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The effects of temperature and liquid crystalline polymer (LCP) on mechanical properties of a blend of polyphenylene sulphide and LCP

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The mechanical properties of polyphenylene sulphide (PPS) and liquid crystalline polymer (LCP) blends were investigated over a range of temperatures. The effect of blend composition on the brittle–ductile transition temperature (B–D) was also studied by differential scanning calorimetry and scanning electron microscopy. Blends of various compositions (PPS/LCP; 90/10, 75/25, 50/50 and 25/75) were prepared and injection moulded. The bending test temperature was varied between − 40 and 150 °C. The results showed a rapid load drop at the B–D transition region. The B–D transition temperature occurred in unannealed pure PPS, 90/10, 25/75 and 50/50 blends around 75 °C whilst in the annealed sample it was observed around 100 °C. In pure LCP and 25/75, no transition occurred. Partial miscibility of PPS and LCP was confirmed by SEM observations, bending modulus and thermal properties. The use of LCP, as a good reinforcing agent which can improve processability and modulus, is discussed.

1. Introduction

There is increasing commercial interest in blending two or more polymers because it provides a unique route for structural modification of properties for specific needs at low cost. In several applications, neat resin may not satisfy all the end-use requirements, while physical and chemical combination of two or more dissimilar components can provide the required balance of properties, such as processability, thermal stability, impact resistance, heat distortion temperature HDT, etc. [1–6]. Both polyphenylene sulphide (PPS) and liquid crystalline polymer (LCP) are speciality polymers and are increasingly attractive for several applications, including connectors for electronic equipment, automobile parts, electrical appliances and coating [7].

Few scientific investigations on the blending of PPS with thermoplastic polymers have been cited in the literature [8–12]. In a recent study [10], it was shown that PPS is immiscible with both polyetherimide (PEI) and polysulphone (PSF) and that the ability of PPS to crystallize is not suppressed within the blends, even with low PPS content. In a similar study conducted in our laboratory [13] using differential scanning calorimetry, we concluded that the presence of LCP had little or no effect on the crystallinity of the blend. Numerous studies have been carried out on LCP blends [13–18] and, in most cases, LCP was found to be immiscible with most thermoplastic polymers but the modulus was enhanced. Siegmann *et al.* [16] reported that in an LCP/PA blend, the mechanical properties increased monotonically with increasing LCP content. The distribution of the LCP phase depends on many factors such as composition, processing conditions, viscosity ratio of the component polymers and the rheological characteristics of the matrix polymer [19].

In this study, the effect of temperature on the bending properties of blends containing PPS and LCP was investigated.

2. Experimental procedure

2.1. Materials

The linear PPS used in this investigation was supplied by Idemitsu Petrochemical Company. The molecular weight was determined in chloronaphthalene by gel permeation chromatography (GPC) at 207 °C. The results were $M_w = 42\,038$, $M_n = 5782$, $M_z = 82\,557$ with polydispersities of 7.27 (M_w/M_n) and 1.96 (M_z/M_w). The commercial-grade LCP was purchased from dealers. The molecular weight could not be determined because it was difficult to find a suitable solvent in which it can be dissolved. The structures of PPS and LCP are given in Fig. 1.

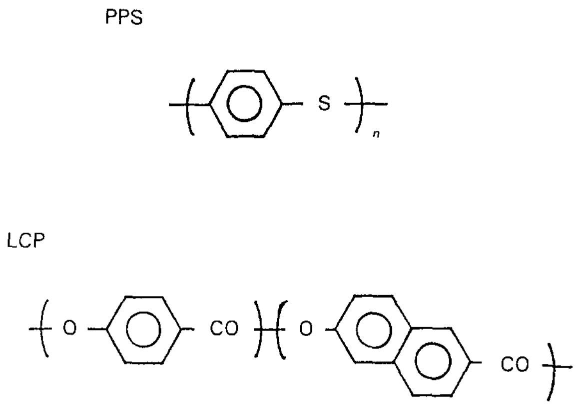


Figure 1 The Structure of PPS and LCP.

2.2. Blending

PPS and LCP pellets were mixed according to the required composition, i.e. 90/10, 75/25, 50/50 and 25/75 PPS/LCP blends. The blending operation was carried out on Toshiba TEM35B-10/1V double-screw blender. The blends were extruded, pelletized and predried at 150 °C for 24 h.

2.3. Injection moulding

PPS/LCP pellets of various compositions were predried at 230 °C for 6 h before moulding. The blends were injection moulded using Toyo Ti-30F6 moulding machine. The moulding conditions were: cylinder temperature 300 °C, injection pressure 4.9 MPa, and mould temperature 100 °C.

2.4. Bending test

The bending test was carried out on Instron Universal Testing Machine, Model 4206. The specimen geometry is shown in Fig. 2. The bending span was 48 mm and the test speed was 2 mm min^{-1}. Test temperature was varied between -40 and 200 °C. Prior to the bending test, some of the samples were annealed at 250 °C for 1 h. Experiments were conducted on batches of five or more and the results averaged.

2.5. Differential scanning calorimetry (DSC)

DSC measurements were carried out using Perkin–Elmer DSC, model DSC7 fitted with a thermal analysis data station. The sample was heated to 320 °C at a heating rate of 20 °C min^{-1} and was allowed to crystallize at a cooling rate of 20 °C min^{-1}. Experiments were conducted on fractured bending test samples at brittle, brittle–ductile (B–D) transition, and ductile regions.

