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In situ compatibilisation of poly(phenylene sulphide)/wholly aromatic thermotropic liquid crystalline polymer blends by reactive extrusion: morphology, thermal and mechanical properties

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Abstract

Compatibilisation of immiscible poly(phenylene sulphide) (PPS)/wholly aromatic thermotropic liquid crystalline polymer (TLCP) blends is reported. In situ compatibilised PPS/TLCP blends were prepared in a twin-screw extruder by reactive blending of PPS and TLCP in presence of dicarboxyl-terminated poly(phenylene sulphide) (DCTPPS). The block copolymer formed during reactive blending, by transesterification reaction between carboxyl groups of DCTPPS and ester linkages of TLCP, is tested for its role as the compatibiliser by studying the morphology, mechanical and thermal properties of the compatibilised PPS/TLCP blends over a wide range of composition. The heat of melting (ΔH_m), crystallisation temperature (T_c) and heat of crystallisation (ΔH_c) of PPS phase are observed to decrease marginally as a result of improvement in the interfacial adhesion between the two phases on compatibilisation. The tensile properties and impact strength of PPS/TLCP blends are seen to improved on compatibilisation. This observation is further supported by morphological features of the blend.

Keywords: Polymer blends; Poly(phenylene sulphide); Thermotropic liquid crystalline polymer

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1. Introduction

Blending conventional thermoplastic polymers with thermotropic liquid crystalline polymers (TLCP) can lead to easier processing and in situ matrix reinforcement [1–3]. Poly(phenylene sulphide) (PPS) and TLCPs are high strength/high temperature speciality polymers that find applications in the aerospace, automotive, marine, electrical and electronic industries. Specific improvement in properties of PPS on blending with wholly aromatic [4–6] and semi-aromatic [7–9] thermotropic liquid crystalline polymers have been reported in the very recent past. Most blends of thermoplastics and TLCPs show poor interfacial adhesion resulting in inferior mechanical properties. In an immiscible polymer blend the desired strong interfacial adhesion and stabilised morphology often requires the presence of appropriate interfacial agents.

Recently, increasing efforts have been directed towards in situ compatibilisation of immiscible polymer blends by reactive extrusion [10–15]. Instead of synthesising the compatibilisers in a separate step, these are created during extrusion through interfacial reactions between the respective functionalised polymers. From a technological point of view, a one step reactive extrusion process is easier to control for cost-effective generation of compatible blends from initially immiscible polymers [15].

Here, we report for the first time the in situ compatibilisation of PPS and Vectra A950, a wholly aromatic TLCP by reactive extrusion in presence of dicarboxyl-terminated PPS (DCTPPS). The carboxyl end groups of PPS can undergo transesterification reaction with ester groups in the Vectra A950 in the molten state leading to the in situ formation of block copolymer comprising PPS blocks and Vectra A950 blocks at the interface between the PPS/Vectra A950 blends during extrusion. The chemically identical PPS block is miscible with PPS matrix while the Vectra A950 block is compatible with Vectra A950 component. The effect of in situ compatibilisation on PPS/TLCP blends was investigated by studying morphology, mechanical and thermal properties.

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2. Experimental

2.1. Materials

Poly(phenylene sulphide) (PPS) (unfilled grade Fortron 0220 A1) and Vectra A950 (unfilled grade), a wholly aromatic thermotropic liquid crystalline polymer [copolyester of 25 mol% of 2-hydroxy-6-naphthoic acid (HNA) and 75 mol% of 4-hydroxy benzoic acid (HBA)] were supplied by Hoechst-Celanese. Dicarboxyl-terminated poly(phenylene sulphide) (DCTPPS) of varying statistically average block lengths ($n = 6, 9, 12$) were prepared by the procedure described previously [9,16].

2.2. Methods

Pellets of PPS and Vectra A950 were manually mixed in the ratio 95/5, 90/10, 75/25, 50/50 (w/w) and dried in an air oven drier at 150°C. DCTPPS was taken as 10% (w/w) with respect to Vectra A950 concentration.

