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Preparation and properties of injection-moulded blends of poly(vinyl chloride) and liquid crystal copolyester

Y.Z. Meng, S.C. Tjong*

Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, People's Republic of China

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Abstract

Blends of poly(vinyl chloride) (PVC) and a liquid crystal copolyester (LCP) were prepared by injection-moulding. The LCP used was a copolyester consisting of 60 mol% *p*-hydroxybenzoic acid (PHB) and 40 mol% poly(ethylene terephthalate) (PET). The mechanical and thermal properties and the morphologies of these blends were investigated. The results showed that the tensile strength and modulus of the blends tend to increase with increasing LCP content for the blends containing LCP content below 15%, and they decreased significantly with further increasing LCP content. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) showed that PVC and LCP are partially miscible for the blends with LCP content < 15 wt% and miscible for the blends with LCP content > 15 wt%. The torque measurements indicated that the viscosity ratio between the LCP and PVC matrix is much smaller than unity. This implied that LCP fibrillation is likely to occur in the PVC/LCP blends. However, scanning electron microscopy (SEM) observations revealed that fine fibrils are only formed in the skin layer of the blends containing LCP content < 15 wt%. Two-phase morphology disappeared in the PVC/LCP blends containing LCP content above 15 wt% owing to the decomposition of LCP during processing.

Keywords: PVC; Liquid crystalline polymer; Miscibility

1. Introduction

In recent years, blends containing thermotropic liquid crystalline polymers (LCPs) and thermoplastics have attracted much research attention [1–10]. The interest comes from two major advantages of blending LCPs with thermoplastics. First, the LCPs exhibit low melt viscosity, hence the addition of a small amount of LCPs to thermoplastics can result in a considerable reduction in the blend melt viscosity thereby improving the processability of engineering plastics. Second, the LCPs generally exhibit a high degree of order in the melt under the conditions of shear and extension during processing. Therefore, the LCP phase can deform into fibrils, and these fibrils then act as the reinforcing element in the blends as a result of the inherent high strength and stiffness of the LCPs. However, the fibrillation of LCP in thermoplastic melts is influenced by several factors. These include LCP concentration, miscibility between LCP and thermoplastics, and processing parameters such as the melt viscosity ratio of LCP to polymer matrix (Vr), melt temperature, flow mode and rate. The effects of these factors on the fibrillation of LCP in a matrix have been extensively reviewed by La Mantia [11].

It is recognized that the processing temperatures of the LCP/thermoplastic blends must be carefully selected. Blends prepared at temperatures near the solid to nematic transition of LCP generally exhibit superior mechanical properties compared with systems fabricated at significantly higher temperatures. This is due to the disintegration of LCP fibrils into droplets at higher processing temperatures. In some cases, the polymer matrix can decompose at elevated temperatures, and this leads to the Vr having a value much lower than unity [6]. Apart from these factors, the selection of compounding conditions also has great impact on the properties of the polymer blends containing LCP. In previous work [6], the LCP phase was observed to disperse into a porous and foamy structure within the compatibilized polyamide 6 matrix owing to the decomposition of the LCP which consisted of *p*-hydroxybenzoic acid (PHB) and poly(ethylene terephthalate) (PET). The decomposition process was prompted by the presence of an acid which derived from maleic anhydride and maleated propylene. In this case, the LCP did not act as a reinforcement for the thermoplastic matrix,

* Corresponding author.

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hence the compatibilized LCP/PA blends exhibited poor mechanical properties.

Poly(vinyl chloride) (PVC) is often categorized as a commodity thermoplastic material. Its properties can be tailored to meet very specific and demanding applications in building and construction, and in electronics and medicinal fields. However, little information is available in the literature concerning the properties of the blends of PVC and rigid LCP. One article concerning the properties of the PVC blends containing LCP was reported recently by Sato and Ujiie [12], and they prepared PVC/semirigid LCP blends by solution blending. However, the LCP used by them was a semirigid thermotropic liquid crystalline polycarbonate [12]. The miscibility and morphology of those blends were examined by means of thermal analysis and scanning electron microscopy (SEM). Their results demonstrated that no phase separation existed in the micrometre level, and the semirigid LCP formed miscible blends with the PVC matrix. The storage modulus of those blends tended to decrease with increasing LCP content, and the blends containing LCP content higher than 50 wt% were extremely brittle.

In this work, injection-moulded blends of PVC with a rigid thermotropic LCP were prepared. The mechanical properties, morphologies and miscibility of the injection-moulded blends were investigated by means of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), SEM and tensile measurements. The effect of the reinforcement action on the PVC, and the correlation between the microstructure of the PVC/LCP blends with the torque, thermal and tensile measurements are discussed.

2. Experimental

2.1. Materials

The LCP used in this work is a copolyester of 60 mol% *p*-hydroxybenzoic acid (PHB) and 40 mol% poly(ethylene terephthalate) (PET) supplied by Beijing Chemical Research Institute (China). Taiwan-made PVC powders (S-60) were used as the matrix material. The processing lubricants for PVC were chemical reagent-grade stearic acid and calcium stearate; tribasic lead sulphate and dibasic lead sulphate were used for the stabilization of the PVC matrix. The LCP pellets were dried in an oven at 100°C for 24 h prior to blending.

