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Morphology, rheological and thermal properties of the melt blends of poly(phthalazinone ether ketone sulfone) with liquid crystalline copolyester

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A novel poly(aryl ether), poly(phthalazinone ether ketone sulfone) (PPESK) copolymer, was synthesized. This high performance polymer was characterized by an extremely high glass transition temperature, extraordinary thermooxidative stability, but poor processability. The melt blends of PPESK and liquid crystal copolyester were prepared. The rheology, morphology and the thermal behaviour of the blends were investigated by means of capillary rheometry, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric and heat deformation analysis. SEM observations revealed that a two-phase microstructure of the blends was formed, and a fibril morphology is created in the PPESK/LCP blends with the exception of PPESK/5%LCP blend. The thermogravimetric and heat deformation analysis indicated that the addition of LCP slightly affected these thermal properties of PPESK/LCP blends. The relationship of morphologies and rheological properties was correlated to explain the experimental results. The possible use of LCP as a processing aid for improving the processability of the novel PPESK was studied and discussed. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(phthalazinone ether ketone sulfone); fibrillation; liquid crystalline copolyester)

INTRODUCTION

Blends of liquid crystalline polymers (LCPs) and thermoplastics have been studied extensively in the past decades. The liquid crystalline phase in the blends shows good promise for improvement of the mechanical performance and processability of these materials. The molecular chains of LCPs are very stiff and have a rigid-rod structure. These molecules tend to align along the flow direction under appropriate processing condition, leading to the formation of fine fibrils within an isotropic matrix. The LCP fibrils can reinforce the thermoplastic matrix, thereby producing the so-called in-situ polymer composites. In addition, the melt viscosity of LCPs is generally much lower than that of conventional thermoplastics. Thus, LCPs can reduce the melt viscosity of polyblends and serve as processing aids. The morphology, rheology and mechanical properties of the blends of LCPs with general-purpose and engineering polymers, e.g. LCP/polypropylene, LCP/polyamides, LCP/polycarbonate, are widely reported in the literature[1–12].

In recent years, there has been growing interest in the development and investigation of the properties of high performance polymers, such as poly(aryl ether)s (PAEs). The typical commercially available PAEs include poly (ether ether ketone) (PEEK) and poly(ether sulfone) (PES)[13–17]. These polymers are based on aromatic backbones, and have high glass transition temperatures (*Tg*). Furthermore, they also exhibit superior mechanical strength, good dimensional stability and solvent resistance. These useful engineering properties make them attractive for application in aerospace, automobile and electrical industries. They can also be considered as suitable matrix materials for high performance polymer composites. However, most high performance polymers show poor processability owing to their high glass transition temperature. In this regard, LCPs have been considered for use as processing aids in reducing the melt viscocity of high performance polymers, and thus the blends become more easily processable and moldable. Some studies have been reported on the preparation and properties of blends of LCPs with high performance polymers. These papers include LCP/PEEK[21], LCP/poly(ether imide) (PEI)[23–25], LCP/polysulfone (PSF)[18–20], LCP/poly(ether amide) (PEA)[22], LCP/poly(ether sulfone) (PES)[18,19], and LCP/polyphenylenesulfide (PPS)[34]. For example, Isayev and Subramanian reported that the addition of LCP to PEEK leads to improvement in Young's tensile and flexural modulus but no improvement in the break strength[21]. However, less information is available in the literature on the rheological behaviour of PAEs blended with LCP. Recently, Bennett and Farris have synthesized poly(aryl ether ketone)/LCP copolymers based on the reaction of LCP mesogen, biphenol and a crystal-disrupting substituted monomer[26]. Their work was aimed at reducing the melt viscosity of poly(aryl ether ketone)s by the incorporation of LCP into the high performance polymer. They have reported the thermal and microstructural properties of such synthesized copolymers, but no rheological properties.