2.3. Reactive blending

The melt blending of the PPS, Vectra A950 and DCTPPS was done with Berstroff co-rotating twin-screw extruder (E0.0004/91) by the procedure described previously [16].

2.4. Processing

2.4.1. Injection moulding

The blends as well as respective polymers were injection moulded into test specimens after drying in a air oven at 150°C for 8 h. Injection moulding was carried out in an Arburg all rounder 220-90-350 injection moulding machine. The pure polymers were processed under conditions recommended by the manufacturers. The conditions chosen for the processing of blends was a suitable compromise between those used for the respective homopolymers (Table 1). The moulded specimens consisted of standard test bars for tensile and impact tests.

2.5. Testing and analysis

2.5.1. Thermal properties

Thermal properties of extruded PPS/Vectra A950 blend samples were measured by Mettler TA 4000 series differential scanning calorimeter. 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 crystallisation tests, as described by Elder and Wlochowics [17]. The sample masses were kept constant (6.0 ± 0.1 mg) throughout the analysis so as to minimise the effect of mass change on the enthalpy change. The heats of fusion and crystallisation were determined from the peak area in the d.s.c. thermogram. The melting transition temperature (T_m) and crystallisation temperature (T_c) were calculated from the peak maxima of the thermograms in the second heating and cooling scan of samples, respectively.

2.5.2. Tensile properties

Tensile properties were measured according to ASTM D-638 using an Instron testing machine (4204). The strain rate was 5 mm/min for tensile strength and elongation measurements and 1 mm/min for determining the elastic modulus. The dimensions of the test bars were 15.4 × 1.2 × 0.3 cm.

2.5.3. Impact properties

The impact strength of notched and unnotched test specimens were determined according to ASTM D-253 C using a CEAST impact testing machine. The dimensions of the test specimens were 5.0 × 0.6 × 0.3 cm. For PPS and its blends a pendulum of 40 kpcm was used.

2.6. Morphology

The morphology of the fractured surfaces of the extruded and injection-moulded tensile specimen were coated with a 15 nm gold layer and examined by Leica Stereoscan 440 scanning electron microscope.

3. Results and discussion

3.1. In situ compatibilisation

Our approach is to extrude the PPS and Vectra A950 in the presence of dicarboxyl-terminated poly(phenylene sulphide) (DCTPPS) proportional to Vectra A950 concentration using a twin-screw extruder. The carboxyl end groups of DCTPPS can undergo transesterification reaction with ester groups in the Vectra A950 in the molten state leading to the in situ formation of block copolymer comprising PPS blocks and Vectra A950 blocks at the interface between the PPS/Vectra A950 blends during extrusion. Similar results of transesterification reaction between thermotropic polyesters and various reactive components have been reported [13,18,19]. The block copolymer so formed during reactive

Table 1
Processing conditions of PPS, Vectra A950 and PPS/Vectra A950 blends

	1st zone	2nd zone	3rd zone	4th zone	5th zone	Mould temp.
PPS	305	310	315	315	315	130
PPS/Vectra A950	310	310	315	315	315	130
Vectra A950	280	285	290	295	295	130

Table 2
Thermal properties of uncompatibilised and compatibilised PPS/Vectra A950 blends

PPS/TLCP/DCTPPS (%, w/w)	Uncompatibilised						Compatibilised [10% (w/w) of TLCP content]					
	T_m (°C)	ΔH_m (J/m)	T_c (°C)	ΔH_c (J/m)	$T_m - T_c$ (°C)	α	T_m (°C)	ΔH_m (J/m)	T_c (°C)	ΔH_c (J/m)	$T_m - T_c$ (°C)	α
100/0	279	36.0	227	41.4	52	0.25	—	—	—	—	—	—
90/10	279	33.2	232	36.0	47	0.23	280	26.1	229	34.0	51	0.18
75/25	280	24.8	238	29.7	42	0.17	279	17.4	232	23.4	47	0.12
50/50	279	20.3	242	25.8	37	0.14	280	16.1	240	23.0	40	0.11
0/0/100	282	1.8	238	1.5	—	—	—	—	—	—	—	—

T_m, melting peak temperature; $T_m - T_c = \Delta T$, degree of super cooling; ΔH_m, heat of fusion; T_c, crystallization temperature; ΔH_c, heat of crystallization; α, degree of crystallinity

blending could play the role of compatibiliser by its preferential location at the interface, with consistent blocks being diffused into the corresponding blend phase of the same chemical structure. This will promote the miscibility by reducing the interfacial tension between the PPS and Vectra A950 phases. It is interesting to study the compatibilising efficiency of this block copolymer by investigating morphology, mechanical and thermal properties of the PPS/Vectra A950 blends over a wide range of composition.

