Effects of Novel Thermotropic Liquid Crystalline Polyester with Aryl-Ether Linkages on the Processability and Properties of Poly(ether ether ketone)s Fibers

Ting Wu, Pengqing Liu, Xiao Wang, Luxian Zeng, Guangdou Ye, Jianjun Xu

State Key Laboratory of Polymer Materials Engineering (Sichuan University), College of Polymer
Science and Engineering of Sichuan University, Chengdu 610065, China
Correspondence to: J. Xu (E-mail: xujj@scu.edu.cn)

ABSTRACT: A series of composite fibers based on poly(ether ether ketone)s (PEEK) and a novel thermotropic liquid crystalline polye-therarylates (PEAR) with the aryl-ether linkages, have been prepared by melt spinning. The impact of PEAR on PEEK is investigated by rheological measurements, differential scanning calorimetry, thermal gravimetric analysis, wide angle X-ray diffraction and scanning electron microscope, orientation degree test and mechanical properties test, etc. The results show that the flowing curves of the blends can be divided into three regions: the first shear thinning region, the shear thickening region, and the second shear thinning region; meanwhile, the PEAR can function as a processing aid by reducing the viscosity of PEEK, thus the processing can be carried out at relatively low temperatures. Although, they are partially compatible, the mechanical properties of the post-treatment fibers have been improved by 14% after adding 2% PEAR to PEEK. The crystallinity of the as-spun fibers increases from 22.47 to 42.10%, suggesting that PEAR can act as nucleating agent. Regretfully, both of the initial degradation temperatures and the maximal degradation temperatures decrease with the increase of the PEAR content. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Poly(ether ether ketone) (PEEK) is widely used as a high performance material, due to its outstanding heat resistance and thermal stability, high mechanical properties, excellent antiultraviolet properties, good stability of the dielectric properties over a broad frequency and temperature range, etc.[1–3] The primary commercial PEEK (Victrex) based on hydroquinone (HQ) and 4,4′-difluorobenzonphenone (DFBP), is only soluble in 98% sulfuric acid due to its rigid structure and close chain packing, which determines it can be processed only by thermoplastic processing methods. PEEK has not only high melting point around 344°C but also high melting viscosity, therefore its processing temperature is high up to 400°C.[4] All of the above determines that the processing of PEEK consumes high energy, has high requirement of the equipment sealing performance and brings about high loss of the equipment.[5] Thus, How to improve the processability of PEEK has received much attention.

There are many approaches to improve the processability of PEEK. The first one is to synthesize new types of readily soluble PEEKs, which can be processed into films by casting or used as coating. Although the solubility of PEEK can be improved, there are some problems, such as the weakness of the thermal stability, the disappearance of crystallization and high cost of the monomers and synthesis, etc.[6–10] The second one is to decrease the melting temperature T_m with the impairment of the heat resistance, which is meaningless. The third one is to compound with another polymer with low melting viscosity, such as polyether sulfone (PES). PES is useful to decrease the melting viscosity of PEEK, but the thermal properties and mechanical properties were diminished after adding PES.[11,12]

Polymer blending based on thermoplastics and thermotropic liquid crystalline polymer (TP/TLCP) is a useful and attractive approach.[13–18] TLCP with high strength and stiffness, high chemical resistance, good thermal properties, and low melting viscosity can function as a processing aid by reducing the viscosity of TP matrix during compounding, thereby easing the processability of TP.[19] Moreover, the TP matrix can be reinforced due to the formation of TLCP fine fibrils, giving rise to the development of polymer composites that are commonly known as *in situ* composites.[20] The *in situ* composites based on TLCP and several kinds of TP, e.g., poly(ether sulfone) (PES),

polyethylene terephthalate (PET), polycarbonate (PC), polyamide 6 (PA6), polyphenylene sulfide (PPS), PEEK have been researched.[21–24] However, the mechanical properties of TLCP/TP blends are far behind expectations due to the poor compatibility between the dispersed TLCP phase and TP matrix. What's more, not all of the TLCPs can contribute to improve the processing properties of TPs. Valenza et al.[25] studied the rheological behavior and thermal stability of a TLCP (Vectra-B950, Hoechst-Celanese, US, synthesized by 6-hydroxy-2-naphthoic acid (HNA), p-hydroxybenzoic acid (PA), and terephthalic acid (TPA) with the molar ratio of 60 : 20 : 20.)/PPS blends, and the results showed that Vectra-B950 could not be considered as a good processing aid because the viscosity of Vectra-B950 was lower than that of PPS only at relatively high temperatures and under high shear rates.