2.2. Blending procedure

The PVC resin was initially prepared in a twin-screw Brabender Plasticorder at 180°C and 35 rev min^{-1} by blending 100 parts per hundred (phr) PVC powder with 7 phr tribasic lead sulphate, 3 phr dibasic lead sulphate, 2 phr calcium stearate and 0.5 phr stearic acid. The extrudates were cut into pellets by a pelletizer. The PVC and LCP pellets were mixed in a plastic box before injection-moulding. Dog-bone shaped tensile bars (ASTM D-638) were injection-moulded directly from the PVC and LCP pellets. The LCP contents of PVC/LCP blends were fixed at 0, 5, 15, 25, 35 and 45 wt%. The barrel zone temperatures were set at 210, 210 and 205°C.

2.3. Static mechanical properties

The tensile behaviour of the specimens was determined using an Instron tensile tester (model 4206) at 23°C with a relative humidity of 50%. A crosshead speed of 1 mm min^{-1} was used in the measurements. The gauge length of the specimens was 57 mm. At least five specimens of each composition were tested and the average values reported.

2.4. Morphology observation

The morphologies of the fracture surfaces of all blends 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 prior to SEM examinations.

2.5. Differential scanning calorimetry (DSC)

DSC measurements were carried out using a Perkin-Elmer calorimeter (model DSC-7) from 30 to 250°C at a heating rate of 10°C min^{-1} under a protective nitrogen atmosphere.

2.6. Torque measurements

Torque values for the blends and pure polymers were measured using a Brabender Plasticorder batch mixer at 210°C and 30 rev min^{-1} for 5 min. The chamber volume was 50 cm^3. For each examination, 30 g material were added into the batch.

2.7. Dynamic mechanical analysis (DMA)

DMA of the injection-moulded specimens were conducted using a Du Pont dynamic mechanical analyser (model 983) at a fixed frequency of 1 Hz and an oscillation amplitude of 0.2 mm. The temperature range studied was from -40 to 150°C with a heating rate of 2°C min^{-1}.

2.8. Thermogravimetric analysis (TGA)

The decomposition process of the specimens from 50 to 650°C under a protective helium-atmosphere (200 ml min^{-1}) was determined with a thermogravimetric analyser (Seiko model SSC/5200). The heating rate employed was 10°C min^{-1}.

Table 1
Effects of temperature on the tensile properties of injection-moulded PVC and LCP specimens

Material	Temperature (°C)	Tensile strength (MPa)	Tensile modulus (MPa)	Strain-at-break (%)	Tensile energy (J)
PVC	180	45.52	1397	27.93	26.30
	200	44.85	1390	25.96	25.69
	210	44.52	1365	26.35	24.23
LCP	190	21.49	1386	1.965	0.5344
	200	38.67	2660	1.649	0.8227
	210	62.79	3314	2.557	2.023

3. Results and discussion

3.1. Tensile properties

As mentioned above, processing temperatures play a decisive role in fibrillation of LCP domains in PVC/LCP blends since PVC decomposes readily at processing temperatures higher than 170°C, particularly at temperatures higher than 190°C. On the other hand, a stabilized PVC does not degrade at 170°C. The processing temperature for rigid LCP is generally higher than 200°C. In order to avoid thermal degradation of the PVC matrix of PVC/LCP blends, we first investigated the effects of temperature on the mechanical properties of pure PVC and LCP. Table 1 lists the tensile properties for PVC resin and LCP. It can be seen that the injection-moulding temperatures of 180–210°C have little effect on the tensile properties for PVC resin. The tensile strength decreases very slightly with increasing temperatures from 180–210°C. However, the processing temperatures have a significant effect on the mechanical properties of injection-moulded LCP specimens. It can be seen that the tensile strength and modulus of the specimens fabricated at 210°C are three times higher than those prepared at 190°C. The LCP specimens fabricated at 210°C exhibit better mechanical properties because the LCP domains can deform into a well-oriented structure at a temperature above its melting point (~210°C). In this context, we select the processing temperature of PVC/LCP blends at 210°C.

Fig. 1a and Fig. 1b show the variations between the tensile strength and modulus with LCP content, respectively. It is clear that the tensile strength and modulus increase with increasing LCP content up to 15 wt%, and their values are above those predicted from the rule of mixture. However, both strength and modulus decrease dramatically with further increasing LCP content. This abnormal behaviour is similar to that of compatibilized LCP/PA polyblends [7], in which we indicated that the decreasing trend in the mechanical strength of these polyblends is associated with the degradation of LCP catalysed by the presence of an acid, i.e. free maleic anhydride. Lee and Dibenedetto [13] and Yoda et al. [14] reported that the LCP consisting of PHB and PET can decompose easily into carbon dioxide and acetaldehyde during processing, thereby resulting in a material with a very low molecular weight [13]. Thus, it is likely that the LCP phase of PVC/LCP blends degrades readily during injection-moulding. Fig. 2 shows the plot of strain at break versus LCP content. Clearly, the strain at break decreases sharply with increasing LCP content. Moreover, the tensile energy at break also exhibits a similar decreasing tendency with LCP content (Fig. 3). These results imply that the blends become extremely brittle as the LCP content increases.

