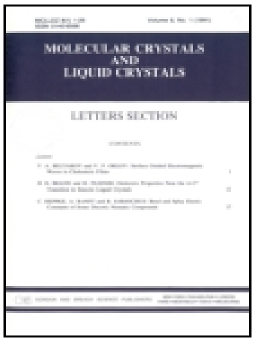

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In situ composites based on blends of PEEK and thermotropic liquid crystalline polymer

Zong Cheng Miao[a], Dong Wang[b], Yan Xing[c], Hong Gao[c], and Jingjing Zhang[c]

[a]Department of Applied Statistics and Science, Xijing University, Xi'an, Shaanxi Province, China; [b]University of Science and Technology Beijing, Beijing, PR China; [c]China Academy of Space Technology, Beijing, PR China

ABSTRACT
A series of blends were prepared by mixing pellets of the thermotropic liquid crystalline polymers (TLCP) with poly (ether ether ketone)(PEEK) in the dry state under injection mouldingmolding conditions. The mechanical properties of blends were measured, and it is proved that the mechanical properties of blends are better than those of their matrix. Compared with the thermoplastic matrix, the tensile modulus and strength of the blends increased obviously, with the addition of only 2 wt% LCP. At the same time, the addition of TLCP decreased the melt viscosity of the blends.

KEYWORDS
In-situ Composites; thermotropic Liquid Crystalline; poly(ether ether ketone)

Introduction

High- performance thermoplastic poly (ether ether ketone)s (PEEK) have outstanding thermal and mechanical properties. Nonetheless, there is room for improvement, if they are to be using in many commercial applications [1]. Although they are melt processable, PEEK have relatively narrow melt processing windows limited at lower temperatures, because of high viscosity and at higher temperatures by their thermal instability. By melt blending the PEEK with thermotropic liquid crystalline polymers (LCPs) [2–5], the limitation can be overcome.

In recent years, *in -situ* composites containing thermotropic liquid polymers (LCPs) have received increasing attention because of their scientific and technological importance [6–14]. The premise behind the *in -situ* composite concept is the existence of an immiscible mixture of LCP and isotropic polymer, in which the dispersed LCP phase is deformed into a fibrillar form during processing, acting as a reinforcing phase. Consequently, significant improvements in physical properties can be achieved by using a small portion of LCP.

In this sense, *in -situ* composites are akin to short fiber reinforced thermoplastic composites. The two most distinct advantages are: (1) the reinforcing fibrillar structure is formed *in-situ, i.e.*, the formation of the reinforcing phase and the composite itself is completed in a single step. A separate process to produce the reinforcing fiber, as in short fiber reinforced composites, is unnecessary. Hence it is a potentially economical process to generate high performance materials; (2) LCP functions as a processing aid, because of its extremely low melt viscosity, thereby making the use of high viscosity thermoplastics possible. Obviously, the *in situ* composite concept offers a new method for tailoring physical properties of polymers

CONTACT Zong Cheng Miao ✉ miaozongcheng@xijing.edu.cn 🖃 Department of Applied Statistics and Science, Xijing University, Xi'an, Shaanxi Province, China

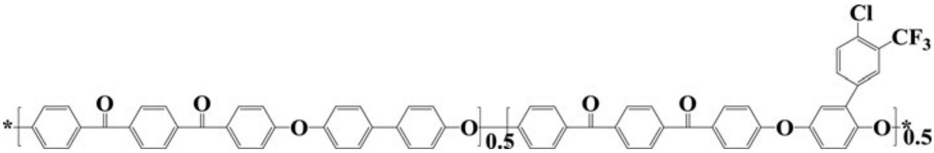

Figure 1. The chemical structure of LCP.

without having to go through expensive chemical procedures. However, the addition of TLCP decreases the viscosity of whole blend systems, so that TCLP/PEEK blends have torque much lower than PEEK. The *in situ* hybrid composite has its advantage in the aspect of processing.

In this paper, the use of liquid crystalline polymers (LCPs) blended with thermoplastics to form *in -situ* composites has been studied. The objective is to enhance the mechanical properties of the thermoplastic and decrease torque of PEEK.

Experimental

Materials

The LCP used in this work was a wholly aromatic copoly(aryl ether ketone) synthesized by our laboratory [15] and the chemical structure was depicted in Figure 1. It shows the nematic state in the temperature range of 279–371°C. T_g of the LCP was 150°C. The poly(ether ether ketone) (PEEK) was purchased from JHPM company. Pellets of the PEEK and the LCP were dried in a convection oven at 150°C for at least 48 h before using.

Processing

Composite strands (fibers) were produced by mixing pellets of the LCP and PEEK in the dry state, feeing the mixture through an extruder and drawing the resulting strand. The extruder was a twin-screw extruder with a WPZXK30P9P twin-screw extruder (Germany). The down-stream barrel temperatures were set at 350°C. The matrix and the LCP pellets were mixed in a specific weight ratio and tumbled together before injection molding. The LCP/matrix blends containing x wt% LCP and y wt% matrix. Time, for the melt blending in a mixer could be used to characterize the processability of blended systems.

Injection molding

Dog-bone-shaped tensile bars were injection molded using an injection molder. Rectangular plaques for flexure and impact tests were also injection molded. The processing conditions used were as follows: the temperature in the barrel was 350°C and the mold temperature was 150°C.

Instrumentation

Differential scanning calorimetry measurements were conducted on a Mettler Toledo DSC 821^e under a nitrogen atmosphere. Heating rate was 20°C/min. Tensile properties of the extruded stands were measured on a SHIMADZU AG-1 Testing machine (10 m/min). Flex properties of the extruded stands were measured on a SHIMADZU AG-1 Testing machine

Table 1. Mechanical properties of the blends.

