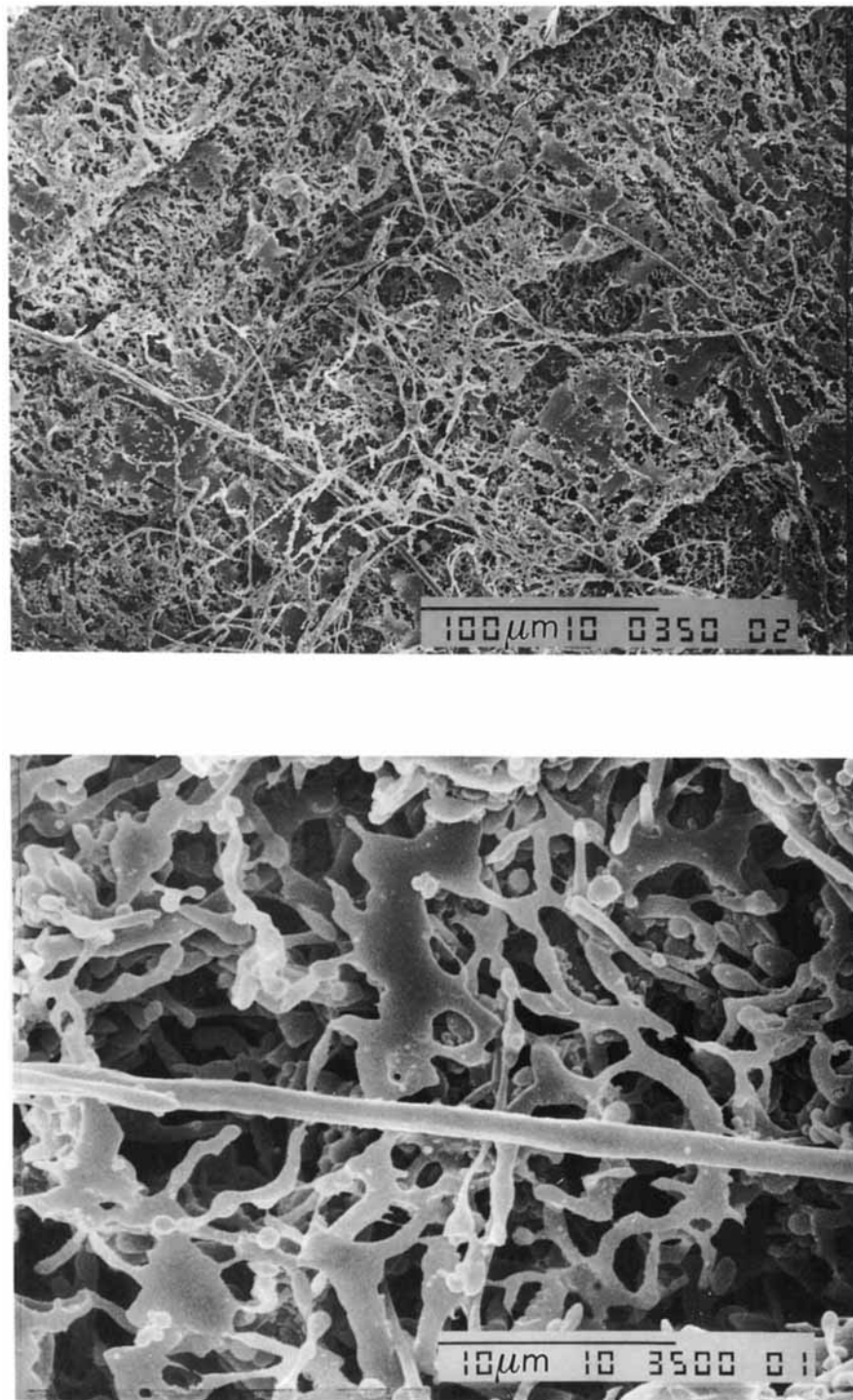


Figure 8 (Continued from the previous page)

duced from commercial VA [Fig. 3(b)] and, also, with respect to the 90/10 blend prepared with a small amount of the alleged compatibilizer (Fig. 13). Moreover, the adhesion between PSu and VA seems

somewhat enhanced. Although the possible differences in molecular weight and composition between commercial VA and the LCP produced in our laboratory in the presence of PSu may be partly re-

