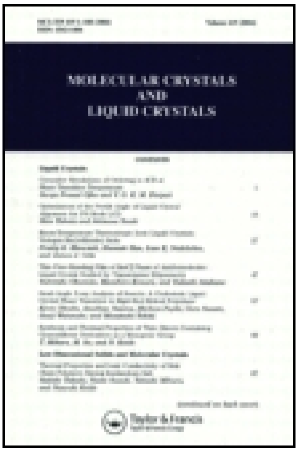

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The Nucleating Effect of a Semiflexible Liquid-Crystalline Polymer for the Crystallization of Poly(Phenylene Sulfide)

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THE NUCLEATING EFFECT OF A SEMIFLEXIBLE LIQUID-CRYSTALLINE POLYMER FOR THE CRYSTALLIZATION OF POLY(PHENYLENE SULFIDE)

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Abstract Blends of poly(phenylene sulfide) and a semiflexible liquid-crystalline polymer have been prepared, in the whole range of concentration, by melt mixing. The effect of the LCP phase on the crystallization of PPS has been studied by non-isothermal and isothermal calorimetry. It has been found that the addition of only 2-5% LCP into PPS strongly increases the crystallization rate of the latter polymer. This effect has been interpreted as the result of an increased nucleation density. The morphology of the blends, studied by scanning electron microscopy, has shown that the two polymers are incompatible, although the phase dispersion is good. Under elongational flow, the dispersed phase shows a distinct tendency toward fibrillation.

INTRODUCTION

During the last two decades, the blends of commercial thermoplastics with liquid-crystalline polymers (LCPs) have attracted the attention of researchers, due to the expected benefits offered by the processing-aid and the reinforcing effects played by the LCP phase, at loadings as low as 5-20%.[1] When the host resin is a crystalline polymer, the LCP phase may also influence the crystallization process. This effect has, in fact, been observed for a number of systems, in the past.[2-6]

A few years ago, we carried out a systematic study of the crystallization kinetics of poly(phenylene sulfide) (PPS) blended with a commercial, wholly aromatic copolyesteramide (Vectra-B950, by Höchst-Celanese).[7-10] We found that the presence of a very low amount of the LCP (2-5%), leads to a pronounced acceleration of the isothermal crystallization of PPS, and to an increase of the dynamic crystallization temperature. This effect, which may be beneficial for, e.g., the injection molding operations used for manufacturing PPS articles, has been interpreted in terms of an increased nucleation density.

PPS is a semicrystalline engineering polymer which is finding increasing application as either unfilled and filled resin.[11] The morphology and the properties of the fabricated PPS articles have been shown to depend, not only on the adopted processing conditions, but also on the nature of the fillers, since the latter may influence the degree of crystallinity and the rate of crystallization. For neat PPS, the maximum crystallization rate has been observed in the 170°C range. It has also been shown that an increase of the molecular mass leads to a reduction of both the crystal growth rate and the velocity of bulk crystallization.[12, 13] The presence of fibrous fillers, especially aramid fibers, was found to increase the PPS crystallization rate, and this effect was interpreted in terms of a faster heterogeneous nucleation taking place in the composite.[14-16] The crystallization of PPS blended with different thermoplastic polymers was also studied by several researchers, and the effect of the second component was found to depend on the nature of the added polymer. Thus, the addition of either high density polyethylene,[17, 18] or poly(ethylene terephthalate),[19] was observed to increase the rate of PPS crystallization, but the reverse was found when polystyrene was used as the second component of the blend.[20] Whatever the effect on the crystallization kinetics could be, the degree of crystallinity of PPS was always found to decrease with increasing the concentration of the other polymer.[17-20]

In the present investigation, the kinetics of crystallization and the morphology of PPS (Ryton GR02), blended with a semiflexible LCP (SBH 1:1:2), recently developed by Eniricerche,[21] have been studied.

