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Preparation and Characterization of High-Performance Poly(ether ether ketone) Fibers with Improved Spinnability based on Thermotropic Liquid Crystalline Poly(aryl ether ketone) Copolymer

Jiashuang Luan,[1,2] Shuling Zhang,[1] Mei Zhang,[2] Zhi Geng,[1] Yang Wang,[1] Guibin Wang[1]

[1]College of Chemistry, Engineering Research Center of High Performance Plastics, Ministry of Education, Jilin University, ChangChun 130012, China

[2]College of Quartermaster Technology, Jilin University, Changchun 130062, China

Correspondence to: G. Wang (E-mail: wgb@jlu.edu.cn)

ABSTRACT: High-performance poly(ether ether ketone) (PEEK) fibers were prepared by melt-spinning in the presence of thermotropic liquid crystalline poly(aryl ether ketone) copolymer (FPAEKLCP). The rheological and mechanical properties, birefringence, orientation, and crystallization of the resulting PEEK/FPAEKLCP fibers were characterized by using a melt flow indexer, capillary rheometer, single fiber electronic tensile strength tester, polarized light microscopy (PLM), and wide-angle X-ray diffraction (WAXD), respectively. The results indicate that the melt viscosity of PEEK significantly reduced by introducing FPAEKLCP, followed by the improvements in the spinnability and the quality of as-spun fibers. The tensile properties of PEEK/FPAEKLCP fibers mainly depend on the content of FPAEKLCP, drawing temperature, drawing ratio, and annealing processes. Moreover, the tensile strength and modulus of PEEK/FPAEKLCP fibers are obviously higher than those of neat PEEK fibers under the same processing conditions. This should be attributed to an enhancement in the orientation and crystallization of PEEK compounded with FPAEKLCP. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

KEYWORDS: fibers; manufacturing; mechanical properties; structure–property relations; rheology

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INTRODUCTION

Poly(ether ether ketone) (PEEK) is one of the most important kinds of high-performance engineering thermoplastics, and has extensive applications in the aviation, automotive, medical, and electrical industries owing to the excellent mechanical performance, good thermal stability, and chemical resistance, and so on.[1] Therefore, PEEK fibers have a unique combination of mechanical properties that are stable under extreme environmental conditions. Whether it is at high temperature, extreme moisture, alkaline or acidic environments, there is almost no other fiber that will do a comparable job.

For PEEK fibers, numerous efforts have been devoted to improving their mechanical properties by the changes of processing parameters in the past few decades. For example, Shimizu et al.[2,3] studied on the relationship between the drawing ratio and the mechanical property of PEEK fibers, whereas Lee et al.[4] investigated the effect of the drawing temperature and drawing speed on the mechanical property of PEEK fibers. Hence, there were almost no reports on how to improve the spinnability and the quality of as-spun fibers, and further enhance the mechanical properties of PEEK fibers by the changes of PEEK resin, i.e., the reduction of PEEK melt viscosity. The raw PEEK resin of the fibers in all above research was from Victrex plc. However, no scientific research on PEEK fiber was carried out by using Chinese PEEK resin. PEEK resin was successfully industrialized in China in 2003 and the different molding products, rod of PEEK and so on were developed, so this study was focused on preparation and characterization of PEEK fibers to use Chinese PEEK resin.

It is well known that high melting temperature and high melt viscosity are characteristic of PEEK. These are also the primary drawbacks associated with their processing and applications.[5–8] The conventional processing aids are unsuitable for PEEK resin because of their low degradable temperature. Thermotropic liquid crystalline polymers (TLCPs) are excellent candidates for the processing aids owing to the unique rod-like molecule, anisotropy, low melt viscosity, a high degree of order in the melt under shear and elongational flow fields.[9–12] Nevertheless, the usual TLCPs could not meet the needs of process because of the unmatched processing temperature and poor compatibility with PEEK resin.[13] In order to find a suitable processing aids, we

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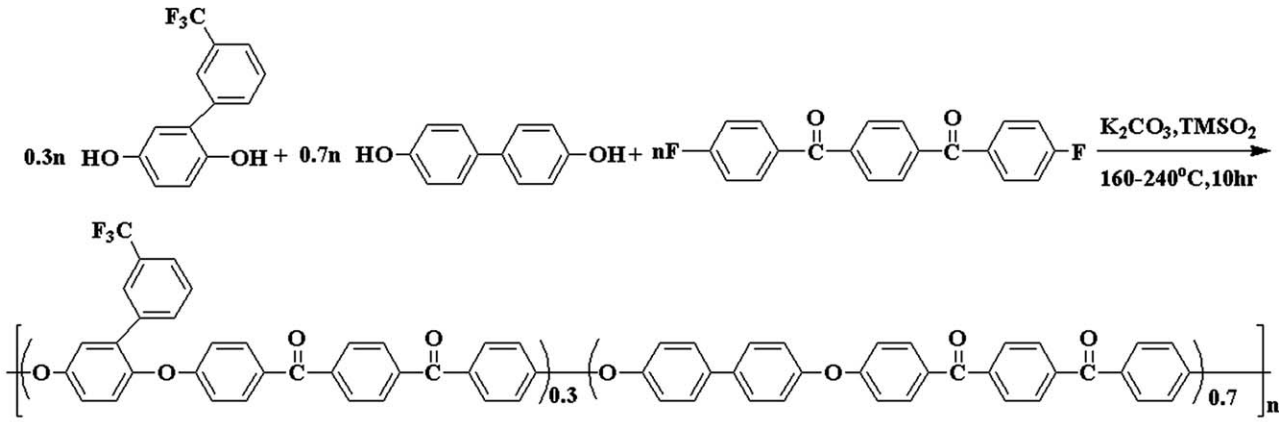

FPAEKLCP (FH0.3)

Scheme 1. The synthetic route of FPAEKLCP.

previously synthesized a novel thermotropic liquid crystalline poly(aryl ether ketone) copolymer (FPAEKLCP).[1] FPAEKLCP possesses the matched processing temperature and the similar structure with PEEK resin, but also decreases the melt viscosity of PEEK, thereby improves the spinnability and the quality of as-spun fibers to obtain a high-performance PEEK fiber.