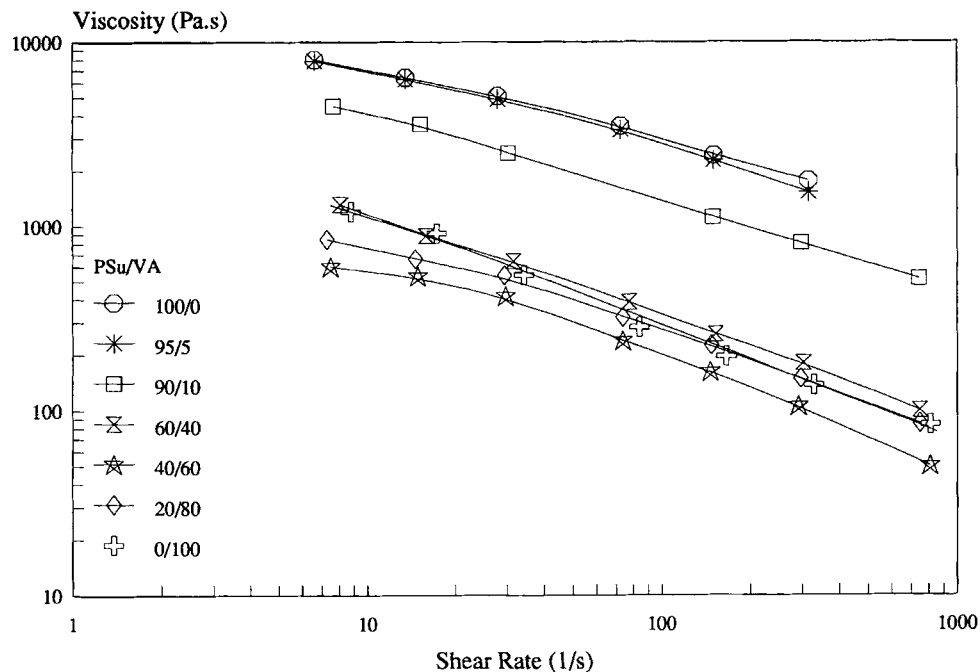


Figure 9 Viscosity curves of PSu, VA, and their blends, measured at $T = 290^{\circ}\text{C}$.