3.2. Thermal properties

3.2.1. Melting behaviour

Fig. 1 show typical d.s.c. curves corresponding to second heating scans of PPS, Vectra A950, uncompatibilised and compatibilised 75/25% (w/w) PPS/TLCP blends containing 10% (w/w) DCTPPS with respect to Vectra A950 concentration. Thermal properties are tabulated in Table 2. From Table 2 it is very clear that the heat of melting (ΔH_m of neat PPS = 36.0 J/m, uncompatibilised 50/50% (w/w) PPS/Vectra A950 blend = 20.3 J/m and compatibilised 50/50% (w/w) PPS/Vectra A950 blend = 16.1 J/m) of the blends in all composition decreases on reactive compatibilisation. The introduction of interacting groups by chemical modification of a polymer or by copolymerisation can result in a negative contribution to the enthalpy of mixing. A decrease in the enthalpy of PPS/Vectra A950 blend (ΔH_{mixing}) on reactive compatibilisation indicates the presence of favourable interactions between PPS and Vectra A950.

Usually the melting transition and glass transition of blend components undergo an inward migration on compatibilisation as a direct consequence of mutual dissolution of the two components. The glass transition temperatures (T_g) of the PPS phase and Vectra A950 phase in the PPS/Vectra A950 blends are not distinguishable due to the close proximity of T_g of both components (~100°C). The melting endotherms of the two polymers also overlap, with the melting point of Vectra A950 being in the range of 282°C and the PPS being around 279°C. Therefore, compatibilisation does not affect the glass transition and melting transition temperature of the respective blend components in PPS/Vectra A950.

3.2.2. Crystallisation behaviour

Fig. 2 shows typical d.s.c. thermograms corresponding to second cooling scans of PPS, Vectra A950 and 75/25% (w/w) PPS/Vectra A950 blends compatibilised with 10 wt%

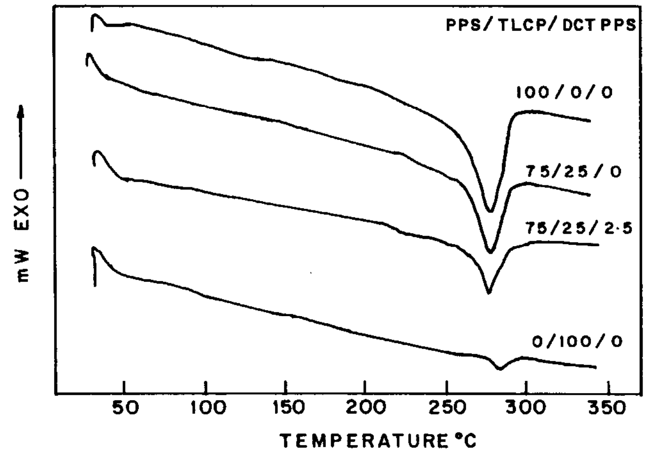


Fig. 1. D.s.c. thermograms corresponding to second heating scans of PPS, Vectra A950, uncompatibilised 75/25% (w/w) PPS/Vectra A950 blend and compatibilised 75/25% (w/w) PPS/Vectra A950 blend containing 10 wt% DCTPPS with respect to Vectra A950 concentration.