With this goal in mind, in this study, first the FPAEKLCP were synthesized. Subsequently, a series of PEEK fibers were prepared by melt-spinning in the presence of FPAEKLCP. Then, the effect of the content of FPAEKLCP, drawing temperature, drawing ratio, and annealing processes on the performance of PEEK/FPAEKLCP fibers was explored. Finally, a high-performance PEEK compounded with FPAEKLCP fiber was optimized.

EXPERIMENTAL

Materials

Fiber grade PEEK [melt flow index: 22 g (10 min)$^{-1}$; glass transition temperature (T_g): 145°C; melting point (T_m): 337°C; the temperature of 5% weight loss (T_d^5): 558°C] was obtained in powder form by Changchun Jilin University Super Engineering Plastics Research Co. (China).

FPAEKLCP (FH0.3) was prepared according to the procedure described previously in our lab.[1] The inherent viscosity of FPAEKLCP was 0.64 dL g^{-1}; T_g: 13 °C; T_m: 297°C; liquid crystal-to-isotropic transitions (T_i): 365°C; T_d^5: 532°C. The synthetic route of FPAEK was shown in Scheme 1.

Preparation of PEEK/FPAEKLCP Blends

PEEK resin and FPAEKLCP (FH0.3) in powder form were dried at 80°C for 12 h prior to blending, and the weight fraction of FPAEKLCP in the blends was 0, 2, 4, 6, or 8 wt %. PEEK resin and FPAEKLCP were first pre-mixed with a high-speed mixer, then the pre-dispersion mixture was further blended by using a Haake PTW16/25p co-rotating twin-screw extruder at a screw speed of 120 rpm and a temperature profile of 320/340/355/355/355/340°C. Finally, the resulting blends were cut into granules for melt-spinning.

Melting Spinning of PEEK/FPAEKLCP Blends

The PEEK/FPAEKLCP blends granules were dried at 120°C for 8 h before spinning. The spinning and drawing of PEEK fibers were carried out on the high temperature experimental spinning equipment developed by Beijing Paigu, China. The schematic diagram of the machine was shown in Figure 1(a). The extrusion temperature of the polymer was maintained at 380–400°C, and the spinning speed of melt spinning was controlled in the range of 0.1–1.0 km min^{-1}.

To investigate the effect of drawing temperature (DT) on the structure and properties of PEEK/FPAEKLCP fibers, as-spun fibers (which the weight fraction of FPAEKLCP in the blends was 2, 4, or 6 wt %, spun with a wind up speed of 300 m/min) were drawn by the equipment in Figure 1(b) at various temperatures (120, 140, 160, 180, 200, 220, 240, 260, and 280°C), and the drawing ration (DR) was fixed at 3.0 as well as the annealing process was carried out at 260°C for 2 h. To investigate the effect of the drawing ratio on the structure and properties of PEEK/FPAEKLCP fibers, as-spun fibers (which the weight fraction of FPAEKLCP in the blends was 4 wt %, spun with a wind up speed of 300 m/min) were drawn with the different draw ratio (1.5, 2.0, 2.5, and 3.0), and the drawing temperature was maintained at 240°C as well as the annealing process was carried out at 260°C for 2 h.

Characterization

The rheological properties were investigated by using an America Dynisco polymer test LCR7001 capillary rheometer in the shear rate range of 1–5000 s^{-1}. Melt flow index (MFI) was measured by using a melt flow indexer (Jilin University, China) according to the ASTM D 1238. The test temperature was 400°C, and the weight was 5 kg. PEEK/FPAEKLCP blends were fed into stuff canister and pre-melted for 5 min. The birefringence (Δn) of the fibers was observed using a Leica (German) polarizing microscope equipped with a break compensator. The value of the birefringence was obtained from the eq. (1)[14]:

$$\Delta n = \frac{(\alpha + \pi n)\lambda}{\pi d} \quad (1)$$

where α is the rotation angle of the analyzer rotated until the innermost interference fringe merged using a Sennarmont