In the present work, a new type of thermotropic liquid crystalline polymer—polyetherarylate (PEAR) derived from 1,3-bis(4'-carboxyphenoxy)benzene, 1,4-diacetoxybenzene, and p-acetoxybenzoic acid has been synthesized through melt transesterification process. It has the same linkages with PEEK, such as the aryl-ether linkages (—O—), which is expected to improve the compatibility between TLCP and PEEK. To investigate the effects of PEAR on the processability and properties of PEEK, the rheological behavior of the blends with the PEAR weight ratios of 0, 2, 6, and 10% has been studied by high-pressure capillary rheometer and verified by the melt spinning. Moreover, the thermal properties, crystallinity, mechanical properties and morphology of these composite fibers have been investigated by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), wide angle X-ray diffraction (WAXD), and scanning electron microscope (SEM), etc.

EXPERIMENTAL

Materials

The PEEK was Victrex 2000P with melting point of 344°C, manufactured by Degussa.

The TLCP was PEAR (shown in Figure 1), synthesized from 1,3-bis(4'-carboxyphenoxy)benzene, 1,4-diacetoxybenzene, p-aceroxybenzoic acid through melt transesterification process with the molar ratio of 1 : 1 : 1. IR (KBr): 1735 cm^{-1} ($v_{C=O}$), 1599–1467 cm^{-1} (—Ar—, $v_{C=C}$), 1200–1060 cm^{-1} (δ_{C-O-C}), 1007 cm^{-1} ($v_{Ar-O-Ar}$). The inherent viscosity [η] was 0.81 dL g^{-1}, which was determined with an Ubbelohde viscometer ($4 - \varphi$ 0.6, which means the capillary diameter is 0.6 mm and the capacity of measuring bulb is 4 mL). The melting temperature determined by the second heating DSC curve was 285°C. The initial degradation temperature was 424°C. The polarized optical microscopy (POM) photographs (shown in Figure 1) were tested by Leica DMLP POM (Germany) with a heating stage (THMS600, Linkam Scientific Instruments, China). From Figure 1, the nematic phase of PEAR exhibited a characteristic bright texture due to its birefringence, suggesting the PEAR was a thermotropic liquid crystalline polymer. Moreover, it can maintain its liquid crystalline state from 360 to 390°C, which is the processing temperature range of PEEK.

Blends Preparation

The blends based on PEAR and PEEK were prepared by DFT-100 high speed versatile distintegrator (DFT-100, Jinpeng
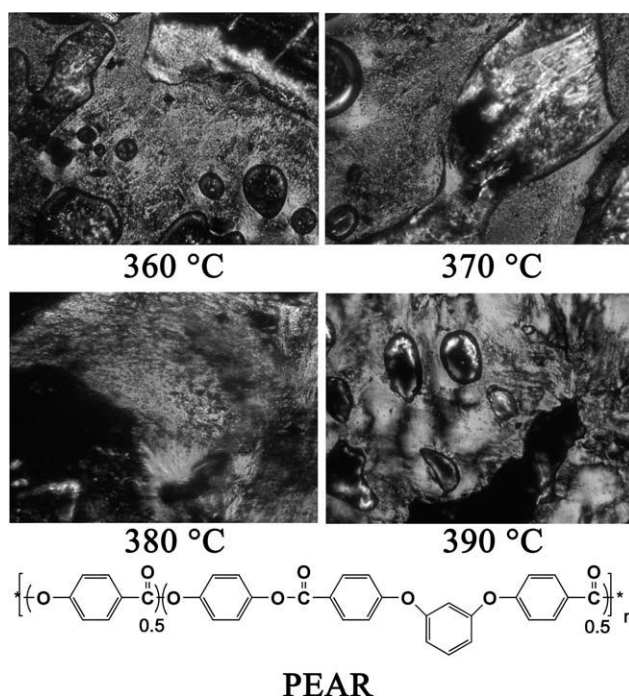

Figure 1. Optical polarized photographs of the PEAR at the temperatures of 360, 370, 380, and 390°C (magnification ×200).