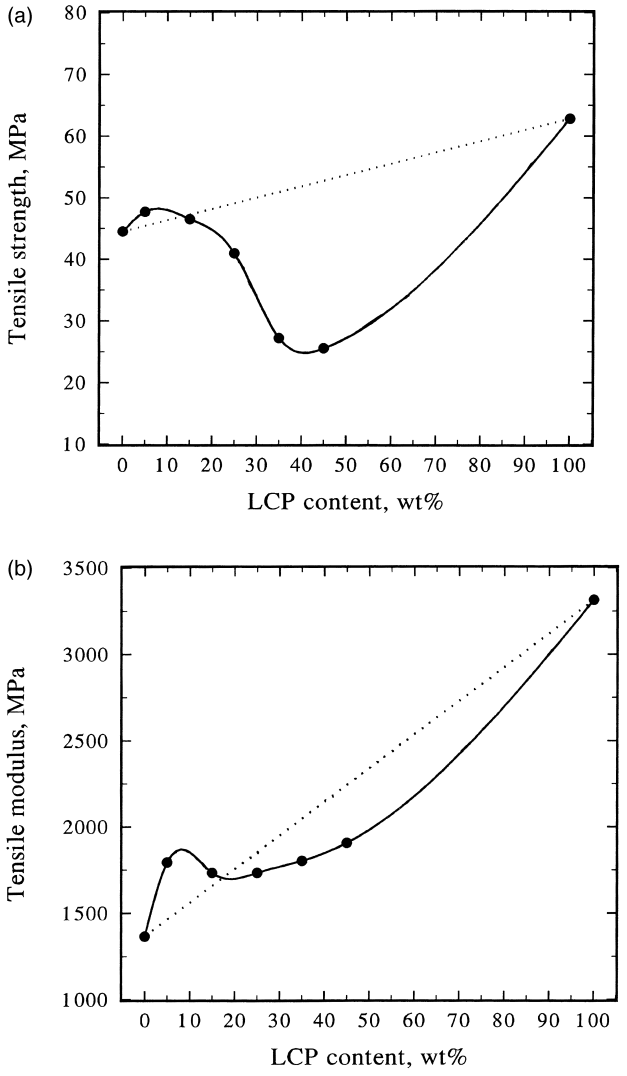

Fig. 1. Variation of (a) tensile strength and (b) modulus with LCP content for the PVC/LCP blends.

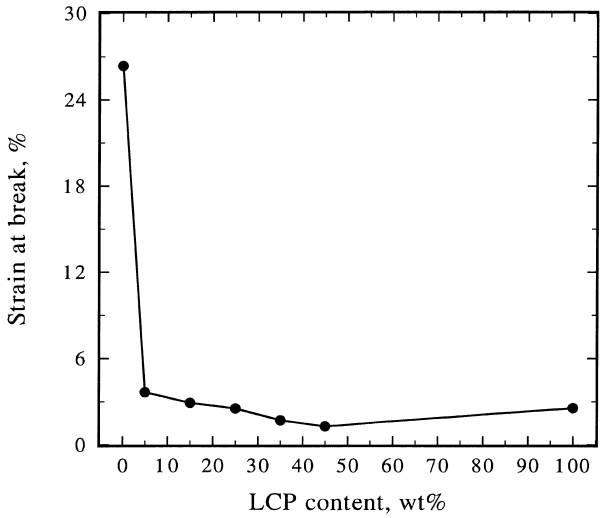

Fig. 2. Strain at break versus LCP content for the PVC/LCP blends.

3.2. Torque behaviour

Several researchers have studied the flow behaviour of thermoplastic/LCP blends [15–18]. It is commonly observed that LCP fibrillation occurs when the viscosity ratio of LCP to the polymer matrix is smaller than or near unity. The relationships between the torque value and mixing time for PVC resin and LCP are depicted in Fig. 4. The torque value is generally related to the viscosity of the polymers. For PVC, the torque value increases with increasing mixing time up to 1.5 min, thereafter it levels off. The increase in torque value resulted from the thermal decomposition or dehydrochlorination of PVC, as dehydrochlorination leads to the formation of conjugated double bonds in PVC. Furthermore, discolouration is observed for the PVC samples after the torque test. In general, the molecular chain with conjugated double or sp^2 bonds is more rigid than that with single or sp^3 bonds. On the other hand, the torque value for LCP decreases with increasing