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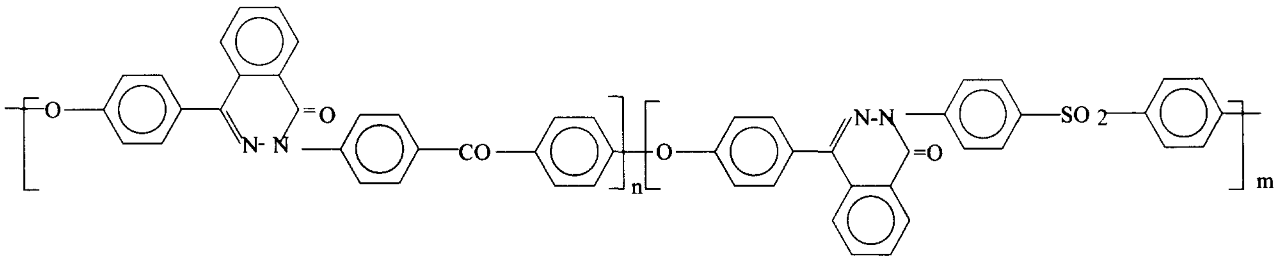

Figure 1 Chemical structure of PPESK

In our earlier paper[27], we synthesized the novel poly (phthalazinone ether ketone sulfone) (PPESK) from bis(4-fluorophenyl) ketone, bis (4-chlorophenyl) sulfone and 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one. The synthesized polymers have extremely high glass transition temperature ($Tg = 290°C$) and thermooxidative stability. Furthermore, PPESK is characterized by superior mechanical properties, satisfactory solubility and good flame retardancy. PPESK can potentially be used as a high temperature membrane material, and also in hot impregnating varnish used in harsh environmental conditions. However, the PPESK is difficult to process due to its rigid amorphous molecular structure. In the previous work[27], the blends of PPESK with two kinds of oligomers were prepared and investigated in order to improve the processability of PPESK. This work attempts to improve the processability of PPESK by blending it with LCP, and to investigate the rheological and morphological behaviours of the blends of PPESK with LCP.

EXPERIMENTAL

Materials

The amorphous matrix, poly(phthalazinone ether sulfone ketone) (PPESK) used in this work was synthesized from bis(4-fluorophenyl) ketone, bis (4-chlorophenyl) sulfone and 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one according to the procedure reported by Berard and Hay[28]. The synthetic procedure for PPESK was reported in our previous work[27]. The PPESK used in this work had a composition of sulfone/ketone ratio of 3/1, and its chemical structure is shown in *Figure 1*. The LCP used in this work was Vectra A950® obtained from Hoechst Celanese Corporation. This LCP is a copolymer with composition based on 27 mol% of 2,6-hydroxynaphthoic acid (HNA) and 73 mol% of p-hydroxybenzoic acid (HBA). The materials were dried in an oven at 130°C for 48 h before mixing.

Sample preparation

Melt blends of PPESK with 5, 10, 15, 25 and 35 wt% LCP were prepared. The blending was performed in a Brabender Plasticorder equipped with a mixing chamber at 350°C and 20 rev/min for 5 min. The blends produced from the Brabender mixer were then compression molded into plates under a pressure of 10 MPa at 350°C. The plates were finally cut into small pellets for the rheological determinations and other measurements.

Rheological measurements

Rheological properties of pure polymers and blends were measured using a Rheograph capillary rheometer (model 2003). The entrance effect was taken into account due to the low *L/D* ratio. Capillaries with diameters of 2 mm and *L/D* ratios of 5, 10 and 15 were used for the rheological characterization of pure materials. However, a capillary with 2 mm diameter and 30 mm long ($L/D = 15$) was used for the measurements of the viscosity of blends. The entrance angle of the capillary was 180°. The Rabinowitch correction was applied to all experimental data. The shear rate range investigated was within $1-10^4\ s^{-1}$. The extrudates from the rheometer were quenched into a cold water bath in order to preserve the microstructure developed during the flow.

Differential scanning calorimetry (DSC)

DSC measurements were carried out using a Perkin–Elmer calorimeter (model DSC-7) from 30 to 350°C at a heating rate of 10°C/min under a protective nitrogen atmosphere.

Thermogravimetric analysis (TGA)

TGA of the specimens from 100 to 700°C was carried out under a protective nitrogen atmosphere using a thermal gravimetric analyser (Seiko model SSC/5200). The heating rate employed was 20°C/min.

Vicat softening temperature (Tv) **measurements**

Tv measurements were performed according to ASTM D1525 procedure using a Vicat softening temperature measurement apparatus (model HS-4). Test specimens with 13 mm square and 3 mm thick were used for the *Tv* measurements. The specimens were placed in a bath containing phenyl-silicon-oil. The temperature of the bath was raised uniformly at a rate of 50°C/h. The temperature at which the needle displaced 1 mm was noted and reported as the *Tv* value.

