Properties of a blend of poly(phenylene ether) with a liquid-crystalline polymer

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Blends of a thermotropic liquid-crystalline polymer with poly(phenylene ether) are investigated in the melt and solid state. Melt flow properties are examined using a number of different flow regimes – ranging from simple shear to flows with an extensional component. The blends are shown to be largely immiscible in the molten state, with the addition of liquid-crystalline polymer reducing the blend viscosity. This viscosity reduction is seen to be more effective in the case of flows that contain an extensional flow history. The morphology associated with these blends is oriented liquid-crystalline polymer fibrils suspended in a poly(phenylene ether) matrix. Thermal and mechanical analysis indicates that the two polymers are practically immiscible in the solid state with the possibility of slight intermixing. Crystallization data indicates that the presence of the LCP phase may encourage crystallinity of the poly(phenylene ether) phase.

(**Keywords: liquid-crystalline polymer; polymer blends; rheology; mechanical properties; immiscible blends**)

INTRODUCTION

Technological and economic imperatives in the plastics industry have led to much research and development in polymer blends. The ability to melt-blend plastics readily and inexpensively has been the impetus for much work in this area.

Utracki[1] has classified the types of possible blends according to thermodynamic considerations as miscible and immiscible. Miscible blends in which the component homopolymers are mixed on an intimate, molecular scale show properties intermediate between those of the homopolymers. Immiscible systems are multiphase and usually demonstrate properties that can vary widely from those of the two constituent homopolymers. If the materials are immiscible, much care has to be taken to define and control the blend concentrations and the thermomechanical history of the mixing and processing steps, since these aspects can strongly affect blend morphology and thus rheological and mechanical properties. This has been exploited commercially with the dispersion of fine, elastomeric particles in polymers to improve fracture toughness.

While the majority of blends studied have dealt with polymers that exhibit conventional isotropic melts, increasing interest is being directed to blends of thermoplastics with liquid-crystalline polymers (LCPs). As a class of polymers, LCPs have become available commercially only in the last few years. They consist of rigid, largely aromatic-based polymer chains, which show an anisotropic, low-viscosity melt between the melting transition and the isotropic phase. Most commercial LCPs are random copolyesters[2] and have high modulus and strength due to the high degree of orientation of the rigid chains. In addition, they have excellent chemical resistance and barrier properties typical of polyesters.

The incorporation of these materials into conventional thermoplastics has the ability to provide 'molecular reinforcement'[3] via melt-blending techniques. The low-viscosity LCP minority phase when processed under certain conditions forms stiff, fibre-like dispersions elongated in the direction of flow, called fibrils, which have the effect of stiffening a lower-modulus matrix. In this sense it is similar to oriented, chopped reinforcing fibres (such as those of glass and carbon) added to a thermoplastic material for reinforcement. However, conventional reinforcement fibres result in increased viscosity and wear of processing machines. The addition of an LCP phase leads to a decrease in viscosity (and thus increased processibility), lower wear and other improved properties such as dimensional stability[4].

It should be noted that the modulus of injection-moulded LCP is much lower than that of glass fibres (5 GPa compared to 75 GPa) and is much more temperature-dependent. However, the modulus of highly oriented LCP fibres can be around 55 GPa[5], and imposing a post-extrusion draw ratio in blend processing can lead to increased fibrillation of the LCP phase and a composite modulus some eight times greater (for a 20% LCP blend) than for a blend that is not post-drawn[6]. The combination of reinforcement in tandem with lower viscosities and other property improvements has stimulated much interest in thermoplastic/LCP blends.

Most thermoplastics have been found to be immiscible with the LCPs, although a degree of compatibility with certain LCPs that contain an ethylene terephthalate

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component has been reported with polycarbonate and poly(ethylene terephthalate) (PET)[7].

A two-phase morphology is thought to be desirable since its existence is proposed to be related to the viscosity reduction[8] and reinforcement mechanism (discussed in more detail later). Some interphase adhesion is found with certain polymers[9] and is expected to lead to improved tensile strengths. Most work has been done with the LCP as the minority phase ($<20\%$), although Jaffe[8] points out that much interest could be placed on blends where the majority component is the LCP. The addition of a thermoplastic component to the LCP could result in better properties perpendicular to the flow direction, improved fracture toughness and improved weldline strength of LCP materials.

In this work we investigate LCP blends with poly(2,6-dimethyl-1,4-phenylene ether) (PPE), a high-glass-transition-temperature thermoplastic showing good toughness, chemical and electrical properties and possessing one of the lowest specific gravities (1.06) of engineering polymers[10]. As a homopolymer its viscosity necessitates a high processing temperature and as such suffers from oxidative degradation due to the methyl groups[11], affecting its solid-state properties.

This material is rarely processed unblended. It is found to be compatible in all concentrations with polystyrene[12] and is sold commercially blended with high-impact polystryene (HIPS) by a number of manufacturers. While processibility is improved, favourable PPE properties such as modulus and heat distortion temperatures (HDT) are necessarily influenced by those of the more flexible component. This makes PPE a good candidate for blending with LCP. Such a blend has been reported in the last year by us[13] and in a very recent paper by Limtasiri *et al.*[14]. A recent conference proceeding[15] detailed studies of LCP with a commercial PPE/HIPS commercial blend – essentially a ternary blend with two miscible phases. The interest in studying a PPE/LCP blend is to develop a reduced-viscosity system that maintains the modulus and HDT of PPE and to investigate the possibility of interactions between these two aromatic polymers.

MATERIALS

The LCP used in this work is a copolyester of 73% *p*-hydroxybenzoic acid (HBA) and 27% 2,6-hydroxynaphthoic acid (HNA) sold by Hoechst-Celanese as Vectra A950 (LCP). Being largely insoluble, its precise chemical characterization is difficult, but it is believed to be a random copolymer with a degree of polymerization of about 350[16].

PPE was supplied by GE Plastics, Victoria, Australia. It was used without any further additives.

EXPERIMENTAL PROCEDURE

Prior to blending, the LCP and PPE were dried overnight under vacuum at a temperature of 120°C.

Blends of various LCP concentrations were prepared in the molten state in an instrumented Haake Internal Mixer with Banbury rotors. Consistent 50 cm^3 volumes of both neat and blended material were used to ensure that torque could be quantitatively compared between batches and hence the internal mixer could be used as a torque rheometer. Blending was performed at 320°C and at 40 rev min^{-1}. Mixing times were varied, dependent on the attainment of constant melt temperature.

Material was also prepared using a Brabender Plasticorder and a ribbon die. Scanning electron microscope (SEM) analysis of the two phases present in the ribbon extrudate was performed on fracture surfaces produced by extending the specimens to failure. The SEM used was a JEOL JSM-840 Scanning Electron Microscope.

