Effects of thermal treatment on poly(ether ether ketone)

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The effects on poly(ether ether ketone) (PEEK) of thermal treatment in a particular temperature range in air have been studied. When PEEK is annealed in a partially melted state at a very high temperature, above its original melting point, both crosslinking and crystallization occur. The crosslinking takes place in the melted part in this case, while the crystallization occurs on the surface of the unmelted crystal residues. They lead to the characteristic double-melting peaks of PEEK, representing two distinct crystals. The low-temperature peak arises from the crystals formed during cooling after the treatment, and the higher peak is associated with crystals thickened in the process of annealing. With increasing the annealing time, the low-temperature peak decreases due to the variation in crosslinking of the melted part of PEEK, while the high-temperature peak, which is usually above 350°C, increases and may exceed the equilibrium melting point of PEEK if the annealing time is long enough.

(Keywords: poly(ether ether ketone); thermal treatment; crystallization; crosslinking; melting behaviour)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a high-temperature, high-strength aromatic thermoplastic which is currently attracting interest because of its useful engineering properties[1,2]. As a semicrystalline polymer, whose properties depend on its crystalline structure, PEEK has received detailed study with regard to the effects of thermal treatment. It was revealed that PEEK could crystallize from its melting state or amorphous glass state when treated at a temperature below its original melting point, and the crystallization which would affect the melting behaviour of PEEK depended on the thermal history and the conditions of thermal treatment[3–7]. As found for several other polymers, such as poly(ethylene terephthalate) (PET), double-melting peaks affected by the treatment were found in PEEK. The peaks have been proposed to be related to a melting and recrystallization phenomenon of one initial crystal morphology, which is characteristic of the prior crystallization history[3,8,9], or to be associated with distinct morphologies or crystals[6,10,11].

When PEEK is treated at a temperature just above its original melting point, self-seeding crystallization may occur. Bassett *et al.*[11] have reported that a sharp high-temperature peak, which is related to well-composed lamellae, appeared when PEEK was annealed at 340°C. It was found in our work, that the annealing effects in the temperature range 340–350°C were very complicated. After the treatment, PEEK shows double-melting peaks which represent two distinct crystals, and one of the two melting peak temperatures may surpass the equilibrium melting point of PEEK. In this paper, a detailed study will be given.

EXPERIMENTAL

PEEK powder (grade 450P, ICI) was used in this work. Specimens for thermal analysis were prepared in the following way: PEEK powder was placed in an aluminium pan and heated at 20°C min^{-1} in a CDR-1 d.s.c. to a certain temperature, which had been calibrated with tin and zinc. It was then annealed in air at that temperature for a specific time followed by cooling naturally to room temperature. Specimens for wide-angle X-ray scattering (WAXS) analysis were obtained by annealing the cold-pressed plate of PEEK powder in an oven in air and then cooling naturally to room temperature.

A Perkin–Elmer DSC-2 was used to analyse the thermal behaviour of the specimen, with a 10°C min^{-1} heating rate or a -10°C min^{-1} cooling rate being selected in all analysing experiments unless otherwise indicated. Melting points and heats of fusion were calibrated initially by scanning indium and lead at the same rate. Nitrogen atmosphere was used to protect the specimen in the analysis. WAXS examination of the specimen was carried out in a Rigraky Giggefex vertical diffractometer in the transmission mode at 40 kV and 30 mA.

RESULTS AND DISCUSSION

Figure 1 shows the d.s.c. traces of PEEK powder and the thermally treated specimens. The specimens were obtained by annealing PEEK powder in air at 332, 337, 342 or 347°C for 4 h. PEEK shows a sharp melting peak only when the annealing temperature T_a is lower than its original melting point T_{m_0} (340°C), but double-melting peaks when T_a is higher than T_{m_0}. The single sharp peak