2.6. Scanning electron microscopy

The morphology of the blends was examined by scanning electron microscopy using a Jeol, Model JSM-5200 at 15 kV accelerating voltage. The fracture surface was examined with specific reference to skin and core morphologies. All samples were coated with gold and examined at a magnification of 1000.

2.7. Measurement of viscosity

The viscosity of the blends was measured by using Shimadzu Capillograph with capillary die of diameter $D = 1$ mm, and length to diameter ratio $L/D = 20$. Extrusion of the pellets through the capillary was carried out at 320 °C.

3. Results and discussion

3.1. Effect of temperature

The load–displacement curves of neat PPS, LCP and their blends are shown in Fig. 3. All data reported are average values because there was no significant scatter in bending properties. Brittle failure occurred in neat PPS, 90/10, 75/25 and 50/50 PPS/LCP blends, whilst in neat LCP and 25/75 blend the failure was ductile. A well-pronounced yield drop occurred in 25/75 sample. The presence of LCP in 90/10, 75/25 and 50/50 blends had no effect on the shape of the load–displacement curves which are similar to that of neat PPS. This observation may indicate the strong influence of PPS in the blend. Typical load–displacement curves of representative blend (75/25) at various temperatures are depicted in Fig. 4. The mode of failure in both unannealed and annealed samples ranges from brittle to ductile depending on the test temperature. At -40 °C, the sample failed in a brittle manner, whilst at higher temperature, ductile failure ensues. The bending modulus as a function of temperature is shown in Fig. 5 for unannealed and annealed samples. Thus, three failure modes (brittle, brittle–ductile and ductile) can be observed in the figure. A sharp B–D transition occurred in neat PPS, 90/10, 75/25 and 50/50 blends. In 25/75 blend and neat LCP, no clear B–D transition point can be detected. The B–D transition temperatures of all the blends are tabulated in Table I. In the

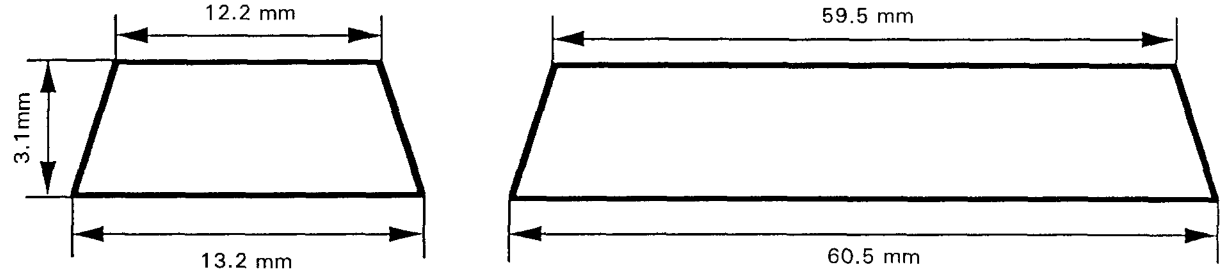


Figure 2 Bending specimen geometry.

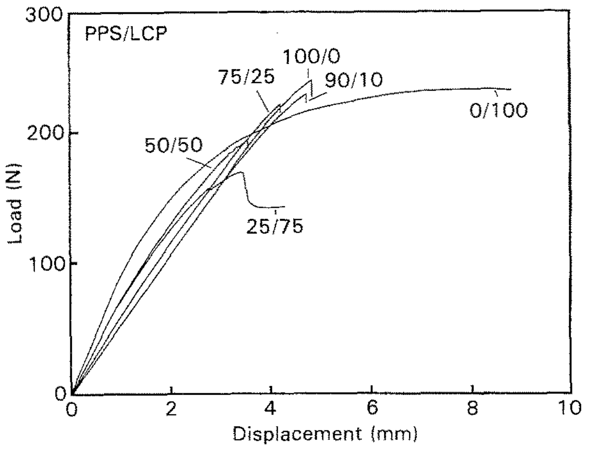


Figure 3 Load–displacement curves of pure PPS, LCP and their blends.

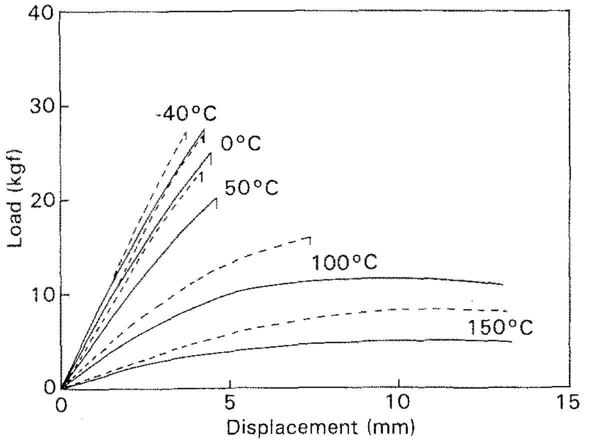


Figure 4 Load–displacement curves of representative blend (75/25) at various temperatures; (——) unannealed and (···) annealed specimens.

