

Preparation and Characterization of High-Strength Poly(ether ether ketone) Films

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ABSTRACT: High-strength poly(ether ether ketone) (PEEK) films were prepared through melt extrusion followed by stretching. The tensile strength, orientation, and crystallization behaviors of PEEK films were characterized by universal testing machine, thermomechanical analysis, wide-angle X-ray diffraction, and differential scanning calorimetry. The results indicated that the tensile strength of PEEK films mainly depended on the stretching rate (v), stretching temperature (T), and stretching ratio (λ_L). Moreover, the tensile strength of the stretched PEEK film (333 MPa) was almost four times higher than that of the unstretched PEEK film (87 MPa) under an optimized condition. This is attributed to a synergistic effect of orientation and crystallization in the stretching process, and the influence of orientation is stronger than that of the crystallization on the improvement of the tensile strength of PEEK films. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40172.

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INTRODUCTION

Poly(ether ether ketone) (PEEK) is a kind of semicrystalline thermoplastic polymer with outstanding properties, including high-temperature resistance, superior mechanical properties, and excellent chemical resistance.^{1,2} In order to expand its application fields, PEEK has developed different types of products, such as plates, rods, pipes, fibers, and films. Recently, PEEK films have attracted much attention due to a unique combination of properties, like high-temperature performance, mechanical strength, chemical resistance, electrical insulation, excellent wear and abrasion resistance, radiation resistance, and low-moisture absorption.^{3–11} They successfully meet increasing demands for lightweight, durable, low cost, and eco-friendly application design in a broad range of markets including electronics, acoustics, aerospace, automotive, industrial, energy, and more.^{12–18}

Nevertheless, PEEK films are still facing a challenge, that is, whether they can be used in certain harsh environments, such as to meet the need of a higher strength. Understanding the interactions between processing parameters and the development of structural characteristics is required to control the properties of polymeric materials. Most of the reported studies have focused on the optical property, fracture behavior, and surface functionalization of PEEK films,^{19–22} whereas there is no research on how to improve the tensile strength of PEEK films by the change of processing parameters. This is the focal point of interest in the present study. Therefore, series of PEEK films

prepared under different stretching condition were investigated with the aim of gaining the enhanced understanding of process (stretching rate, stretching temperature, and stretching ratio)–structure (orientation and crystallization)–property (tensile strength) relationships and with the ultimate aim of obtaining high-strength PEEK films.

EXPERIMENTAL

Material

Commercial grade (APTIV film 2000 series) PEEK cast films of 70- μm thickness was provided by Victrex. APTIV film 2000 series, which exhibit glass transition temperature (T_g) at 143°C and melt temperature (T_m) at 342°C, are amorphous films.

Samples Preparation

Rectangle-shaped samples of 80 mm (length) \times 40 mm (width) were cut from the amorphous PEEK films. The samples were clamped and mounted on the uniaxial stretching system inside an environmental chamber with a constant temperature heating device. The distance between the clamps was 40 mm. The series stretched PEEK films were obtained by controlling the stretching rate (v), stretching temperature (T), and stretching ratio (λ_L) of rectangle-shaped samples in the stretching process. The heat treatment time was same when the PEEK films were prepared. The PEEK films samples of the largest stretching ratio need the longest stretching time in the preparation of all samples. The longest stretching time was used as the standard time

of heat treatment for all samples. All PEEK films samples were kept inside heating device at a constant temperature for the standard time so that the heat treatment time was same.

Characterization. Dumbbell-shaped samples of 40 mm (length) \times 10 mm (width) were cut from the origin and stretched PEEK films. Tensile strength of dumbbell-shaped samples was performed on a Shimadzu AG-1 universal testing machine (UTM) without a strain gauge-type extensometer at room temperature. A cross-head speed of 2 mm/min was employed. The average values of at least five tests were reported.

The orientation of the origin and stretched PEEK films was evaluated by coefficient of thermal expansion (CTE), which included the longitudinal CTE along the stretching direction of the films and the transverse CTE perpendicular to the stretching direction of the films. The data on CTE were obtained by Mettler–Toledo TMA/SDTA 841° thermomechanical analysis (TMA) in the range of 25°C–160°C. The heating rate was 5°C/min, and the test mode was film stretching.

