回火對無定形聚醚醚酮膜的影響

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摘　　要

本文探討回火對無定形聚醚醚酮(PEEK)薄膜的影響。將原為無定形的 PEEK 薄膜回火可得不同結晶度的 PEEK。回火的 PEEK 薄膜以示差掃描熱卡計(DSC)，紫外線-可見光光譜儀及 X 射線繞射儀分析描述之。回火溫度對回火 50 分鐘之後的 PEEK 薄膜的影響很大。因此，在 163℃下將無定形 PEEK 薄膜回火而得不同結晶度的 PEEK 薄膜試片。由 DSC，可見光透過率數據以及 X 射線繞射譜可看出當回火溫度提高或回火時間增長，PEEK 薄膜試片的結晶度有增高的趨勢。DSC 及可見光透過率數據亦顯示在 163℃下回火超過 40-50 分鐘之間，PEEK 薄膜試片有最快的結晶速率。而結晶度對 PEEK 薄膜試片的抗張性質有所影響。

關鍵詞：聚醚醚酮、結晶度、回火、熱性質、透光率。

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Effect of Annealing on an Amorphous Polyetheretherketone Film

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Abstract

The effect of annealing on an amorphous polyetheretherketone (PEEK) film is described in this article. PEEK film samples of different crystallinity were obtained by annealing originally amorphous PEEK films. The annealed PEEK film samples were characterized a differential scanning calorimeter (DSC), ultra-violet(UV)-visible spectrometry and X-ray diffraction. The annealing temperature affected the crystallinity of PEEK film greatly after an annealing time of 50 min. Thus, an annealing temperature of 163℃ was chosen for obtaining PEEK film samples of different crystallinity. It can be seen that as the annealing temperature or time increases, the crystallinity follows an increasing trend. The DSC and light transmittance data show that the crystallization rate seems to reach a maximum around 40-50 min at an annealing temperature of 163℃. Furthermore, the crystllinity affects the tensile properties of the PEEK film significantly.

Keywords: polyetheretherketone, crystallinity, annealing, thermal properties, light transmittance

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1. INTRODUCTION

Polyaryletherketones such as polyetheretherketone (PEEK) and polyetherketoneketone (PEKK), exhibit outstanding heat resistance, mechanical properties and chemical resistance, and are considered as high performance engineering plastics [May, 1988; Clagett, 1987;Brydson, 1982; Schwarts and Goodman, 1982]. Some performance characteristics of the polyaryletherketones are significantly affected by the crystallinity, and various properties and the crystalline properties of the polyaryletherketones have been characterized in the literature [Cebe et al. 1987; Hsiao, 1993; Lu and Capel 1996; Jar and Shanks 1996; Wolf and Fu 1996; Ji et al. 1997; Ke and Wu 1998; Liu et al. 1999; Wang et al. 1999; Fougnies et al. 1999; Clayden 1999; Daly et al. 1999; Ozden et al. 1998; Qiu et al. 2000; Abate et al. 2002; Mamdan and Swallowe 1996].

In this article, amorphous PEEK films were annealed to obtain samples of different crystallinity, and various properties were characterized.

2. EXPERIMENTAL

The amorphous PEEK (450G) film samples of 0.05 mm thickness (obtained from Polymics, Pennsylvania, USA) were annealed by a program controllable HMO PC-900 high temperature oven (Fashing Inc., Taiwan). The chosen annealing temperatures were from 140 to 200℃, and the annealing time internals were from 10 to 1000 min.

The thermal properties of the annealed PEEK films from 100 to 380℃ were determined by a Perkin Elmer DSC 7(differential scanning calorimeter) at a scanning rate of 20℃/min under nitrogen. The UV-visible spectra of the annealed PEEK films were determined by a Hitachi 2001 UV spectrophotometer at a scanning rate of 200nm/min. The X-ray diffraction patterns of annealed PEEK films were recorded by a Mac Science MXP-18 at a scanning rate of 4°/min. The tensile stress-strain data of dumb-bell shaped film specimens were determined by an Instron 4469 Universal Testing Machine at an extension rate of 20 mm/min at 23℃, and the gauge length used was 25 mm.