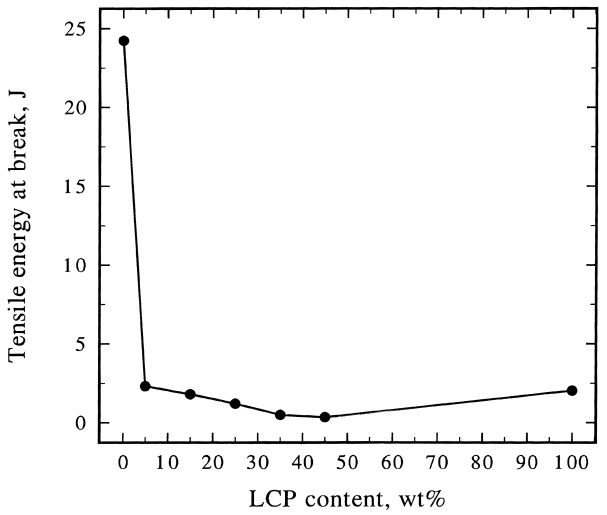

Fig. 3. Tensile energy at break versus LCP content for the PVC/LCP blends.

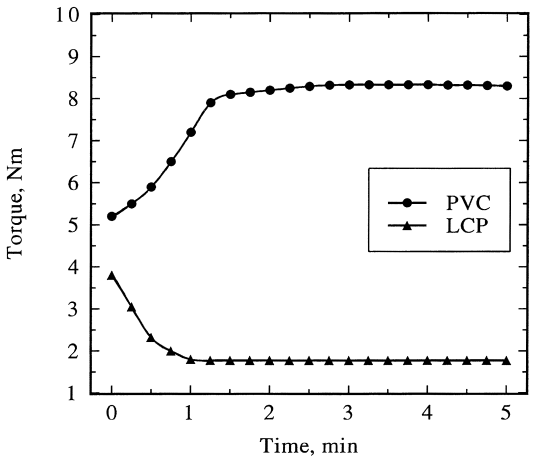

Fig. 4. Torque versus mixing time for PVC and LCP at 210°C.

mixing time during the initial loading indicating that LCP molecular chains begin to orient in the melt. After 1 min, the torque reaches a steady-state value. It should be noted that the melt viscosity of LCP is much lower than that of the PVC matrix, thus producing a Vr value smaller than unity and thereby favouring the formation of LCP fibrils within the PVC matrix. However, the Vr values shown in Fig. 4 do not correlate well with the LCP morphologies of the PVC/LCP blends as observed by SEM. The reasons for this will be discussed later.

Fig. 5 shows the torque value versus mixing time for the PVC/LCP blends at 210°C. It is evident that the torque values decrease considerably with increasing LCP content. This decrease with LCP content is more evident when the results are replotted as in Fig. 6. The results demonstrate that the processability of PVC can be greatly improved by the addition of LCP. Moreover, the melt viscosities of all the blends tend to decrease with increasing mixing time with the exception of the PVC/5% LCP blend. A reduction in melt viscosity with time indicates that the LCP phase of the PVC/LCP blends decomposes during processing since the melt viscosities for both LCP and PVC achieve steady values after 1.5 min.

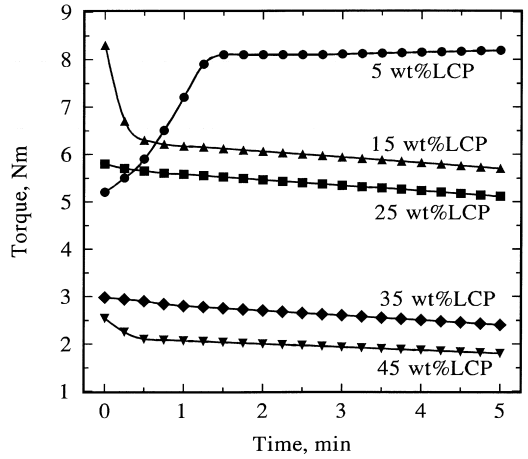

Fig. 5. Torque versus mixing time for the PVC/LCP blends at 210°C.

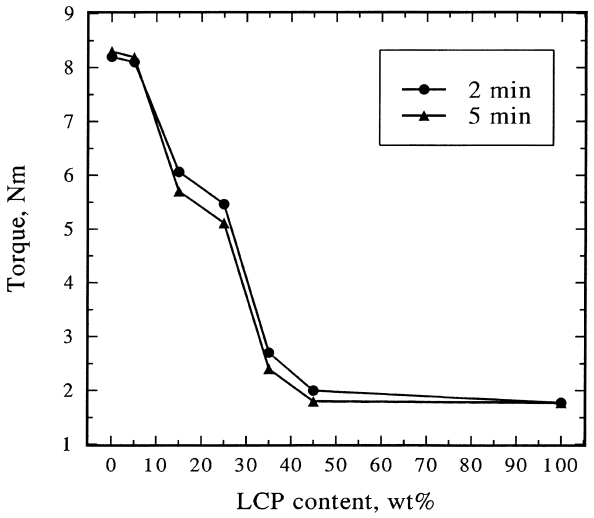

Fig. 6. Relationships between torque and LCP content for the PVC/LCP blends mixed at 2 and 5 min, respectively.