TABLE I Brittle-ductile transition temperatures in PPS/LCP blend

PPS/LCP	B–D Transition Temperature (°C)	
	Unannealed	Annealed
100/0	75	100
90/10	75	100
75/25	75	100
50/50	–	–
25/75	–	–
0/100	–	–

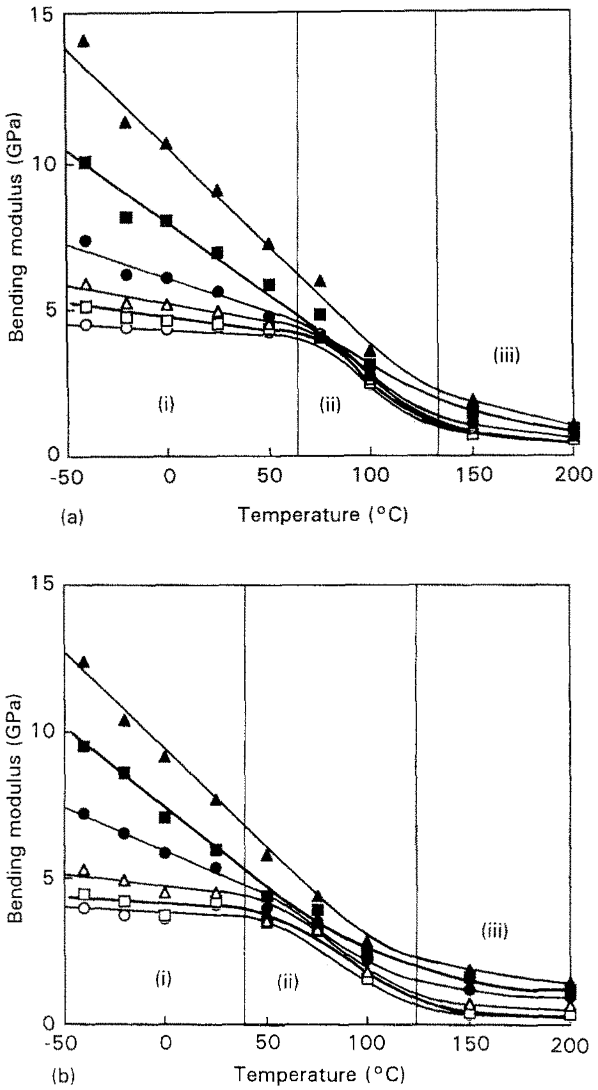


Figure 5 Bending modulus of PPS/LCP blends as a function of temperature: (i) brittle region, (ii) B–D transition region; (iii) ductile region. (○) 100/0, (□) 90/10, (△) 75/25, (●) 50/50, (■) 25/75, (▲) 0/100.

unannealed sample, transition occurred around 75 °C and in annealed samples, it was observed around 100 °C. Where transition occurred, LCP content had no effect. A similar situation for bending strengths is shown in Fig. 6. In general, bending moduli and strengths of annealed samples were higher than those of unannealed ones. It is well documented that in glassy polymers, brittle failure which occurred at low temperature favours crazing, whilst the ductile failure at high temperature promotes shear yielding [20, 21]. Matsushige *et al.* [20] on polystyrene (PS) and polymethyl methacrylate (PMMA), pointed out that ductile–brittle transition is a direct result of the alteration in deformation mode from yielding to crazing. In this investigation on speciality polymers (PPS and LCP), crazes were not observed in the brittle region. The modes of failure in this case may be conceptualized as those involving breaking of the untangled tie molecules in the brittle region and stretching and fibre pull-out in the ductile region. Representative scanning electron micrographs of fractured surfaces in the brittle, B–D and ductile regions are shown in Fig. 7.

3.2. Miscibility of the blend

Miscibility is the tendency or capacity of the components to form a uniform blend, i.e. the blend is homogeneous down to the molecular level. In our previous studies [13], using differential scanning calorimetry (DSC), we argued that PPS was partially miscible with LCP; the present study, therefore, cemented such argument. The present investigation may serve as an alternative method to determine the miscibility of the

