# Blends of a thermotropic liquid-crystal polyester with poly(phenylene sulphide)

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Blends of a thermotropic liquid-crystalline polymer (LCP), based on a copolyester of hydroxynaphthoic acid and hydroxybenzoic acid, with an engineering thermoplastic, poly(phenylene sulphide) (PPS), were prepared using a co-rotating twin-screw extruder. The blends were subsequently injection moulded to study their mechanical, dynamic, impact and morphological characteristics. Rheological studies have indicated a higher shear viscosity of the LCP as compared to PPS, with the shear viscosity of some of the blends being higher than that of the LCP. Dynamic and thermal studies have indicated overlapping temperature transitions of the pure components. Therefore, based on these measurements it is not possible to make a conclusion about the compatibility of the blends. Thermogravimetric studies have indicated the poor thermal stability of the blends when compared to the pure materials. The tensile and impact properties of these blends were found to increase with the addition of LCP. However, the pure LCP exhibits the highest properties. The morphology of the blends has indicated their incompatibility and the formation of LCP droplets in the matrix of PPS at nearly all concentrations of LCP, with the formation of the skin–core morphology being clearly visible at LCP content greater than 25%.

**(Keywords: blends; polyester; poly(phenylene sulphide); liquid-crystalline polymer; characterization)**

## INTRODUCTION

Much attention has been focused by the polymer industry on the area of high-performance plastics, as these materials have shown immense diversified applications. The latest in these series are the thermotropic liquid-crystalline polymers (LCP). In the anisotropic melt stage they exhibit much lower viscosities than the isotropic phase of flexible chain polymers. This characteristic of the LCPs makes them easily processable[1].

Blending of polymers to obtain a blend of superior mechanical and impact properties and better thermal stability has been adopted by the polymer industry for a long time[2]. Blends that are a mixture of two or more polymers may be physically compatible or incompatible[3]. In incompatible blends, depending on the viscosity and the volume fraction, one component is dispersed in the other. The resultant morphology of the blends so formed is largely governed by interfacial tension, ratio of viscosities and strain rate, with high strain rates favouring fibrillation[4]. Blends of LCPs with engineering thermoplastics are fast gaining popularity. The LCP phase in these blends, owing to their lower viscosity than the thermoplastic phase, forms fibres of LCP in the matrix of the thermoplastic material, resulting in the formation of self-reinforced or *in situ* composites[5–12]. The viscosity of these composites is observed to be lower than that of the thermoplastic polymer, thereby making the processing of these blends easier.

In many cases the blends of LCPs with engineering thermoplastics show improved mechanical, impact and processing characteristics. Usually, these blends involve the incorporation of an LCP of lower viscosity in the matrix of the thermoplastic material. The present study involves the LCP–thermoplastic polymer blend where the LCP has a higher shear viscosity than the thermoplastic polymer. Therefore, the main objective of this work has been to study the mechanical, dynamic, impact, thermal and morphological characteristics of such blends. An explanation of the observed mechanical properties of the blends from the knowledge of the morphology is given.

## MATERIALS

The thermotropic liquid-crystalline polymer used in this study was Vectra A950 supplied by Hoechst-Celanese Company. This LCP is a wholly aromatic copolyester consisting of 25 mol% of 2,6-hydroxynaphthoic acid (HNA) and 75 mol% of *p*-hydroxybenzoic acid (HBA). The thermoplastic used in this study was poly(phenylene sulphide), grade P-6, which was obtained as a powder from Phillips Petroleum Company.

## EXPERIMENTAL PROCEDURE

Blends of the above-mentioned materials were prepared using a co-rotating twin-screw extruder ZSK-30 (Werner Pfleiderer Corp.). The PPS powder was initially run through the extruder at 285°C to obtain pellets of the material so as to facilitate better mixing with the LCP pellets. Blends of LCP composition ranging from 2.5% to 90% were prepared.

Rheological measurements on these blends and the pure materials were carried out using an Instron capillary rheometer (model 3211). A capillary die of diameter $D = 0.001\,57$ m with a length-to-diameter ratio $L/D$ of 28.7 was used. All measurements were carried out at a temperature of 300°C in a shear rate range of $1$–$10^3\ \mathrm{s}^{-1}$. No entrance pressure correction was applied.

The transition temperatures of the blends and the pure

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materials have been evaluated using a differential scanning calorimeter (DuPont 9900). Temperature scans from 40 to 350°C at a heating rate of 20°C $\mathrm{min}^{-1}$ were carried out. The thermal stability of the blends was investigated using a DuPont 990 Thermogravimetric Analyzer. The samples were kept at 300°C for a period of 60 min and the weight loss was recorded.

Injection moulding of the blends and the homopolymers was carried out using a reciprocating screw injection moulding machine (Boy 15S) with a maximum clamping force of 150 kN and a maximum shot size of $3.6 \times 10^{-5}\ \mathrm{m}^3$. The injection moulding runs were carried out at a melt temperature of 300°C, a mould temperature of 90°C and a volumetric flow rate of $4.5 \times 10^{-5}\ \mathrm{m}^3\ \mathrm{s}^{-1}$.

Tensile properties of the blends were investigated using a Monsanto Tensiometer (T-10). Testing of minitensile bars (MTBs) was carried out using a cross-head speed of 0.005 m $\mathrm{min}^{-1}$ and a gauge length of 0.01 m. Six samples of each composition were tested and the average values recorded. The impact tests of self-reinforced tensile bars (STBs) were carried out using an Izod Impact Tester (Testing Machine Inc.), according to ASTM D-253 C.

Dynamic mechanical tests were carried out using a dynamic mechanical thermal analyser (Polymer Laboratories Inc.). Experiments were carried out in flexural mode using N/C clamps on samples of dimensions $0.014 \times 0.0031 \times 0.0015\ \mathrm{m}^3$ employing a frequency of 1 Hz and a heating rate of 2°C $\mathrm{min}^{-1}$.

Studies on the morphology of the blends were carried out using a scanning electron microscope (model SX-40, ISI Inc.). For these studies, samples of the MTBs were fractured in liquid nitrogen and vacuum coated using a gold–palladium plasma for a period of 2 min.

