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Poly(phenylene sulphide)/thermotropic liquid crystalline polymer blends: a comparative study of thermal properties, phase behaviour and morphology of blends generated by different techniques

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Blends of poly(phenylene sulphide) and poly(ethylene terephthalate-*co*-oxybenzoate), an aliphatic–aromatic thermotropic liquid crystalline polymer (TLCP), were prepared by different blending techniques and their thermal properties, phase behaviour and morphology were compared using differential scanning calorimetry (d.s.c.), polarized light optical microscopy (p.l.o.m.) and scanning electron microscopy (s.e.m.). Melting transitions and phase behaviour of the blends were dependent on the preparation method. While blends prepared by the precipitation method appeared monophasic, those prepared by melt-mixing were seen to be phase separated. The melt-mixed blends show macrophase-separated morphology indicating poor phase mixing whereas the co-precipitated blends of the same composition exhibit a disperse-type morphology, as observed by p.l.o.m. In comparison to melt-mixed blends, co-precipitated blends were seen to be uniform and continuous. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Fibre-reinforcement has been used for many years to increase the engineering performance of thermoplastics[1]. Such composite materials have found applications in the aircraft, aerospace vehicles, automotive, marine and electronic industries. The reinforcing materials are traditionally inorganic such as graphite, boron and glass. The use of inorganic fibres and fillers in thermoplastics leads to an increase in melt viscosity and lowers the ease of processing. Reinforcement through the addition of thermotropic liquid crystalline polymers (TLCPs) to thermoplastics has been investigated over the last few years with encouraging results[2–13]. The principal goal is to achieve improvements in mechanical properties by using TLCPs to reinforce flexible thermoplastics through the *in situ* formation of fibres. Blending is also considered as a possible route to overcome the highly anisotropic physical properties of TLCPs that can be problematic in many applications. The low melt viscosity of the TLCPs can reduce the overall melt viscosity of the blend and thus act as a good processing aid. Moreover, the TLCP phase has been shown to influence the crystallizability of the thermoplastic matrix.

Poly(phenylene sulphide) (PPS) and TLCPs are high strength/high temperature speciality polymers that find applications in the electrical and electronic industries[2]. Several studies[3–7] have been published on the blends of PPS with wholly aromatic TLCPs such as Vectra-A950 (copolyester of 25 mol% 2-hydroxy-6-naphthoic acid (HNA) and 75 mol% 4-hydroxybenzoic acid (HBA)) and Vectra-B950 (copolyester of 60 mol% 2-hydroxy-6-naphthoic acid, 20 mol% terephthalic acid and 20 mol% 4-aminophenol). Subramanian and Isayev[3] found that for effective reinforcement and improvement of mechanical properties, the viscosity of the TLCP must be lower than that of the PPS at the processing temperature. The mechanical properties estimated for PPS/Vectra-A950 were lower than that of TLCP and no fibrillation of the TLCP phase in the matrix was found. Previous studies[4,5] led to the conclusion that maximum fibrillation occurs when the melt viscosity ratio of the original components is close to unity. The presence of fibres seems to be a necessary attribute for improving the mechanical properties. Thus, the viscosity ratio between the dispersed phase and the matrix is an important factor for the phase morphology of the blends. Magagnini *et al.*[4] found that the melt viscosity of PPS was considerably reduced in the presence of Vectra-B950. The inherent low melt viscosity of the TLCP melt is one reason for this reduction. Change of flow pattern of the blend is another reason. Heino and Seppala[5,6] reported that PPS/Vectra-A950 blends were two-phase systems and that the properties were dependent on miscibility, interfacial adhesion between the blend components, and orientation of the TLCP phase.

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In a series of previous papers[7–9], we have reported the thermal behaviour, crystallization kinetics and phase morphology of blends of PPS and poly(ethylene terephthalate-*co*-oxybenzoate), an aliphatic–aromatic thermotropic liquid crystalline copolyester (TLCP). This TLCP was found to be very effective in improving the crystallization behaviour of PPS[7,8].