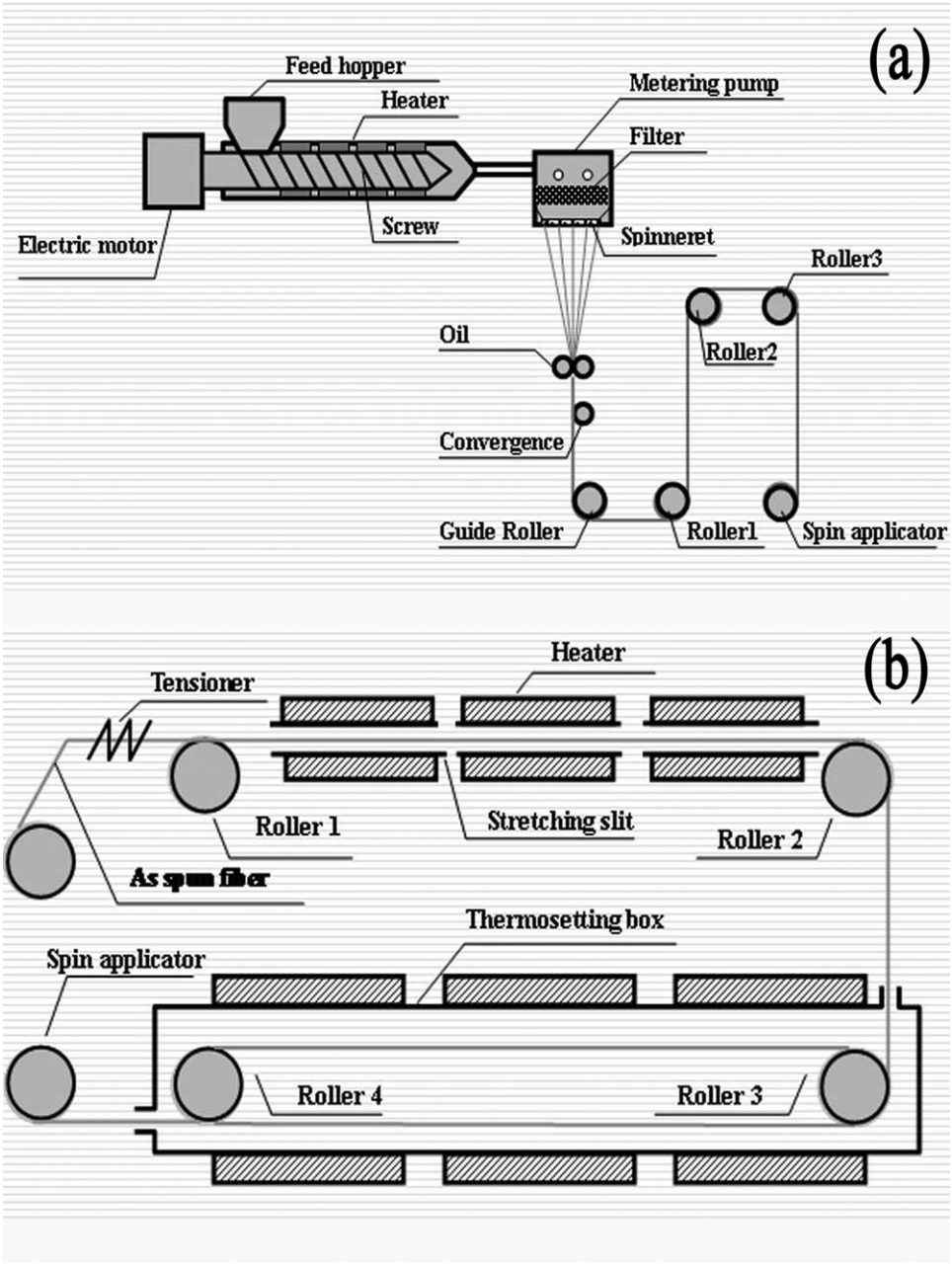

Figure 1. Schematic diagrams of (a) melting spinning equipment and (b) post-treatment equipment.

compensator in a compensator slot, n is the number of interference fringe. λ is the wavelength of monochromatic light (589.3 nm), d is the diameter of a fiber, and π is 180°. The tensile properties of the fibers were measured by using the Single Fiber Electronic Tensile Strength Tester (Shandong Laizhou, China) equipped with standard fiber grips operating at room temperature. The rate of the tensile was 20 mm min^{-1} and the gauge length was 20 mm in accordance with the GB/T-14337(CN) standard. The average values of at least 20 samples were reported. WAXD measurements were performed by using an Empyrean || X-ray diffractometer (PANalytical B.V., Netherlands), using Cu $K\alpha$ radiation (λ = 0.1542 nm) with a step size of 0.02° in the 2θ ranging from 10° to 40°, operated at 60 kV and 60 mA. The intensity curves are obtained by some corrections like air scattering and polarization effect.

RESULTS AND DISCUSSION

Rheological Properties of PEEK/FPAEKLCP Blends

In order to investigate the effect of the addition of FPAEKLCP on the melt viscosity of PEEK, melt flow index (MFI) and steady shear flow properties were measured. In Figure 2(a), MFI of the PEEK/FPAEKLCP blends is obviously higher than that of neat PEEK resin (MFI = 22 g $(10\ min)^{-1}$). Even with a 2 wt % FPAEKLCP addition, the MFI increases to about 27 g $(10\ min)^{-1}$. With further increasing FPAEKLCP content, the MFI value of 8 wt % FPAEKLCP blend is up to about 39 g $(10\ min)^{-1}$. The

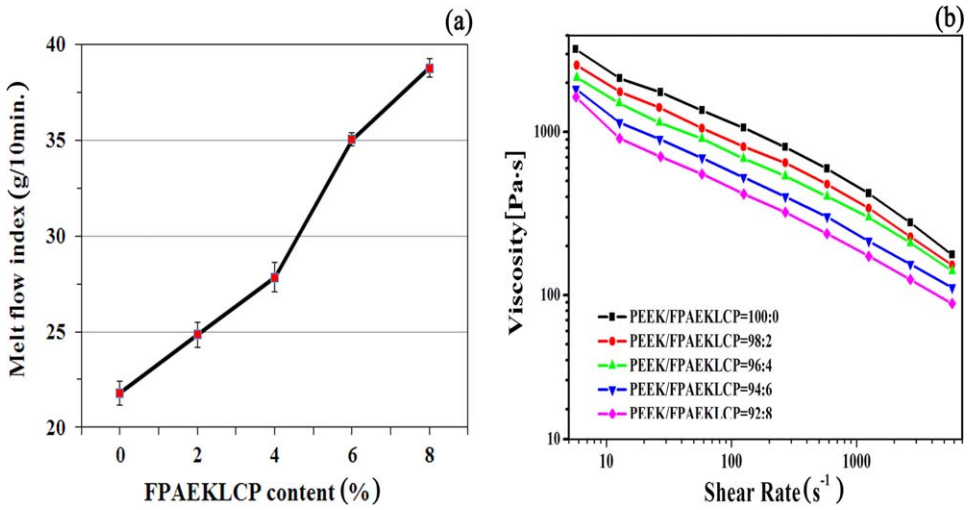

Figure 2. (a) Effect of FPAEKLCP loading on the melt flow index of PEEK/FPAEKLCP blends. (b) The relationships between the apparent viscosity and the shear rate at 400°C for neat PEEK and PEEK/FPAEKLCP blends. [Color figure can be viewed in the online issue, which is available atwileyonlinelibrary.com.]

relationships between steady shear viscosity and shear rate for neat PEEK and PEEK/FPAEKLCP blends are exhibited in Figure 2(b). All samples show the typical shear thinning behavior, i.e., shear viscosity decreases continuously with increasing shear rate. In the case of PEEK/FPAEKLCP blends, their shear viscosities are lower than that of pure PEEK resin at the same shear rate, and the reduced trend becomes more apparent with the increase of FPAEKLCP content in the blends. Based on the above results, it is expected that the spinnability and the quality of PEEK resin would be significantly improved by the addition of FPAEKLCP due to the reduction in the melt viscosity of PEEK. This contributed to the preparation of high-performance PEEK fibers.

