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Mechanical properties of injection moulded blends of polypropylene with thermotropic liquid crystalline polymer

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Blends of a thermotropic liquid crystalline polymer (LCP) with polypropylene (PP) were injection moulded. The LCP exhibited a higher viscosity than that of PP. Static and dynamic mechanical measurements, Izod impact tests, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA) were performed on these blends. The static tensile tests show that the tensile modulus and strength of PP are improved with the addition of LCP. The improvement in mechanical properties is associated with the formation of LCP fibrils as evidenced by SEM observations. Dynamic studies on these blends show an increase in the storage modulus but a decrease in loss factor with the addition of LCP. Furthermore, TGA measurements show that the thermal stability of PP is improved substantially with the addition of LCP.

1. Introduction

Recently, a number of attempts have been made to improve the mechanical properties of polymers through the physical blending. Blending of thermotropic liquid crystalline polymer (LCP) with other thermoplastics is attractive for a number of reasons. LCPs are known to show liquid crystalline order and flow properties at elevated temperature. They also exhibit low melt viscosity and low coefficient of thermal expansion [1–3]. The viscosity of the blends is lower than that of the thermoplastic materials, thus they can be easily fabricated using conventional thermoplastic processing techniques. During processing of the blend, the LCP phase may be deformed into a fibrillar structure, thereby producing an *in-situ* composite reinforcement.

The LCP/thermoplastic blends have been reported to be mainly immiscible [4, 5] or partly miscible if the polymers are fairly similar, e.g. a polyester type LCP and a polyester [6–8]. The LCP does not mix properly with thermoplastics, a two-phase morphology is typically formed in binary blend. The morphology of the LCP dispersed phase in immiscible polymer blends plays a key role in the determination of final mechanical properties. Morphologies ranging from spherical droplets to long fibrils have been observed. Good reinforcement is achieved when the LCP phase is deformed into fibres oriented in the flow direction. Furthermore, the reinforcing effect of the LCP phase depends on the volumetric composition, on viscosity ratio between the LCP and matrix, and on the flow field encountered during processing. Generally, the viscosity of the LCP dispersed phase is lower than that of the thermoplastics for the formation of fibres [9, 10]. Among these factors, the flow field has been found to be of primary importance for a specific LCP/thermoplastic blend. Kohli *et al.* [11] reported that the LCP dispersed phase was elongated more effectively in the entrance region by the extensional stress. Shear flow is generally ineffective at developing these fibrillar morphologies.

Injection moulded composite materials are increasingly being used in semistructural applications because they allow mass production of small, complex shapes with high dimensional accuracy. However, the polymers are subjected to a complex environment of stress and thermal gradients during injection moulding. The melt orientation and cooling rate can differ dramatically from the mould walls to the centre or core of the moulding. As a result, characteristic skin-core morphologies are known to develop in semicrystalline polymers, especially polypropylene [12]. When short glass fibres are present, the mouldings are characterized by inherent anisotropy and a layered microstructure due to the fibre orientation varies from the skin to the core section [13]. In injection moulded LCP/polymer blends, a skin-core morphology was regularly observed, particularly at high LCP concentrations [9, 14]. In the skin layer there are more oriented fibrillar LCP domains, while in the core the LCP domains are less oriented or in spherical form.

The morphology and mechanical properties of LCP/thermoplastic blends reported in the literature were mostly concerned with the blends where the LCP has a lower viscosity than the thermoplastic material [7, 9, 11]. Isayev and Subramanian have investigated the mechanical properties of the LCP/PEEK (poly (ether ether ketone)) blends where the LCP has a high

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shear viscosity than the thermoplastic polymer [10]. They reported that substantial improvements in tensile and flexural modulus were observed with the addition of LCP. However, there was no improvement in the break strength with the addition of the LCP [10]. In this work, isotactic polypropylene (PP) is chosen as the matrix material because its viscosity is smaller than that of the LCP under high shear rate conditions. Furthermore, PP is widely used in various fields in view of its relatively low cost and ease of processing. For these reasons, PP has been widely studied both as a homopolymer and as a component of blends. This paper aims to study the effect of LCP content on the morphology and mechanical properties of the injection moulded PP/LCP blends.