EXPERIMENTAL

PPS was kindly supplied by Phillips Petroleum International S.R.L., Milan. The sample, Ryton GR02, was a pale amber, translucent, pelletized material. The polymer was dried in a vacuum oven at 120°C for at least 48 h, before use. This treatment led to cold crystallization and the material became opaque. The MFI, measured according to ASTM D1238 (5 Kg, 316°C) was 9.78 g/min.

SBH 1:1:2 was a LC random copolyester composed of sebacic acid (S), 4,4'-dihydroxybiphenyl (B), and 4-hydroxybenzoic acid (H) units, in the 1:1:2 molar ratio, under development at Eniricerche S.p.A., Milan. This LCP also was dried under vacuum at 120°C for 48 h, before being used.

The blends, with an SBH content of 0, 2, 5, 10, 20, 40, 60, 80 and 100% w/w, were prepared in a 30 ml mixer attached to a Brabender Plasticorder. Blending was done under nitrogen, in order to minimize the chemical modifications undergone by PPS, when held at high temperature in the presence of air.[22] The conditions used were as follows: temperature 290°C, mixing time 3-4 min, speed 100 rpm.

The thermal analysis of the blends has been carried out with a Perkin Elmer differential scanning calorimeter (DSC-4), equipped with a data station. The calorimeter was calibrated with indium and zinc standards. All the DSC heating traces were recorded with a rate of 20°C/min, whereas the cooling scans were done using different rates, namely 5, 10, 20 and 40°C/min. The samples, ca. 15 mg, were heated at 330°C for 10 min, before each cooling scan, and before the isothermal crystallization experiments. This treatment grants the destruction of the crystalline nuclei, without measurably altering the characteristics of the materials .

For pure PPS, the isothermal crystallization analysis was made in a temperature range between 200 and 240°C. For the blends, due to the faster crystallization of PPS, the explored interval was higher: 240-250°C, for the blends with 2-5% SBH, and 210-230°C, for the blends with 80% SBH. The specimens, were held at 330°C for 10 min and were then cooled down to the selected crystallization temperature with a rate of 200°C/min. The heat evolved during the isothermal crystallization was recorded, and the fraction X_t of polymer crystallized at time t was evaluated from the ratio of the area of the exotherm at time t to the total area. The latter was determined by back extrapolation of the baseline obtained after the end of crystallization. The starting time of crystallization (t = 0) was taken as the onset of the exothermic peak.

The melting temperature (Tm) of the isothermally crystallized specimens was determined by a DSC scan carried out directly from Tc up to 330°C, with a rate of 10°C/min.

SEM investigation was carried out on blend specimens fractured under liquid nitrogen and coated with gold, by means of a Jeol T-300 scanning electron microscope.

Spinning experiments were made with a laboratory extruder, equipped with a die of 0.9 mm diameter and L/D = 0.45. The filament was drawn with a draw ratio of ca. 10.

RESULTS AND DISCUSSION

Non-isothermal calorimetry

The DSC traces, measured with a rate of 20°C/min for some of the PPS/SBH blends, are presented in Figures 1a (heating scans) and 1b (cooling scans), along with those of the neat polymers. The traces of the blends with a SBH content in the 0-40% range show a single transition associated with the fusion/crystallization of the PPS phase; the transition due to the LCP phase cannot be detected, probably because the apparent transition