Effect of Drawing Temperature on the Properties of PEEK/FPAEKLCP Fibers

Usually, synthetic fibers could meet the needs of product after they were post-drawn, so the properties of PEEK/FPAEKLCP fibers mainly depend on the drawing temperature, drawing ratio, and annealing processes beside the content of FPAEKLCP. Effect of the drawing temperature on the tensile strength and modulus of neat PEEK fibers and PEEK/FPAEKLCP fibers are presented in Figure 3. Whether neat PEEK fibers or PEEK/FPAEKLCP fibers, their tensile strength, and modulus first increase then decrease with the increase of the drawing temperature, and reach a maximum at 240°C. This should be ascribed that the movement of PEEK segments in fibers enhanced with

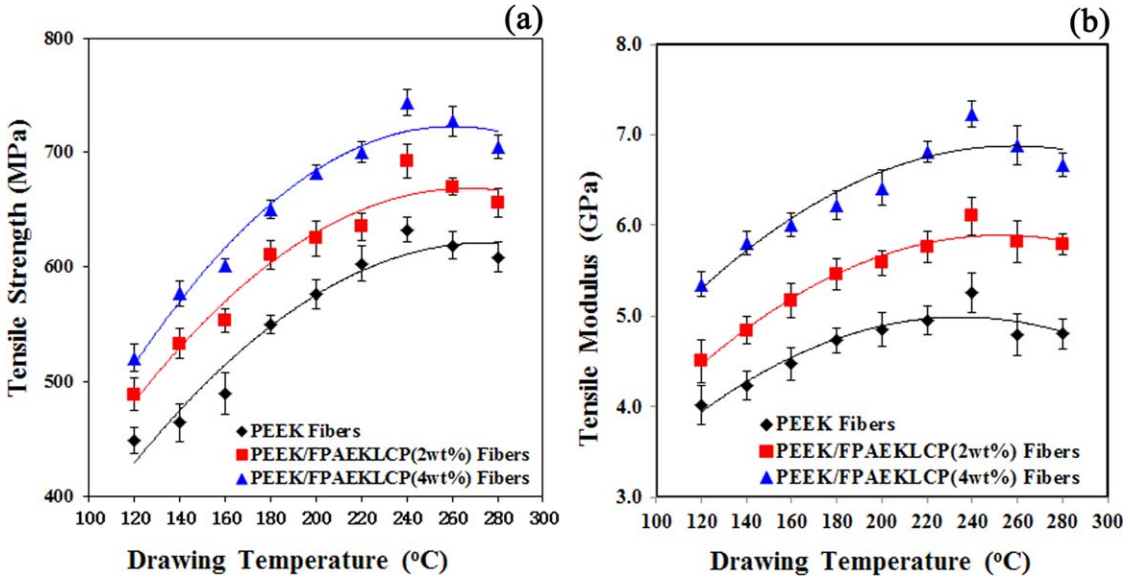

Figure 3. Effect of the drawing temperature on the (a) tensile strength and (b) modulus of neat PEEK fibers and PEEK/FPAEKLCP fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

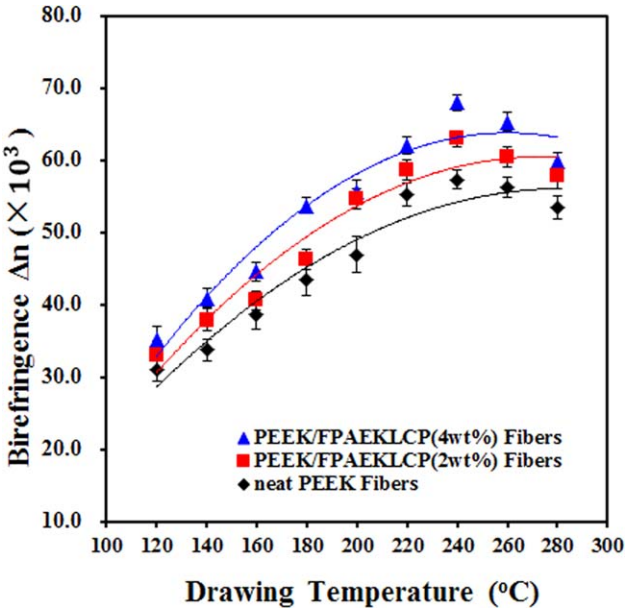

Figure 4. Dependence of the birefringence values of neat PEEK fibers and PEEK/FPAEKLCP fibers on the drawing temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

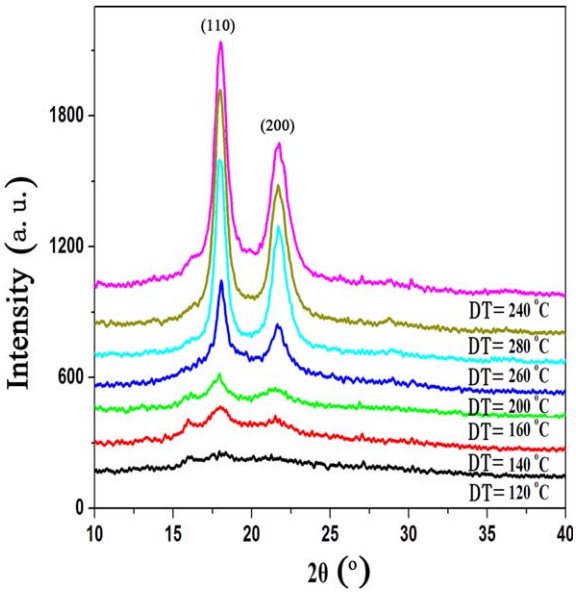

Figure 5. WAXD profiles of PEEK/FPAEKLCP (4 wt %) fibers at the different drawing temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increasing the drawing temperature. As a result, the orientation and crystallization tended to be more perfect, followed by the improvements in the tensile strength and modulus of fibers. However, the disorientation tended to become stronger with further increasing the drawing temperature. Hence, the tensile strength and modulus of fibers decreased. The measurement of birefringence (Δn) is the most widely used criterion for anisotropic features of fibers. A higher value of birefringence indicates a higher degree of molecular orientation.[15] From Figure 4, it could be found that the birefringence values of all fibers first increase and then decrease with increasing the drawing temperature, and achieve a maximum at 240°C. The data on the birefringence well confirmed the aforementioned viewpoint about the dependence of the orientation and the drawing temperature. WAXD profiles of PEEK/FPAEKLCP (4 wt %) fibers at different drawing temperature are shown in Figure 5. It could be seen that the peak width at half height and peak height increase with increasing the drawing temperature, indicating that the enhancement of orientation and crystallization in fibers.