2. Experimental procedure

The thermotropic liquid crystalline polymer used in this study is Vectra A130. It is a blend of Vectra A950 and 30 wt % glass fibre. Vectra A950 is a wholly aromatic copolyester consisting of 25 mol % of 2,6-hydroxynaphthoic acid (HNA) and 75 mol % of *p*-hydroxybenzoic acid (HBA). The PP matrix is a commercial product of Himont Company (Pro-fax 6331) with a melt flow index of 12.

Both polymer pellets of PP and LCP were dried in an oven at 70 and 150 °C, respectively. The pellets containing 9, 13, 17, 23, 29, 33, and 50 wt % LCP were tumbled together in a box before injection moulding. They were then moulded with a Chen Hsong injection moulding machine (model JM4 MKII-C). Standard dogbone tensile bars (ASTM-638) were produced. The injection moulding conditions are listed in Table I.

Static mechanical properties of the specimens were tested in an Instron tensile tester (model 4206) at a crosshead speed of 1 mm min^{-1} and an extensometer with a guage length of 50 mm. Five specimens of each composition were tested and the average values reported.

Specimens for the Izod test were prepared from the central longitudinal section of the injection moulded tensile bars. The impact tests (ASTM D-256) were carried out on these specimens using an Ceast impact tester equipped with both personal computer and software.

The decomposition process of the specimens from room temperature to 600 °C under a protective nitrogen atmosphere was determined with a thermal gravimetric analyser (model Seiko SSC/5200). The heating rate employed was 20 °C min^{-1}.

Dynamic mechanical properties of the injection moulded specimens were obtained by a Du Pont dynamic mechanical analyser (model 983) at a fixed frequency of 1 Hz and an oscillation amplitude of 0.4 mm. The temperature range studied was from − 80 to 160 °C with a heating rate of 1 °C min^{-1}.

The morphologies of the fracture surfaces of the blends studied were observed in a scanning electron microscope (Jeol JSM 820). The specimens were fractured in liquid nitrogen and the fracture surfaces were coated with a thin layer of gold before observation.

3. Results and discussion

Fig. 1 shows the typical stress–strain curves of the PP and the blends. It can be seen that pure PP exhibits a yield stress and necking followed by homogeneous drawing. The strain at break of PP exceeds more than 500%. However, the strain at break of the blends decreases dramatically with increasing LCP concentrations. The blends containing 23% LCP and above show an elongation at break of less than 5%. Fig. 2 shows the elongation at break of the blends as

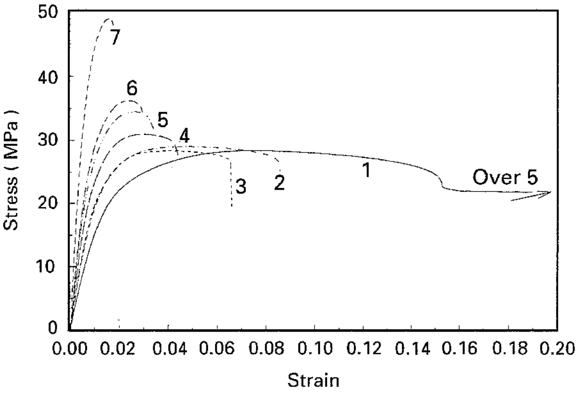


Figure 1 Stress–strain curves of PP/LCP blends. —— (1) Pure PP; -·- (2) 13% LCP: --- (3) 17% LCP; ——— (4) 23% LCP; ·—···— (5) 29% LCP; ---- (6) 33% LCP; --- (7) 50% LCP.