## RESULTS AND DISCUSSION

### *Rheological properties*

The flow curves of pure PPS, LCP and their blends measured at 300°C are depicted in *Figure 1*. It can be seen from the figure that in the shear rate range studied all the melts exhibit a typical non-Newtonian behaviour, with the highest power-law exponent being for the pure LCP and blends of high LCP concentration. The rheological curves of pure PPS and low LCP concentration blends are found to exhibit a slight non-Newtonian behaviour. It is also observed that the viscosity of the LCP is higher than that of PPS. At low shear rates ($10\ \mathrm{s}^{-1}$), the blends of LCP concentration greater than 5% exhibit a higher viscosity than the LCP. The variation of viscosity of the blends as a function of the LCP concentration at two high shear rates is shown in *Figure 2*. It can be seen that the viscosity of the blends exhibits a complex behaviour with an increase in LCP concentration. The blend containing compositions greater than 25% LCP exhibits a viscosity greater than that of the LCP, except the blend containing 50% LCP, exhibiting a viscosity slightly lower than that of the LCP. Similar observations are also made on poly(ether ether ketone) (PEEK)/LCP blends[11], where the addition of the LCP of higher viscosity to the thermoplastic polymer of lower viscosity resulted in an increase in the viscosity of the blends, with the pure LCP exhibiting the highest viscosity. The observations on the increase in the viscosity of the PPS/LCP blends on addition of LCP differ from previous studies[5–8], where the addition of the LCP resulted in a decrease of the viscosity of the blends when compared to the pure thermoplastic polymer. The PPS/LCP blends exhibit some outgassing during measurements of viscosity possibly due to some chemical reaction taking place between the LCP and PPS. However, this outgassing did not show large effects on the viscosity measurements. Studies on PPS/LCP blends by Ramanathan *et al.*[12] have also suggested some chemical interaction between these materials leading to chemical reactions, thereby resulting in blends of inferior quality.

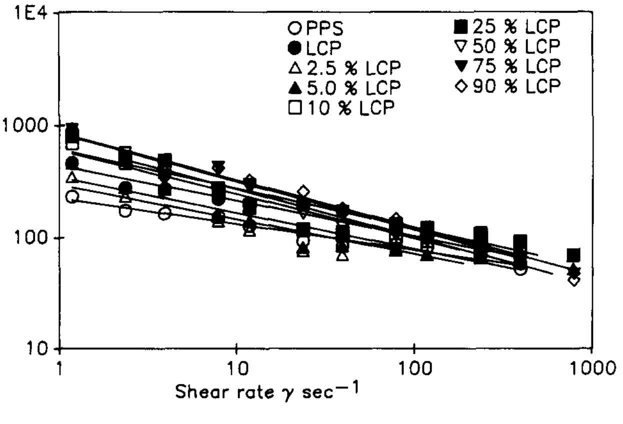

**Figure 1** Variation of viscosity with shear rate for PPS/LCP blends at 300°C

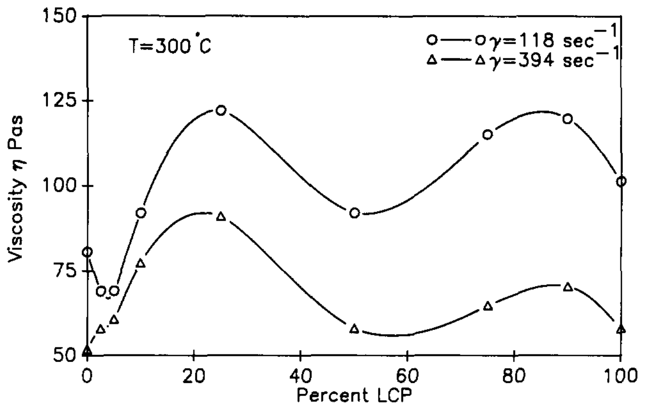

**Figure 2** Variation of viscosity with LCP concentration for PPS/LCP blends at two shear rates

It can be seen from *Figure 1* that there is no intersection between the flow curves of pure PPS and the LCP under the temperature and shear rate range studied. Tsebrenko[13], who studied flexible thermoplastic blends, has suggested that maximum fibrillation occurs in blends during shear flow when the viscosity curves of the components cross over where the viscosity ratio is equal to unity. Studies on some LCP/polymer blends, viz. the polycarbonate (PC)/LCP[6] and the PEI/LCP[7] systems, have indicated maximum fibrillation in these systems at high shear rates when the viscosity of the thermoplastic material was much higher than the viscosity of the LCP.

### *Thermal studies*

The results of d.s.c. studies on the neat polymers and their blends are shown in *Figure 3*. It can be seen that the glass transition temperatures of the individual components in the blends are not clearly distinguishable due to the close proximity of $T_g$ of both components (about 100°C). The melting endotherms of the two materials also overlap, with the melting point of the pure

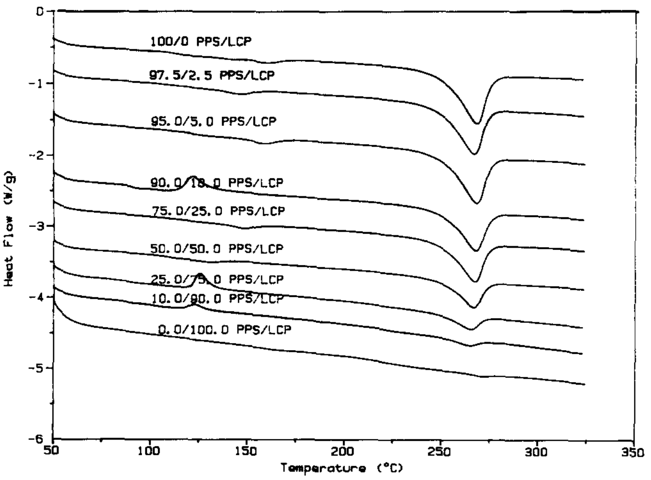

**Figure 3** D.s.c. thermograms of PPS/LCP blends at a heating rate of 20°C min$^{-1}$

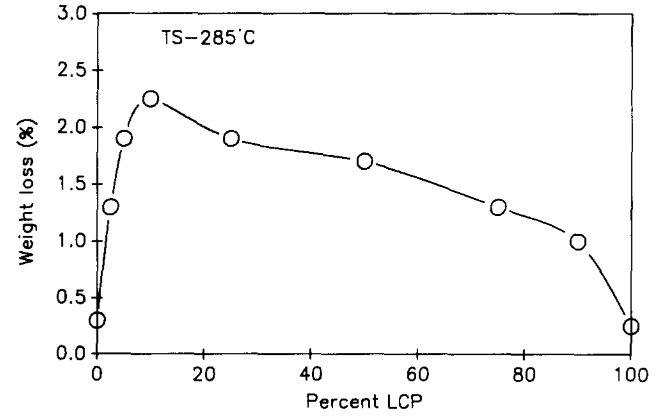

**Figure 4** Weight loss as a function of LCP concentration for PPS/LCP blends when held at a temperature of 330°C for a period of 60 min

LCP being in the range of 275°C and the PPS being around 269°C. Blends of LCP composition 10%, 75% and 90% exhibit a small exotherm at around 125°C corresponding to the crystallization temperature of PPS. The reason for the appearance of this peak only in the blends mentioned above is not clear.

