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Poly(caprolacton)/Liquid crystalline polymer blends: phase behaviour and mechanical properties

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The blend behaviour of a thermoplast (polycaprolacton) and a liquid crystalline polyester was investigated. The blending was performed via a common solution and rapid precipitation. The blends exhibited a two-phase structure with one phase being the pure thermoplast and the second a mixture of the thermoplast with the liquid crystalline polymer (LCP). The mixed phase can be interpreted as a lyotropic LCP phase with the thermoplast acting as the solvent. At low LCP concentrations ($< 2\%$), the Young's modulus, E, of the blend is increased by more than a factor of two, but higher LCP concentrations do not increase the mechanical properties as drastically.

1. Introduction

Due to their high stiffness and strength, thermotropic main-chain liquid crystalline polymers (LCPs) are of interest in various technological applications [1]. Disadvantages are their relatively high costs and difficulties in processing [1, 2]. In recent years several attempts have been made to mix commercial thermoplastic polymers with LCPs to combine the properties of LCPs and thermoplastic polymers [3–5]. In the ideal case, LCPs and thermoplastics are mixed on the molecular level with the rigid LCP chains acting as reinforcing fibres in the flexible thermoplastic matrix. This is known as the concept of molecular reinforcement [6]. In these molecular composites, two possible arrangements of the rigid-rod molecules in the thermoplastic matrix can be suggested. One possibility is that the rigid-rod molecules are isotropically dispersed in the matrix; the alternative, especially at higher LCP contents, is that the rods are aligned parallel to each other within domains, but still diluted by thermoplastic chains, in other words a lyotropic solution of the LCP in the thermoplastic matrix.

While metastable isotropic mixtures of thermoplasts with LCPs have been prepared in several cases [7–12], lyotropic LCP/thermoplast mixtures are as yet unknown. In this thermal and morphological study of blends consisting of commercial poly(caprolacton) (PCL) and a liquid crystalline poly(ester), we report on the existence of LCP/thermoplast mixed phases with liquid crystalline behaviour under certain conditions. The mechanical properties of the blends were investigated to obtain information about the reinforcement effectivity. The experimental results are related to theoretical approaches based on the modification of the Halpin Tsai theory by Nielson [13].

2. Experimental procedure

A commercial poly(caprolacton) (PCL-700), traded by Union Carbide, was utilized as thermoplastic polymer. Its molecular weight (M_w) is about 40 000 with a melting point of 60 °C.

The LCP is a liquid crystalline polyester which is wholly aromatic in the main chain; its chemical formula is given in Fig. 1, and the synthesis is described elsewhere [14]. It forms a liquid crystalline melt at 207 °C, the LC-isotropic transition appears at about 440 °C under chemical decomposition.

Blend preparations were carried out by coprecipitations from common solutions of both components in dichloromethane/trifluoroacetic acid (7:1) mixtures into a large amount of methanol. The chosen PCL-700/LCP-ratios were 100:0, 99:1, 95:5, 90:10 by weight, respectively. The blends were washed several times in methanol and subsequently dried in vacuum for 12 h. For mechanical tests the precipitated blend materials were pressed between heating plates at 70 °C. The resulting specimens were quenched into ice water. The stress–strain behaviour of the specimens was examined with a Zwick 1445 tensile testing machine. Samples were 5.0 cm in length, 1.0 cm in width and 0.1 cm in thickness. Polarizing light microscopy was carried out with a Reichert-Jung POLIVAR/microscope on a heating stage. The thin films were