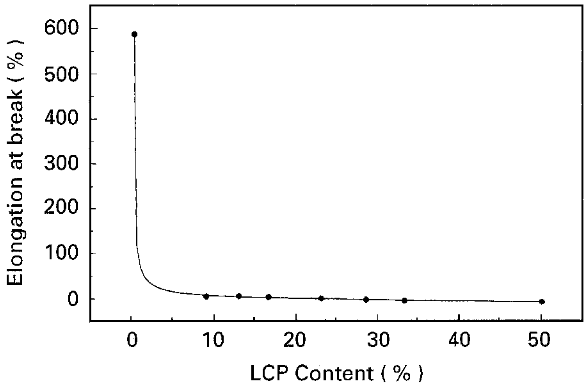


Figure 2 Elongation at break versus LCP composition in PP/LCP blends.

TABLE I Injection moulding processing parameters for PP/LCP blends

	Temperature (°C)				Pressure (kg cm^{-2})	
Samples	Cylinder Zone 1	2	3	Mould	Injection	Holding
PP	225	225	230	50	1050	850
PP/LCP	285	285	290	50	1050	850

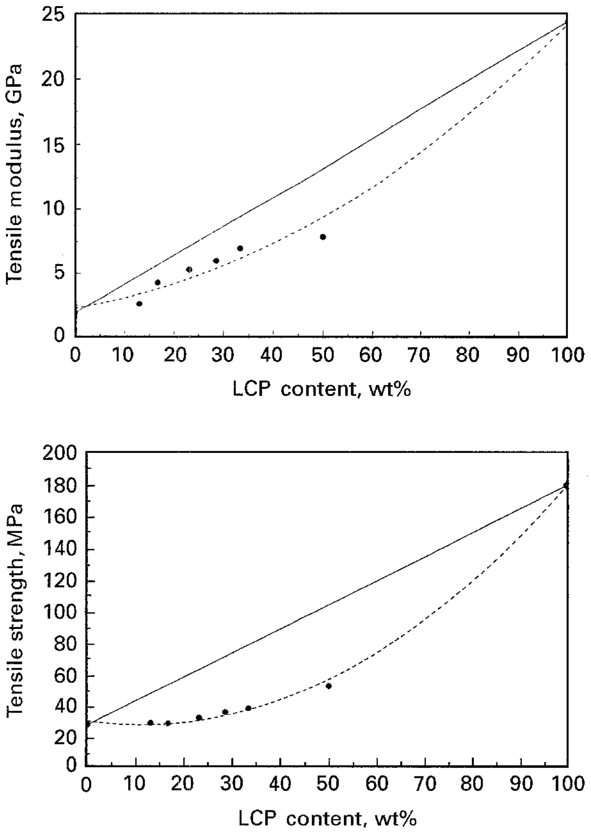


Figure 3 Variation of (a) tensile modulus and (b) tensile strength with LCP content for PP/LCP blends. • Experimental data; ---- fitting curve; —— mixing rule.