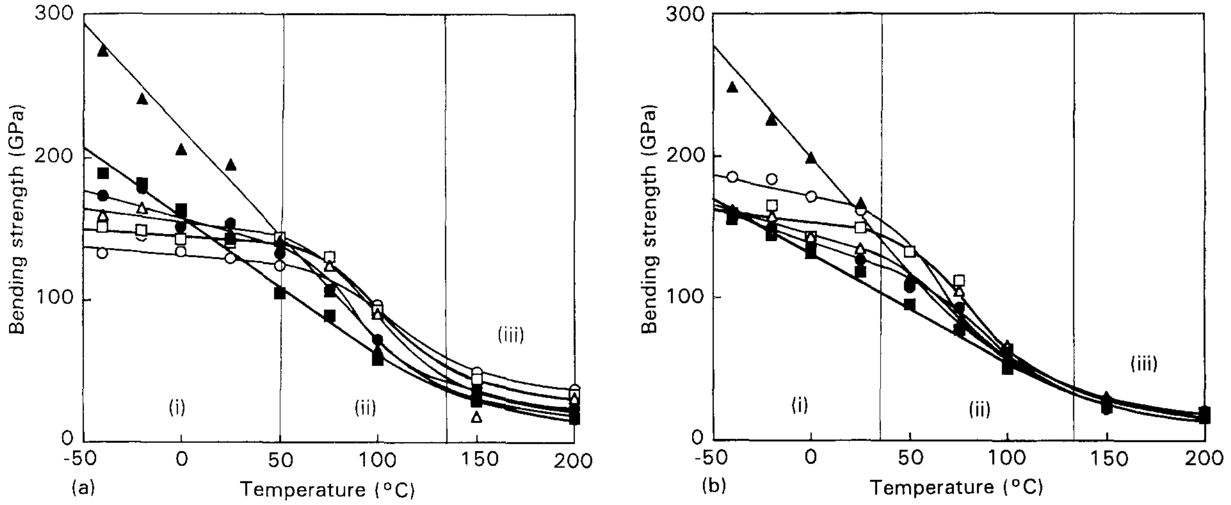
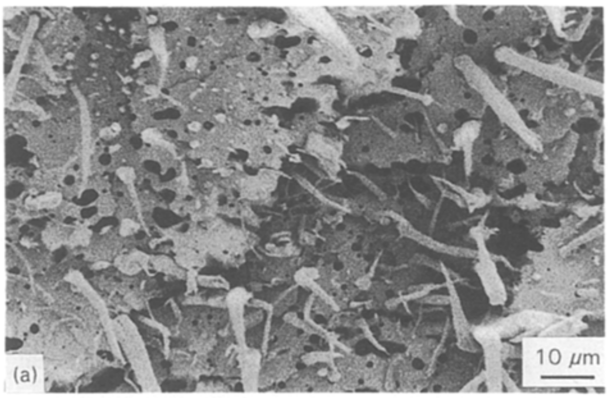
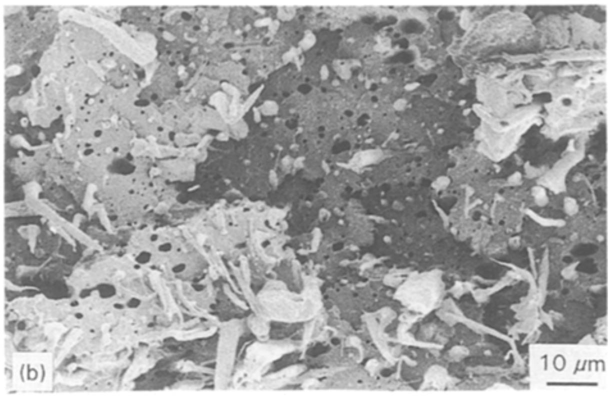


Figure 6 Bending strength of PPS/LCP blends as a function of temperature: (i) brittle region; (ii) B–D transition region; (iii) ductile region. For key, see Fig. 5.





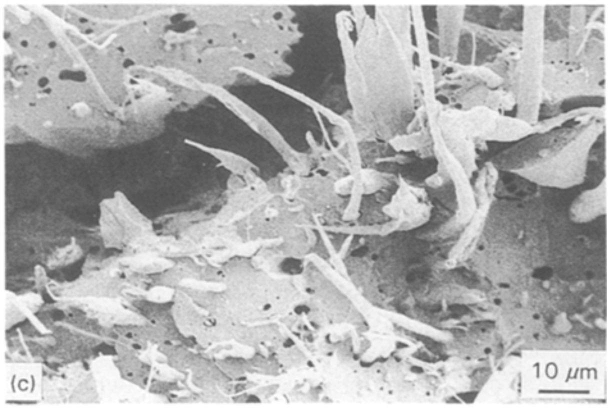


Figure 7 Scanning electron micrographs of a fractured surface of representative blend (75/25): (a) brittle region, (b) B–D transition region and (c) ductile region.

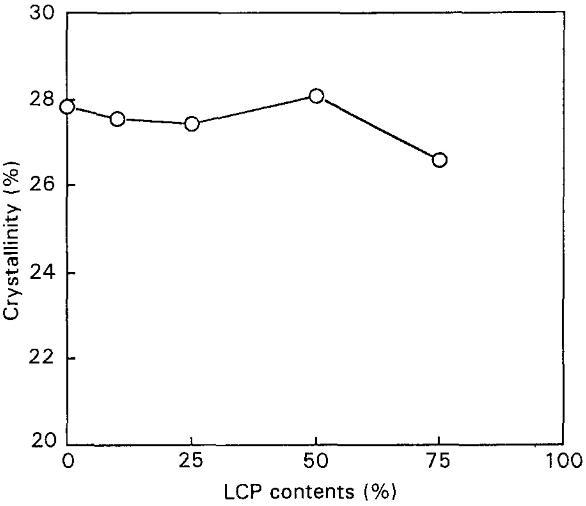


Figure 8 Blend crystallinity as a function of LCP content.

components. The influence of PPS in the blend is confirmed by

(a) the shape of load–displacement curves; pure PPS, 90/10, 75/25 and 50/50 were similar (Fig. 3);

(b) rapid load drop at the B–D transition; rapid load drop occurred in pure PPS, 90/10, 75/25 and 50/50 blends; and

(c) the B–D transition temperature; the presence of LCP had no influence on the temperature at which transition occurred.