The manner in which two polymers are blended together is of vital importance in controlling the phase morphology and to the ensuing properties of blends. Most common techniques for preparing the blends are melt-mixing, solution blending and co-precipitation. Published literature regarding the effect of blending techniques and conditions on the morphology and phase behaviour of PPS/TLCP blend system is rather limited. In this paper, we present a comparative study on the thermal properties, phase behaviour and morphology of PPS/TLCP blends produced using different blending techniques. Thermal analysis by differential scanning calorimetry (d.s.c.) is employed to compare the melting and crystallization behaviour of the blends. The influence of blending techniques on the phase behaviour was investigated with polarized light optical microscopy (p.l.o.m.), and scanning electron microscopy (s.e.m.).

EXPERIMENTAL

Materials

PPS used was a commercial grade Ryton V-1 (M_w = 60 000) manufactured by Phillips Petroleum Company, USA. This material showed a melting point of 282°C and the ΔH was 43.2 J g^{-1}. The aliphatic–aromatic thermotropic liquid crystalline polymer (TLCP) was synthesized from 70 mol% poly(ethylene terephthalate) and 30 mol% 4-acetoxybenzoic acid[14]. It was termed as P37. The intrinsic viscosity of the PET used was 0.6 dL g^{-1}. The TLCP exhibited birefringence when heated up to 300°C and then cooled down. This aliphatic–aromatic TLCP showed a glass transition temperature of 65°C and crystal to nematic transition at 197°C. 1-Chloronaphthalene was obtained from Aldrich Chemical Co., USA, and was used without further purification.

Preparation of blends

Melt-mixing. Powders of the TLCP and PPS were dried at 130°C under vacuum for 48 h prior to mixing. The PPS/TLCP blends with a TLCP content of 10, 20, 30, 50, 75 or 90% (wt/wt) were prepared in a 30 ml mixer attached to a Brabender Plasticorder at 300°C and 100 rev min^{-1} for 5 min under a nitrogen atmosphere. Blank samples of both PPS and TLCP were subjected to the same treatment.

Co-precipitation. The autoclave (made by Parr Reactor Co., USA) was charged with PPS and TLCP (blend compositions same as melt-mixed blends) in 1-chloronaphthalene and heated at 260°C for 5 min under a nitrogen atmosphere. The reactor was cooled to room temperature and the polymer mixture was precipitated in acetone. Blends were dried at 150°C in a vacuum oven for 1 week to remove 1-chloronaphthalene.

Thermal analysis

Thermal properties were measured by a Mettler TA4000 series DSC. The apparatus was calibrated with indium at different scanning rates. The lag between sample and pan holder temperature was also taken into account, and computed through indium crystallization tests as described by Eder and Wlochowicz[15]. The weights of the samples were kept constant (6.0 ± 0.1 mg) throughout the analysis so that the effect of weight change on enthalpy change could be minimized. A standard scanning rate of 20°C min^{-1} was used for heating and cooling cycles. The heats of fusion and crystallization were determined from the peak area of the d.s.c. thermograms.

Polarized light optical microscopy

The phase behaviour of PPS/TLCP blends generated by different blending techniques was investigated by a hot stage coupled Leitz microscope under crossed polarizers. The blend samples were sandwiched between a microslide and a cover glass and were melted at 320°C for 1 min under slight pressure. The slides containing thin film (20–30 μm) were then quickly transferred to the preheated hot stage (at 320°C) and observed under polarizers.

Scanning electron microscopy

The morphology of the blend surfaces was studied using a Leica Stereoscan 440 scanning electron microscope. The melt-mixed and co-precipitated blends were moulded into strips using a compression moulding press unit under identical conditions (at 300°C for 4 min). These strips were freeze-fractured at liquid nitrogen temperature and the fractured surface were coated with a thin layer of gold prior to the observation.

RESULTS AND DISCUSSION

Thermal properties

Melting behaviour. d.s.c. heating thermograms of PPS and TLCP as well as PPS/TLCP blends prepared by melt-mixing and co-precipitation methods are shown in *Figure 1*. In co-precipitated blends, the endothermic peaks corresponding to the melting transition of TLCP are absent, whereas in melt-mixed blends the intensity of melting transition peak of TLCP increases with its concentration.