The results of the thermal stability studies on the blends and pure material are shown in *Figure 4*. It can be seen from the figure that the weight loss in the blends is much higher than that in the pure materials. This poor stability of the blends may be due to the chemical interaction between the components. Such interactions between LCPs and thermoplastic polymers have been observed in PEEK/LCP blends[11], where LCP was Xydar SRT-300, and PPS/LCP blends[12]. In the latter study, dynamic mechanical measurements have been used in contrast to the capillary rheometry used in the present work.

### *Mechanical properties*

Minitensile bars of LCP/PPS blends show ductile fracture up to 10% LCP and brittle fracture at higher LCP concentrations. The variation of the break stress of the blends as a function of LCP concentration is shown in *Figure 5*. It can be seen that the break stress shows a small increase even at low LCP concentration till a concentration of 25% LCP. Then, it shows a monotonic increase at higher LCP concentrations, with the pure LCP exhibiting the highest value of break stress. Previous studies on LCP/thermoplastic polymer blends[5–9] have indicated improvement in the mechanical properties of the blends of certain compositions when compared to the homopolymers. The results obtained in the system under consideration can be interpreted based on the observed rheological behaviour. Previous studies essentially involved the blends of an LCP with a thermoplastic material where the LCP has a much lower viscosity than that of the thermoplastic material. Because of this fact LCP fibrils were formed in the matrix of the thermoplastic material, leading to composites with superior mechanical properties. In the system under consideration the thermoplastic material exhibits a lower viscosity than the LCP. Under these conditions no reinforcement of the matrix by the LCP is apparently possible. In such cases, it has been found[11] that the LCP forms globules in the matrix of the thermoplastic, which does not contribute to the increase in the mechanical properties.

The variation of the secant modulus of these blends as a function of the LCP concentration is shown in *Figure 6*. It can be seen that the secant modulus shows an increase with LCP concentration, with the pure LCP showing the highest value of the secant modulus. The observed modulus has been compared with the predicted modulus in accordance with the law of mixtures. It can be seen that the predicted modulus values are higher than those experimentally observed.

The elongation to break values of these blends as a function of the LCP concentration are shown in *Figure*

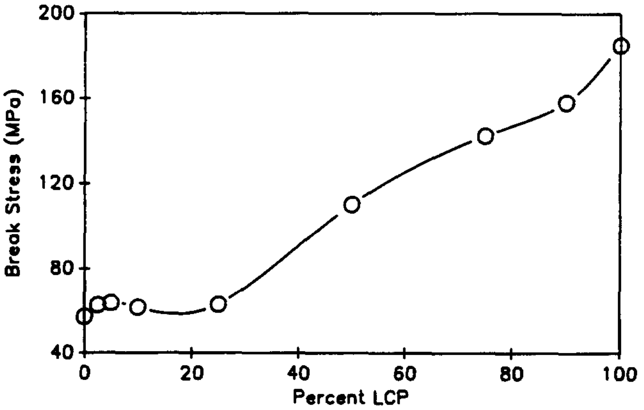

**Figure 5** Break strength as a function of LCP concentration for PPS/LCP blends injection moulded as MTBs

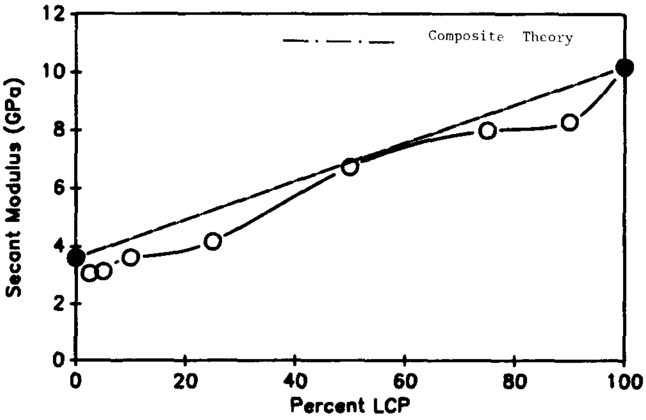

**Figure 6** Secant modulus (at 1% strain) as a function of LCP concentration for PPS/LCP blends injection moulded as MTBs

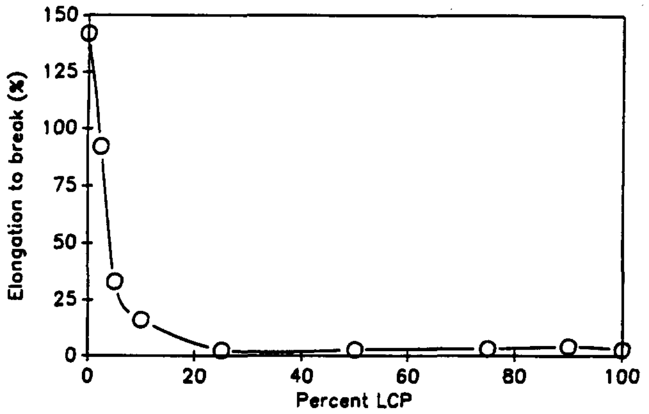

**Figure 7** Elongation to break for PPS/LCP blends injection moulded as MTBs

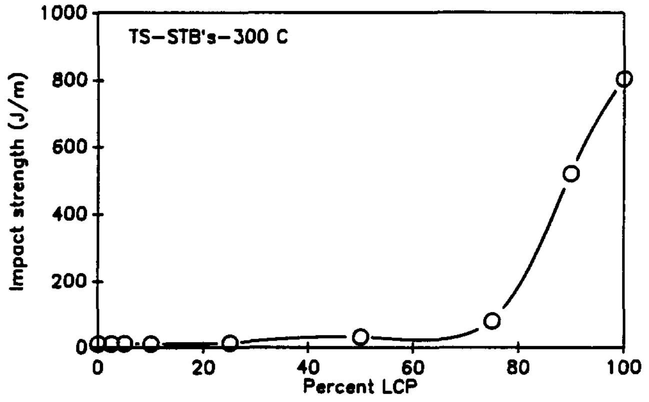

**Figure 8** Impact strength *versus* LCP content for PPS/LCP blends injection moulded as STBs

7. The elongation to break decreases with the addition of the LCP, with blends up to an LCP concentration of 10% exhibiting a ductile behaviour. The elongation to break drastically decreases in blends of LCP concentration greater than 10% LCP, with blends containing an LCP concentration of 25% and above showing a typical brittle failure. Similar observations on the decrease in the elongation to break on addition of LCP have been made by many previous workers[6,7,9].

The variation of the impact strength of the blends as a function of the LCP content are shown in *Figure 8*. The impact strength shows a very marginal increase up to a concentration of 75% LCP, when a drastic increase is noted for the blend containing 90% LCP. Once again the pure LCP exhibits the highest value of impact strength.

