



Thermal Stability of Poly(*p*-phenylenebenzobisoxazole) Fibres

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ABSTRACT

The thermal degradation behaviour and service lifetime of poly (*p*-phenylenebenzobisoxazole) (PBO) fibres, prepared by our group, were investigated. The thermal degradation processes of the PBO fibres were studied using TG-DTG at heating rates of 5.0, 10.0, 15.0, 20.0 K.min⁻¹ under atmospheric air and at heating rate of 10.0 K.min⁻¹ under nitrogen atmosphere, respectively. The thermal decomposition process of PBO fibre occurs in a single step in the air, being especially prominent between 900 K and 960 K. The thermal degradation kinetics of the PBO polymer under the non-isothermal condition, gave values for activation energy *E* and the pre-exponential factor *A* as 142.51±10 kJ.mol⁻¹ and 2.43×10⁷±10⁵ min⁻¹, respectively. Under nitrogen condition, the thermal degradation has started above 907 K. The thermal stability of PBO in the nitrogen atmosphere was 80 K higher than that in the air atmosphere. Moreover, the oxygen played an important role in the degradation, which initiated the degradation of PBO. The decomposition gases of the PBO were analyzed by TG- FTIR. It was found that CO, CO₂ and H₂O were the main compounds during the PBO degradation in the air. PBO fibre is transformed into charred material which is stable enough and has no aromatic species. The PBO fibre can be used for long time as the temperature is less than 300°C in air. The service lifetime of the PBO fibres was estimated by the kinetics of thermal degradation, and the lifetime equation at weight-loss of 5% was deduced from the equation $\ln t = -19.954 + 17141 / T$.

Key Words:

PBO fibres;
degradation;
stabilization;
thermogravimetric analysis;
service lifetime.

INTRODUCTION

Poly(*p*-phenylene-2,6-benzoxazole) (PBO) fibre, which is a new kind of high performance rigid-rod isotropic crystal polymers, has excellent thermal stability, solvent resistance, remarkable tensile strength and modulus [1-4]. The applications of PBO might be brought up to the higher demand.

The properties of PBO relating to the structure, thermal degradation and mechanics have been studied in detail [5-8]. However, the properties of PBO, such as the durability and the service lifetime, have not been systematically reported. In previous research works, the thermal properties of PBO were

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investigated from different research angles, including the relative fire resistance (flammability, smoke, and the type of combustion products) of PBO sheets and carbon fibre/PBO matrix composites [9], the degradation mechanisms due to moisture or acid presence, and the radiation effect from the UV spectrum [10,11], the ultraviolet and hydrolytic stability of the benzoxazole ring structure [12]. In addition, the kinetics of thermal degradation of PBO was studied by TG in dynamic nitrogen gas [13,14].

The reactions of degradation abide by Arrhenius kinetics. If the data of the kinetics of thermal degradation are obtained, the thermal properties of materials in the whole temperature range can be known. In this respect the temperature-dependent service lifetime can also be calculated. These data are only valid for the actual temperature under consideration [15,16].

In this paper, the TG-DTG-FTIR technology, which has never been used in the study of thermal performance of polymers, is adopted to study the thermal stability (under pyrolytic and thermo-oxidative conditions) of PBO fibre prepared by our group. On the basis of kinetic parameters, the lifetime for high temperature is calculated. The thermal stability of commercial PBO fibres is compared with that of PBO fibres produced in the laboratory. The thermal degradation kinetics of the PBO fibre was studied under non-isothermal condition. The thermodynamic properties of PBO and the service lifetime at higher temperature play an important role in helping us not only to find out the properties of the high performance organic fibres and the composites in different temperatures, but also to exploit their potential applications to a large extent.

EXPERIMENTAL

Materials

4,6-Diamino-1,3-benzenediol/terephthalate (TA salt) was prepared from 4,6-diamino-1,3-benzenediol and terephthalic acid. PBO was prepared from TA salt in polyphosphoric acid using solution polycondensation. Polymerization reaction was performed in a kettle reactor and in a twin-screw extruder as described in previous work [17]. The limiting viscosity number was above 25.4 dL/g. The polymerization solutions were directly spun into fibres via a dry-jet wet-spinning process (the process variable of spinning: the draw ratio was 30, the temperature was 175°C, the dilute phosphoric acid as coagulant, and the multihole spinneret was 0.2×32 mm). The fibre was completely washed in running water and then dried in vacuum. The tensile strength as high as 4.5 GPa and the tensile modulus as high as 260 GPa for the prepared as-spun PBO fibres were reached. The process of synthesis of PBO fibre is shown in Figure 1.