3. RESULTS AND DISCUSSION

The amorphous PEEK film samples were annealed at temperatures of 140-200℃ for 50 min. Typical UV-visible spectra of the film samples annealed at various temperatures for 50 min are shown in Figure 1. It can be seen that the annealing temperature affect the visible light transmittance significantly. Since the loss of the visible light transmittance is mainly due to the light scattering of the crystallites, the crystallinity of the film samples would follow an increasing trend as the annealing temperature increases after annealing for 50 min, as expected. As the annealing temperature is 150℃ (or below), there is no significant change in transmittance as compared to the un-annealed PEEK film. As the annealing temperature is 170℃ (or above), the film samples lose transmittance greatly in the visible region due to crystallization. The depress in visible light transmittance is only slight after annealing at 160℃ for 50 min. Thus an annealing temperature of 163℃ was chosen for obtaining PEEK film samples of different crystallinity.

The UV-visible spectra of the PEEK film samples annealed at 163℃ for various time intervals are shown in Figure 2. It can be seen that the transmittance in the visible region follows a decreasing trend as the annealing time increases, indicating that the crystallinity increases with annealing time, as expected. Taking the change rate of the transmittance for comparison, the crystallization rate seems to reach a maximum around 40-50 min at an annealing temperature of 163℃.

Typical first run DSC heating of the annealed PEEK film samples are shown in

Figure 3. The thermal properties are summarized in Table 1.

Table 1. Thermal properties of annealed PET sheets.

Annealing temperature	Annealing time	T_g (℃)	T_{cc} (℃)	ΔH_{cc} (J/g)	T_m (℃)	ΔH_m (J/g)
140℃	50 min	143	177	-35.8	338	35.6
160℃	50 min	144	176	-36.0	339	34.6
170℃	50 min	156	188-	-2.8	338	34.6
180℃	50 min	---	---	---	340	34.7
200℃	50 min	---	---	---	240	35.0
163℃	10 min	142	175	-35.2	339	34.3
163℃	20 min	144	175	-34.5	340	35.0
163℃	30 min	143	175	-32.7	340	33.7
163℃	40 min	147	178	-32.7	347	33.9
163℃	50 min	156	175	-15.1	338	34.3
163℃	100 min	156	182	-8.3	337	36.1
163℃	200 min	161	184	-4.8	339	34.9
163℃	500 min	161	185	-4.2	338	34.5
163℃	1000 min	163	187	-3.0	339	33.9

Within the annealing temperature range of 100 to 380℃, the first run DSC heating curve of unannealed PEEK sample exhibit a step inflection corresponding to the glass transition, an exotherm corresponding to cold crystallization and an endotherm corresponding to melting. The mid-point of the step inflection is taken as the glass transition temperature (T_g), the peak temperature of the endotherm is taken as the cold crystallization temperature (T_{cc}), and the peak temperature of endotherm is taken as the melting point(T_m).

As the annealing temperature is 160℃ or below, the peak area of T_{cc} is close to that of T_m, indicating that these PEEK film sample would be almost amorphous. The peak area of T_{cc} decrease drastically for the PEEK film sample annealed at 170℃ for 50 min, indicating that the sample exhibit rather high crystallinity. For the PEEK film samples annealed at 163℃, as the annealing time increases, the area of the T_{cc} decreases. It can be seen from Table 1 that the crystallinity follows an increasing trend as the annealing temperature is raised for 50 min of annealing or as the annealing time increases at 163℃, as expected. The trend of the crystallinity obtained from DSC data is consistent with the UV/visible data.

