

Skin-core morphology of *in situ* composites based on polycarbonate and a liquid crystalline polymer

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The outstanding mechanical properties of an engineering liquid crystalline polymer (LCP) can be attributed to the self-reinforcement effect due to its rigid rod-like molecular structure [1-4]. High strength and high stiffness liquid crystalline polymer fibres, e.g. Kevlar and Vectran have been developed and commercialized [5, 6]. Recently there has been increasing interest in blending thermotropic liquid crystalline polymers with conventional isotropic polymers. Liquid crystalline polymer fibre reinforcement can be formed *in situ* in an isotropic polymer matrix via a melt blending process [7-26]. The structure and morphology of the *in situ* composites may be controlled by varying the processing conditions and rheological history of the blends. Blends of LCPs with conventional polyesters [7, 8], nylon [9], polycarbonate [10-13], polystyrene [11, 14], polypropylene [15, 16], polysulphone [17], poly[ether imide] [18] and poly[phenylene sulphide] [19] have been studied. For extrusion-blended materials, the structure and mechanical properties were found to be closely related to the extrusion conditions, in particular the draw-down ratio. Most researchers have attempted to explain the changes in mechanical properties in terms of the morphology of the LCP phase in the blends, with the most widely used techniques to study the morphology being scanning electron microscopy (SEM) and X-ray diffraction (XRD) [7, 12].

Transmission electron microscopy (TEM) has been widely used to study the crystalline structure of liquid crystalline fibres [4, 6, 20, 21] and the morphology of multiphase polymer systems [22]. Analysis has revealed detailed information on the crystalline structure of aramid and thermotropic liquid crystalline polyester fibres and the development of skin-core morphology of such fibres [4, 21]. These findings were related to the properties and sample processing conditions.

The work reported in this letter is concerned with the application of the TEM technique to the analysis of blends of a liquid crystalline polymer and polycarbonate. The microstructure and morphology

of the blends, in particular the development of *in situ* LCP fibrils in the polycarbonate matrix during melt extrusion, was examined. TEM analyses have indicated that there is a differentiation in the fibril morphology at the skin and core region of the extrudates. It is understood that these fibrils are ultimately responsible for the reinforcement effects in such *in situ* composites. Hence the molecular ordering and geometric morphology of these fibrils affect significantly the mechanical properties, such as the strength and stiffness of the blends.

The blending of a main chain thermotropic liquid crystalline polymer (Vectra B950, Hoechst Celanese) and a bisphenol-A polycarbonate (Lexan 151, General Electric) was carried out using a co-rotating twin screw extruder, the processing details having been described elsewhere [12]. Blends of two different compositions (10 wt% and 30 wt% of LCP in polycarbonate) were prepared in the present study and the draw-down ratio was kept constant at about 12. The extrudates obtained, typically about 1 mm in diameter, were embedded in a cold-curing Spur resin of suitable hardness. Ultra-thin sections (thickness <100 nm) of the blends were cut using a diamond knife on a Reichert Jung Ultracut-E ultramicrotome. The cutting was carried out longitudinally perpendicular to the direction of drawing with ultra-thin sections from both the outer skin and the inner core region being prepared.

The ultra-thin samples of these blends were examined using a 200 kV Hitachi 8100 STEM operated under TEM mode. A low electron beam dose was used to avoid beam damage on the polymers. Bright field images of the *in situ* composites were obtained without any staining processes. Selected area diffraction patterns were obtained from areas of 500 nm in diameter.

Fig. 1 shows the TEM bright field images obtained from a blend containing 10 wt% LCP. TEM micrographs were taken of the ultra-thin samples sectioned from the skin and the core regions of the extrudate. A distinct two-phase structure was observed in the blend with the LCP phase dispersed

within the polycarbonate matrix. High-contrast TEM images were observed without using any sample staining procedure because of the relatively large difference in electron density in these two polymers. A higher electron density would be expected in the LCP phase since it is a fully aromatic copolyester amide and has a highly ordered molecular structure. The formation of *in situ* LCP fibrils in the direction of extrusion and drawing is evident from these micrographs indicating that an *in situ* fibre reinforced composite was produced, though morphological differences between the skin and core regions were noticeable. The LCP phase appears mostly fibrous with occasional particle morphology in the skin region of the extrudate. The fibrils are mostly longer, smaller in diameter and well defined as shown in Fig. 1a and b. The diameter of these fibrils ranges from tens of nanometres to 300 nm. Fig. 1c and d show that a fibrous LCP phase was also formed in the core region of the extrudate. However, these fibrils are less well-defined and tend to be thicker and shorter compared to those formed in the skin region. Typical diameter ranges from 200 to 500 nm. Furthermore, a significant amount of the LCP is in the form of ellipsoidal or spherical particles in the core region. This skin-core morphology is most likely due to the differences in the extent of shear and extensional flow experienced by the dispersed LCP phase.