The structure surfaces of the origin and stretched PEEK films were observed with a Shimadzu SSX-550 Superscan scanning electron microscope (SEM). The samples were gold-sputtered before scanning.

The orientation and crystallization of the origin and stretched PEEK films were investigated by Rigaku D/max-2500 X-ray

diffractometer with CuK α radiation ($\lambda = 0.154$ nm) as the X-ray source. The 2θ scan data were collected at 0.05° intervals over ranges of 10°–60° and scan speed was 10°(2 θ)/min.

The crystallization properties of the origin and the stretched PEEK films were measured using Mettler–Toledo DSC821° differential scanning calorimetry (DSC) at a heating rate of 10°C/min under nitrogen. The degree of crystallinity was determined using eq. (1):

$$\chi(\%) = (\Delta H_m - \Delta H_c) / \Delta H_f^0 \times 100 \quad (1)$$

where χ is the degree of crystallization, and ΔH_m represents the enthalpy of melting, ΔH_c is the enthalpy of crystallization, ΔH_f^0 represents the heat of fusion of 100% crystalline to be 130 J/g.²³

RESULTS AND DISCUSSION

The stretching rate (v), stretching temperature (T), and stretching ratio (λ_L) are three important processing parameters in the subsequent stretching process for PEEK films produced by melt extrusion.

Influence of Stretching Rate (v) on Tensile Strength of PEEK Films

Figure 1(a) shows the dependence of the tensile strength on stretching rate for PEEK films. From Figure 1(a), it can be observed that the tensile strength of PEEK films first increases