Typical X-ray diffraction patterns of the PEEK film samples annealed at different temperatures for 50 min are shown in Figure 4. As the annealing temperature is 160℃ or below, the film samples show no explicit diffraction peak. There is only a broad peak due to amorphous scattering. As the annealing temperature is from 170 to 200℃, the film samples show some explicit diffraction peak. For the sample annealed at 200℃ for 50 min, the diffraction peaks are at d spacings of 0.314, 0.398, 0.435 and 0.478 nm. The data are consistent with those described in the literature. Typical X-ray diffraction patterns of the PEEK film samples annealed at 163℃ for different time intervals are shown in Figure 6. As the annealing time is 40 min or shorter, the film samples show only a broad peak due to amorphous scattering. Interesting is that some film samples are partially crystalline, but no obvious diffraction peak has been detected. One possible reason is that the crystalline phase cannot behave continuously for these samples. It can be seen from Figure 6 that the wide angle X-ray diffraction analysis has limit signal to noise ratio, and some discrete crystalline domains might not be seen by the instrument. As the annealing time is 50 min or longer, the film samples can display diffraction peaks. As the annealing time increases, some diffraction peaks tend to become sharper and sharper, indicating the crystallinity increases accordingly. The trend is consistent with the visible light transmittance and DSC data.

Typical tensile stress vs. strain curves of the annealed PEEK film samples are shown in Figure 6. All the film samples exhibit yield behavior, and rather high elongation at break. The tensile properties are summarized in Table 2. It can be seen that the annealing condition, thus the crystallinity, affects the tensile properties to some extent. As the crystallinity increases, the initial tensile modulus and the yield strength follow an increasing trend, as expected. Although the tensile strength tends to increase with the crystallinity, there is another factor, namely the elongation at break affects the measured tensile strength. Higher elongation at break tends to let the film samples exhibit higher tensile strength. Interesting is that the increase in the crystallinity doesn't lower the elongation at break. In fact, all the film samples exhibit rather high elongation at break, and some film samples with higher crystallinity even exhibit higher elongation at break as show in Table 2. One possible explanation is that the test temperature (23℃) is below the glass transition temperature, and the presence of the crystallite toughens the materials. This means the reasonable increase in the crystallinity wouldn't sacrifice the toughness of the PEEK film.

Table 2. Tensile properties of the annealed PEEK films

Annealing temperature	Annealing time	Tensile modulus (GPa)	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)
140℃	50 min	2.2	75	76	130
150℃	50 min	2.2	75	80	130
160℃	50 min	2.3	71	80	150
180℃	50 min	2.7	95	85	140
200℃	50 min	2.6	90	90	180
163℃	10 min	2.2	75	76	130
163℃	20 min	2.2	69	79	140
163℃	30 min	2.2	70	80	130
163℃	40 min	2.3	71	80	150
163℃	50 min	2.3	75	86	140
163℃	100 min	2.6	87	84	150
163℃	200 min	2.5	85	95	170
163℃	500 min	2.6	86	98	170
163℃	1000 min	2.6	85	95	160

4. CONCLUSION

An annealing temperature of 163℃ has been chosen for obtaining PEEK film samples of different crystallinity. It can be seem that as the annealing temperature or time increases, the crystallinity follows an increasing trend. The DSC and light transmittance data show that the crystallinity after 50 min of annealing is much higher than that before 40 min of annealing at 163℃. Thus, the crystallization rate seems to reach a maximum around 40-50 min at an annealing temperature of 163℃.

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Figure Captions

Figure 1. Typical UV/visible spectra of the PEEK film samples annealed at various temperatures for 50 min.