3.3. Dynamic mechanical properties

Fig. 7 shows the storage modulus versus temperature for PVC, LCP and their blends. It can be seen that the relationship between the storage modulus and LCP content is similar to that of the static tensile modulus as shown in Fig. 1b. Fig. 8 shows the plots of tan delta versus temperature for the PVC/LCP blends. It is apparent that all the curves exhibit one peak or a glass transition temperature T_g with the exception of the PVC/5% LCP blend. The thermal properties of PVC/LCP blends are presented in Table 2. The T_g values of PVC and LCP are 84.4 and 112.0°C, respectively. The PVC/5% LCP blend exhibits two T_gs (84.45 and 113.2°C) indicating that PVC and LCP phases in this blend are immiscible. However, only one T_g is observed for the PVC/LCP blends containing LCP content higher than 5 wt%. Moreover, the T_g peaks tend to shift towards higher temperatures with increasing LCP content (Table 2) indicating that miscible blends are formed in these cases. It is well known that the C–Cl bonds of the

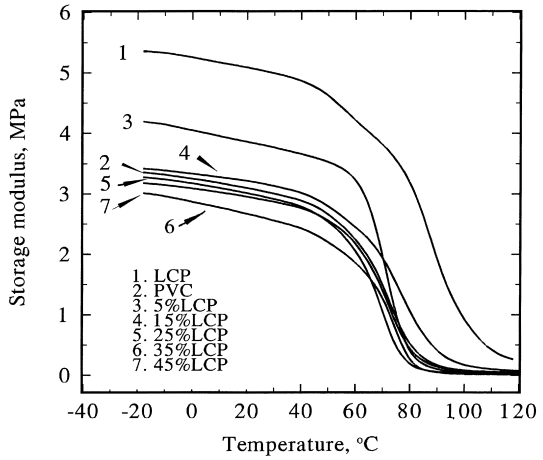

Fig. 7. Storage modulus versus temperature for PVC, LCP and their blends.

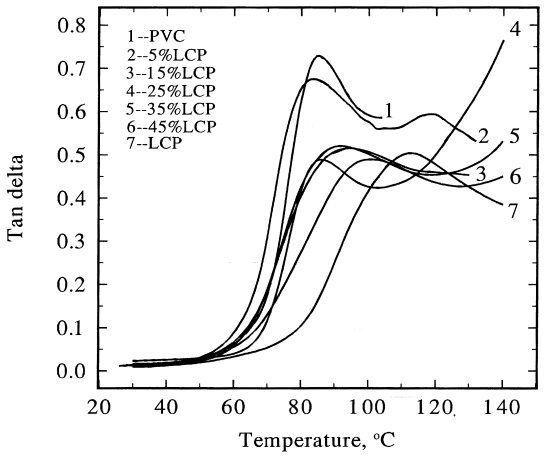

Fig. 8. Tan delta versus temperature for PVC, LCP and their blends.

PVC chain exhibit very strong polarity, and such polarity in turn leads to the H–C bond possessing strong electrophilicity. Therefore, the carbonyl groups in LCP can develop stronger hydrogen bonds with hydrogen atoms of PVC as shown in Fig. 9. These hydrogen bonds act as an effective compatibilizer for the PVC/LCP blends. The compatibilizer enhances the interaction between PVC and LCP, thereby producing a miscible blend. PVC is known to form miscible blends with various thermoplastic polymers containing ester and/or ether linkages such as polyester and vinyl acetate copolymers [19–22], poly(ethylene oxide) [23] and poly(methylene oxide) [24]. The miscibility between the matrix and reinforcement of a polymer melt blend has a dramatic effect on its mechanical properties. Generally, a miscible blend exhibits a poorer mechanical strength because of the loss of reinforcement of a polymer component. As mentioned above, the decomposition of LCP in the PVC matrix during processing results in the break-up of LCP fibrils. They consequently form a miscible blend. This is the case for the blends with LCP content above 15 wt%.

3.4. Thermal stability

Fig. 10 shows the typical DSC curves for different PVC samples. It can be seen that the T_g of both PVC samples is located at 84.4°C. However, an additional peak is located at 121.6°C for the PVC specimen subject to extrusion and injection-moulding at 210°C. The peak at 121.6°C relates to the processing history as documented in the literature [25,26].

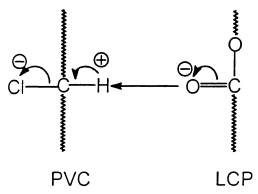

Fig. 9. Formation of hydrogen bonds in the PVC/LCP blends.