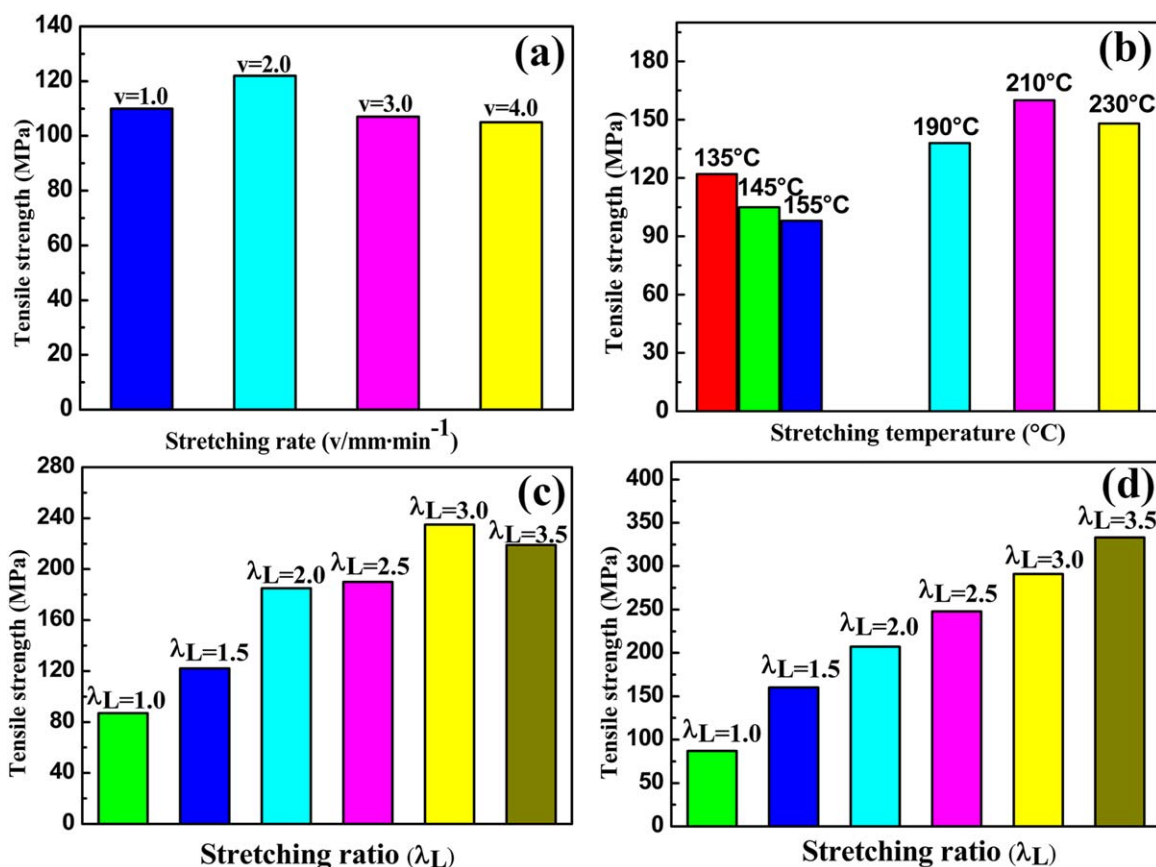


Figure 1. Dependence of tensile strength on (a) stretching rate ($T = 135^\circ\text{C}$, $\lambda_L = 1.5$), (b) stretching temperature ($v = 2$ mm/min, $\lambda_L = 1.5$), (c) stretching ratio ($T = 135^\circ\text{C}$, $v = 2$ mm/min) and (d) stretching ratio ($T = 210^\circ\text{C}$, $v = 2$ mm/min) for PEEK films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

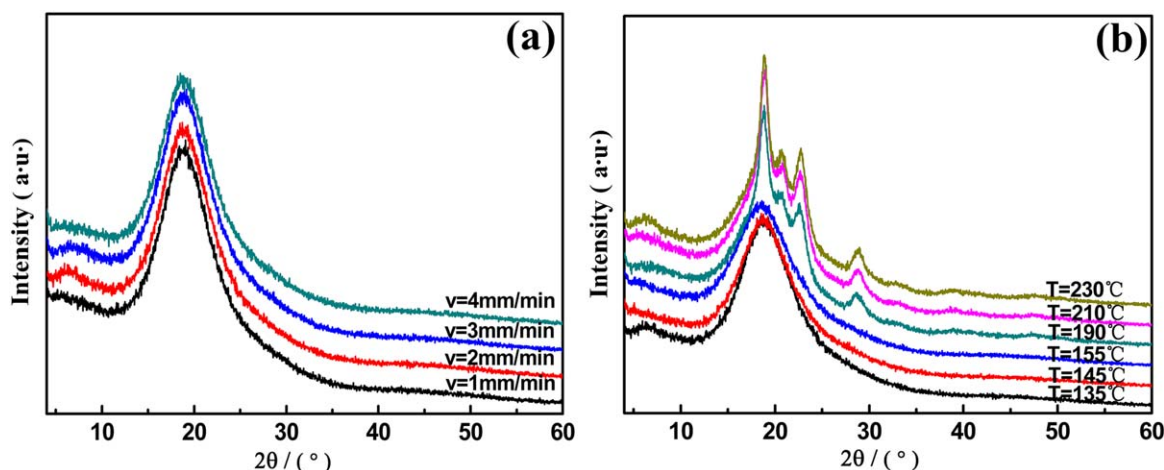


Figure 2. Wide-angle X-ray diffraction patterns of PEEK films with different stretching rate (a) and stretching temperature (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

then decreases with increasing the stretching rate ($T = 135^{\circ}\text{C}$, $\lambda_L = 1.5$). Additionally, wide-angle X-ray diffraction (WAXD) patterns of PEEK films with different stretching rate are demonstrated in Figure 2(a). As revealed by Figure 2(a), there is only a diffused peak for PEEK films with different stretching rate, indicating that the state of aggregation of the obtained PEEK films ($T = 135^{\circ}\text{C}$, $\lambda_L = 1.5$) is amorphous and is not dependent on the stretching rate.

In order to have a clear understanding on how the stretching rate affect the tensile strength of PEEK films, the CTE of PEEK films ($T = 135^{\circ}\text{C}$, $\lambda_L = 1.5$) with different stretching rate are exhibited in Table I. The longitudinal CTE of PEEK films first decreases and then increases with increasing the stretching rate, whereas the transverse CTE of PEEK films first increases and then decreases. This means that the orientation effect of molecular chains first enhances ($v \leq 2$) and then weakens ($v > 2$) with the increase of the stretching rate. This phenomenon well explains the dependence of tensile strength on stretching rate should be attributed to the dependence of orientation on stretching rate. On the one hand, the orientation of PEEK molecular chains is enhanced with increasing the stretching rate, resulting in the increase of tensile strength. On the other hand, the fracture probability of PEEK molecular chains increases with increasing the stretching rate, leading to the decrease of tensile strength. As a result, the orientation or tensile strength of PEEK film is the highest at $v = 2$ mm/min.