Testmart, China, spindle speed is 24,000 r min^{-1}). The two polymers were added into the distintegrator with the PEAR weight ratios of 0, 2, 6, and 10%, respectively. Then the samples were blended for 30 s. To release the water and solvents, the blends should be vacuum dried for at least 2 h at 200°C.

Fibers Preparation

The as-spun fibers of the neat PEEK and PEAR/PEEK were prepared through melt spinning process with the spinneret of single hole ($D = 0.8$ mm, $L/D = 8/1$). First, the blends were melted and extruded by the single screw, and then the melt formed into the as-spun fibers through spinneret orifice, running rollers and winder. The main processing parameters were as follows: processing temperatures were 365, 370, and 380°C, spinning speed was 5.85 m min^{-1}, while winding speed was 340 m min^{-1}. Finally, these as-spun fibers were subjected to the post treatment with the dry hot stretching at 210°C (the draw ratio was 3.4) as well as the heat setting at 200°C (heat setting time was 51 s).

Measurements

The rheological measurements were carried out by a high-pressure capillary rheometer (Rosand RH7D, Malvern, England) with a screw diameter of 1 mm and capillary length-to-diameter (L/D) of 16. The measurements were performed in the shear rate range of 20–2000 s^{-1} at the temperatures of 370, 380, and 390°C, respectively. About 20 g blended powder was used as test sample.

DSC was carried out using DSC 204F1 (Netzsch, Germany) at a heating rate of 10°C min^{-1} in flowing nitrogen (20 cm^3 min^{-1}). The temperature range evaluated was from 50 to 380°C and about 4 mg fiber powder was used as test sample.
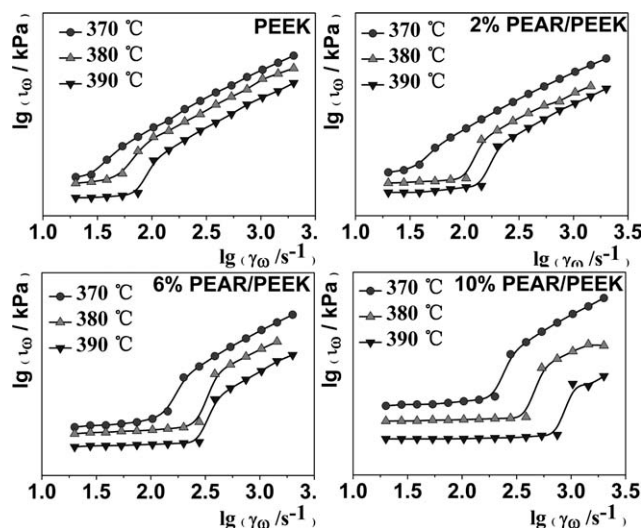
Figure 2. Plots of lg τ as a function of lg γ_ω for the blends at different temperatures.

The temperature and heat enthalpy were calibrated with indium standard before the equipment running. The calculation of crystallinity ($X_c\%$) is according to equation:

$$X_c\% = \left[(\Delta H_m + \Delta H_{rc})/(w \times \Delta H^\theta)\right] \times 100\%;$$

where, ΔH^θ represents the melting enthalpy of the 100% crystalline PEEK ($\Delta H^\theta = 130$ J g^{-1}), ΔH_m is the melting enthalpy of the sample and ΔH_{rc} is the recrystallization enthalpy, and w represents the weight percentage of PEEK component in the composite fibers.[26]

TGA were measured with a thermo gravimetric analyzer (SDTQ600, TA) using a heating rate of 20°C min^{-1} in N$_2$ at a flow rate of 100 cm^3 min^{-1}. The temperature range evaluated was from the room temperature to 800°C. About 3–4 mg fiber powder was used as test sample.