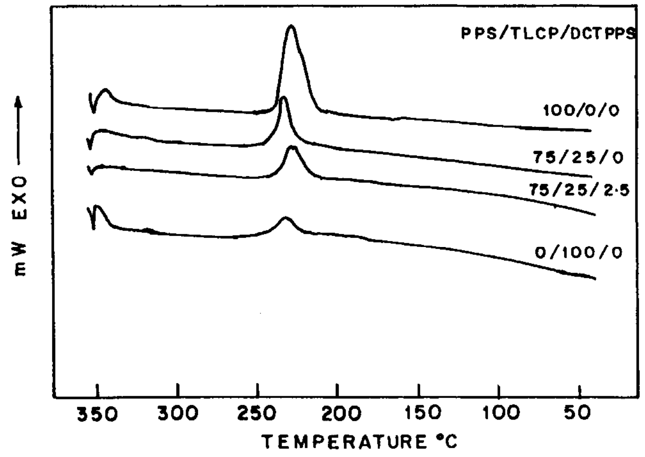


Fig. 2. D.s.c. thermograms corresponding to second cooling scans of PPS, Vectra A950, uncompatibilised 75/25% (w/w) PPS/Vectra A950 blend and compatibilised 75/25% (w/w) PPS/Vectra A950 blend containing 10 wt% DCTPPS with respect to Vectra A950 concentration.

DCTPPS. In Fig. 2 only one crystallisation exotherm could be seen in the cooling traces of blends on account of the low crystallisation enthalpy of Vectra A950. The crystallisation temperature (T_c) and heat of crystallisation (ΔH_c) decrease on compatibilisation as seen in Table 2. The crystallisation temperatures (T_c) are those corresponding to the exothermic peak maxima, corrected as described by Elder and Wlochowicz [17].

The crystallisation temperature (T_c) and heat of crystallisation (ΔH_c) of PPS phase decreases on compatibilisation, indicating that it retards the PPS crystallisation process. The crystallisation peak corresponds to the PPS phase in the compatibilised 75/25% (w/w) PPS/Vectra A950 blend containing 10 wt% DCTPPS (with respect to Vectra A950 content) was at 232°C while in the uncompatibilised blend it was at 238°C. In the compatibilised blend, the temperature range over which PPS crystallises also broadened and its intensity decreased dramatically. This indicates that the compatibilisation process marginally slows down the crystallisation rate of the PPS phase. The crystallisation rate of PPS was depressed in the compatibilised blends as seen from an increase in the degree of supercooling ($T_m - T_c = \Delta T$). Such a decrease in the crystallisation temperature and increase in the supercooling of PPS phase are known to arise on compatibilisation of incompatible blends [19–32].

3.2.3. Degree of crystallinity

The degree of crystallinity (α) of the PPS phase in both uncompatibilised and compatibilised blends are tabulated in Table 2. The ΔH_m of Vectra A950 recorded is rather small (1.8 J/m) as compared to that of PPS (36.0 J/m). Therefore, the degree of crystallinity (α) has been calculated from the enthalpy of fusion normalised to the PPS content assuming that the contribution of the Vectra A950 phase is negligible [20]. A value of 146.2 J/g was estimated by Maemura et al. [21] for enthalpy of fusion of 100% crystalline PPS. The heats of melting (ΔH_m) and hence the degree of crystallinity (α) of the compatibilised blends are decreased significantly as compared to a uncompatibilised blend of similar composition as shown in Table 2. The formation and presence of PPS-Vectra A950 block copolymer is expected to alter the PPS crystallisation, especially in the vicinity of the interface. This observation is in accordance with previous studies of crystallinity of compatibilised blends [9,22–29]. Chang and co-workers [18,19,26] observed a reduction in the degree of crystallinity of polypropylene (PP) in PP/Vectra A950 blends in presence of ethylene–glycidyl methacrylate copolymer (EGMA). They concluded that the EGMA undergoes interchange reactions with Vectra A950 resulting in EGMA–g-Vectra A950 block copolymer which interferes the crystallisation of PP. Ahn et al. [22,32] reported a reduction in the crystallinity of polyacrylate (Par)/polyamide-6 (PA-6) blends in presence of Par-b–PA-6 copolymer. An effective compatibiliser increases the mutual solubilities of the various components, which causes a reduction in the crystallinity of thermoplastic matrix in the thermoplastics (TP)/TLCP blends. The d.s.c. results led us to conclude that the increased interactions between the phases modified the crystallisation behaviour of the blend components.