Table I. Coefficient of Thermal Expansion of PEEK Films with Different Stretching Rate $T = 135^{\circ}\text{C}$, $\lambda_L = 1.5$

Stretching rate (mm/min)	Longitudinal CTE (ppm/k)	Transverse CTE (ppm/k)
1.0	6.45	88.78
2.0	-4.99	91.43
3.0	4.39	91.35
4.0	4.61	90.06

Influence of Stretching Temperature (T) on Tensile Strength of PEEK Films

Figure 1(b) presents the dependence of the tensile strength on stretching temperature for PEEK films. From Figure 1(b), it can be seen that the tensile strength of PEEK films exhibits the different tendency in the different temperature range ($v = 2$ mm/min, $\lambda_L = 1.5$). When the stretching temperature is less than or equal to 155°C ($T \leq 155^{\circ}\text{C}$), the obtained PEEK films is amorphous, as proven by Figure 2(b). As revealed by Figure 2(b), there is only a diffused peak for PEEK films ($T \leq 155^{\circ}\text{C}$). Therefore, the change of the tensile strength is determined by the orientation rather than the crystallization. CTE of PEEK films with different stretching temperature is demonstrated in Table II.

From Table II, it can be found that the longitudinal CTE of PEEK films gradually increases with increasing the stretching temperature ($T \leq 155^{\circ}\text{C}$), whereas the transverse CTE of PEEK films gradually decreases. This suggests that the disorientation of molecular chains tends to become stronger with the increase of the stretching temperature ($T \leq 155^{\circ}\text{C}$), followed by a gradual decline in the tensile strength of PEEK films.

When the stretching temperature is greater than or equal to 190°C ($T \geq 190^{\circ}\text{C}$), the obtained PEEK films is crystalline, as proven by Figure 2(b). As revealed by Figure 2(b), there are the

Table II. Coefficient of Thermal Expansion and Degree of Crystallization of PEEK Films with Different Stretching Temperature ($v = 2$ mm/min, $\lambda_L = 1.5$)

Stretching temperature ($^{\circ}\text{C}$)	Longitudinal CTE (ppm/k)	Transverse CTE (ppm/k)	Degree of crystallization (%)
135	-4.99	91.43	Amorphous
145	12.41	83.86	Amorphous
155	42.74	79.17	Amorphous
190	36.79	76.42	26.20
210	27.68	85.65	27.86
230	38.92	74.56	29.74

three sharp peaks indexed as 110, 200, and 020²⁴ for PEEK films ($T \geq 190^\circ\text{C}$). Hence, the change of the tensile strength depends on two aspects of orientation and crystallization. From Table II, it can be observed that the degree of crystallization of PEEK films slightly increases with increasing the stretching temperature ($T \geq 190^\circ\text{C}$), whereas the disorientation of PEEK films first weakens ($210^\circ\text{C} \geq T \geq 190^\circ\text{C}$) then enhances ($T = 230^\circ\text{C}$). This should be attributed that the formation of crystallization limits the occurrence of the disorientation at lower temperature ($210^\circ\text{C} \geq T \geq 190^\circ\text{C}$), but the restricted effect weakens at higher temperature ($T = 230^\circ\text{C}$). The result is that the tensile strength of PEEK films is the highest at $T = 210^\circ\text{C}$.

It is necessary to be noted that the stretching temperature is at least 135°C , otherwise it would be difficult to obtain the intact films owing to the rigidity of PEEK molecular chains. In order to avoid the occurrence of the disorientation effect and obtain the PEEK films with high strength as much as possible, 135°C and 210°C were chosen as the stretching temperature of the amorphous and crystalline films, respectively.