Table 2
Thermal properties for PVC, LCP and their blends

Material	T_g^1 (°C)	T_g^2 (°C)	$T_{-5\%}$ (°C)	T_{max}^1 (°C)	T_{max}^2 (°C)
PVC	84.40	–	282.7	301.2	477.2
PVC/5% LCP blend	84.45	113.20	259.4	300.1	445.1
PVC/15% LCP blend	93.24	–	264.3	296.3	447.7
PVC/25% LCP blend	92.10	–	268.1	295.0	445.3
PVC/35% LCP blend	92.07	–	270.4	297.5	447.6
PVC/45% LCP blend	102.30	–	271.5	295.2	446.5
LCP	112.00	–	418.1	462.5	–

Fig. 11 shows the weight loss and derivative weight loss plots for PVC and LCP. It can be seen that the thermal stability of LCP used in this work is much higher than that of PVC. Moreover, the weight loss curve of PVC exhibits two flat regimes in the temperature range studied. It is evident that these two stages correspond to the dehydrochlorination of the PVC matrix and to the thermal decomposition of the dehydrochlorinated PVC which consists mainly of conjugated double bonds. Thus, the decomposition temperatures for LCP and dehydrochlorinated PVC are essentially identical owing to the conjugated double bonds exhibiting a similar thermal stability as the aromatic chain. From Fig. 11, two decomposition peaks for PVC can also be seen in the derivative weight loss curve, and they are designated as T_{max}^1 and T_{max}^2, respectively. These two peak temperatures are listed in Table 2. This table reveals that the T_{max}^1 and T_{max}^2 for the PVC/LCP blends decrease with increasing LCP content for LCP content smaller than 15 wt%, and then level off with further increasing LCP content.

Fig. 12 shows the plots of weight loss versus LCP content for PVC and its blends. The 5% weight loss temperatures ($T_{-5\%}$) for each blend are also listed in Table 2. It can be seen that the variation trend for $T_{-5\%}$ with LCP content is similar to that for T_{max}^1 or T_{max}^2. This implies that the introduction of LCP into the PVC matrix does not improve the thermal stability of the PVC/LCP blends although the thermal stability of LCP used in this work is much higher than that of PVC. Moreover, both strength and modulus of the PVC/LCP blends decrease dramatically with increasing LCP content as shown in Fig. 1a and Fig. 1b. This abnormal behaviour is associated with the degradation of LCP catalysed by the presence of an acid, i.e. HCl derived from the dehydrochlorination of PVC. For the PVC/LCP blend system, it can therefore be concluded that LCP appears to degrade chemically with the incorporation of LCP into PVC, hence poor mechanical properties result. This view is also discussed in the mechanical properties section and is supported by the results presented there.

3.5. Blend morphology

For injection-moulded specimens, a skin–core structure is usually developed in the moulded parts where highly oriented molecules are only found in the skin layer. A high degree of fibril orientation resulted from the extensional flow at the advancing flow front and from rapid cooling near the mould surface [8,27–30]. Fig. 13a and Fig. 13b show the SEM fractographs of the skin and core section of PVC/5% LCP injection-moulded blends, respectively. From Fig. 13a, it can be seen that the LCP domains of the skin section deform into fine and short fibrils. However, the LCP phase of the core section disperses into ellipsoids (Fig. 13b). Moreover, only few cavities can be observed in the core section indicating that good compatibility exists between the PVC matrix and LCP. As the LCP content of the blend is increased to 15 wt%, the

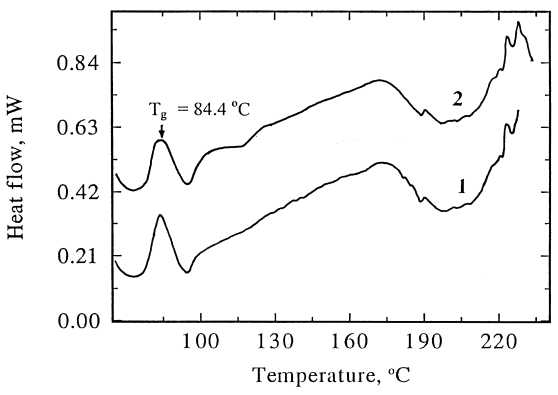

Fig. 10. DSC curves of (1) pure PVC resin and (2) PVC sample subject to extrusion and injection-moulding at 210°C.

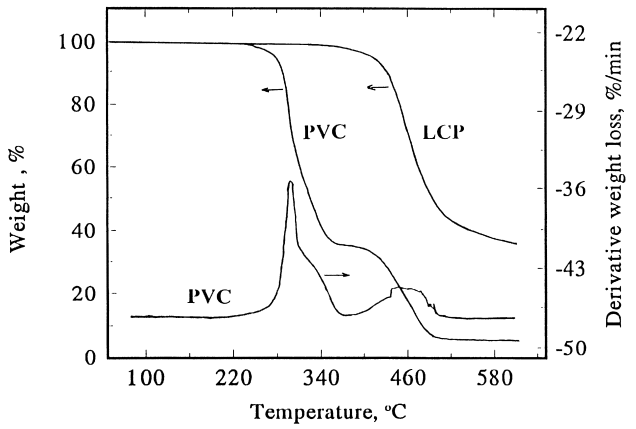

Fig. 11. Weight loss and derivative weight loss curves for PVC and LCP.

