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Study on the thermal degradation of high performance fibers by TG/FTIR and Py-GC/MS

Guang Ming Cai · Wei Dong Yu

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Abstract The thermal degradation behaviors of Kevlar 49, Kevlar 129 (Poly(*p*-phenylene terephthamide), Nomex (polyisophthaloyl metaphenylene diamine), and PBO (poly(*p*-phenylene benzobisoxazole)) fibers were measured by TG/FTIR and Py-GC/MS. The characteristic temperatures of the fibers in air were obtained by TG. It indicated that the initial degradation temperature of the PBO is the highest. The initial degradation temperature of Nomex fiber is the lowest, but the end decomposition temperature of Nomex is the highest. The gases released by the pyrolysis in air were mainly CO_2, CO, H_2O, NO, and HCN, also containing a small amount of NH_3, and the absorption peaks of CO_2 were the strongest. The results of Py-GC/MS showed that CO_2 and benzene were the most pyrolysis fragment. With the change of pyrolysis temperature, the chromatogram and mass spectra results take a large variety. The pyrolysates can help us to study the pyrolysis process of high performance fibers.

Keywords High performance fiber · Thermal degradation · Pyrolysis · TG/FTIR · Py-GC/MS

G. M. Cai (✉) · W. D. Yu
College of Textile, Wuhan Textile University, 430073 WuHan, Hubei, People's Republic of China
e-mail: guangmingcai2006@163.com

W. D. Yu
Textile Materials and Technology Laboratory, Donghua University, 201620 Shanghai, People's Republic of China

Introduction

It is well known that polymers have been applied to various fields in our daily life. The high performance fibers have great thermal stability, which were widely used as thermal protective materials. Many studies have discussed the thermal stability of Kevlar and Nomex fiber by TG and obtained the characteristic temperature of degradation in the last few decades [1–7]. And some studies reported the effects of temperature on the tensile properties of aramid fiber and [8, 9]. PBO shows a heat resistance about 100 °C higher than PPTA (Poly(*p*-phenylene terephthalamide) and there have been some reports about thermal analysis of PBO fibers [10, 11]. The thermal degradation of PBZT and PBZO was studied using Py-GC/MS [12]. The characteristic temperature of basalt fiber was also obtained [13]. Although the considerable efforts have been devoted to study the high performance fibers structure, thermal properties, and their relationship, and thermal stability and thermal degradation of aramid fibers, but there are few publications on the comparison in their thermal stability and analysis of thermal degradation process by TG/FTIR and Py-GC/MS.

In this article, the thermal degradation of Kevlar 49, Kevlar 129, Nomex, and PBO fibers were studied by TG/FTIR and Py-GC/MS. Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy was used to obtain the thermogravimetric progress of the fiber and identification of volatile thermal products at the same time. The pyrolysis processes of Kevlar 49, Kevlar 129, Nomex, and PBO fibers were analyzed, and the pyrolysates of different temperatures were obtained using Py-GC/MS. As a result, volatile thermal products, temporarily non-reactive, thermally stable and fragments can be detected, which can be used to interpret their thermal degradation behavior.

Table 1 The specifications of samples

Samples	Manufacturer	Linear density/dtex
Kevlar 49	Du pont (USA)	2.2dtex
Kevlar 129	Du pont (USA)	1.68dtex
Nomex	Du pont (USA)	2.2dtex
PBO	TORY (Japan)	1.68dtex

Experiment

Materials

Four types of high performance fibers were collected, including Kevlar 49, Kevlar 129, Nomex, and PBO. The specifications are listed in Table 1.

Methods

Thermal degradations of high performance fibers were performed in a TG 209 F1 Iris device. The thermal scanning mode ranges from 50 to 800 °C at a programming heating rate of 20 °C min^{-1} in air atmosphere with a gas flow of 20 mL min^{-1}. Each of the samples was controlled within 5–6 mg in primary mass and held in an alumina crucible, and then the loss of the sample mass was measured under a temperature program. The TG curves were recorded and displayed simultaneously during the measurement. Regarding to the temperature parameters, they are the initial temperature of decomposition (T_0), the temperature of half decomposition ($T_{1/2}$), and the end decomposition temperature (T_t), respectively. Fourier transform infrared spectroscopy (Nicolet Corporation U.S., NETXUS750 type) was used to analyze the component of release gas. The thermal degradation products during experimental process were blew into the infrared testing pool by carrier gas and were analyzed. The spectral range is 400–4000 cm^{-2} and the resolving power is 1 cm^{-2}.