### *Morphological studies*

*Figure 9* shows the SEM micrographs of the skin and core regions of a 2.5/97.5 LCP/PPS blend. Few LCP droplets are present in the skin and core regions, with the average diameter of the droplets being about 8 μm in the skin and 3–15 μm in the core. In the case of the 5/95 blend shown in *Figure 10*, the skin region indicates more or less spherical domains of LCP with an average diameter of about 10 μm. The core region indicates fine spherical domains of the LCP, with the diameter of the domains being about 2–3 μm. In the case of the blend containing 10% LCP (*Figure 11*), the skin exhibits the formation of ellipsoids of LCP of average diameter 8–10 μm whereas the core exhibits the formation of globules of LCP in the PPS matrix with diameter as high as 15–20 μm. Blends containing 25% LCP exhibit a rather interesting morphology (*Figure 12*). The morphology of the skin regions indicates the formation of fine droplets of the LCP in the matrix of the thermoplastic material, with the average diameter of the droplets being around 1 μm. The core region, however, shows droplets of slightly larger diameter of about 2 μm. In the blends containing 50% LCP (*Figure 13*) the skin region indicates the formation of droplets of LCP about 3 μm. The core region exhibits a rather interesting morphology with the presence of ellipsoids and flakes of the LCP, with the average diameter of the ellipsoids being about 2 μm and that of the flakes being around 6 μm. Although the mechanical properties of these blends showed a gradual increase with LCP concentration, no fibrillation of LCP was observable in the matrix of these blends. Similar observations have been made by Vinogradov and Yarklykov[14] in their studies on polyoxymethylene–copolyamide blends, where the microstructure of the blend has been correlated to the blend viscosity and shear stress. The blend exhibiting a greater viscosity than the parent materials tended to exhibit globules of one component in the other depending on their viscosities. The blend containing 75% LCP (*Figure 14*) indicates once again the formation of ellipsoids of the LCP in the

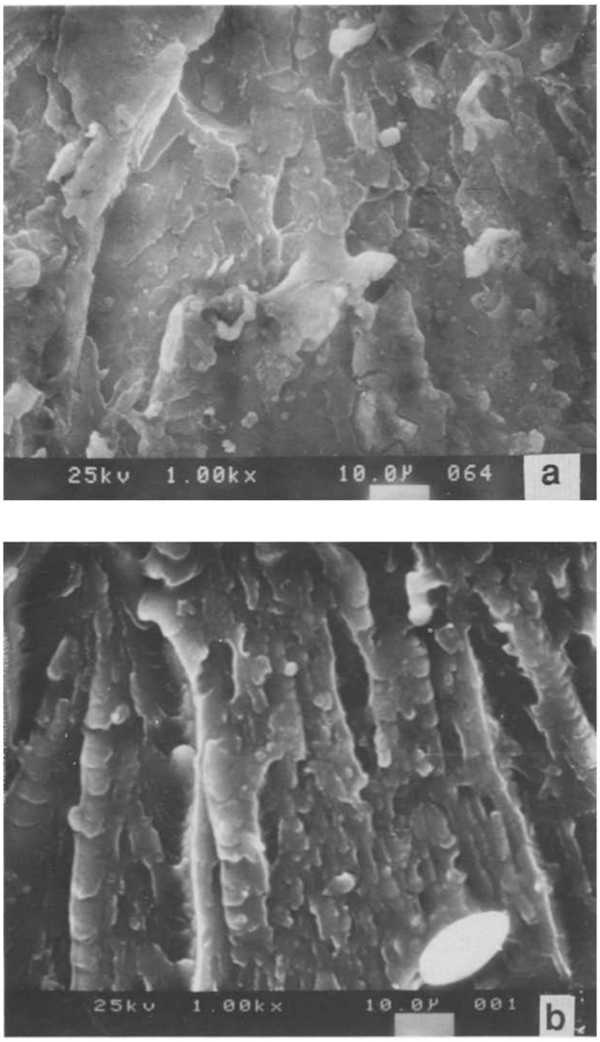

**Figure 9** SEM micrographs of a fractured surface of an MTB of a 2.5/97.5 LCP/PPS blend: (a) skin region; (b) core region

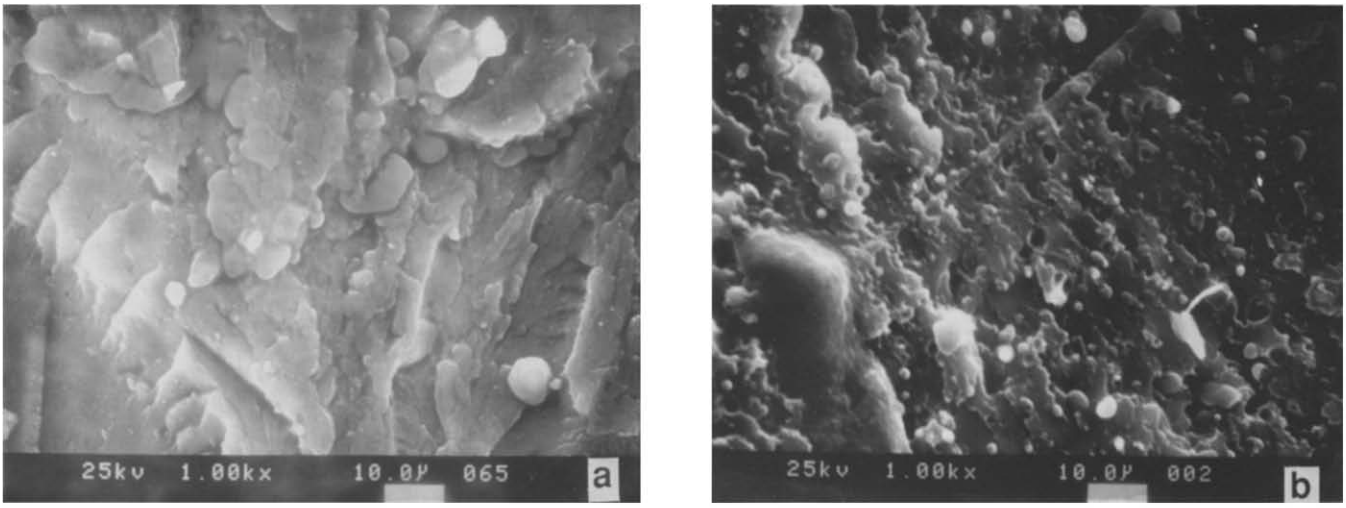

**Figure 10** SEM micrographs of a fractured surface of an MTB of a 5.0/95.0 LCP/PPS blend: (a) skin region; (b) core region