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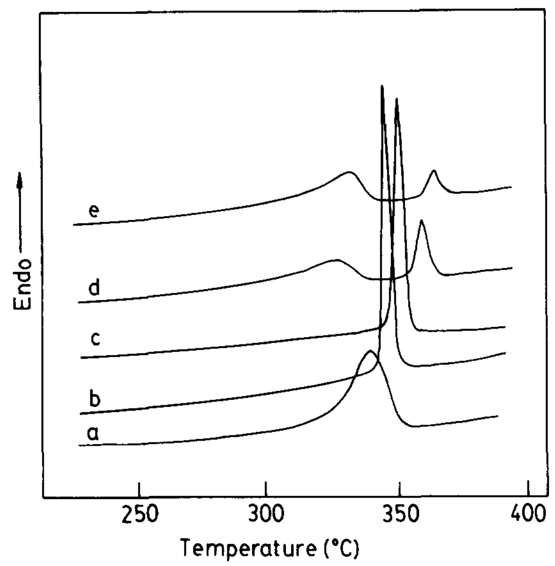

Figure 1 Melting endotherms of PEEK annealed at different temperatures. Scanning rate 10°C min^{-1}. (a) PEEK powder. Samples annealed in air for 4 h at: (b) 332°C; (c) 337°C; (d) 342°C; (e) 347°C

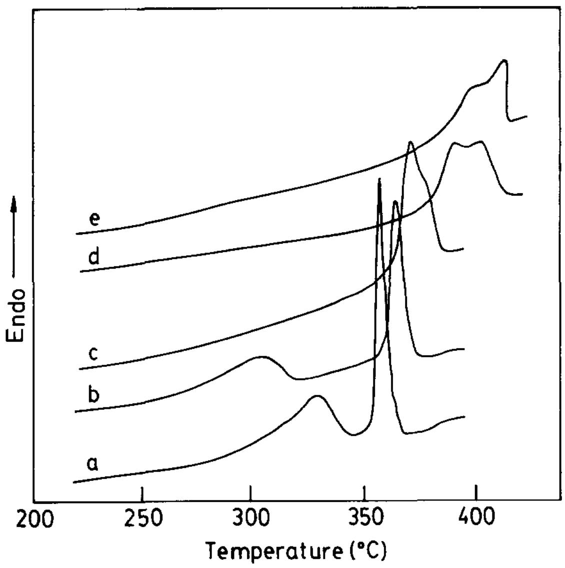

Figure 2 Melting endotherms of PEEK annealed at 342°C for different times. Scanned at 10°C. Samples annealed in air for: (a) 3 h; (b) 7 h; (c) 20 h; (d) 46 h; (e) 72 h

arises from the crystal perfection in the treatment, and the double peaks are thought to be due to a complicated structure variation. By comparison with the melting behaviour of PEEK reported previously, a distinction is made between the double peaks with those obtained by annealing PEEK at a temperature below T_{m_0}. The lower peak temperature of the former is in the range 280–345°C, and the higher peak is over 350°C, while the lower and higher peak temperatures of the latter are in the range 210–330°C and 334–350°C, respectively[5,8]. It is therefore known that PEEK is characterized by a new and special double-melting behaviour when it is annealed at very high temperature above its T_{m_0} in air.

The double-melting behaviour depends on the annealing time and annealing temperature as shown in *Figure 2* and *Table 1*. With increasing time, the peak temperature T_{m_1} and heat of fusion ΔH_{f_1} of the low-temperature melting peak decrease until the peak disappears, while T_{m_2} and ΔH_{f_2} of the high-temperature peak continue to increase. The existing higher peak divides further into two peaks ($T_{m_{21}}$ and $T_{m_{22}}$) when the annealing time is long enough. If the annealing temperature is raised, T_{m_1}, ΔH_{f_1} and T_{m_2} rise while ΔH_{f_2} falls. It was also noted that PEEK only showed the low-temperature peak when it was annealed at 352°C.

