

# Rheological Behavior and Thermal Stability of Poly(Phenylene Sulfide)/Vectra-B950 Blends

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## SYNOPSIS

Blends of polyphenylene sulfide (PPS) with a commercial, wholly aromatic, liquid crystalline polymer (LCP), Vectra-B950, have been prepared by melt-blending. Their rheological behavior has been studied in order to determine if the LCP displays a processing aid ability, and under what conditions it gives rise to potentially reinforcing fibrils dispersed in the PPS matrix. The problem of the thermal stability of PPS/LCP blends, which has been considered by some authors as the main obstacle to the production of usable materials due to the evolution of gaseous substances during processing, has been discussed. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Liquid crystalline polymers (LCPs) are being actively investigated as blend additives in the 5–25% composition range for thermoplastic polymers, in view of their potential as processing aids and reinforcing agents.<sup>1</sup> Whereas the lowering of the melt viscosity of thermoplastics brought about by LCPs is a fairly common feature, an appreciable reinforcing effect can be observed only if the dispersed LCP phase undergoes a pronounced fibrillation during blend processing. In practice, the use of appropriate processing conditions involving high extensional flow is required to attain such LCP fibrillation and, in addition, the viscosity of the LCP should be slightly lower than that of the matrix. On the other hand, these LCP/thermoplastic blends, which have been referred to as *in situ* composites,<sup>2</sup> do not wear the machinery surfaces during processing, and this may mean a further advantage if they are compared with common melt processible fiber-filled composites. Moreover, if the thermoplastic matrix is a crystallizable polymer, the LCP phase may also act as

a nucleating agent,<sup>3</sup> thus improving the crystallization kinetics and, thereby, making the injection molding operations easier.

In previous papers,<sup>4–6</sup> some of us demonstrated that, in blends of poly(phenylene sulfide) (Ryton GR02, by Phillips) (PPS) with a thermotropic LC copolyesteramide (Vectra-B950, by Hoechst-Celanese) (VB), the LCP phase strongly accelerates the crystallization of PPS, with no reduction of the degree of crystallinity. These results, together with the observation that the micrographs of the fracture surfaces of blend samples seemed to indicate a satisfactory interphase adhesion, led us to conclude that the PPS/VB blends could deserve further study, in order to evaluate the possible processing-aid and reinforcing effects of the LCP.

During the last few years, a number of papers have appeared in the scientific literature, dealing with the morphology, the rheology, and the bulk properties of blends of PPS with LCPs.<sup>7–12</sup> Thus, Baird and co-workers<sup>7–9</sup> studied the rheology and the morphology of blends of a high molecular weight PPS sample with a number of LCPs, including Vectra-A900 (VA), a LC copolyester sold by Hoechst-Celanese, containing 73% 4-hydroxybenzoic acid (HBA) and 27% 2-hydroxy-6-naphthoic acid (HNA) moieties. They found that, despite of the favorable rheological properties of the two compo-

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nents (the melt viscosity of PPS was considerably higher than that of VA, in the whole frequency range investigated), no elongation of the LCP particles could be induced by any of the processing techniques used. Moreover, the blends appeared foamy, with no interphase adhesion, and poor mechanical properties. These authors assumed that a gas was produced by unspecified chemical reactions taking place between the two components of the blends or, perhaps, between PPS and some of the VA additives.

Similar results were obtained by Subramanian and Isayev<sup>10</sup> in a study of blends of PPS (of lower molecular weight) and Vectra-A950 (a 75/25 HBA/HNA copolyester). In this case, however, the rheological properties of PPS and of the LCP were unfavorable for the production of an *in situ* composite, because the viscosity of PPS was lower than that of VA. Thus, no LCP fibrillation and no substantial property improvement was expected for these blends. These authors, as well, made the hypothesis that, during processing, PPS and VA give rise to chemical reactions leading to gas evolution and to the formation of large cavities in the blend matrix.

Seppälä, Heino, and Kapanen,<sup>11</sup> on the contrary, failed to notice any sign of a chemical reaction taking place between PPS and Vectra-A950, in blends prepared at ca. 290°C in a corotating twin screw extruder. The blends, after injection molding at 310–325°C, displayed good fibrillation of the LCP phase, improved mechanical properties, and enhanced dimensional stability and heat deflection temperature. Thus, although the interphase adhesion was found to be poor, these authors concluded that VA can be considered as a good reinforcing agent for PPS. These results were confirmed in a subsequent paper<sup>12</sup> dealing with extruded strands of the same PPS/VA blends. Here also, an increase of both modulus and strength was obtained as a result of the addition of VA into PPS, and the reinforcing effect was attributed to the LCP fiber formation, which was particularly evident in the skin region of the extrudates, and was higher the higher the LCP concentration and the draw ratio. The good formation of VA fibers was in agreement with expectation, because the viscosity ratio of VA to PPS, at 310°C, was found to be 0.2–0.4, in the 500–10,000 s<sup>-1</sup> shear rate range. The SEM observation of the fracture surface of the extrudates, however, revealed a porous morphology that had not been observed in injection molded specimens. This porosity, which was considered as the cause for the reinforcing effect being lower than that found by the same authors in, e.g., PET/VA and PP/VA blends, was attributed

to a lack of interfacial adhesion between the blend components.

In view of the apparent discrepancy in the literature data concerning the possibility of occurrence of high temperature chemical interactions between PPS and some of the investigated LCPs, we decided to carry out a study of the thermal stability of the system PPS/VB that we had investigated previously from the point of view of the PPS crystallization process.<sup>4–6</sup> In this article we also present the results of a rheological, morphological, and dynamic-mechanical characterization of these PPS/VB blends, in the whole composition range.

## EXPERIMENTAL

PPS was a pelletized experimental grade (Ryton GR02) generously supplied by Phillips Petroleum International S.R.L., Milan. The MFI, measured according to ASTM D1238 (5 kg, 316°C) was 97.8 g/(10 min). VB was a commercial, wholly aromatic LC copolyesteramide (Vectra-B950), sold by Hoechst-Celanese, synthesized from terephthalic acid (20 mol%), 4-aminophenol (20 mol%) and 2-hydroxy-6-naphthoic acid (60 mol%). Both polymers were dried in a vacuum oven at 120°C for at least 48 h before use.