Rheometry of the blends was undertaken with the defined flows of a Weissenberg Cone-and-Plate Rheometer and a Monsanto Instron Capillary Rheometer over a range of shear rates. In the cone-and-plate rheometer the tests were performed at 320°C using a cone angle of 3°45′ and a diameter of 25 mm. Compression-moulded discs of 0.79 mm were introduced into the preheated chamber. All samples were flushed with nitrogen during residence in the test chamber, with runs lasting typically 10–20 min. Capillary rheometry was performed using a die of 0.92 mm (L/D ratio of 22) at a melt temperature of 310°C. In this rheometer the shear stress was varied and the time to extrude a known volume of material was measured. The Rabinowitsch–Mooney procedure was used to correct shear rate. Limited quantities of sample prevented a wider range of dies being used and hence the Bagley correction was not applied.

The thermal properties of the solidified blends were characterized by a Perkin–Elmer DSC-7 to study the glass transition, melting and crystallization phenomena of the two systems. Temperature scan rates of 10°C min^{-1} for heating and 5°C min^{-1} for cooling were used. Mechanical properties of the blends were measured as a function of temperature using a Rheometrics Dynamic Mechanical Analyzer (RSA II) from ambient up to 250°C. Compression-moulded thick films were tested in dual cantilever geometry at 10 Hz and at 5°C min^{-1}.

RESULTS AND DISCUSSION

Blends of concentrations 0, 10, 20, 30, 40, 50, 75 and 100% (weight per cent of the LCP component) were prepared in the Haake internal mixer. Typical mixing curves (torque vs. mixing time) are shown in *Figure 1* for the range of blends prepared at 310°C. After about 6 min the samples appeared to be uniformly mixed and the torque stabilized to a constant value. *Figure 2* shows the value of the stabilized, plateau torque as a function of LCP content.

The plateau torque from internal mixers is a good indicator of melt viscosity[17] and has been used as such in other LCP blends[18]. A good correlation with more conventional capillary melt rheology, relating shear stress to torque and rotor speed to shear rate, has been demonstrated. As all our experiments are done at constant rotor speed, torque is a measure of viscosity under the flow conditions in the mixer (shear stress/shear rate). This is not necessarily the best way to determine viscosity vs. composition data for polymer blends, since in immiscible blends strain rate is more likely to differ across the interfaces than stress[1] and hence comparisons of viscosity for blends of varying concentrations is best done at constant stress. However, as this represents constant torque, this is much more difficult to achieve in this experimental configuration.

The level of torque reached is shown in *Figure 2* as a function of the weight per cent of LCP. According to

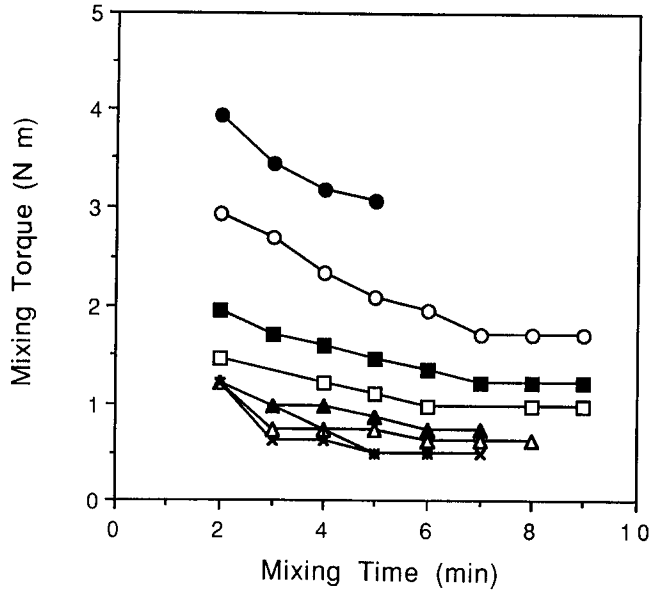

Figure 1 Mixing torque vs. mixing time for blends prepared at 320°C with the following weight per cent of the LCP component: (●) 0% (pure PPE), (○) 10%, (■) 20%, (□) 30%, (▲) 40%, (△) 50%, (×) 75%, (+) 100% (pure LCP)

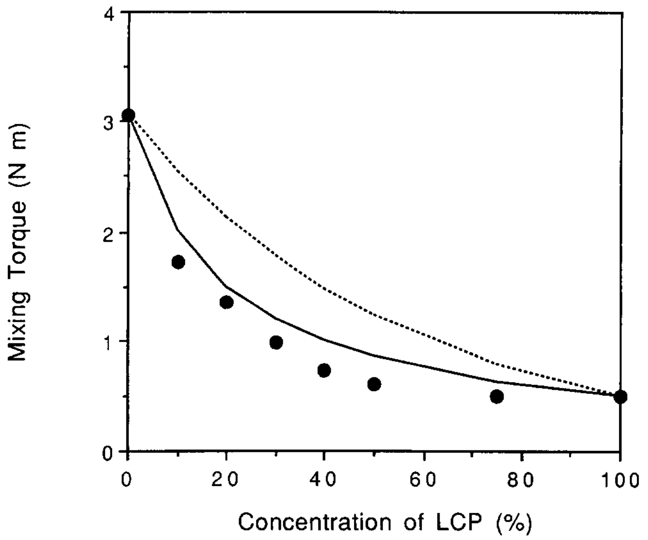

Figure 2 The plateau torque level in mixing as a function of LCP concentration (●). The two curves represent the equations from De Meuse and Jaffe[18] for a miscible melt (equation (1), dotted curve) and for an immiscible melt (equation (2), full curve)

De Meuse and Jaffe[18], the two extreme composition-dependent viscosity relationships are given by the following:

miscible melts

$$\ln \eta_{BL} = w_1 \ln \eta_1 + w_2 \ln \eta_2 \qquad (1)$$

immiscible melts

$$1/\eta_{BL} = w_1/\eta_1 + w_2/\eta_2 \qquad (2)$$

where η is shear viscosity, w the weight fraction and the subscripts 1, 2 and BL refer to pure LCP, PPE and the blend respectively.

These are included in *Figure 2* as a full curve (immiscible) and a dotted curve (miscible). The material appears to show immiscible behaviour in the molten state since equation (2) better approximates the data points than the miscible curve. The nature of the data and the shape of the immiscible plot demonstrate that the addition of small amounts of LCP results in a marked decrease in viscosity. A 50% reduction with the addition of about 12 wt% LCP is observed. Rapid decreases in viscosity with small additions of LCP are found in several other immiscible LCP systems[19,20].