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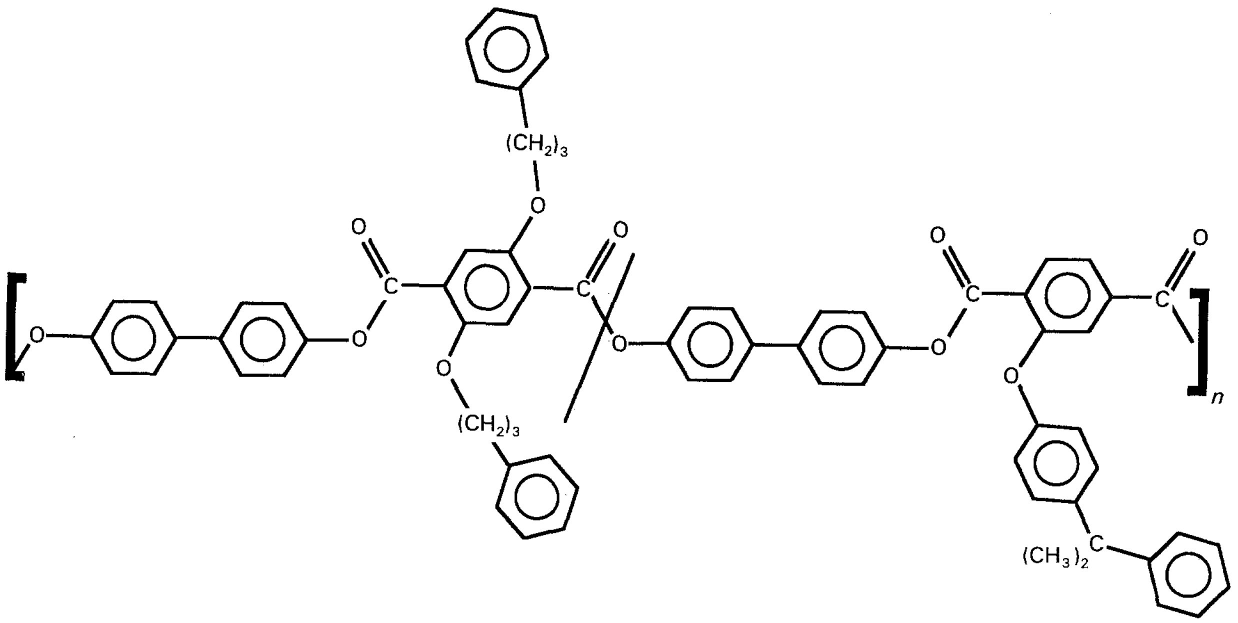

Figure 1 Chemical structure of the LCP used in the present work.

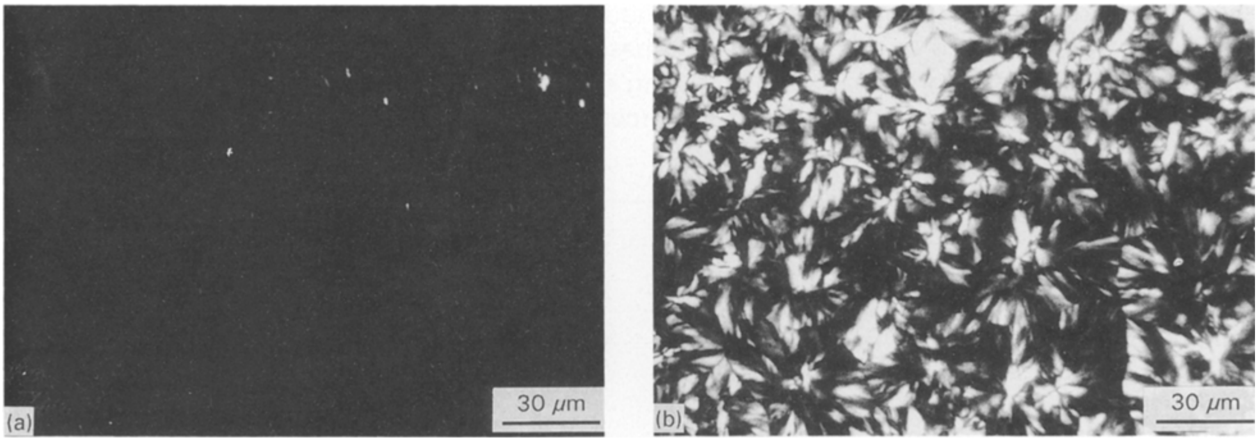

Figure 2 (a) Optical micrograph (crossed polarizers) of the pure PCL, sheared between glass slides at 70 °C and photographed at 70 °C. (b) The same sample as in Fig. 2a after crystallization.

oriented by pressing and shearing the blends between glass slides above the melting point of the PCL-700 at various temperatures. Differential scanning calorimetry (DSC) was carried out with a Heraeus TA 500S, with a heating rate of 10 °C min^{-1}.