The occurrence of phase separation in blends is observable in d.s.c. thermograms by the absence of any change in either the glass transition temperature or melting transition temperature or enthalpy of transitions from those corresponding to the original polymer components[16]. The absence of the endothermic peak corresponding to melting transition of TLCP in the co-precipitated PPS/TLCP blends of 80/20, 70/30 and 50/50 compositions in *Figure 1* could be due to (i) the absence of phase separation or (ii) microphase separation not detectable by d.s.c. However, in the present blend system, it is difficult to interpret any interactions, either chemical or physical, between the PPS and TLCP[8,9]. Moreover, in the case of homogeneous miscible blends the melting endotherm should have shifted to temperatures intermediate between that of the two homopolymers[11,17] and this shift is not observable for the PPS/TLCP blends in *Figure 1*. Therefore, the hypothesis (ii), that microphase separation is not detectable by d.s.c., is more appropriate to describe the blends prepared by co-precipitation.

The minimum domain size required for the detection of phase separation by d.s.c. is considered to be of the order of 20 nm[18]. Schurer *et al.*[19] have reported that in d.s.c. thermograms the transition corresponding to the minor component may appear reduced in intensity if the dispersed phase is smaller. In the case of melt-mixed blends, the

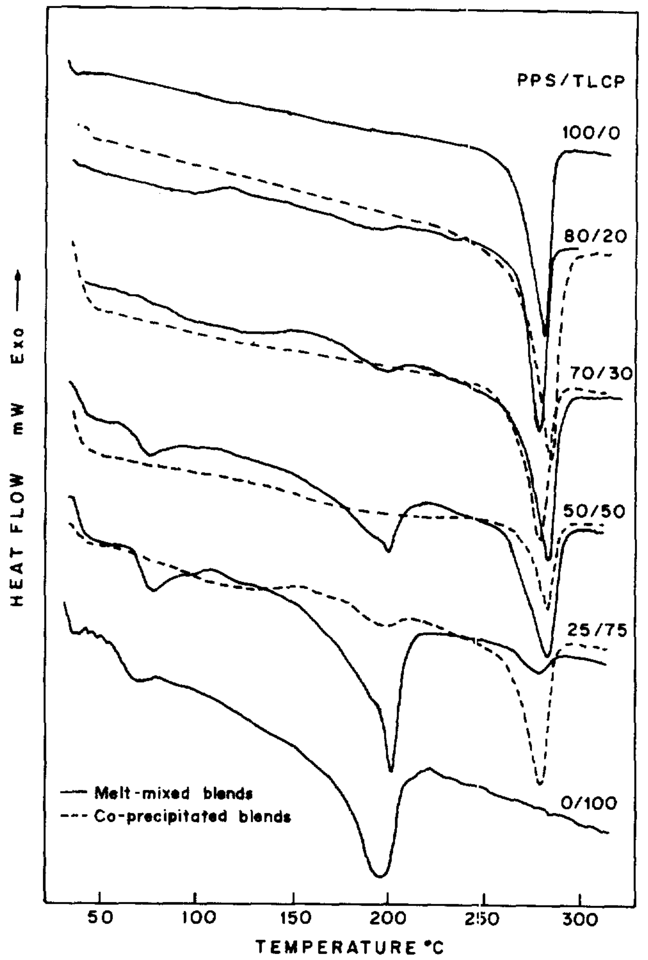


Figure 1 D.s.c. thermograms (second heating scan) of melt-mixed and co-precipitated PPS/TLCP blends at the heating rate 20°C min^{-1}