The torque rheometry data showed little change in torque once the temperature stabilized. This indicated (given the dependence of viscosity on morphology) that most of the deformation in a mixing chamber takes place very early on, during the melting stage, and that continued blending does little to affect morphology. This has been reported recently by Favis[21], who made direct experimental observations of morphology *versus* mixing time in mixing chambers in other immiscible polymer blend systems.

Figure 3 shows the viscosity vs. shear-rate data at 320°C for the blends determined by cone-and-plate rheometry. Again the addition of LCP results in a decrease in melt viscosity. The flow of neat LCP and PPE and intermediate blends is non-Newtonian and decreases as a function of shear rate. This corresponds with the literature, in which both LCP[22] and PPE[23] show non-Newtonian behaviour.

However, the nature of the decrease in viscosity as a function of concentration is different in cone-and-plate geometry when compared with the internal mixer data, with small concentrations not as effective in reducing viscosity. This is best seen in *Figure 4* where the blend viscosity at 320°C (expressed as a fraction of the PPE viscosity) is plotted as a function of concentration for cone-and-plate shear rate of 1 s^{-1}. It can be seen that 35% LCP component is required to reduce the blend viscosity to half that of neat PPE (compared with 20% in the case of the internal mixer data).

Figure 5 shows viscosity vs. shear-rate data at 310°C from capillary rheometry. As with the cone-and-plate data, pseudoplastic behaviour is also observed. When compared to the cone-and-plate data (*Figure 4*), the viscosity decreases more rapidly with LCP, similar to the

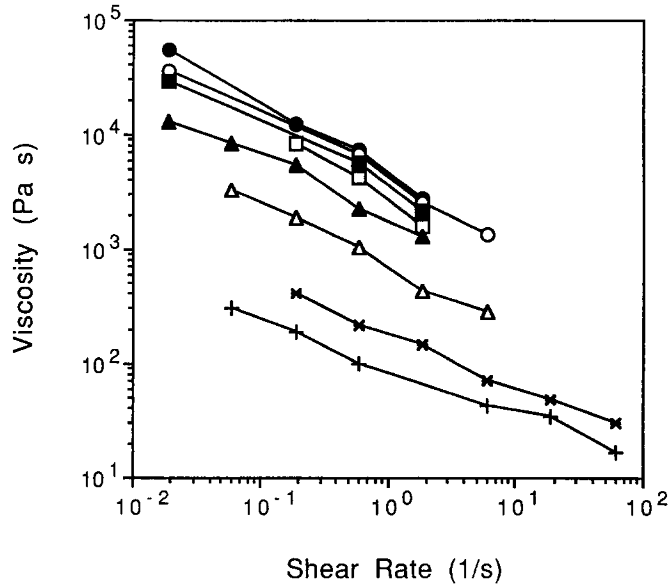

Figure 3 Shear viscosity vs. shear rate for blends of varying LCP concentrations for the cone-and-plate rheometer at 320°C. Same symbols as for *Figure 1*

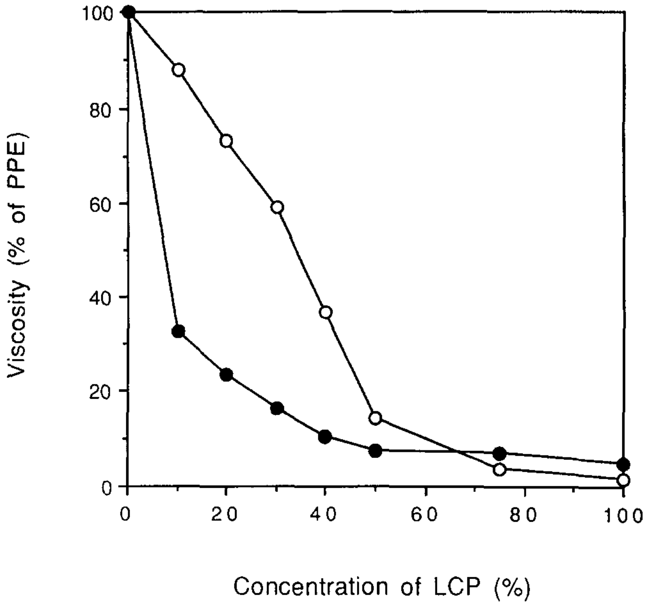

Figure 4 Cone-and-plate shear viscosity data at $\dot{\gamma} = 1\ \mathrm{s}^{-1}$, $T = 320°\mathrm{C}$ (○) and capillary rheometry shear viscosity at $\dot{\gamma} = 200\ \mathrm{s}^{-1}$, $T = 310°\mathrm{C}$ (●) plotted as a ratio of the PPE viscosity at each set of conditions

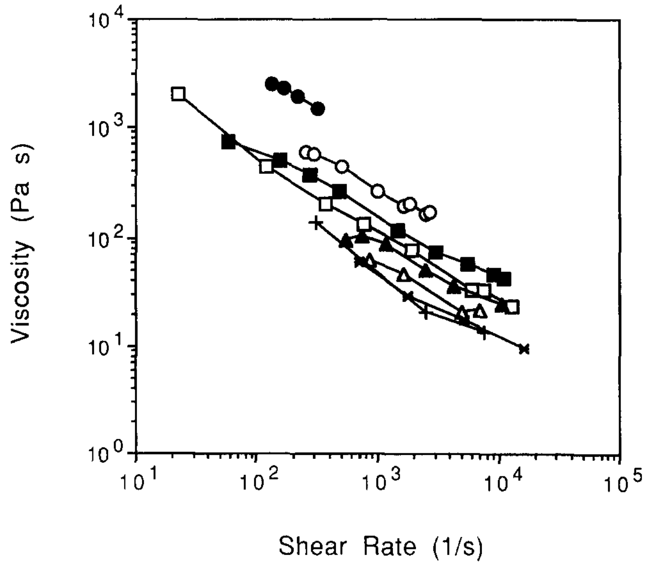

Figure 5 Capillary rheometry shear viscosity data as a function of shear rate for blends of varying LCP concentration at 310°C (same symbols as for *Figure 1*)

behaviour seen with the internal mixer in *Figure 2*. The similarity in both the capillary rheometry and internal mixer data is related to the mechanism by which the LCP materials reduce viscosity. Recent work by Limtasiri *et al.*[14] with this system also showed a decrease in viscosity. The decrease in blend viscosity they found, particularly at low blend concentrations, was not as great as in our capillary rheometry or torque data, possibly because of the lower shear rates (and hence weaker extensional flows) they employed.

