Structure and mechanical properties of the extruded blends of a liquid crystalline polymer with polypropylene

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Blends of a thermoplastic, isotatic polypropylene (PP) and a liquid-crystalline polymer (LCP) based on a copolyester of hydroxynapthoic acid and hydroxybenzoic acid, were extruded. The LCP exhibited a higher viscosity than that of the PP under the extrusion conditions. Calorimetric, microscopic, static and dynamic mechanical tests were performed on these blends. Differential scanning calorimetry thermograms indicated that the crystallization temperature of PP increases slightly with increasing LCP content. Scanning electron microscopy examinations revealed that the LCP phase was elongated into microfibrils in the blends investigated. However, some undeformed spherical droplets were dispersed in the PP matrix in addition to microfibrils for the blends containing high LCP concentrations. Static tensile tests showed that the addition of LCP to PP results in an increase of the modulus of elasticity but a decrease in tensile strength. The storage modulus of the extruded blends was found to increase with the addition of LCP.

1. Introduction

It is well known that the mechanical properties of polymers, e.g. stiffness, strength, can be greatly enhanced by the addition of fibres. However, the melt viscosity is increased strongly by the incorporation of fibres in the polymeric melt, leading to problems of longer production cycles and increased power consumption. Moreover, the fibres are probably subjected to fracture during the processing of a viscous melt by extrusion or injection moulding [1].

Thermotropic liquid-crystalline polymers (LCPs) are materials that retain a high degree of orientation in the liquid-crystal state. They result from the incorporation of rigid mesogenic groups in the backbone of the polymer chains [2]. Compared with other engineering plastics, the LCPs have a much lower viscosity and are frequently added to improve the processability of engineering plastics without decreasing their mechanical properties [3–5]. The melt blends of conventional isotropic polymers with LCPs are sometimes called *in situ* composites. Fibrillar structures are most often formed in these materials and the self reinforcement leads to high stiffness, strength and low coefficient of thermal expansion [6]. They may be competitive with glass fibre-reinforced plastics in applications where processability and low density are key requirements.

A number of main-chain LCPs have been commercialized. They are based primarily on copolymers of hydroxybenzoic acid (HBA) and 2,6-hydroxynapthoic acid (HNA) [7]. For example, Vectra A950 produced by Hoechst–Celanese company consists of

25 mol% HNA and 75 mol% HBA. The principal application of LCPs today is injection-moulded precision parts, particularly for the electronic interconnect device industry [6]. As the prices of LCPs are relatively expensive, much work has concentrated on using these materials as reinforcements for composites or in blends of two or more polymers, where they constitute a minor component [6, 8–11].

The LCP/thermoplastic blends have been reported by several workers to be immiscible [8, 12] or a partially miscible pair [13]. The LCP does not mix properly with thermoplastics, thus the blends consist of two separated phases. The morphology of the dispersed phase in immiscible polymer blends plays an important role in the determination of the final physical properties. The formation of fibrillar LCP phase in the matrix improves the mechanical properties of the blends. However, the fibrillar structure formation depends on the ability of the rigid LCP molecules to orient in the direction of melt flow.

Taylor [14] has studied the effects of different parameters on the elongation of a suspended immiscible droplet in a Newtonian fluid. He found that the droplet tends to elongate when the ratio between the viscosity of the droplet and the viscosity of the suspending liquid is small. Thus LCP fibrillation is likely to occur in the LCP/thermoplastic blends when the viscosity ratio of LCP to matrix is smaller than or near unity.

Recent work on the blends containing LCP were mainly concentrated on the engineering polymers with their matrix materials exhibiting a higher melt

viscosity than the LCP. In this work, isotatic poly-propylene (PP) is chosen as the matrix, because its viscosity is smaller than the LCP under high shear-rate conditions. This paper aims to investigate the morphology, structure and mechanical properties of the extruded thermoplastic composite containing a LCP.

2. Experimental procedure

The main-chain thermotropic liquid crystalline polymer used in this work is Vectra A130 produced by Hoechst–Celanese Co. This LCP is Vectra A950 containing 30 wt% glass fibre. The PP matrix material is the commercial product of Himont (pro-fax 6331) with a melt flow index 12 g/10 min.

Before mechanical mixing, both polymer pellets of PP and LCP were separately dried in an oven operated at 70 and 150 °C. The blends with LCP composition ranging from 9–33 wt% were prepared in a twin-screw Brabender ($L/D = 7$, $D = 41.8$ mm) with an attached slit die of 50×0.5 mm^2. The barrel temperatures from root to the die were maintained at 285, 285, 290 and 290 °C, respectively. The rotation speed of the screw was kept at 40 r.p.m. The extruded ribbons with a thickness of ~ 0.4 mm were taken up in air by a chill roll. Compression-moulded plates were prepared at 220 °C with a laboratory hydraulic press operated at a pressure of 10 MPa. The ribbons were stacked and aligned unidirectionally in the mould prior to compression.

The apparent viscosity of all PP/LCP blends was obtained by using the Brabender mixer equipped with a round die ($L/D = 30$, $D = 1$ mm) without entrance effects correction. The extrusion conditions for viscosity measurements were similar to those of the ribbon fabrication. The shear rate used was $\sim 6 \times 10^3$ s^{-1}.