Drastic skin-core differentiation in the phase morphology was also observed in blends containing 30 wt% of LCP as shown in Fig. 2. Well-defined fibrils with relatively uniform length and diameter are formed in the extrusion and drawing direction in the skin region of the extrudate. These fibrils are typically of about 100 nm in diameter and are uniformly dispersed in the polycarbonate matrix (Fig. 2a and b). The fibrils formed in the core region, on the other hand, are much less uniform and tend to be thicker and shorter, as can be seen from Fig. 2c and d. The diameter of the fibrils is averaged at around 300 nm, which is three times thicker than those formed in the skin region. Similar to that observed earlier in the blend containing 10 wt% LCP, substantial amounts of spherical and ellipsoidal LCP particles are found in the core region of the blend containing 30 wt% LCP. This shows that LCP fibrils formed in the core region of the extrudate are less in number and of poorer quality. It is therefore implied that the fibrils formed in the skin region have greater reinforcement effects on the polycarbonate matrix since they have a higher aspect ratio and possibly better mechanical properties due to the higher degree of molecular orientation [1–3]. More quantitative information on the crystalline structure and skin-core morphology of the *in situ* composites will be discussed later in the results obtained using the selected area electron diffraction (SAD) tech-

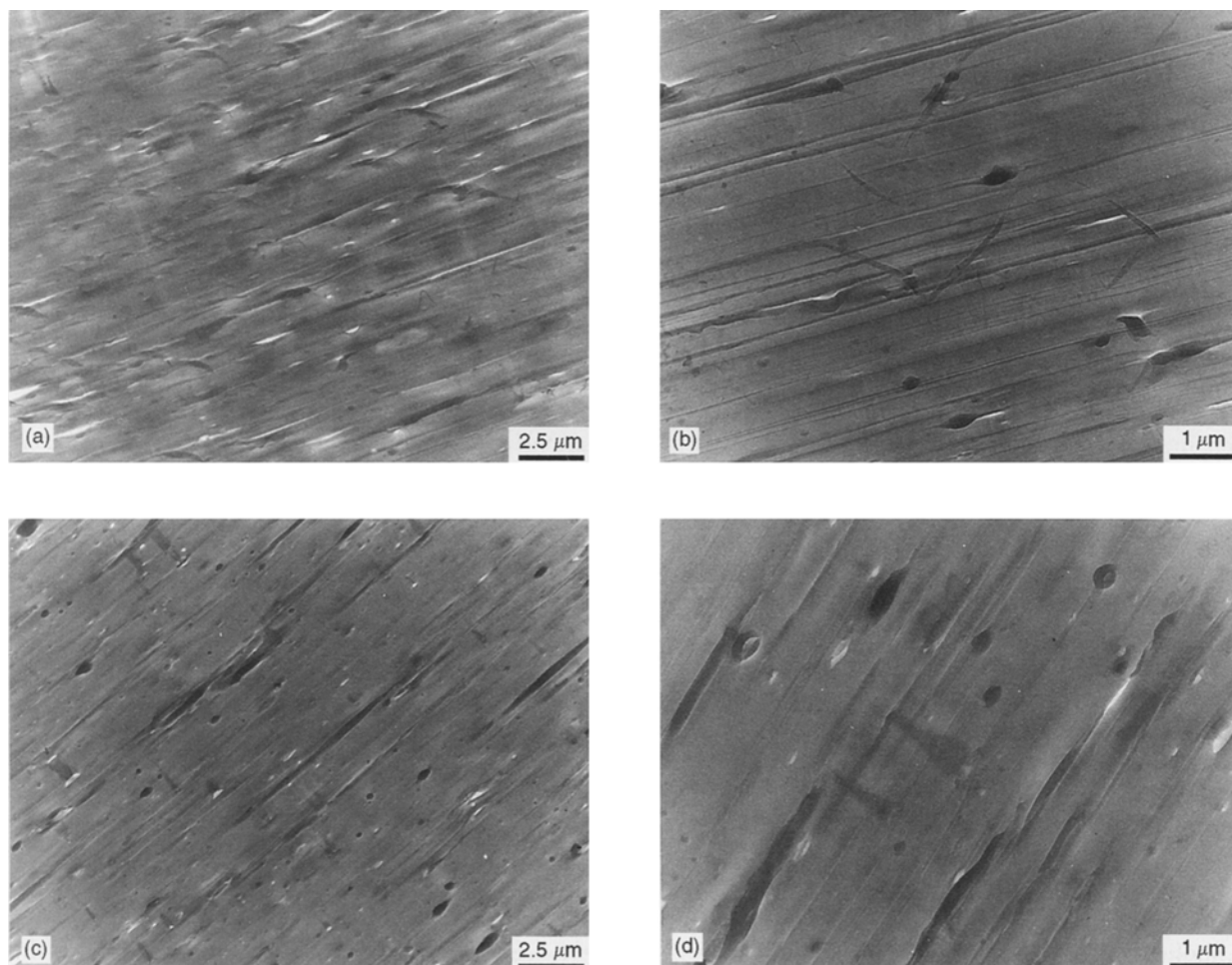


Figure 1 Bright field TEM micrographs of the *in situ* composite containing 10 wt% LCP: (a) and (b) skin region; (c) and (d) core region.