3. Results

Figs 2a and b and 3a–c are optical micrographs obtained under crossed polarizers of pure PCL and of a blend PCL/LCP (99:1 weight ratio), respectively. Both samples were sheared at 70 °C and photographed at 70 °C, at room temperature and after reheating to 70 °C. While no anisotropy is seen in the pure thermoplastic polymer (Fig. 2a), remarkable birefringence attributed to molecular orientation within individual very small domains can be seen in the blend (Fig. 3a). This birefringence is maintained when keeping the sample at 70 °C for several hours (more than 24 h). Cooling the blend to room temperature results in the spherulitic crystallization of the non-birefringent part of the sample, but the birefringent domains remain. Reheating results in an unchanged texture compared to Fig. 3a. The sizes of the domains depend on concentration, their orientation depends on shear rate but not on temperature until 130 °C is reached. Those domains are also visible in the polarizing microscope in non-sheared samples, but the orientation of an individual domain can have an arbitrary direction. Shearing the blends above 130 °C but below 200 °C changes the shape and size of the domains. With higher shearing rates, larger domains appear with a more extended geometry in shearing direction (higher aspect ratio) (compare Fig. 4a and b). Again, these domains are stable in size and orientation with annealing up to 200 °C for several hours. The volume fraction of the domains is determined mainly by the concentration of the LCP but not so much by temperature. Cooling and re-heating the sample again does not change the domain pattern (Fig. 4c and d). Annealing a blend above 200 °C destroys the domain geometry. The same area of a blend is seen in Fig. 5a and b, after shearing at 150 °C (Fig. 5a) and after subsequent heating to 220 °C (Fig. 5b), respectively. The disappearance of the domains into a (more fibrillar) network is evident. This network has lost its

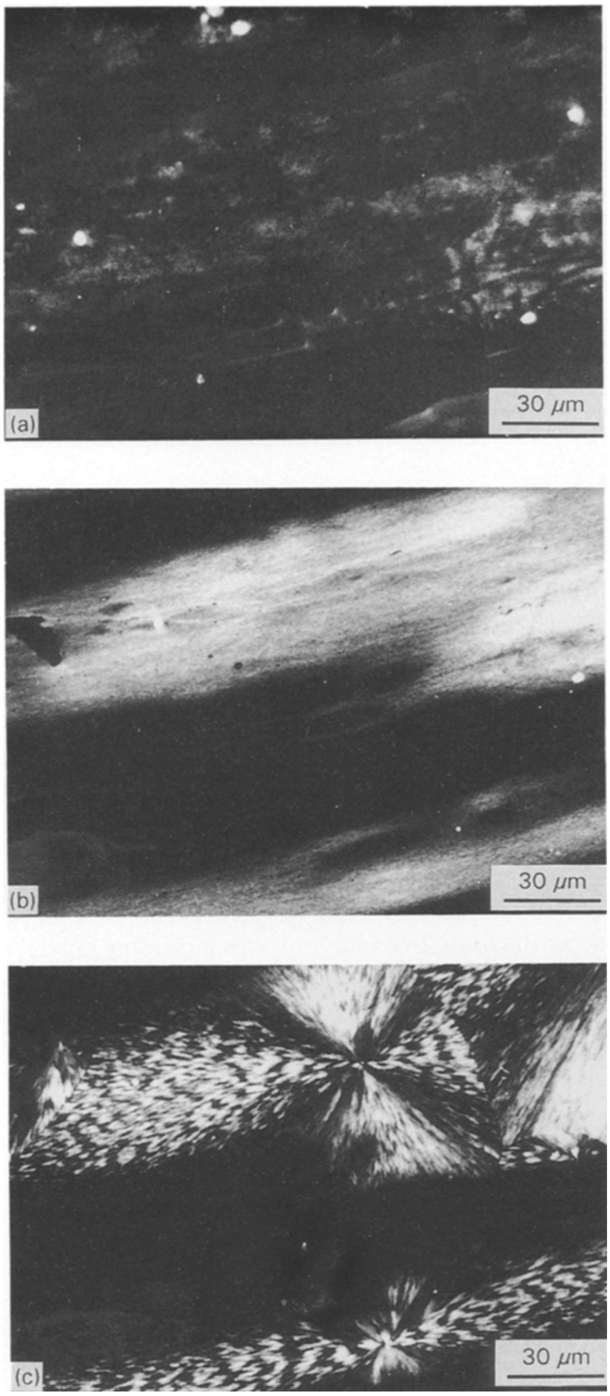

Figure 3 (a) PCL/LCP-blend (99:1) after shearing at 70 °C. The sample is oriented for minimal transmission between the polarizers (photographed at 70 °C). (b) The same area as in Fig. 3a but oriented for maximal transmission. (c) The same area as in Fig. 3a, b after crystallization.