The degree of orientation of the molecular chain was determined by measuring the transmitting time of the ultrasonic wave between two transducers coupled to the specimens. The measurements were carried out by an SCY-III model fiber sonic velocity meter (Donghua University, People's Republic of China). f represents the chain orientation factor of the fiber,

which can be calculated according to equation $f = 1 - \left(\frac{C_u}{C}\right)^2$; where, C and C_u represent the sonic velocity of the above samples and unoriented PEEK sample, respectively. $C_u = 1.487$ km s^{-1}, was carried out by the free-run PEEK fibers instead of unoriented fibers.

WAXD measurements were performed on a X'Pert Pro (Philips) X-ray diffractometer operating in the 2θ range of 5–40° at a scanning rate of 12° min^{-1} with nickel filtered Cu Kα radiation ($L = 1.54$ Å) at room temperature. The parallel monofilament fiber was bundled onto a glass slide and fixed to the sample holder. The data analysis was performed by MDI Jade 5.0 software.

The morphology of the fibers was investigated with the field-emission scanning electron microscope (FSEM) (FEI Sirion-200, USA) at ambient condition. SEM figures of the oblique profile of the as-spun fibers were used to investigate the compatibility of two phases, while SEM figures of the surface of the as-spun fibers were used to study the impact of PEAR on the processability of PEEK.

Tensile mechanical properties of the fibers, including breaking strengths and elongation at break, were tested with tensile strength tester (YG061, China) at the room temperature. Initial length is 20 mm, tensile speed is 20 mm min^{-1}. Single fiber was used for this study and an average of 10 replicas was used.

RESULTS AND DISCUSSION

Processability

The effects of PEAR on the processability of PEEK fibers have been investigated by rheological measurements. Figure 2 represents the shear stress τ_ω − shear rate γ_ω relationships of the blends with the PEAR weight ratios of 0, 2, 6, and 10% at the temperatures of 370, 380, and 390°C, respectively. It can be found that the samples are not always a typical non-Newtonian fluid at the investigated shear rate range. It can be divided into three regions. Region I is the shear thinning region in low shear rate. lg τ_ω is almost invariable with the elevating of lg γ_ω in this region, which demonstrates that the apparent viscosity of PEAR/PEEK melt rapidly decreases. This may be due to the disentanglement and the orientation of the molecular chains under the shear stress; As a result, the apparent viscosity decreases. Region II is the shear thickening region. With further increase of the shear rate, there is a mutation area where lg τ_ω sharply
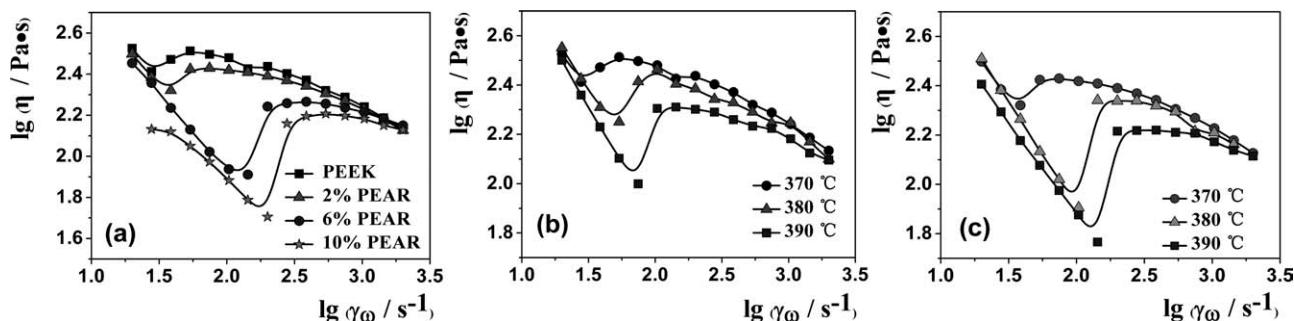

Figure 3. Plots of lg η as a function of lg γ_ω for the samples: (a) samples with the PEAR contents of 0, 2, 6, and 10% at 370°C; (b) neat PEEK at different temperatures; (c) samples with 2% PEAR at different temperatures.