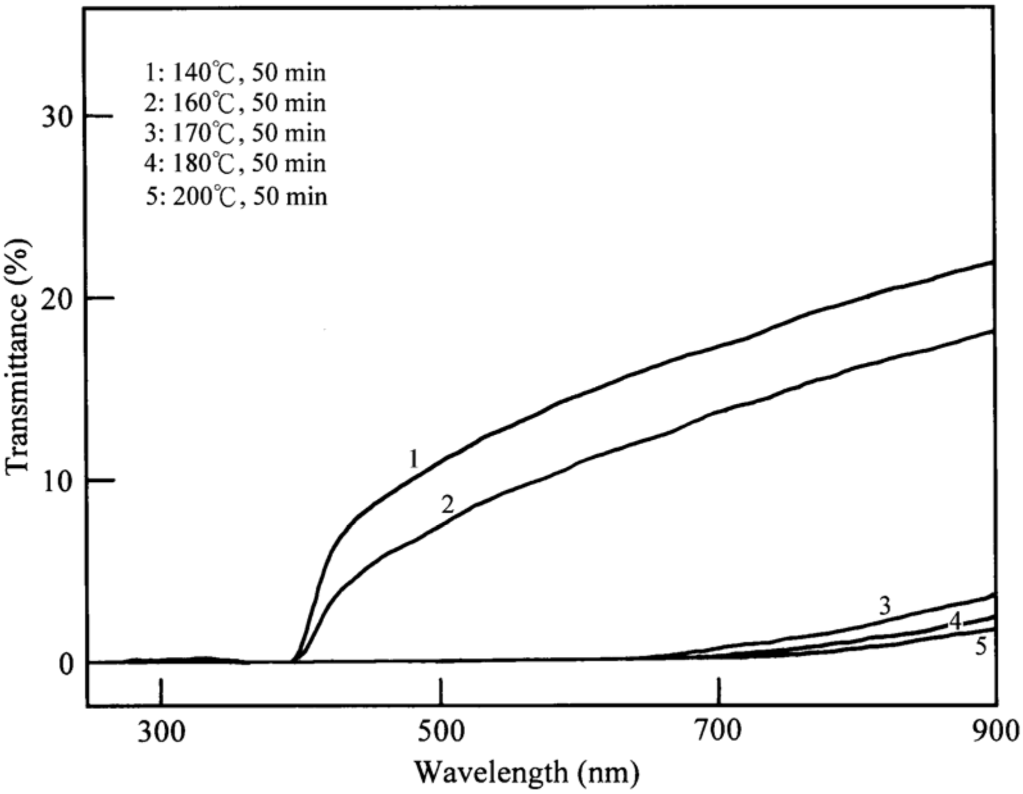
Figure 2. UV/visible spectra of the PEEK film samples annealed at 163℃ for various time intervals.

Figure 3. Typical first run DSC heating curves of annealed PEEK film samples.

Figure 4. Typical X-ray diffraction patterns of the PEEK film samples annealed at various temperatures for 50 min.

Figure 5. Typical X-ray diffraction patterns of the PEEK film samples annealed at 1630℃ for various time intervals.

Figure 6. Typical tensile stress vs. strain curves of annealed PEEK film samples.