The average percentage crystallinity as a function of LCP content is presented in Fig. 8. As can be seen in the figure, PPS maintains its crystallinity in the blend even when the PPS content was as low as 25%. This further indicates that PPS is partially miscible with LCP. Thus, if both polymers were miscible, a significant change in crystallinity would be expected. Ther-

TABLE II Thermal Properties of PPS/LCP blend: (a) brittle region, (b) ductile region and (c) brittle-ductile transition region

(a)

PPS/LCP	Unannealed Sample			Annealed Sample		
	T_m (°C)	T_c (°C)	ΔH (Jg^{-1})	T_m (°C)	T_c (°C)	ΔH (Jg^{-1})
100/0	279.4	243.2	38.43	286.2	246.6	47.92
75/25	279.0	245.2	29.50	289.0	243.6	37.22
50/50	278.2	243.8	18.60	282.2	243.6	24.45
0/100	284.8	231.8	1.69	283.0	231.6	2.81

(b)

PPS/LCP	Unannealed Sample			Annealed Sample		
	T_m (°C)	T_c (°C)	ΔH (Jg^{-1})	T_m (°C)	T_c (°C)	ΔH (Jg^{-1})
100/0	278.1	242.8	40.39	288.4	246.5	47.48
75/25	280.2	245.4	29.14	287.6	243.9	35.21
50/50	278.8	244.0	19.49	281.7	243.2	25.14
0/100	276.0	231.8	0.82	280.8	231.6	2.87

(c)

PPS/LCP	Unannealed Sample			Annealed Sample		
	T_m (°C)	T_c (°C)	ΔH (Jg^{-1})	T_m (°C)	T_c (°C)	ΔH (Jg^{-1})
100/0	281.0	242.7	40.36	276.9	241.9	42.41
75/25	278.5	245.5	29.96	279.6	244.5	36.01

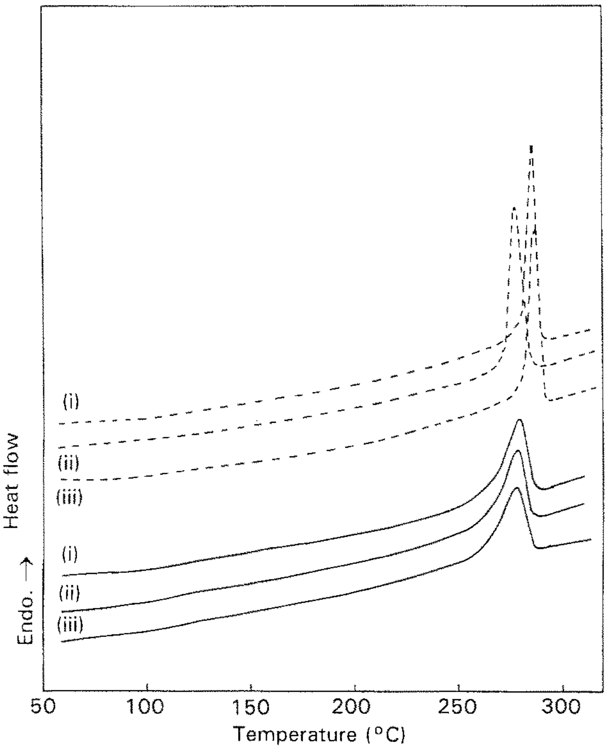


Figure 9 Representative (75/25) DSC thermograms of PPS/LCP blends: (——) unannealed, (···) annealed: (i) brittle region, (ii) B–D transition region and (iii) ductile region.

mal properties of the representative blends in the brittle (−40 °C), B–D transition (70 and 100 °C) and ductile (150 °C) regions are shown in Table II. The representative DSC thermograms are depicted in Fig. 9 for unannealed and annealed samples. In all cases, the melting temperatures, T_m, of annealed samples were higher than those of the unannealed ones. This was due to relaxation of molecules in the annealed state. There was no significant difference in thermal properties obtained in all three regions.

3.3. Effect of LCP in the blend

Traditionally, glass and carbon fibres are widely used as reinforcing agents in academic and industrial communities. These fibres are known to improve the mechanical properties. One large disadvantage is that processing becomes more difficult due to increased viscosity which, in most cases, is higher than the parent polymer. LCP is a speciality polymer and a good substitute for glass and carbon fibres. In this present work, two main advantages of LCP content in PPS/LCP blends were noted; improved processability and stiffness.

The viscosity as a function of LCP content in the blend is shown in Fig. 10. As can be seen in the figure, viscosity reduces with increasing LCP. As pointed out by Van Oene [22], the rheology of the polyblend is influenced by the melt structure which depends on the characteristics of the phases such as viscosity ratio, interaction, flow conditions and mixing mode. In this case, it may be concluded that in all the blend compositions, the LCP domains were well dispersed in the PPS matrix, and lubricate the PPS, thereby reducing the viscosity. Thus, addition of as little as 10% LCP resulted in about 15% reduction of viscosity from that of the pure PPS. With 25% LCP content, the reduc-

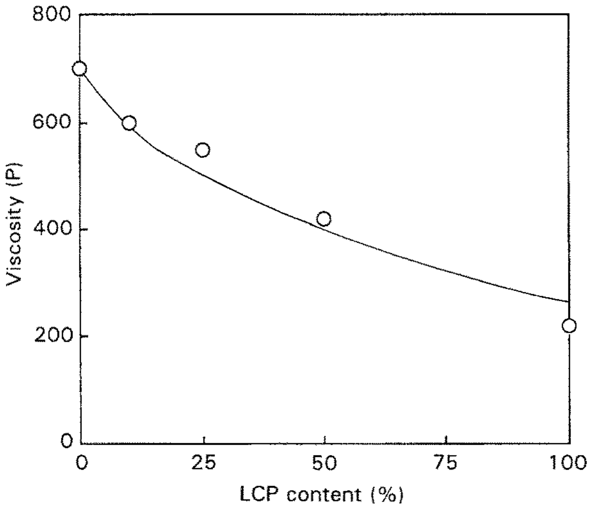


Figure 10 Melt viscosity of PPS/LCP blends as a function of LCP content.

tion was 21%; in 50/50 PPS/LCP blend, the viscosity was reduced by about 43%; and in pure LCP, the viscosity of LCP was about 72% lower than that of PPS. One major advantage of LCP content during processing of PPS/LCP blend is that wear and tear of machine parts due to abrasion is reduced as a result of the low viscosity.