The differential scanning calorimetry (DSC) measurements were conducted from 50–300 °C under a nitrogen atmosphere using Perkin–Elmer thermal analysis system (model DSC-7). Indium, and zinc standards were used for temperature calibration. In the test the specimen was initially heated to 300 °C at a rate of 10 °C min^{-1}, held 5 min at this temperature and then cooled at a rate of 10 °C min^{-1}. A second heating run to 300 °C was subsequently performed after recording the DSC cooling traces.

Static mechanical properties of all the materials were determined on a standard tensile bar (ASTM D-638) cut out from the compression-moulded plates in the flow direction. Stress-strain curves were recorded using an Instron tensile tester (model 4206) at a cross-head speed of 1 mm min^{-1}.

A scanning electron microscope (SEM) was used to examine the morphology of the extruded ribbons both in the flow and transverse directions. The specimens were fractured in liquid nitrogen and the fracture surfaces were coated with gold.
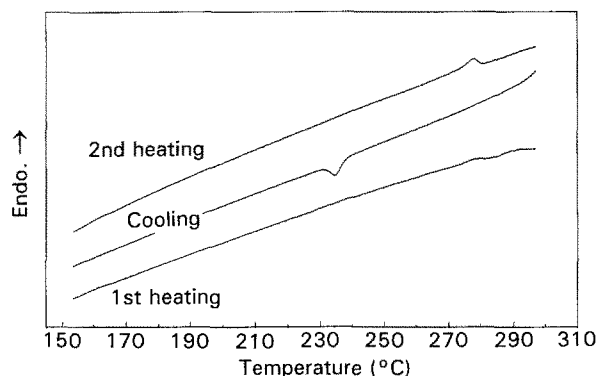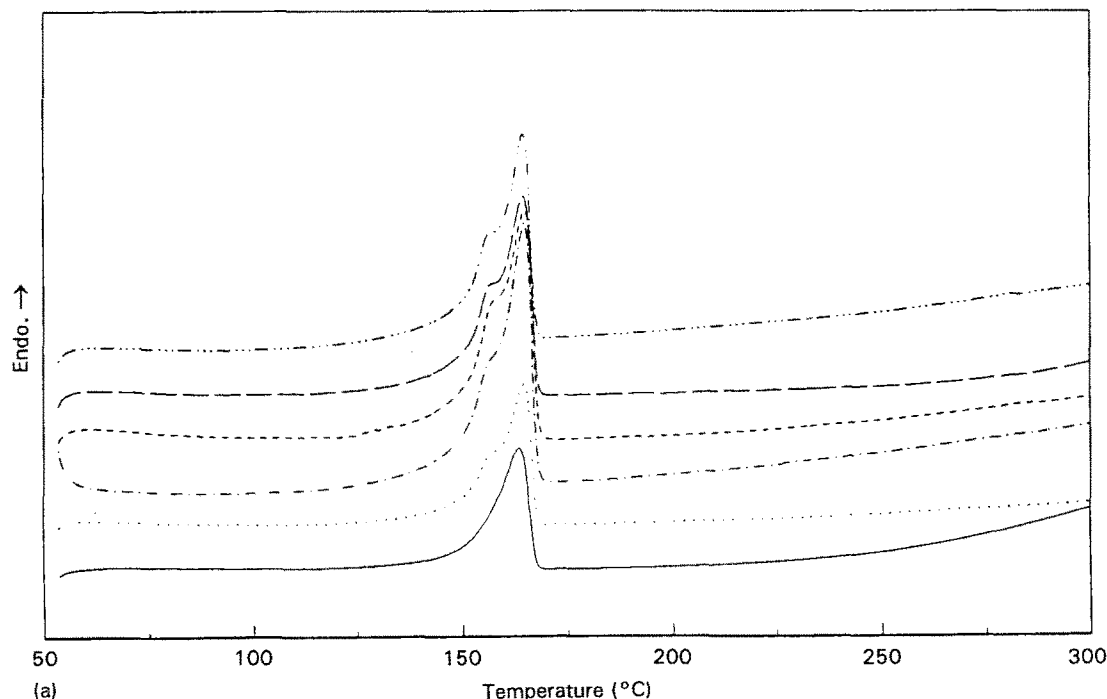

Figure 1 DSC heating and cooling curves for pure LCP.

Figure 2 DSC curves of PP/LCP blends (a) first heating run; (b) cooling run; (c) second heating run. (——) PP, (···) 9% LCP, (---) 17% LCP, (---) 23% LCP, (— —) 29% LCP, (······) 33% LCP.

(b)