Thermal Analysis

TG-FTIR (thermogravimetric analysis connected with Fourier transform infrared spectroscopy) was used for the analysis of weight loss and the decomposition gases of the PBO. The TG-FTIR includes a TG 209 thermal analysis system (Germany NETZSCH) and a FTIR monitor (Germany Bruker Vector 22). The sample (about 5 mg) was placed in Al₂O₃ crucibles, and the analysis was performed at heating rates of $\beta = 5.0, 10.0, 15.0, 20.0 \text{ K}\cdot\text{min}^{-1}$ under air atmosphere and $\beta = 10.0 \text{ K}\cdot\text{min}^{-1}$ nitrogen atmosphere from 293 K to 1473 K, respectively.

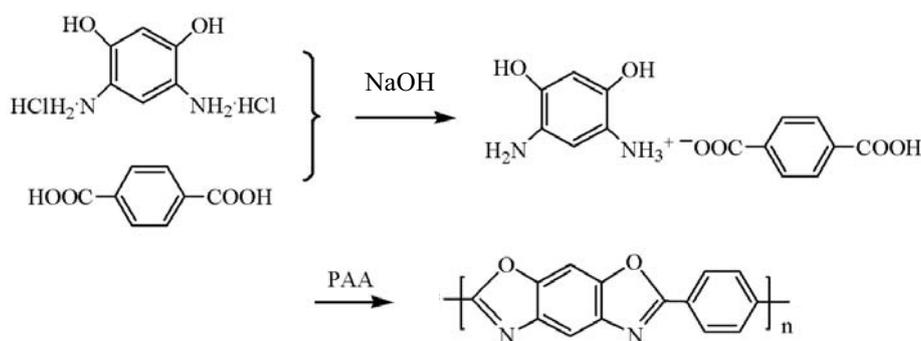


Figure 1. Synthesis of PBO fibre.

RESULTS AND DISCUSSION

Thermal Decomposition Behaviour

Figure 2 shows the curve of TG-DTG at the heating rate of $10 \text{ K}\cdot\text{min}^{-1}$ of PBO fibre under air atmosphere, while Figure 3 shows that of PBO fibre under nitrogen atmosphere.

It is observed from Figures 2 and 3 that the DTG curves slightly decline in the initial stages due to loss of water around 373 K. This is consistent with the DSC results reported in ref 18. Under air condition, the thermal degradation is occurred above 883 K and finally a residue of about 3 wt% is formed at 1200 K, and the significant changes occur between 900 and 995 K. While under nitrogen condition, the degradation of PBO fibres begins at higher temperature (about 907 K), and a large amount of residue is formed (about 16 wt%) which is stable up to 1200 K. The basic data of decomposition of PBO is given in Table 1.

The thermal stability of PBO in the nitrogen atmosphere is 80 K higher than that in the air atmosphere. This is because oxygen plays a critical role at the initial stage of degradation in polymers. Due to the higher thermal stability of PBO in the nitrogen atmosphere, the amounts of volatile substances are lower than in the air atmosphere, while the temperature of volatile substance is much higher than that in the air atmosphere. These analyses indicate the strong influence of oxygen on the thermal degradation of the fibres and different decomposition reactions in air and nitrogen.

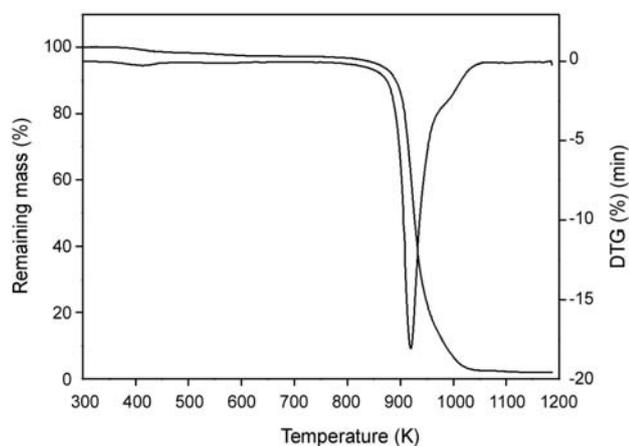


Figure 2. TG-DTG curves of PBO fibre in air.