Figure 3 and *Table 2* show the results of scanning the specimens at different rates. T_{m_1} decreases but T_{m_2} increases at higher scanning rates, in contrast to the well-known polymeric double-melting behaviour corresponding to crystal reorganization. In the case of reorganization occurring, the peak temperature of the low-temperature endotherm increases with increased scanning rate due to non-equilibrium of the original crystals, while the peak temperature of the high-temperature endotherm decreases as a result of decreased size and perfection of the recrystallized crystals[12–15]. When PEEK is treated at a temperature below its original

Table 1 Melting data of annealed PEEK

Annealing temperature (°C)	Annealing time (h)	Low-temperature peak		High-temperature peak	
		T_{m_1} (°C)	ΔH_{f_1} (J g^{-1})	T_{m_2} (°C)	ΔH_{f_2} (J g^{-1})
342	1	338.6	22.6	357.8	11.3
	3	330.7	19.2	359.0	13.4
	5	321.7	15.9	362.9	15.0
	7	304.8	10.9	365.7	17.1
	10	288.4	5.4	369.4	18.0
	20	–	–	373.4	19.2
	46	–	–	393.3, 404.8	21.2
	72	–	–	403.6, 416.6	22.1
347	1	354.4	33.4	363.6	1.7
	3	341.3	30.9	364.5	2.9
	5	336.5	27.6	365.6	3.8
	7	321.5	22.2	368.6	4.6
	10	308.6	16.3	370.7	5.4

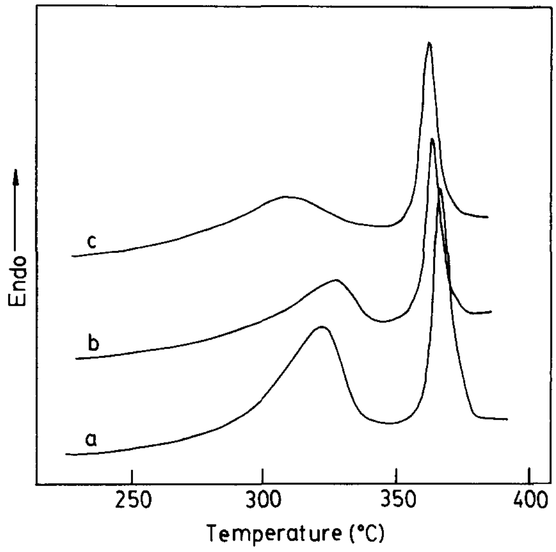

Figure 3 Effects of scanning rate and thermal history on the melting endotherm of PEEK annealed in air at 342°C for 5 h. Scanning rate: (a) 40°C min^{-1}; (b) 10°C min^{-1}; (c) second run at 10°C min^{-1} after scanning at 10°C min^{-1} to 345°C and then cooling at −160°C min^{-1} to room temperature

Table 2 Melting peak temperature at different scanning rates for PEEK annealed at 342°C for 5 h

Scanning rate (°C min^{-1})	T_{m_1} (°C)	T_{m_2} (°C)
10	321.7	362.9
40	314.4	368.1
80	310.5	370.8

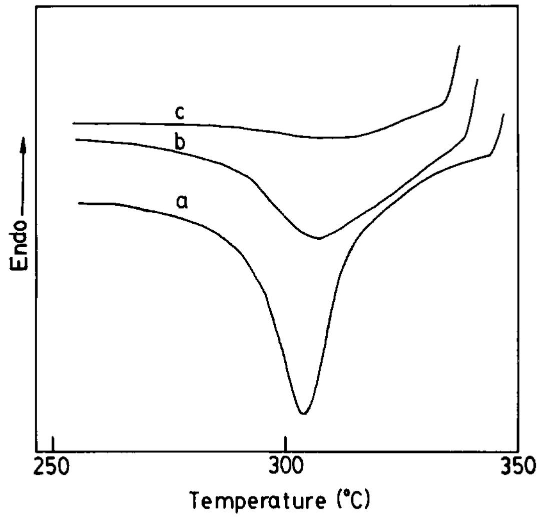

Figure 4 Melt crystallization of PEEK during cooling from different temperatures. Scanning rate −10°C min^{-1}. PEEK was held for 1 min at (a) 347°C; (b) 342°C; (c) 337°C