In addition, the effect of the content of FPAEKLCP on the mechanical properties of the series PEEK/FPAEKLCP fibers drawn at various temperatures is shown in Figure 6. It could be seen that the tensile strength and modulus of PEEK/FPAEKLCP fibers drawn at all studied temperatures first increase then

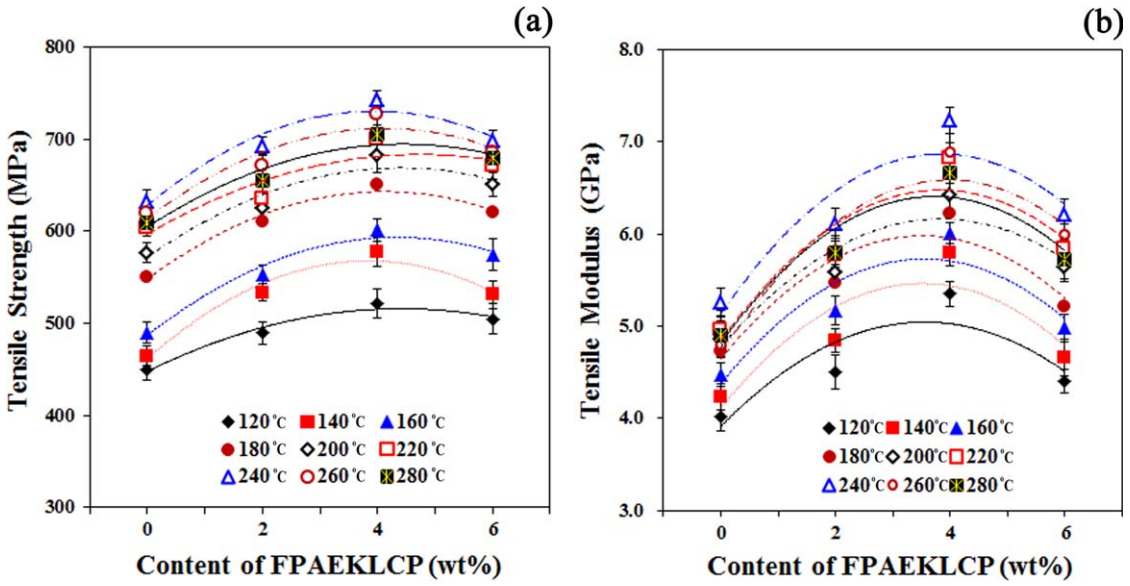

Figure 6. Effect of the content of FPAEKLCP on the (a) tensile strength and (b) tensile modulus of the series PEEK/FPAEKLCP fibers drawn at various temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