orientation in the shear direction having the typical nematical grizzle texture of the pure LC-polyester. DSC traces of all the samples exhibit a melting endotherm at 60–65 °C, which corresponds to the melting of the PCL crystals. The intensities of the melting peaks, which can be related to the crystallinity of the samples, decrease with increasing LCP content faster than expected from a two-component (pure PCL and LCP) system. Fig. 6 shows the normalized crystallinity related to the pure PCL ($x_{\text{rel}} = 1$) as depending on the LCP content. In Fig. 7a and b, the changes of the Young's modulus (E) normalized to the pure PCL and

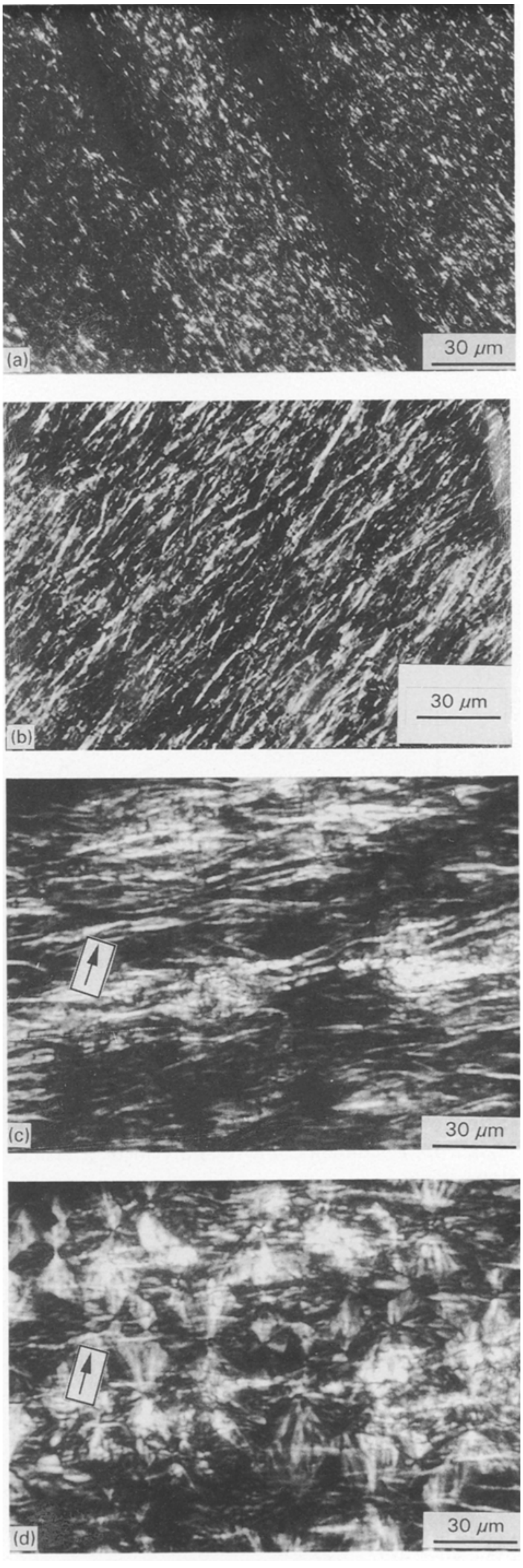

Figure 4 (a) PCL/LCP-blend (99:1) after shearing at 150 °C, lower shearing rate. (b) The same blend after shearing at 150 °C with a higher shearing rate. (c) PCL/LCP-blend (9:1) after shearing at 150 °C. (d) The same area as in Fig. 4c, after crystallization of the PCL at 35 °C. The domain structure is also visible within spherulites (arrows).