Blends LCP/PEEK	Tensile strength (MPa)	Youngs' moduli (GPa)	Elongation (%)	Flex strength (MPa)	Flex moduli (GPa)	Izod impact (KJ/m^2)
0%	80.8	1.85	7.2	117	2.51	14.3
1%	88	1.92	7.3	120	2.60	12.8
2%	110	2.42	7.5	143	2.84	7.0
3%	94.6	2.1	7.2	131	2.60	9.26

(5 mm/min). The Izod impact properties of the blends were measured on a XJ-6 Impact Testing machine. The arithmetic average and the standard deviation of the tensile properties were calculated using a minimum of five samples. The mechanical tests were carried out at room temperature. The change of torque was recorded with the help of Haake Rheomix 600. A volume of 50 ml mL for each blend was melt blended with a rotor speed of 30 rev/min and 60 rev/min for 10 min at 350°C.

Results and discussion

Thermal properties

The results of DSC traces show that T_g and T_m of the blends are almost same to those of the matrix. T_g are about 143°C, and T_m are about 334°C. Detecting T_g is one of the most effective methods, for characterizing the miscibility of blends, when the component polymers have a T_g difference larger than 20°C. $\mathrm{T_g}$ of LCP is 150°C, T_m of matrix is 279°C and T_i of matrix is 371°C. The difference of them is lower than 20°C and the content of LCP in PEEK is very small so the effect of LCP is low level too. However, the glass transition temperature corresponding to the LCP phase remains relatively unchanged (within experimental error) regardless of the blend composition.

Mechanical properties

The tensile properties of blends are shown in Table 1. As can be seen, all tensile properties of PEEK/LCP are higher than those of PEEK. The tensile strength increases up to 2% LCP content, and then decreases at 3% LCP content. The flexure test and notched impact strength of blends is tabulated in Table 1. As can be seen, the impact strength of LCP/PEEK is worse than that of PEEK, and the trends of flex tests is the same to tensile test. The data shows that when the content of LCP is 2%, the tensile properties and the flex properties are the best, but the impact properties are the worst among a series of blends.

Rheological

The rheological properties of the neat polymers are of great importance to the processing study. The viscosities of the components and their blends as a function of time, measured by a rheometer at corresponding extruding temperatures at 350°C, are shown in Figure 2. The PEEK and LCP are only measured below 370°C and are too low to measure at higher temperature. The apparent viscosity of the LCP/ PEEK blends with 2 wt% LCP content are lower than that of other LCP contents.

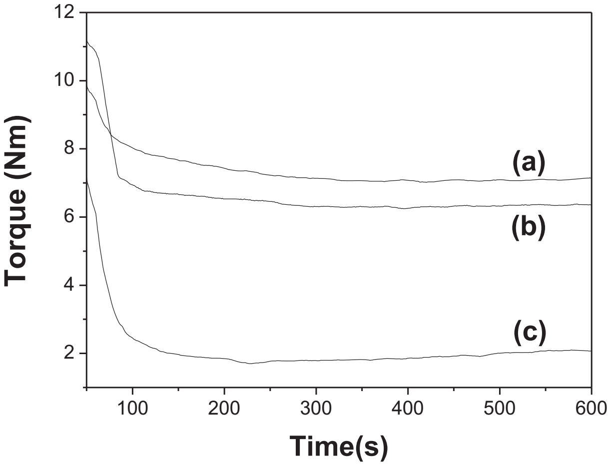

Figure 2. The rheological properties of the blends with difference LCP content, a: PEEK; b: 1 wt% LCP; c: 2 wt% LCP.

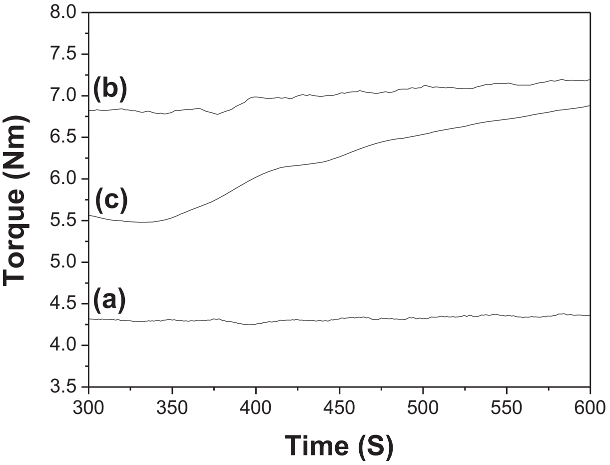

Figure 3. The rheological properties of the blends with 3 wt% LCP content at difference shear rate and temperatures, a: 30 rev/min at 350°C; b: 60 rev/min at 350°C; c: 60 rev/min at 370°C.

Figure 3 shows the rheological behavior of PEEK and LCP/ PEEK blends with difference shear rate and temperature. Its apparent viscosity increases greatly with shear rate up to 60 rev/min. If the temperature was increased, the viscosity would be decreased (see in Figure 3, Part c). The increase of viscosity is due to the crosslink of PEEK (see in Figure 3, Part b and c).

Conclusions

We processed a series of blends by mixing pellets of the LCP and PEEK in the dry state. The thermal properties of the blends almost were same to those of matrix. The some mechanical properties of the blends were better than their matrix. Compared with the thermoplastic matrix, the tensile modulus and strength of the in situ composite had increased by 1.3 times and 1.4 times, respectively, with the addition of only 2 wt% LCP. The addition of LCP decreased the melt viscosity of the blend.

Acknowledgments

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