Kinetic Study on Pyrolysis of Polyphenylene Sulfide under Different Oxygen Concentrations

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Abstract—Kenitic of thermal degradation of PPS were studied undernitrogen, oxygen and airin formal works. The integral Coats-Redfern method based on single heating rate is employed for the kinetic analysis of the pyrolysis processunder different oxygen concentrations. The results indicated that only one stage occurred under pure nitrogen atmos- phere while two stages occurred under oxidative atmosphere. Maximal mass loss rate and apparent activation energy of the first stage varies little (Maximal mass loss rate of first degradation stage stabilizes $(4.3\pm0.5)\%\cdot min^{-1}$, and apparent activation energy of the first degradation stage fluctuate around $170kJ\cdot mol^{-1}$) while corresponding kinetic parameters of the second stage increase linearly with increasing oxygen concentrations (at 10%, 20%, 30%, 40%, 50%, 60%) , in addition, apparent kinetic compensation effect of PPS under oxidative atmosphere was also discovered and discussed. The isokinetic temperature T_S is 505°C and 522.4°C respectively with heating rate of $10k\cdot min^{-1}$ and $20 k\cdot min^{-1}$.

Keywords-PPS;apparent activation energy; pre-exponen-tial factor; apparent kinetic compensation effect; different oxygen concentrations

I. Introduction

Polyphenylene sulfide has been widely used in auto-mobile, chemical, building material industry and environ-mental protection for the sake of excellent fire retardancy, heat durability, corrosion resistance and mechanical property since industrialized production[1]. Instability of outermost electron of the divalent sulphur atom results in its tendency to lose electrons and react with oxygen atom, furthermore, the macromolecular chains broken and degradation occurs[2]. The mechanical properties such as breaking tenacity and elongation of PPS fiber was investigated[3][4][5],kinetic analyzed thermal behaviors of PPS in the present only concentrates on the nitrogen atmosphere, air atmosphere, or the comparison of them. In order to study the effects of oxygen on the degradation of polyphenylene sulfide, a set of thermagravimetric experiments under different oxygen concentrations were carried out.

II. Experimental section

Thermo gravimetric experiments were conducted on Netzsch STA 449F3 analyzer and Proteous thermal software. Approximately, 6mg of polyphenylene sulfide fiber samples from Toray of Japan were used for each experiment. Samples were heated from 30°C to 700°C with two heating rates $(10K\cdot min^{-1}, 20K\cdot min^{-1})$ under N_2-O_2 mixture with different oxygen concentration (0%, 10%, 20%, 30%, 40%, 50%, 60%), and all tests were carried out with a total flow rate of $100ml\cdot min^{-1}$.

III. Results and discussion

A. Pyrolysis characteristic analysis

Thermogravimetry (TG) curves under various oxygen percentages are illustrated in Fig.1 and Fig.2 respectively for heating rates of 10k/min and 20k/min. Initial degradation temperature stabilize around 480°C and increase with the increasing heating rates. In pure nitrogen the degradation involves only one stage with the weight loss ratio of 43% and terminated pyrolysis temperature of 580°C and 595°C for two heating rates respectively. When oxy- gen is present, two degradation stages occur and the first stage is independent of oxygen concentration with the TG curves nearly overlapped. In addition, the terminated temperature of first stage is located in range of 550-610°C and 575-615°C and decrease with the increasing oxygen percentages. Divergence could be illustrated in the second stage obviously, TG curve moves forward and degradation quickens with the increase of oxygen concentration.
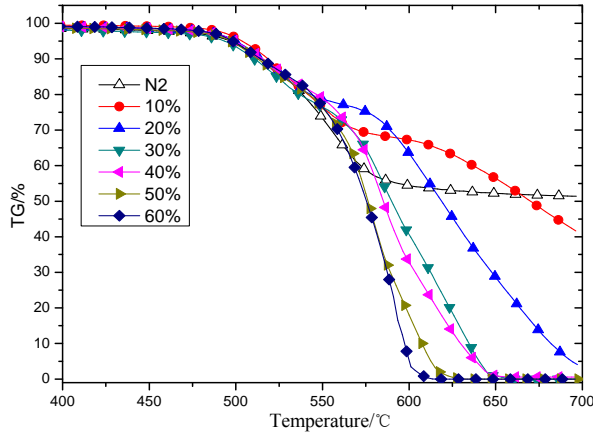
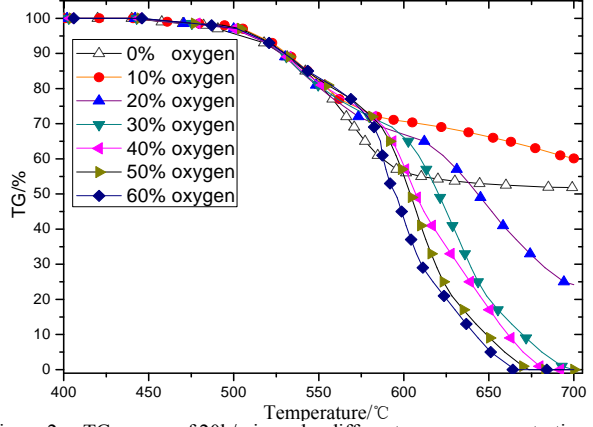Figure 1.   TG curves of 10k/min under different oxygen concentrations