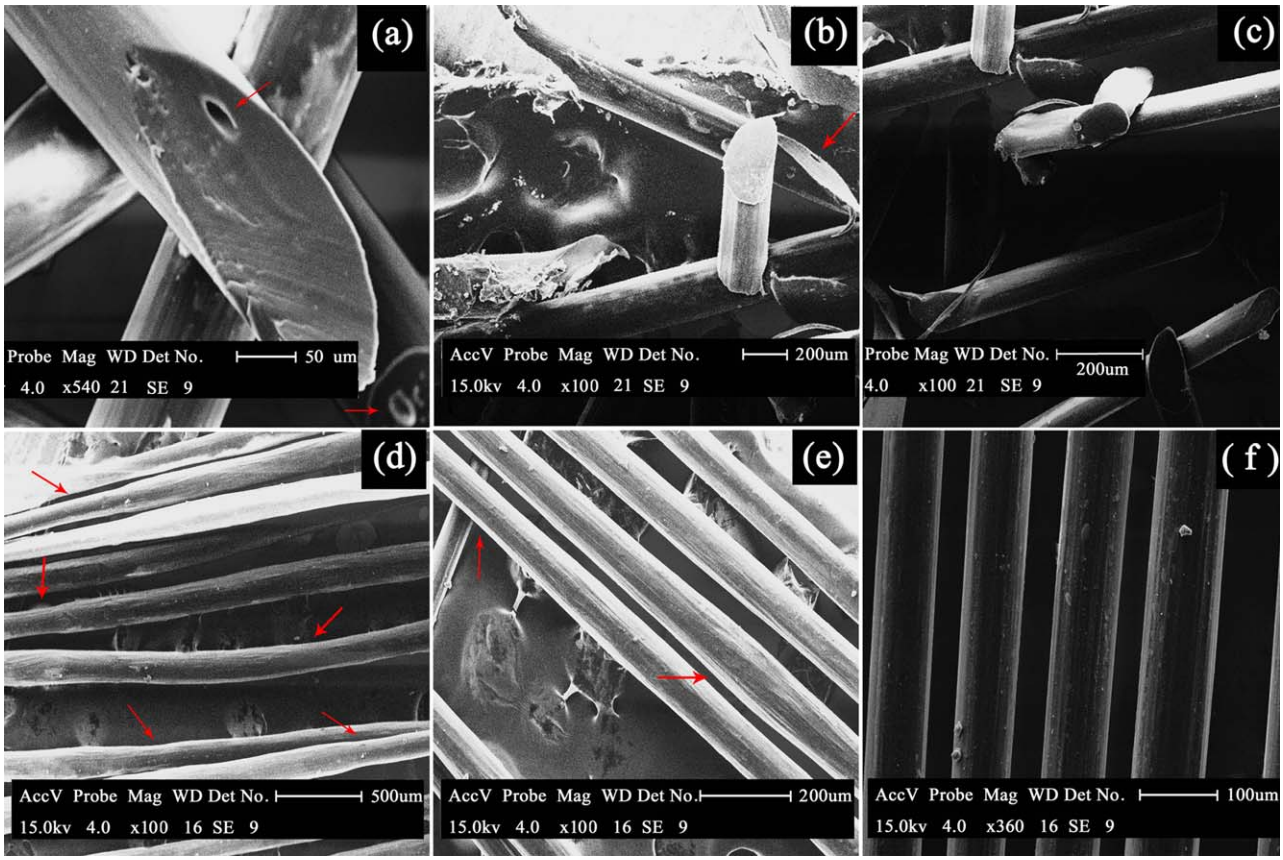

Figure 7. Photomicrographs of the fracture surface of the (a) neat PEEK fibers, (b) PEEK/FPAEKLCP (2 wt %) fibers, (c) PEEK/FPAEKLCP (4 wt %) fibers; Photomicrographs of the surface of (d) neat PEEK fibers, (e) PEEK/FPAEKLCP (2 wt %) fibers, (f) PEEK/FPAEKLCP (4 wt %) fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decrease with the increase of the FPAEKLCP content, and reach a maximum at the loading of 4 wt %. Increasing the content of FPAEKLCP helps to improve the spinnability and the quality of as-spun fibers. However, if the content of FPAEKLCP is too high, the tensile strength and modulus of PEEK/FPAEKLCP fibers decrease, which results from the dilution of FPAEKLCP to

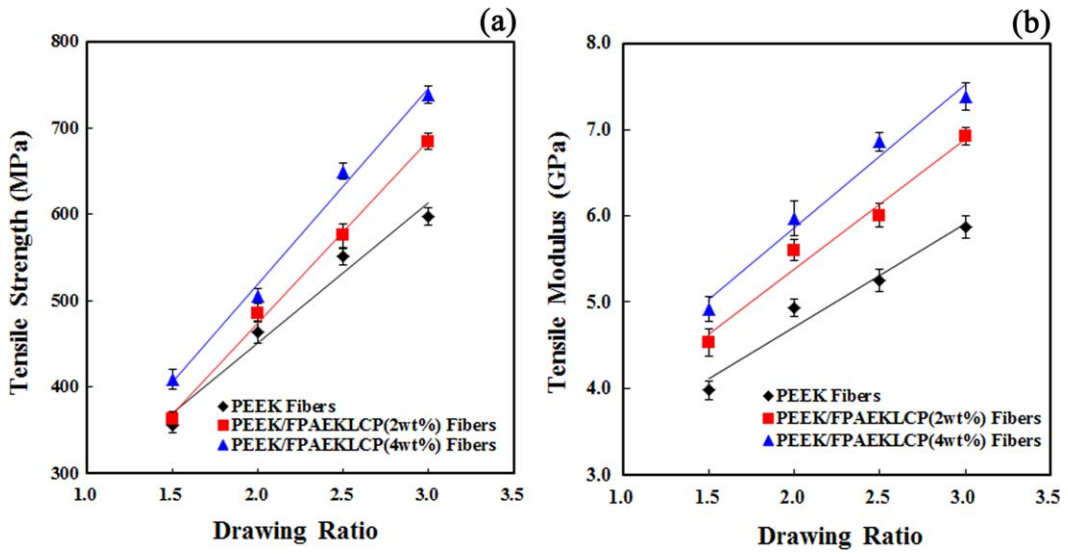

Figure 8. Dependence of (a) tensile strength and (b) tensile modulus on the drawing ratio for neat PEEK fibers and PEEK/FPAEKLCP fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

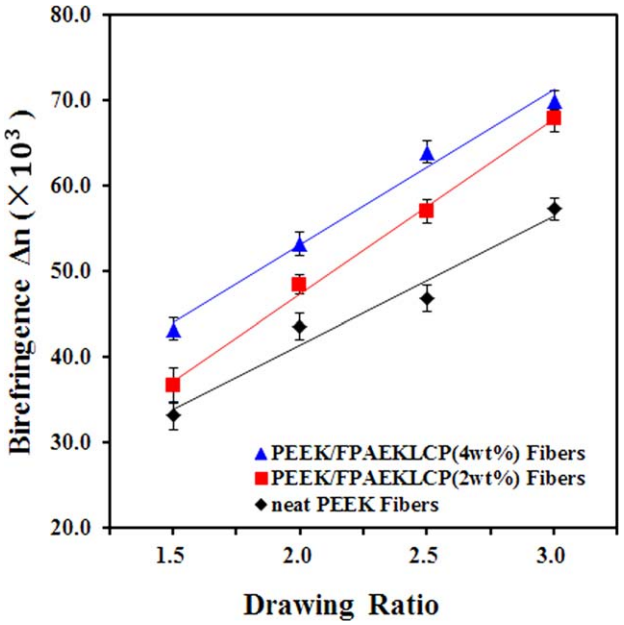

Figure 9. Dependence of the birefringence value on the drawing ratio for neat PEEK fibers and PEEK/FPAEKLCP fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

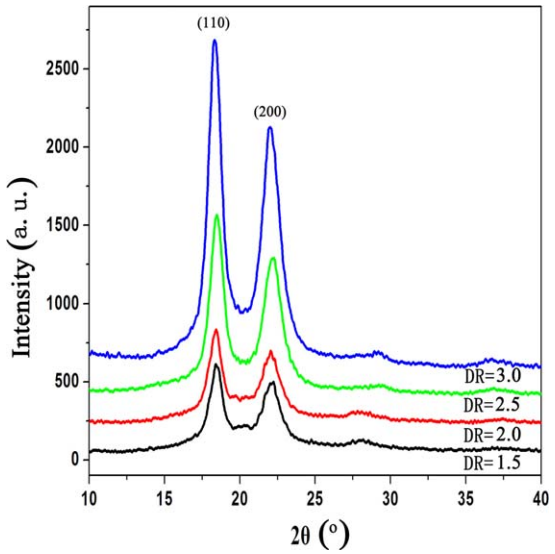

Figure 10. WAXD profiles of PEEK/FPAEKLCP(4 wt %) fibers with different drawing ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