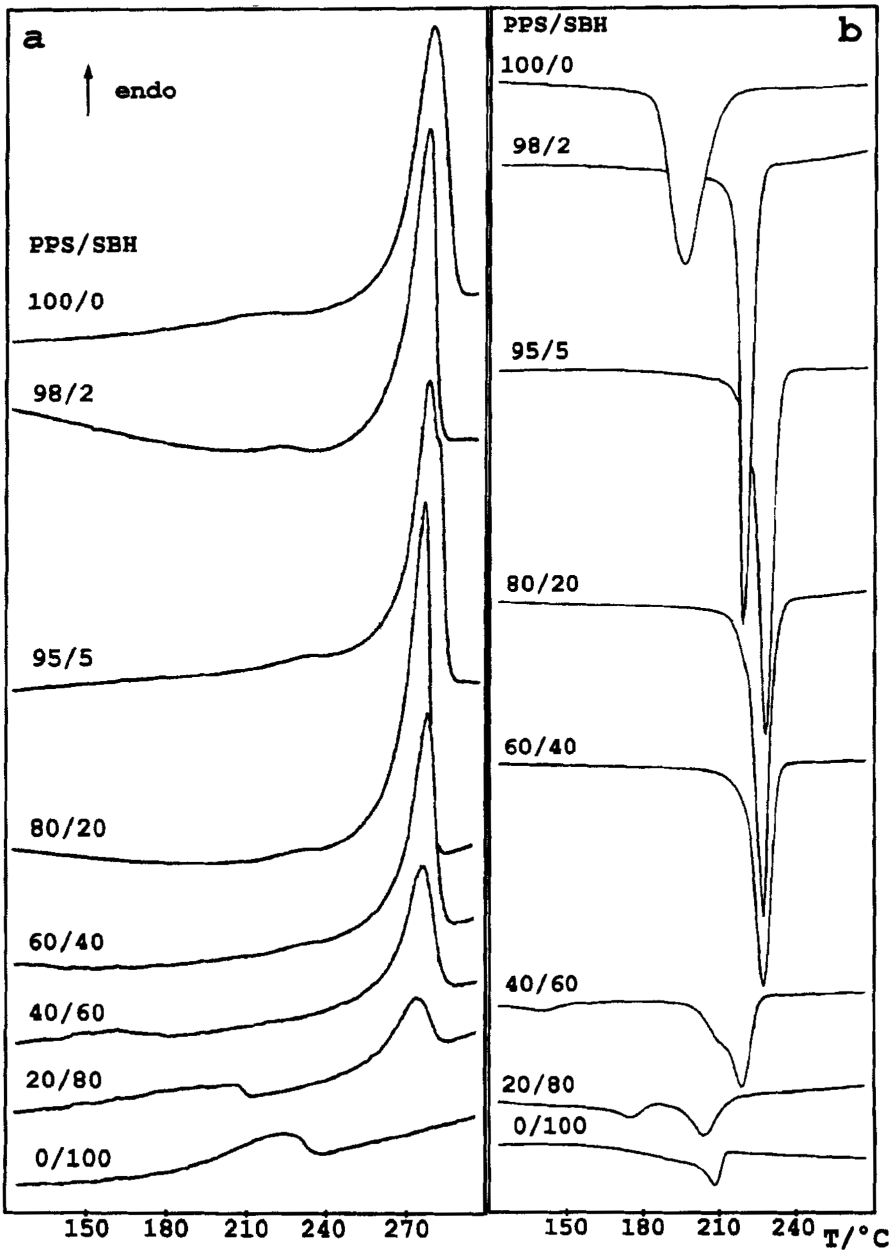

FIGURE 1 DSC heating (a) and cooling (b) traces of PPS/SBH blends. Scanning rate 20°c/min.

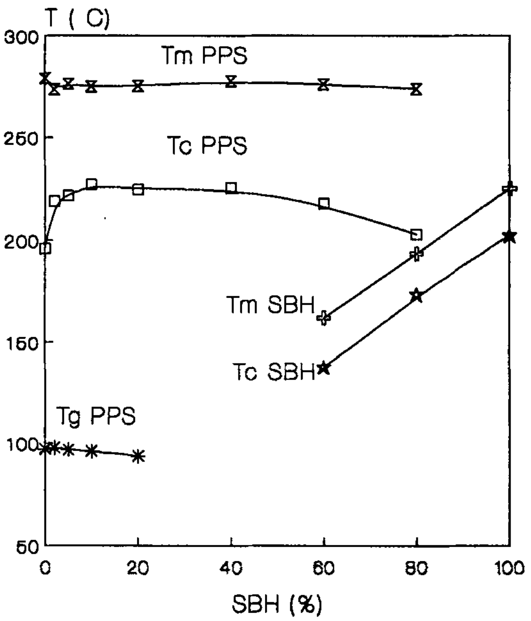

FIGURE 2 Dependence of the transition temperatures of PPS/SBH blends on the LCP content.