melting point, the behaviour of the obtained double-melting peaks has been found to be similar to this and the same explanation has been given by Lee and Porter[8] and Blundell[9]. It is thus believed that the two melting peaks seen in this experiment represent two morphologically different crystals or lamellar species. This was confirmed by changing the scanning schedule. When scanning is stopped at a temperature T_s between these two peaks, namely 345°C in *Figure 3b*, whereafter the specimen is cooled quickly and rescanned at the same rate, the lower peak moves to a lower temperature and broadens, while the higher peak remains unchanged (*Figure 3c*). Since the low-temperature peak will move to higher temperature and exceed T_s in the case of crystal reorganization occurring[8], it is impossible that the high-temperature peak of the annealed PEEK, shown in this work, is related to the melting and recrystallization of the initially formed crystals.

The low-temperature peak of the double peaks of PEEK represents the crystals formed in the process of cooling after annealing is finished. By using d.s.c., it is known that a large amount of PEEK is melted and a small part is unmelted when it is annealed at a temperature above its original melting point. A simple example is that the melted PEEK makes up 70.2% when PEEK is heated in d.s.c. at 10°C min^{-1} to 342°C, and 91.2% when heated to 347°C. Most of the melted PEEK will remain uncrystallized during annealing but crystallizes when it is cooled after the treatment. The crystallization of this part of PEEK during cooling can be detected with d.s.c. *Figure 4* shows the results for PEEK cooled at −10°C min^{-1} from different temperatures, at which it had been held for 1 min in nitrogen. The result, that the exothermic heat of crystallization increases when the annealing temperature is increased, indicates the increased content of melted PEEK in this case. This is in agreement with the temperature-dependent results of the heat of fusion ΔH_{f_1} of the low-temperature peak (seen in *Table 1*).

In the sample preparation, the melt crystallization of the melted part of PEEK was observed when PEEK was cooled in d.s.c. after annealing. If PEEK is quenched when the treatment is finished and then scanned in d.s.c., a cold crystallization will be seen, which is affected by the annealing. As observed in *Figure 5*, the quenched PEEK shows an exothermic peak which moves to higher temperature with increasing the annealing time and will disappear if the time is long enough. The cold crystallization arises from the amorphous PEEK formed from the melted part during quenching. The rise in the peak temperature and fall in the exothermic heat indicate that crystallization has been hindered after annealing. These results are consistent with the melting results of the low-temperature peak. As shown in *Table 1*, T_{m_1} and ΔH_{f_1} decrease with annealing time. Also, the low-temperature melting peak will disappear if the melt crystallization of the annealed PEEK during cooling or its cold crystallization during heating cannot be observed. It is suggested that partial crosslinking has occurred in the melted part of PEEK during annealing, because crosslinking may hinder the crystallization of PEEK and cause such an increase of crystallization temperature and such decreases of crystallization heat, melting temperature and heat of fusion[16,17]. Crosslinking was further confirmed by the fact that the annealed PEEK could only be partially dissolved in 98% sulfuric acid, in which untreated PEEK dissolves completely.

It is interesting that T_{m_1} increases when the annealing temperature is increased (shown in *Table 1*), in contrast to the melting behaviour of PEEK reported by Day *et al.*[18]. They found that the single-melting peak temperature of PEEK was lowered with increased temperature when PEEK was treated in the range 380–420°C in air. Since PEEK is partially melted below 350°C and thoroughly melted above 380°C, the conditions in our experiments are different from those of Day *et al.* We think our result is related to the extent of