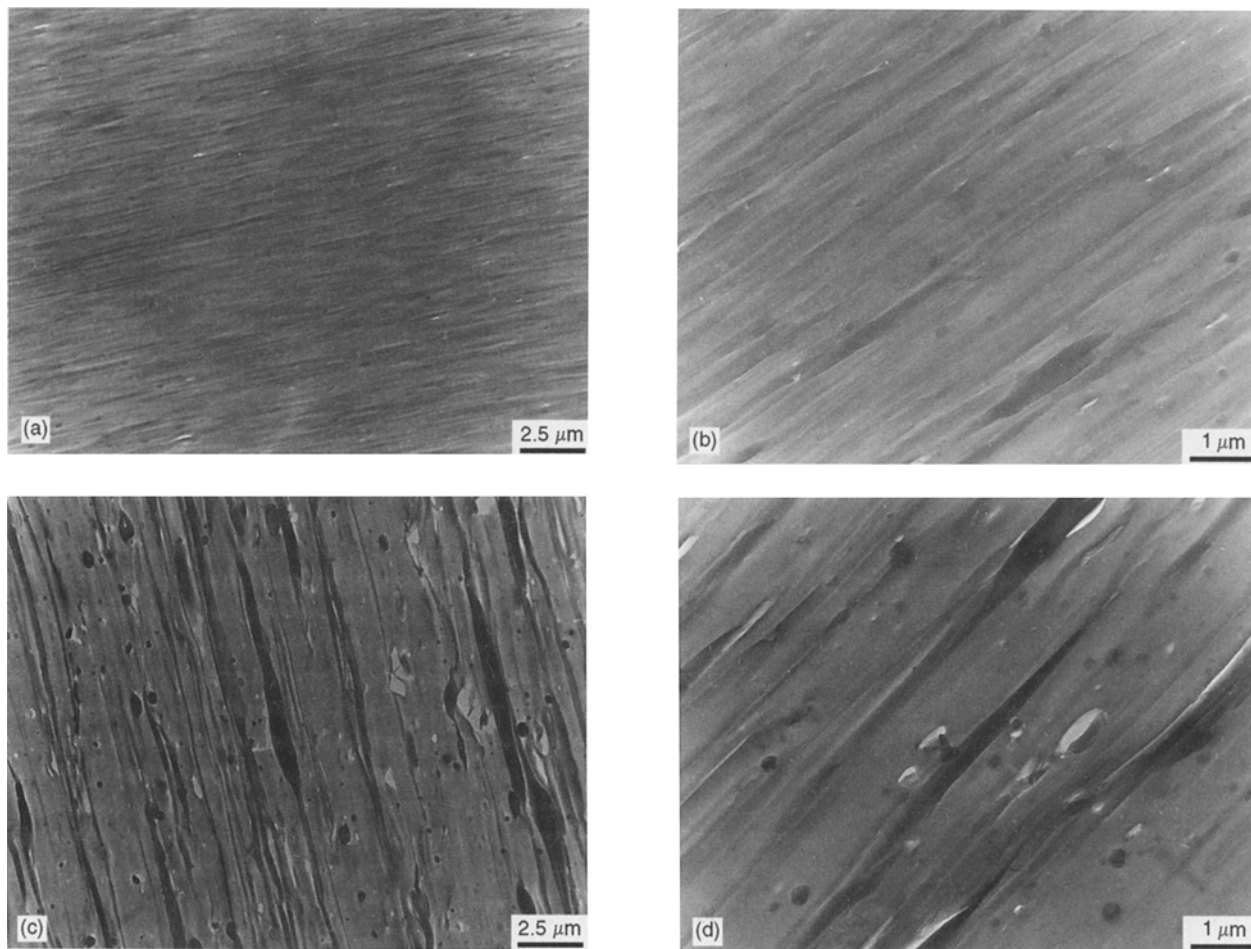


Figure 2 Bright field TEM micrographs of the *in situ* composite containing 30 wt% LCP: (a) and (b) skin region; (c) and (d) core region.

nique. In fact, the skin–core differentiation phenomenon has been reported in pure LCPs, such as aramid fibres [21], thermotropic LCP extrudates [4, 6] and injection moulded objects [4, 23]. The high degree of molecular orientation in the skin was attributed to the high shear strain rate and fast cooling rate experienced in this region. In particular, it was found that the melt flow of an LCP through a restricted channel, such as the capillary die of an extruder, was typically in a plug-like form with a rather flat velocity profile [24, 25]. This means that only the region near the wall of the die set or spinneret is subjected to a high shear rate, and the core region of the extrudates or fibres experiences little shear. In the case of an *in situ* composite extrudate, a two-phase polymer blend, similar higher shear was experienced in the skin region during extrusion, and hence the LCP phase there would be extended into finer and longer fibrils with a higher degree of molecular orientation than those in the core region. Furthermore, this highly ordered fibrous structure in the skin was subsequently “frozen-in” in the polycarbonate matrix due to the faster cooling rate, while the extended LCP phase in the core region would have more time to relax back into a less-ordered structure.