The Py-GC/MS experiments were carried out with a 2020IS Pyroprobe pyrolyzer coupled to a GC/MS-QP2010 gas chromatograph and mass spectrometer. Powder sample (5–10 mg) was set in the platinum cup and dropped to the pyrolysis quartz capillary. The pyrolysis was carried under helium carrier gas at a flow rate of 50 mL min^{-1}, and the temperature is 600, 700, and 750 °C, respectively, and the pyrolysis time is 12 s. The GC column was a SDB-5MS (30 m × 0.25 mm × 0.25μm), and the GC oven temperature was initially held at 40 °C for 3 min, was programmed to 250 °C at 10 °C min^{-1}, and held for 10 min. The temperature of GC/MS interface was set at 300 °C. Mass spectra were recorded under electron impact ionization energy of 70 eV, and the flow rate was kept constant. The MS detector was scanned from 29 to 600 m/z at scan rate of 1.8 scan s^{-1}. The data were searched in the NIST Library 107.

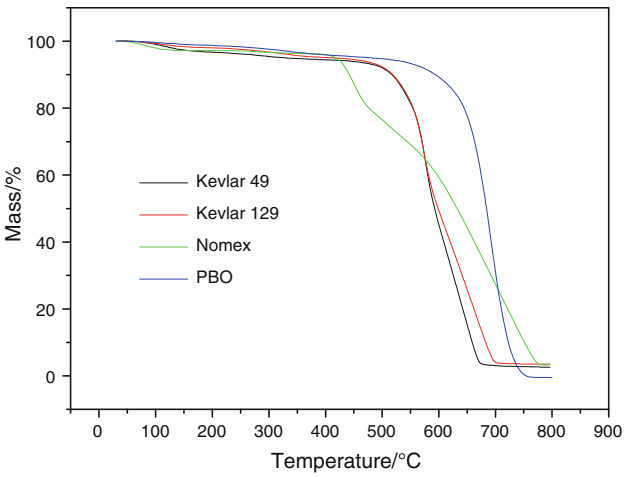


Fig. 1 TG curves of high performance fibers in air

Results and discussions

Thermal degradation analysis of high performance fibers byTG-DTA/FTIR

The TG curves of high performance fibers in air studied were shown in Fig. 1. The characteristic temperature of fibers can be obtained from the curve of TG by the method of Ref. [7]. Table 2 showed the characteristic temperature of fibers. It indicated that the initial degradation temperature of the PBO is the highest. The initial degradation temperature in air, T_o, is in the range of 423.7–648 °C and in the order of PBO > Kevlar 49 > Kevlar 129 > Nomex. It can be concluded that the PBO fiber is the best in thermal stability; the following are the two Kevlar fiber, and then Nomex fiber. PBO fiber shows the most stable thermal property of the tested samples, which is associated with its production procedure where no isomer occurs. The temperature of half decomposition in air, $T_{1/2}$ is in order of PBO > Nomex > Kevlar 129 > Kevlar 49. The T_o of Nomex fiber is the lowest, but the T_t of Nomex is the

Table 2 The characteristic temperature of high performance fibers in air

T/°C	Kevlar 49	Kevlar 129	Nomex	PBO
T_o	548.1	542.4	423.7	648.0
$T_{1/2}$	592.7	598.6	632.24	683.9
T_t	643.7	660.4	784.2	726.5

T_o is the initial temperature of the decomposition; $T_{1/2}$ is the temperature of half decomposition; T_t is the end temperature of decomposition