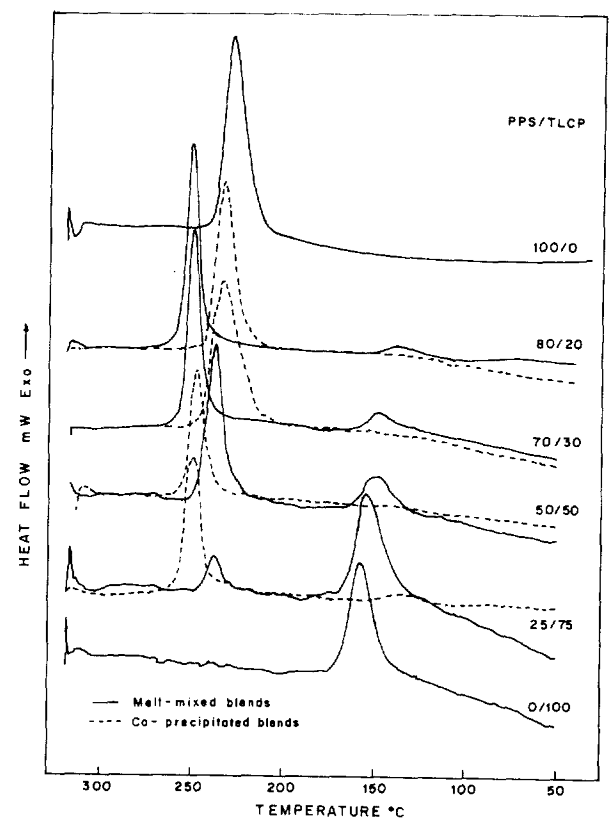


Figure 2 D.s.c. crystallization exotherms (second cooling scan) of melt-mixed and co-precipitated PPS/TLCP blends at the cooling rate 20°C min^{-1}

domains of the dispersed TLCP phase exist as comparatively large in size and therefore can be easily detectable by d.s.c. as shown in the heating thermogram presented in *Figure 1*.

Crystallization behaviour. The crystallization exotherms of pure PPS and PPS/TLCP blends prepared by melt-mixing and co-precipitation methods are shown in *Figure 2*. The crystallization temperatures (T_c), presented in *Table 1*, are those corresponding to the exothermic peak maxima and are corrected as described by Eder and Wlochowicz[15]. In co-precipitated blends, the exothermic peaks corresponding to the TLCP crystallization are absent, whereas in melt-mixed blends the peak intensity of the crystallization exotherm of TLCP increases with its concentration. The crystallization temperature (T_c) and hence the rate of crystallization of the PPS phase increases with the TLCP content up to 30% and decreases on further addition for melt-mixed blends. On the other hand, T_c and hence the rate of crystallization of the PPS phase in the co-precipitated blends steadily increases with TLCP content as shown in *Figure 2*.

These observations are similar to the melting behaviour discussed in the previous section. The dispersed TLCP phase in co-precipitated blends crystallize to form the microphase not detectable by d.s.c. whereas in melt-mixed blends the PPS and TLCP crystallize into separate phases as shown in the d.s.c. exotherm presented in *Figure 2*. The TLCP phase accelerates the crystallization of PPS phase in both melt-mixed and co-precipitated blends. Due to its low melt-viscosity[8,9], the molten TLCP phase provides enough chain mobility to cause rapid crystallization of the PPS phase.

Degree of crystallinity. The degree of crystallinity, α, of the PPS phase in both melt-mixed and co-precipitated blends plotted against the TLCP content is presented in *Figure 3*. The degree of crystallinity, α, was calculated from the enthalpy of crystallization normalized to the PPS content, assuming that the contribution of the TLCP phase is negligible[20]. A value of 146.2 J g^{-1} was estimated by Maemura *et al.*[21] for the enthalpy of fusion of 100% crystalline PPS. For melt-mixed blends, the degree of crystallinity of PPS remains almost constant up to 30 wt% TLCP content and then reduces with further addition of TLCP. In the case of the co-precipitated blends, the degree of crystallinity steadily decreases with TLCP concentration.