Figure 2.   TG curves of 20k/min under different oxygen concentrations

As is shown in Fig3 and Fig4,corresponding with two stages of TG curves, two peaks displayed on the derivative thermogravimetry(DTG) curves under oxidative atmosphere. Similarly, first stage of DTG curves is nearly overlapped while the peak temperature decreases and the temperature range of a whole weight loss peak narrows with the increase of oxygen concentration in second degradation stage. At the same time, in comparison with 10k/min,the peak temperature are higher and the peak range are wider at the heating rate of 20k/min,which is corresponding with the conclude of M.X.Fang[6].This phenomenon can be explained by thermal hysteresis quality under different heating rates, time of receiving heat is more adequate with the lower heating rate, then both of the initial and terminated temperature move toward lower direction.
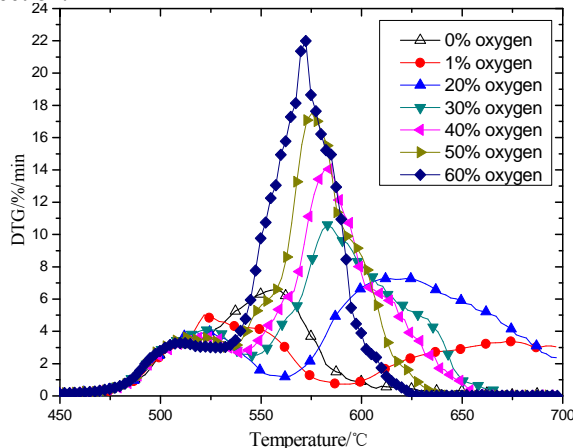

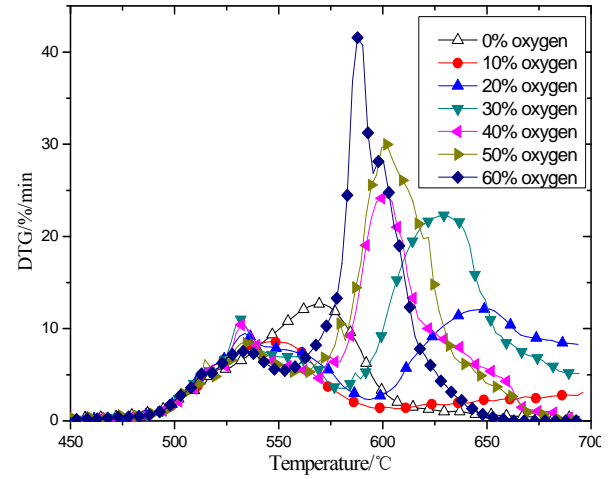Figure 3.   DTG curves of 10k/min under different oxygen concentrations

Figure 4.   DTG curves of 20k/min under different oxygen concentrations

Peak value of DTG in two stages of PPS under different oxidative atmosphere are showed in Fig5.The value of first stage vary little but in the second stage change distinctly with the increasing oxygen concentration, a strong linear relationship also be found between the maximal degradation rate and the oxygen concentration with the fitting degree of 0.986(β=10K/min) and 0.942(β=20K/min).
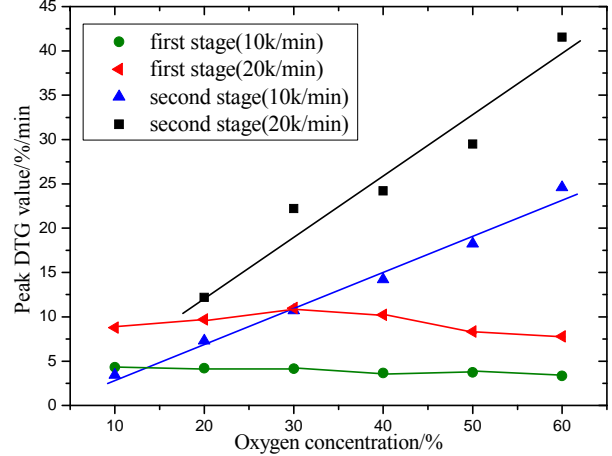