Influence of Stretching Ratio (λ_L) on Tensile Strength of PEEK Films

From Figure 1(c,d), it can be found that the tensile strength of PEEK films undergoes a significant enhancement (~ 3 times for amorphous films stretched at $T = 135^\circ\text{C}$ and $v = 2$ mm/min or approximately four times for crystalline films stretched at $T = 210^\circ\text{C}$ and $v = 2$ mm/min), indicating that the increase of the stretching ratio can greatly improve the tensile strength of PEEK films. In comparison with other polymer films with high strength, such as PP, PTT, PTFE, and PET,^{25–28} PEEK films possess a higher strength suitable for the application in certain harsh environments. The difference of the stretching behaviors is that the tensile strength of PEEK films stretched at 135°C presents a first increased ($1 \leq \lambda_L \leq 3$) and then decreased ($\lambda_L = 3.5$) trend with increasing the stretching ratio, whereas the tensile strength of PEEK films stretched at 210°C presents a tendency of the continuous increase ($1 \leq \lambda_L \leq 3.5$). The phenomenon is ascribed that the molecular chains of rigid PEEK stretched at the lower temperature are more likely to break compared with the higher temperature under the premise of a relatively high stretching ratio ($\lambda_L = 3.5$). It is necessary to point out that even the stretching temperature is higher ($T = 210^\circ\text{C}$), if the stretching ratio exceeds 3.5, the molecular chains will reach the limit of their extension, resulting in the

damage of PEEK films. Therefore, the maximum stretching ratio for the amorphous films is 3, while the maximum stretching ratio for the crystalline films is 3.5.

CTE of PEEK films with different stretching ratios are exhibited in Table III. The longitudinal CTE of PEEK films stretched at 135°C first decreases and then increases with increasing the stretching ratio, whereas the transverse CTE of PEEK films stretched at 135°C first increases and then decreases. This means that the orientation of molecular chains first enhances ($1 \leq \lambda_L \leq 3$) and then weakens ($\lambda_L = 3.5$) with the increase of the stretching ratio. The trend well explains the dependence of the tensile strength on the stretching ratio for PEEK films shown in Figure 1(c). The longitudinal CTE of PEEK films stretched at 210°C continuously decreases with increase in the stretching ratio, while the transverse CTE of PEEK films stretched at 210°C gradually increases. This suggests that the orientation of molecular chains progressively strengthens ($1 \leq \lambda_L \leq 3.5$) with the increase of the stretching ratio. The trend well illustrates the dependence of the tensile strength on the stretching ratio for PEEK films presented in Figure 1(d).

In order to observe the orientation, the state of PEEK film produced by melt extrusion before and after stretching was visualized by SEM, as shown in Figure 3. For the original or unstretched film analyzed [Figure 3(a)], no preferential arrangement of molecular chains is found in all examined areas. However, for the stretched films analyzed [Figure (b,c)], whether the stretching temperature is lower or the higher, a large numbers of the preferential arrangement of molecular chains along the stretching direction are observed in all examined areas. This proves that the stretching leads to the occurrence of orientation for PEEK films.

Additionally, WAXD patterns of PEEK films with different stretching ratios at 135°C and 210°C are demonstrated in Figure 4. As revealed by Figure 4(a), there is only a diffused peak for PEEK films with different stretching ratios at 135°C , indicating that the lower stretching temperature promotes the formation of the amorphous PEEK films. As demonstrated by Figure 4(b), there are the three sharp peaks indexed as 110, 200, and 020²⁴ for PEEK films with different stretching ratios at 210°C , hinting that the higher stretching temperature induces the formation of the crystalline PEEK films. Therefore, the improvement in the tensile strength of PEEK films stretched at the lower temperature (below and close to the glass transition temperature of PEEK, $T \leq 155^\circ\text{C}$, $T_g = 143^\circ\text{C}$ ²⁹) origins from the single effect of

Table III. Coefficient of Thermal Expansion and Degree of Crystallization of PEEK Films with Different Stretching Ratios ($v = 2$ mm/min, $T = 135^\circ\text{C}$ and 210°C)

Stretching ratio	Stretched below T_g (135°C) amorphous film		Stretched above T_g (210°C) crystalline film		
	Longitudinal CTE (ppm/k)	Transverse CTE (ppm/k)	Longitudinal CTE (ppm/k)	Transverse CTE (ppm/k)	Degree of crystallization (%)
1.0	66.03	73.94	66.03	73.94	0
2.0	-20.26	109.35	30.71	92.49	28.83
2.5	-23.62	112.54	-0.77	92.57	31.68
3.0	-27.28	123.53	-3.67	110.56	33.10
3.5	-11.21	108.75	-28.70	157.61	36.76

