

CHAPTER 4

SYNTHESIS OF COMPATIBILISER¹ AND COMPATIBILISATION OF PPS/PET-OB BLENDS²
In this chapter the synthesis and characterisation of a compatibiliser for poly(phenylene sulphide) (PPS)/poly(ethylene terephthalate-co-oxybenzoate) (PET/OB) blend system is presented. The block copolymers synthesised by melt-transesterification of dicarboxyl terminated (PPS) with PET/OB, a semi-aromatic thermotropic liquid crystalline polymer (TLCP), were characterised using Fourier transform infra-red spectroscopy (FTIR), differential scanning calorimetry (DSC), x-ray diffraction (XRD) and polarised light optical microscopy (PLOM). The effect of factors such as mole percent of oxybenzoate, weight percent of PPS to PET/OB content and melt-transesterification time at 300 °C on the thermotropic character and crystallisability of the copolymers were also investigated. The crystallisability and thermotropic character were observed to depend on the extent of interchange reactions between the respective segments, which in turn, are dictated by the composition of PET-OB and the transesterification time. The thermotropic character and crystallisability of the copolymers were significantly influenced by factors such as mole percent of oxybenzoate, weight percent of PPS to PET/OB content and melt-transesterification time (at 300 °C) etc. The efficiency of this copolymer to compatibilise PPS/PET-OB blends was tested. While compatibilised blends appeared monophasic, uncompatibilised blends were seen to be clearly phase separated. The uncompatibilised blends showed macrophase-separated-morphology indicating poor phase mixing whereas the compatibilised blends of the same composition exhibited a disperse type morphology, as observed by PLOM.
4.1 INTRODUCTION

Blending conventional thermoplastic polymers with thermotropic liquid crystalline polymers (TLCPs) can lead to easier processing and in situ matrix reinforcement. The properties of blends are strongly influenced by the morphology as a consequence of incompatibility and phase separation. The addition of block or graft copolymers represents the most researched approach to the compatibilisation of blends. Daccord and Sillion reported the preparation of block copolymers of PPS telechelics with other polymers. Heitz et al reported block copolymers of carboxyl terminated telechelic PPS with polyamides and polyesters.

An ideal fibril-reinforced microcomposite based on thermoplastics (TP)/thermotropic liquid crystalline polymer (TLCP) blend should comprise of a TP matrix and longer and finer TLCP fibrils (with high aspect ratio) with good interfacial adhesion between the two. The phase stabilisation of PPS blends with TLCPs can be improved by using compatibilisers. However, recent studies have shown that most of the compatibilised 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 compatibilisation must not cause the loss of fibrous morphology.

In this Chapter, the synthesis and characterisation of block copolymers of dicarboxyl terminated poly(phenylene sulphide) (DCTPPS) and poly(ethylene terephthalate-co-oxybenzoate) (PET/OB), a semi-aromatic thermotropic liquid crystalline
polymer, are discussed. The compatibilising efficiency of these block copolymers for PPS/PET-OB blend system was evaluated. Thermal analysis by differential scanning calorimetry (DSC) was employed to compare the melting and crystallisation behaviour of the uncompatibilised and compatibilised blends. The influence of compatibilisation on the phase behaviour were investigated with polarised light optical microscopy (PLOM) and scanning electron microscopy (SEM).

4.2 EXPERIMENTAL

4.2.1 Materials

PPS used was a commercial grade Ryton V-1 manufactured by Phillips Petroleum Company, U.S.A. The 4-chlorobenzoic acid, sodium sulphide and N-methyl pyrrolidinone procured from commercial source were used after purification. This material showed a melting point of 282 °C and the ΔH was 43.2 J/g. The aliphatic-aromatic thermotropic liquid crystalline polymer (TLCP) was synthesised and characterised as described in Section 2.2.1.