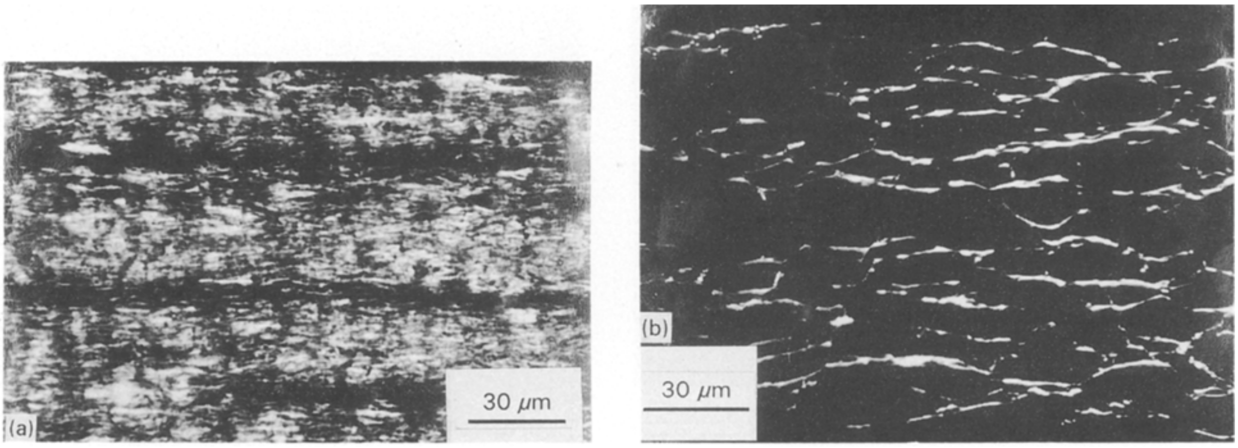

Figure 5 (a) PCL/LCP-blend (99:1) after shearing at 150 °C. (b) The same area of the sample after heating to 220 °C.

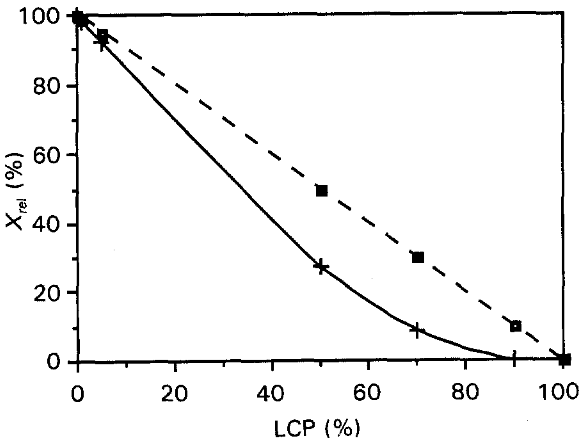

Figure 6 Relative crystallinity (x_{rel}) (continuous line) as dependent on LCP content. The dashed line is the calculated crystallinity under the assumption that both components do not interact.

the elongations to break as a function of the LCP content are shown. A remarkable increase of the Young's modulus by more than a factor of two can be observed in blends containing only 1 wt% LCP, while their elongation at break decreases drastically. At higher LCP contents, the reinforcement efficiency slows down.

4. Discussion

Several binary lyotropic systems of rigid-rod polymers and monomeric solvents are known [15, 16]. Flory [17] discussed the molecular arrangements of those systems and came to the conclusion that above a critical concentration the rigid-rod macromolecules and the monomeric solvent form a one-phase lyotropic liquid crystalline order.

Ternary systems consisting of rigid-rod and flexible macromolecular chains in a monomeric solvent were also investigated by Flory [18]. He predicted a phase separation into two solutions with increasing polymer contents: lyotropic rigid-rod macromolecules, flexible chains and solvent (lyotropic LCP system), and isotropic flexible macromolecules and solvent (isotropic system) for macromolecules without any attractive interactions. With partial miscible macromolecules, both phases consist of a lyotropic ordered and an isotropic phase with high and low LCP contents, respectively [19, 20].

Lyotropic LCP behaviour of rigid-rod macromolecules with flexible macromolecules as the solvent has not been reported until now. Seurin *et al.* [21] published data on the phase behaviour of semirigid hydroxypropylcellulose (HPC) and oligomeric poly(ethyleneglycole) (PEG) having a degree of poly-