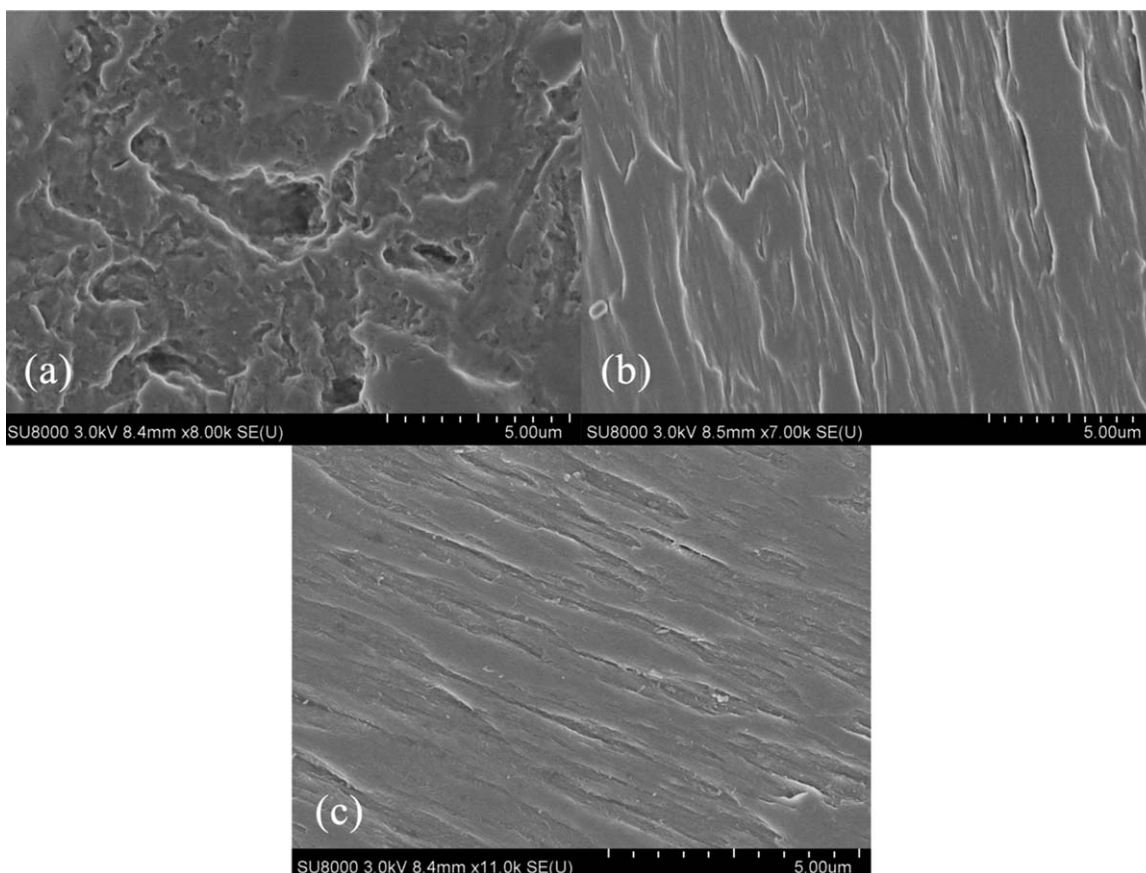


Figure 3. Typical SEM micrographs from the surface of (a) the unstretched film, (b) the stretched PEEK film ($T = 135^{\circ}\text{C}$, $v = 2$ mm/min, $\lambda_L = 3.0$) and (c) the stretched PEEK film ($T = 210^{\circ}\text{C}$, $v = 2$ mm/min, $\lambda_L = 3.0$).

orientation, whereas the enhancement in the tensile strength of PEEK films stretched at the higher temperature (above the glass transition temperature of PEEK, $T \geq 190^{\circ}\text{C}$, $T_g = 143^{\circ}\text{C}$) result from the synergistic effect of orientation and crystallization. Based

on the above reason, if the stretching ratio is the same, the tensile strength of PEEK films stretched at the higher temperature is better than that of PEEK films stretched at the lower temperature. The result is consistent with the data in Figure 2(c,d).