This marked difference in the degree of crystallinity may be due to the fact that the degree of mixing is more intimate in co-precipitated blends as compared to the melt-mixed blends of similar composition. The addition of a second polymer to a semicrystalline polymer can act as a diluent, which could either decrease crystallinity by decreasing concentration and number of nuclei, or increase crystallinity by enhancing nucleation or increasing the chain mobility[22]. The degree of crystallinity, α, is known to be a measure of degree of phase mixing[9,23]. The degree of crystallinity is known to decrease on compatibilization of incompatible blends[23]. From these observations, we may conclude that the degree of crystallinity of the PPS phase depends on the extent of phase separation between the

Table 1 Comparison of thermal data of PPS phase in melt-mixed and co-precipitated PPS/TLCP blends

PPS/TLCP	Melt-mixed blends			Co-precipitated blends		
%(wt/wt)	T_m (°C)	T_c (°C)	ΔH_c (J g^{-1})	T_m (°C)	T_c (°C)	ΔH_c (J g^{-1})
100/0	282	237	43.9	282	237	43.9
90/10	280	252	43.8	281	239	35.1
80/20	279	251	44.0	280	243	33.6
70/30	281	252	35.1	278	245	32.1
50/50	280	247	32.1	279	249	26.3
25/75	278	245	26.2	279	251	24.9
10/90	277	243	23.4	278	249	22.0

T_m, melting peak temperature; T_c, crystallization peak temperature; ΔH_c, heat of crystallization

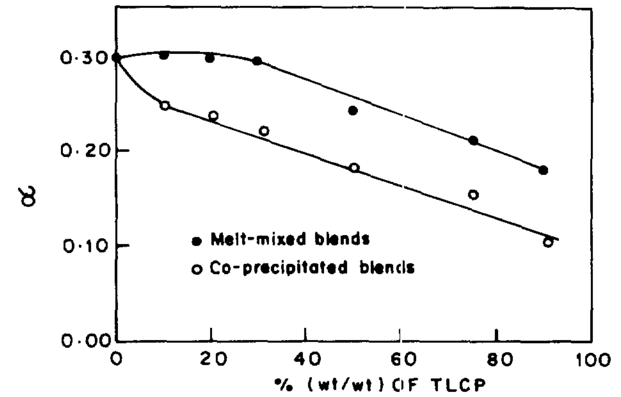


Figure 3 Effect of TLCP content on the degree of crystallinity (α) of the PPS phase in both melt-mixed and co-precipitated blends

PPS phase and the TLCP phase, which in turn, depends on the blending technique used for the preparation of PPS/TLCP blends.

Morphology

Polarized light optical microscopy. Figure 4(a)–(f) shows the optical micrographs under cross polarizers of PPS and PPS/TLCP blends (in the molten state at 320°C) produced by melt-mixing and co-precipitation. At this temperature, the domains of TLCP alone are observable under cross polarizers as these are in the anisotropic nematic state. *Figure* 4(a) and (b) shows a comparison between the TLCP domain size of melt-mixed and co-precipitated blends under identical conditions. A liquid–liquid phase separation in the melt prior to crystallization is observable in PPS/TLCP blends produced by melt-mixing as well as by co-precipitation. In the co-precipitated blends, the TLCP domains are relatively smaller and are more uniformly dispersed within the PPS matrix (*Figure* 4(b), (d) and (f)) whereas in the melt-mixed blends, the TLCP phase exists as a separate phase in the PPS matrix (*Figure* 4(a), (c) and (e)).

Scanning electron microscopy. Figure 5(a)–(d) shows the scanning electron micrographs of PPS and PPS/TLCP blends prepared by melt-mixing and co-precipitation. The melt-mixed blends show macrophase-separated morphology in *Figure* 5(a), (c) and (e) indicating poor phase mixing whereas the co-precipitated blends of the same composition (*Figure* 5(b), (d) and (f)) exhibit a disperse-type morphology. In the blend containing 50% TLCP (*Figure* 5(e)), the TLCP phase exists as fibrils whereas in the corresponding co-precipitated blend (*Figure* 5(f)) no fibrils are observed. The fibrillation observed in the melt-mixed blend (*Figure* 5(e)) is due to a deformation force which plays a major role in the melt-mixing of polymers.