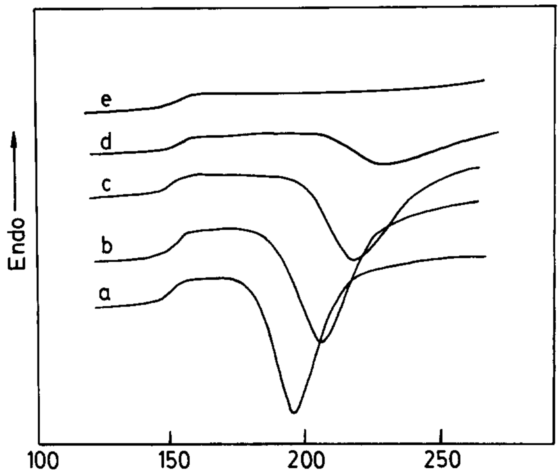

Figure 5 Cold crystallization of the annealed PEEK. Scanning rate 10°C min^{-1}. PEEK was quenched after annealing at 342°C for: (a) 1 h; (b) 3 h; (c) 5 h; (d) 7 h; (e) 20 h

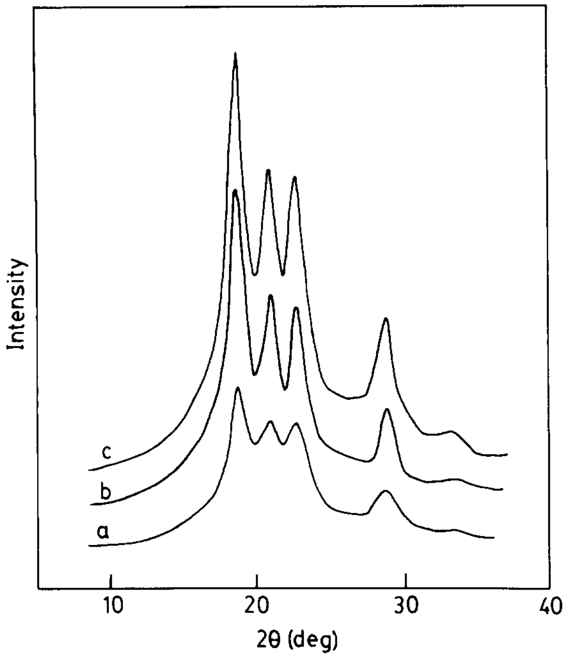

Figure 6 WAXS of PEEK. PEEK was quenched after annealing in air at 344°C for: (a) 20 h; (b) 7 h; (c) PEEK powder

contact of PEEK with air, the presence of which is very important for the crosslinking of PEEK[16,17]. It was observed that the obtained PEEK remained granulated when the annealing temperature was 342°C, but agglomerated when the temperature was 347°C. It is suggested that more air is in contact with PEEK in the process of annealing at 342°C, causing a higher degree of crosslinking in the melted part. The influence of air on the crosslinking of PEEK was emphasized by treating PEEK in nitrogen. For example, a T_{m_1} of 337.9°C was obtained when PEEK was annealed at 342°C in nitrogen for 3 h. This is higher than the T_{m_1} value when PEEK is treated at the same temperature for the same time but in air (found in *Table 1*).

The high-temperature melting peak corresponds to the crystalline structure established when PEEK is annealed. The crystallization onto the unmelted part of PEEK is suggested to be responsible for the structure formation. This was proved by the fact that such a melting peak appeared when PEEK was scanned directly in d.s.c. immediately after being annealed. Also, as seen in *Figure 2* and *Table 1*, T_{m_2} and ΔH_{f_2} increase with increasing the annealing time, indicating the increase in thickness of the lamellae during the treatment. A similar increase in the melting point was found in polyethylene, and self-seeding crystallization was considered to be the cause[19]. It has been mentioned that the T_{m_2} value is over 350°C, i.e. higher than the original melting point of PEEK, and the extraordinary phenomenon is that T_{m_2} may surpass the equilibrium melting point of PEEK. For instance, $T_{m_{21}}$ is 403.6°C and $T_{m_{22}}$ is 416.6°C when PEEK is annealed at 342°C for 72 h. But the equilibrium melting point is 395°C, as obtained by Blundell and Osborn[3], and 389°C according to Lee and Porter[8].