enthalpy of this polymer (ca. 8 J/g) is much lower than that of PPS (ca. 36 J/g). For the blends with a higher LCP content (60-80%), two transitions can be observed, which are clearly separated from each other, and can be safely assigned to the fusion/crystallization of the two phases.

In Figure 2, the temperatures of melting (Tm) and crystallization (Tc) of the blend components are plotted as a function of the LCP content. The dependence of the glass transition temperature (Tg) of the PPS phase, which could be measured reliably only for the blends with low SBH content, is also shown in Figure 2. It may be seen that Tg and Tm of the PPS phase are practically independent of blend composition. This indicates that SBH is insoluble in the PPS phase. On the other hand, the decrease of Tm and Tc of the SBH phase, with increasing the concentration of PPS, may mean that the latter is partially soluble in the LCP.

The DSC traces in Figure 1b, as well as the plot of Figure 2, show that Tc of the PPS phase increases strongly upon addition of small amounts of SBH (2-5%); at higher SBH loadings, Tc remains almost constant, and finally decreases when the LCP content exceeds ca. 60%, i.e., beyond the phase inversion. The finding that PPS crystallizes at a higher Tc, under dynamic conditions, if loaded with small amounts of SBH, is an indication that this semiflexible LCP acts as a nucleating agent for PPS. It must be

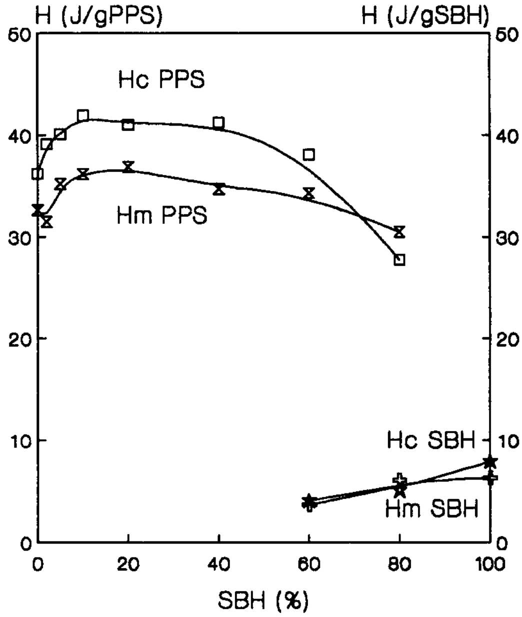

FIGURE 3 Dependence of the transition enthalpies of PPS/SBH blends on the LCP content.

emphasized that SBH is in the nematic state, in the temperature range of crystallization of PPS.

The enthalpies of the phase transitions undergone by the blends components (in J/g of the corresponding phase) are plotted in Figure 3, vs. the SBH content. The slight decrease of the enthalpy associated with the SBH transition, with increasing the PPS content, may perhaps be taken as a confirmation of the hypothesis that PPS is partially soluble in the LCP. The enthalpies of fusion/crystallization of the PPS phase increase by ca. 15% in the 0-10% SBH concentration range, remain practically constant in the 10-50% interval, and finally decrease beyond the phase inversion. The appreciable increase of the enthalpy of the PPS transition, resulting from the addition of rather small amounts of SBH, shows that this LCP does not only nucleate the crystallization of PPS, but also raise its degree of crystallinity.