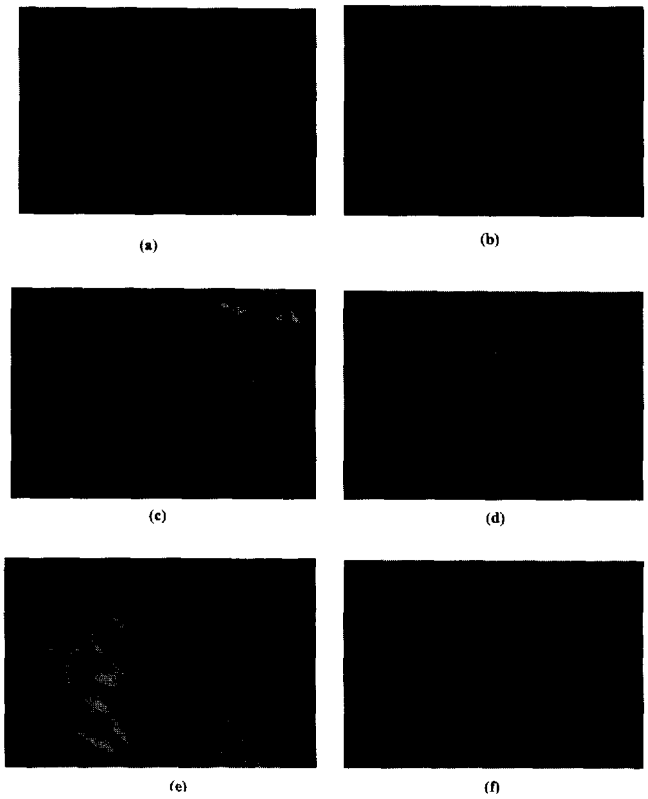
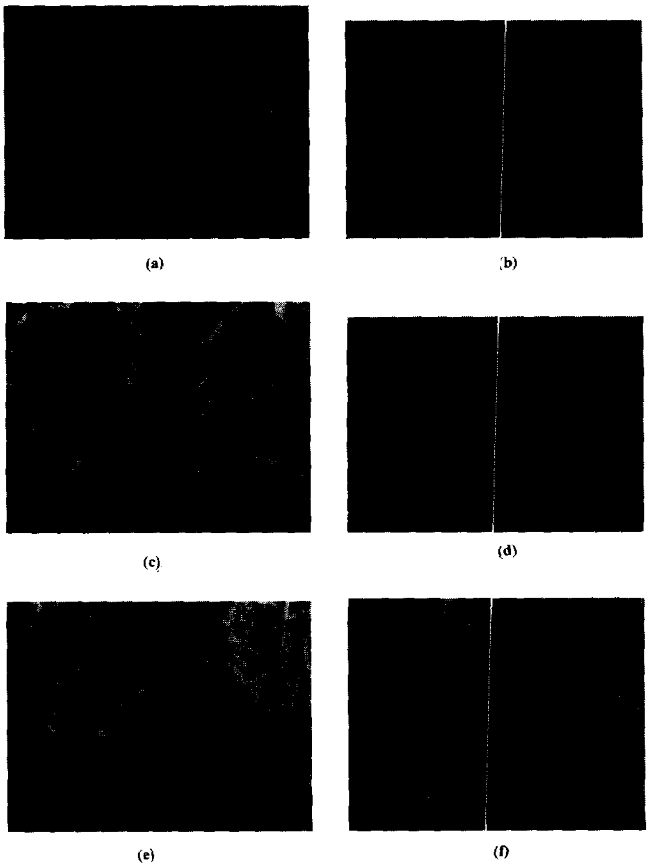


Figure 4 Optical micrographs (same magnification, 100 ×) of the phase behavior and morphology of melt-mixed and co-precipitated PPS/TLCP blends at various compositions at 320°C. Melt-mixed: (a) 80/20, (c) 70/30 and (e) 50/50% (wt/wt). Co-precipitated: (b) 80/20, (d) 70/30 and (f) 50/50% (wt/wt)