To investigate the reason for such high values of T_{m_2}, WAXS was used to analyse the crystal structure. It was found that the treatment could affect the crystallinity of PEEK but not its crystal unit cell. As shown in *Figure 6*, the intensities of the annealed PEEK, of which sample A (*Figure 6a*) shows only the high-temperature peak in d.s.c. and sample B (*Figure 6b*) shows double peaks, are lower than those of untreated PEEK (*Figure 6a*), while their scattering angles are the same as those of the latter. Therefore, there is no possibility that the unusually high T_{m_2} value is caused by the change of the unit cell dimensions of PEEK. Besides, other factors that may influence the melting point of a polymer, such as lamellar thickness, heat of fusion and surface free energy, cannot be used to explain the unusually high T_{m_2} value either. According to the Thomso–Gibbs equation[20], any polymeric melting point is lower than its equilibrium melting point because the thickness of any real lamella is always finite. It is thought that two possible cases might be responsible for the result. The first is related to the chain structure from the lamellae[21]. It is known, on the basis of the discussion given later, that crosslinking has occurred in the chains from the obtained lamellae. The crosslinking structure might hinder the motion of the chains on the lamellar surface, and therefore hinder the melting of the lamellae, because melting begins on the surface[8]. Another possibility might be associated with the known value of the equilibrium melting point of PEEK. Since the value is extrapolated, and any small experimental error may result in a great difference, the obtained value, whether 395°C or 389°C, might be lower than the real one.

Following the above discussion, which shows the occurrence of crosslinking and crystallization of PEEK at the same time when PEEK is annealed in air at a temperature above its original melting point, the recrystallization behaviour of the annealed PEEK was studied. *Figure 7* shows the d.s.c. curves of the annealed PEEK during cooling after melting at 430°C for 5 min in nitrogen, while *Figure 8* is the result of rescanning the samples. Only one exothermic peak could be seen when the samples were cooled, and one endothermic peak when they were rescanned. It is suggested that all the molecules are involved in crosslinking, because there should be two crystallization peaks or two melting peaks if some molecules do not crosslink while others crosslink deeply. This is confirmed by the result that double-crystallization

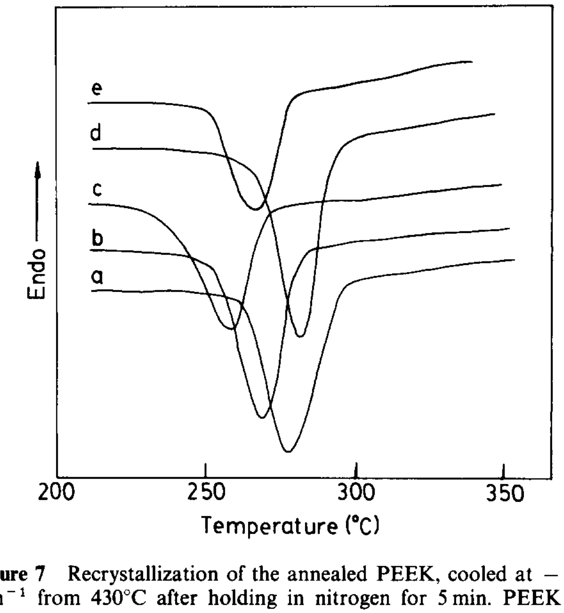

Figure 7 Recrystallization of the annealed PEEK, cooled at −10°C min^{-1} from 430°C after holding in nitrogen for 5 min. PEEK was annealed once at 342°C for: (a) 1 h; (b) 3 h; (c) 5 h; and at 347°C for (d) 1 h; (e) 5 h