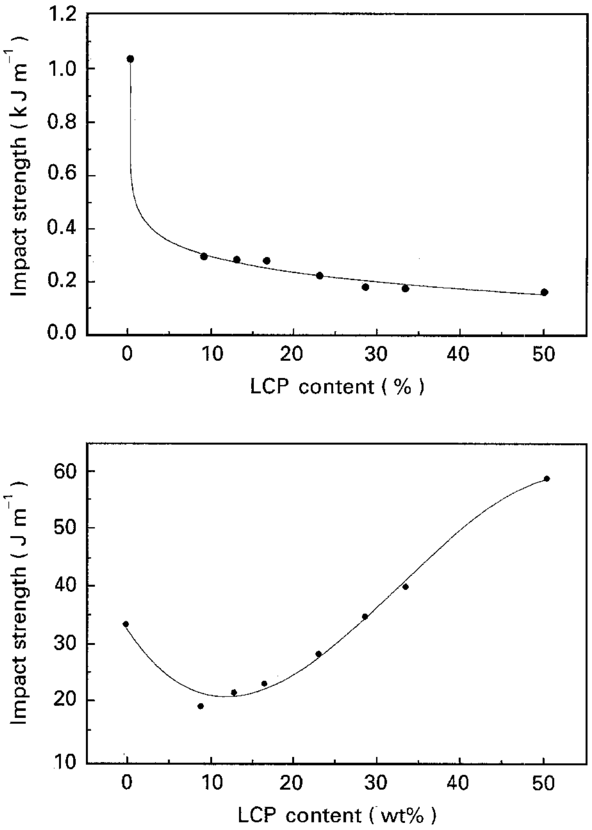
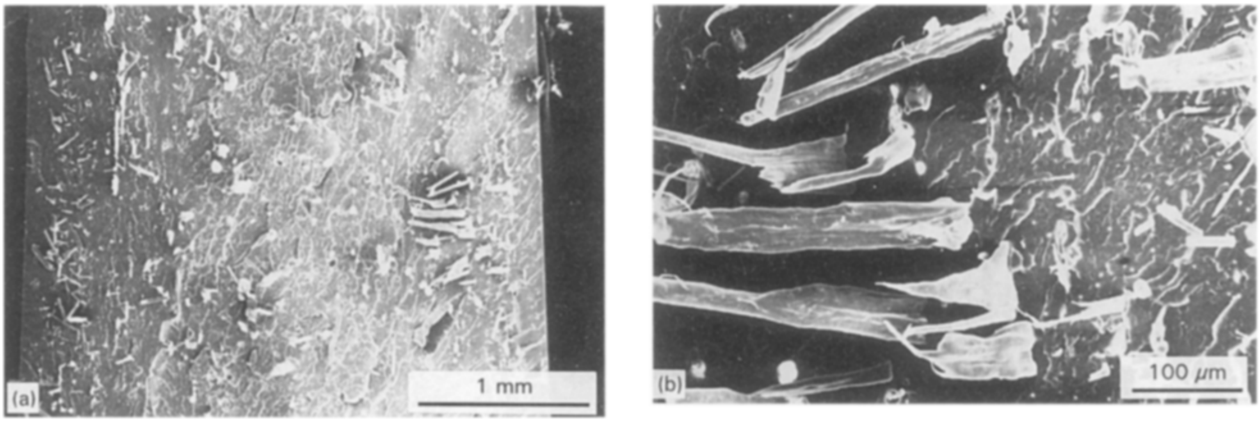


Figure 4 (a) Unnotched Izod impact strength and (b) notched Izod impact strength as a function of LCP content.

a function of the LCP concentration. The pure PP shows extensive plastic deformation upon slowly drawing, thus it exhibits the highest value of elongation. Addition of 9% LCP to the pure PP leads to a marked decrease in the elongation at break. A slight decrease in elongation is observed with further addition of LCP. Therefore, the addition of LCP made the material more brittle.

Fig. 3(a) and (b) show the variation of tensile modulus and strength with LCP concentration. From Fig. 3(a), the modulus of the blends shows an increase up to an LCP concentration of 50%. However, little change in the tensile strength is observed at LCP concentrations up to 17%. As the LCP concentration reaches 23%, a monotonic increase in strength is observed. The results of the tensile tests indicated that LCP acted as a mechanical reinforcement in the blends. The magnitude of the reinforcing effect depended significantly on LCP content. The blends containing high LCP concentrations exhibit high tensile modulus and strength, and low toughness. These are typical mechanical behaviours of fibre reinforced composites. It should be noted that the moduli of the blends lie below those obtained from the rule of mixture, and the strength also lies below the rule of mixture. As mentioned above, immiscible polymer blends form multiphase materials and exhibit poor mechanical properties as a result of poor adhesion between phases. Mechanical properties of immiscible blends generally fall below those predicted by the rule of mixing. Obviously, better mechanical properties would be obtained if the adhesion between PP and LCP phases is improved. Datta *et al.* [15] reported that the compatibilizing agent based on a maleic anhydride grafted PP can be used to promote the interfacial adhesion, thereby results in significant improvements in tensile strength and modulus of PP/LCP blends.