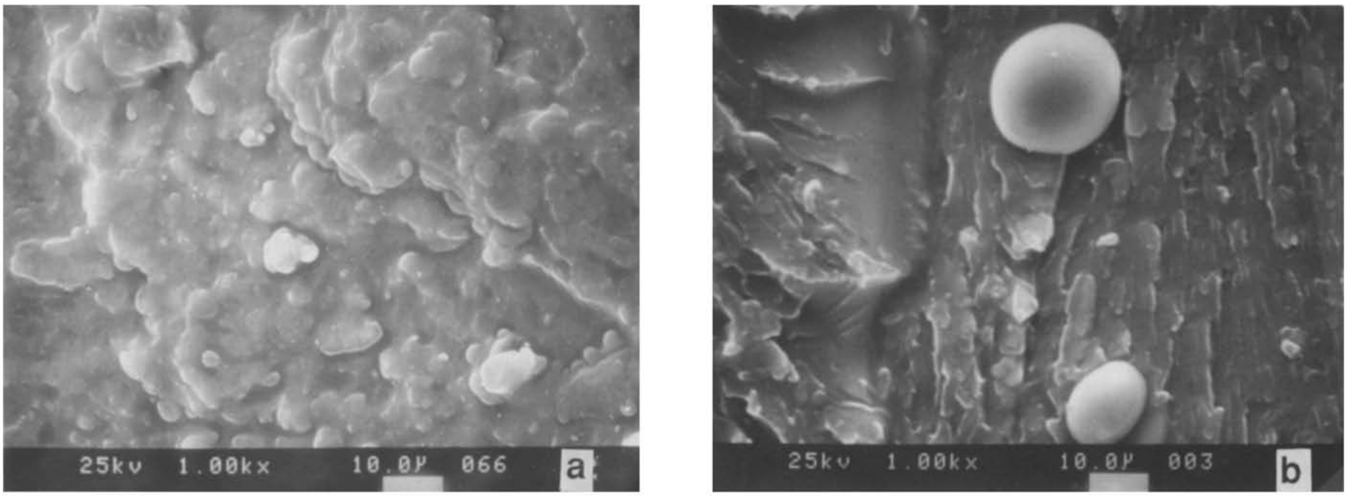

**Figure 11** SEM micrographs of a fractured surface of an MTB of a 10.0/90.0 LCP/PPS blend: (a) skin region; (b) core region

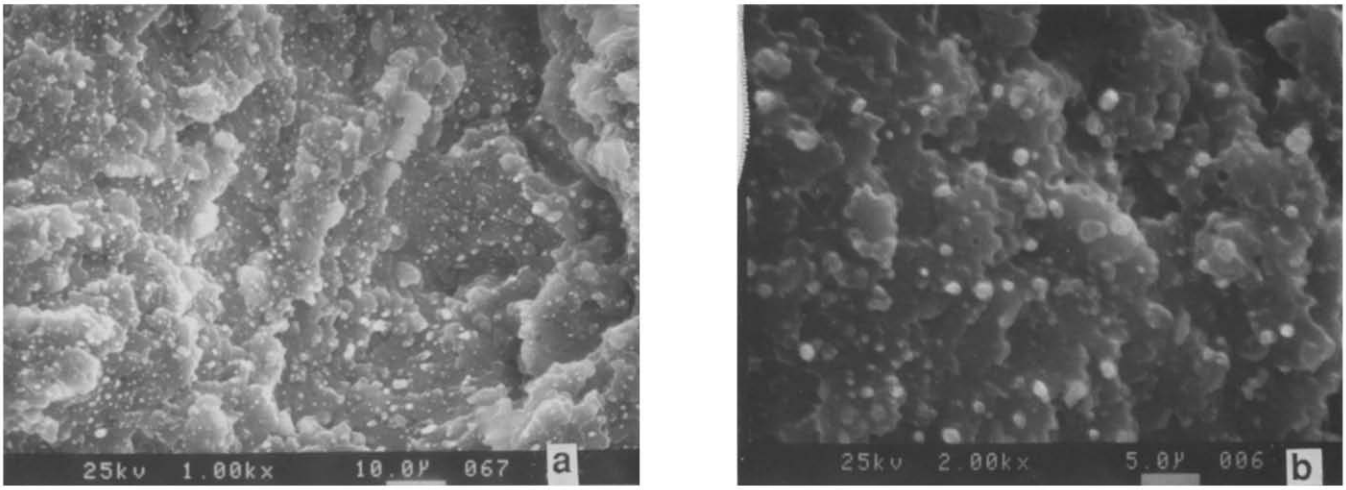

**Figure 12** SEM micrographs of a fractured surface of an MTB of a 25.0/75.0 LCP/PPS blend: (a) skin region; (b) core region

skin region of diameter 2–3 $\mu$m with the core region exhibiting ellipsoids of rather large diameter (about 10 $\mu$m). The blend containing 90% LCP (*Figure 15*) exhibits a slightly different morphology than the other blends. The skin region exhibits the formation of flakes of the LCP of about 10 $\mu$m whereas the core region indicates the formation of ellipsoids and flakes, with the average diameter of the ellipsoids being around 2 $\mu$m and that of the flakes being around 5 $\mu$m.

The distinct development of a skin–core morphology in the above blends is observable only at concentrations of LCP greater than 25%. Previous studies[7,15–20] on the

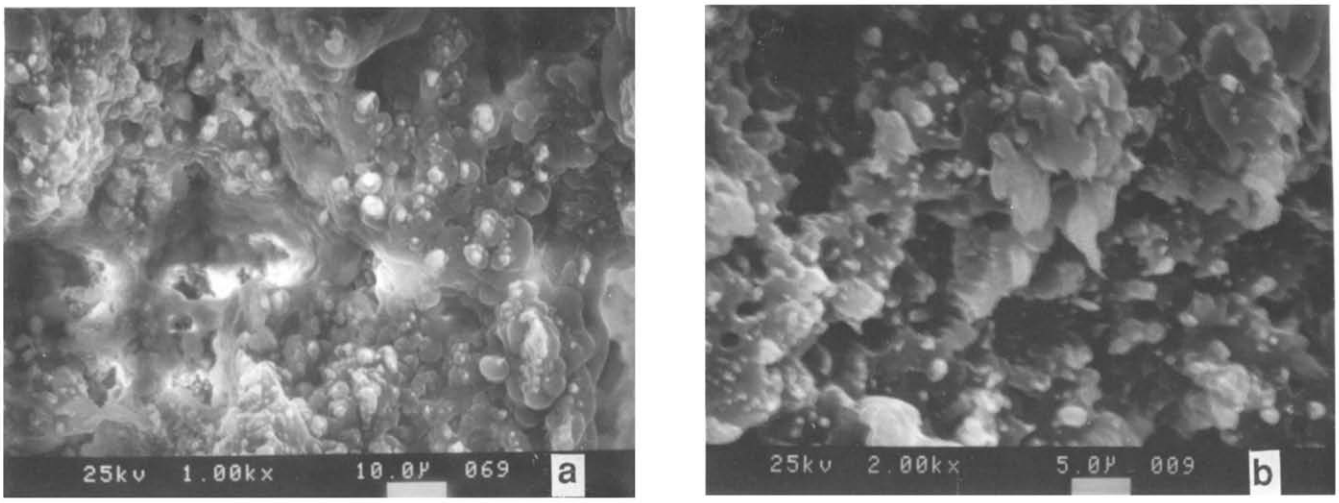

**Figure 13** SEM micrographs of a fractured surface of an MTB of a 50.0/50.0 LCP/PPS blend: (a) skin region; (b) core region