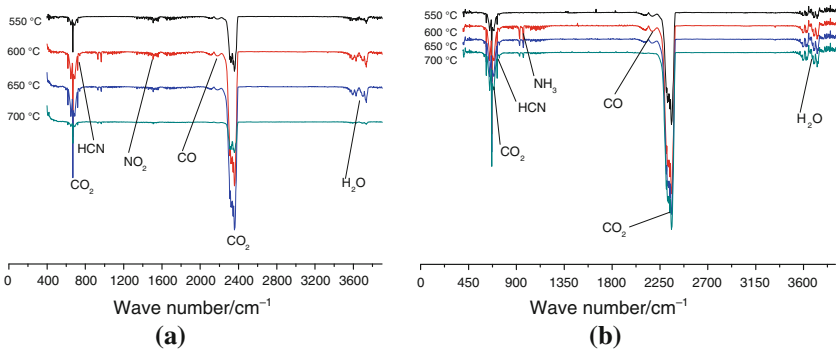


Fig. 2 FTIR spectra of degradation in air **a** Kevlar 49; **b** Kevlar 129

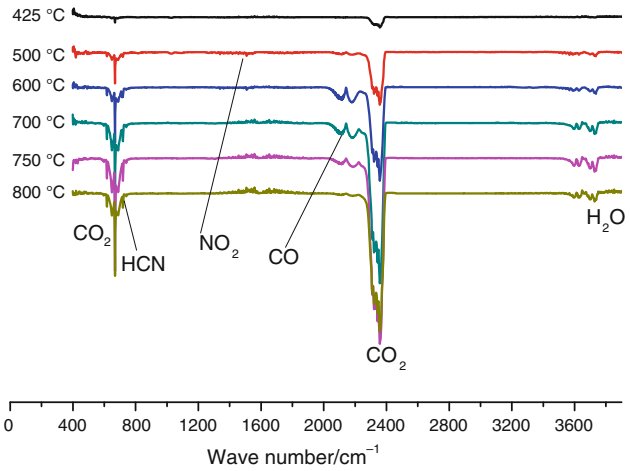


Fig. 3 FTIR spectra of degradation of Nomex in air

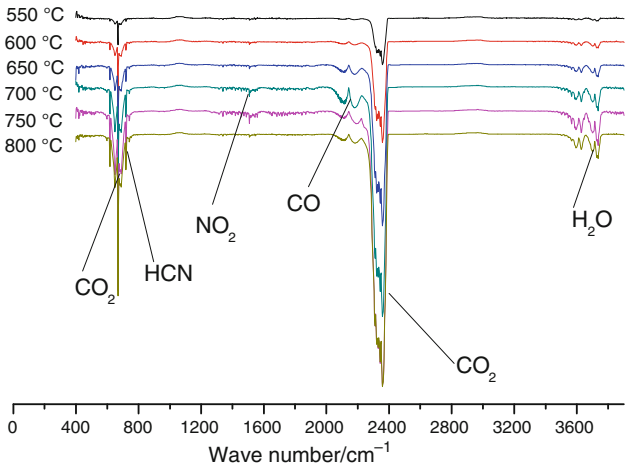


Fig. 4 FTIR spectra of degradation of PBO in air

highest. It indicated that the decomposition rate of Nomex fiber is the lowest. The TG curve of Nomex indicates that it decomposes in two stages and the second decomposition step occurs slowly.

Using the TG-DTA/FTIR, we investigated the gas phase during the thermal degradation of four kinds of high performance fibers. Three-dimensional image of time, wavenumbers and absorbance of volatiles can be observed by TG-DTA/FTIR. The FTIR spectra of volatiles at different temperatures are shown in Figs. 2, 3, and 4. The FTIR spectra of Kevlar 49 fiber volatiles at 550, 600, 650, and 700 °C are shown in Fig. 2a. The volatile compounds were identified as HCN, CO, CO_2, NO_2, and H_2O. In Fig. 2a, the degradation was not strong at 550 °C with only absorption peaks of CO_2, NO_2, and H_2O, and the absorption peaks of HCN and CO were faint. When the temperature rises to 600 °C, a few weak bonds in the heterocycles were broken, and the absorption peaks of HCN, CO, CO_2, NO_2, and H_2O appeared. When the temperature reached 650 °C, the absorption peaks of HCN, CO_2, NO_2, and H_2O became more apparent. The absorption peak of CO decreased and CO_2 exhibited strong absorption peak, which is due to further oxidation of CO in air. When the temperature continued to increase to 700 °C, it was clear that the CO peak disappeared; at the same time, we can see that HCN, NO_2, and H_2O peaks became weak. It was obvious that the Kevlar 49 fiber almost completely decomposed at 700 °C.