The temperature of dynamic crystallization of the PPS phase (Tc) was also measured using different cooling rates, namely 5, 10, 20, and 40°C/min. The dependence of Tc on the SBH content, observed at different cooling rates, is shown in Figure 4. It is readily seen that the increase of Tc in the SBH concentration range 0-5% is higher the higher the cooling rate: with a cooling rate of 5°C/min, Tc grows by ca. 20°, whereas the increase becomes of ca. 40° with a cooling rate of 40°C/min. This means that the dynamic

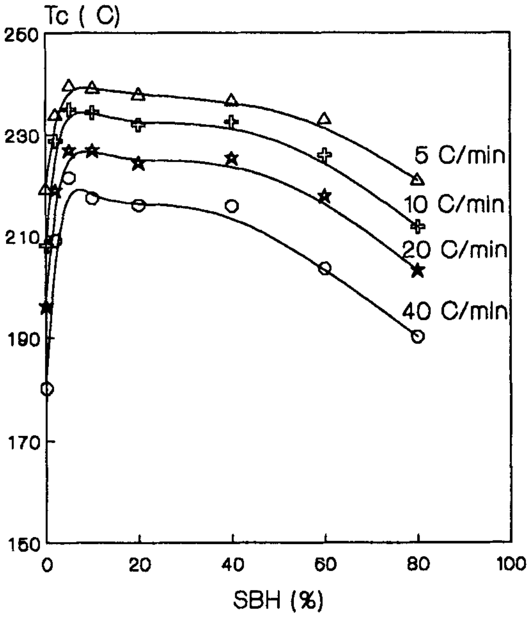

FIGURE 4 Dependence of the dynamic crystallization temperature of the PPS phase on the LCP content, for different cooling rates.

crystallization of PPS is less cooling-rate sensitive when the polymer is loaded with small amounts of LCP. Such behavior, which is similar to that described for the case of PPS blends with a wholly aromatic LCP,[7] seems to be peculiar for LCP fillers. In fact, other fillers, such as glass and carbon fibers, mineral fillers, etc., have been shown to display a reduction of their nucleating ability toward crystallizable polymers, such as polypropylene[23], upon increasing the cooling rate.

The results obtained from dynamic DSC measurements show that the two polymers under investigation are practically immiscible, although some evidence for a partial solubilty of PPS into SBH has been obtained. These results also demonstrate that small amounts of the semiflexible LCP added into the PPS matrix lead to a noticeable increase of both the crystallization temperature and the degree of crystallinity of the latter.

Isothermal calorimetry

The isothermal crystallization behavior of the PPS/SBH blends was studied by rapidly cooling the blends specimens from 330°C down to the selected temperature Tc, and recording the heat evolution as a function of time. The Tc range investigated varied with the blend composition in the interval 210-250°C, and, as already stated, the SBH component was in the nematic state, at these temperatures. Thus, a single exotherm was recorded, corresponding to the isothermal crystallization of the PPS phase. From the exothermic peaks, the figures for the the fraction X_t of PPS crystallized at time t were calculated and, from the plots of X_t vs. log(t), the values of t½ (half-crystallization time) were determined.

In Figure 5, t½ is plotted as a function of blend composition. It may be seen that, at every Tc, the addition of SBH into PPS dramatically lowers t½. The observed decrease of t½ is of ca. one order of magnitude. The dependence of t½ on the SBH content, shown in Figure 5, can be compared to that of the dynamic Tc, shown in Figure 4. Here also, in fact, the stronger effect is found in the 0-5% SBH range; higher amounts of added SBH have practically no effect, and, finally, beyond the phase inversion, the effect becomes lower the higher the SBH content.