Fig. 4(a) and (b) show the unnotched and notched Izod impact strength for the blends versus LCP concentrations. It is apparent in these figures the notched impact values of all the blends studied are much lower than those of unnotched specimens. It is generally known that the unnotched impact strength is influenced by the energy for crack initiation and propagation, whereas the notched impact strength is associated with the energy dissipation for crack propagation. Moreover, it is evident in Fig. 4(a) that the presence of LCP reduces the total energy absorbed during impact for all blends investigated. In the impact test, the greatest amount of energy is absorbed when the impact force is spread throughout the target and the entire specimen participates in dissipating the energy. Pure PP meets this condition and it shows the highest value of total absorbed energy. As the adhesion between the LCP and PP is relatively poor, consequently the total energy absorbed decreases with the addition of LCP. The unnotched impact energies and the area under the stress–strain curves (Fig. 1) are both considered to be measures of toughness. Both sets of data show the same trend, i.e. an initial sharp decrease followed by a slight decrease with further addition of LCP. From Fig. 4(b), an initial decrease in notched impact strength is observed at low LCP



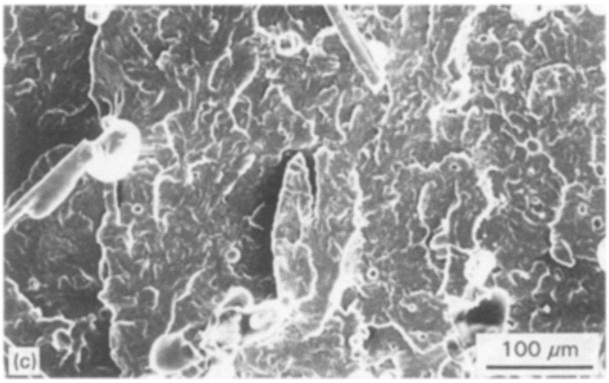


Figure 5 (a) SEM micrograph of the fracture surface of PP/9% LCP blend. A higher magnification of (b) skin layer and (c) core section of micrograph shown in (a).

concentrations up to 9% LCP. Blends with an LCP concentration greater than 13% LCP show a substantial increase in the impact strength values. This implies that the LCP phase tends to improve the resistance of polymer to crack propagation. Such LCP phase is expected to form fibrillar network within the specimens with high LCP additions during injection moulding. A similar increase in the notched impact strength with increasing LCP additions has been observed in polyethylene terephthalate (PET)/LCP blends [7]. An island model was developed by Brostow and colleagues to explain the effect of LCP on crack propagation of the PET/LCP blends [7].

Fig. 5(a) shows the SEM micrographs of the fracture surface of the PP/9%LCP blends. Higher magnifications of the skin and the core regions of the same specimen are shown in Figs 5 (b–c), respectively. These micrographs illustrate that the LCP phase tends to elongate into fibrils near the skin region. The diameter of the LCP fibrils varies from 20–30 μm. However there are only fewer fibrils exist near the core region. Moreover, some voids are observed in the core region indicating poor adhesion between the LCP and PP (Fig. 5(c)). As the LCP content increases, numerous high extended fibrils are formed in both skin and core sections (Figs. 6(a–c)). Furthermore, the skin–core structure does not develop for blends containing high LCP concentrations. Fig. 7(a) and (b) show the SEM micrographs of the PP/33%LCP blend following dissolution of PP matrix in boiling xylene solution. It can be seen from these micrographs