PPS/VB blends were prepared in a 30 mL mixer attached to a Brabender Plasticorder. The blending conditions, unless otherwise stated, were as follows: temperature, 290°C; rate, 100 rpm; time, 3–4 min. Neat PPS and VB were subjected to the same treatment, before characterization, for safe comparison.

Rheological measurements were made using a capillary viscometer, Rheoscope 1000 by CEAST, at 290 and 320°C. The capillary had 1 mm diameter and an L/D ratio equal to 40. The Rabinowitch correction was applied to all experimental data, whereas the Bagley corrections were neglected due to the high L/D ratio. For viscosity/temperature measurements, the temperature of the capillary was continuously lowered, with a rate of 5°/min.

The morphology of the blends was studied by scanning electron microscopy (SEM), using a Jeol T300 apparatus. The specimens were fractured under liquid nitrogen and the fracture surface was coated with gold. For SEM analysis, several kinds of specimens were used. Sometimes, small pieces of material, as received from the mixer, were employed; in other cases, extruded strands were produced with the capillary viscometer, or with the MFI apparatus, either without or with afterdrawing. The filament

could be drawn either manually or by use of counter rotating rolls.

Thermogravimetric measurements were made with a Mettler TG50 apparatus either in nitrogen or in air atmosphere. Dynamic measurements were done with a heating rate of 20°/min; isothermal experiments were made by heating the specimens with a rate of 50°/min up to 330°C and recording the weight loss during 1 h period at this temperature.

The dynamic mechanical properties were determined with a Polymer Laboratories DMTA apparatus, using compression-molded specimens, at a frequency of 1 cps and a heating rate of 10°/min.

## RESULTS

The viscosity curves of the PPS/VB blends, measured at 290 and 320°C, are shown in Figure 1. PPS displays a quasi-Newtonian behavior, with some shear thinning at the highest shear rates. The shear thinning behavior of VB is more pronounced, the viscosity curve of this material showing a Newtonian plateau only at the lowest shear rates. At  $T = 290^\circ\text{C}$ , the viscosity curves of PPS and VB intersect at a fairly high shear rate, whereas, at 320°C, the viscosity of the LCP is lower than that of PPS in the whole range.

All the blends exhibit non-Newtonian behavior over the whole gradient range studied. Because, contrary to both neat components, the blends have no Newtonian plateau at low shear rates, they are not expected to obey the empirical rule according to which the viscosity–composition curve should have a minimum, at low LCP concentrations, when the viscosity of the LCP is higher than that of the thermoplastic matrix.<sup>13</sup> In the investigated system, in fact, the viscosities of the blends tend to exceed those of both pure components, under low shear conditions. At high shear rates, the viscosities of the blends are intermediate between, or, sometimes lower than, those of the neat components. The variation of viscosity of the blends as a function of the VB concentration, at different shear rates, is shown in Figures 2 and 3, for measurements made at 290 and 320°C, respectively. It may be observed that the experimental points are indicative of a relative minimum, at 290°C and at low shear rates, for the blend with 60% VB (Fig. 2). A similar trend was described by Subramanian and Isayev<sup>10</sup> for PPS/VA blends in which the LCP represented the more viscous component. However, although the scatter of the points is perhaps too high to be attributed to experimental errors, we are not able to offer any reasonable explanation for such a minimum, and this is why we drew the tentative connecting curves as

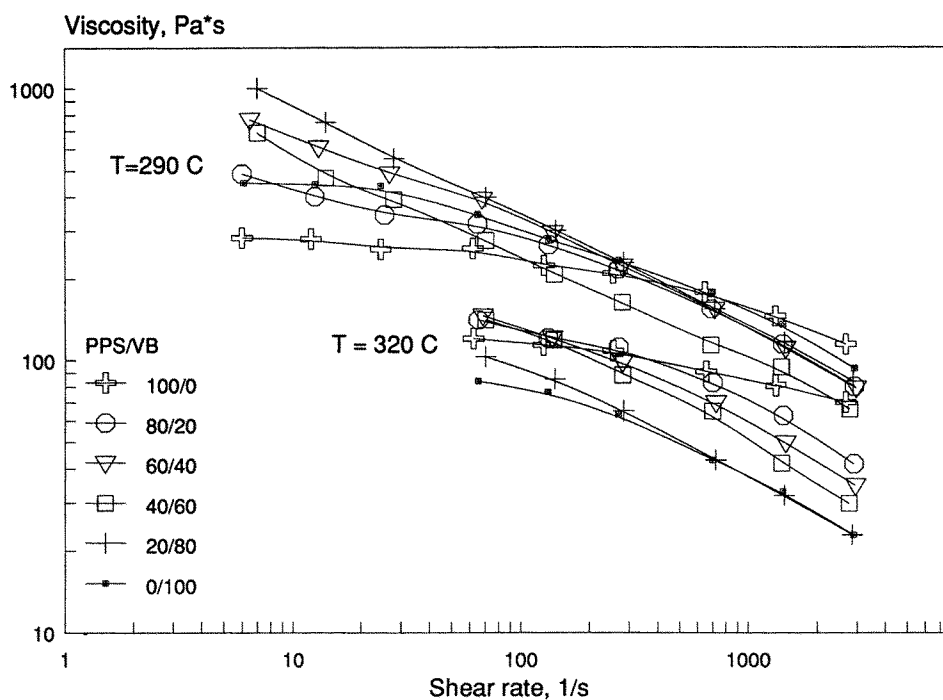
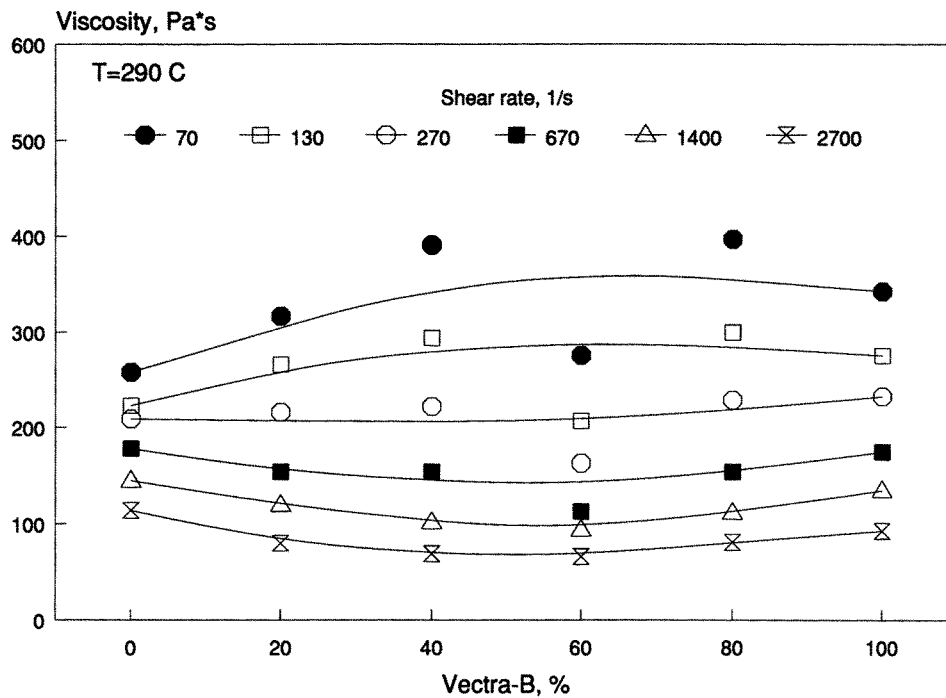