As already pointed out, the strong increase of both non-isothermal and isothermal crystallization rates of PPS, due to the addition of SBH, has been interpreted in terms of an increased nucleation density. This hypothesis was supported by the observation of the textures shown by thin films of neat PPS and its blends with SBH, when viewed between crossed polarizers, after identical crystallization treatments. The dimensions of the PPS spherulites were, in fact, at least ten times smaller in the blends. It might be argued that, under this hypothesis, the PPS crystallization rate should be found to increase further

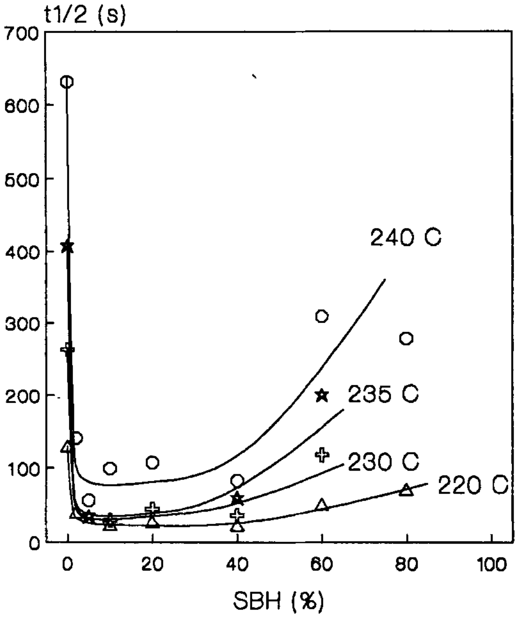

FIGURE 5 Dependence of the half-crystallization time t½ of PPS, in PPS/SBH blends, on the LCP content and the isothermal crystallization temperatures

upon increasing the SBH concentration beyond the 5-10% level. However, as discussed below, the dimensions of the dispersed SBH particles were shown to increase on increasing the LCP content in the blend, and this may explain, at least in part, why the nucleation density does not increase any more, above a certain SBH concentration.

The crystallization kinetics of the PPS phase was analyzed by means of the Avrami Equation

$$X_t = 1 - \exp(-k \times t^n) \tag{1}$$

where k is the rate constant of crystallization and *n* is the Avrami exponent, which can be related to the type of nucleation and to the geometry of crystal growth. The values of *n* and k were determined from the slopes and the intercepts of the linear plots of $\log[-\ln(1-X_t)]$ vs. $\log(t)$.

The isothermal crystallization parameters are collected in Table 1.

The average values of the Avrami exponents *n* of both neat PPS and its blends (with the exception of the 20/80 PPS/SBH blend) are in the 2.5-3 range. With the commonly accepted assumption that *n* may be lowered below 3 by, e.g., the formation of sheaf-like structures not fully developed into spherulites, and/or impingement effects, this can be

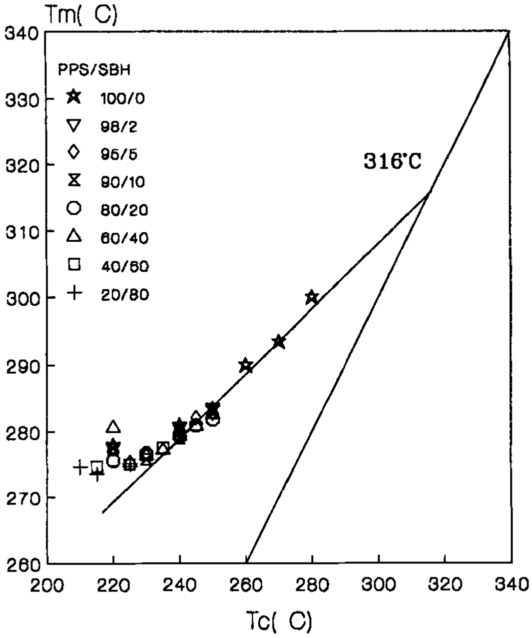

FIGURE 6 Fusion temperatures of isothermally crystallized PPS phase in PPS/SBH blends vs. crystallization temperature.

TABLE 1 Isothermal crystallization parameters of the PPS phase of PPS/SBH blends.