Dicarboxyl terminated poly(phenylene sulphide) (DCTPPS) of varying statistically average chain length (n = 6, 9 and 12) and poly(ethylene terephthalate-co-oxybenzoate) (PET-OB), an aliphatic-aromatic thermotropic liquid crystalline polymer (TLCP) with oxybenzoate content 30, 45 and 60 mole percent, were synthesised by established procedures. Block copolymers of DCTPPS and PET-OB (75/25, 50/50, 25/75 wt./wt.%) were synthesised by melt-transesterification at 300 °C under reduced nitrogen pressure for varied times in the range of 60, 90, 120 and 180 minutes. A 80 mL
Figure 4.1 Laboratory scale reaction set-up for the synthesis of PPS-PET/OB block copolymer.
glass lined electrically heated reactor depicted in Figure 4.1 was used for polymer synthesis. The reactor had two parts for charging/stirring the reactants and for nitrogen purging. It could be maintained isothermally at any temperature between ambient temperature and 400 °C. A provision for measuring the side product was made as shown in Figure 4.1.

4.2.2 Measurements

IR spectra of PPS-PET/OB block copolymers were recorded on a Perkin Elmer 16 PC FTIR spectrometer using potassium bromide discs. Thermal transitions in copolymers were estimated with a Mettler DSC 30 differential scanning calorimeter under nitrogen atmosphere using sample weight of 6.0±0.1 mg. Samples were analysed in the temperature range of 30-350 °C in both heating and cooling cycles at a rate of 20 °C/minute. Melting transition temperatures determined from the peak maxima and the enthalpy changes ($\Delta H$) corresponding to heating and cooling were calculated from the area under the peak of the DSC thermogram. Instrument calibrations made were as described in Section 2.2.3. The block copolymers were observed by a hot stage coupled Leitz microscope under crossed polarisers in the temperature range over which transitions were observed by DSC. X-ray diffraction study of copolymer samples were performed with Philips PW 1730 X-ray diffractometer using Cu Kα-radiation.
4.2.3 Preparation of Blends

Powders of the PET-OB and PPS were dried at 130 °C under vacuum for 48 h prior to mixing. The uncompatibilised and compatibilised PPS/PET-OB blends with a PET-OB content in the range 10, 20, 30, 50, 75 and 90 % (wt./wt.) were prepared in a 30 ml mixer attached to a Brabender Plasticorder at 300 °C and 100 rpm for 5 minutes under nitrogen atmosphere. The amount of compatibiliser fixed to 10 wt.% with respect to PET-OB concentration. Blank samples of both PPS and PET-OB were subjected to the same treatment.

4.2.4 Polarised light optical microscopy

The phase behaviour of compatibilised and uncompatibilised PPS/PET-OB blends was investigated by a hot stage coupled Leitz microscope under crossed polarisers by the procedure described in Section 2.2.4.

4.2.5 Scanning electron microscopy

Morphology of the blend surfaces were studied using a Leica Stereoscan 440 scanning electron microscope as discussed in Section 2.2.5.

4.3 RESULTS AND DISCUSSION

Dicarboxyl terminated poly(phenylene sulphide) (DCTPPS) of varied statistically average degree of polymerisation were synthesised by reacting 4-chloro benzoic acid, 1,4-dichloro benzene and sodium sulphide (Na₂S) in N-methyl-2-pyrrolidone (NMP) at 250 °C in a Parr reactor. The mole ratio of 4-chloro benzoic acid : 1,4-dichloro
benzene was varied to prepare dicarboxyl terminated PPS telechelics of varied chain length \((n=6, 9, 12)\) (Scheme 1). While the empirical formula of the telechelics are supported by the elemental analysis, the actual block length within the given system would indeed be a varied one, with an average corresponding to that dictated by the 4-chloro benzoic acid:1,4-dichloro benzene mole ratio. The melting transition occurs at 280 °C.

The PET/OB copolymers were synthesised from virgin fibre grade poly(ethylene terephthalate) (PET, intrinsic viscosity = 0.6 dL/g) and 4-acetoxy benzoic acid at 275 °C, first at atmospheric pressure and later at 0.5 Torr till the removal of final traces of acetic acid. Three random copolymers of PET:OB 70:30, 55:45 and 40:60 were synthesised. The intrinsic viscosity in 60/40 (v/v) phenol/1,1,2,2-tetrachloro ethane ranged from 0.33 for 70:30 to 0.65 dL/g for 40:60 PET:OB. The generalised structure of this random copolymer is presented in Scheme 1. The liquid crystalline transition of PET/OB is around 200 °C and glass transition temperature is around 70 °C.