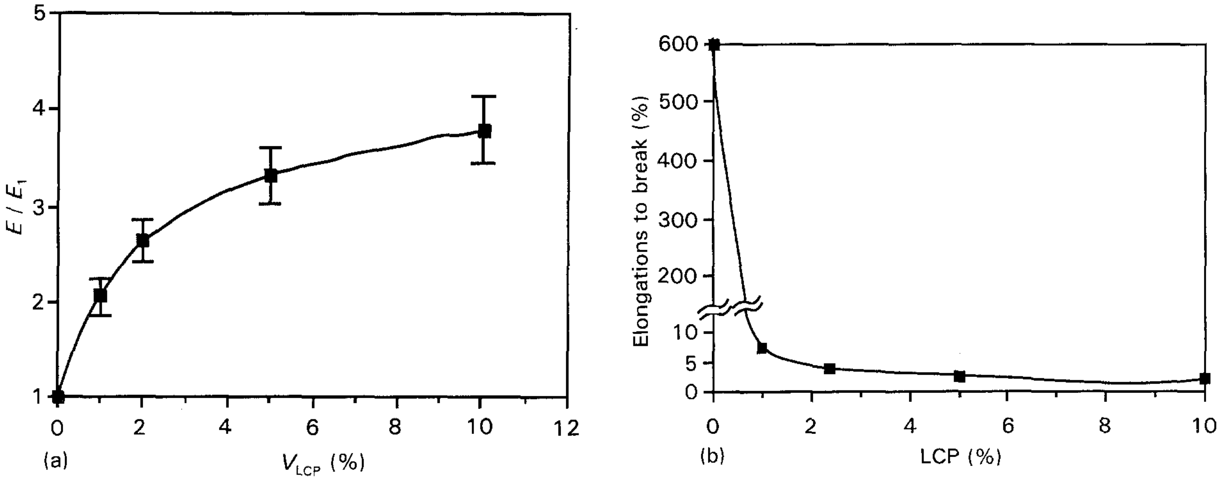

Figure 7 (a) Normalized Young's moduli E/E_1 (E = Young's modulus of the blends) as dependent on LCP concentrations. (b) Elongations to break as depending on LCP concentration.

merization of six, and found a liquid crystalline mixed phase. However, complete phase segregation occurred when using PEG with a higher degree of polymerization.

Our results from polarizing light microscopy and thermal analysis also suggest a two-phase morphology. One phase consists of the pure thermoplastic PCL and the other of a liquid crystalline lyotropic phase from the LC-polyester with the PCL as the solvent. The pure PCL phase was established from the crystallization behaviour (the melting point did not change with composition) and the occurrence of the PCL spherulites in the blend (Figs 2 and 3). Thermomechanical measurements did not provide any evidence for a change of T_g in the PCL. Closer examination of the optical micrographs (see Fig. 4c and d) shows that the LCP domains, visible in the pure PCL melt (Fig. 4d), are also visible embedded within the PCL spherulites.

Unfortunately, proof of the second phase being a lyotropic LCP phase could not be obtained by thermal analysis measurements. With our instruments, a T_g of the LCP-containing phase in the blends was detected neither in the DSC nor in the thermo-mechanical measurements. The evidence for liquid crystalline domains within the sample is straightforward from Figs 3–5, but the domains can either consist of the pure LCP or of a mixed phase of LCP and PCL.

Our conclusion of a mixed phase results from the observation that under the same shearing conditions as in the blends, it was not possible to orient the pure LCP due to its high viscosity up to temperatures of $\sim 200\,^{\circ}\mathrm{C}$, while the domains in the blends can easily be oriented under the same shearing conditions above 130 °C. Above 200 °C a phase separation from the mixed phase into the pure LCP phase occurs (Fig. 5a and b). In Fig. 8, a sketch of our proposed morphology is shown: the as-prepared samples (Fig. 8a) contain very small cylindrically shaped lyotropic LCP/PCL domains having a statistical orientation in the PCL matrix. Shearing the samples at 70 °C results in a rotation of the domains with their long axis into the shearing direction (Fig. 8b). Shearing the samples at elevated temperatures (between 130 and 200 °C) orients the domains by a viscose deformation and consequently increases the aspect ratio of the domains (Fig. 8c). Also, a fusion of single domains into larger ones can occur. Finally, decomposition of the domains into the pure phases occurs above 200 °C. No conclusion can be drawn if the lyotropic LCP phases are thermodynamically stable below 200 °C or are unstable, and their decomposition is kinetically hindered. The domains were observed just below 200 °C for several hours in the light microscope without a change in their shape.