Temperature (°C)
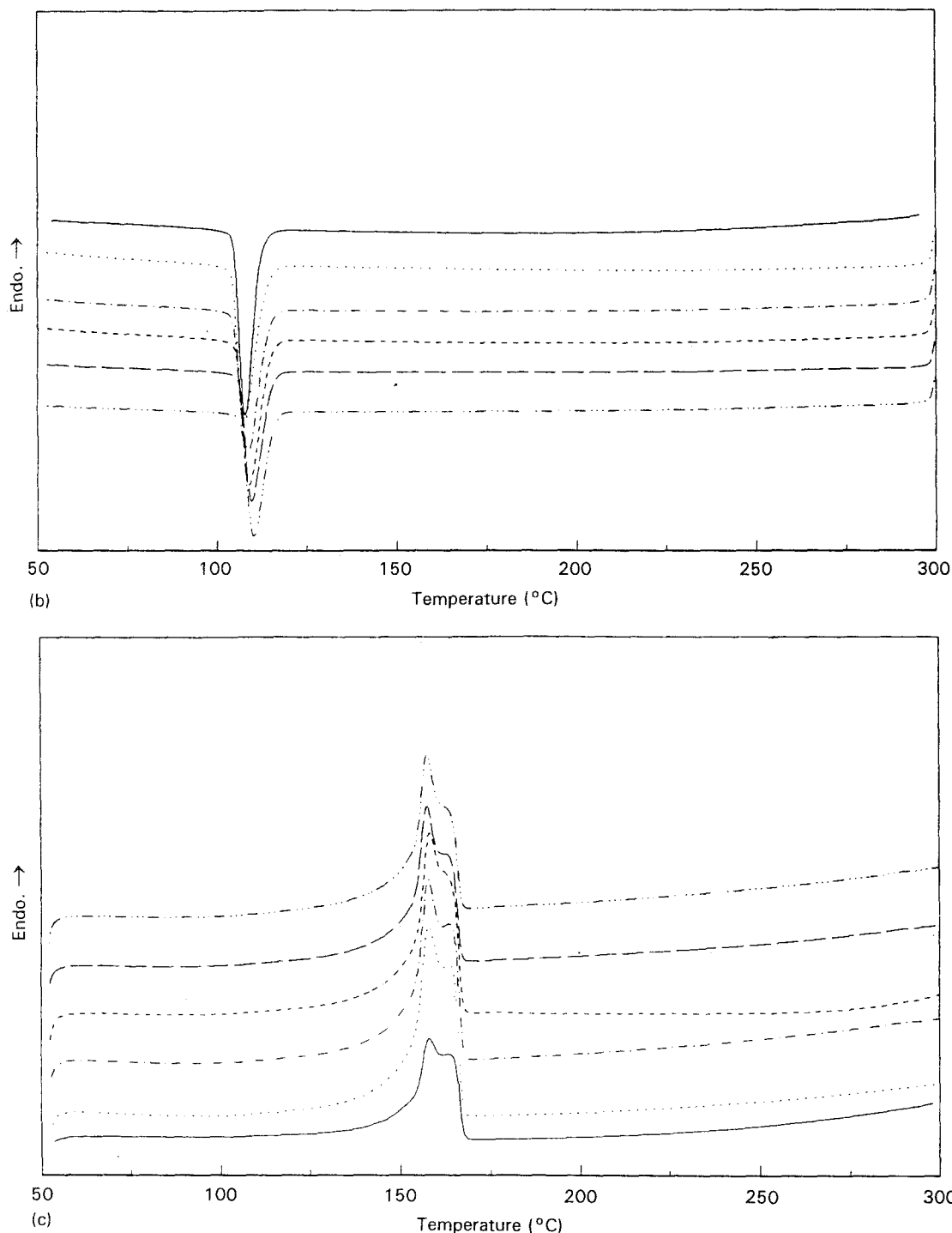
(c)

Temperature (°C)

Figure 2 (continued).

Dynamic mechanical analysis (DMA) of the extruded ribbons was performed in a Du Pont dynamic mechanical analyser (model 983) at a fixed frequency of 1 Hz and an oscillation amplitude of 0.1 mm. The temperature range of study was from -80 to $150\,°C$, and the heating rate was $1\,°C\,\text{min}^{-1}$.

3. Results and discussion

Fig. 1 shows typical DSC heating and cooling curves of the pure LCP. The pure LCP exhibits an endothermic peak at about $273\,°C$ during heating, which is associated with the transition from crystalline to nematic mesophase state [15, 16]. On cooling, the nematic to crystalline transition is observed at $\sim 237\,°C$. No distinct glass transition could be detec-

ted by DSC measurements. The thermal properties of Vectra A130, as shown in Fig. 1, are similar to that of Vectra A950 [15]. The DSC traces of PP/LCP blends are shown in Fig. 2 and the relevant numerical results are listed in Table I. The heat of fusion and crystallization of the blends are obtained by normalizing the measured values over the PP content.

From Table I, it is seen that the melting points of all the blends remain practically constant, i.e. the difference in melting temperature is within $\pm 1\,°C$. However, a slight increase of the crystallization temperature is observed when LCP is added. Moreover, the heat of crystallization, (ΔH_c), appears to increase slightly with increasing LCP content. Several workers [17, 18] have reported that the heat and degree of crystallization of the matrix polymer are increased by

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the addition of LCP. They suggested that the LCP acts as nucleating sites for the crystallization of the polymeric matrix during solidification [18–20].

Fig. 3a shows typical spherulitic morphology generated in PP, where the spherulitic morphology of PP/9% LCP is shown in Fig. 3b. It can be seen in Fig. 3b that the transcrystalline morphology is formed in the blend. This morphology is regarded as a nucleation-induced crystallization at the interfacial region or mesophase in most polymer blends [21]. In this region with higher nucleation activity, crystallization of PP begins at a lower supercooling. As PP is generally known to exhibit semicrystalline structure, the crystallinity is increased slightly by the presence of LCP phase (Table I). However, the enhancement of the crystallization is more pronounced in other LCP/thermoplastic blends where the matrix polymer exhibits an amorphous structure [17].