The PPS-PET/OB block copolymers were synthesised by uncatalysed melt-transesterification between DCTPPS and PET/OB at 300 °C. The composition of DCTPPS, PET/OB as well as the weight ratio of DCTPPS and PET/OB were all varied to synthesise a rich variety of block copolymers. In addition, a definite weight ratio of PPS : PET/OB, from DCTPPS of a specific chain length and PET/OB of a particular composition, was allowed to react for varied times at 300 °C to alter the PET/OB sequence as well as its block length.
The PPS-PET/OB copolymers were suspended in 60:40 (v/v) phenol : 1,1,2,2-
tetrachloro ethane mixture under stirring for 24 hours at room temperature. PET/OB is
soluble in this solvent system at a concentration of 0.5 gm/dL. The insolubles were
filtered off and the filtrate was poured into a number of solvents like methanol in which
PET/OB is insoluble. No precipitation was observed indicating the absence of unreacted
PET/OB in the final product. This indicates of the formation of PPS-PET/OB copolymer.
IR spectra of PPS-PET/OB copolymer exhibited the characteristic aliphatic and aromatic
ester C=O stretching occurring at 1718 and 1738 cm\(^{-1}\) respectively and the
sulphur linkage (-S-) at 814 cm\(^{-1}\). A typical polarised light optical microscope photograph
at 300 °C of 50/50 wt./wt.% PPS-PET/OB block copolymer from 55/45 mole ratio
PET/OB is shown in Figure 4.2. The dark domains correspond to isotropic PPS rich
phase while an anisotropic PET/OB rich phase was observed in the form of a thread-like
texture. This observation further supports the formation of block copolymer comprising
PPS blocks and PET/OB blocks. Similar morphology has been observed for segmented
block copolymers with crystallisable hard segments and amorphous soft segments.
Wilkes and coworkers\(^{23}\) studied microstructure of various copolymers comprising
crystallisable hard segments and non-crystallisable soft segments and observed copolymer
exists as phase separated.

4.3.1 Effect of oxybenzoate (OB) content

The liquid crystallinity as well as liquid crystalline transition of PET/OB segment is
sensitive to the mole % of OB. At OB content ≤28 mole %, the mesogène-unit, carboxy-
1,4-phenylene oxy carboxy-1,4-phenylene carboxy, is diluted at the expense of increasing concentration of PET and the thermotropic character disappears. Above 50 mole % of OB the average mesogen length increases while the flexible spacer remains unchanged.

**Scheme 1**

**SCHEME 1**

![Scheme 1 Diagram](image)

DiCarboxyl terminated polyphenylene sulfide (DCTPPS)

\[
\text{HOOC} \left( \begin{array}{c}
\text{S} \\
\text{S}
\end{array} \right)_n \text{COOH}
\]

where \( n = 6, 9, 12 \)
Figure 4.2 Typical optical micrograph of 50/50 (wt./wt.%) PPS-PET/OB (containing 45 mole % OB) block copolymer.
Figure 4.3 DSC thermograms (second heating) showing the effect of oxybenzoate content (with respect to the PET content) on the thermal behaviour of block copolymer; (a) Heating scans; (b) Cooling scans.
and consists of dimethylene units arising from 1,2-ethanediol. Above 60 mole % of OB non-melting oxybenzoate blocks are formed and thermotropic character disappears. This study has been restricted to 30-60 mole % of OB.

The DSC thermograms corresponding to heating and cooling scans of typical 50:50 (wt./wt.%) PPS:PET/OB with 30, 45 and 60 mole % OB (with respect to PET) are shown in Figure 4.3(a) and (b). The thermal properties tabulated in Table 4.1.