Morphology observations

The morphologies of the fracture surfaces of all melt blends were observed in a scanning electron microscope (SEM, model JEOL JSM 820). The specimens used for SEM observations were taken from the strands extruded from the rheometer. The specimens were fractured in liquid nitrogen and the fracture surfaces were coated with a thin layer of gold prior to SEM examinations.

RESULTS AND DISCUSSION

Rheological behaviour

Figure 2a and *b* show the viscosity versus shear rate data for the pure LCP and PPESK matrices at different temperatures, respectively. Apparently, the LCP and matrix in the studied range of temperatures exhibit a non-Newtonian flow behaviour. The viscosity of the LCP decreases with increasing temperature. The LCP viscosity shows little variation between 250°C and 265°C, but it tends

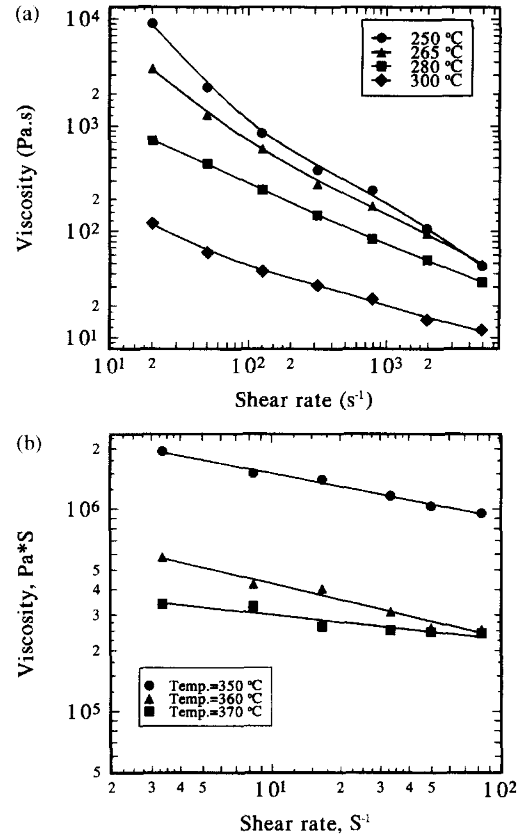

Figure 2 Viscosity versus shear rate for (a) LCP and (b) PPESK matrix at various temperatures

to decrease significantly when the temperatures reach 283°C and above. It can also be seen from *Figure 2a* that the viscosity of the LCP decreases sharply with increasing shear rate because the LCP molecules become more oriented in the flow direction as the shear rate increases. On the other hand, the PPESK exhibits a much higher viscosity than LCP, and is less shear rate dependent owing to its rigid molecular chain (*Figure 2b*). It is evident that the viscosity of PPESK decreases sharply at temperatures of 350 and 360°C. The variation in viscosities at temperatures between 360 and 370°C is small, particularly in the high shear rate region. Generally, polymers with rigid molecular chain have higher flowing activation energy and are sensitive to temperature. It is believed that such a small decreasing tendency in melt viscosity between 360 and 370°C is caused by crosslinking reactions of PPESK at temperatures higher than 360°C as evidenced by traces of un-endcapped end group[29]. Therefore, raising the processing temperatures is not an effective alternative to reduce the melt viscosity of PPESK. *Figure 3* shows the viscosity curves for the PPESK/LCP blends at 340°C. Apparently, the viscosities of PPESK/LCP blends are significantly lower than that of the pure PPESK over the entire range of shear rate studied, and they appear to decrease monotonically with increasing LCP content. Moreover, the addition of LCP renders the blends more subject to shear-thinning. This indicates that there exists a plasticizing effect when PPESK is blended with LCP. The viscosities of the PPESK/LCP blends have values lower than 10^3 PaS in the range of shear rates between 10^2–10^3 s^{-1}, indicating that the processability of the PPESK is greatly improved by blending with LCP.

The viscosity versus shear rate curves for PPESK, LCP and their blends at 340°C are shown in *Figure 4* for the purpose of comparison. It can be seen that the PPESK exhibits the highest viscosity, followed by PPESK/LCP blends and LCP. The PPESK blends exhibits a monotonical shear-thinning behaviour over the entire range of shear rates studied. However, the PPESK/LCP blends show more pronounced shear-thinning than the PPESK matrix. This is associated with the ease of alignment of the LCP molecular chain along the flow direction.