3.3. Mechanical properties

There are conflicting reports on the mechanical properties and morphological features of PPS/Vectra A950 blend systems. Previous studies indicate that the mechanical properties of PPS does not show great improvement on blending with Vectra A950. Ramanathan et al. [33] observed that the chemical reaction between the PPS and Vectra A950 during blending results in porous structure which leads to poor mechanical properties. We studied the same blend system in wide range of compositions and have not observed any chemical reaction between the PPS and Vectra A950. We observed a fibril morphology and mechanical reinforcement for PPS/Vectra A950 blends. The tensile strength of neat PPS (82 MPa) improves on blending with Vectra A950 (PPS containing 25 wt% Vectra A950 shows 87 MPa) as revealed in the Table 3. But this improvement in mechanical properties is only marginal on account of phase separation and lack of adhesion between the blend components. This observation agrees with that of Heino and Seppala [2,3] who studied the same blend and concluded that there is no chemical reaction between the PPS and Vectra A950.

Tensile bars of uncompatibilised PPS/Vectra A950 blends show brittle fracture, whereas compatibilised blends show ductile fracture. This is presumed to be due to the crack preferentially occurring under stress at defects such as

Table 3
Mechanical properties of PPS/TLCP blends

PPS/TLCP/DCTPPS (%, w/w)	Uncompatibilised[a]			Compatibilised [10% (w/w) of TLCP content]		
	Toughness (J/m)	Tensile modulus (MPa)	Break Stress (MPa)	Toughness (J/m)	Tensile modulus (MPa)	Break stress (MPA)
100/0	1058	3697	82	—	—	—
90/10	—	3987	84	970.3	3649	89
75/25	—	4803	87	810.1	6632	98
50/50	—	5584	96	798.2	9345	108
0/100	572	6447	115	—	—	—

[a] Toughness of uncompatibilized blend could not be measured

Table 4
Impact strength of PPS/TLCP Blends

PPS/TLCP/DCTPPS (wt%)	Uncompatibilised		Compatibilised [10% (w/w) of TLCP content]	
	Unnotched (kJ/m^2)	Notched (kJ/m^2)	Unnotched (kJ/m^2)	Notched (kJ/m^2)
100/0	27.0	—	—	—
90/10	22.1	18.4	36.8	29.6
75/25	24.0	13.6	41.3	31.1
50/50	21.0	16.4	46.4	33.2
0/100	80.0	—	—	—

voids exists at the interface between the PPS and Vectra A950 phases in uncompatibilised PPS/Vectra A950 blends. The compatibilised blends show ductile fracture with improved toughness (elongation at break) as a direct consequence of miscibility and improved stress transfer between the two phases. Tensile properties and impact strength are improved on compatibilisation of PPS/Vectra A950 blends. The tensile strength of the uncompatibilised 75/25% (w/w) PPS/Vectra A950 blend is 87 MPa, whereas that of compatibilised 75/25% (w/w) containing 10% DCTPPS (with respect to Vectra A950) is 98 MPa as shown in Table 3. In uncompatibilised blends, void exists between the interfaces causing poor stress transfer between the phases which results in the inferior mechanical properties. The enhancement in the tensile modulus of the in situ compatibilised PPS/Vectra A950 blends points to an improved interfacial adhesion.

The impact strength of the blend is greatly dependent upon the dissipation capacity of the impact energy through