The Tg, ascribable to PET/OB in PPS-PET/OB block copolymer, decreases marginally with increase in OB content. This decrease in glass transition temperature of PET/OB (Tg of PET is 80 °C) with OB mole % has been attributed to an enhanced randomisation which increases the segmental mobility within PET/OB. The nematic

<table>
<thead>
<tr>
<th>OB content. mole %</th>
<th>Tg °C</th>
<th>Tm °C</th>
<th>L.C. transition °C</th>
<th>ΔHm J/gm</th>
<th>Tc °C</th>
<th>ΔHc J/gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>71</td>
<td>272</td>
<td>194</td>
<td>23.4</td>
<td>198</td>
<td>22.5</td>
</tr>
<tr>
<td>45</td>
<td>69</td>
<td>268</td>
<td>192</td>
<td>25.3</td>
<td>179</td>
<td>19.8</td>
</tr>
<tr>
<td>60</td>
<td>65</td>
<td>271</td>
<td>191</td>
<td>27.1</td>
<td>159</td>
<td>17.3</td>
</tr>
</tbody>
</table>

Tg: glass transition temperature, Tm: melting transition temperature, L.C. transition: liquid crystalline transition, ΔHm: heat of fusion (normalised to weight fraction of DCTPPS), Tc: crystallisation temperature, ΔHc: heat of crystallisation
Figure 4.4 X-ray diffraction profiles of 50/50 wt./wt.% PPS-PET/OB block copolymer.
liquid crystalline transition ascribable to PET/OB occurs approximately at 193 °C. The endotherm at 270 °C in Figure 4.3(a) corresponds to melting of PPS. This points to a microphase separation between the two blocks.

The heat of crystallisation (obtained by integration of exothermic peak corresponding to the crystallisation of PPS segments in the copolymer) reduced with an increase in OB content as observed in Figure 4.3(b) and Table 4.1. When the OB content attains 60 mole %, the crystallisation peak of PPS segments disappears indicating that the crystallisation of PPS blocks is hindered perhaps due to an interaction between PPS blocks and PET/OB segments in PPS-PET/OB copolymer. The non-melting OB blocks decrease the mobility of crystallisable PPS chains and thereby inhibit their crystallisation. These findings are supported by x-ray powder diffraction studies shown in Figure 4.4. Here, the peak height and the area under the peak corresponding to the PPS blocks are seen to reduce with increase in oxybenzoate content indicating a reduction in the crystallinity of PPS segments.

4.3.2 Dependence of DCTPPS:PET/OB composition

The DSC thermograms corresponding to heating and cooling scans of PPS-PET/OB copolymers with 0, 25, 50 and 75 wt.% PET/OB content (OB content fixed at 45 mole %) are shown in Figure 4.5(a) and (b) and thermal properties are compiled in Table 4.2.
Figure 4.5  DSC thermograms (second heating) showing the effect of PET-OB content on the thermal behaviour of 50/50 wt./wt.% PPS-PET/OB block copolymer: (a) Heating scans; (b) Cooling scans.
Table 4.2: Effect of TLCP content on the thermal behaviour of PPS blocks in copolymer

<table>
<thead>
<tr>
<th>TLCP content wt. %</th>
<th>Tg °C</th>
<th>Tm °C</th>
<th>L.C. transition °C</th>
<th>ΔHm J/gm</th>
<th>Tc °C</th>
<th>ΔHc J/gm</th>
<th>αc,PPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>68</td>
<td>279</td>
<td>-</td>
<td>35.6</td>
<td>222</td>
<td>33.1</td>
<td>0.24</td>
</tr>
<tr>
<td>25</td>
<td>72</td>
<td>272</td>
<td>192</td>
<td>24.4</td>
<td>201</td>
<td>22.4</td>
<td>0.16</td>
</tr>
<tr>
<td>50</td>
<td>71</td>
<td>267</td>
<td>191</td>
<td>22.1</td>
<td>198</td>
<td>17.4</td>
<td>0.15</td>
</tr>
<tr>
<td>75</td>
<td>69</td>
<td>265</td>
<td>192</td>
<td>18.7</td>
<td>193</td>
<td>15.7</td>
<td>0.12</td>
</tr>
</tbody>
</table>