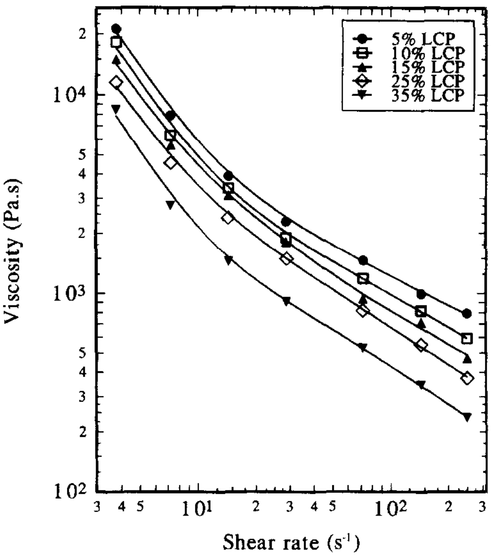

Figure 3 Viscosity versus shear rate for the PPESK/LCP blends at 340°C

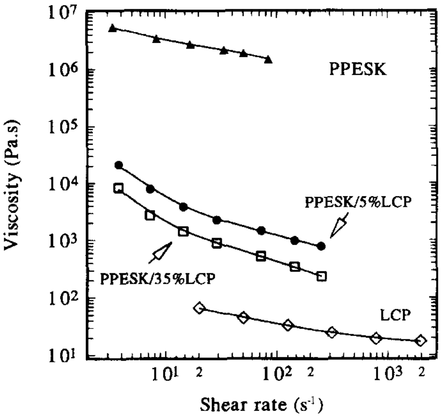

Figure 4 Viscosity versus shear rate for PPESK, LCP and their blends at 340°C

Figure 5a and *b* show the plots of viscosity-composition curves for the PPESK/LCP blends at shear rates of 14.4 s^{-1} and 72.0 s^{-1}, respectively. From these figures, it is evident that the addition of a small amount of LCP (5 wt%) leads to a very sharp decrease in the melt viscosity of PPESK/LCP blends. Further increasing LCP content above 5 wt% only results in a steady decrease of the melt viscosity of the blends. A drastic reduction of the viscosity associated with the LCP addition to polymers is generally well-established[30,31]. However, the two-phase flow behaviour of polymers, in general, is a complicated phenomenon, particularly when one component is a liquid crystal polymer owing to the possible anisotropy of the liquid thermotropical crystal phase[32,33]. Basically, two types of viscosity-composition curves are observed. For a blend in which the two neat polymers have different but closer viscosities, the blends

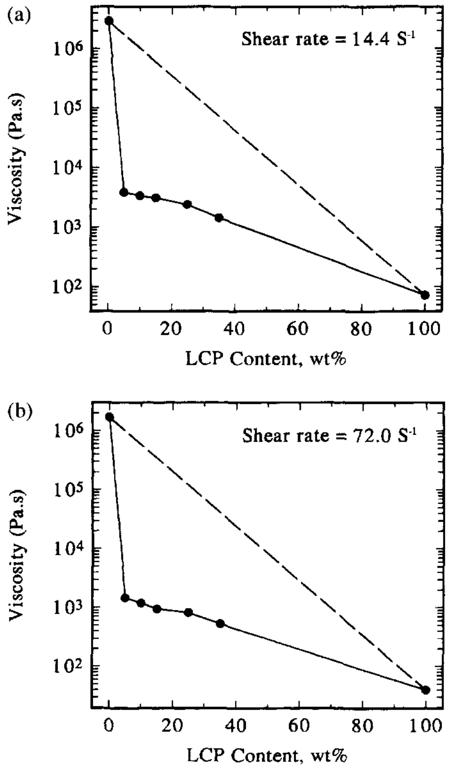

Figure 5 Viscosity-composition curves for PPESK/LCP system at a shear rate of (a) 14.4 s^{-1} and (b) 72.0 s^{-1}. The dash line is predicted from equation (1)