Table I. The Processability of the Neat PEEK and PEAR/PEEK Blends

Samples	Processing temperature (°C)	Spinning pack pressure (MPa)	Unstable flow severity	Texture of the as-spun fibers	Filament breakage severity
PEEK	365	1.60 ± 0.10	Serious	Rough	Frequent
	370	1.55 ± 0.10	Relatively serious	Rough	No
	380	1.05 ± 0.10	Normal	Smooth	No
2% PEAR/PEEK	365	1.60 ± 0.05	Relatively serious	Rough	Relatively frequent
	370	0.70 ± 0.05	Normal	Smooth	No
6% PEAR/PEEK	365	1.60 ± 0.05	Serious	Rough	Frequent
	370	0.60 ± 0.05	Serious	Rough	Frequent
10% PEAR/PEEK	365	1.55 ± 0.05	Serious	Rough	Frequent
	370	0.40 ± 0.05	Serious	Rough	Frequent

increases, suggesting that the apparent viscosity of PEAR/PEEK melt rapidly increases. The shear thickening behavior may be brought about by the slight physical crosslink structure, which may result from the enhanced intermolecular force of the ordered area or the tangles between main chain and branched chain (as we know, the absolute linear polymer does not exit). Region III is the second shear thinning region, where the apparent viscosity decreases with the further elevating of the shear rate. This is because the slight physical crosslink structure is destroyed at relative high shear rate.

Figure 3(a) shows the effect of the PEAR content on the rheological behavior. It can be seen that the viscosities of the blends sharply drop with the addition of PEAR, suggesting that PEAR can act as a processing aid by reducing the viscosity of PEEK melting during processing. The main reason can be explained by the morphological changes of PEAR and PEEK chains in capillary die. The PEAR chains are easy to orientate under the shear conditions, leading to the orientation of the PEEK chain and the drop of the viscosity. It can also be found that the range of shear rate in the first shear thinning region becomes wider and wider, the shear thickening region tends to more and more significant and the second shear thinning region becomes more and more gentle with the increase of the PEAR content. This may be because the PEAR can make it easier for the orientation of the PEEK molecular chains at a relative high and wide range of shear rate, however, the bigger the orientation degree is, the more easily the slight-physical crosslink structure forms in the ordered area, which results in the rising of the melting viscosity. With further increase of the shear rate, the viscosity drops more gently after adding the PEAR, suggesting that PEAR lowers the sensitivity of the viscosity to the shear rate; as a result, the processability tents to be more stable.

Figure 3(b, c) shows the effect of the temperature on the viscosity of the samples, which has similar effect with that of the PEAR content. Because it is easier for the molecular chains to move at higher temperature; the high temperature is beneficial to the orientation at a relative high and wide range of the shear rate.

The rheological behavior of the PEEK/PEAR blends suggests that PEAR is benefit to drop the melting viscosity of the blends. Moreover, the improvement of processability of the blends must be verified by the melt spinning. Table I shows the key parame-

ters in the melt spinning of the blends with different weight ratios at different temperatures. It can be seen that the processing conditions of the neat PEEK is rather poor. At the temperatures below 380°C, the viscosity of the melting is too high to steady flow, leading to filament breakage and producing rough fibers. The spinning pack pressure of all the samples is much bigger at 365°C than that at relative high temperatures. This is due to that the PEEK is not completely plasticized at 365°C, leading to filament breakage and producing rough fibers. What's more, the spinning pack pressure decreases with the increase of the PEAR content at the same temperatures, indicating that the PEAR is really benefit to drop the melting viscosity of the blends. After adding 2% PEAR into the PEEK, it can obtain smooth as-spun fibers with breakage-free at relatively low temperature of 370°C. However, with the rising of the PEAR, the processing condition became poor again, which may be due to the partially compatibility. As we know, the two components have different responses to the flow field. TLCP component has the tendency to move to shell of the capillary under the condition of shear stress. The more TLCP, the more easily the orientated chains will move to the surface, thereby leading to unstable flowing.