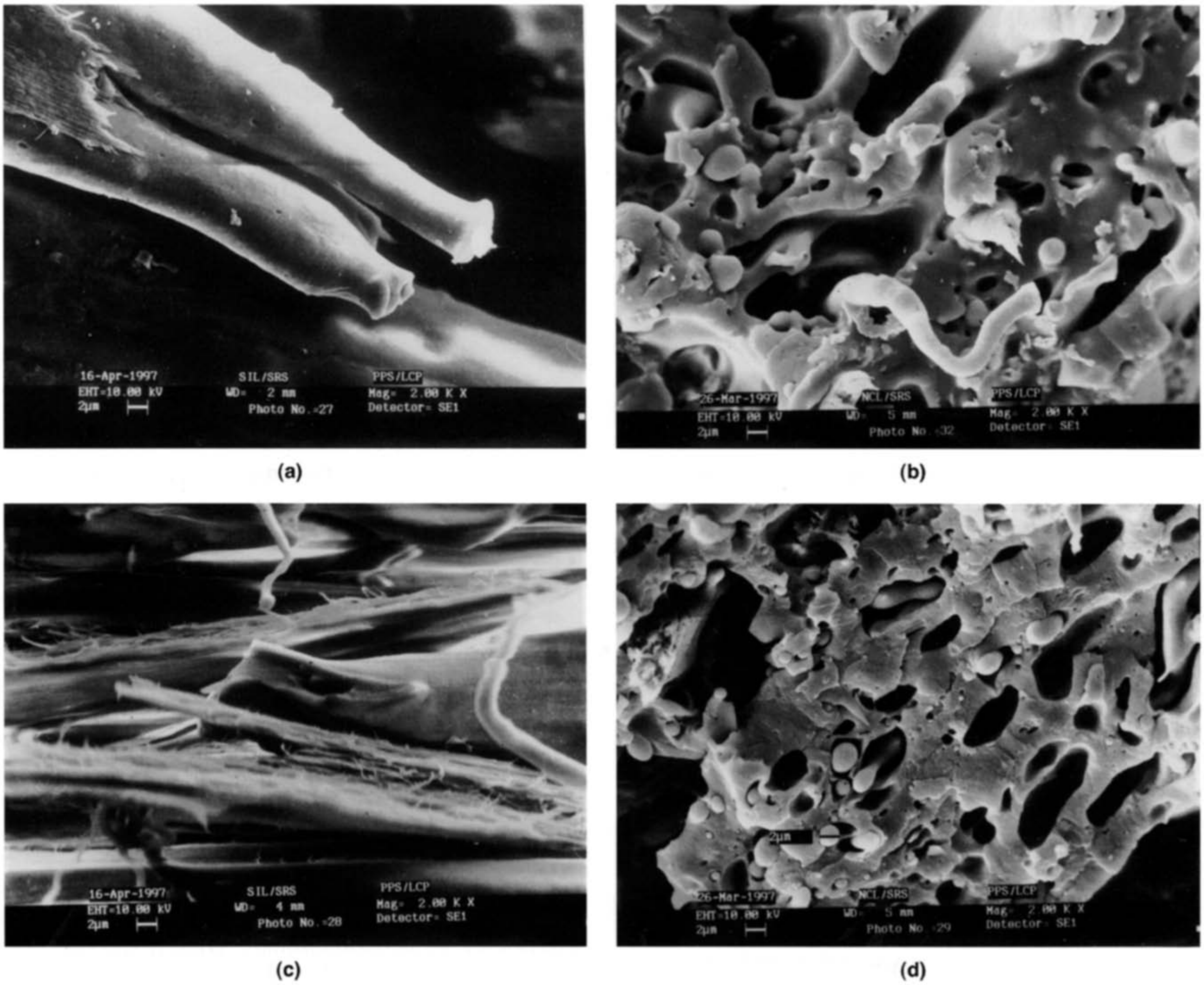