The morphology of PPS/LCP depicted in Figs 11–14 contained LCP fibrils in the skin region and droplets in the core region. These morphological observations made by SEM confirmed that both fibrils and droplets were present in polyblends and they may change from one type to another depending on blend composition and flow condition [16]. The plate-like skin and core regions of parent PPS polymer is shown in Fig. 15. In all the blends (except 25/75), the skin region contains fibrils of LCP about 2–4 μm embedded in PPS matrix. The core region, on the other hand, contains fine droplets (irregular diameter) of LCP. Both fibril and droplet diameter increase with increasing LCP content. In 25/75 blend, a network structure similar to that of pure LCP (Fig. 16) was observed in both skin and core regions. These SEM observations correlate well with the observed brittle–ductile transition region, i.e. clear transition points were detected in pure PPS, 90/10, 75/25 and 50/50 PPS/LCP blends. In 25/75 blend and pure LCP, clear B–D transition points could not be detected.

Because LCP was argued above to be a form of reinforcing agent, the rule of mixtures, which is applicable to composite materials, may also be adopted for calculating the modulus. Thus, the modulus of unidirectional fibre-reinforced composite can be calculated as follows [19]

$$E_c = E_1V_1 + E_2V_2 \quad (1)$$

where E_c is the composite modulus, E_1 and E_2 are the moduli of the reinforcing LCP and the matrix, respectively, and V_1 and V_2 are their volume fractions.

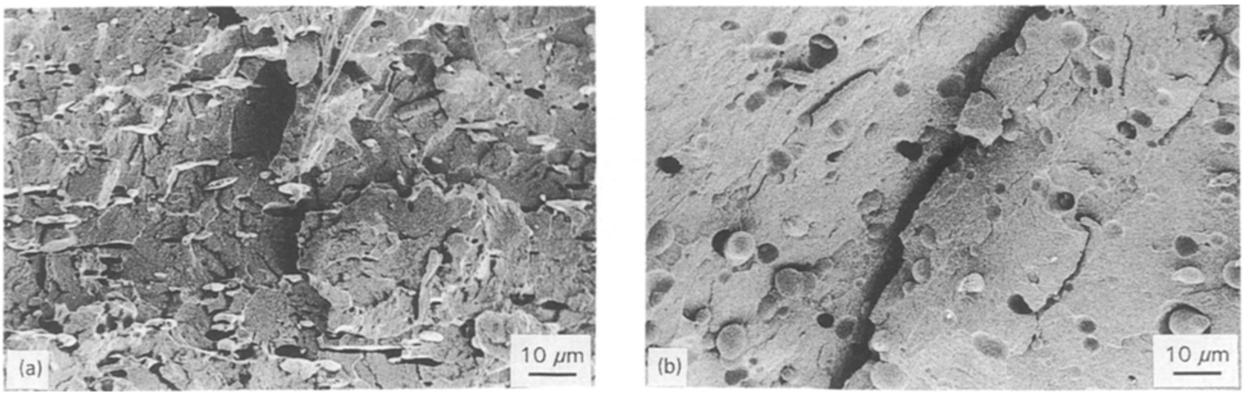


Figure 11 Scanning electron micrographs of a fractured surface of 90/10 PPS/LCP blend: (a) skin region; (b) core region.

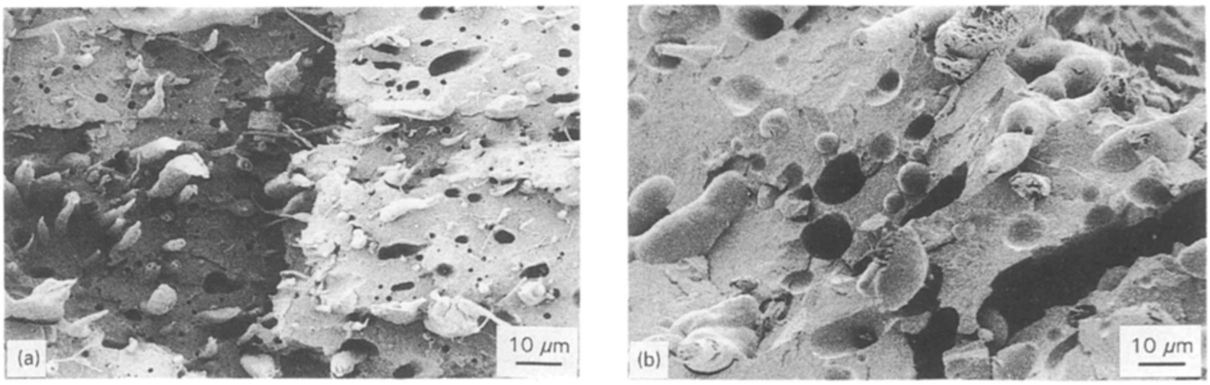


Figure 12 Scanning electron micrographs of a fractured surface of 75/25 PPS/LCP blend: (a) skin region; (b) core region.