Properties of the Fibers

Thermal Properties. The two components have different molecular structures and heat resistant, which results in the influence on the properties. The thermal properties of these as-spun fibers were evaluated by means of DSC and TGA. DSC results are listed in Table II and showed in Figure 4(a). All the samples show an obvious exothermic peak at relatively low temperatures

Table II. DSC Data of PEAR/PEEK As-Spun Fibers

Samples	T_{rc}[a]/°C	T_m[b]/°C	T_c[c]/°C	X_c[d]/%
PEEK	168	344	301	22.47
2% PEAR/PEEK	166	343	303	30.97
6% PEAR/PEEK	164	341	304	36.80
10% PEAR/PEEK	162	342	303	42.10

[a]T_{rc} represents the recrystallization temperature, [b]T_m represents the melting points, [c]T_c represents the crystallization temperature, [d]X_c represents the crystallinity.
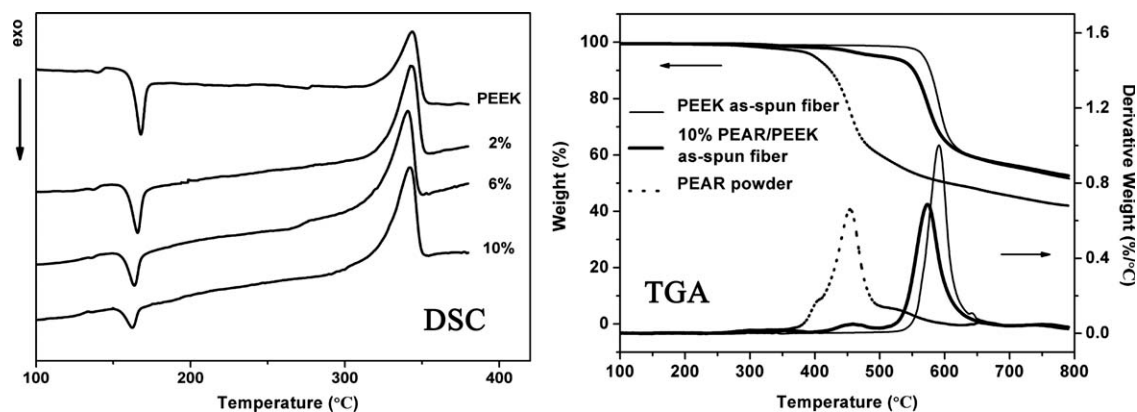
Figure 4. DSC and TGA curves of the samples: (a) DSC curves of the as-spun fibers (first heating); (b) TGA curves of PEEK and 10% PEAR/PEEK as-spun fibers and the neat PEAR powder.

and an obvious endothermic peak at higher temperatures in the DSC heating trace, which represents the recrystallization peaks and melting peaks, respectively. There is little change in the melting temperatures of all the samples, suggesting that the addition of PEAR has little influence on the heat resistant of PEEK. However, the recrystallization peak shifts to the lower temperature as the PEAR weight ratio increases. This is because PEAR is easy to orientate under shear conditions, leading to the disentanglement and the orientation of PEEK chain for the slippage between those two phases, as a result, it becomes easier for these relatively ordered molecular chains to enter the crystal lattice.

Moreover, the crystallization peak determined by the DSC cooling trace tends to shift to the higher value as the weight ratio of the PEAR/PEEK increases. As we know, it is rather hard for TLCP to crystallize owing to its rigid molecular chains, meanwhile the crystal nucleus are unstable in high temperature. But the PEAR are in liquid crystalline state at 300°C, the domains or the defects in the mesogenic phase can function as nucleating agent, which gives rise to the crystallization of the PEEK chains at higher temperatures. For the same reason, the crystallinity of the as-spun fibers tends to rise with the increase of the PEAR content.

Thermal stabilities of these as-spun fibers were evaluated by TGA under nitrogen atmosphere. The blended samples decompose in two steps [seen in Figure 4(b)] except the neat one. The first step represents the decomposition of the PEAR component, while the second one represents the decomposition of the PEEK component. The results are listed in Table III. It can be seen that both of the initial degradation temperatures (T_{id}) and the maximal degradation temperatures (T_{md}) decrease with the increase of the PEAR content due to the relatively poor thermal stabilities of the PEAR. However, there is little change in the char yields at 800°C for all the blended samples and the neat PEEK sample, suggesting that the addition of PEAR has little influence on the decomposition behavior of PEEK.