Fig. 4 shows the variation in viscosity of the PP/LCP blends versus LCP concentrations at 290 °C. It is observed in this figure that the viscosity of pure PP is smaller than that of pure LCP. Furthermore, the viscosity of the blends decreases with increasing LCP concentration and is less than that of the PP phase. A significant reduction in viscosity is observed in the blend containing 75% LCP. A minimum is observed in the viscosity composition curve. This minimum tends to occur when the viscosity of LCP is higher than the matrix or the viscosity of the two components

is similar [22, 23]. A reduction in viscosity can possibly be attributed to the polymer chains in LCP tending to orient and align themselves in the flow direction by shearing force, thereby promoting slippage between the chains [11, 24].

Fig. 5a–c show scanning electron micrographs of the fracture surfaces of extruded blends containing various LCP contents. It can be seen in Fig. 5a that only one elongated LCP fibre is observed in the PP/9% LCP blend. The fibre is at its earlier stage of its formation due to its ellipsoidal morphology. The formation of LCP fibres becomes quite pronounced at and above 17% LCP. Poor adhesion between LCP fibre and PP is indicated by the smooth surface of fibre pull-out from the matrix. These LCP fibres can be observed in both skin and core region, thus the skin–core structure is less pronounced in thin extrudates when one compares it with that of the injection-moulded specimens. Fig. 6a–c show the SEM fractographs of the extruded ribbons containing various LCP contents fractured perpendicular to the processing direction. At 9% LCP blend (Fig. 6a), voids are observed in the micrographs indicating some fibres have been pulled out of the PP matrix. The fibres appear to be poorly oriented in high LCP content blends.

As the morphology of LCP phase plays a key role in improving the mechanical properties of the PP/LCP blends, it is necessary to extract the LCP particles

TABLE I DSC results of the LCP/PP blends

	Parameter[a]	PP	9%LCP	17%LCP	23%LCP	29%LCP	33%LCP
First	T_{mp} (°C)	165.32	164.50	164.84	165.00	164.38	164.19
heating	T_{mo} (°C)	154.35	155.55	155.17	154.26	154.49	155.88
run	ΔH_f (J g^{-1})	89.20	88.88	86.64	88.89	87.74	92.46
	T_{cp} (°C)	105.26	107.59	108.80	109.12	109.76	110.30
Cooling	T_{co} (°C)	111.01	113.82	113.59	115.03	115.33	115.81
run	ΔH_c (J g^{-1})	95.05	93.73	96.18	96.79	97.66	100.56
Second	T_{mp} (°C)	158.85	157.81	157.78	158.17	157.45	157.52
heating	T_{mo} (°C)	152.05	152.69	152.99	153.22	153.03	153.23
run	ΔH_f (J g^{-1})	92.53	94.14	92.21	97.44	94.81	98.31

[a]T_{mp}, melting peak temperature; T_{mo}, melting onset temperature; T_{cp}, crystallization peak temperature; T_{co}, crystallization onset temperature; ΔH_f, heat of fusion; ΔH_c, heat of crystallization.
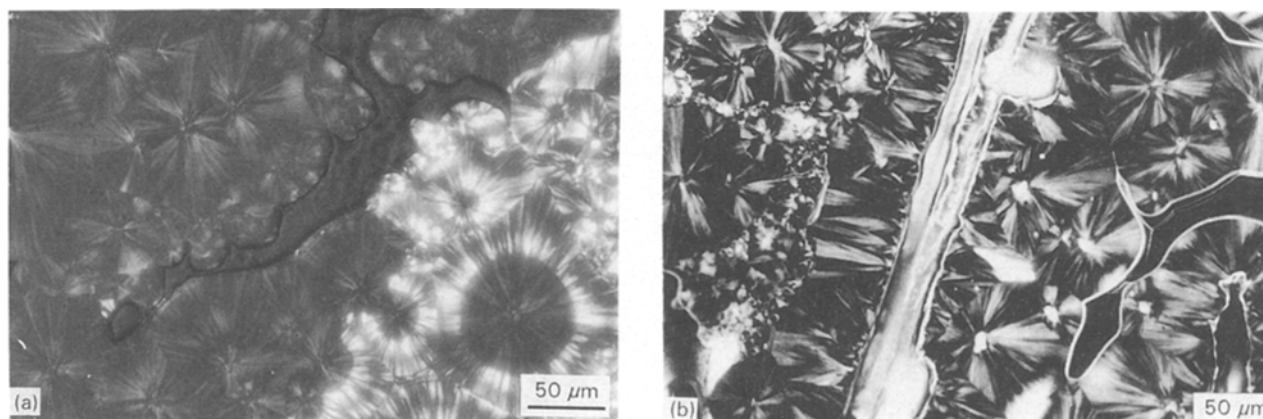