The copolymerisation alters the melting behaviour of both PPS and PET/OB in PPS-PET/OB block copolymer. The intensity of liquid crystalline transition peak is enhanced at higher PET/OB concentration while the melting transition temperature and the corresponding enthalpy values of PPS blocks (normalised to the weight fraction of PPS) are depressed. The existence of distinct endothermic peaks corresponding to the PPS and PET/OB in the DSC thermograms [Figure 4.5 (a)] points to a microphase separation between the PPS and PET/OB in the PPS-PET/OB block copolymer. This observation is further supported by optical microscopy. The intensity of crystal-nematic
transition peak of copolymer reduces with PPS content, as shown in Figure 4.5 (a) and Table 4.2, as a direct consequence of loss of rigid and axially symmetrical configuration (mesogen) of the copolymer. No glass transition temperature \( (T_g) \) corresponding to DCTPPS and PPS blocks in the PPS-PET/OB block copolymer were observable. However, the \( T_g \) of PET/OB was found to increase on copolymerisation with DCTPPS perhaps due to an antiplasticising effect of crystallisable PPS blocks on the amorphous phase of PET/OB as observed in block copolymers of PET/OB with polysulphones.\(^{24}\)

The degree of crystallinity relative to PPS \((\alpha_{c,pps})\) segments in PPS-PET/OB was estimated from the heat of fusion \((\Delta H)\) determined by DSC according to the following equation:

\[
\alpha_{c,pps} = \frac{\Delta H}{\Delta H^m}
\]

where \( \Delta H^m \) is the heat of fusion of 100\% crystalline PPS, \( \Delta H^m = 146 \text{ J/g} \).\(^{25}\) \( \alpha_{c,pps} \), the degree of crystallinity of PPS segment in PPS-PET/OB copolymer with 25, 50, 75 wt.% PET/OB were 0.16, 0.15, 0.12 while that of the pure DCTPPS was 0.24 (Table 4.2).

The crystallisation temperature \((T_c)\) of PPS segments in PPS-PET/OB copolymer was found to decrease with an increase in PET/OB content as shown in Table 4.2. The PPS segment in PPS-PET/OB copolymer with 25 wt. \% PET/OB content crystallises at 201 °C while the DCTPPS crystallises at 222 °C. On copolymerisation, the crystallisability of PPS segments are depressed, probably by the inhibition of the regular chain packing desirable for crystallisation by the introduction of PET/OB through extensive interchange reactions. Heitz and coworkers\(^{13-15}\) discussed similar reduction in
the crystallisability of PPS blocks in block copolymers of PPS with polyamides polyesters. The PET/OB segments act as diluent for the crystalline PPS blocks.

4.3.3 Effect of reaction time

The DSC thermograms corresponding to heating and cooling scans of copolymers (50 wt.% PET/OB composed of 45 mole % OB) synthesised by varying reaction times, 60, 90, 120 and 180 minutes are shown in Figure 4.6(a) and (b) and the thermal properties are presented in Table 4.3. The longer reaction times would lead to a more randomised PET/OB sequences due to transesterification reactions.

At longer reaction times (120 or 180 minutes), the liquid crystalline transition of the PET OB segment in copolymer is seen to disappear. This could be explained as follows: At the beginning of reaction (0-15 minutes) acetic acid distills out indicating that DCTPFS preferably reacts with the acetoxy end groups of PET/OB. This leads to the formation of an AB type block copolymer since starting PET/OB is monofunctional in acetoxy end groups. Therefore, PET/OB block retains its initial sequence and hence its liquid crystalline properties. At longer reaction times, interchange reactions occur between terephthaloyl and DCTPPS units which slice PET/OB block and incorporate PPS segments. This slicing lowers the axial ratio and the chain no longer possesses the structure needed to exhibit liquid crystallinity.
Figure 4.6  DSC thermograms (second heating) showing the effect reaction time content on the thermal behaviour of 50/50 wt./wt.% PPS-PET/OB block copolymer. (a) Heating scans; (b) Cooling scans.
Table 4.3: Effect of reaction time on the thermal behaviour of copolyester