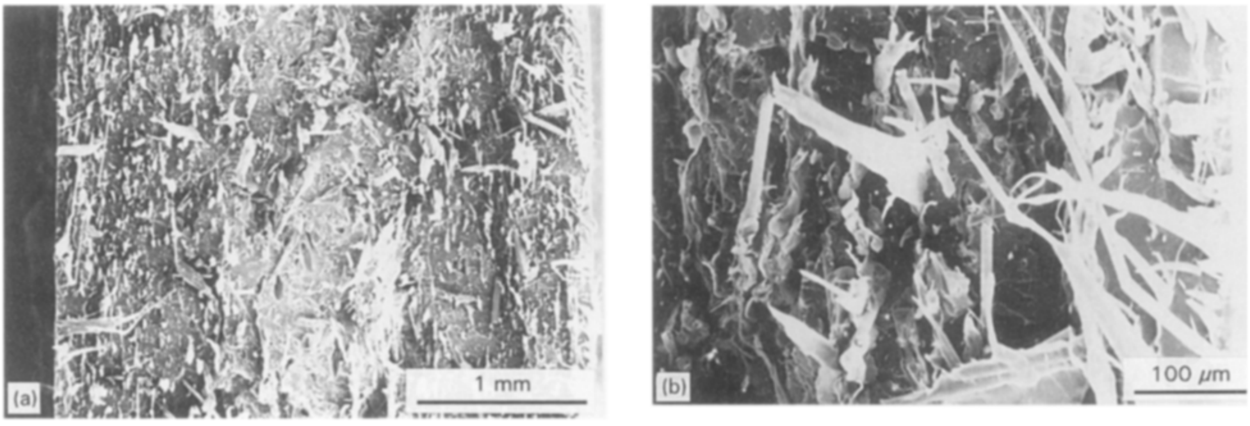


Figure 6 (a) SEM micrograph of the fracture surface of PP/33% LCP blend. A higher magnification of (b) skin layer and (c) core section of micrograph shown in (a).

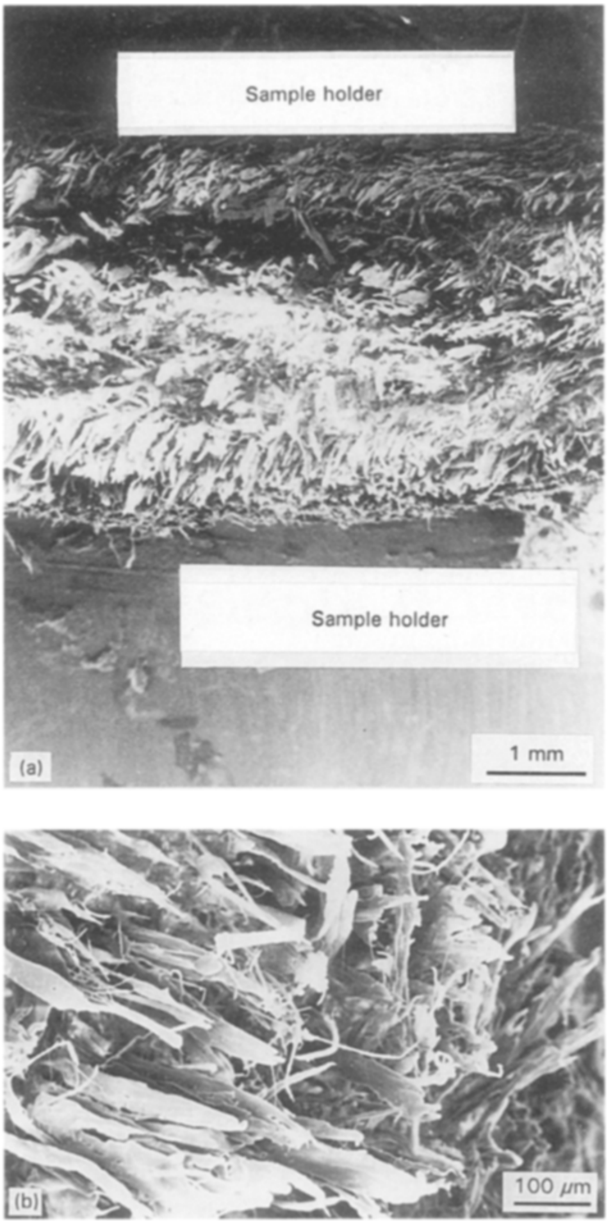


Figure 7 SEM micrograph of the LCP phase in PP/33% LCP blend after dissolving the PP matrix in boiling xylene. (a) A low magnification showing an overall view of the specimen; (b) skin region.