Figure 2b showed the FTIR spectra of Kevlar 129 fiber volatiles at 550, 600, 650, and 700 °C. It can be seen that the decomposition volatiles of Kevlar 129 fiber are HCN, CO, CO_2, NO_2, and H_2O. The degradation process of Kevlar 129 is similar with Kevlar 49 fiber. The absorption peaks of HCN, CO, and NO_2 were not obviously at 550 °C. The absorption peaks of HCN, CO_2, NO_2, and H_2O became more apparent with the increase of temperature. When the temperature reached 700 °C, the CO peak disappeared. Unlike Kevlar 49 fiber thermal decomposition, the absorption peaks of HCN, CO_2, NO_2, and H_2O still appeared at 700 °C, which showed the Kevlar 129 fiber not completely decomposed at 700 °C.

According to TG curve, the infrared spectra of decomposition products of Nomex fiber at 425, 500, 600, 700, 750, and 800 °C were analyzed. Figure 3 showed the FTIR spectra of volatiles at different temperatures. It can be seen that the decomposition products of Nomex fiber were HCN, NO_2, CO, CO_2, and H_2O. When the temperatures

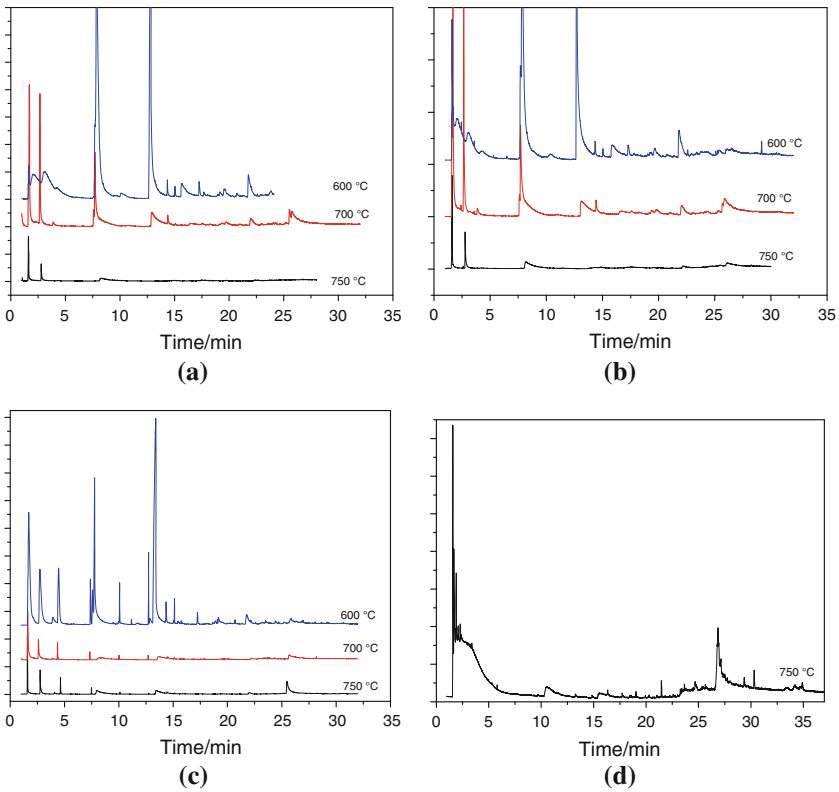


Fig. 5 Chromatograms of the pyrolysate of high performance fibers at different temperatures

were 425 and 500 °C, the thermal degradation of Nomex fiber was not obvious and only CO_2 absorption peak appeared. A small amount of weak aromatic heterocyclic bonds broke in fibers in this temperature. When the temperature reached 600 °C, H_2O, HCN, NO_2, and CO absorption peaks appeared. It showed that the breakage of molecular chain increased, and hydrolysis occurred. When the temperature reached 700 °C, the absorption peaks of HCN, NO_2, CO, CO_2, and H_2O were increased. When the temperature continued to rise to 800 °C, the absorption peak of HCN, NO_2, CO, and H_2O became weak. It clearly shows that the end decomposition temperature of Nomex is higher than Kevlar fiber.