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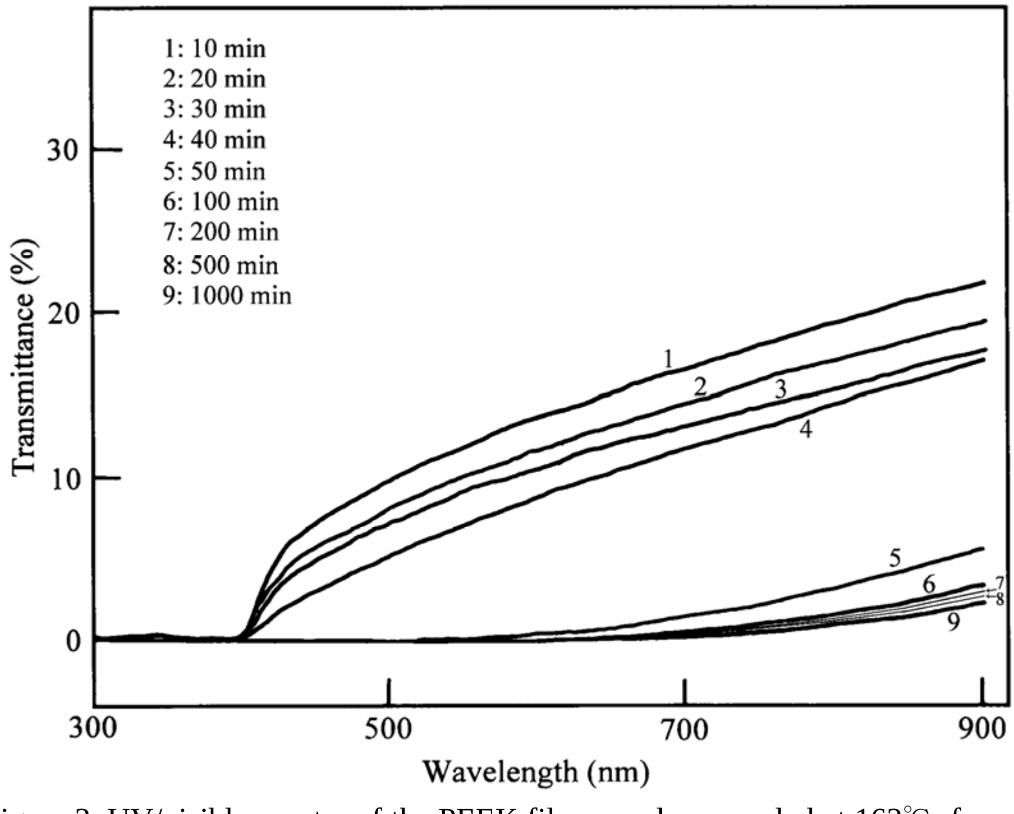
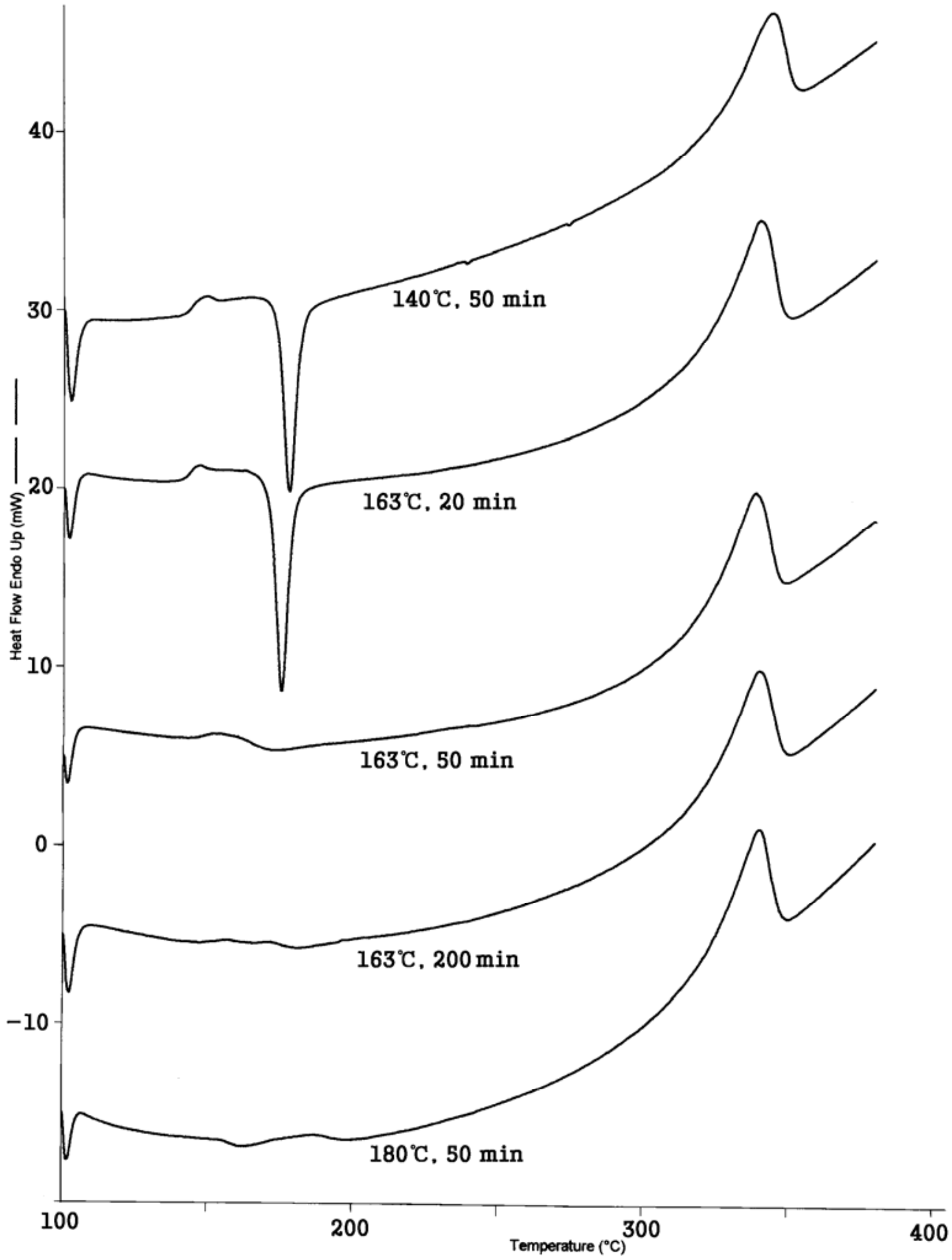