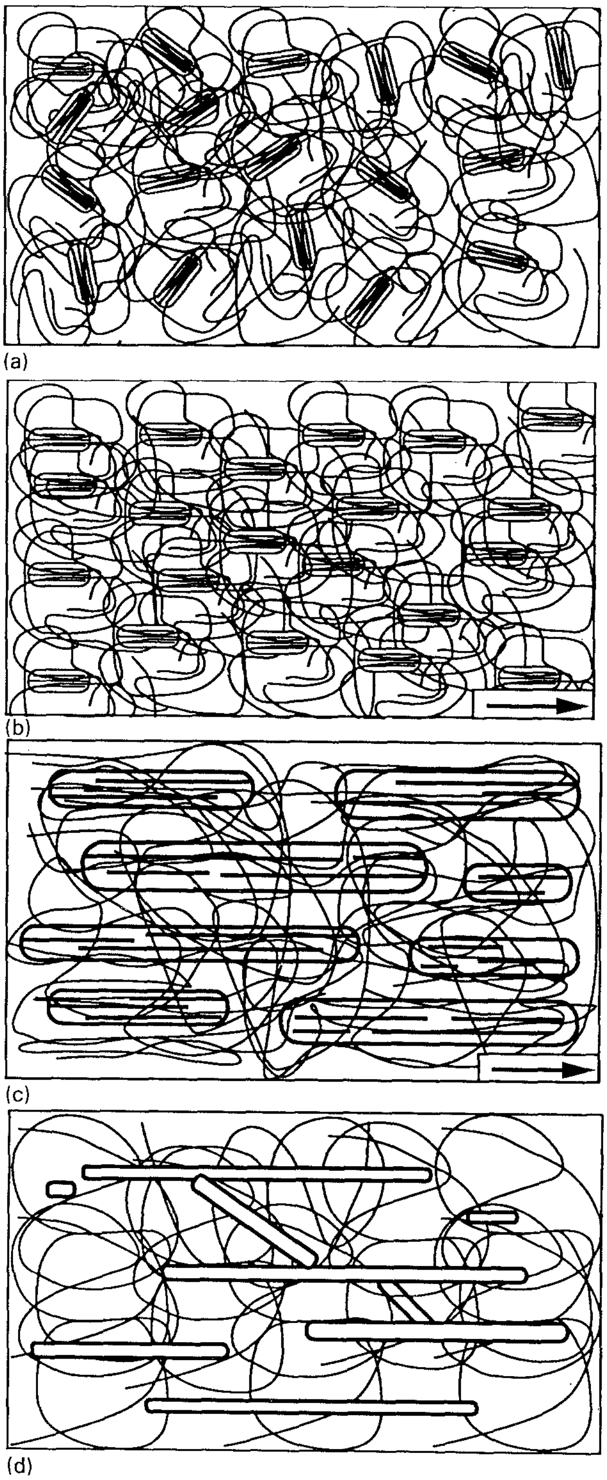

Figure 8 Sketches of the morphologies in the blends. The parallel lines (domains) indicate the lyotropic LCP phase (Fig. 8a–c). (a) Unoriented domains in the non-sheared blends. (b) Oriented domains after shearing at 70 °C. The arrow indicates the shearing direction. (c) Coarsened and elongated domains after shearing at 150 °C. (d) Phase separation into the pure components after annealing above 200 °C. The rods indicate the pure LCP domains.

A direct correlation between the morphologies of the samples and their mechanical properties would be very speculative for the blends used in our investigations. As only samples with the as-prepared morphology (Fig. 8a) were used for the mechanical tests, neither their compositions and the volume fraction of the domains, nor their shapes, are really known. Additionally, the crystallinity of the matrix PCL is changing with LCP content (Fig. 6), and influences the mechanical properties of the matrix. For an analysis of the data using the Halpin–Tsai equation, and their modification by Nielson [13], all the above-mentioned parameters should be known. Using a Young's modulus of 150 GPa [22] for the lyotropic LCP domains and 0.36 GPa for the PCL matrix (as measured from the pure PCL sample) a hypothetical aspect ratio of $L/D = 300$ (L is persistent length, D is diameter of the macromolecules of the LCP) was calculated for the blend with 1% LCP and $L/D = 40$ for the blend with 10% LCP.

Experimental investigations are under way on similar systems but with amorphous matrices, in which the parameters for the Halpin–Tsai equation can be more easily determined.

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