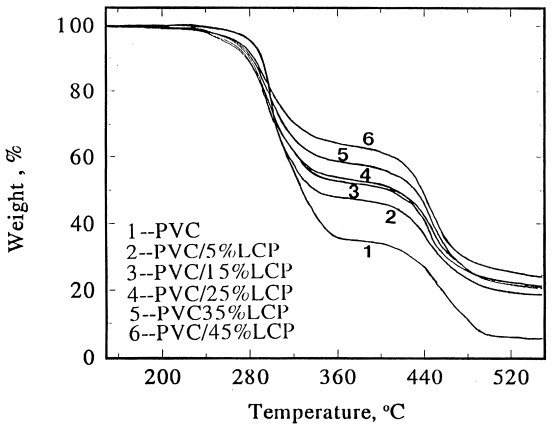

Fig. 12. Weight loss curves for PVC resin and its blends containing various LCP contents.

morphologies of the PVC/15% LCP specimen are basically similar to those of PVC/5% LCP specimen (Fig. 14a and Fig. 14b). It should be noted that the dispersed LCP droplets have very small diameters ($< 1\ \mu$m). The result demonstrates that PVC is partially miscible with LCP or miscible at the micrometre level. As the LCP content is further increased up to 25 wt%, LCP fibrillation does not take place in the PVC/LCP blends owing to the thermal degradation of LCP. The miscibility between PVC and LCP tends to be enhanced with increasing LCP content. It is believed that the improved miscibility results from the degradation of the LCP within the PVC matrix since polymers of a melt blend with lower molecular weight have better miscibility than those with higher molecular weight. The fractographs of the core region of the blends containing LCP $\geq$ 25 wt% no longer exhibit two-phase morphologies (Fig. 15b and Fig. 15c), demonstrating that PVC and LCP are miscible in these cases.

4. Conclusions

Injection-moulded blends of poly(vinyl chloride) and liquid crystal copolyester were prepared. The results showed that the tensile strength and modulus appeared to increase with increasing LCP content for the blends with LCP content lower than 15 wt%, and they decreased significantly with further increasing LCP content. Thermal analyses indicated that PVC and LCP are partially miscible for the blends containing LCP content $<$ 15 wt%, and miscible at LCP content above 15 wt%. The torque measurements showed that the

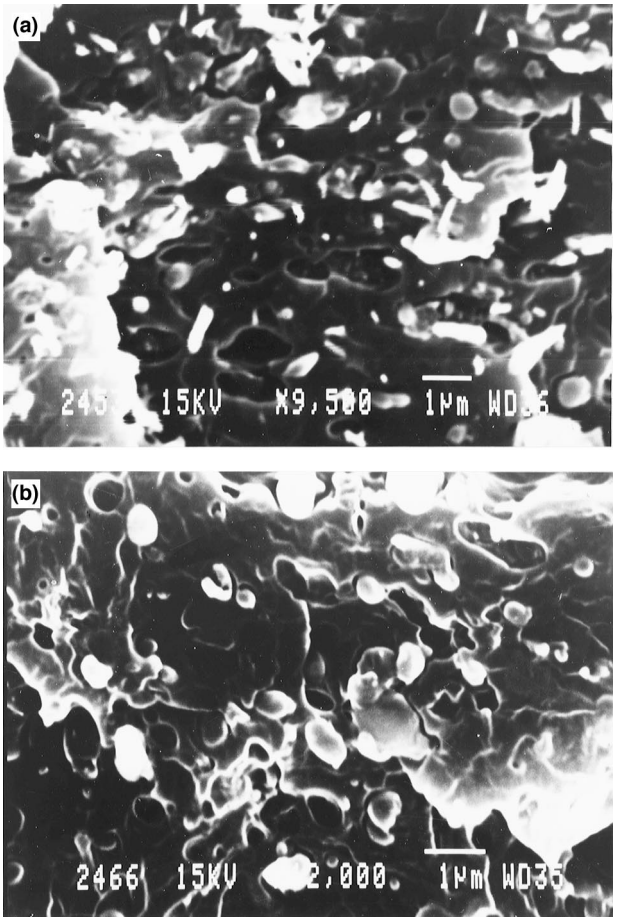

Fig. 13. SEM fractographs of (a) skin and (b) core sections of the injection-moulded PVC/5% LCP specimen.