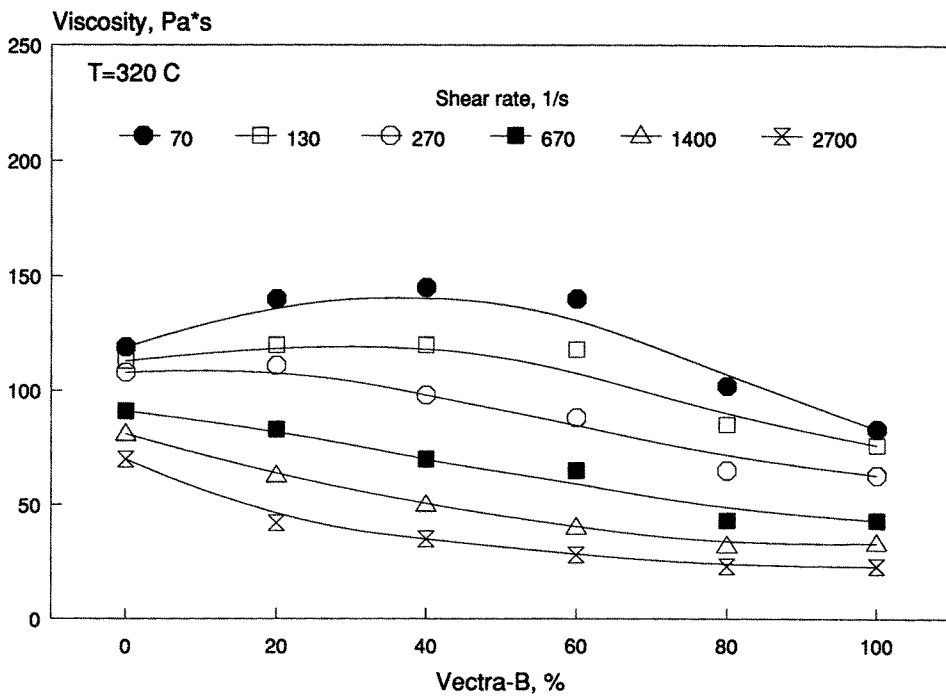
Figure 1 Viscosity curves of the PPS/VB blends, measured at 290 and 320°C.



**Figure 2** Viscosity vs. composition curves, measured at  $T = 290^{\circ}\text{C}$  and different shear rates.

shown in Figure 2. Independent of this point, the observation of Figures 2 and 3 leads to conclude that, at both 290 and 320°C, the viscosity-composition

curves lay above the straight line representing the rule of mixtures at low shear rates, and below this line at high shear rates. Thus, the addition of VB



**Figure 3** Viscosity vs. composition curves, measured at  $T = 320^{\circ}\text{C}$  and different shear rates.

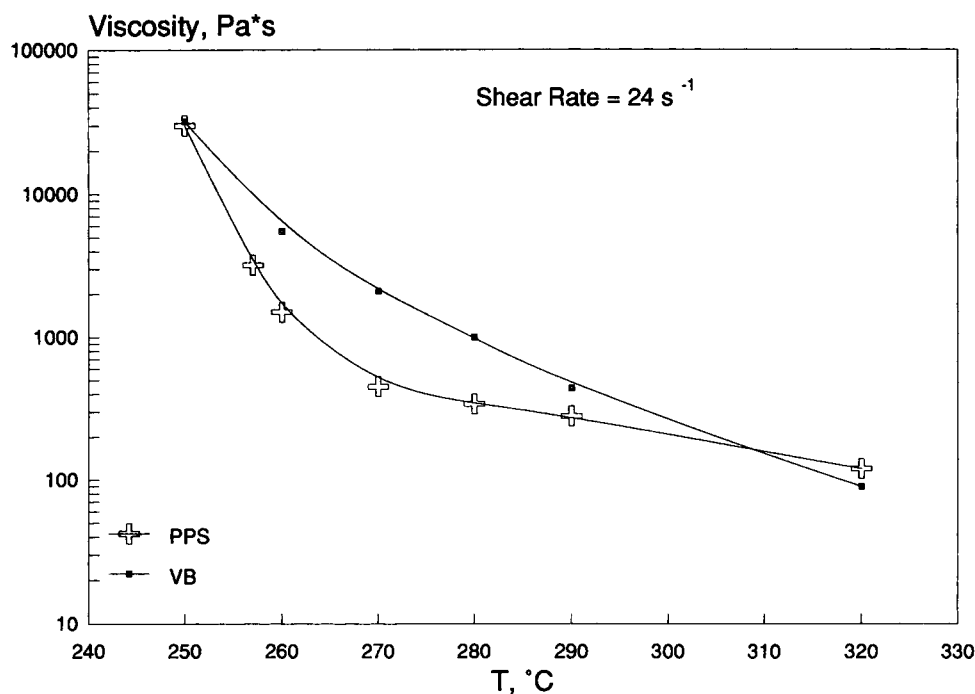
into PPS leads to a viscosity reduction only under very high shear conditions, the effect being more pronounced at 320°C. Under low shear rates, on the contrary, an increase of the PPS viscosity is observed as a result of the addition of small amounts of VB. It may be concluded that, for the system investigated, the LCP displays rather limited processing-aid ability, if any.