Crystallinity. The crystal form of as-spun fibers and post treatment fibers have been studied by WAXD Figure 5 shows the WAXD figures of neat PEEK and 2% PEAR/PEEK fibers.

The left figure indicates that crystallinity of as-spun fibers is too low to view the crystal diffraction peaks; after the post treatment, the crystallinity of fibers is increased obviously. The XRD patterns of those two samples show strong reflections with four peaks $2\theta = 18.76°$, $22.42°$, $24.74°$, and $26.67°$, which are assigned as (110), (111), (200), and (211), respectively. This implies that the adding of PEAR has little impact on the crystal form of PEEK.

Morphology. The morphology of the PEAR/PEEK as-spun fibers are now considered. As we know, the molecular structures of these two components are different, and they have different responses to flow field. Thus, the PEAR has great influence on the morphology of the composite fibers. Figure 6(a–d) shows the scanning electron micrographs of the oblique profile of the PEAR/PEEK as-spun fibers formed at 370°C. As shown in the figure, there are obvious interfaces and even gaps in the oblique profile and the PEAR phase is dispersed in the PEEK matrix as cylinders or fine fibrils along the flow direction, which demonstrates that these two components are half-compatible. The more the PEAR, the more the gaps of the unit area. Figure 6(e–h) shows the scanning electron micrographs of the surface of the PEAR/PEEK as-spun fibers formed at 370°C. The surface of the neat PEEK as-spun fiber is rough and uneven thickness, while that of the 2% one is smooth with uniform thickness, suggesting that it can improve or avoid the phenomenon of the melt broken by the means of adding 2% PEAR. However, with

Table III. TGA Data of the PEEK and PEAR/PEEK As-Spun Fibers and the PEAR Power

Samples	T_{id}[a]/°C	T_{md}[b]/°C	Char yield[c]/%
PEEK	567	591	51.62
2% PEAR/PEEK	555	583	52.46
6% PEAR/PEEK	539	577	51.45
10% PEAR/PEEK	502	573	52.62
PEAR powder	424	495	42.02

[a]T_{id} represents 5% weight loss temperature, [b]T_{md} represents the maximum rate of decomposition temperature, [c]Residual weight percentage at 800°C in nitrogen.
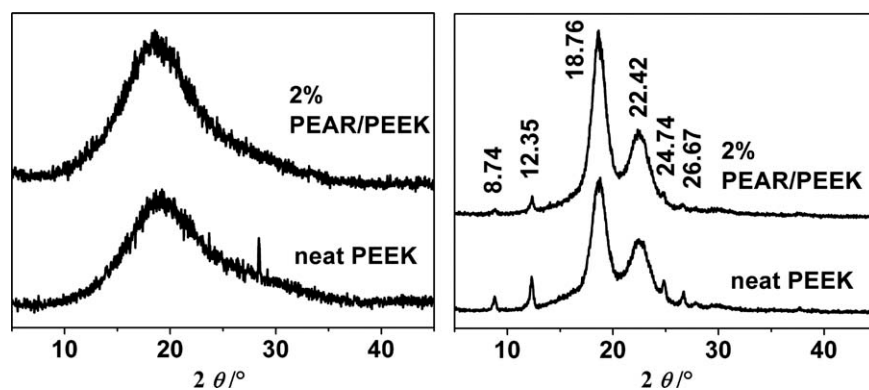
Figure 5. WAXD patterns of neat PEEK and 2% PEAR/PEEK fibers: left: as-spun fibers, right: post treatment fibers.
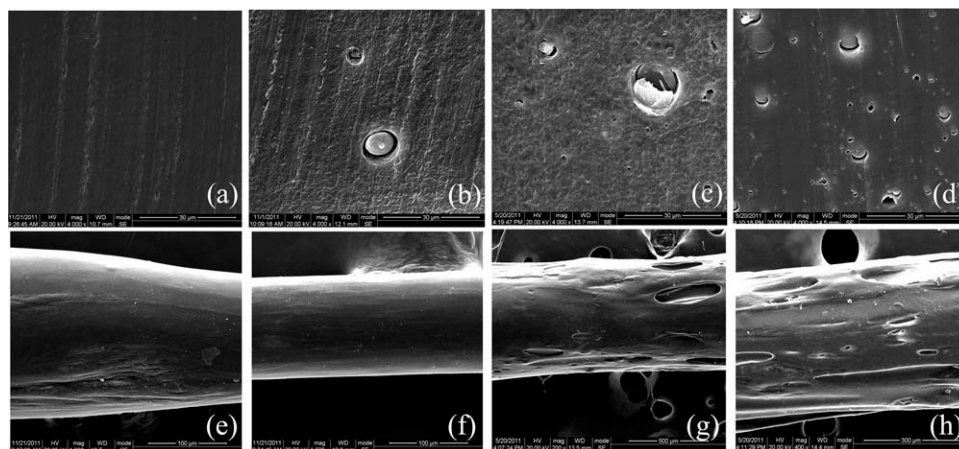