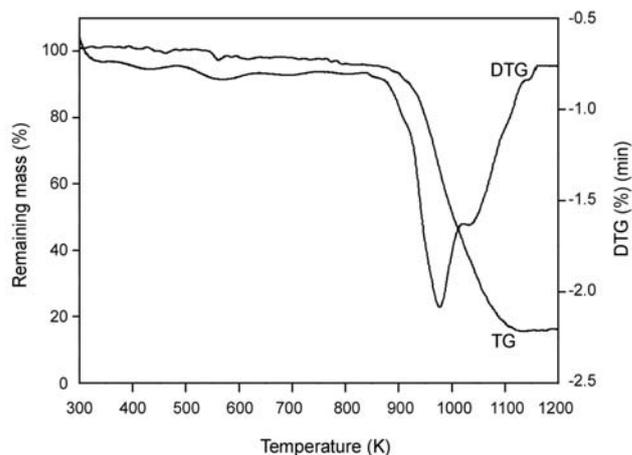


Figure 3. TG-DTG curves of PBO fibre in nitrogen atmosphere.

The high-temperature degradation of PBO may have two modes: the scission of the heterocyclic ring and the scission of the C-C single bond connecting to benzene ring. The pyrolytic decomposition of PBO is apt to begin with the scission of the heterocyclic ring which can bring about dicyanobenzene products. These products finally turn into the major volatile products such as CO_2 , HCN among others. In the air atmosphere the degradation of PBO is explained by thermo-oxidation mechanism. The oxidation accompanying high-temperature degradation can accelerate the decomposition of fibre. The activation energy of degradation and the residues of PBO fibre in the air are much lower than degradation under nitrogen (Table 2). Maybe that is because the PBO high-temperature degradation can generate scission and form the oxygenous structures. The oxygenous structures can accelerate the generation of the scission and free

Table 1. Basic data of thermal decomposition of PBO.

Thermal decomposition data	Nitrogen	Air
Peak temperature (K)	977	919
Residue at 1200 K (wt%)	16	3
Temperature at the onset of degradation (K)	907	883
Temperature at the end of degradation (K)	1160	1040
Temperature range of the degradation (K)	920~1100	900~960

Table 2. Invariant kinetic parameters of PBO fibres.

Atmosphere	E (kJ.mol ⁻¹)	A	n	Temperature range (°C)	Source of data
Nitrogen	327±15	2.6×10 ¹⁴ ±10 ¹³ (s ⁻¹)	-	500-800	Data obtained
Air	85±5	1.7±0.1 (s ⁻¹)	-	400-900	Ref [22]
Nitrogen	-	-	-	-	Data obtained
Air	142.51±10	2.43×10 ⁷ ±10 ⁵ (min ⁻¹)	1.88	500-800	Calculated

radicals, which can accelerate chain transfer, generate the new decomposition and free radicals transfer.

It can be seen from the above that the heat-resistance of PBO fibre is very good, especially under nitrogen atmosphere, which is attributed to the highly conjugated system and great stiffness of the PBO molecule.

Figure 4 shows the thermal degradation curves corresponding to dynamic experiments carried out at different heating rates: 5, 10, 15 and 20 K/min. The onset decomposition temperature increased along with the augment of heating rates under air atmosphere.

Gas Phase Analysis

The gas phase during the degradation of PBO was investigated using the TG-FTIR spectrometer. The gases collected from the degradation of PBO were analyzed by FTIR, and the results are shown in Figure 5. The absorption bands of CO (region