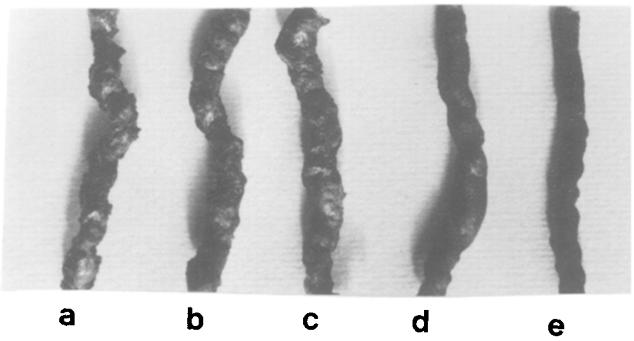

Figure 6 Photograph of PPESK/LCP blends extruded at 340°C. (a) PPESK/5%LCP, (b) PPESK/10%LCP, (c) PPESK/15%LCP, (d) PPESK/25%LCP, (e) PPESK/35%LCP

viscosities are intermediate or lower than those of the parent components. For a blend where the matrix has a much higher velocity than LCP, however, the melt viscosities of the blends are between those of the neat components[34]. The PPESK/LCP blends investigated belong to the latter case. The viscosity-composition relation is generally described by the following equation[35]:

$$\log\eta_b = \varpi_1\log\eta_1 + \varpi_2\log\eta_2 \qquad (1)$$

where η_b is the viscosity of a blend, η_1 and η_2 are the viscosities of component 1 and 2, ϖ_1 and ϖ_2 are the weight fractions of component 1 and 2, respectively. The viscosity-composition curves predicted from equation (1) are plotted (dashed line) in *Figure 5a* and *b*. It appears that the viscosities of the blends investigated are significantly lower than the line predicted from equation (1). It is believed that the improvement in the processability is associated with the ease of deformation of LCP domains[23]. In addition, the LCP phase with a relative low viscosity tends to coagulate between the capillary wall and blend, thereby allowing the molecular chains to slide past each other with relative ease, leading to a sharp fall in melt viscosity with increasing LCP content.

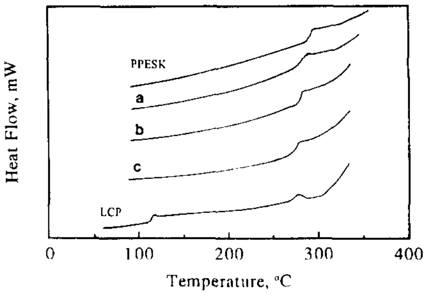

Figure 7 DSC traces for neat PPESK, LCP and their blends. (a) PPESK/10%LCP, (b) PPESK/15%LCP, (c) PPESK/25%LCP

Figure 6 shows a photograph of the extruded strands for PPESK/LCP blends. Analysis of the extrudate surfaces indicates that the LCP content plays a key role for smooth flow. Smooth surfaces can only be observed for the blends containing higher than 25 wt% LCP. It is considered that melt instability occurs in the blends containing less than 10 wt% LCP, which is associated with the sharp decrease in melt viscosity with increasing LCP content. Therefore, the die swell decreases with increasing LCP content in the blends.

Thermal properties

Figure 7 shows the DSC traces of neat PPESK, LCP and the PPESK/LCP blends. Apparently, the *Tg* of the PPESK is located at about 290°C. The *Tg* of the LCP is located at about 120°C, whilst the melting point is detectable at 283°C. For the PPESK/LCP blends, only one *Tg* peak is observed (280–288°C), and it is slightly lower than that of neat PPESK, showing that a plasticizing effect occurs for the PPESK blending with LCP phase. However, despite the fact that the molecular structures of PPESK and LCP are aromatic and rigid, the PPESK/LCP blend is basically an immiscible two-phase system as revealed by the SEM micrographs in the next section.

Figure 8a and *b* show the weight loss and derivative weight loss curves versus temperature for the PPESK/LCP blends. The 5 wt% loss temperature of pure PPESK is about 508°C, while pure LCP is about 515°C. The 5 wt% loss temperatures for PPESK/LCP blends are between those of the parent components. From *Figure 8a*, it can be seen that the 5% weight loss temperatures of PPESK/LCP blends increases slightly with increasing LCP content. The maximum weight loss peaks occur at 593°C for neat PPESK and 530°C for LCP, respectively. Apparently, the thermal stability of the PPESK is slightly improved with the LCP addition.