Figure 3 Optical micrographs of (a) the spherulites formed in pure PP, and (b) the spherulites and transcrystalline structure formed in PP/9% LCP at 230 °C (air-cooled).
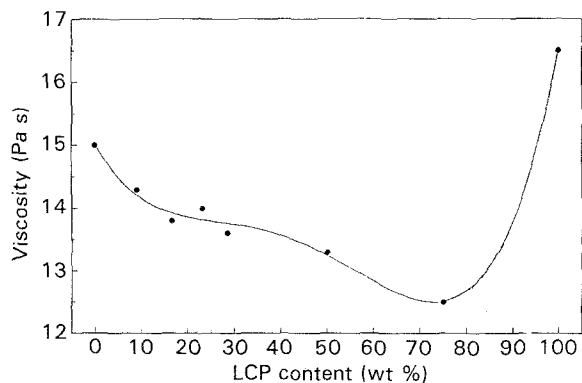
Figure 4 Apparent viscosity of the PP/LCP blends versus LCP concentrations (shear rate $\simeq 6 \times 10^3 \, s^{-1}$, $L/D = 30$, $D = 1$ mm).
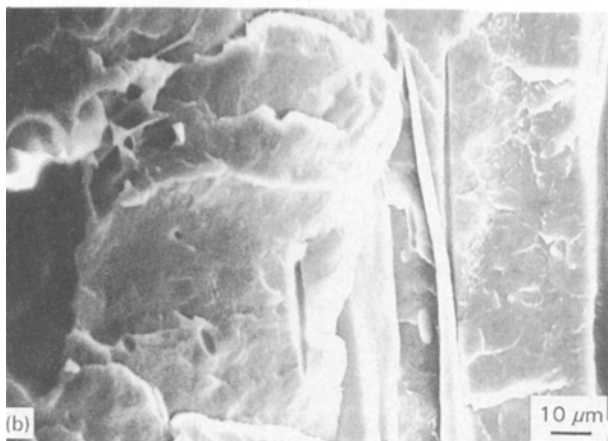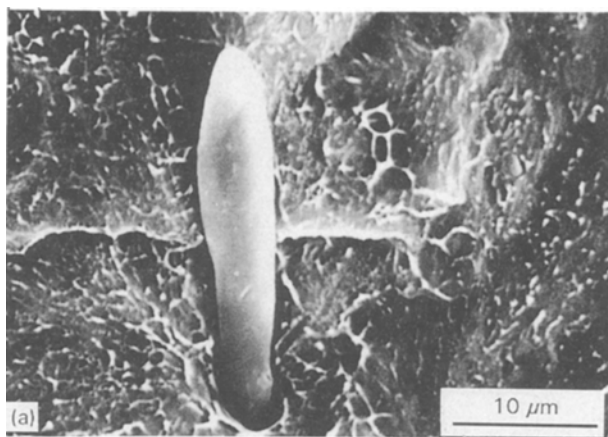

Figure 5 Scanning electron micrographs of the fracture surfaces of (a) PP/9% LCP, (b) PP/17% LCP and (c) PP/29% LCP, after being chopped parallel to · the flow direction at liquid-nitrogen temperature.
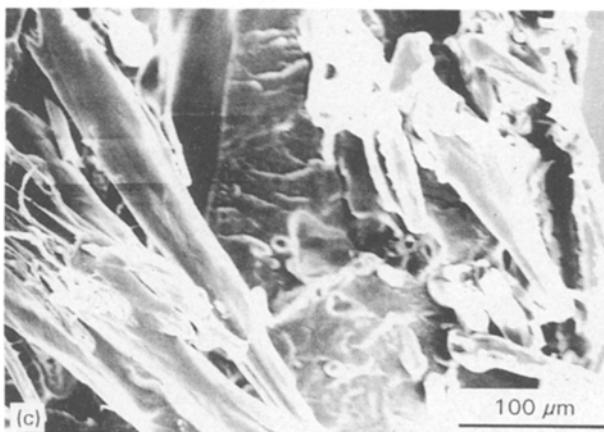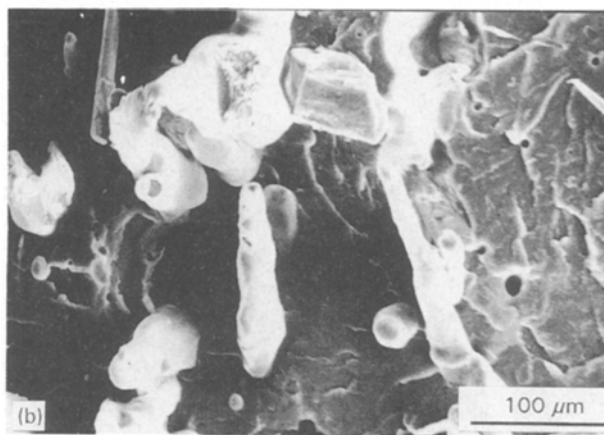

Figure 6 Scanning electron micrographs of various PP/LCP blends fractured perpendicular to flow direction. (a) PP/9% LCP; (b) PP/29% LCP; (c) PP/33% LCP.