Blend	Tc (°C)	t½ (s)	n	k × 10^7 (s^{-n})
100/0	240	631	3	0.0021
	235	407	3	0.0285
	230	263	2.9	0.056
	225	170	2.74	4
	220	128	2.76	9
	200	35	2.56	733
98/2	250	221	2.45	34
	240	81	2.85	771
95/5	250	122	2.77	104
	240	38	3	1010
90/10	250	156	2.5	
	245	92	2.77	101
	240	65	2.77	336
	230	23	2.66	12309
80/20	250	181	2.5	28
	245	132	2.77	25
	240	74	2.77	167
	230	32	2.85	2859
60/40	245	172	2.5	1935
	240	52	2.5	5261
	230	32	2.5	42963
	225	17		
40/60	235	128	2.5	304
	230	99	2.25	3355
	225	65	2.46	4016
	215	30		67379
20/80	225	144	1.42	12065
	215	75	1.74	49916
	210	56	1.48	90953

taken as an indication that the crystallization of PPS involves heterogeneous nucleation and tridimensional crystal growth, and that this mechanism does not change appreciably, in the presence of the LCP.

As for the rate constant of isothermal crystallization, it may be observed that the values found for the blends are invariably much higher than those for neat PPS. Thus, the same k value obtained for neat PPS at, e.g., Tc = 200°C may be found for the 2-40% SBH blends at Tc ≈ 240°C, and, for those with 60-80% SBH, at Tc ≈ 230°C. As for neat PPS, the kinetic parameters are in agreement with literature data.[15]

The melting temperatures of the isothermally crystallized samples are plotted as a function of Tc in Figure 6. The linear dependence of Tm on Tc, for Tc > 240°C, can be described by Equation 2[24]

$$Tm = Tm^\circ(1 - 1/Y) + Tc/Y \tag{2}$$

where Tm° is the thermodynamic melting point of the crystallized component, and Y is a constant related to the crystal size and perfection. It may be observed that the experimental values found for the blends fit a single straight line, for Tc > 240°C, and extrapolation of this line leads to a thermodynamic melting point of the PPS phase (Tm°=316°C), which is independent of blend compoasition.

Morphology

The morphology of the PPS/SBH blends was studied by scanning electron microscopy (SEM). The specimens were either in the form of blocks of material, as received from the melt mixing operation (Figure 7a, b, c), or in the form of fibers prepared as described in the experimental section (Figure 7d, e, f). A two phase structure of the blends was always observed, thus confirming that the two components are practically immiscible. The interphase adhesion is not very good, but there is no sign of voids due to evolution of gases produced by chemical interactions between the components, as found by Baird et al.[25], and by Subramanian and Isayev[26] for PPS blends with a commercial wholly aromatic LC copolyester. The phase inversion is found to occur in the 40-60% SBH range.

At SBH loadings up to 40%, the LCP dispersed phase, in the absence of elongational flow, appears in the form of spherical droplets, whose dimensions progressively increase with the SBH content (Figure 7a, b). In drawn fibers, the SBH particles show a fibrillar geometry, uniformly oriented in the draw direction (Figure 7d, e). When the SBH content is equal to, or higher than, 60%, the LCP forms the continuous phase and the PPS phase appears as spherical or fibrillar particles, depending on the flow conditions, embedded in the fibrous matrix (Figure 7c, f).