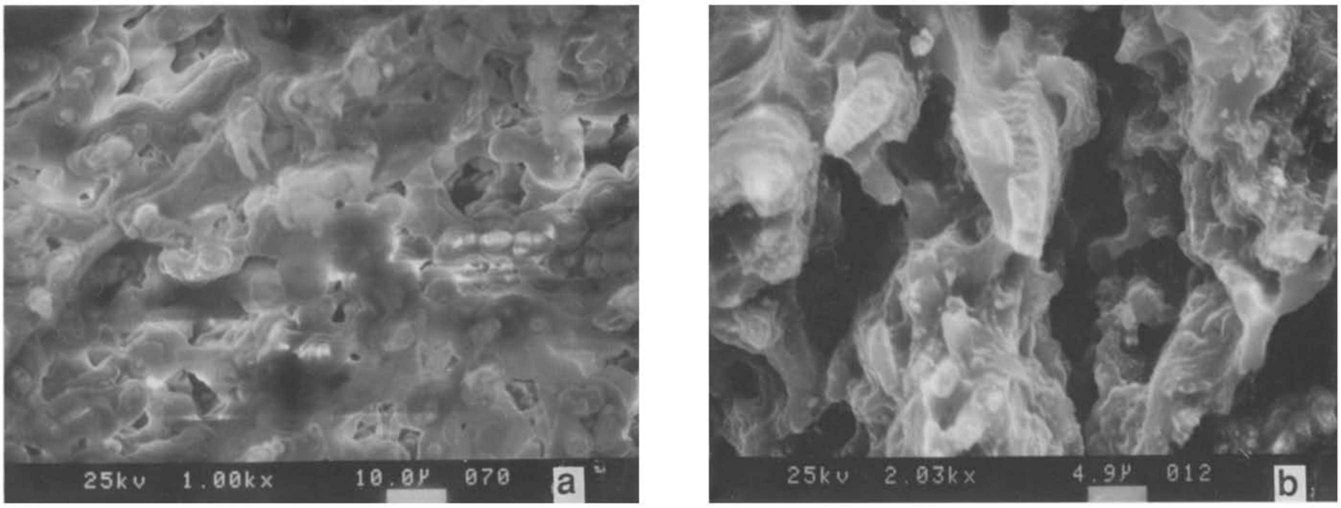

**Figure 14** SEM micrographs of a fractured surface of an MTB of a 75.0/25.0 LCP/PPS blend: (a) skin region; (b) core region

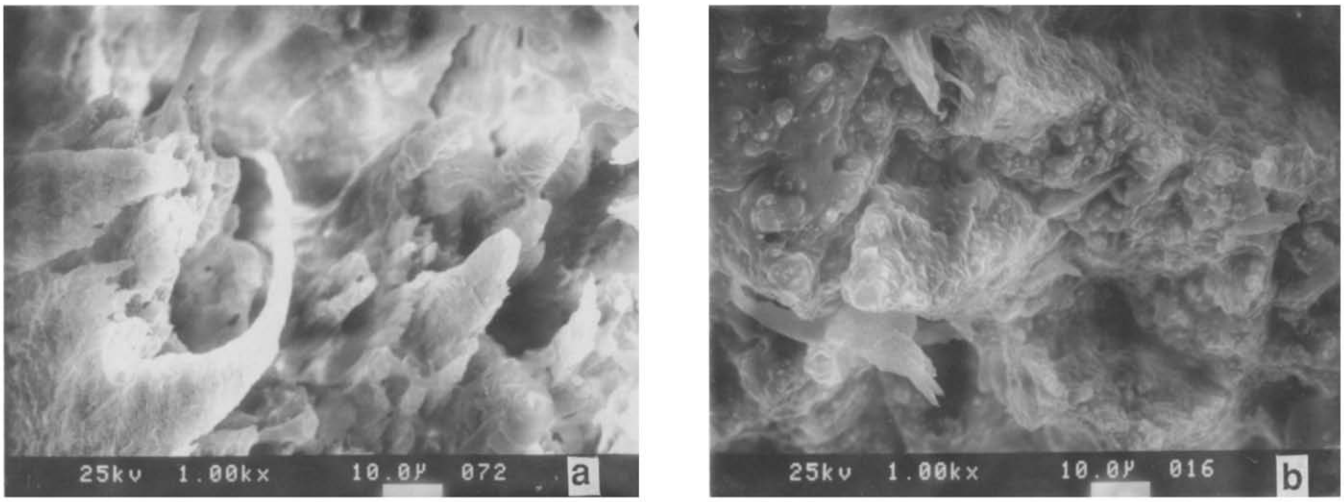

**Figure 15** SEM micrographs of a fractured surface of an MTB of a 90.0/10.0 LCP/PPS blend: (a) skin region; (b) core region

development of such morphologies in pure LCPs and thermoplastics have also indicated the formation of such morphologies during injection moulding as being due to the freezing of the orientation in the layer in contact with the mould due to the steep temperature gradients. *Figures 16–19* show the skin–core morphologies in the PPS/LCP system under consideration at LCP concentrations of 25, 50, 75 and 90%. The gradual increase in the mechanical properties of these blends when compared to the blends with lower LCP concentrations can be attributed to the

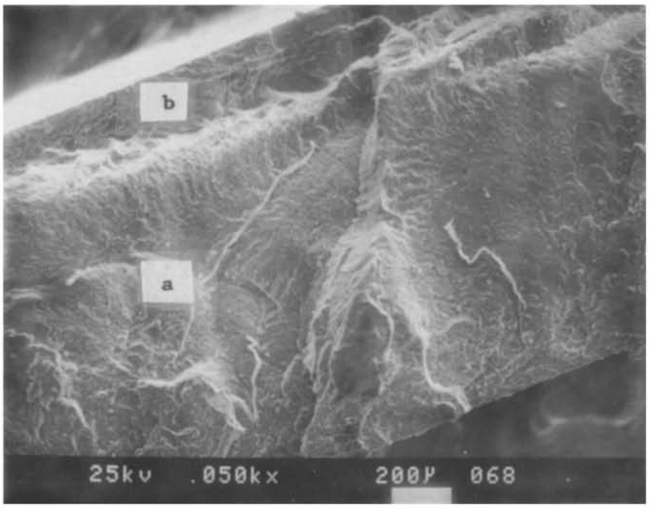

**Figure 16** Skin-core morphology of a fracture surface of an MTB of a 25.0/75.0 LCP/PPS blend: (a) core region; (b) skin region