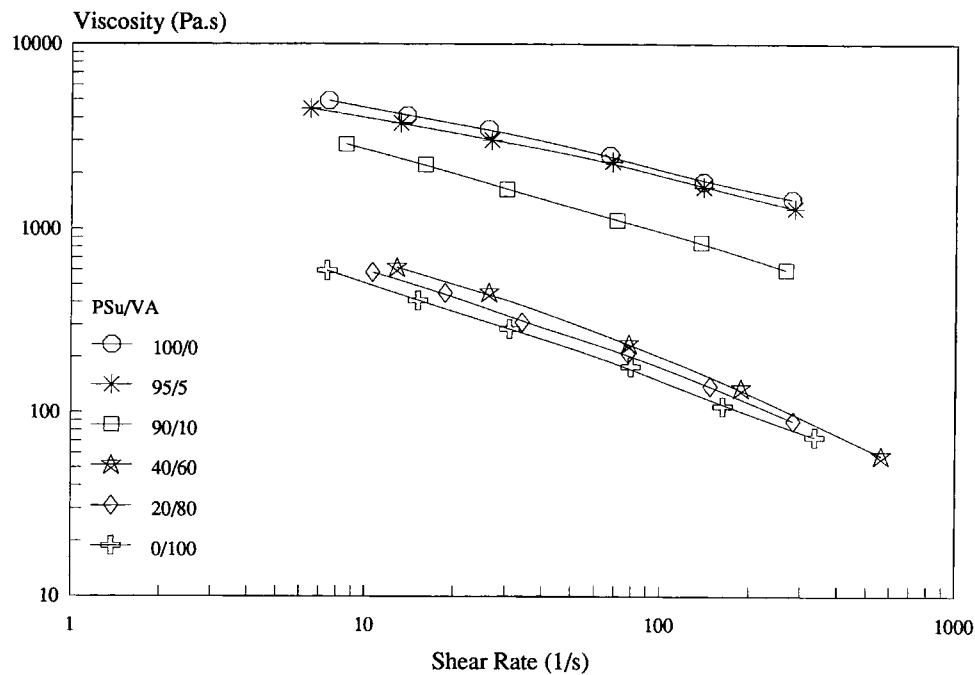


Figure 10 Viscosity curves of PSu, VA, and their blends, measured at $T = 300^{\circ}\text{C}$.

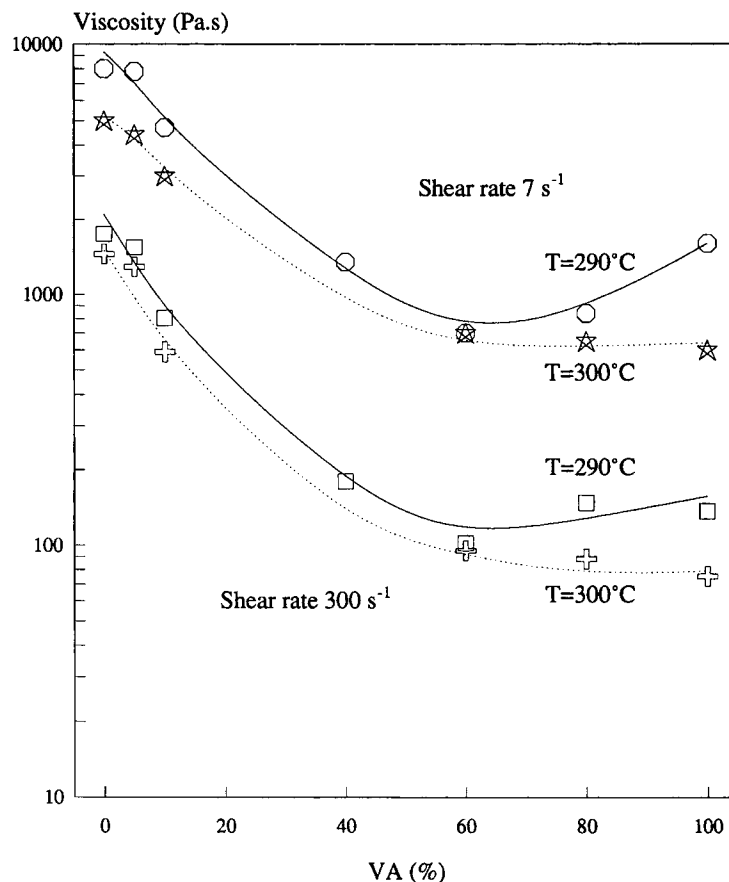


Figure 11 Viscosity-composition curves of PSu/VA blends, measured at two shear rates (7 and 300 s^{-1}) and at two temperatures (290 and 300°C).

responsible for the observed differences in the morphology of the blends, we believe that the apparent improvements obtained by this technique encourages further studies in this direction.

CONCLUSION

It has been demonstrated that the PSu/VA blends are composed of two immiscible phases showing poor compatibility and very low interphase adhesion. Despite this, the LCP droplets can be deformed into oriented fibrils under elongational flow conditions, thus leading to a possible reinforcement of the PSu matrix, as found by others.⁹⁻¹¹ The morphology of the blends was found to depend markedly on the flow conditions, and this was demonstrated not only by the above-mentioned (and well-known) defor-

mation of the LCP particles in elongational flow, but also by their tendency to coalesce into large domains, and to migrate toward the outer layer of, e.g., extruded rods, under appropriate flow conditions.