<table>
<thead>
<tr>
<th>Reaction time, minutes</th>
<th>Tg</th>
<th>Tm</th>
<th>L.C. transition</th>
<th>ΔHm</th>
<th>Tc</th>
<th>ΔHc</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>71</td>
<td>279</td>
<td>193</td>
<td>24.3</td>
<td>202</td>
<td>23.1</td>
</tr>
<tr>
<td>90</td>
<td>71</td>
<td>274</td>
<td>192</td>
<td>21.6</td>
<td>195</td>
<td>21.4</td>
</tr>
<tr>
<td>120</td>
<td>67</td>
<td>270</td>
<td>189</td>
<td>18.8</td>
<td>185</td>
<td>18.7</td>
</tr>
<tr>
<td>180</td>
<td>69</td>
<td>268</td>
<td>-</td>
<td>15.4</td>
<td>178</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Tg: glass transition temperature; Tm: melting transition temperature; L.C. transition: liquid crystalline transition; ΔHm: heat of fusion (normalised to weight fraction of DCTPPS); Tc: crystallisation temperature; ΔHc: heat of crystallisation.

The thermograms corresponding to the cooling scan of the copolymers are presented in Figure 4.6(b). The crystallisation temperature (Tc) and heat of crystallisation (ΔH) are seen to decrease with increasing transesterification time indicating extensive interchange reactions resulting in a random copolymer.

In conclusion, the liquid crystalline properties and the crystallisability of copolymer are greatly influenced by the extent of interchange reactions, the mole percent of oxybenzoate with respect to the PET, the PPS:PET/OB weight ratio and reaction time.
4.4 Comparison of Uncompatibilised and compatibilised PPS/PET-OB Blends

Compatibilisation can interact in complex ways to influence the final blend properties: (i) Reduce the interfacial tension in the melt causing an emulsification effect and resulting in an extremely fine dispersion of one phase in another; (ii) Increase the adhesion at phase boundaries giving improved stress transfer and (iii) Stabilise the dispersed phase against growth during annealing, modifying the phase boundary interface. Thus, it will be interesting to investigate the effect of compatibilisation of block copolymer comprising PPS blocks and PET-OB blocks on the thermal behaviour and phase morphology of the PPS/PET-OB blends.

4.4.1 Thermal properties

4.4.2 Melting behaviour

DSC heating thermograms of pure PPS, PET-OB, uncompatibilised PPS/PET-OB and compatibilised PPS/PET-OB blends were shown in Figure 4.7. In compatibilised blends, the endothermic peaks corresponding to the melting transition of PET-OB are absent whereas in melt-mixed blends the intensity of melting transition peak of PET-OB increases with its concentration. Phase separations in blends can be identified in DSC thermograms by the absence of any change in the glass transition temperature, melting transition temperature or enthalpy of transitions from those corresponding to the original polymer components. The absence of the endothermic peak corresponding to melting transition of PET-OB in the compatibilised PPS/PET-OB blends in Figure 4.7 could be due to the absence of phase separation. The degree of
Figure 4.7  DSC thermograms (second heating) of uncompatibilised and compatibilised PPS/PET-OB blends at the heating rate 20 °C/minute.
Table. 4.4. Comparison of thermal data of PPS phase in uncompatibilised and compatibilised PPS/PET-OB Blends

<table>
<thead>
<tr>
<th>PPS/PET-OB</th>
<th>Uncompatibilised blends</th>
<th>Compatibilised blends (10% w.r.t. PET-OB content)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% (wt./wt.)</td>
<td>Tm (°C)</td>
<td>Tc (°C)</td>
</tr>
<tr>
<td>100/0</td>
<td>282</td>
<td>237</td>
</tr>
<tr>
<td>90/10</td>
<td>280</td>
<td>252</td>
</tr>
<tr>
<td>80/20</td>
<td>279</td>
<td>251</td>
</tr>
<tr>
<td>70/30</td>
<td>281</td>
<td>252</td>
</tr>
<tr>
<td>50/50</td>
<td>280</td>
<td>246</td>
</tr>
<tr>
<td>25/75</td>
<td>278</td>
<td>244</td>
</tr>
<tr>
<td>10/90</td>
<td>277</td>
<td>243</td>
</tr>
</tbody>
</table>