Figures 6 and *7* are representative photomicrographs of the fracture surfaces of ribbons of LCP/PPE blends of various concentrations produced by the Brabender single-screw extruder with a slit die. The flow regime in this system is similar to the capillary rheometer, with elongational flow prior to the die followed by shear between the die walls. They show fibrils of LCP suspended in the PPE matrix, indicating immiscibility in the solid state. The predominant nature of the LCP is as highly elongated fibrils aligned in the direction of the extruded strip. The adhesion between the two phases appears poor, as seen by the relatively unstrained nature of the emergent fibrils and the clean hole left following the pull-out of an LCP fibril.

It is generally accepted that, in blends which include a minor phase of lower viscosity, the minor phase becomes elongated and the blend viscosity reduced[24]. It is also accepted that a lower-viscosity minor phase becomes elongated into fibrils provided there is sufficient quantity of the minority phase (greater than about 10% LCP)[25] and there are extensional flows involved – such as high rates of flow through the entrance to the capillary rheometer[26]. Indeed, elongational flows can be effective in deforming and stretching spherical droplets even if the minor-phase droplet viscosity is higher than that of the matrix polymer[27].

Taylor[28] and others[29] have studied two-phase systems of Newtonian fluids and found the viscosity ratio, interfacial tension and applied shear stress were crucial to the resultant drop morphology.

A number of workers have applied these ideas,

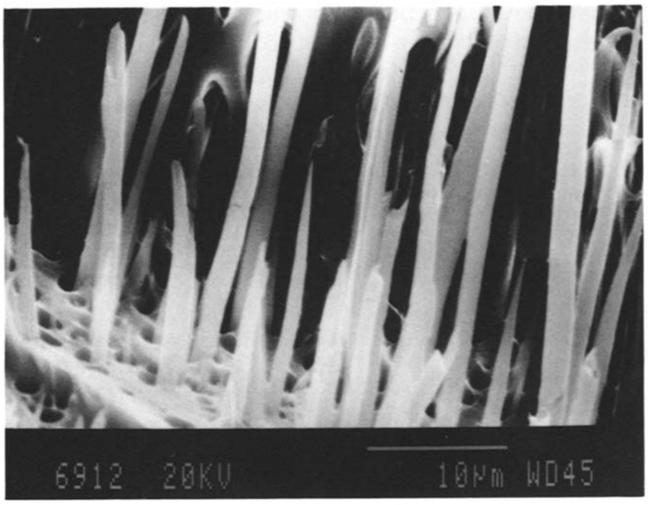

Figure 6 SEM micrographs of extrudate cut perpendicular to the flow with composition 20% LCP/80% PPE

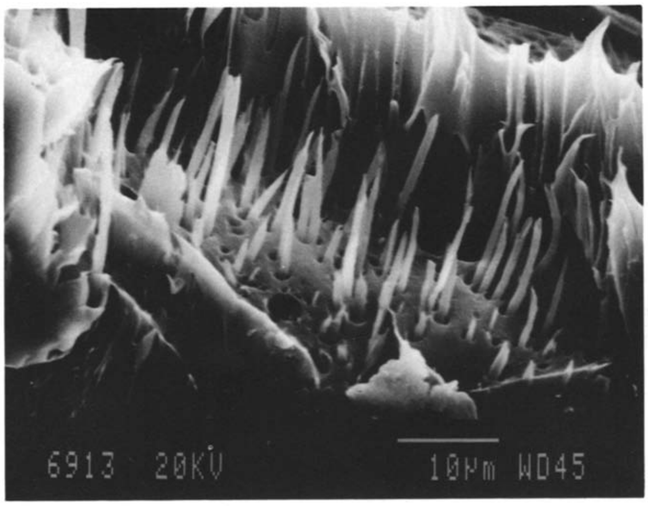

Figure 7 SEM micrographs of extrudate of composition 10% LCP/90% PPE. Same preparation procedure as *Figure 6*

including that of the importance of drop viscosity to matrix viscosity (viscosity ratio), to LCP blend systems[9,20,26]. All agree that some form of elongational deformation is necessary to produce fibrillation. Weiss *et al.*[30] showed that purely spherical droplets were formed when examining the morphology of polystyrene/LCP blends following simple shear flow. This lack of good alignment of the LCP phase in shear flow is consistent with high interfacial tension in LCP blends (demonstrated by gross phase separation, poor adhesion and a resulting lack of deformation of the LCP fibrils in the SEM photographs described above).

The results of the model Newtonian systems of Taylor[28] and Rumscheidt *et al.*[29] described above represent the simplest blend systems. In LCP/PPE and other immiscible polymer blends, both phases may often show increasingly complex non-Newtonian and viscoelastic melt behaviour. It has been reported that the main influence of the viscoelastic nature of the component melts is on the nature of droplet break-up[31]. Given that elongational flow fields are required to stretch the LCP phase, it is unclear what part a *shear* viscosity ratio plays in determining the effectiveness of LCP fibrillation, which is essentially an *elongational* flow problem. Bentley and Leal[32] found in work on simple fluids that by altering the shear viscosity ratio the effect on droplet morphology was similar, independent of whether the flow was in simple shear or extension. This could be due to the fact that shear and extensional viscosity are directly proportional in simple fluids (Trouton's rule). Direct extensional viscosity measurement is difficult in polymer melts[1], but it is known that elongational flow properties can vary widely and independently of shear properties, and we feel that determination of the extensional viscosity ratio of the two phases (or some related variable) is a neglected but important parameter in fully understanding fibril formation in these LCP blend systems.

The results shown in *Figures 2* and *4* seem to indicate that simple shear flows are less able to produce an effective viscosity reduction when compared with extensional flow regimes. Such extensional flow occurs in the entrance to the capillary rheometer and in the complex flows in the internal mixer. Data of Blizzard and Baird[19] indicated that they too found that more effective viscosity decrease occurred in capillary rheometry, especially at low LCP concentrations in an LCP/PET system. Morphological examination by them indicated that pure shear flow induced only spherical droplets and that increasing the shear rate only served to decrease particle size. However, flow through a capillary readily produced fibrils. Weiss *et al.*[30] showed that addition of small amounts of LCP to polystyrene actually *increased* the viscosity in pure shear flow, while similar additions to polystyrene in capillary flow *reduced* the viscosity. They proposed that the spherical droplets observed in shear flow would rotate and tumble, increasing viscous dissipation and increasing viscosity. Consideration of our results and those of other workers indicates that fibrillar formation (due to a component of extensional flow) is the most effective way of utilizing the LCP component to reduce blend viscosity. It should be noted that, when comparing cone-and-plate and capillary data of ourselves and other workers[30,33], the shear rates of capillary rheometry exceed those of cone-and-plate data and direct comparison at a particular shear rate is not usually possible. However, indications are that the effect of higher shear-rate cone-and-plate experiments would be merely to reduce droplet size without improving substantially the blend viscosity reduction by fibrillar formation.