The rheological behavior of the blends, which is characterized by a marked negative deviation from the additivity rule, which might be interpreted in terms of a processing aid effect played by VA with respect to PSu, is certainly complicated by the formation of an LCP layer on the outer part of the polymer strand that acts as a lubricant.

The synthesis of a copolyester having the same chemical structure of commercial VA, carried out in the presence of PSu, has led to a blend characterized by apparently improved interphase properties. The use of this "synthetic" blend as an additive for the PSu/VA blends had the effect of improving the LCP dispersion within the matrix, but hardly enhanced the adhesion between the phases.

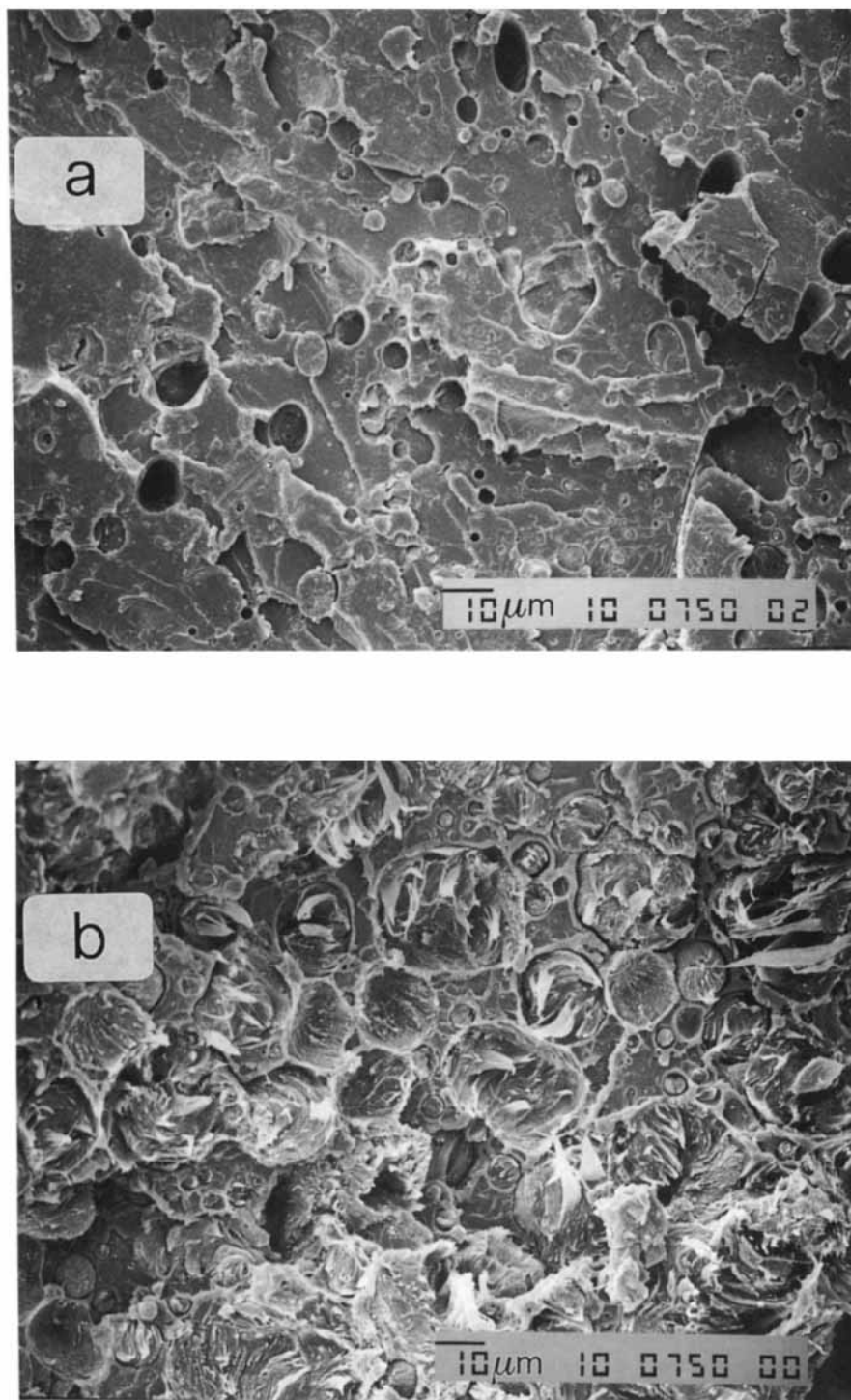


Figure 12 SEM micrographs of PSu/VA blends prepared by synthesizing the LCP in the presence of commercial PSu. (a) 80/20; (b) 20/80.

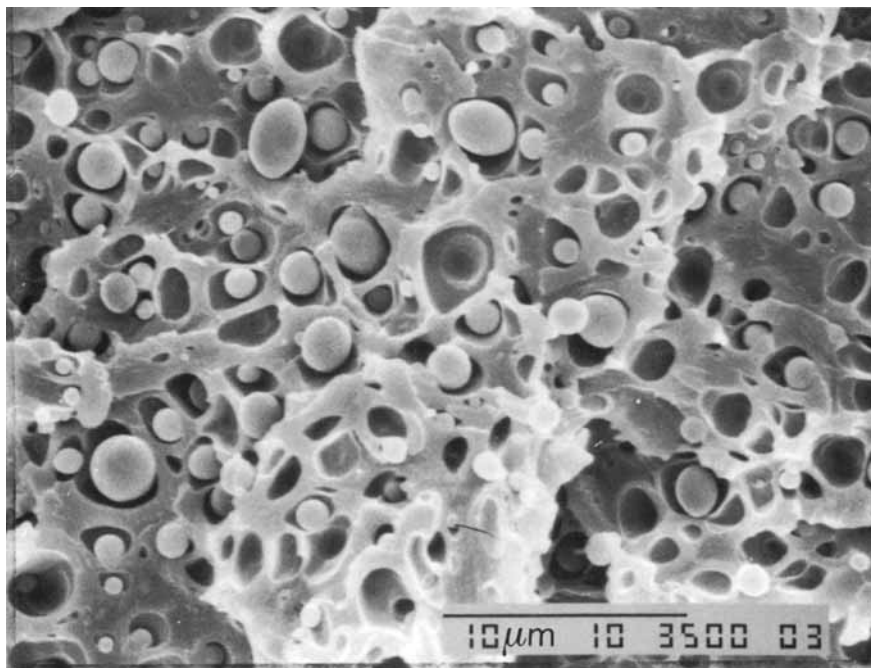


Figure 13 SEM micrograph of a 90/10 PSu/VA blend containing 4% (w/w) of the “synthetic” 20/80 blend shown in Figure 12(b).