The Vicat softening temperatures (*Tv*) for neat PPESK and PPESK/LCP blends are tabulated in *Table 1*. The *Tv*'s slightly decrease with increasing LCP content, and the heat-resistance of matrix PPESK is essentially not affected by blending with LCP.

Morphology observations

It is generally known that the viscosity ratio between the LCP and thermoplastic matrix (*Vr*) plays a crucial role in the LCP fibrillation. The *Vr* must be close to unity or less for the formation of LCP fibrils. In this work, the *Vr* for the

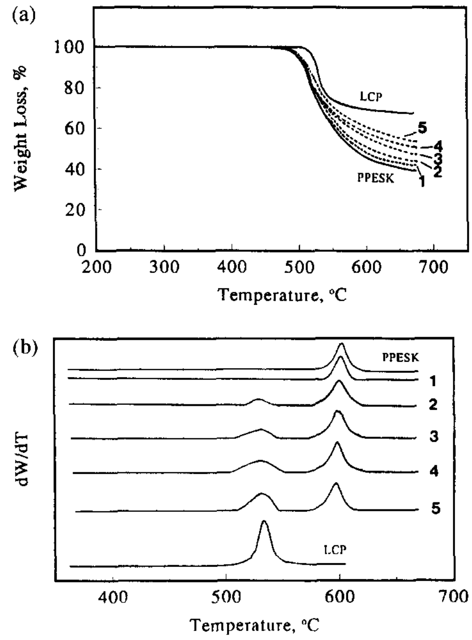

Figure 8 (a) weight loss and (b) derivative weight loss curves for neat PPESK, LCP and their blends. (1) PPESK/5%LCP, (2) PPESK/10%LCP, (3) PPESK/15%LCP, (4) PPESK/25%LCP, (5) PPESK/35%LCP

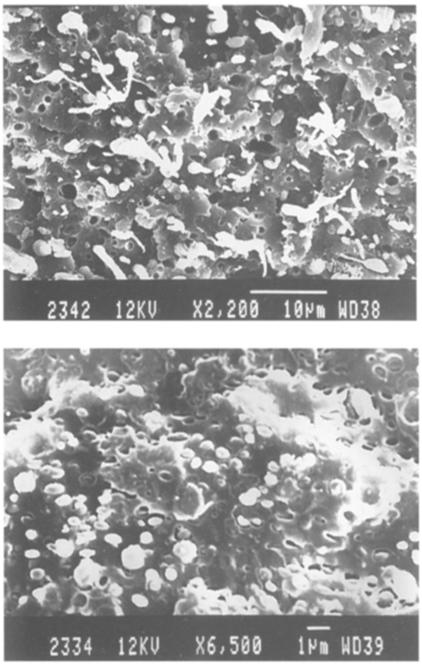

Figure 10 SEM micrograph of the PPESK/10%LCP blend extruded at a shear rate of (a) 250 s^{-1} and (b) 14.4 s^{-1}

Table 1 The Vicat softening temperatures for neat PPESK and PPESK/LCP blends

Material	PPESK	5 wt%LCP	10 wt%LCP	15 wt%LCP	25 wt%LCP	35 wt%LCP
Tv (°C)	243	241	240	237	232	226

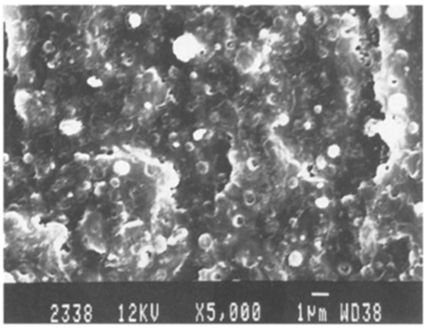

Figure 9 SEM micrograph of the PPESK/5%LCP blend extruded at a shear rate of 250 s^{-1}