Figure 2. UV/visible spectra of the PEEK film samples annealed at 163℃ for various time intervals.



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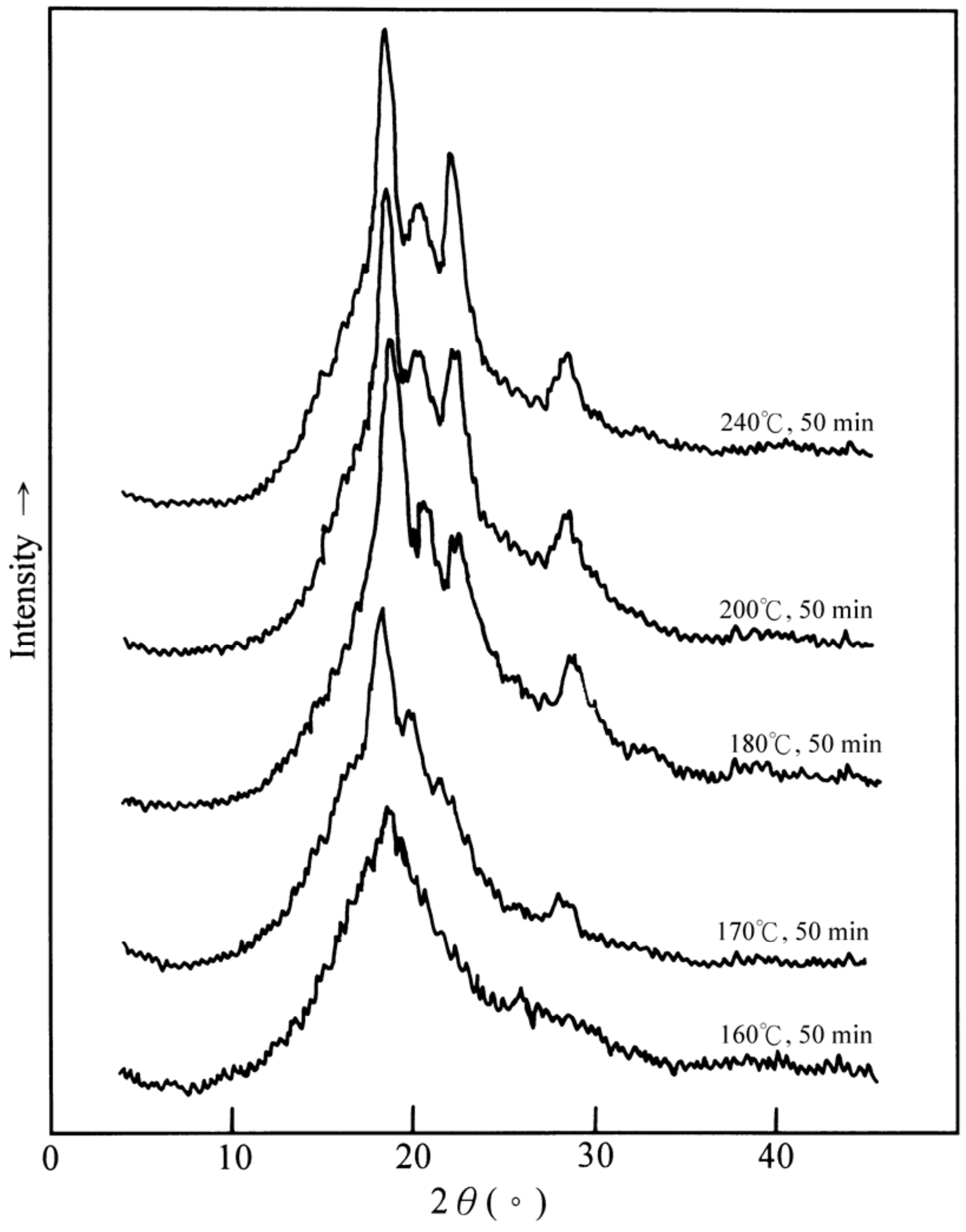