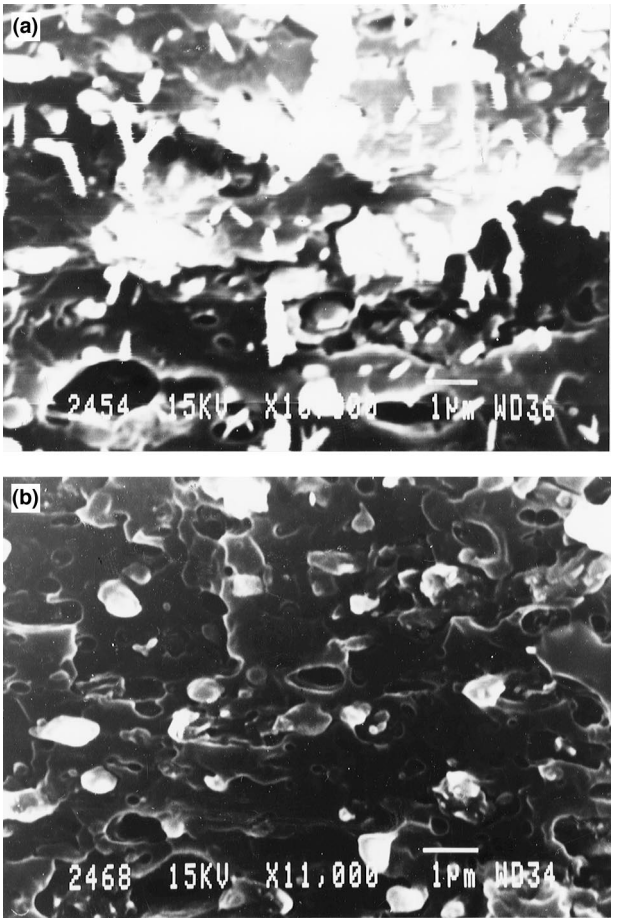

Fig. 14. SEM fractographs of (a) skin and (b) core sections of the injection-moulded PVC/5% LCP specimen.

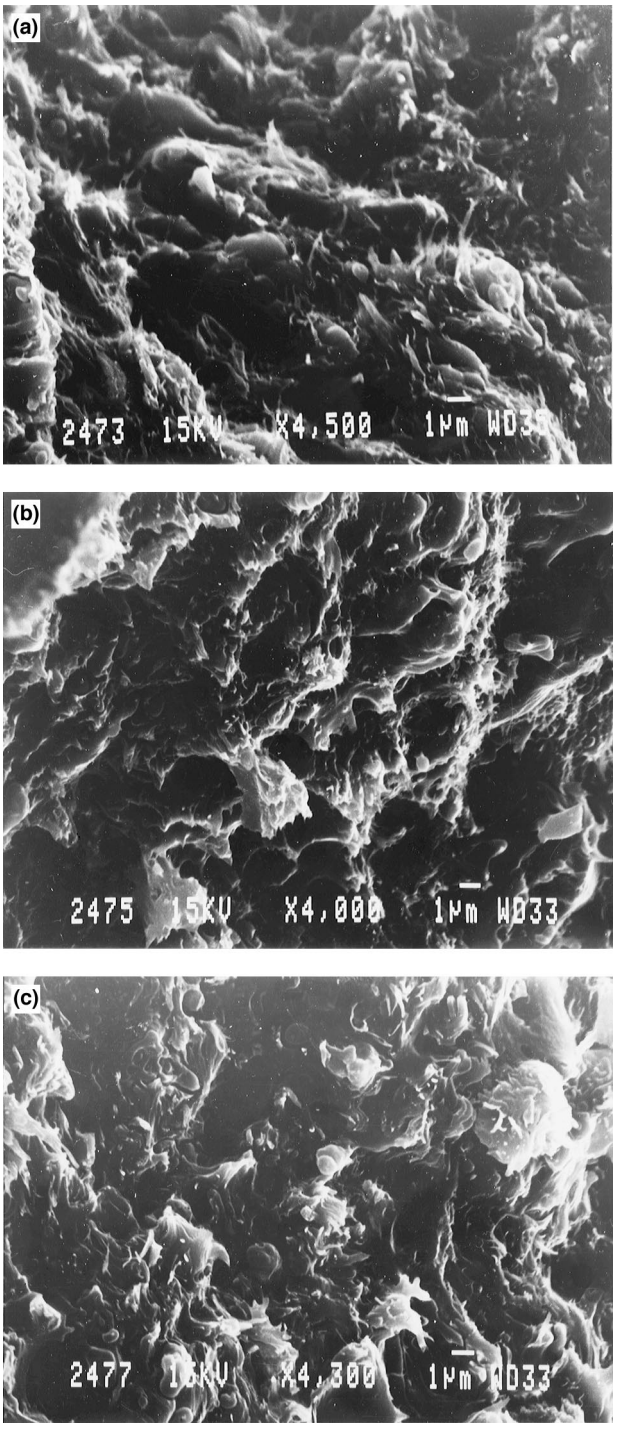

Fig. 15. SEM fractographs of the core section of injection-moulded (a) PVC/25% LCP, (b) PVC/35% LCP and (c) PVC/45% LCP specimens.

viscosity ratio between the LCP and the PVC matrix is much smaller than unity. SEM observations revealed that fine fibrils are only formed in the skin layer of the blends containing LCP content below 15 wt%. The core section of these blends exhibited an ellipsoidal feature. Two-phase morphology disappeared in the PVC/LCP blends with LCP content above 15 wt% owing to the decomposition of the LCP during processing. In this case, the mechanical strength of the PVC/LCP blends with the higher LCP content tended to decrease sharply with increasing LCP content.

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