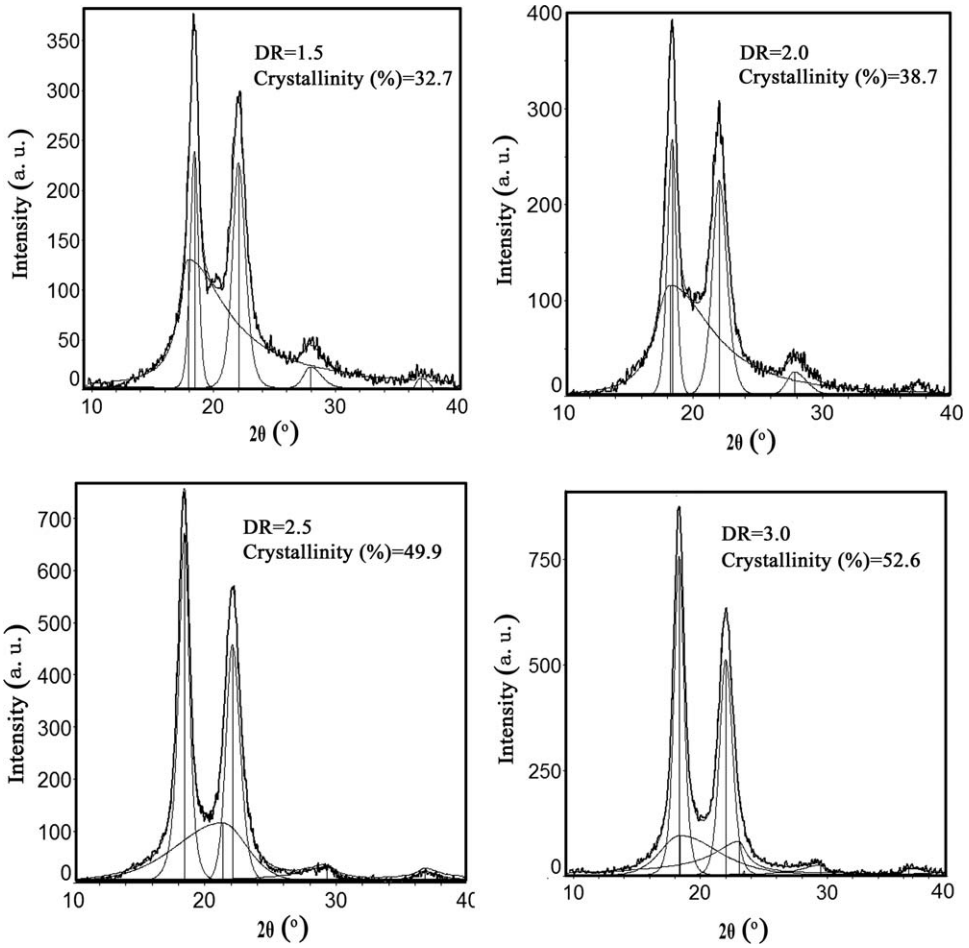

Figure 11. Wide angle X-ray diffraction curve-fitting photographs of neat PEEK fibers and PEEK/FPAEKLCP fibers with drawing.

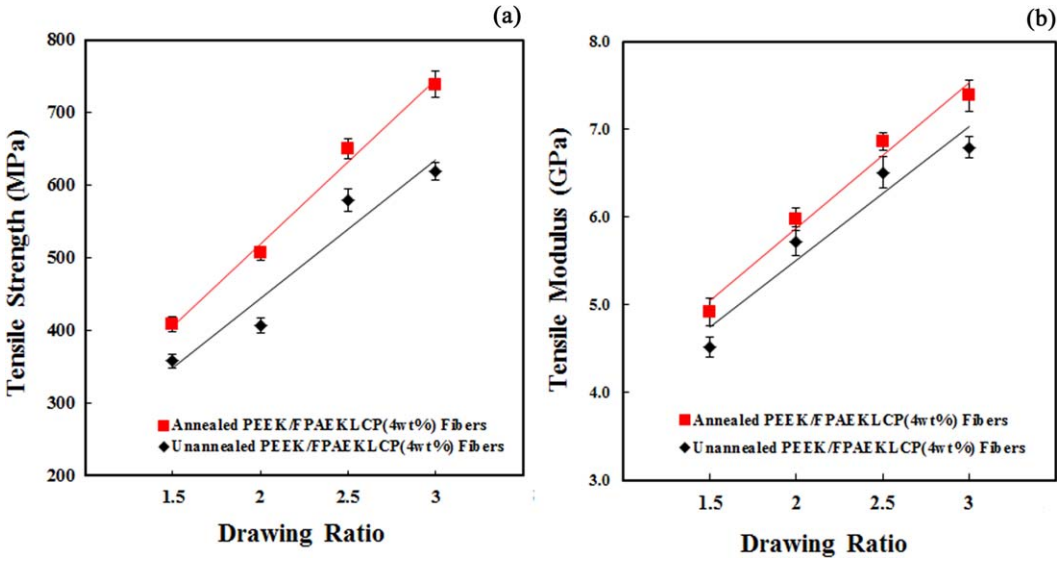

Figure 12. Tensile strength (a) and modulus (b) of unannealed PEEK/FPAEKLCP fibers and annealed PEEK/FPAEKLCP fibers with different draw ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PEEK. After all, the tensile strength and modulus of FPAEKLCP is lower than those of PEEK owing to the lower molecular weight of FPAEKLCP in comparison with PEEK. The morphology of neat PEEK fibers and PEEK/FPAEKLCP fibers was visualized by SEM. Figure 7 well confirmed the aforementioned viewpoint. The fibers with FPAEKLCP proportions of 4.0 wt % are cylindrical with smooth surface and uniform diameter, and there are no irregular striations on their surface and there are hardly any holes in the fibers as shown in Figure 7(c,f). However, neat PEEK fibers and the fibers with FPAEKLCP proportions of 2.0 wt % have irregular striations and a few holes, as shown in Figure 7(a,b,d,e). Low melt viscosity and good spinnability are to assure the good quality and the less defects of fibers. This resulted in relatively good mechanical properties of PEEK fibers.