Figure 4. Typical X-ray diffraction patterns of the PEEK film samples annealed at various temperatures for 50 min.

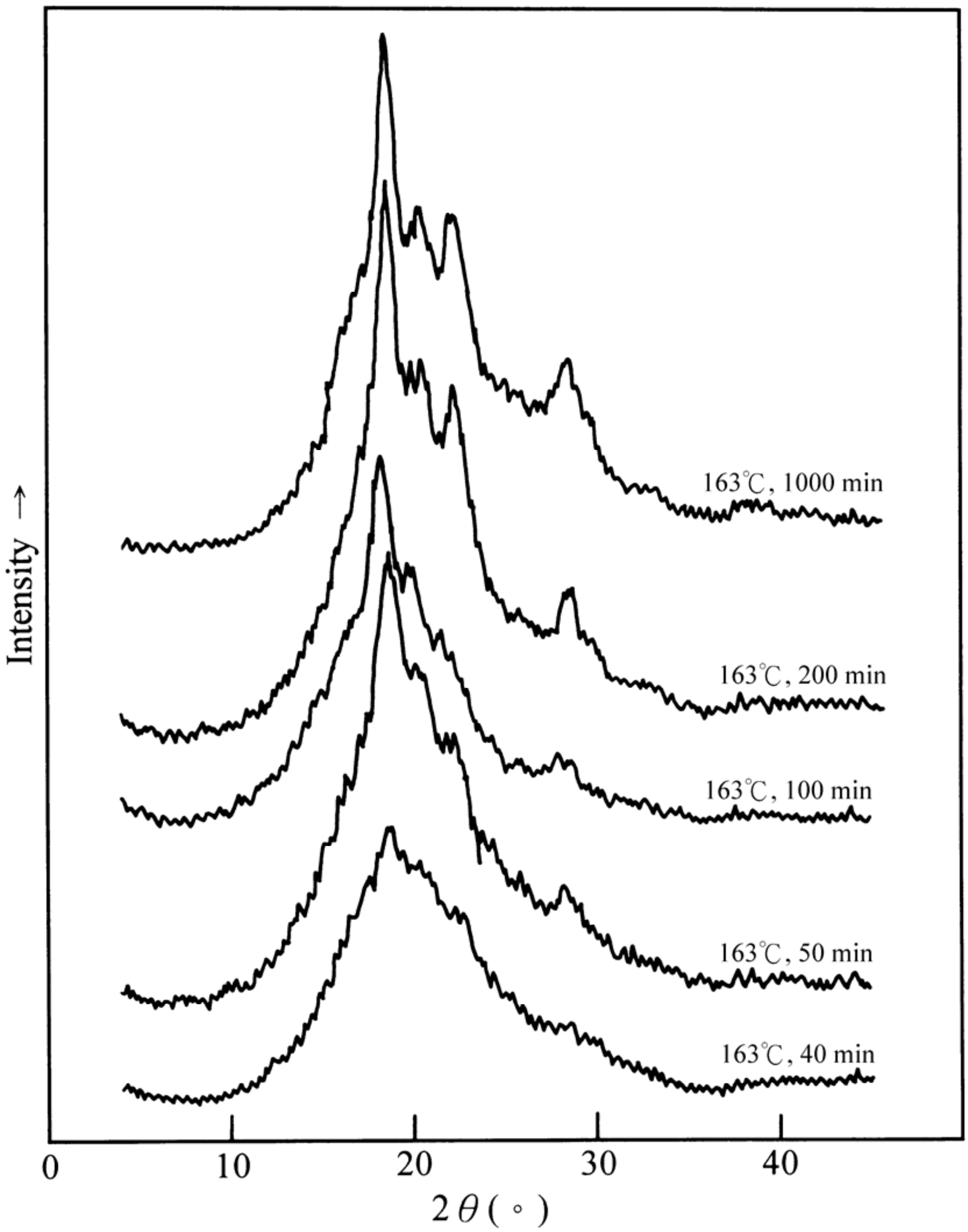
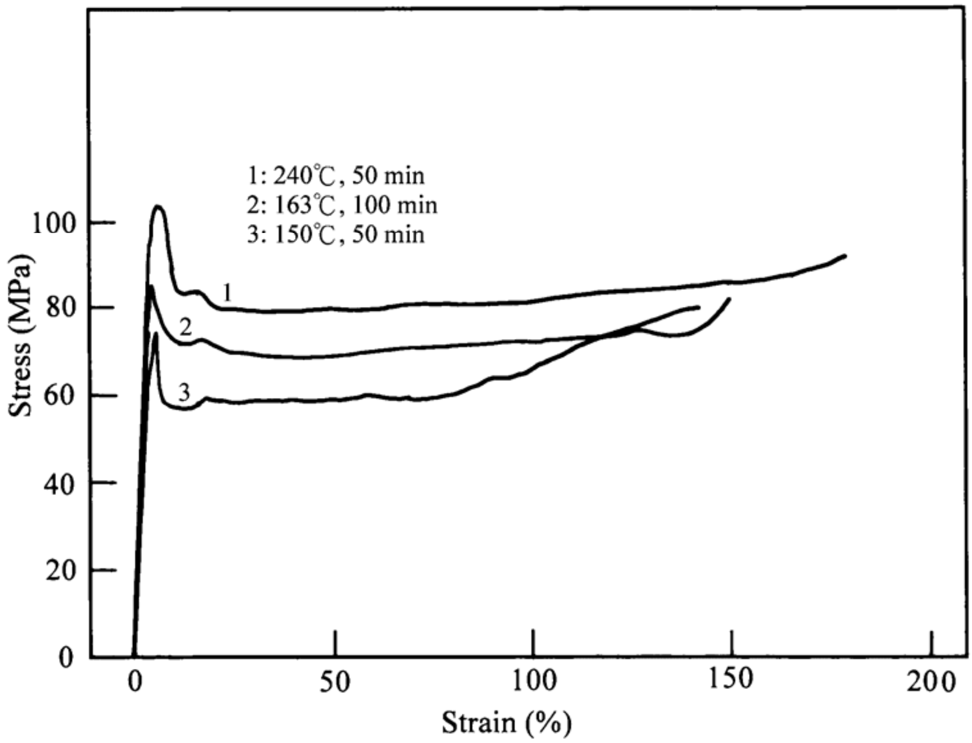


Figure 5. Typical X-ray diffraction patterns of the PEEK film samples annealed at 1630℃ for various time intervals.



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