Figure 5.   Peak DTG value of every stage under different oxygen concentrations

B.   Analysis based on Coats-Redfern method

Coats-Redfern integral method has been generally used to analysis non-isothermal kinetic parameters by calculating data of a TG curve from a single heating rate[7][8][9].The kinetic equation can generally be written as equation (1):

$$\frac{d\alpha}{dt}=k(T)f(\alpha)$$

k(T) is described by Arrhenius equation (2) as follows, which reveals the relation between reaction rate and temperature:

$$k=Ae^{-\frac{E}{RT}}$$

where A is the pre-exponential factor, E is the apparent activation energy and R is the gas constant. $f(\alpha)$ follows the equation (3),where n is the reaction order.

$$f(\alpha)=(1-\alpha)^n$$

Equation (4) shows the conversion rate α, m_t represent the weight of the sample corresponding to time t; m_i and m_∞ are the initial and terminate weight of the sample respectively[10].

$$\alpha=\frac{m_i-m_t}{m_i-m_\infty}$$

Plug equation (2) and equation (3) into equation (1) get equation (5):

$$\frac{d\alpha}{dt}=Ae^{-\frac{E}{RT}}(1-\alpha)^n$$

There Coats-Redfern equation can be obtained by integration of equation (5) as follows[11]:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT}\quad(n\neq1)$$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]=\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT}\quad(n=1)$$

Where β is the heating rate, for generally reaction precess, $E/RT\geq1$ and therefore $1-2RT/E\approx1$，fitting the left of equation (6) and equation (7) versus $1/T$, the apparent activation energy E and pre-exponential factor A can be determined by slope and intercept respectively. Table1 shows the apparent activation energy and pre-exponential factor calculated by this method.

TABLEI. APPARENT ACTIVATION ENERGY CALCULATED BY COATS-REDFERN METHOD

Atmosphere	apparent activation energy and degree of fitting				
	β	E_1	R^2	E_2	R^2
	K/min	kJ/mol		kJ/mol	
0%O$_2$	10	167.71	0.9979	—	—
	20	168.23	0.9992	—	—
10%O$_2$	10	168.02	0.9716	40.05	0.9980
	20	175.43	0.9771	19.41	0.9767
20%O$_2$	10	177.32	0.9747	119.39	0.9989
	20	178.52	0.9817	116.99	0.9980
30%O$_2$	10	175.18	0.9916	155.48	0.9978
	20	173.36	0.9711	162.05	0.9905
40%O$_2$	10	159.17	0.9727	221.14	0.9959
	20	177.87	0.9700	197.05	0.9916
50%O$_2$	10	163.27	0.9760	232.27	0.9961
	20	179.95	0.9743	240.69	0.9928
60%O$_2$	10	153.90	0.9798	270.41	0.9864
	20	163.73	0.9732	308.22	0.9920

Apparent activation energy of the second pyrolysis stage increases with the increasing oxygen concentration with the same heating rate.A strong linear relationship between apparent activation energy of the second stage and oxygen concentration can be found,with the fitting degree of 0.956(β=10k/min) and 0.973(β=20k/min) showed in Fig.6.Apparent activation energy of the first degradation stage fluctuates around 170kJ/mol.
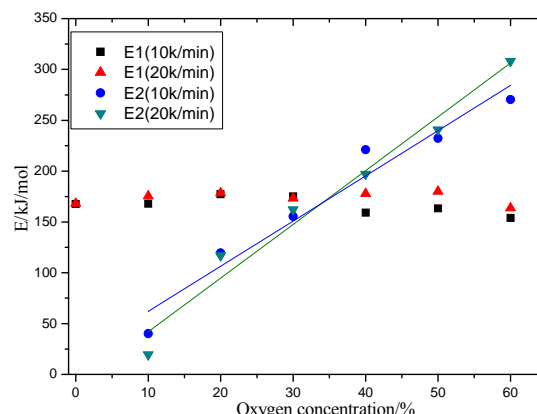