A comparison of the viscosity curves of PPS and VB shows that fibrillation of the LCP can be favored only at high temperatures and high shear rates. On the other hand, because the LCP fibrillation is normally favored using elongational flow conditions such as those prevailing at the entrance of the extrusion die and during the subsequent drawing of the extrudate, and because during this latter stage the temperature of the blend is lowered, it is of interest to study how the viscosities of the two components vary upon cooling. The results of measurements made using a capillary viscometer whose temperature was lowered with a rate of ca. 5°/min are plotted in Figure 4. These measurements were made under a shear rate of 24 s<sup>-1</sup>, which is close to that prevailing during the extrusion of some of the specimens used for the morphological characterization of the blends. It may be noticed that, although at 320°C the viscosity of VB is lower than that of PPS by about 25%, upon cooling, the situation

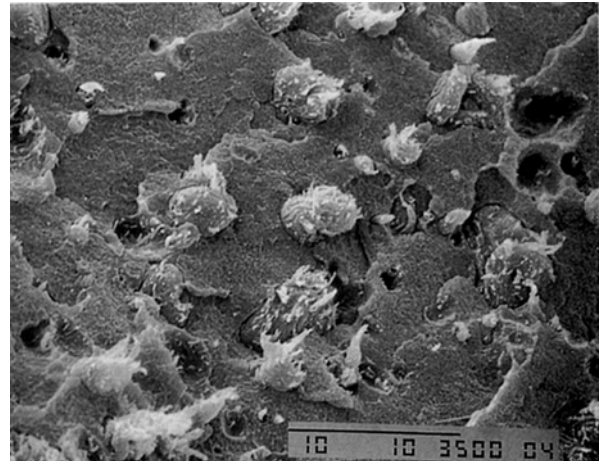
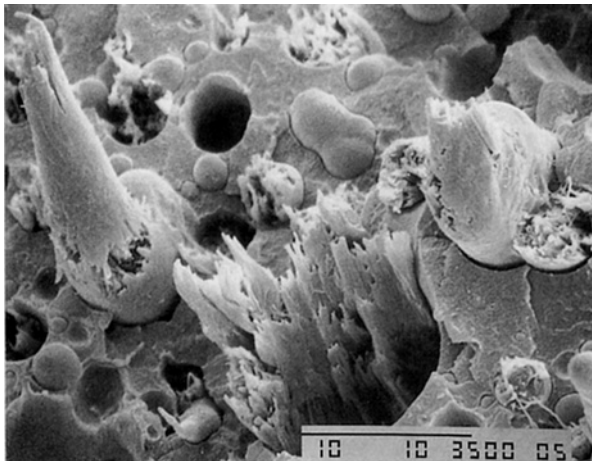
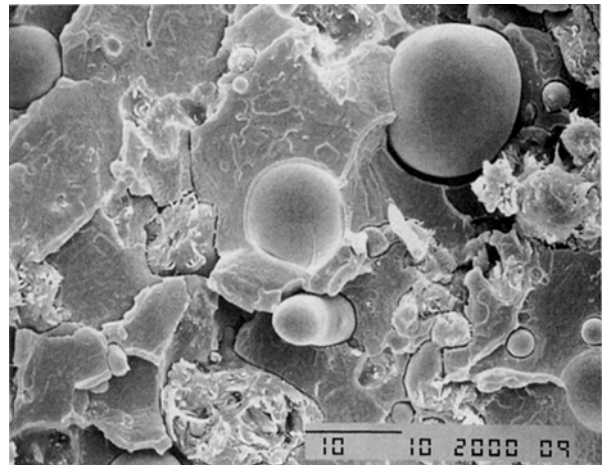
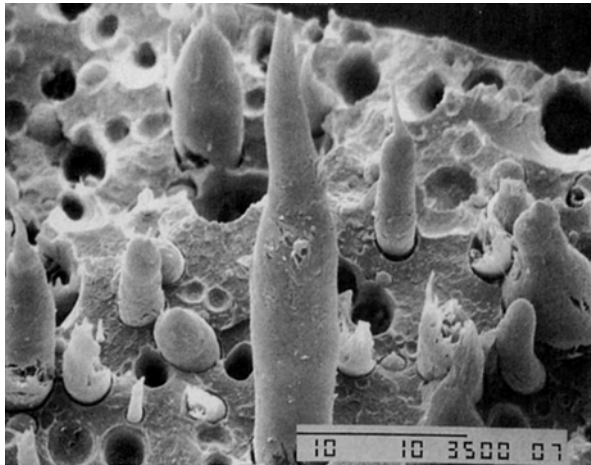
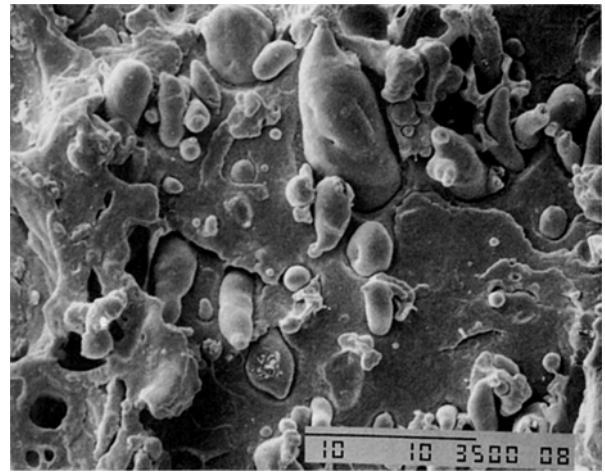
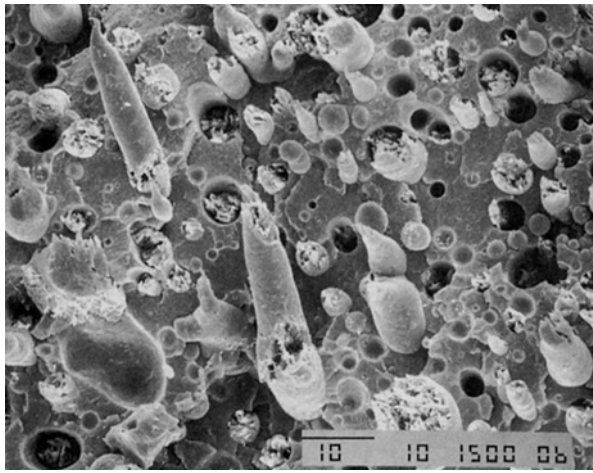
changes very rapidly and, at 280°C, VB is ca. three times as viscous as PPS. Thus, the conditions for the fibrillation of VB during blend processing are not readily obtained: it seems that high temperature extrusion, using dies with convergent entrance, should provide the best results. On the contrary, the use of high draw-down ratios is not expected to help fibrillation because the extrudate temperature falls at the die exit and the viscosity ratio of the two polymers rapidly becomes unfavorable.