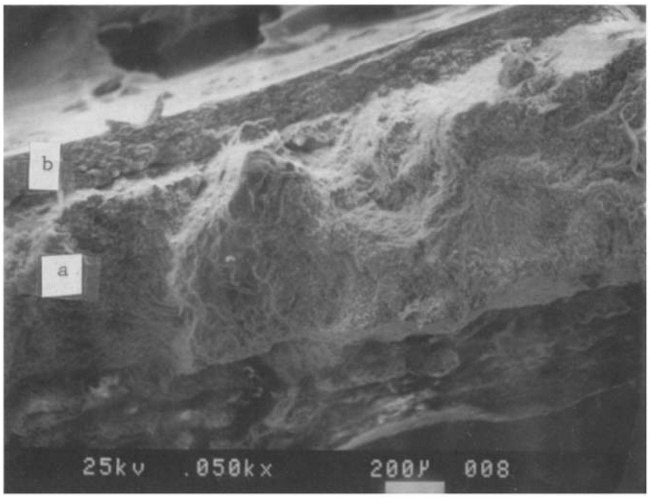

**Figure 17** Skin-core morphology of a fracture surface of an MTB of a 50.0/50.0 LCP/PPS blend: (a) core region; (b) skin region

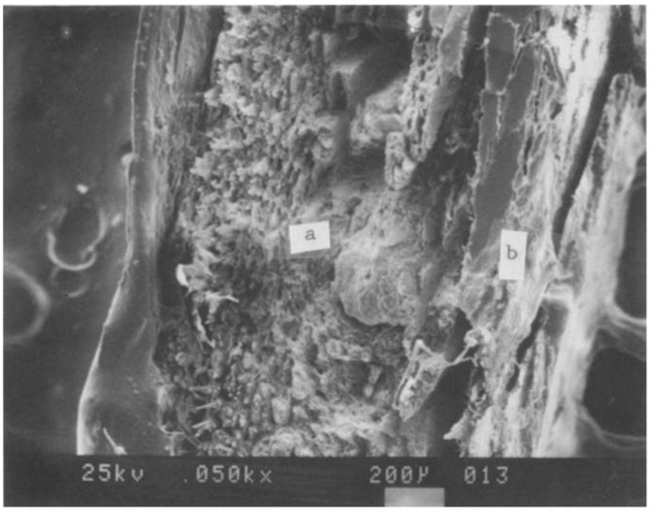

**Figure 18** Skin-core morphology of a fracture surface of an MTB of a 75.0/25.0 LCP/PPS blend: (a) core region; (b) skin region

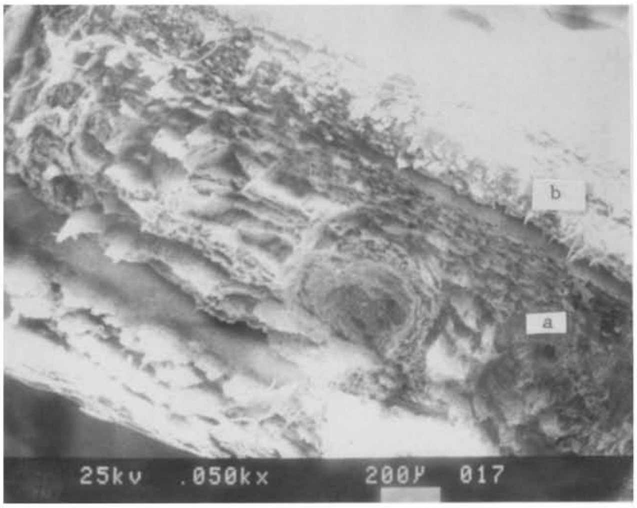

**Figure 19** Skin-core morphology of a fracture surface of an MTB of a 90.0/10.0 LCP/PPS blend: (a) core region; (b) skin region

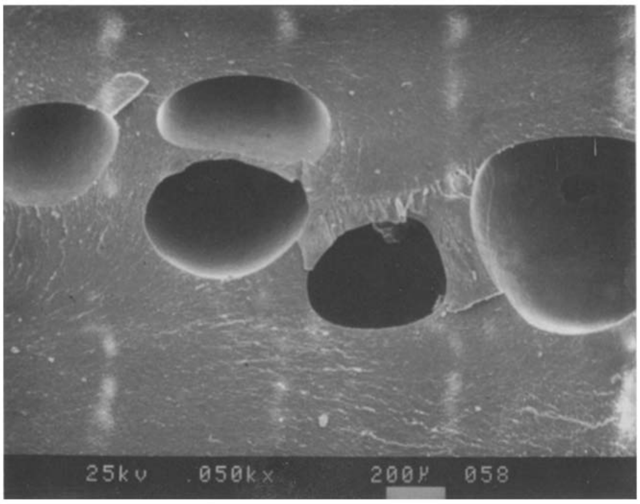

**Figure 20** Void formation in the core of an STB of a 25.0/75.0 LCP/PPS blend

formation of this morphology, with the skin region being capable of carrying a much higher stress than the core region, like in the case of a pure LCP[21].

The SEM micrograph in the core of a 25% LCP STB is shown in *Figure 20*. It can be seen that voids of rather large diameter (around 300 $\mu$m) are observable. Owing to the chemical reaction in these blends, excessive degassing takes place during processing, leading to the formation of voids in the sample[12]. Such degassing, as mentioned before, was also observable during viscosity measurements using a capillary rheometer.