Fig. 3 gives the selected area electron diffraction (SAD) patterns obtained from the skin and core

regions of the two blends. All of the diffraction patterns indicate that the LCP phase has a preferred molecular orientation in the direction of extrusion and drawing. In fact, these diffraction patterns are similar to those obtained from a melt-spun high-strength/high-stiffness thermotropic LCP fibre [4, 6]. However, Fig. 3 also reveals that the LCP fibrils in the skin region give sharper electron diffraction patterns showing a higher degree of preferred orientation in the fibre direction. It should be pointed out that due to the small diameter of the fibrils, the diffraction patterns obtained from a selected area of 500 nm in diameter are more likely representations of the average molecular orientation of several fibrils. It is also worth mentioning that the skin–core differentiation in the phase morphology is more prominent in the blend containing the higher percentage of LCP. This was clearly observed from both the bright field TEM images (Figs. 1 and 2) and the selected area diffraction patterns (Fig. 3) of the materials. The phenomenon is not unexpected since during extrusion the flow of the pure LCP tends to have a plug-like velocity profile whilst the flow of the isotropic polycarbonate should follow a parabolic profile [26]. It is therefore expected that the blends with higher LCP content should render the velocity profile more plug-like. Lower core shear rate results which is in turn responsible for the larger skin–core