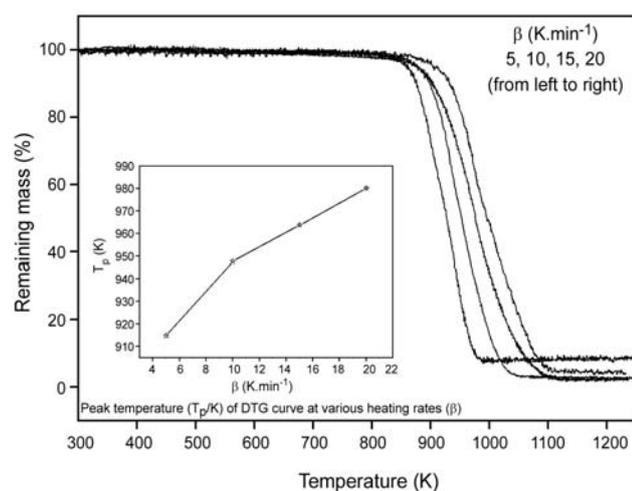


Figure 4. The curves of conversion versus temperature at different temperatures.

2000-2250 cm⁻¹), CO₂ (regions 2250-2400 and 635-720 cm⁻¹) and H₂O (regions 3500-4000 and 1350-1850 cm⁻¹) are detected as major products. It is found that the amount of gases is low in the degradation of PBO and the time used to detect these gases is long. These attribute to the higher thermal stability of PBO. Furthermore, there are no aromatic compounds to be detected as the temperature is raised. This is because PBO is transformed into charred material which is stable enough and has no aromatic species.

The region of 1300-700 cm⁻¹ shows that hydrocyanic acid (HCN) and ethylenic species are evolved in the degradation of PBO at 920 K.

When the degradation reaction happens at 1100 K, the gases such as CO, CO₂ and H₂O molecules are detected as major products once again and as small amount, which is confirmed by the above data, while there are also changes in the evolved products of degraded gases of PBO at 1100 K. When zooming in the spectra, the absorption band of HCN, ethylenic species and aromatic compounds are no longer present but other bands appear in the region 1900-1200 cm⁻¹. This is likely that the nitrogen containing

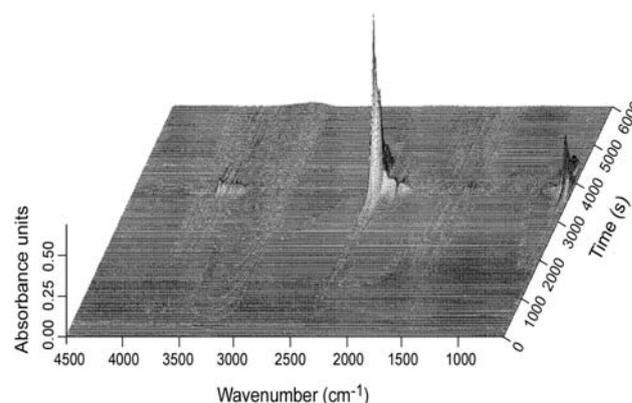


Figure 5. FTIR of spectrum of degrading PBO at different temperatures.

compounds (PBO) are evaporated during the gasification process, which leads to the NO formation in the gas phase.

Service Lifetime

In general, the decomposition of solid polymer can be associated with the reactions. A typical model for kinetic process can be expressed as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp(-E/RT) \cdot (1-\alpha)^n \quad (1)$$

Where α is the degree of conversion, $(1-\alpha)^n$ is the differential expression of a kinetic model function [19]. E is the activation energy (J/mol), R is the constant (8.314 J/mol.K), A is pre-exponential factor (min^{-1}), T as the absolute temperature (K), β is the constant heating rate ($\beta = dT/dt$ (K/min)) and $[A \exp(-E/RT)]$ is the decomposition rate constant k , according to the Arrhenius law.

According to literature [19,20], the concept, the service lifetime t_f (min), was introduced. As in eqn (1), the variables α and t were apart at first, and then integrated to form eqns (2) and (3) as follows:

$$n \neq 1, \quad t = \frac{(1-\alpha)^{1-n} - 1}{(n-1) \cdot k} \quad (2)$$

$$n \neq 1, \quad t = \frac{-\ln(1-\alpha)}{k} \quad (3)$$

The general service lifetime formulation of materials is as follow [21]:

$$\ln t_f = a + b/T \quad (4)$$

where t_f (min) is the service lifetime at temperature T (K) when the mass-loss is f , a and b are constants.