Figure 6. Scanning electron micrographs of the PEAR/PEEK as-spun fibers formed at 370°C: (a) 0%, (b) 2%, (c) 6%, and (d) 10%a (a–d: oblique plane, magnification ×4000); (e) 0% (×1000), (f) 2% (×1000), (g) 6% (×200), and (h) 10% (×400), (e–h: surface of the fibers).

further increase of the PEAR content, there are more and more channels in the surface of the fibers, indicating once again that the PEAR component has the tendency to move to the surface; as a result, when the content of PEAR is >6%, the melting flow becomes unstable and the processability turns to poor again.

Mechanical Properties. The as-spun fibers of the neat PEEK and the blend with 2% PEAR were subjected to a one-stage dry hot stretching and heat setting, while others could not owing to the terrible texture. Table IV lists the mechanical properties, the chain orientation factors and the crystallinities of the post treatment fibers. It can be seen that, even though there are obvious interfaces in the fibers with 2% PEAR, the mechanical properties of the post treatment fibers have been improved by 14%

compared to that of the neat one, which may be explained by the induced orientation of PEAR on the PEEK molecular chains. Meanwhile, the crystallinity of the post treatment fiber with 2% PEAR is lower than that of the neat PEEK one, which is contrary to the conclusion of the as-spun fibers. It elicits that the induced crystallization of PEAR on the PEEK exists in the forming stage of the as-spun fibers, and the PEAR component inhibits the growth of the PEEK crystals.

CONCLUSIONS

In the present study, we have investigated the effects of PEAR on the processability and properties of PEEK fibers. The results show that the flowing curves of the blends can be divided into

Table IV. Properties of the Post-Treatment Fibers

Samples	Breaking strengths (cN/dtex)	Standard deviation (%)	Elongation at break (%)	Standard deviation (%)	f^{a}	Crystallinity[b] (%)
PEEK	4.04	7.66	9.17	8.27	0.77	63.81
2% PEAR/PEEK	4.59	11.68	6.32	15.85	0.79	60.68

[a]f represents the chain orientation factor of the fiber, [b]Tested by wide angle X-ray diffraction.

three regions: the first shear thinning region, the shear thickening region and the second shear thinning region, and the former two regions are more obvious with the increase of PEAR content or elevated temperature. What's more, the PEAR can function as a processing aid by reducing the viscosity of PEEK matrix so that the processing can be carried out at relatively low temperature. Although, they are partially compatible, the mechanical properties of the post treatment fibers have been improved by 14% after adding 2% PEAR to the PEEK matrix. However, with the increase of the PEAR, the processing condition became poor again. The DSC results show that the crystallinity increases from 22.47 to 42.10%, suggesting that PEAR can act as nucleating agent. The TGA results show that both of the initial degradation temperatures and the maximal degradation temperatures decrease with the increase of the PEAR content. In general, the blends based on PEEK and 2% PEAR can exhibit good processing properties and their composite fibers have good mechanical properties and excellent thermal properties.

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