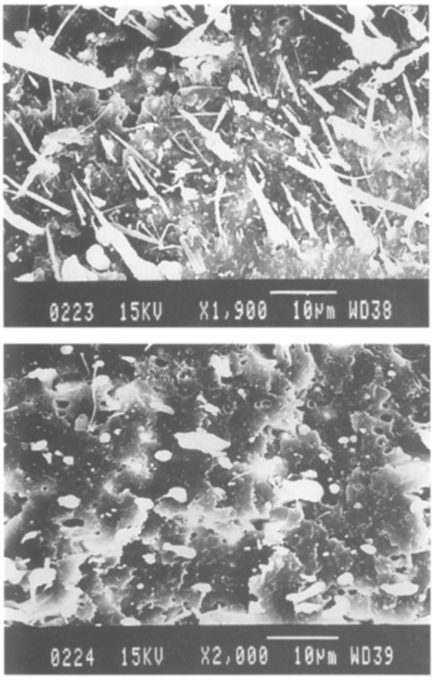

Figure 11 SEM micrograph of the PPESK/15%LCP blend extruded at a shear rate of (a) 250 s^{-1} and (b) 14.4 s^{-1}

PPESK/LCP system is much smaller than unity over the entire range of shear rates investigated. This means that the rheological properties of the PPESK/LCP system favoured the formation of LCP fibrils within the PPESK matrix. In addition, the LCP content also affects the development of a fibril morphology in polyblends.

Figure 9 shows the SEM micrograph of the PPESK/5%LCP blend subjected to a higher shear rate of 250 s^{-1}. It can be seen that the LCP domains disperse as droplets in the matrix. Cavities can hardly be discerned in this micrograph indicating that the interfacial adhesion between the PPESK and LCP is relatively good despite the fact that the PPESK/LCP system still retains two phases. Increasing the LCP content to 10 wt% leads to the formation of elongated LCP ellipsoids in the matrix at a higher shear rate of 250 s^{-1}, whilst the LCP phase remains as spherical droplets at a lower shear rate of 14.4 s^{-1} (*Figure 10a* and *b*). By comparing *Figure 10b* with *Figure 9*, it can be seen that the blends with a higher LCP content (10 wt%) exhibit droplets with larger diameter. Well-developed fibrillation morphologies can be formed in the PPESK/15%LCP blend at the shear rate of 250 s^{-1} and 14.4 s^{-1} (*Figure 11a* and *b*).

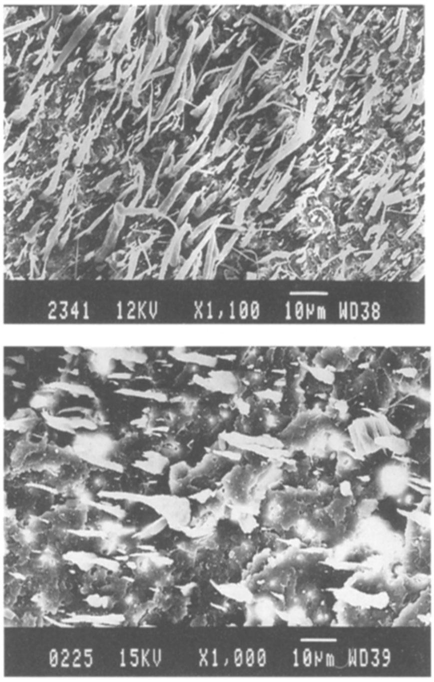

Figure 12 SEM micrograph of the PPESK/35%LCP blend extruded at a shear rate of (a) 250 s^{-1} and (b) 14.4 s^{-1}

Similarly, very fine and well-oriented LCP fibrils are observed in the sample of PPESK/35%LCP blend at low and high shear rates, respectively (*Figure 12a* and *b*). Finally, a skin-core morphology is not observed in the PPESK/LCP blends.

CONCLUSION

A novel poly(aryl ether), poly(phthalazinone ether ketone sulfone), was synthesized and the PPESK/LCP blends were prepared. The morphologies, rheological and thermal properties of the PPESK/LCP blends were investigated. The results showed that the melt viscosity of PPESK/LCP blends decrease with increasing LCP content. This behaviour was derived from the low LCP viscosity coupled with the deformability of LCP domains. The DSC, TGA and Vicat softening temperature measurements showed that the heat-resistance of the PPESK is generally not affected by the LCP addition. SEM observations revealed that LCP droplets are formed in the PPESK/5%LCP blend subjected to low and high shear rates. However, elongated LCP ellipsoids were formed in PPESK/10%LCP blend at a higher shear rate. Well-developed and oriented fine fibrils were developed in the PPESK/LCP blends containing LCP content higher than 10 wt%. It can be concluded that LCP serves as a processing aid as well as reinforcing agent in the polyblends of PPESK and LCP.

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