Based on the invariant kinetic parameters, e.g. the activation energy (E), pre-exponential factor (A), the reaction order (n), the relationship of the service lifetime, and the temperature could be obtained. The t_f might be used as the appraising guideline of thermodynamic properties. At certain temperature, the larger $t_{0.05}$ indicated thermodynamic stabilities. This concept avoided the relative latent tentative, and made better use of the three kinetic parameters to express

Table 3. Service lifetime of PBO fibre by kinetic parameters.

T (K)	$\tau_{5\%}$ (min)	T (K)	$\tau_{5\%}$ (min)
473	$1.2 \times 10^7 \pm 10^4$	673	$2.5 \times 10^2 \pm 6$
523	$3.7 \times 10^5 \pm 10^2$	723	43.1 ± 2
573	$2.1 \times 10^4 \pm 10^2$	773	9.4 ± 0.2
603	$4.8 \times 10^3 \pm 10$	823	2.6 ± 0.1
623	$1.9 \times 10^3 \pm 10$	873	0.9 ± 0.03

the t_f correctly.

As it is observed from Table 2, the kinetic parameters were calculated according to the TG results (Figure 4) by the Flynn-Wall-Ozawa and Coats-Redfern methods as reported in literature [23-25]. The corresponding kinetics of thermal degradation parameters reported in literature [22] are also listed in Table 2. With the aid of these parameters, the mass-loss of 5% lifetime is predicted at 473-873 K in air and listed in Table 3. By substituting the values in Table 3 into eqn (4), the constants a , b , and linear correlation coefficient, r , are obtained by the linear least square method:

Lifetime equation is $\ln t = -19.954 + 17141/T$

Linear correlation coefficient, r , is 0.9999.

The values of the service lifetime of PBO fibre are given in Table 3. The fibre can be used for long time as the temperature in air is less than 300°C. However, the service lifetime of PBO fibre is sharply decreased when the temperature is above 300°C. From Figure 6, it can be seen that the critical temperature (T_c) is 340°C. When the temperature is above 340°C, the fibre has heat resistance, but the performance of fibre cannot be maintained the same as before. Therefore, as ref 26 notes the tensile strength and modulus of PBO fibre are unchanged after 200 h at 300°C under nitrogen atmosphere, and 60% tensile strength is retained after 200 h at 300°C in air.

If 5% weight loss is considered as the only factor, the lifetime of PBO fibre is 350 h (2.1×10^4 min) which is higher than 200 h according to the ref 26 at 300°C in air. However, the lifetime of 350 h of PBO obtained does not include factors of thermal aging degradation, hydrolytic degradation, photodegradation and reduction of tensile strength, etc. Thus, in fact, the diminished mechanical properties of PBO depend enormously on the thermal degradation as

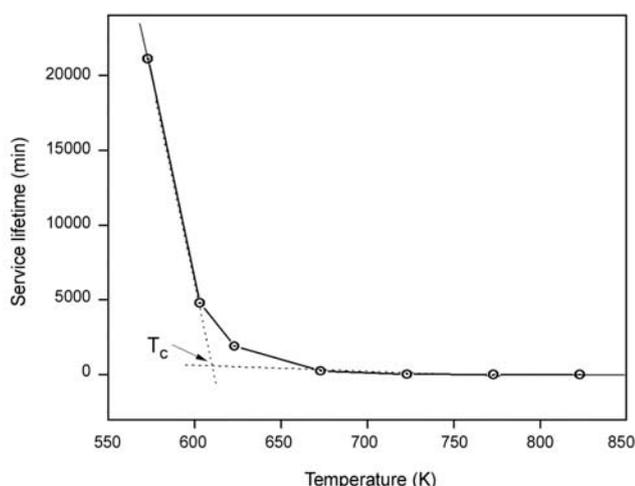


Figure 6. Service lifetime vs. temperature curves of PBO fibre.

well as thermal aging after 350 h at 300°C.

CONCLUSION

PBO fibre has better heat resistance in air and nitrogen atmospheres. The thermal stability of PBO under nitrogen atmosphere is 80 K higher than that under air atmosphere. The substances such as CO, CO₂ and H₂O are examined during the PBO degradation in the air atmosphere. It can be presumed that oxygen plays an important role in the initiation of degradation. The lifetime of PBO fibres is estimated by the kinetics of thermal degradation. At weight-loss of 5% the lifetime equation was deduced to be $\ln t = -19.954 + 17141/T$.

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