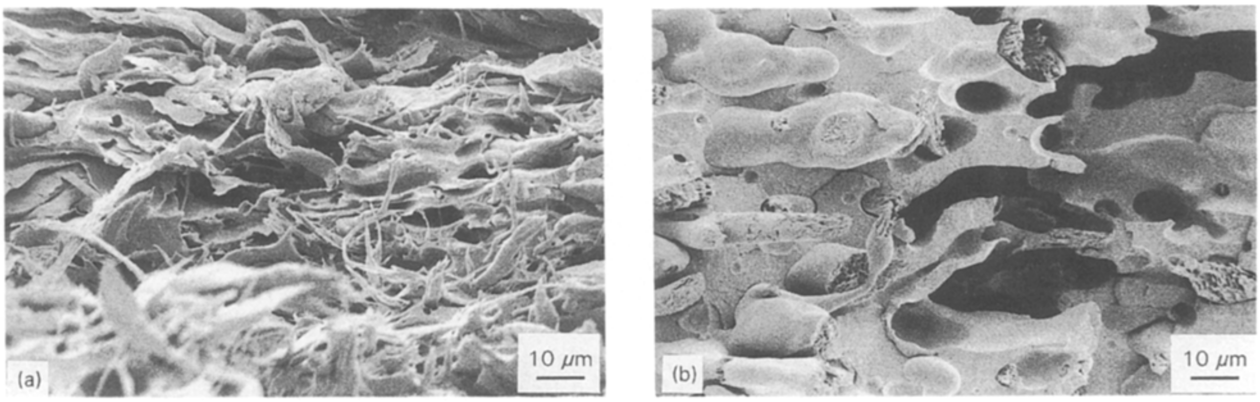


Figure 13 Scanning electron micrographs of a fractured surface of 50/50 PPS/LCP blend: (a) skin region; (b) core region.

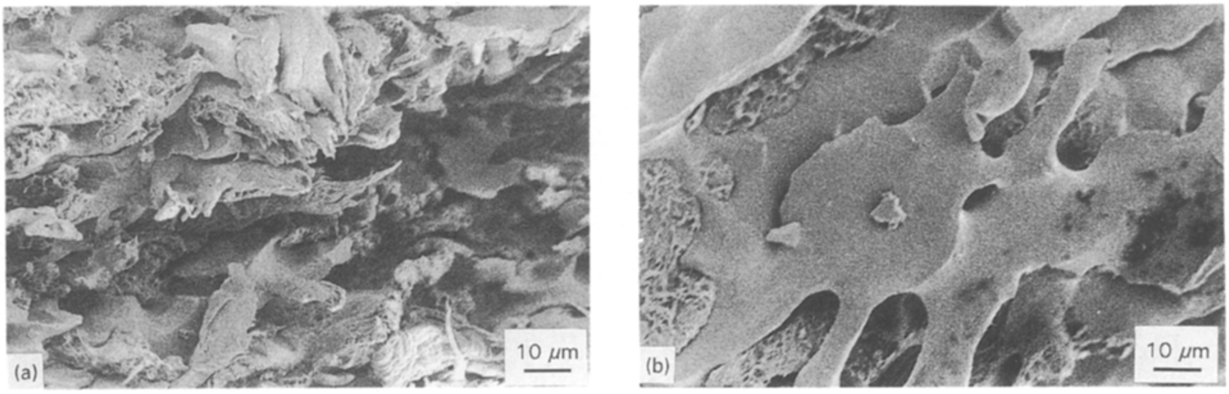


Figure 14 Scanning electron micrographs of a fractured surface of 25/75 PPS/LCP blend: (a) skin region; (b) core region.

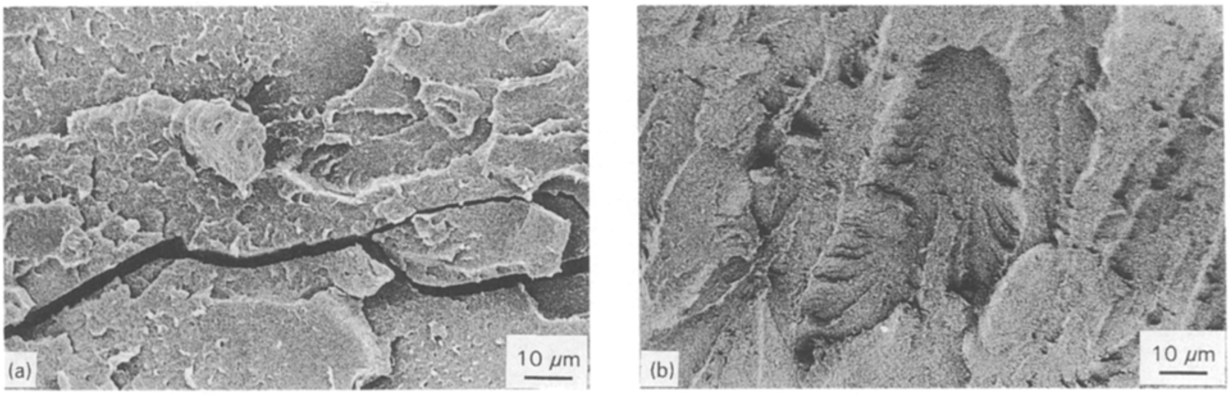


Figure 15 Scanning electron micrographs of a fractured surface of pure PPS: (a) skin region; (b) core region.