The morphologies of extruded strands of a 80/20 PPS/VB blend, prepared at 320°C, with no afterdrawing, using the capillary viscometer equipped with a conical die, are shown in Figure 5. The large VB particles with 2–5 μm diameter are strongly elongated in the flow direction. Many such particles appear fractured rather than pulled out of the matrix, thus showing that, despite of the poor adhesion, there is good contact between the two phases. The LCP dispersion is satisfactory, but there is a wide distribution of the particle sizes. The smaller particles, having a diameter of 0.5–3 μm, have spherical shape.

Similar strands prepared with the same technique at a lower temperature ( $T = 290^{\circ}\text{C}$ ) failed to show LCP fibrils. In fact, as it is shown in Figure 6, most VB particles appeared spherical or globular. In this case too, the specimen preparation, carried out by



**Figure 4** Viscosity vs. temperature curves for PPS and VB, recorded during cooling at 5°/min.



**Figure 5** SEM micrographs of the fracture surface of 80/20 PPS/VB strands prepared at  $T = 320^{\circ}\text{C}$ , with the capillary viscometer, without stretching.

**Figure 6** SEM micrographs of the fracture surface of 80/20 PPS/VB strands prepared at  $T = 290^{\circ}\text{C}$ , with the capillary viscometer, without stretching.

fracturing the strand at the liquid nitrogen temperature, led to the failure of some of the LCP particles.

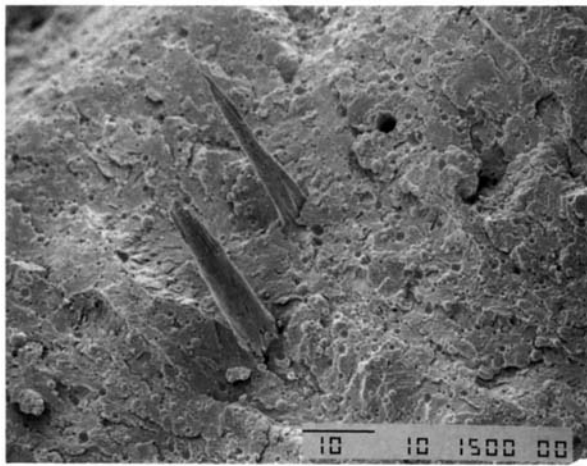
The observation of the morphology of extruded strands prepared in the absence of afterdrawing leads to the conclusion that, as predicted, some VB fibrillation takes place at the die entrance, provided that the extrusion temperature is sufficiently high to grant a favorable viscosity ratio. In any case, as already pointed out in our previous studies,<sup>5,6</sup> the morphology of the blends appeared fairly compact, with no evidence of the large cavities observed by Subramanian and Isayev,<sup>10</sup> and with microvoids which, in most cases, could be thought as being left by LCP particles pulled off upon fracturing the specimen.

An attempt to enhance the VB fibrillation was made by extruding a blend filament at 290–325°C, and pulling it down, either manually, or by the use of counter-rotating rolls. The results were irreproducible. In fact, in some cases a morphology such as that shown in Figure 7a was observed: the larger VB particles (2–5  $\mu\text{m}$ ) were highly elongated in the draw direction, whereas the smaller ones (0.5–2  $\mu\text{m}$ ) were spherical and, still, no sign of cavities in the matrix, or in the interphase region, could be seen. In others, as it is shown in Figure 7b and 7c, a region of the cross-section of the filament appeared rich of microcavities (0.5–2  $\mu\text{m}$  diameter), whereas in other regions of the same specimens, the morphology remained fairly compact. The appearance of a porosity in the blend morphology seemed to be a fortuitous event, although it was noticed that the relevant probability was higher the higher the extrusion temperature and the degree of extension of the extrudate. In fact, the presence of porous regions in the bulk of PPS/VB blends was fairly rare in samples prepared in the mixer or extruded under comparatively low shear. The shape and the dimensions of the microvoids also varied appreciably, as it can be seen from the two other examples shown in Figure 7d and e; in general, both the VB particles and the microvoids were larger the higher the spinning temperature. These results are very similar to those of Heino and co-workers,<sup>11,12</sup> who attributed the porosity of the structure of extruded PPS/VA blends to the exceptionally poor interfacial adhesion rather than to chemical reactions between the blend components, leading to gas evolution, as suggested by others.<sup>7–10</sup> Actually, as it is particularly evident from the micrograph shown in Figure 7c, the formation of microvoids seems to have occurred independently of the contact between the two polymers. This would rule out the hypothesis of a chemical reaction between PPS and the LCP, but cannot be fully ex-