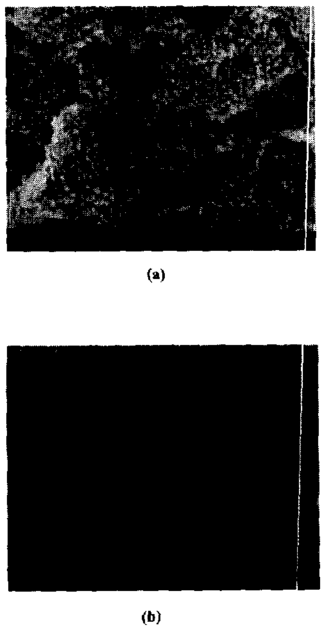
The more uniform and continuous morphology of the co-precipitated blends is a consequence of the intimate dispersion of the TLCP phase within the PPS matrix. This observation is further supported by the scanning electron micrographs at higher magnification exhibited in *Figure 6*. This morphology is comparable to that noted in the case of partially miscible blends. It is difficult to obtain homogeneous mixing of blend components with melt-mixing as a direct consequence of restricted motion polymer chains in the molten state. In that case, the dispersion process is controlled by the shear viscosity of the two polymers. The properties of melt-mixed blends are also strongly influenced by the temperature, time and speed of mixing.

Two polymers which are indeed miscible may form a phase-separated system when solution cast from certain solvents because of differences in the polymer/solvent interaction parameters of the two polymers[24]. In co-precipitated blends, mixing of the two polymers to a homogeneous level is possible because the free motion of



(a) (b) (c) (d) (e) (f)

Figure 5 Scanning electron micrographs showing morphology of freeze-fractured samples of melt-mixed ((a) 90/10, (c) 70/30 and (e) 50/50% (wt/wt)) and co-precipitated ((b) 90/10, (d) 70/30 and (f)50/50% (wt/wt)) PPS/TLCP blends. (TLCP was termed as LCP in micrographs of melt-mixed blends and as P37 in micrographs of co-precipitated blends)



(a) (b)

Figure 6 Scanning electron micrographs at high magnification showing morphology of freeze-fractured samples of (a) melt-mixed and (b) co-precipitated 70/30% (wt/wt) PPS/TLCP blends. (TLCP was termed as LCP in micrographs of melt-mixed blends and as P37 in micrographs of co-precipitated blends)

the polymer chains in the solution state is more compared to the molten state. In addition, rapid removal of solvent from the solution of the two polymers by precipitation using a non-solvent prevents agglomeration and this will lead to homogenization of the components. Therefore, in comparison to melt-mixing and solution casting, co-precipitation is a more convenient and useful alternative for generating molecular composites.

The properties of blends are strongly influenced by their morphology as a consequence of incompatibility and phase separation[25,16,26]. In order to develop an ideal fibril-reinforced microcomposite based on thermoplastics (TP)/ thermotropic liquid crystalline polymer (TLCP), the formation of longer and finer TLCP fibrils with a higher aspect ratio with the TP matrix and an increased interfacial adhesion are the two most important factors[9,23]. The phase stabilization of PPS blends with TLCPs can be improved with the use of compatibilizers. However, recent studies[9,21,27–29] have shown that most of the compatibilized TP/TLCP blends tend to hinder TLCP fibril formation, due to lower interfacial tension and finer dispersed phase domains, even though enhanced interfacial adhesion is obtained. The compatibilization must not cause the loss of fibrous morphology. We are presently exploring different strategies to develop compatibilized PPS/TLCP blends without the loss of fibrous morphology of TLCP.

CONCLUSION

Blends of poly(phenylene sulphide) and poly(ethylene terephthalate-*co*-oxybenzoate), an aliphatic–aromatic thermotropic liquid crystalline polymer (TLCP), were prepared by different blending techniques and their thermal properties, phase behaviour and morphology were compared using differential scanning calorimetry, polarized light optical microscopy and scanning electron microscopy. From these investigations, we could reach the following conclusions: (i) the extent of phase separation is more in melt-mixed blends as compared to co-precipitated blends; (ii) the TLCP phase accelerates crystallization of the PPS phase in both melt-mixed and co-precipitated blends and (iii) the effect of the TLCP phase on the crystallinity of PPS varied with the extent of phase separation between the two components.

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