The mechanism of viscosity reduction in purely shear or extensional/shear flow regimes is not clear. Most workers refer to the fact that the LCP phase 'lubricates' the flow[30]. Some[20,33] assume it is due to migration of LCP to the outside of the flow and reduction of friction at the melt/metal capillary interface. But a review by Weiss *et al.*[30] shows that differing blend morphologies (positions of fibrils) have been observed, depending on materials and processing conditions. Some LCP fibrils migrate to the core while others migrate to a region between the skin and core. Work by Gauthier *et al.*[34] states that viscoelastic fibrils should migrate to a position intermediate between skin and core and, the greater the flow rate, the closer to the capillary core they exist. Experimental evidence of these conclusions has been observed by SEM microscopy of LCP/polystyrene rheometer extrudate[35], although conflicting studies exist which indicate that the LCP fibrils migrate to the surface of injection-moulded samples[36,37]. The more complex nature of flow involved in the filling of an injection mould and the particular rheology of the components involved[35] may be responsible. An interesting study[38] in which the distribution of immiscible phases (of polyethylene and polystryene) in capillary rheometry extrudate was determined by chemical means indicated that the lower-viscosity component resided preferentially in the surface region rather than in the core. The effect was, however, very small. Thus the melt/metal interface explanation has not been demonstrated clearly and may only be a partial reason for viscosity reduction.

It seems likely that the viscosity reduction is due to some sort of interlayer slip between the phases, a slippage that seems more effective in the case of fibrils than the droplets that result from simple shear (although they too cause some shear viscosity reduction). This would occur most likely between phases that show poor adhesion. The immiscibility of PPE and LCP in the molten state would support such a proposition. It is interesting that, in some LCP systems, there is actually a viscosity minimum (blend viscosity lower than either component viscosity) attributed to such mechanisms[26].

Another factor often overlooked is the effect of the pre-blend mix prior to the viscosity measurement for immiscible polymer melts. The nature of the morphology *prior* to any extensional or shear flow in the rheometer must be considered. Even plaques used for cone-and-plate rheometry, usually platen-pressed, are subject to pre-measurement flow histories. Observations by Kiss[9] indicated that the nature of the blending (such as single screw, twin screw or in the injection moulder itself) had little effect on the final mechanical properties, although this conflicts with the results of Isayev *et al.*[38], who showed that different processing histories did affect results in the LCP/poly(ether imide) system.

It can be seen in *Figures 2* and *4* that the shapes of all flow curves look very similar above 50% LCP. That is, the viscosity of the melt is very similar to that of pure LCP, independent of the nature of the flow regime. This has been seen by other workers such as Fruitwala *et al.*[39], who found that phase inversion occurs between 40% and 60% LCP. Above the inversion, the blend takes on the fibrous nature of LCPs, as expected, given the similar viscosity. The phase inversion in these systems has not been studied in great detail. Results in other immisible blend systems have found that it depends not only on concentration but also on the viscosity ratio and shear rate[1]. However, as blends of high LCP become useful (for reasons mentioned in the Introduction), this region may become studied more. It is an interesting observation that even a 45% addition of a highly viscous, isotropic thermoplastic has little effect on the melt viscosity of an LCP. Rheological investigations into the LCP-rich end of the flow spectrum may yield further information about the rheological properties of LCPs themselves.

The next set of results relate to the compatibility in the solid state determined by thermal and mechanical means. In this work glass transitions, melting points and crystallization peaks are examined as a function of blend concentration. If the positions of these various transitions and relaxations are observed to change with concentration, miscibility on a molecular scale is assumed[40].

Figure 8 shows the d.s.c. curves for various blend concentrations (0, 10, 20, 30, 40, 50 and 75% LCP) in the region of the glass transition temperature (T_g) of PPE. It can be seen that the experimental T_g of pure PPE alone is 212°C, close to the literature value of 209°C[41].

Clearly the strength of the transition decreases on dilution with the LCP component. However, a slight decrease in position of T_g is also observed, with the T_g of the blend having a value of about 208°C for 75% LCP, although increasing signal noise prevents a very accurate determination. This lowering of T_g may indicate some miscibility, presumably shifting in the direction of that of the dispersed LCP material. Such behaviour seen by Limtasiri *et al.*[14] in the LCP/PPE system was ascribed to either miscibility or the small size of the dispersed LCP phase. The glass transition of this LCP cannot normally be seen using d.s.c. techniques, but previous dynamic mechanical results indicate that it exists at about 100°C[42] for HBA/HNA copolymers, and this has been confirmed for this precise grade of LCP by dielectric results (90°C)[43].

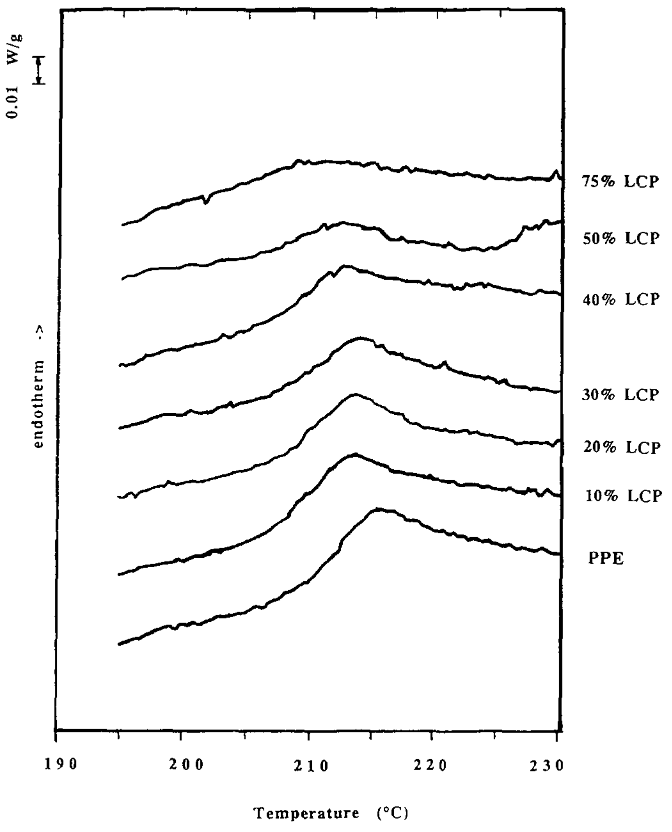

Figure 8 Differential scanning calorimetry heating traces of LCP/PPE blends in the region of the glass transition of PPE