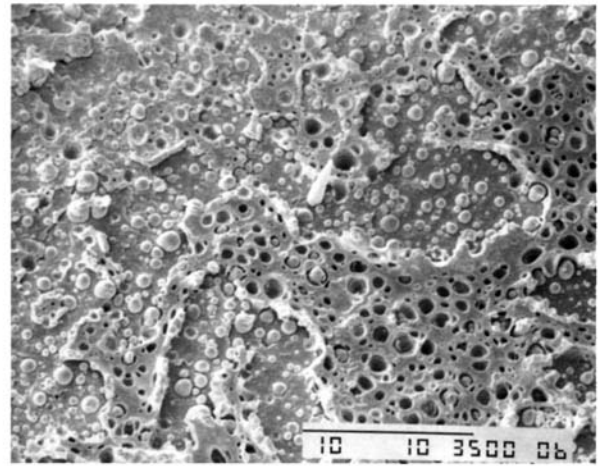
plained on the basis of a reduced interphase adhesion, either. In order to shed more light on the problem, we changed the conditions of blend preparation to see the effect of features such as mixing time (3–90 min), mixing temperature (290–330°C), and presence of moisture (predrying omitted) upon the porosity of the blends. However, no one of these features was found to favor the development of microvoids, and this was taken as a further evidence against the occurrence of chemical reactions involving the two polymers.

This point was investigated further by thermogravimetric analysis. In Figure 8, the weight loss curves obtained on heating neat PPS and a 80/20 PPS/VB blend with a rate of 20°/min are shown. Both samples appear to be fairly stable up to temperatures of ca. 450°C, although the temperature of initial degradation of the blend appears to be about 20° lower than that of pure PPS. The TGA curves measured isothermally, at  $T = 330^\circ\text{C}$ , under nitrogen, are shown in Figure 9. In all cases, the weight loss during the first hour of heating was close to 0.5%, except for pure VB, which displayed a lower value (0.28%). Our results differ appreciably from those found, under comparable conditions, by Subramanian and Isayev<sup>10</sup> who found that the PPS/VA blends undergo weight losses of 1.5–2%, as compared with ca. 0.3% for the neat polymers. However, at least some of the PPS/VB specimens investigated here showed a slightly higher weight loss rate, as compared to neat PPS (cf. Fig. 9).

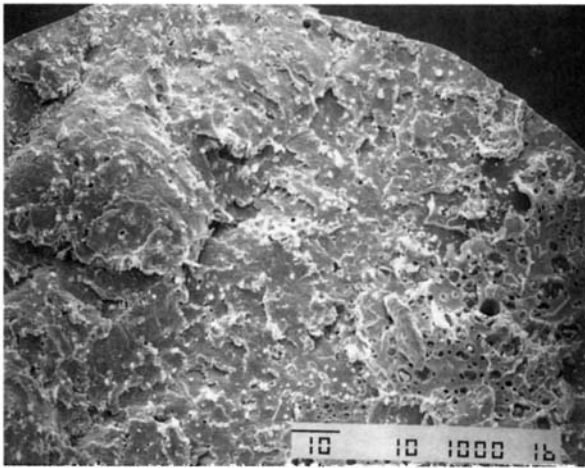
The thermal degradation of PPS was studied by Lum<sup>14</sup> and Markert et al.<sup>15</sup> They found that, while extensive thermal decomposition of PPS does not begin until around 400°C, some outgassing already takes place in the 200–400°C region with evolution of carbon dioxide, sulphur dioxide, and water. It is likely that the formation of these volatile products is catalyzed by traces of ionic substances contained in the PPS bulk as residues of the polymer synthesis catalyst or as impurities. In this light, the gas evolution observed by Baird et al.<sup>7–9</sup> and by Subramanian and Isayev<sup>10</sup> in blends of PPS (by Phillips) with VA could be envisaged as being due to PPS degradation catalyzed by the ionic substances contained into PPS and/or into VA, as suggested by Baird.<sup>9</sup> In turn, the observation by Seppälä and co-workers<sup>11</sup> that no outgassing takes place in injection molded PPS/VA blends could be ascribed to the fact that these authors used a PPS sample of different source (Fortron, by Hoechst Celanese), which is said to be less branched and to have a lower content of ionic impurities. This seems to be confirmed by the fact that a PPS/LCP blend (Vectra V-140) having good