T_m: Melting peak temperature.  
T_c: Crystallisation peak temperature.  
ΔH_f: Heat of Fusion.  
α: Degree of Crystallinity

interaction between two polymers is described by ΔG, comprising of ΔH and ΔS contributions. For a blend to be a single phase, ΔG<0. Since ΔS is negligible for polymers, ΔH dominates in the free energy of mixing in polymer blends. The introduction of interacting groups by chemical modification of a polymer or by
copolymoerisation can result in a negative contribution to the enthalpy of mixing. The enthalpy of mixing ($\Delta H_{\text{mixing}}$) of stiff rigid-rod like liquid crystalline segments with a flexible-coil polymer is mostly positive. From Table 4.4, it is very clear that the enthalpy of mixing ($\Delta H_{\text{mixing}}$) of PPS/PET-OB blend decreases. This points to a favourable interaction between PPS and PET-OB chains on compatibilisation.

4.4.3 Crystallisation behaviour

The crystallisation exotherms of pure PPS, PET-OB, uncompatibilised and compatibilised PPS/PET-OB blends were shown in Figure 4.8. The crystallisation temperatures ($T_c$), presented in Table 4.4, were those corresponding to the exothermic peak maxima and are corrected as described by Elder and Wlochowicz. In compatibilised blends, the exothermic peaks corresponding to the PET-OB crystallisation are absent whereas in uncompatibilised blends the peak intensity of crystallisation exotherm of PET-OB increases with its concentration. Again, in compatibilised blends the crystallisation temperature ($T_c$) and hence the rate of crystallisation of PPS phase passes through a maximum corresponding to 30 mole % PET-OB. On the other hand, $T_c$ and hence the rate of crystallisation of PPS phase in compatibilised blends slightly decreases with increase in PET-OB content as shown in Table 4.4. The dispersed PET-OB phase in compatibilised blends crystallises to form microphase not detectable by DSC where as in uncompatibilised blends the PPS and PET-OB crystallise into separate phases as shown in the DSC exotherm presented in Figure 4.8. The PET-OB phase accelerates
Figure 4.8  DSC exotherms (second cooling) of uncompatibilised and compatibilised PPS/PET-OB blends at the heating rate 20 °C/minute.
the crystallisation of PPS phase in uncompatibilised blends whereas it retards the rate of crystallisation of PPS phase in compatibilised blends. This may be due to the interference of copolymer in the crystallisation of PPS. Similar results of decrease of rate of crystallisation of blends on compatibilisation was reported in earlier studies. Chang and coworkers investigated the effect of reactive compatibilisation of NORYL [poly(phenylene oxide)/polystyrene]/Vectra A950 using styrene-glycidyl methacrylate (SG) as reactive component. They observed that the crystallisation rate of blend components were decreased by in situ formed block copolymer comprising of SG and Vectra A950.

4.4.4 Degree of Crystallinity

The degree of crystallinity, \( \alpha \), of the PPS phase in both uncompatibilised and compatibilised blends plotted against the PET-OB content were presented in Table 4.4. The degree of crystallinity, \( \alpha \), was calculated from the enthalpy of fusion normalised to the PPS content, assuming that the contribution of the PET-OB phase is negligible. A value of 146.2 J/g was estimated by Maemura et al. for enthalpy of fusion of 100% crystalline PPS. For uncompatibilised blends, the degree of crystallinity of PPS remains almost constant up to 30 wt.% PET-OB and then reduces with further increase in PET-OB content. In compatibilised blends, the degree of crystallinity steadily decreases with PET-OB concentration. This observation is consistent with previous reports of
crystallinities of compatibilised blends. Chang and coworkers investigated ethyl-glycidyl methacrylate copolymer (EGMA) as reactive compatibiliser for immiscible blends of polypropylene (PP) and Vectra A900 and observed that the crystallinity of PP phase in compatibilised blends was lower than that of the corresponding incompatibilised blends due to interference in the PP crystallisation by the in situ formed EGMA-g-Vectra A900 copolymers.