from the blends in order to reveal the microstructure of the dispersed phase in more detail. Fig. 7a–e show the morphology of the LCP particles in various extruded PP/LCP ribbons following dissolution of the PP matrix. It is apparent in Fig. 7a that numerous fibrous particles having a non-uniform diameter (~ 40–80 μm) exist in the PP/9% LCP blend. These fibres are inhomogeneously distributed throughout the specimen, as only one fibre is observed prior to dissolution of the PP matrix (Fig. 5a). The fibres appear to be more elongated and uniform in their diameter (15–20 μm) in the PP/17% LCP blend (Fig. 7b). The PP/29% LCP blend shows that the LCP phase consists of some spherical particles in addition to more abundant fibrous particles (Fig. 7c). The presence of small spherical particles indicates that
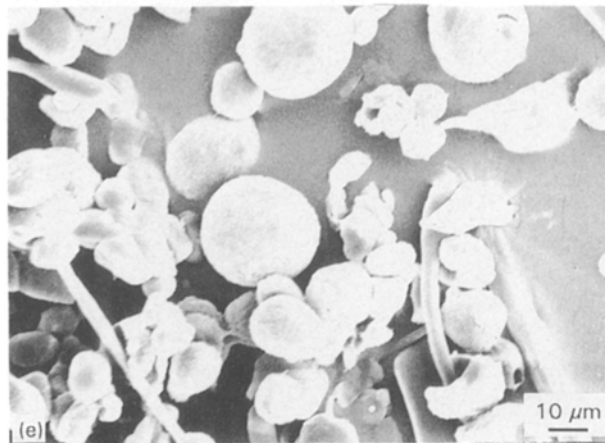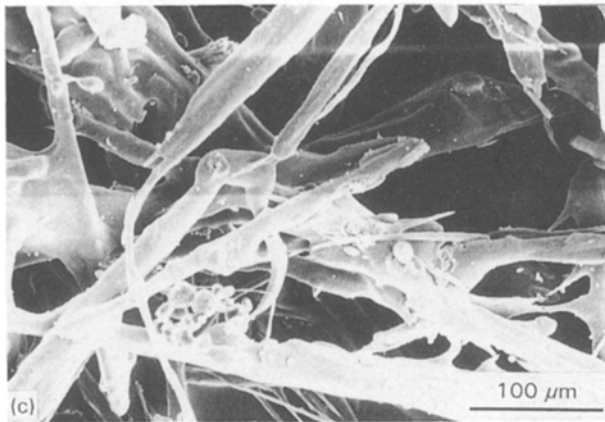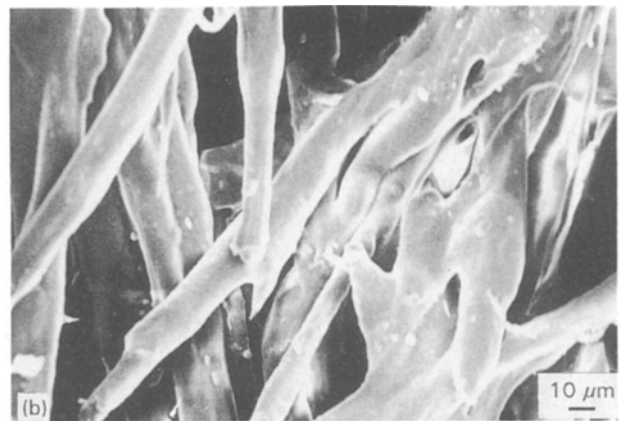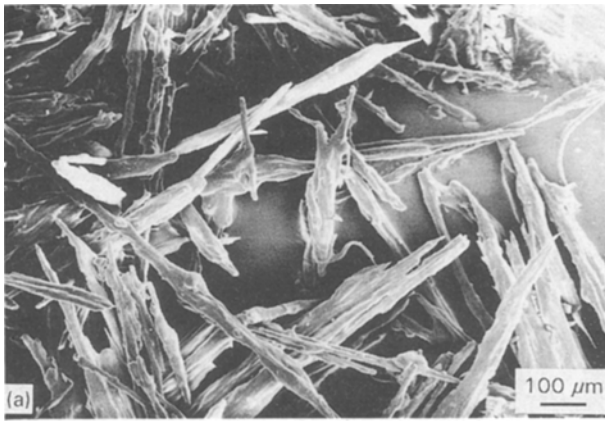
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Figure 7 Scanning electron micrographs of the LCP phase in various PP/LCP blends after dissolving the PP matrix. (a) PP/9% LCP; (b) PP/17% LCP; (c) PP/29% LCP; (d) PP/33% LCP and (e) another area of the same PP/33% LCP specimen.

some of the LCP domains do not deform or elongate into fibrils during extrusion. Fig. 7d shows that the volume fraction of this spherical dispersed phase increases dramatically in the PP/33% LCP blend. In another area of the same specimen, a scanning electron micrograph reveals that the LCP phase consists predominantly of small undeformed particles (Fig. 7e).

As the thickness of compression-moulded bars used for the tensile tests is much thicker than that of the extruded ribbons, it is possible that the width of the unoriented core relative to the oriented skin increases with increasing specimen thickness. However, SEM examinations revealed that the compression-moulded bars do not exhibit skin–core morphology (micrographs not shown).

According to the theory of Taylor [14], low-viscosity dispersed particles are elongated in the flow direction when blended with a higher viscosity poly-meric matrix. The dispersed droplets tend to elongate and burst into fine fibrils, provided that the coalescence of the droplets occurs. In other words, fibres are formed when the ratio of the dispersed phase to matrix viscosity is small. Long fibres that have high aspect ratio are reported to be formed in the PET/LCP, PEEK/LCP systems, etc., as they meet this criterion [11, 25]. However, no fibrillation of LCP is observed in the matrix of PPS/LCP blends where the viscosity ratio is larger than unity [22]. Furthermore, the PPS/LCP blends exhibit a greater viscosity than the parent materials [22]. In present work, the viscosity ratio is slightly larger than unity but the viscosity of the blends is less than that of the parent polymers.
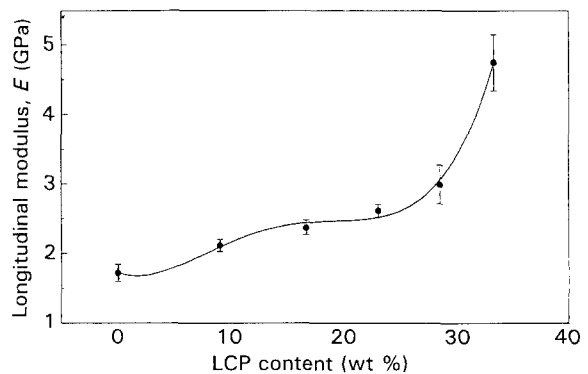