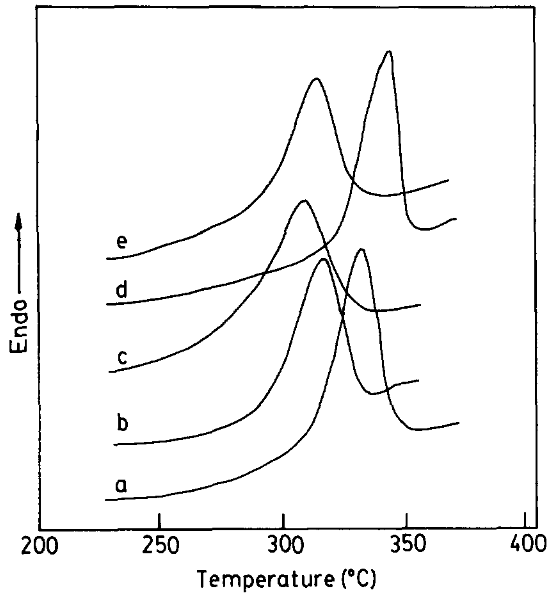

Figure 8 Melting endotherms of the annealed PEEK, scanned at 10°C min^{-1} after holding at 430°C in nitrogen for 5 min and then cooling at -10°C min^{-1}. PEEK was annealed at 342°C for: (a) 1 h; (b) 3 h; (c) 5 h; and at 347°C for: (d) 1 h; (e) 5 h

peaks and double-melting peaks were observed in blends of uncrosslinked PEEK with crosslinked PEEK. The reason is that crosslinking has a great influence on the crystallization and melting behaviour of PEEK[16]. So crosslinking should take place in the molecules that are all in the melt state and those that are partially in the melt state. For the latter, crosslinking is supposed to include their chain folds, chain ends and chain ties from the remaining lamellae, based on the well-known model of lamellae with irregular folding of molecule chains[22]. In this situation, the recrystallization and remelting characteristics of the annealed PEEK are reasonably similar to those of the in-air melt-treated PEEK as reported previously[16,17].

In earlier publications, the lamellar structure of PEEK was reported in detail[5,23,24]. Due to the metastability of the crystal surfaces, melting and crystallization occur on them[8]. Since T_{m_2} and ΔH_{f_2} increase when PEEK is annealed at a temperature above its original melting point, it is considered that crystallization takes place at the surface of the remaining lamellae, and crosslinking should occur further away from the lamellae due to their restriction on the chains. From this consideration, a model, shown in *Figure 9*, is proposed to explain the experimental results. In this model, two regions are distinguished in the melted part: that near the surface of the remaining lamellae is called the crystallization region, and the other, further away, is called the crosslinking region. When PEEK is annealed in air at a temperature in this special range, both crystallization and crosslinking occur.

CONCLUSION

PEEK shows special double-melting peaks which represent two distinct crystals when it is annealed in air in a partially melted state at a temperature above its original melting point. The low-temperature peak arises from the crystals formed during cooling after the treatment. It is affected by the crosslinking that occurs during annealing and depends on the annealing time and temperature. The high-temperature peak is associated with the crystals whose thickness is increased in the process. Its peak temperature, usually over 350°C, may surpass the equilibrium melting point of PEEK obtained by Blundell and Osborn[3] and Lee and Porter[8]. The occurrence of both crystallization at the surface of the remaining lamellae and crosslinking further away from the lamellae when PEEK is annealed, is considered to be the reason for the special melting behaviour.

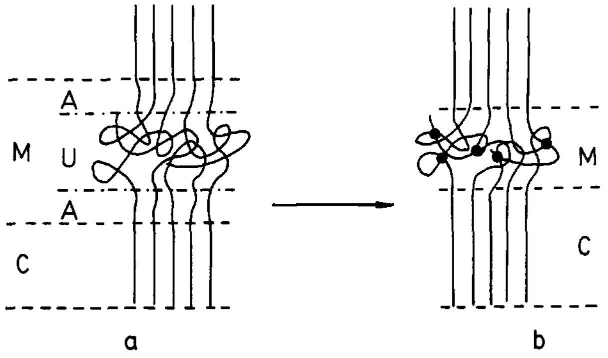

Figure 9 Structural model of PEEK during annealing above its original melting point: (a) at the beginning; (b) some time later. M, melting region; U, region in which crosslinking occurs; A, region in which crystallization occurs; C, crystalline region

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