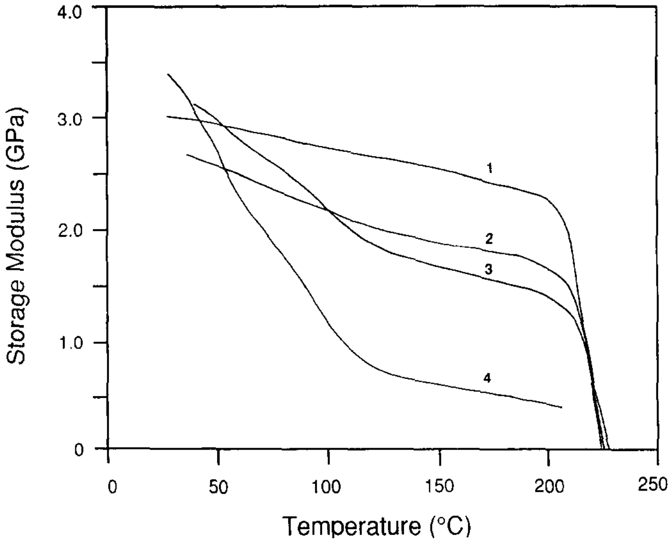

Figure 9 Dynamic mechanical storage modulus data of LCP/PPE blends as a function of temperature with the following weight per cent concentrations of LCP: (1) 0% (pure PPE), (2) 20%, (3) 40%, (4) 100% (pure LCP)

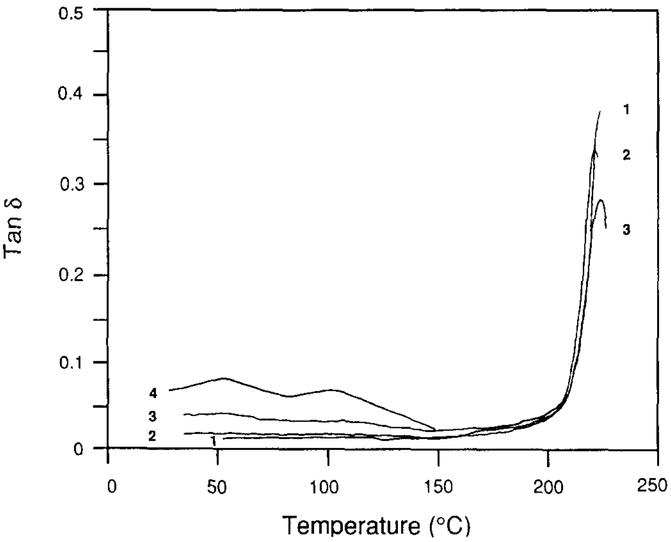

Figure 10 Dynamic mechanical loss (tan δ) as a function of temperature for LCP/PPE blends (same numbering as *Figure 9*)

Therefore, any partial miscibility would be expected to decrease the blend glass transition. The continued presence of a PPE T_g close to the T_g of pure PPE material indicates that PPE exists as essentially a separate phase with some dissolved LCP component. This is confirmed by the dynamic mechanical data shown in *Figures 9* and *10* in which the storage modulus (E') and the ratio of storage to loss modulus (tan δ) are shown as functions of temperature for LCP blend concentrations (0, 20, 40 and 100% LCP), respectively. It can be seen that in the mechanical loss spectra the PPE T_g remains strong and essentially constant in position. It is difficult to scan temperatures higher than the T_g since PPE-rich samples lose their mechanical integrity just above T_g. This very strong T_g is seen in *Figure 9* as the dramatic loss in modulus. Clearly any decrease in T_g is better seen in d.s.c. where dimensional integrity of the sample is not required. In any event, any miscibility is low. The glass transition can be seen in *Figure 10* as a peak at 100°C, as expected. A lower-temperature, secondary relaxation based around 55°C has been assigned previously to localized motion of the naphthyl group[44]. The strength of the LCP glass transition decreases rapidly in *Figure 10* with addition of PPE. This is related to the nature of the LCP glass transition, as well as to pure dilution effects with increasing PPE.

Given the highly oriented nature of the polymer chains, the mechanism of an LCP glass transition is somewhat different than the increased mobility and free volume experienced by randomly coiled chains, such as PPE. Work by Green *et al.*[42] compared the strength of the relaxation in shear and extensional modes. The T_g relaxation is seen to be stronger in shear mode where, given the highly oriented nature of the chains, shear or sliding between chains will be the dominant deformation mechanism, and this greater shear mobility between chains describes the nature of the glass transition.

The storage modulus change is quite interesting as a function of concentration (*Figure 9*). The rapid modulus decrease at about 220°C T_g is seen in the blends with a high PPE component. Blends with sufficient LCP (above about 40%) are found to show the quite rapid decrease in modulus seen in pure LCP. Within the LCP curve one can see the decrease as T_g, as well as at the β relaxation (50°C). It can be seen that, although the dynamic mechanical analyser was only available in the super-ambient mode, the decrease has commenced, even below 30°C. This is indicative of the γ relaxation, due to the motion of the benzoic acid moieties. The continual drop of the LCP modulus over the wide temperature range (even well below T_g) is understandable when one considers that the secondary relaxations are basically limited motions of the same movement of the main chain which results in the glass transition at higher temperatures. It is interesting to observe a cross-over point in moduli of pure PPE and blends near room temperature. The higher modulus of the LCP is only able to be reflected in an improvement at room temperature over the blend modulus for LCP concentrations greater than 20%, otherwise the lower PPE modulus dominates. (It should be noted that the samples discussed here were produced by compression moulding and the LCP phase lacks the high degree of orientation that would be induced in polymer processing that involved higher shear rates and elements of elongational flow.) Higher concentrations of LCP have reduced moduli compared to pure PPE owing to the rather more rapid decrease of LCP modulus in the 100–180°C region.

The positions of the LCP melting peaks were examined from comparative d.s.c. scans (*Figure 11*). Care was taken to produce specimens with the same thermal history since annealing below and above T_m can result in a complex range of physical and chemical modifications of the crystal structure of the LCP, allowing the formation of crystals due to increased movement of the chains or increase in the degree of polymerization in the solid or liquid state[45].

The position of the melting endotherm is not seen to change in position greatly with addition of PPE, although a very slight decrease can be discerned before noise at very low LCP concentrations makes a definite assignment difficult. A melting peak for PPE is not seen. Crystallinity has been observed in the as-received PPE with a reported T_m of between 257°C[7] and 267°C[11]. Because of the small difference between T_g and T_m, there is little time to crystallize and the material is usually classed as amorphous.