Figure 8 Tensile modulus of the compression-moulded blends versus LCP content.
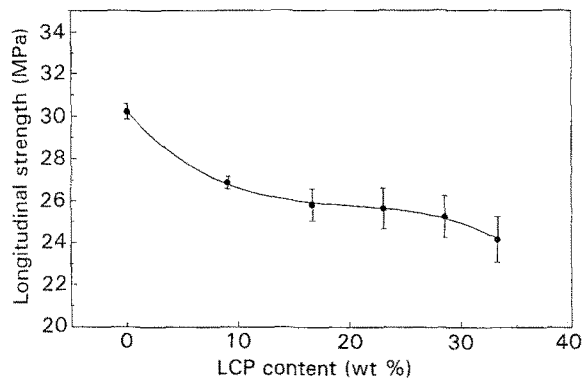
Figure 9 Tensile strength of the compression-moulded blends versus LCP content.

Fibrillation of the LCP phase can still be observed in the PP/LCP system. At high LCP concentrations, the LCP phase with a higher viscosity becomes more difficult to deform and to orient in the flow direction, leading to the formation of both spheres and fibres in the PP matrix.

Figs 8 and 9 show the variation of tensile modulus and tensile strength of the compression-moulded PP/LCP blends versus LCP content, respectively. It can be seen in Fig. 8 that the modulus of the blends gradually increases with increasing concentration of LCP in the blends. However, the addition of LCP reduces the tensile strength, particularly at 33% LCP
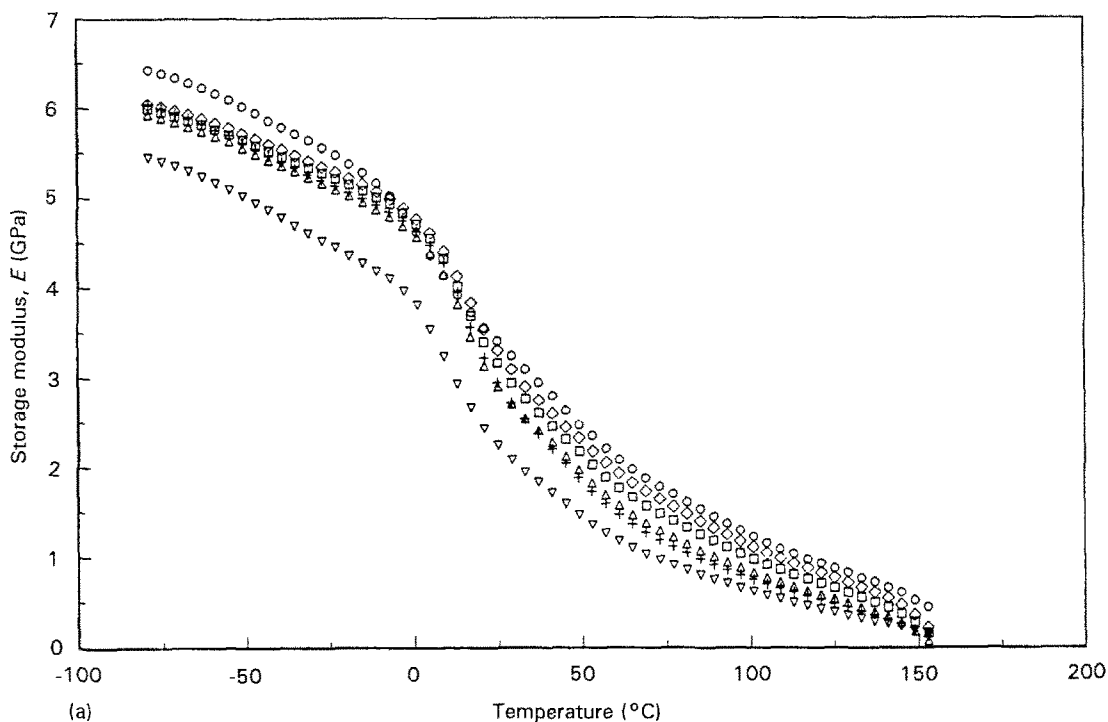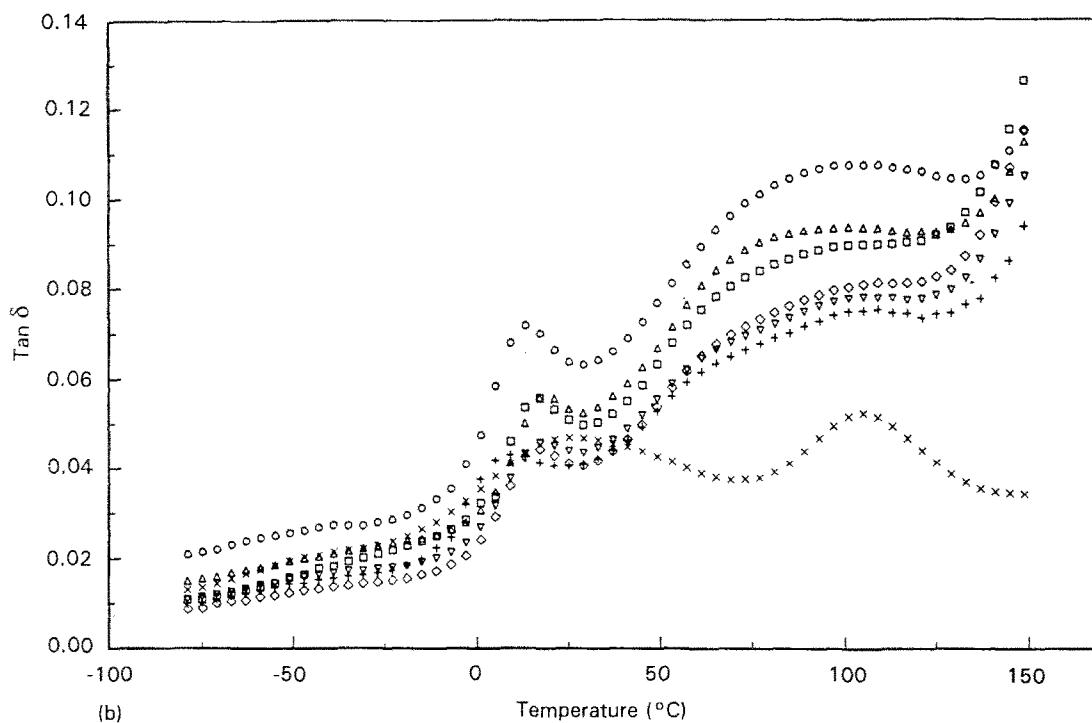
Figure 10 (a) Tensile storage modulus versus temperature for the extruded ribbons; (b) loss factor versus temperature for the extruded ribbons. (a) (○) 33% LCP, (◇) 29% LCP, (□) 23% LCP, (△) 17% LCP, (+) 9% LCP, (▽) PP. (b) (○) PP, (△) 9% LCP, (□) 17% LCP, (◇) 23% LCP, (▽) 29% LCP, (+) 33% LCP, (×) LCP.