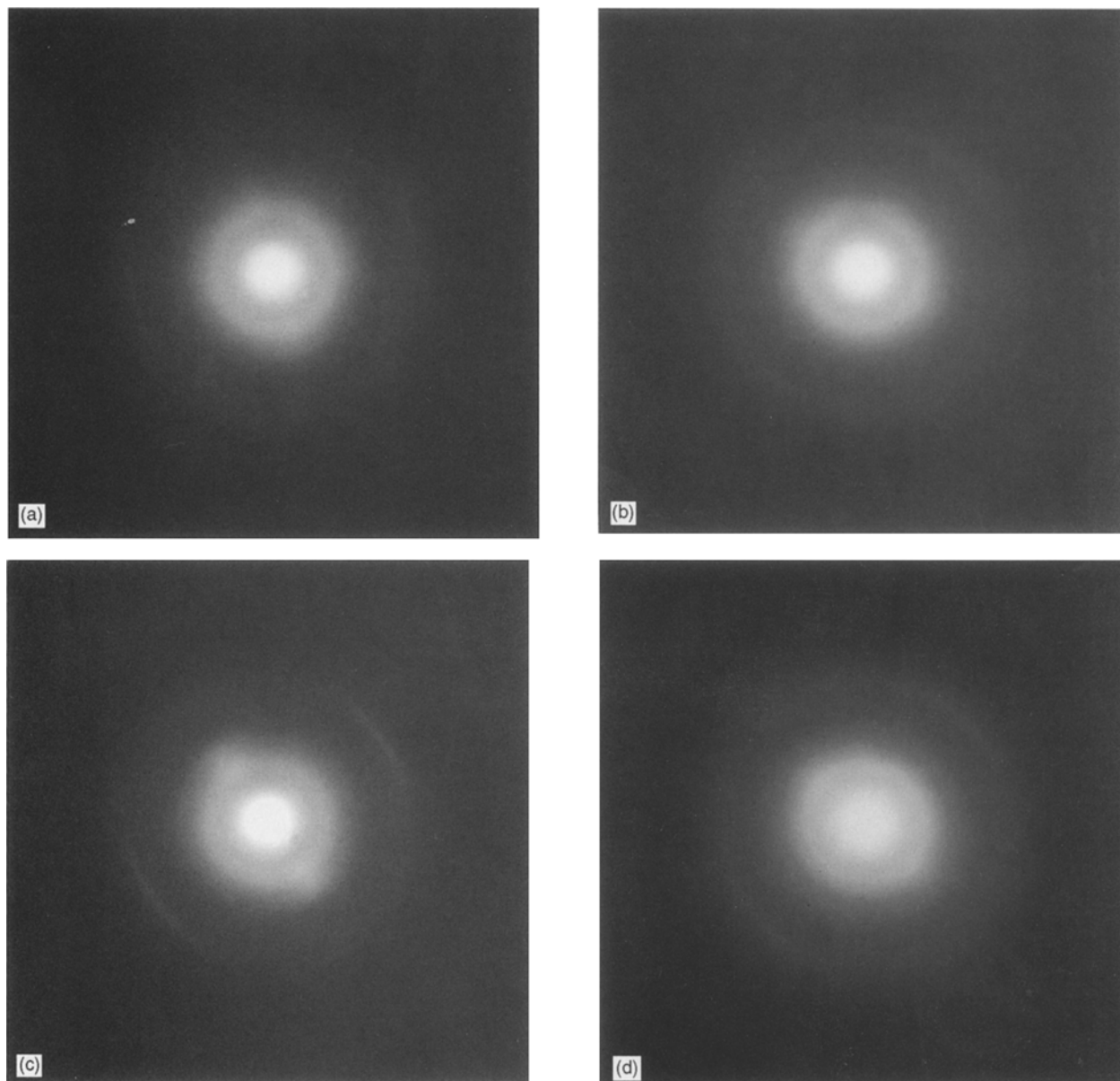


Figure 3 Selected area electron diffraction patterns of the *in situ* composites obtained from: (a) skin of the blend containing 10 wt% LCP; (b) core of the blend containing 10 wt% LCP; (c) skin of the blend containing 30 wt% LCP; (d) core of the blend containing 30 wt% LCP.

differentiation. More detailed study is being carried out to correlate the structure of the *in situ* composites with their rheological characteristics.

Blending of LCP with polycarbonate under controlled blending and extrusion conditions produces *in situ* composites with submicron LCP fibril reinforcement, with typical diameter of around 200–300 nm, as observed under transmission electron microscope. No staining process is necessary to achieve relatively high phase contrast in the TEM bright field images. Distinct skin–core differentiation in morphology was observed in these composite blends, where the fibrils of higher aspect ratios have been formed in the skin region and significant amount of spherical and ellipsoidal LCP particles have been found co-existing with the LCP fibrils in the core region. Selected area electron diffraction patterns have given more quantitative evidence that the LCP fibrils in the skin region of the extrudates have a higher degree of molecular orientation. This

skin–core morphology results because of the differences in the rheological and thermal histories experienced in the skin and core regions of the extrudates. The skin–core differentiation was found to be more prominent in the composite with higher LCP content and this may be attributed to the changes in the velocity profile from parabolic to plug-like in the polymer melts due to the inclusion of the LCP. TEM has been proven a powerful technique to study the microstructure of the *in situ* composites based on LCP. The information obtained should be useful for qualitative and quantitative correlation between the structure of the materials and rheological properties of the LCP-based *in situ* composites.

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