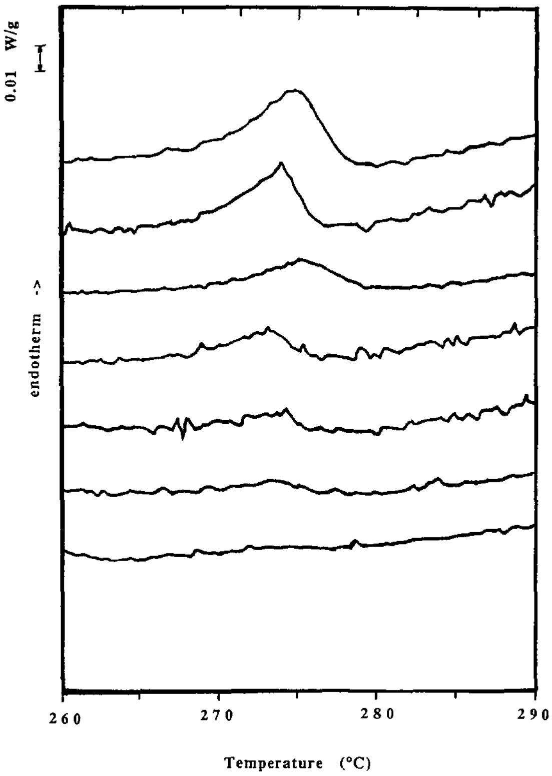

Figure 11 Differential scanning calorimetry heating traces of various LCP/PPE blends in the region of the melting transition of the LCP component

The recrystallization peaks upon cooling the various blends are shown in *Figure 12*. In each case the samples were held at 300°C for 5 min after heating and cooled at 5°C min^{-1}. The pure LCP shows a crystallization point maximum of about 234°C, similar to that reported in such systems[46]. It was not seen to move very much with addition of PPE. It appears from the melting and crystallization data that the LCP phase is only very slightly invaded by a PPE component.

In the 50% LCP blend a sharp series of peaks occurred at about 232°C. These peaks were found to be repeatable for a number of experiments. It is proposed that these are due to induced crystallization peaks of the PPE phase, occurring, as one would expect, between the T_m (267°C) and the T_g (212°C) of the PPE phase. Similar results have been seen in other LCP/thermoplastic blends where the thermoplastic phase was PET[47] or nylon-6[48] and the crystallinity of the thermoplastic phase was increased. The situation with PPE is slightly different because we are reporting the presence of a crystallization endotherm existing where previously (in the pure PPE form) none existed. This is ascribed to the highly oriented, fibrillated LCP phase promoting crystallization by providing nucleating sites or the oriented sites forming templates for crystallization of the thermoplastic phase to occur. Clearly such mechanisms are of interest since the

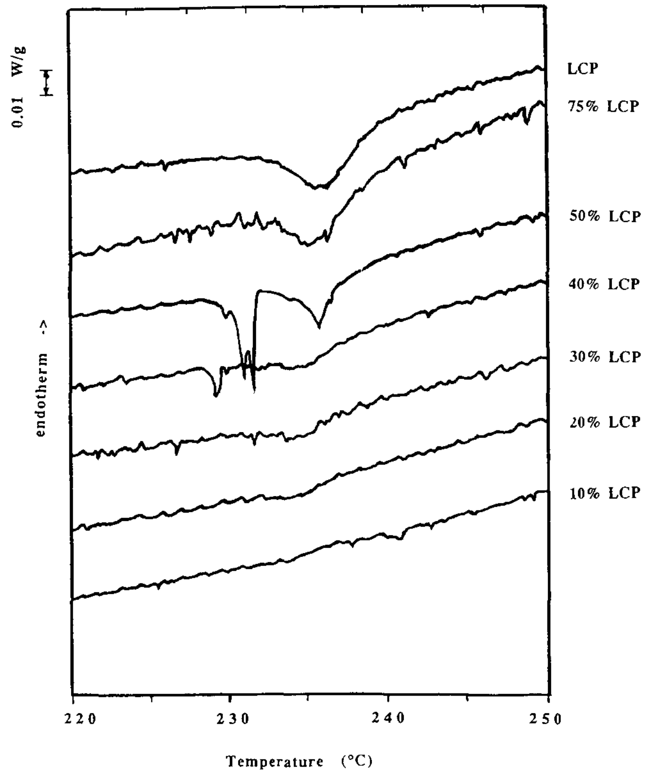

Figure 12 Differential scanning calorimetry cooling traces of various LCP/PPE blends in the region of the recrystallization temperature of LCP

possibility of property enhancement due to induced crystallinity exists. The explanation that the peaks relate to LCP crystallization at greater degrees of undercooling seems less likely. The reason why 50% PPE seems to be an optimal concentration for inducing crystallization and why there are multiple peaks is not yet understood. One possibility is that a certain concentration of LCP is required to effectively nucleate the crystallinity. Perhaps at very high concentrations of LCP insufficient PPE exists to produce a measurable crystallization exotherm. Such multiple peak behaviour has been seen by us in other LCP blend systems[49].

CONCLUSIONS

The addition of liquid-crystalline polymer to the highly viscous PPE is seen to be advantageous. The addition of LCP decreases blend viscosity, aiding processing and reducing potential thermal degradation of the temperature-sensitive PPE matrix by allowing processing at lower temperatures.

In the molten state the blends are immiscible and the nature of the viscosity–concentration relationship is related to the flow regime. All regimes (cone-and-plate, capillary flow and torque rheometry) show a monotonic decrease in viscosity with the addition of LCP. The viscosity decrease in simple shear (cone-and-plate) was not as effective in reducing viscosity as in the other flow regimes. The strong correlation in behaviour of the data from the capillary and torque rheometers indicates that the presence of extensional flow is important in enhanced viscosity reduction. Fibrils of liquid-crystalline polymer oriented in the direction of flow were observed for flows with an extensional shear flow history. The nature of the viscosity reduction is proposed to be largely due to interlayer slip of the phases. This would be more effective in the case of fibrils that arise due to elongational flow than for spherical particles often seen in blends undergoing simple shear flow.

Thermal and mechanical testing show that the materials are practically immiscible in the solid state. A slight intermixing of phases may have occurred; however, glass transitions, melting exotherms and recrystallization exotherms are greatly unaffected over the wide range of concentrations studied.

Interesting crystallization behaviour was observed for the 50% LCP/50% PPE blend in which reproducible, sharp crystallization peaks were found below the crystallization temperature of the LCP. We propose that these are due to crystallization of the PPE phase, possibly initiated by some template or nucleating effect of the LCP phase. Such behaviour has been seen only rarely in other LCP blends and may be desirable in improving blend properties.

Mechanical properties inferred from the storage modulus results show that the presence of LCP reinforces blends at room temperature. However, owing to the constant, steady decrease in LCP modulus with temperature, the modulus of the blend becomes dominated by the stiffness of the PPE phase, which essentially reinforces the LCP material at higher temperatures.