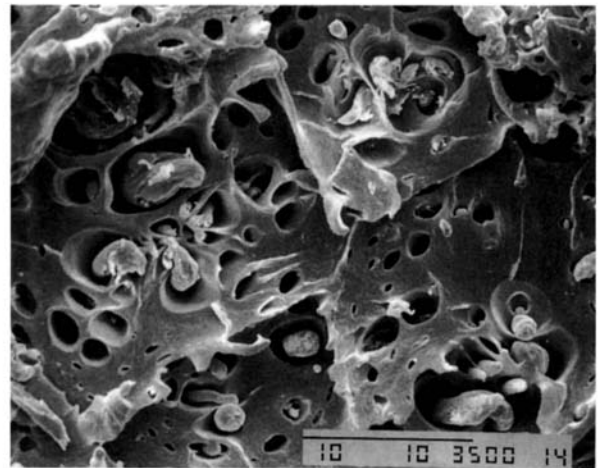
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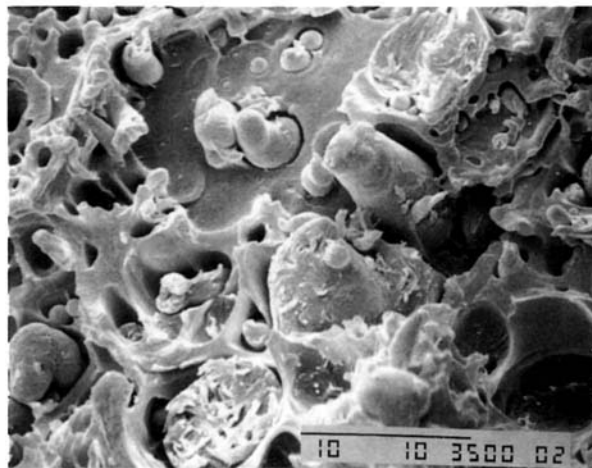
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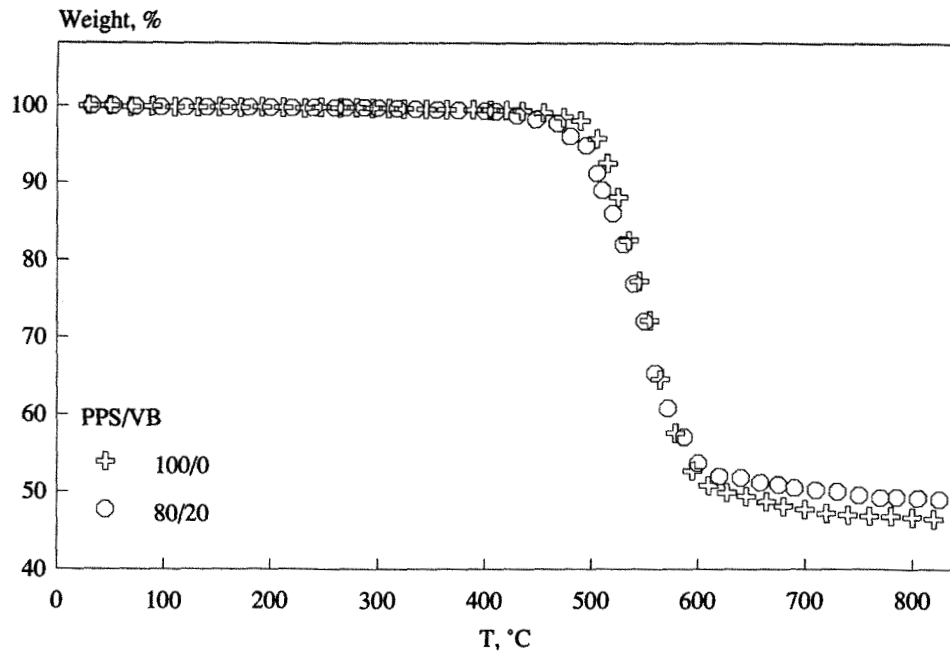
(d)



(e)

**Figure 7** SEM micrographs of the fracture surfaces of PPS/VB filaments prepared using the MFI apparatus with the indicated conditions. (a) 80/20 blend,  $T = 300^\circ\text{C}$ , conical die ( $D = 0.7\text{ mm}$ ,  $90^\circ$ ), draw ratio (DR) equal to 10; (b) 90/10 blend,  $T = 300^\circ\text{C}$ , cylindrical die ( $D = 1\text{ mm}$ ,  $L/D = 40$ ), DR = 10; (c) 80/20 blend,  $T = 300^\circ\text{C}$ , cylindrical die ( $D = 1\text{ mm}$ ,  $L/D = 40$ ), DR = 10; (d) 90/10 blend,  $T = 310^\circ\text{C}$ , cylindrical die ( $D = 1\text{ mm}$ ,  $L/D = 40$ ), DR = 40; (e) 80/20 blend,  $T = 318^\circ\text{C}$ , cylindrical die ( $D = 1\text{ mm}$ ,  $L/D = 40$ ), DR = 90.



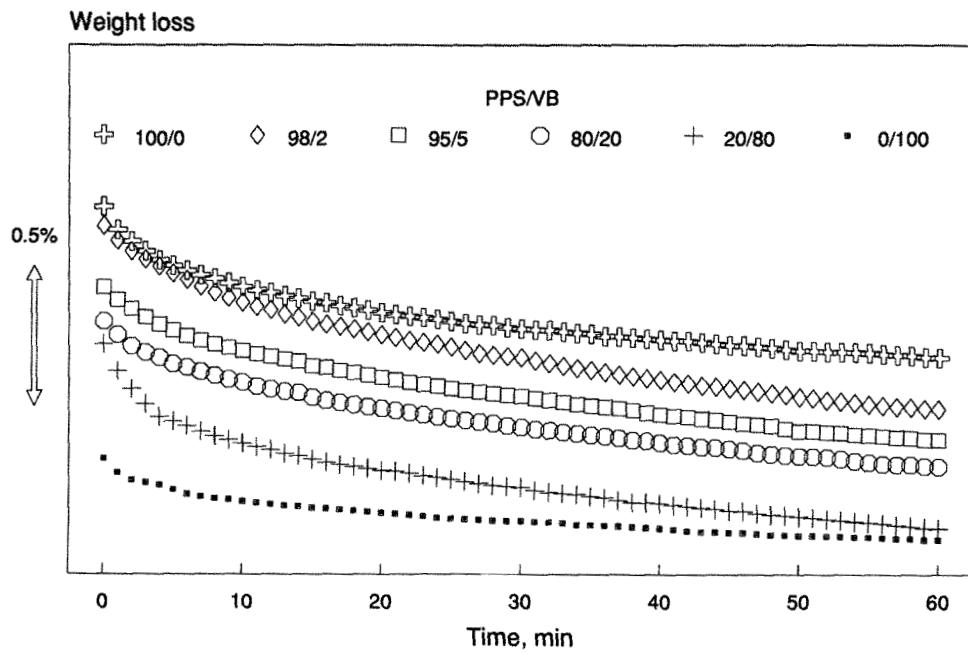


**Figure 8** Thermogravimetric curves for neat PPS and 80/20 PPS/VB, measured under nitrogen with a heating rate of 20°/min.