blends. The pure PP shows ductile plastic deformation and necking occur in the specimen during the tensile tests. The polymer blends containing up to 17% LCP also exhibit ductile fracture. Above 17% LCP blends, brittle fracture predominates. On the basis of static mechanical tests, it appears that the addition of LCP has a much larger effect on the modulus than the strength. Mithal *et al.* [26] reported that the tensile strength of *in situ* composites decreases markedly when LCP is blended with low intrinsic viscosity PET. However, the tensile modulus is found to increase with increasing LCP content. They attributed this to the absence of fibrillar networks in the blends due to the poor processing conditions [26]. Isayev and Subramanian [27] indicated that there was no improvement in the tensile strength of the blends with the addition of LCP which had a higher viscosity than the matrix polymer, whereas the addition of the LCP results in an increase of the flexural modulus. As discussed above, good reinforcement can be achieved in the blends when the spherical particles are deformed into fibres in the flow direction. These oriented fibres carry a significant applied load, thereby reinforcing the matrix. Thus the presence of poorly oriented fibrils and a high concentration of undeformed spherical particles in the blends investigated, lead to a substantial decrease in the mechanical tensile strength. Furthermore, because of their incompatibility, poor adhesion between the PP and LCP also results in a decrease in tensile strength [28].

As mentioned above, the LCP (Vectra A130) used in this work was reinforced with 30 wt% glass fibre. It seems likely that the presence of glass fibres in a LCP has little reinforcing effect in the blends. Chivers and Moore [29] reported that the tensile strength of LCP is not improved by adding glass fibres. A similar observation in glass fibre-reinforced LCP was made by Voss and Friedrich [9]. They pointed out that the tensile strength of LCP is not improved by the addition of glass fibres, because the fibre–matrix bonding is relatively poor [9].

Fig. 10a and b show the dynamic mechanical properties of the extruded PP/LCP blends. The storage modulus is observed to increase with LCP concentrations. The loss factor, tan δ, spectrum of Vectra A130 shows a broad peak at ~ 25 °C and a rather sharp peak at 108 °C. The tan δ peak located at ~ 25 °C can be identified as a relaxation associated with the naphthoic sequences [15], whereas the peak located at 108 °C is associated with the glass transition, T_g. The T_g of PP is located at ~ 18 °C, and the addition of LCP to PP results in a reduction of the peak height of this transition (Fig. 10b). The loss peaks are indicative of the relative amount of damping or energy loss in the material. A decrease in the intensity of the loss peak implies that a reduction occurs in the efficiency of the material in dissipating mechanical energy.

4. Conclusions

1. DSC measurements show that the temperature and heat of crystallization of the blends increase slightly with increasing LCP content.

2. SEM fractographs reveal that the LCP micro-

fibrils are formed in the blends investigated. The fibres are not well oriented in the flow direction. Furthermore, some undeformed LCP particles are observed in high LCP blends.

3. Static tensile tests show that the addition of LCP to PP results in an increase of the tensile modulus but a decrease in tensile strength.

4. Dynamic mechanical tests indicate that the storage modulus of the blends increase with increasing LCP content.

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