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REFERENCES

1 Utracki, L. A. 'Polymer Blends and Alloys', Hanser, New York, 1989
2 Noel, C. and Navard, P. *Prog. Polym. Sci.* 1991, **16**, 55
3 Takayanagi, M., Ogata, T., Morikawa, M. and Kai, T. *J. Macromol. Sci.–Phys.* (*B*) 1980, **17**(4), 591
4 Apicella, A., Nicodemo, L., Nicolais, L. and Weiss, R. A. in 'Handbook of Polymer Science and Technology' (Ed. N. E. Cheremisinoff), Marcel Dekker, New York, 1989, Ch. 20
5 Sarlin, J. and Tormala, P. *J. Appl. Polym. Sci.* 1990, **40**, 453
6 Weiss, R. A., Chung, N. S. and Dutta, D. *Polym. Prepr.* 1989, **30**(2), 544
7 Zhuang, P., Kyu, T. and White, J. L. *Polym. Eng. Sci.* 1988, **28**, 17
8 Jaffe, M. Proc. 2nd Int. Congr. on Compatibilizers and Reactive Polymer Alloys, New Orleqns, Louisiana, 7–9 March 1990, pp. 243–252
9 Kiss, G. *Polym. Eng. Sci.* 1987, **27**(6), 410
10 Brydson, J. A. 'Plastic Materials', Butterworth Scientific, London, 1982
11 Dick, J. 'Compounding Materials for the Plastics Industry', Noyes, New Jersey, 1987
12 MacKnight, W. J., Karasz, F. E. and Fried, J. in 'Polymer Blends' (Eds D. R. Paul and S. Newman), Academic Press, New York, 1978, Vol. I
13 Turek, D., Simon, G. P. and Tiu, C. Proc. 5th Natl Conf. on Rheology, Melbourne, 27–29 June 1990, pp. 119–122
14 Limtasiri, T. and Isayev, A. I. *J. Appl. Polym. Sci.* 1991, **42**, 2923

15 Crevecour, G. and Groenickx, G. Proc. IUPAC Symp. on Speciality Polymers, Singapore, 7–9 November 1990, pp. 78–79
16 Windle, A., Viney, C., Golombok, R., Donald, A. M. and Mitchell, G. R. *Faraday Discuss. Chem. Soc.* 1985, **79**, 55
17 Goodrich, J. E. and Porter, R. S. *Polym. Eng. Sci.* 1967, **7**, 45
18 De Meuse, M. T. and Jaffe, M. *Mol. Cryst. Liq. Cryst. incl. Nonlin. Opt.* 1988, **157**, 535
19 Blizzard, K. G. and Baird, D. G. *Polym. Eng. Sci.* 1987, **27**(9), 653
20 Beery, D. and Siegmann, A. *Polym. Eng. Sci.* 1991, **31**(6), 451
21 Favis, B. D. *J. Appl. Polym. Sci.* 1990, **39**, 285
22 Wissbrun, K., Kiss, G. and Cogswell, N. *Chem. Eng. Commun.* 1987, **53**, 149
23 Lee, H., Stoffey, D. and Neville, K. 'New Linear Polymers', McGraw-Hill, New York, 1967
24 Barid, D. G. and Ramanathan, R. in 'Multiphase Macromolecular Systems' (Ed. B. M. Culbertson), Plenum Press, New York, 1989
25 Isayev, A. and Modic, M. *Polym. Compos.* 1987, **8**(3), 158
26 La Mantia, F. P., Valenza, A., Paci, M. and Magagnini, P. L. *Polym. Eng. Sci.* 1990, **30**(1), 7
27 Han, C. D. 'Multiphase Flows in Polymer Processing', Academic Press, New York, 1981
28 Taylor, G. I. *Proc. R. Soc.* (*A*) 1934, **146**, 501
29 Rumscheidt, F. D. and Mason, S. G. *J. Colloid Sci.* 1961, **16**, 238
30 Weiss, R. A., Huh, W. and Nicolais, L. *Polym. Eng. Sci.* 1987, **27**(9), 684
31 Han, C. D. and Funatsu, K. *J. Rheol.* 1978, **22**, 113
32 Bentley, B. J. and Leal, L. G. *J. Fluid Mech.* 1986, **167**, 241
33 La Mantia, F. P., Valenza, A., Paci, M. and Magagnini, P. L. *J. Appl. Polym. Sci.* 1989, **38**, 583
34 Gauthier, F., Goldsmith, H. L. and Mason, S. G. *Trans. Soc. Rheol.* 1971, **15**(2), 297
35 Weiss, R. A., Huh, W. and Nicolais, L. in 'High Modulus Polymers' (Eds A. E. Zacharides and R. S. Porter), Marcel Dekker, New York, 1988
36 Joseph, E. G., Wilkes, G. L. and Baird, D. G. *ACS Polym. Prepr.* 1983, **24**(2), 304
37 Siegmann, A., Dagan, A. and Senig, S. *Polymer* 1985, **26**, 1325
38 Isayev, A. I. and Swaminathan, S. Proc. 3rd Annu. Conf. on Advanced Composites, Detroit, Michigan, 15–17 September 1987, pp. 259–267
39 Fruitwala, H., Kohl, A., Chung, N. and Weiss, R. Proc. 2nd Int. Congr. on Compatibilizers and Reactive Polymer Alloys, New Orleans, Louisiana, 7–9 March 1990, pp. 253–258
40 Fried, J. R. in 'Developments in Polymer Characterization–4', Applied Science, London, 1990, Ch. 2
41 Manson, J. A. and Sperling, L. H. 'Polymer Blends and Composites', Plenum Press, New York, 1976
42 Green, D. I., Davies, G. R., Ward, I. M., Alhaj-Mohammed, M. H. and Abdul-Jawad, S. *Polym. Adv. Technol.* 1990, **1**, 41
43 Simon, G. P. unpublished data
44 Blundell, B. J. and Buckingham, K. A. *Polymer* 1985, **26**, 1623
45 Economy, J. in 'Liquid Crystal Polymers' (Eds R. A. Weiss and C. K. Ober), American Chemical Society, Washington, DC, 1990
46 De Meuse, M. T. and Jaffe, M. *Polym. Adv. Technol.* 1990, **1**, 81
47 Sharma, S. K., Tendolkar, A. and Misra, A. *Mol. Cryst. Liq. Cryst. incl. Nonlin. Opt.* 1988, **157**, 597
48 Takayanagi, M., Ogata, T., Morikawa, M. and Kai, T. *J. Macromol. Sci.-Phys.* (*B*) 1980, **17**(4), 591
49 Simon, G. P. and Narasimhan, V. unpublished data