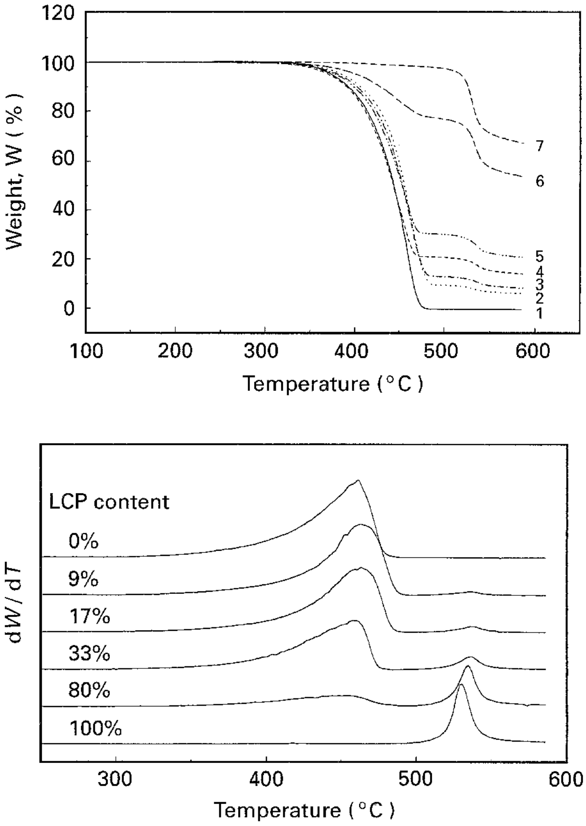


Figure 8 (a) Weight loss and (b) derivative weight loss curves of PP/LCP blends. —— (1) Pure PP; ····· (2) 9% LCP; ·–·– (3) 17% LCP; --- (4) 23% LCP; ·—···— (5) 33% LCP; –·–– (6) 80% LCP; ——— (7) LCP.

that the PP/33%LCP does not display a skin-core morphology. Long fibrils are formed extensively in the skin and core sections of this specimen,

In general, the fibres in the skin layer are highly oriented along the injection flow direction. The orientation of these fibres is caused by elongation flow in the melt advancing front region (fountain flow). It has been reported that the orientation tends to become transverse to the flow direction near the core region [16]. In the present work, fibrillation of LCP phase are observed in the blends despite the fact that the LCP exhibits a higher melt viscosity than the PP. The formation of LCP fibrils leads to an increase in both tensile modulus and strength for the blends (Fig. 3(a) and (b)). These fibrils therefore effectively reinforce the PP matrix. According to the theory of Taylor [17], low viscosity particles are elongated in the flow direction when blended with a higher viscosity polymeric matrix. 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. Long fibres are reported to form in the injection moulded amorphous nylon/LCP, PET/LCP blends etc. as they meet these criteria [9, 18]. On the other hand, Isayev and Subramanian reported that the tensile modulus of PEEK is improved with the addition of LCP. In this case, the LCP has a higher shear viscosity than the PEEK [10]. However, the break strength of the PEEK/LCP blends is not improved by adding LCP. This is because the LCP phase does not elongate into fine fibrillar structures [10].

We now consider the thermal behaviour of the blends as determined by thermogravimetric analysis (TGA) and dynamic mechanical measurements. The results of the TGA studies on the blends are shown in Fig. 8(a) and (b). Pure PP tends to decompose between 320 °C and 476 °C with the DTG peak temperature located at ~460 °C. A significant weight loss occurs in the PP before 476 °C. The thermal stability of LCP is much better than that of the PP as evidenced by a relatively lower weight loss of the LCP. The decomposition of LCP commences at 517 °C with the DTG peak temperature occuring at ~529 °C. The TGA curves also indicate that the weight loss of the blends decreases with increasing LCP content. Thus the stability of the blends is improved with LCP addition. However, it has been reported that the weight loss of some LCP/thermoplastic blends is much higher than that in the pure materials possibly due to the chemical interaction between the components [10, 19].