According to TG curve of PBO fiber, the main loss took place from 550 to 750 °C. Figure 4 was infrared spectra of volatiles from 550 to 800 °C. The main decomposition products of PBO fiber were HCN, NO_2, CO, CO_2, and H_2O. At 550 and 600 °C, the absorption peaks of CO_2 and H_2O appeared, and HCN, NO_2, and CO were not apparent. When the temperature reached 650 °C, the absorption peaks of HCN, CO, CO_2, NO_2, and H_2O became more apparent. Chemical reactions, involving complicated depolymerization, irregular breaking, hydrolysis, and recombination took place after 650 °C. With elevating the temperature, at 800 °C the absorption peaks of NO_2 and H_2O became weak, and the absorption peak of CO_2 was increased. The reason was that carbons in phenyl begun to produce CO_2 after C, N, and O in Heterocycles were oxidized.

Thermal pyrolysis process analysis of high performance fibers by Py-GC/MS

With the change of pyrolysis temperature, the chromatogram and mass spectra results take a large variety. Figure 5a–d is the chromatogram of the pyrolysis products of Kevlar 49, Kevlar 129, Nomex, and PBO fiber, respectively. It can provide useful information on the mechanism of the thermal degradation in polymers. In this study, Kevlar 49, Kevlar 129, and Nomex fibers are pyrolyzed under the same conditions to understand and compare their degradation mechanisms. In Fig. 5a–c, the temperature changes form 600 to 750 °C, and when the temperature rises to 750 °C, the pyrolysis products of fiber take an apparent decreasing. It can be found the pyrolysis products are the most at 600 °C. From 600 to 750 °C for Kevlar 49 and Kevlar 129 fiber, the changes happen mainly in the decrease of aromatic compositions.

Py-GC/MS was taken at a temperature point and afforded the advantages of the separation power of gas-chromatography coupled with the identification power of mass spectrometry. As a result, temporarily non-reactive volatile fragments can be detected. However, in TG/FTIR, the samples were heated continuously, the fragments are kept

Table 3 Pyrolysate of high performance fibers at different temperature

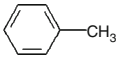
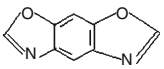
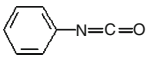
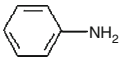
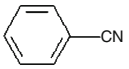
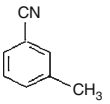
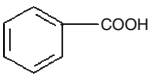
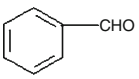
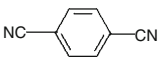
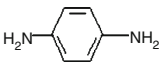
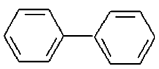
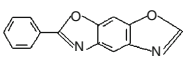
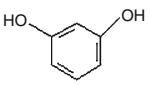
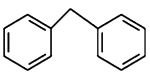
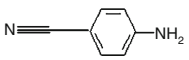
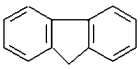
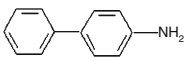
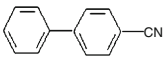
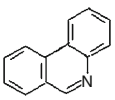
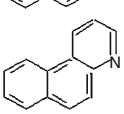
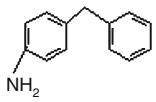
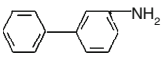
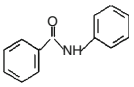
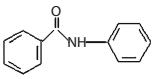
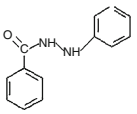
Compound	MM	Kevlar 49 P. A.			Kevlar 129 P. A.			Nomex P. A.			PBO P.A.
		600 °C	700 °C	750 °C	600 °C	700 °C	750 °C	600 °C	700 °C	750 °C	750 °C
CO_2	44	12.74	20.93	32.05	21.87	20.72	24.42	20.9	36.7	18	23.8
C_5H_8	67			0.25						0.116	
	78	5.12	16.18	19.5	3.13	16.42	16.24	10.56	13.99	11.2	9.92
	92	0.44	0.93	1.14	0.99	0.93	0.73	3.84	0.87	1.45	3.97
	160										1.32
	119						0.33				
	93	4.44	2.43		6.81	1.79		9.01	7.8	8.77	
	103	39.1	24.98	40.3	33.81	26.36	35.07	12.21	8.75	12.8	14.72
	117	0.94			0.78						
	122							2.61	0.89		
	106							0.17			
	128	23.99					0.97	0.38			8.07
	108	0.94	17.99		19.98	14.14	1.38	35.6	21.66	14.91	1.26
	154	0.58	1.12		0.55	1.3	1.56	0.83	1.09	0.59	
	160										34.7
	110										2.28
	168	0.33	0.15		0.35			0.11			
	118	4.41	3.53		4.25	2.42					
	166	0.81	0.39		0.86	0.45					
	169	0.26									
	179	0.17	0.51			0.67					
	179	0.36			0.11			0.87			
	179				0.15						