Effect of Drawing Ratio on the Properties of PEEK/FPAEKLCP Fibers

Dependence of tensile strength and tensile modulus on the drawing ratio for neat PEEK fibers and PEEK/FPAEKLCP fibers is presented in Figure 8. Either neat PEEK fibers or PEEK/FPAEKLCP fibers, their tensile strength and tensile modulus gradually improved with increasing the drawing ratio, which should be attributed to an enhancement in the orientation and crystallization of molecular chains, as proven by Figures 9 and 10. Dependence of the birefringence value on the drawing ratio for neat PEEK fibers and PEEK/FPAEKLCP fibers is shown in Figure 9. In general, an increase in the birefringence value represents the enhancement of molecular orientation. As the drawing ratio increased, the molecular orientation of neat PEEK fibers and PEEK/FPAEKLCP fibers became more orderly along the fiber axis. Thus, the birefringence value increased. The birefringence of PEEK/FPAEKLCP fibers is higher than that of neat PEEK fibers at the same drawing ratio, which maybe result from the improvement in the pre-orientation of as-spun PEEK/FPAEKLCP fibers by introducing FPAEKLCP. WAXD profiles of PEEK/FPAEKLCP (4 wt %) fibers with different drawing ratio are presented in Figure 10. It could be seen that the peak widths become narrower as the order and orientation with increasing the drawing ratio. Decreasing peak width at half height and increasing peak height is an indication of the increased crystal and orientation. It was worth mentioning that the crystallinity also increased with increasing the drawing ratio as shown in Figure 11. The degree of crystallinity was calculated by using a curve-fitting procedure suggested by Blundell and Osborn.[16] It also explained one of the reasons for the improvement of the tensile strength and tensile modulus of fibers was derived from the change of the crystalline

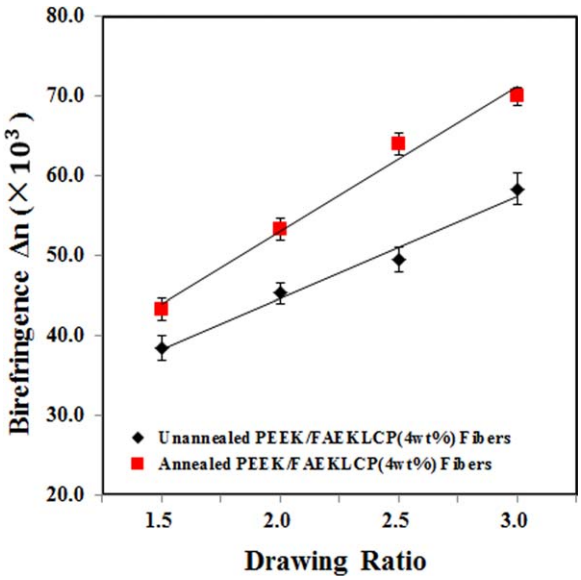

Figure 13. The birefringence value of unannealed PEEK/FPAEKLCP (4 wt %) fibers and annealed PEEK/FPAEKLCP fibers with different draw ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

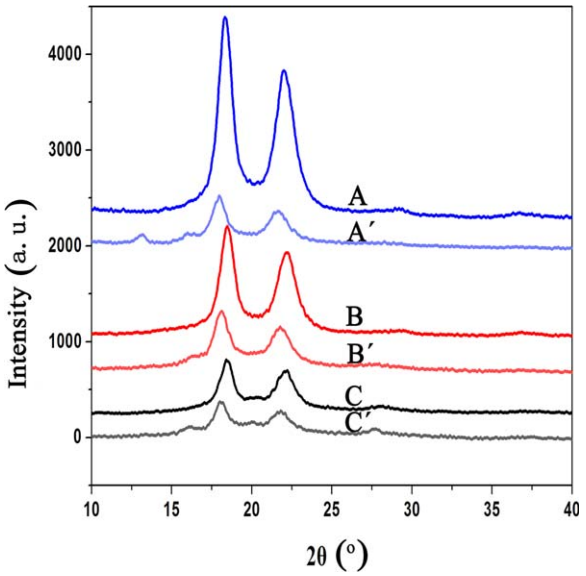

Figure 14. WAXD profiles of PEEK/FPAEKLCP (4 wt %) fibers before and after annealing. A: annealed and the drawing ratio of 3.0, A′: unannealed and the drawing ratio of 3.0; B: annealed and the drawing ratio of 2.5, B′: unannealed and the draw ratio of 2.5; C: annealed and the drawing ratio of 1.5, C′: unannealed and the drawing ratio of 1.5. [Color figure can be viewed in the online issue, which is available atwileyonline library.com.]

aspect, such as the increased crystalline size, the degree of perfection of the crystals, and the crystallinity.

Effect of Annealing on the Properties of PEEK/FPAEKLCP Fibers

The annealing also helps to improve the molecular orientation and crystallization besides the drawing.[17,18] The tensile strength and modulus of the annealed PEEK/FPAEKLCP fibers are higher than those of the unannealed PEEK/FPAEKLCP fibers in Figure 12. The enhancements in the tensile properties should be due to the improvement in the molecular orientation and crystallization arising from the annealing process, as confirmed by Figures 13 and 14. After annealing, the increased birefringence (Figure 13) and the decreased peak width at half height as well as the enhanced peak height (Figure 14), proved the above mentioned viewpoint. This meant that both the annealing and the drawing had a similar role in improving the tensile strength and tensile modulus of fibers.

CONCLUSIONS

The melt viscosity of PEEK decreased markedly and the spinnability of PEEK improved by introducing thermotropic liquid crystalline poly(aryl ether ketone) copolymer (FPAEKLCP). As a result, the tensile strength and modulus of PEEK/FPAEKLCP fibers are obviously higher than those of pure PEEK fibers under the same processing conditions, which should be due to an enhancement in the orientation and crystallization of PEEK compounded with FPAEKLCP. A high-performance PEEK fiber with the tensile strength of 770 MPa and the tensile modulus of 7.6 GPa was prepared under the optimized conditions, such as the FPAEKLCP content of 4 wt %, the drawing temperature of 240°C, the drawing ratio of 3.0, and annealing at 260°C for 2 h. The emergence of such a fiber based on Chinese PEEK resin will be lower price and undoubtedly helps to broaden its applications.

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