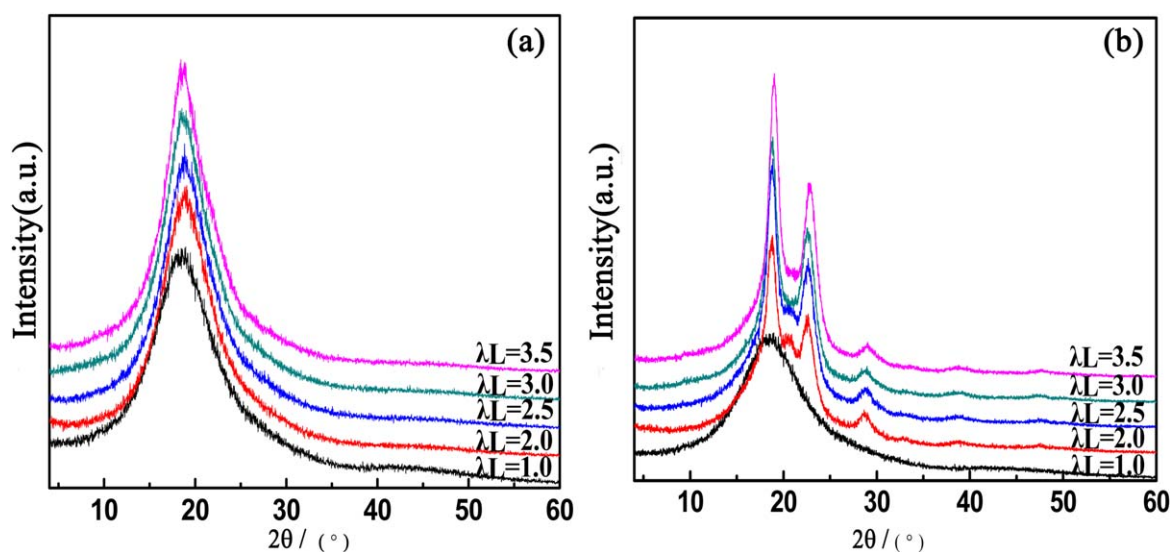


Figure 4. Wide-angle X-ray diffraction patterns of PEEK films with different stretching ratios at 135°C (a) and 210°C (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

From Table III, it can be found that degree of crystallization of the stretched PEEK films slightly increases with the increase of the stretching ratio, and degree of crystallization of all films is less than 37%. In order to evaluate the orientation and crystallization which has a stronger effect on the improvement of the tensile strength of PEEK films, an experiment was carried out. The details were that PEEK film produced by melt extrusion was treated at 280°C for 4 h to obtain the unstretched PEEK film with a higher degree of crystallization (40.83%). It can be found that the tensile strength of the unstretched PEEK film with a higher degree of crystallization (100 MPa) does not show a significant improvement compared with that of the PEEK film produced by melt extrusion (87 MPa). However, the tensile strength of the PEEK film produced by melt extrusion at least increases 70 MPa after the stretching ($v = 2$ mm/min, $\lambda_L = 1.5$, $T = 210^\circ\text{C}$), as shown in Figure 2(d). Therefore, the influence of orientation is stronger than that of the crystallization on the improvement of the tensile strength of PEEK films. In this study, the stretching mode is the longitudinal stretching, rather than first the longitudinal and then the transverse stretching due to the occurrence of the shrinkage phenomenon along the longitudinal direction during the transverse stretching process.

CONCLUSIONS

PEEK films produced by melt extrusion were stretched along the longitudinal direction and the corresponding stretching conditions were optimized. Under the optimized conditions, the experimental results indicated that the tensile strength (230 MPa) of the amorphous PEEK film obtained at the lower stretching temperature ($v = 2$ mm/min, $\lambda_L = 3$, $T = 135^\circ\text{C}$) is almost three times higher than that of the unstretched PEEK film due to a single effect of orientation. Moreover, the tensile strength (333 MPa) of the crystalline PEEK film obtained at the higher stretching temperature ($v = 2$ mm/min, $\lambda_L = 3.5$, $T = 210^\circ\text{C}$) is almost four times higher than that of the unstretched PEEK film owing to a synergistic effect of orientation and crystallization, and the influence of orientation is stronger than that of the crystallization on the improvement of the tensile strength of PEEK films. In summary, how to achieve the adjustment of the structure (orientation and crystallization) of PEEK films by the change of processing parameters (the stretching rate, stretching temperature, and stretching ratio), thereby to achieve the control of the property (tensile strength) of PEEK films, the enhanced understanding of process–structure–property relationships helps to obtain the PEEK films with high strength. For PEEK film obtained through melt extrusion followed by stretching, which possesses the high strength beside the high-temperature resistance, excellent chemical and radiation resistance, superior electrical insulation, and low moisture absorption, is particularly suitable for some of the harsh environments in the aeronautics industry.