This marked difference in the degree of crystallinity is due the improved interfacial adhesion in compatibilised blends as compared to the uncompatibilised blends of similar composition. The addition of a second polymer to a semicrystalline polymer acts as a diluent, which could either decrease crystallinity by decreasing concentration and number of nuclei, or increases crystallinity by enhancing nucleation or increasing the chain mobility. Degree of crystallinity, $\alpha$, is known to be a measure of degree of phase mixing. The degree of crystallinity is known to decrease on compatibilisation of incompatible blends. Thus, the degree of crystallinity of PPS phase depends on the extent of phase separation between the PPS phase and PET-OB phase.

4.4.5 Morphology

4.4.5.1 Polarised light optical microscopy

The optical micrographs under cross polariser of uncompatibilised and compatibilised PPS/PET-OB blends (in molten state at 320 °C) are presented in Figure 4.9 (a)-(d). At this temperature, the PET-OB domains alone are observable under cross
Figure 4.9 Optical micrographs (same magnification; 100 X) of the phase behaviour and morphology of uncompatibilised and compatibilised PPS/PET-OB [% wt./wt.] blends of differing compositions at 320 °C. (a) Pure PPS; (b) uncompatibilised 70/30; (d) uncompatibilised 50/50; (c) compatibilised 70/30 and (e) compatibilised 50/50 blends.
polarisers as these are in the anisotropic nematic state. The liquid-liquid phase separation
is observable in both uncompatibilised and compatibilised PPS/PET-OB blends. A
comparison can be made between uncompatibilised and compatibilised blends under
identical conditions by observing the domain size of PET-OB in Figure 4.9 (a) and (b).
In compatibilised blends [Figure 4.9 (a)], the PET-OB domains are relatively smaller and
are more uniformly dispersed within PPS matrix whereas in the uncompatibilised blends
[Figure 4.9 (b)] a wide size distribution is noted due to distinctive phase separation and
an aggregation of the PET-OB phase.

4.4.5.2 Scanning electron microscopy

The SEM micrographs uncompatibilised and compatibilised PPS/PET-OB blends
are shown in Figures 10 (a) and (b). The uncompatibilised blends show macrophase-
separated-morphology as seen from Figures 10 (a) indicating poor phase mixing whereas
in the compatibilised blends of the same composition [Figures 10 (b)] disperse type
morphology was observed. The more uniform and continuous morphology of
compatibilised blends is a consequence of intimate dispersion of PET-OB phase within
the PPS matrix.
Figure 4.10 SEM micrographs showing morphology of freeze-fractured samples of uncompatibilised [(a) 90/10, (c) 70/30 & (e) 50/50 % (wt./wt.)] and compatibilised [(b) 90/10, (d) 70/30 & (f) 50/50 % (wt./wt.)] PPS/PET-OB blends
4.5 CONCLUSION

The thermotropic character and the crystallisability of the block copolymer, comprising poly(phenylene sulphide) and poly(ethylene terephthalate-oxy benzoate) blocks, were greatly influenced by the extent of interchange reactions, which in turn depends on the mole percent of oxybenzoate (with respect to the PET content), PET/OB content and reaction time.

The compatibilising efficiency of the block copolymer for poly (phenylene sulphide) and poly(ethylene terephthalate-co-oxybenzoate) (PET-OB), an aliphatic-aromatic thermotropic liquid crystalline polymer (TLCP), blend system was tested. Thermal properties, phase behaviour and morphology of uncompatibilised as well as compatibilised blends of PPS and PET-OB were compared using differential scanning calorimetry, polarised light optical microscopy and scanning electron microscopy. From these observations, we concluded: (i) PPS-PET/OB block copolymer is a suitable compatibiliser for PPS-PET/OB blend system; (ii) homogenisation of morphology occurs on compatibilisation; (iii) the PET-OB phase accelerates crystallisation of PPS phase in uncompatibilised blends whereas it retards crystallisation of PPS phase in compatibilised blends and (iv) the effect of PET-OB phase on crystallinity of PPS varied with extent of phase separation between the two components.
4.6 REFERENCES AND NOTES