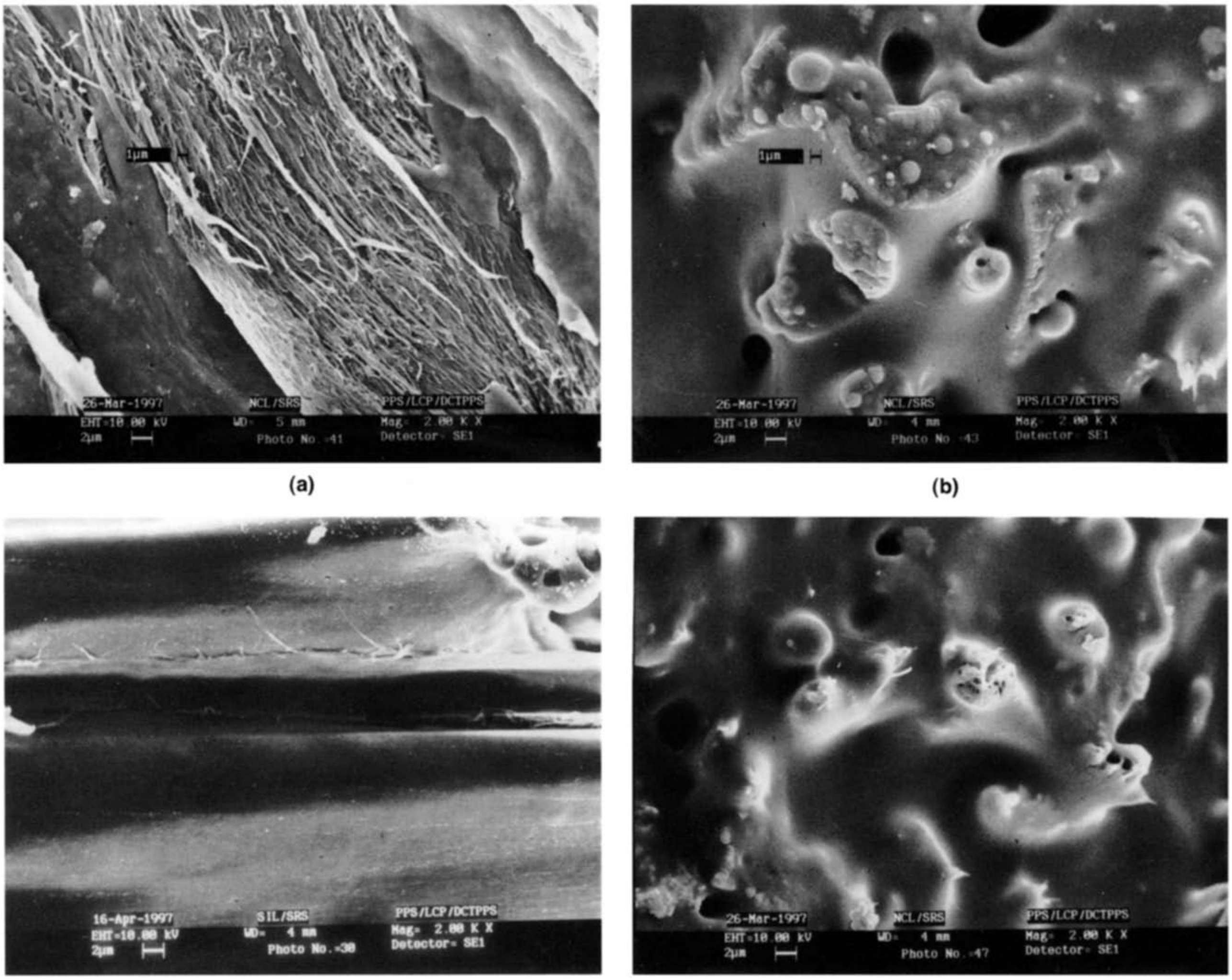