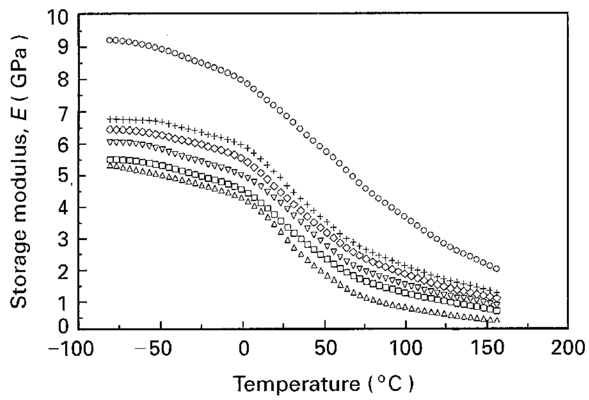


Figure 9 Storage modulus versus temperature for the PP/LCP blends. △ PP; □ 17% LCP; ▽ 23% LCP; ◇ 29% LCP; + 33% LCP; ○ 50% LCP.

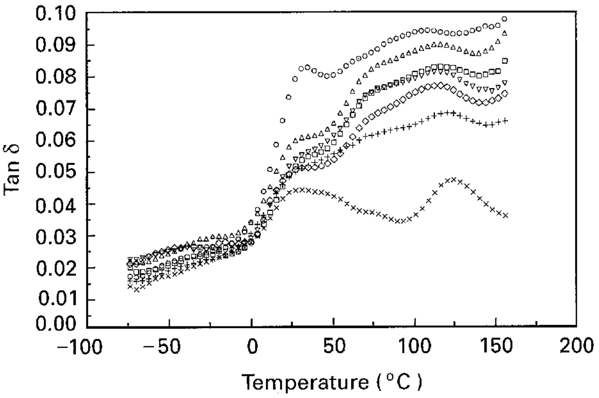


Figure 10 Loss factor versus temperature for the PP/LCP blends. ○ PP; △ 17% LCP; □ 23% LCP; ▽ 29% LCP; ◇ 33% LCP; + 50% LCP; × LCP.

Fig. 9 shows the variation of the storage modulus for the blends with temperature. The storage modulus of pure PP decreases sharply near the glass transition temperature (T_g) of ~28 °C. Furthermore, the storage modulus of the blends increases with increasing LCP concentrations. Such behaviour is similar to that of the static tensile modulus as discussed previously. Fig. 10 shows the loss factor (tan δ) versus temperature for the PP/LCP blends. The LCP exhibits two loss peaks which are located at 25 °C and 108 °C, respectively. The loss peak at 25 °C is identified as a relaxation peak associated with the napthoic process [20], whereas the peak located at 108 °C is associated with the glass transition. The T_g of PP locates at 28 °C and the incorporation of LCP into the PP matrix leads to a broadening of this transition peak and a decrease in intensity. It has been reported that the degree of crystallization of the matrix polymer is increased by the addition of LCP [21]. Since the relaxation associated with T_g is in the amorphous phase, specimens with a higher degree of crystallinity tend to exhibit a smaller loss peak.

4. Conclusions

1. Static tensile tests show that the addition of LCP to PP results in an increase of both tensile modulus and strength but a decrease in elongation at break. The improvement in tensile modulus and strength is associated with the formation of LCP fibrils as evidenced by SEM examinations.
2. Izod impact tests reveal that the unnotched impact strength decreases with increasing LCP content. The impact energies experience an initial sharp decrease followed by a slight decrease with further addition of LCP.
3. The thermal stability of PP was improved with the incorporation of LCP phase.
4. Dynamic mechanical measurements show that the storage modulus of the blends increases with increasing LCP content whereas the loss factor decreases with increasing LCP concentration.

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