Table 3 continued

Compound	MM	Kevlar 49 P. A.			Kevlar 129 P. A.			Nomex P. A.			PBO P.A.
		600 °C	700 °C	750 °C	600 °C	700 °C	750 °C	600 °C	700 °C	750 °C	750 °C
	183				0.1						
	169	0.8	1.23			1.52		0.69	1.08	0.19	
	197	4.03	3.83	6.76	5.51	4.15	6.79	0.16	6.01	3	
	197	0.31	3.7		0.17	1.22					
	212	0.23	3.1		0.4	7.65	12.51	2.07	6.93	27.9	

MM molecular mass; P.A. Peak area

for more time to form more stable compounds, and the unstable fragment can hardly be detected. In fact, only several main volatiles were searched by TG/FTIR. The identified fractions in Py-GC/MS, CO_2 had a considerable proportion. This was corresponding to the strong absorption peak of CO_2 in TG-DTA/FTIR.

In Table 3, the pyrolysates of four kinds of high performance fibers, which were identified by mass spectra, were listed in the order of retention times. About 30 evolved gaseous products were obtained, and the peak area indicates every pyrolysate percentage at a designated temperature. With temperature changing, the fragments of pyrolysis are changing. Of course, GC/MS only gives partial products in the pyrolysates, but the pyrolysates can help us study the pyrolysis process of fibers. The different pyrolysates of four kinds are because of the recombination of fractured chemical bond. The recombination of chemical bond is random and achieve temporary stability.

The pyrolysates of Kevlar 49 and Kevlar 129 at 600, 700, and 750 °C were shown in Table 3. It showed that the CO_2, benzene, and benzonitrile are the main fragments at 600 °C. With temperature elevating, the percentages of CO_2 and benzene are increasing. The percentage of CO_2, benzene and benzonitrile nearly reached at 80% at 750 °C. The gaseous products obviously decreased at 750 °C, only five evolved gaseous products were obtained. It indicated that the aromatic compounds decompose with increase in temperature and form more stable benzene.

The main pyrolysates of Nomex is 1,4-diaminobenzene at 600 °C. With temperature elevating, the percentages of CO_2 and benzene are increasing and the percentage of 1,4-diaminobenzene is decreasing. The percentage of CO_2 reached 36.7% at 700 °C. When the temperature increases, the percentages of CO_2 and benzene decreases at 750 °C. It showed that the Nomex fibers are still decomposing. This was corresponding to the high terminal decomposition temperature of Nomex fiber.

The pyrolysis of PBO at 750 °C was researched. The results showed that the repeating unit of PBO molecular chain was the main fragment, and CO_2 and benzene also kept great yields in all pyrolysates. It indicated that the depolymerization was the main reaction. The fragments of repeating unit of PBO molecular chain can hardly be detected by infrared spectrum.

Conclusions

The thermal degradations of the high performance fibers Kevlar 49, Kevlar 129, Nomex, and PBO in the air were characterized by TG-DTA/FTIR. And the characteristic temperatures of the kinds of fibers in air were obtained. The heat resistance of PBO fiber was the best, and decomposition temperature of the beginning was the highest. Despite the beginning decomposition temperatures of the Nomex fibers were the lowest and less than 450 °C, the termination decomposition temperature was close to 800 °C. The gases released by the pyrolysis in air were mainly CO_2, CO, H_2O, NO, and HCN, also containing a small amount of NH_3, and the absorption peaks of CO_2 were the strongest. The pyrolysis processes of Kevlar 49, Kevlar 129, and Nomex were analyzed using Py-GC/MS. It was found that the proportion of CO_2 is large in pyrolysis products; and more small molecules containing benzene

ring appeared in the pyrolysis products. There were more volatile fragments of Kevlar 49, Kevlar 129 at 600 and 700 °C, and the volatile fragments were reduced at 750 °C. However, there were still more volatile fragments of Nomex than Kevlar fiber at 750 °C.

The pyrolysis temperature of PBO fiber was higher. The repeating unit of PBO molecular chain was the main fragment, and CO_2 and benzene also kept great yields in all pyrolysates.

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