Fig. 3. SEM micrograph showing skin morphology of uncompatibilised PPS/Vectra A950 blends: (a) perpendicular to injection flow direction, skin region; (b) core region of the same specimen; (c) parallel to injection moulded direction, skin region; (d) core region of the same specimen.

the matrix and the delivery of the internal stress of the continuous phase to the dispersed phase. So the interfacial condition between the phases is important. The impact strength of a blend is very sensitive to changes in interfacial adhesion [24]. Thus, the impact strength was measured for both notched and unnotched specimens. Most of the compatibilised blends did not fail in the unnotched impact test. The notched impact strength yielded more information on the behaviour of the material. The impact strength of the in situ compatibilised blends was significantly improved as shown in Table 4. The Izod unnotched impact strength of uncompatibilised 75/25% (w/w) PPS/Vectra A950 blend is 13.4 J/m, whereas for the compatibilised blend of the same composition it is 39.1 J/m due to enhanced adhesion at the interface on compatibilisation.

3.4. Morphology

The fractured surface morphologies of the injection-moulded specimen were inspected on the planes perpendicular and parallel to the injection flow directions in both the core and near-skin regions. Fig. 3 shows scanning electron micrograph of the uncompatibilised PPS/Vectra A950 (75/25) blend. Fig. 3(a) was taken from the plane perpendicular to the injection flow direction, at the skin region, where the Vectra A950 fibrils are fairly long (high aspect ratio), with most of them being pulled out from the PPS matrix which is an indication of poor interfacial adhesion. Fig. 3(b) shows the morphology at the core region for the same specimen as Fig. 3(a), where the Vectra A950 phase exists as large spherical particles. Fig. 3(c) shows the micrograph obtained on the plane parallel to the flow direction near the skin region. This shows the presence of larger number of long Vectra A950 fibrils. Fig. 3(d) shows voids at the interface between PPS matrix and Vectra A950 fibrils as a result of poor interfacial adhesion, which results in the inferior mechanical properties. This kind of skin-core dispersed phase morphology has been observed in many polymer blends as a result of the shear difference and



(a) (b)

(c) (d)

Fig. 4. SEM micrograph showing core morphology of compatibilised PPS/Vectra A950 blends: (a) perpendicular to injection flow direction, skin region; (b) core region of the same specimen; (c) parallel to injection moulded direction, skin region; (d) core region of the same specimen

quenching rate difference in a typical injection-moulding process [34]. Previous studies [30,31] on the development of such morphologies in pure Vectra A950 and thermoplastics have also indicated the formation of such morphologies during injection moulding arise from the freezing of the orientation in the layer in contact with the mould due to the steep temperature gradient. The development of skin-core morphology is observable only at Vectra A950 concentrations exceeding 25 wt%. The increase in the mechanical properties of blends with higher concentration of Vectra A950 can be attributed to the formation of skin-core morphology, with the skin region being capable of carrying a much higher stress than the core region, as in the case of Vectra A950 [34,35].

Fig. 4 shows the morphologies of the compatibilised PPS/Vectra A950/DCTPPS (75/25/2.5) blend, observed at the same locations (same magnification) as described earlier. Fig. 4(a) shows that the improved interfacial adhesion of this compatibilised blend fractured the Vectra A950 fibrils, instead of pulling them out of the matrix. Fig. 4(b) shows clearly the interfacial bonding between the PPS matrix and Vectra A950 fibrils. This observation reveals that the compatibilisation does not affect the extent of fibrillation. This observation is significant from a technological point of view because these fibrils are essential for the reinforcement of the matrix, and lead to enhanced mechanical properties. In previous studies [28,29], compatibilisation was shown to alter the fibril morphology of the Vectra A950 phase which causes inferior mechanical properties. Fig. 4(c) shows that the size of the Vectra A950 dispersed droplets are considerably smaller than that of the corresponding uncompatibilised blend (Fig. 3(c)) and this observation further supports claim of better compatibilisation. At the core region (Fig. 3(d)) the size of the Vectra A950 droplets becomes rather small indicating an improved compatibility between the PPS and Vectra A950. By properly choosing the processing conditions and compatibiliser compositions, the mechanical properties can be improved further.

4. Conclusion

The effect of in situ compatibilisation on thermal properties, mechanical properties and morphology of PPS/Vectra A950 blends were investigated. The decrease in the heat of melting, crystallisation temperature and heat of crystallisation of PPS phase in PPS/Vectra A950 blends on compatibilisation points to the presence of favourable interaction between the blend components. Tensile and impact properties of the compatibilised blends are enhanced indicating an improvement in the interfacial adhesion between the components. Toughness of the blend increases on compatibilisation. In situ reactive compatibilisation of PPS/Vectra A950 blends result in uniform and continuous morphology. Compatibilisation does not affect the extent fibrillation of Vectra A950 phase within PPS matrix. Both uncompatibilised and compatibilised PPS/Vectra A950 blends exhibit skin-core morphology. The Vectra A950 fibres are present more in the skin region, but less in the core region, especially at higher Vectra A950 content. It has been concluded that the in situ compatibilisation of PPS/Vectra A950 blends using DCTPPS as reactive component is an efficient way to produce PPS/Vectra A950 molecular composites with unique properties.

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