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REFERENCES

1. Wang, H. S.; Wang, G. B.; Li, W. L.; Wang, Q. T.; Wei, W.; Jiang, Z. H.; Zhang, S. L. *J. Mater. Chem.* **2012**, *22*, 21232.
2. Zhang, S. L.; Wang, H. S.; Jiang, Z. H.; Wang, G. B. *Appl. Phys. Lett.* **2012**, *101*, 012907.
3. Jonas, A.; Kegras, R. *Polymer* **1991**, *32*, 2691.
4. McGrail, P. T. *Polym. Int.* **1996**, *41*, 103.
5. Cebe, P.; Hong, S. D. *Polymer* **1986**, *27*, 1183.
6. Talbott, M. F.; Springer, G. S.; Berglund, L. A. *J. Compos. Mater.* **1987**, *21*, 1056.
7. Sarasua, J. R.; Remiro, P. M.; Pouyet, J. *J. Mater. Sci.* **1995**, *30*, 3501.
8. Qiao, H. B.; Guo, Q.; Tian, A. G.; Pan, G. L.; Xu, L. B. *Tribol. Int.* **2007**, *40*, 105.
9. Mandal, S.; Alam, S. *J. Appl. Polym. Sci.* **2010**, *117*, 849.
10. Geng, Z.; Zhang, S. L.; Mu, J. X.; Huo, P. F.; Lu, Y. N.; Luan, J. S.; Wang, G. B. *J. Appl. Polym. Sci.* **2013**, *129*, 3219.
11. Ba, J. Y.; Geng, Z.; Mu, J. X. *J. Appl. Polym. Sci.* **2013**, *130*, 193.
12. Lu, Z. P.; Friedrich, K. *Wear* **1995**, *181*, 624.
13. Werner, P.; Altstadt, V.; Jaskulka, P.; Jacobs, O.; Sandler, J. K. W.; Shaffler, M. S. P.; Windle, A. H. *Wear* **2004**, *257*, 1006.
14. Goyal, R. K.; Tiwari, A. N.; Negi, Y. S. *J. Appl. Polym. Sci.* **2012**, *124*, 4612.
15. Ha, S. W.; Hauert, R.; Ernst, K. H.; Wintermantel, E. *Surf. Coat. Tech.* **1997**, *96*, 293.
16. Avanzini, A.; Donzella, G.; Mazzu, A.; Petrogalli, C. *Tribol. Int.* **2013**, *57*, 22.
17. Harrass, M.; Friedrich, K.; Almajid, A. *Tribol. Int.* **2010**, *34*, 635.
18. Murari, A.; Barzon, A. *Vacuum* **2003**, *72*, 327.
19. Arkhireyeva, A.; Hashemi, S. *Eng. Fract. Mech.* **2004**, *71*, 789.
20. Zhao, H. X.; Li, R. K. Y. *Mech. Mater.* **2006**, *38*, 100.
21. Henneuse-Boxus, C.; Dulière, E.; Marchand-Brynaert, J. *Eur. Polym. J.* **2001**, *37*, 9.
22. Daver, F.; Blake, A.; Cakmak, M. *Macromolecules* **2009**, *42*, 2626.
23. Bcakci, S.; Cakmak, M. *Polymer* **2002**, *43*, 149.
24. Karacan, I. *Fiber Polym.* **2005**, *6*, 206.
25. Bedia, E. L.; Murakami, S.; Senoo, K.; Kohjiya, S. *Polymer* **2002**, *43*, 749.
26. Jeong, Y. G.; Bae, W. J.; Jo, W. H. *Polymer* **2005**, *46*, 8297.
27. Morioka, T.; Kakiage, M.; Yamanobe, T.; Komoto, T.; Higuchi, Y.; Kamiya, H.; Arai, K.; Murakami, S.; Uehara, H. *Macromolecules* **2007**, *40*, 9413.
28. Gupta, S.; Dixit, M.; Sharma, K.; Saxena, N. S. *Surf. Coat. Technol.* **2009**, *204*, 661.
29. Pan, G. I.; Guo, Q.; Zhang, W. D.; Tian, A. G. *Wear* **2009**, *266*, 1208.