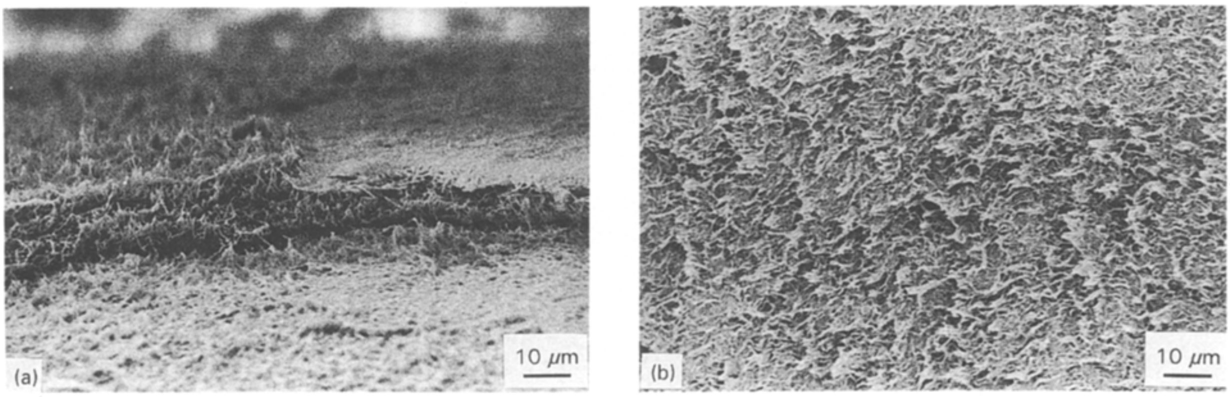


Figure 16 Scanning electron micrographs of a fractured surface of pure LCP: (a) skin region; (b) core region.

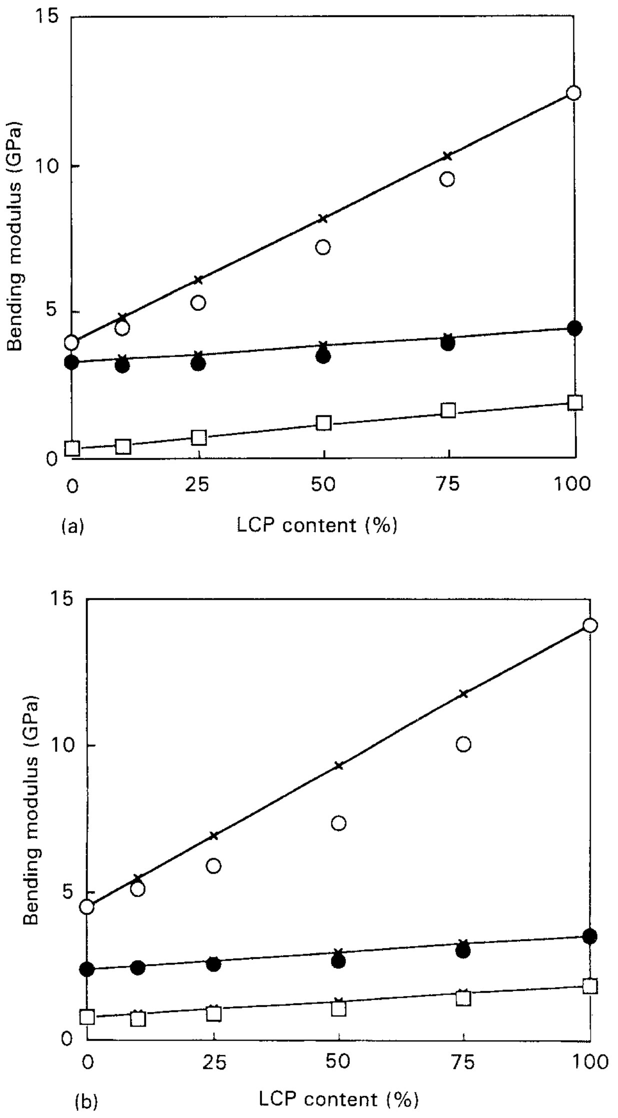


Figure 17 Bending modulus of PPS/LCP as a function of LCP content for comparison with composite theory. (×) Calculated value, and (o) brittle, (●) B–D transition, (□) ductile regions

Fig. 17 compares the results of experimental values of bending moduli and the calculated values using composite theory. The figure shows the effect of LCP content in the brittle, B–D transition and ductile regions. There was a good correlation between the calculated and the experimental values in both the unannealed (a) and annealed (b) samples. This agreement may be due to the alignment of LCP microfibrils as confirmed by scanning electron micrographs. However, because composite theory had been widely used to evaluate the modulus of glass or carbon fibre-reinforced composites, the theory can also be applied to LCP/thermoplastic blend. As can be seen in Fig. 17, the effect of LCP in the blend was higher in the brittle region than in the ductile region. Thus, bending modulus increases with increasing LCP content. In the B–D transition region, the LCP content had no effect on bending modulus.

4. Conclusion

It has been demonstrated that LCP is a good reinforcing agent comparable with glass or carbon fibre. LCP was found to be partially miscible with PPS but its influence in the blend was the increase in modulus and reduction of melt viscosity. The brittle–ductile transition temperature was not influenced by the LCP content. PPS, on the other hand, maintains its crystallinity in the blends, as confirmed by the results.

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