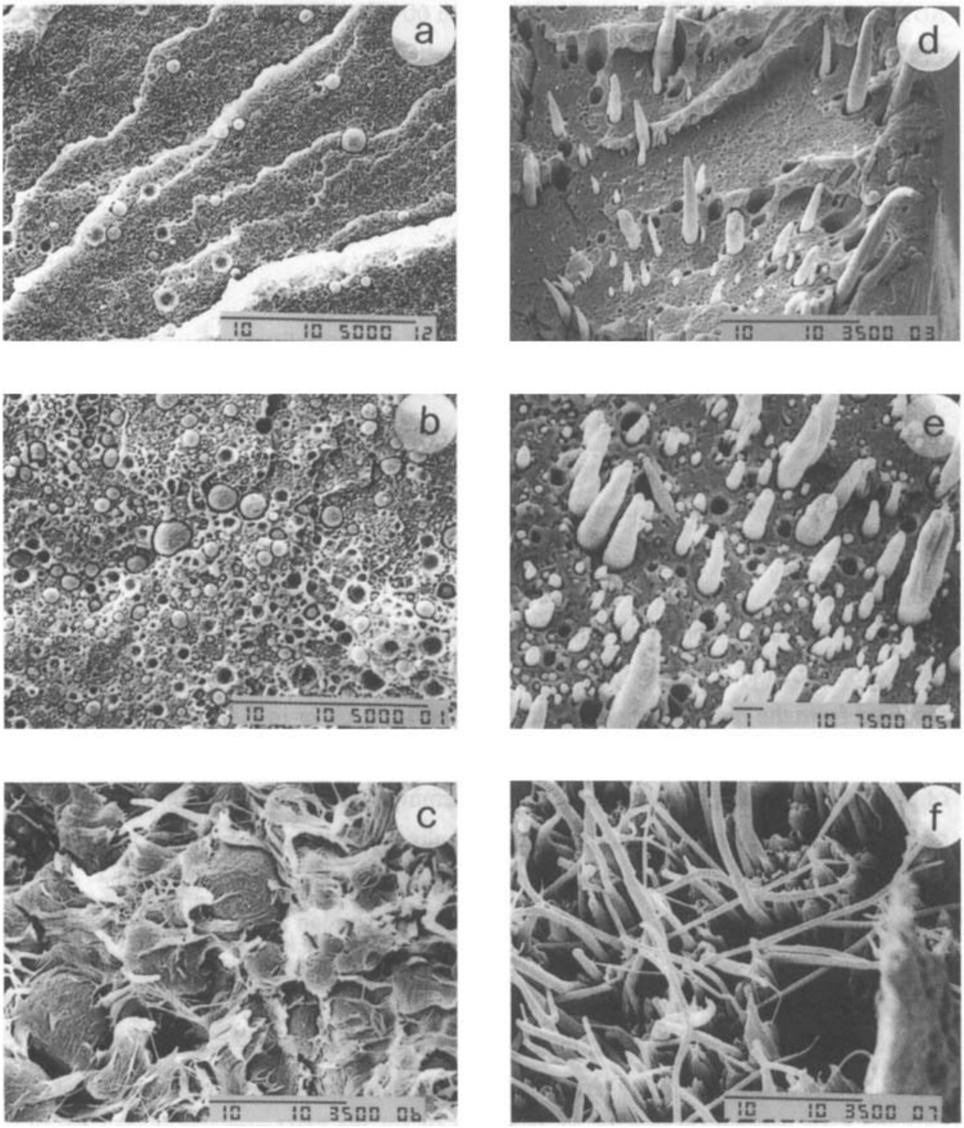

FIGURE 7 SEM micrograph of the fracture surfaces of PPS/SBH blends specimens. (a) 95/5; (b) 80/20; (c) 40/60; (d) 90/10, fiber; (e) 80/20, fiber; (f) 40/60, fiber.

CONCLUSION

It has been shown that the addition of a semiflexible, thermotropic LCP into commercial PPS gives rise to practically immiscible blends. The dispersed phase shows a pronounced tendency to fibrillate under elongational flow conditions. The non-isothermal and isothermal calorimetric investigation has demonstrated that the LCP, which is in the nematic state in the temperature region where PPS crystallization occurs, causes a strong acceleration of the crystallization of PPS. Since this effect is observed even at very low LCP loadings (2% w/w), it may be argued that the in situ addition of such low LCP amounts into PPS might produce some advantage for the injection molding of the latter resin, without any appreciable deterioration of the properties of the finished articles and with no increase of their cost.

ACKNOWLEDGMENT

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