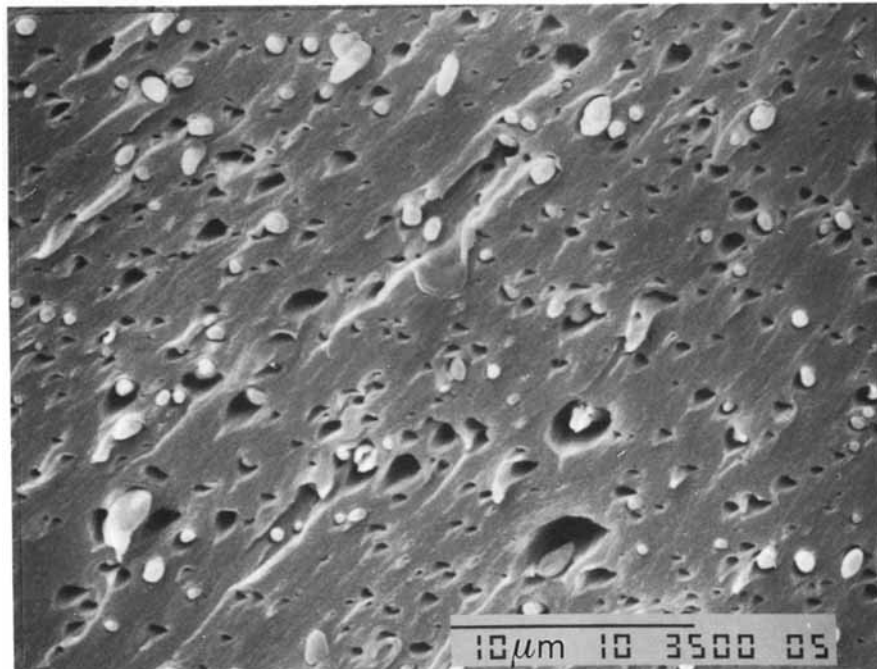


Figure 14 SEM micrograph of a 90/10 PSu/VA blend obtained by mixing appropriate amounts of commercial VA and the “synthetic” 20/80 blend shown in Figure 12(b).

This work was supported financially by the Italian National Research Council (C.N.R.), Progetto Finalizzato "Chimica Fine," and by the Russian Academy of Sciences, and was carried out within the bilateral project on "New Materials Based on Thermotropic Liquid Crystal Polymers."

REFERENCES

1. F. P. La Mantia, Ed., *Thermotropic Liquid Crystal Polymer Blends*, Technomic, Lancaster, 1993.
2. K. G. Blizard and D. G. Baird, *Polym. Eng. Sci.*, **27**, 653 (1987).
3. D. Beery, S. Kenig, and A. Siegmann, *Polym. Eng. Sci.*, **31**, 451 (1991).
4. D. Beery, S. Kenig, and A. Siegmann, *Polym. Eng. Sci.*, **31**, 459 (1991).
5. W. G. Perkins, A. M. Marcelli, and H. W. Frerking, Jr., *J. Appl. Polym. Sci.*, **43**, 329 (1991).
6. M. S. Silverstein, A. Hiltner, and E. Baer, *J. Appl. Polym. Sci.*, **43**, 157 (1991).
7. A. Datta, H. H. Chen, and D. G. Baird, *Polymer*, **34**, 759 (1993).
8. M. T. Heino and J. V. Seppälä, *J. Appl. Polym. Sci.*, **48**, 1677 (1993).
9. V. G. Kulichikhin, O. V. Vasil'eva, I. A. Litvinov, E. M. Antipov, I. L. Parsamyan, and N. A. Platé, *J. Appl. Polym. Sci.*, **42**, 363 (1991).
10. M. H. B. Skovby, J. Kops, and R. A. Weiss, *Polym. Eng. Sci.*, **31**, 954 (1991).
11. S. M. Hong, B. C. Kim, K. U. Kim, and I. J. Chung, *Polym. J.*, **23**, 1347 (1991).
12. A. Golovoy, M. Kozlowski, and M. Narkis, *Polym. Eng. Sci.*, **32**, 854 (1992).
13. M. Kozlowski, in *Processing and Properties of Liquid Crystalline Polymers and LCP Based Blends*, D. Acierno and F. P. La Mantia, Eds., ChemTec Publ. Co., Toronto, 1993.
14. L. A. Utracki, *Polymer Alloys and Blends: Thermodynamics and Rheology*, Hanser Publ., Munich, 1989.
15. V. I. Metelkin and V. S. Blekht, *Kolloid. Zh.*, **46**, 476 (1984).
16. D. Beery, S. Kenig, and A. Siegmann, *Polym. Eng. Sci.*, **33**, 1548 (1993).

Received March 28, 1994

Accepted July 13, 1994