### *Dynamic studies*

*Figure 21* shows the variation of the storage modulus for the blends up to an LCP concentration of 25% with temperature. The pure PPS exhibits a rather sharp decrease in the value of the storage modulus at the glass transition region corresponding to the temperature range 70–100°C. The presence of a plateau region where the storage modulus remains more or less the same is

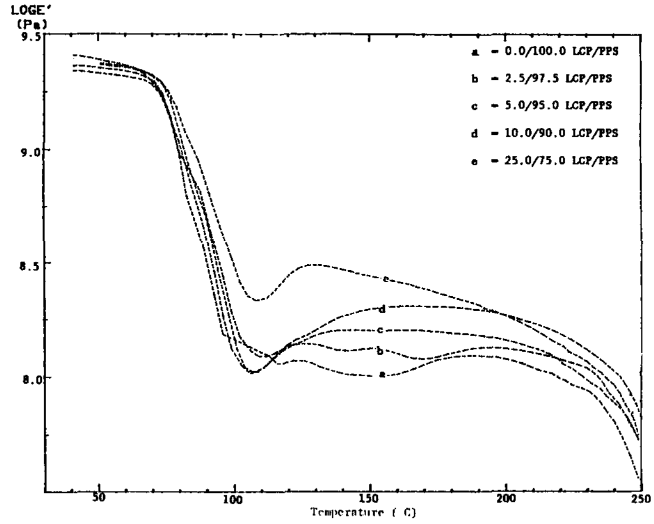

**Figure 21** Storage modulus *versus* temperature for PPS/LCP blends injection moulded as MTBs

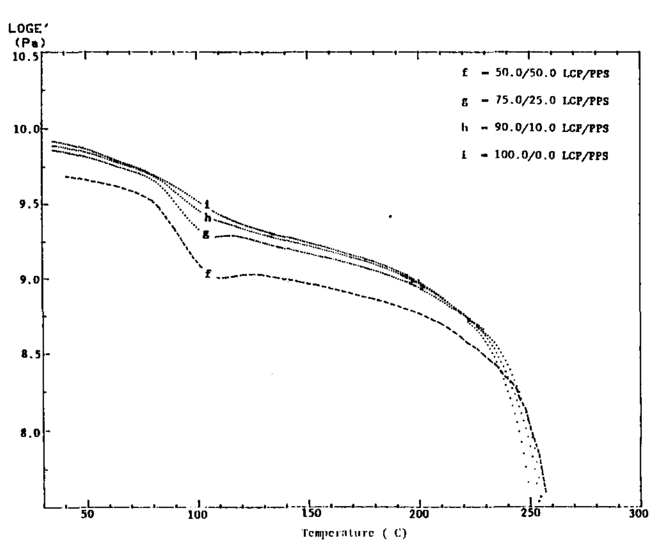

**Figure 22** Storage modulus *versus* temperature for PPS/LCP blends injection moulded as MTBs

observed at temperatures above the glass transition region up to a temperature of 240°C. The drastic fall in the modulus value at temperatures above 240°C is seen, corresponding to the onset of the melting point of the material. Blends containing higher LCP concentrations exhibit a less steep fall in the modulus value at the glass transition temperature. A shift in the plateau to higher modulus values is also observed. This trend can be attributed to the presence of the LCP of high intrinsic storage modulus in the matrix of these blends. The results for blends of LCP concentration greater than 50% and that on pure LCP are shown in *Figure 22*. These blends exhibit a much smaller decrease in the storage modulus value at the glass transition region. It must be mentioned that the glass transition temperatures of the LCP and the thermoplastic under consideration overlap and so do their melting points. The values of the storage modulus at 40°C are found to increase with LCP concentration (*Figure 23*).

Similar observations have been made by Weiss *et al.*[22,23], where the incorporation of an LCP into a matrix of a thermoplastic material has been found to yield blends with a higher storage modulus than the thermoplastic material.

The variation of the loss factor of the blends with temperature is shown in *Figure 24*. The magnitude of the loss peak and its sharpness are found to decrease with the increase in LCP content. The loss peaks are indicative of the efficiency of the material in dissipating mechanical energy, with a lower-magnitude loss peak indicating lower mechanical-energy-dissipating capacity. The temperature corresponding to the maximum of the loss factor is normally associated with the glass transition temperature, which is in the present case seen to be the same for the pure polymers and their blends. Thus, a conclusion about the compatibility of PPS and LCP cannot be made based on d.s.c. and thermomechanical analysis. However, the morphological observation shows that the pair of polymers is incompatible.

## CONCLUSIONS

Blends of PPS/LCP are studied. It has been shown that for effective reinforcement and betterment of mechanical properties the LCP must have a viscosity lower than that of the thermoplastic material at the processing temperature. This was not the case in the blends studied. The

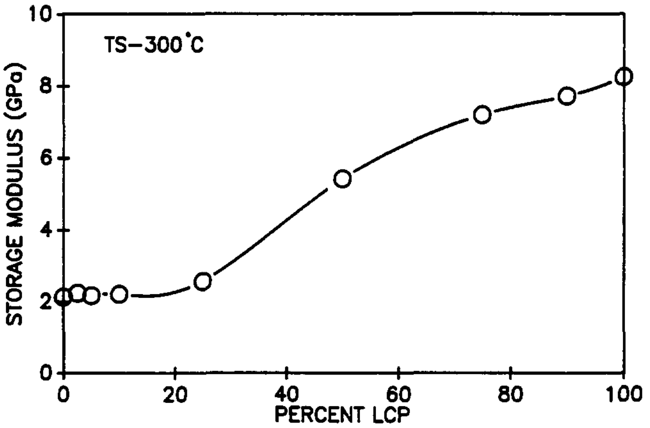

**Figure 23** Storage modulus *versus* LCP content for PPS/LCP blends injection moulded as MTBs

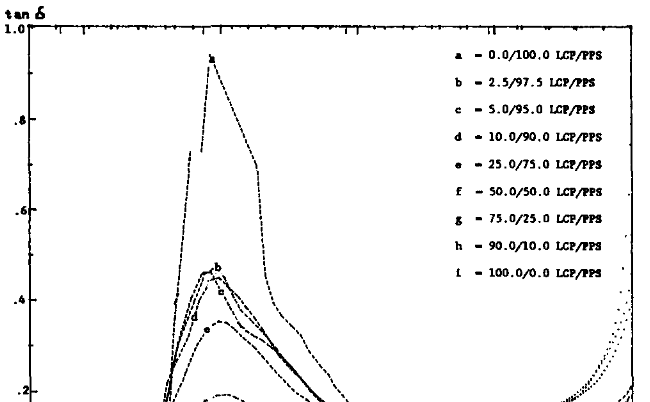

**Figure 24** Loss factor *versus* temperature for PPS/LCP blends injection moulded as MTBs

mechanical properties of these blends showed an increase with LCP concentration; however, they were lower than the values obtained in the case of the pure LCP. No fibrillation of the LCP in the matrix was found. The presence of fibres seems to be a necessary attribute for improvement in the mechanical properties. The morphological studies on these blends have indicated the formation of either ellipsoids or globules of LCP in the matrix, except in the 90% LCP blend, where flakes of LCP phase are observed. The thermal stability of these blends was found to be inferior when compared to the pure materials. The blends were found to exhibit degassing during processing, leading to void formation in the injection-moulded samples. The dynamic moduli of these blends were found to increase with LCP concentration, owing to the formation of a skin–core morphology, as has been seen from SEM studies on blends with an LCP concentration of greater than 25%.

## ACKNOWLEDGEMENT

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