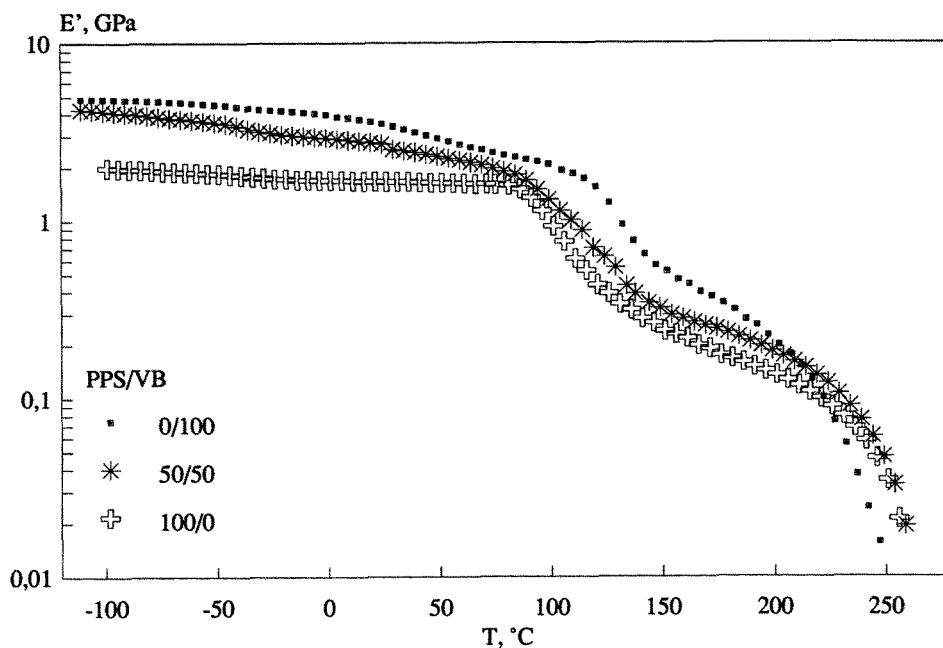
processibility, high HDT, superior weld line strength, and good dielectric properties is presently under development at Hoechst.

The dynamic mechanical characterization of the

PPS/VB blends, which were tested in the form of compression molded bars, confirms that, under the conditions used by us, no significant outgassing takes place. In fact, as it is shown in Figures 10 and 11,



**Figure 9** Isothermal weight loss curves measured at 330°C, for neat PPS and VB, and their blends.

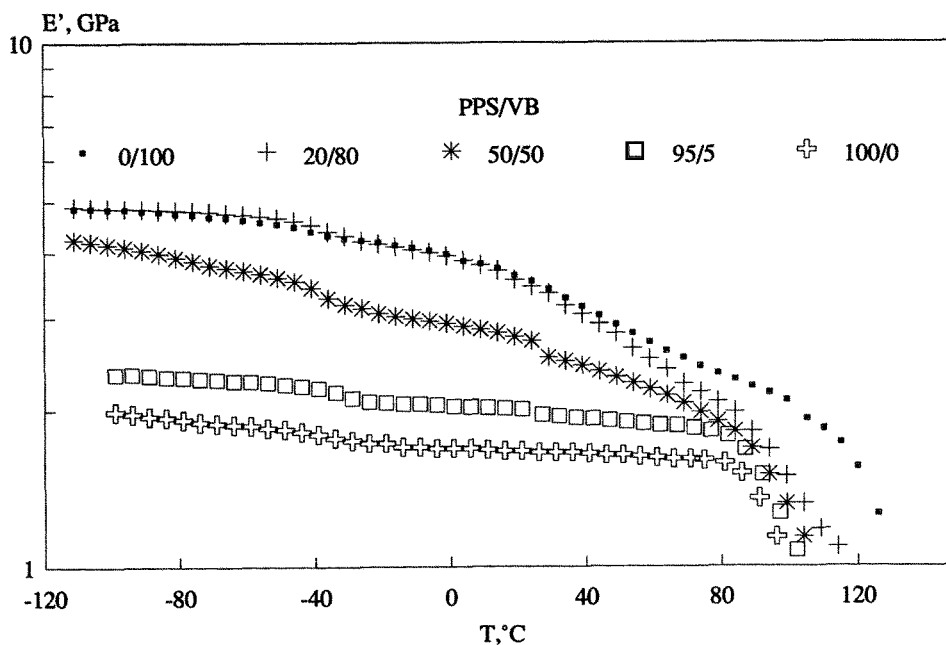


**Figure 10** Young's modulus vs. temperature, in the  $-100 \parallel +270^\circ\text{C}$  range, for PPS, VB, and their 50/50 blend.

their elastic modulus is intermediate between those of the components, at room temperature. It is interesting to notice that a comparatively small addition of PPS to VB leads to an appreciable modulus lowering in the 90–200°C region, and to a modulus increase at higher temperatures.

### CONCLUSIONS

PPS and VB are incompatible polymers, and their blends are characterized by poor interphase adhesion. Because the viscosity of VB is lower than that of PPS only at relatively high temperatures and un-



**Figure 11** Young's modulus vs. temperature, in the  $-100 \parallel +130^\circ\text{C}$  range, for PPS, VB, and some of their blends.

der high shear rates, this LCP cannot be considered as a good processing aid, at least for the PPS grade used in this work. A study of the rheology-morphology relations has shown that a partial LCP fibrillation can be obtained upon extrusion at 320°C.

The formation of a microporosity, which has been observed occasionally, in extruded strands, particularly when these were drawn at the die exit, has been explained as due to the poor adhesion between the two phases which tend to get separated upon straining, and/or to a partial PPS thermal degradation catalyzed by ionic substances, rather than to chemical reactions taking place between PPS and the LCP.

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