Figure 6. Change rules of activation energy calculated by Coats-Redfern method

C. Analysis of the kinetic compensation effect

Apparent activation energy and pre-exponential factor calculated above increase with increasing oxygen concentration. The mathematical expression of kinetic compensation effect can be described as $\ln A=aE+b$[7][12],which denotes that the pre-exponential factor increase with the increasing activation energy. Equation (8) can be transformed from the formula of kinetic compensation effect:

$$A=C_0e^{aE}$$

Where $C_0=e^b$ is constant term, then plug equation (8) into equation (2) and the relationship between reaction rate K and activation energy E can be described as equation (9):

$$K=C_0e^{E\left(a-\frac{1}{RT}\right)}$$

The temperature $T=\dfrac{1}{aR}$ is called isokinetic temperature which can be denoted as T_S, and the effect of activation energy on reaction rate mainly include two aspects[13]:

1. When T<T_S, the coefficient $\alpha-\dfrac{1}{RT}\rangle0$, and then the reaction rate K decreases with the increase of activation energy E.

2. When T>T_S, the coefficient $\alpha-\dfrac{1}{RT}\langle0$,and then the reaction rate K decreases with the increase of activation energy E.

Obvious kinetic compensation effect also discovered according to the solved kinetic parameters of polyphenylene sulfide under different oxygen concentrations. The linear fitting of lnA and E is carried out based on the parameters in Table III and described as Table II and Fig.7, calculated isokinetic temperature T_S is 505°Cand522.4°C

respectively when heating rate is 10k/min and 20k/min.The temperature corresponding to second pyrolysis stage is greater than T_S, therefore the degradation rate of PPS increases with the increase of activation energy.

TABLEII.   KINETIC COMPENSATION EFFECT FORMULA OF PPS

β (K/min)	Linear formula	R^2	T_S(°C)
10	lnA=0.1546E-11.32	0.9999	505
20	lnA=0.1512E-11.38	0.9999	522.4

TABLEIII.   PRE-EXPONENTIAL FACTOR CALCULATED BY COATS-REDFERN METHOD

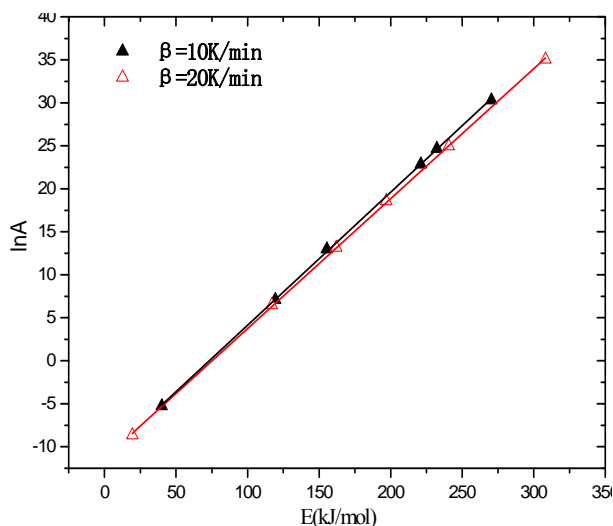| Atmosphere	Pre-exponential factor		
	β	A_1	A_2
	K/min	min^{-1}	min^{-1}
10%O_2	10	4.31×10^6	0.52×10^{-2}
	20	1.74×10^7	0.18×10^{-3}
20%O_2	10	2.05×10^7	1.21×10^3
	20	3.23×10^7	6.55×10^2
30%O_2	10	1.75×10^7	4.37×10^5
	20	1.4×10^7	5.21×10^5
40%O_2	10	1.13×10^6	8.50×10^9
	20	2.74×10^7	1.19×10^8
50%O_2	10	2.38×10^6	5.14×10^{10}
	20	3.60×10^7	7.02×10^{10}
60%O_2	10	5.03×10^5	1.45×10^{13}
	20	2.92×10^6	1.69×10^{15}

Figure 7.   The kinetic compensation effect analysis curves of PPS

IV.   CONCLUSIONS

1)Only one stage occurs in inert atmosphere while two stages occur in oxidative atmosphere in the pyrolysis process of polyphenylene sulfide. Initial degradation temperature of first stage remains at around 480°C and increasing oxygen concentration decreases the initial and terminate temperature of second stage.

2)Maximal mass loss rate of first degradation stage stabilizes (4.3±0.5) %•min^{-1}, apparent activation energy of the first degradation stage fluctuate around 170kJ•mol^{-1} while both increase linearly with oxygen concentration in second stage.

3)Since the kinetic and pyrolysis parameters follow kinetic compensation effect and the temperature range of second stage is greater than isokinetic temperature, both of the apparent activation energy and degradation rate increase with the increasing oxygen concentrations, and isokinetic temperature T_S is 505°C and 522.4°Crespectively when heating rate is 10k•min^{-1} and 20 k•min^{-1}.

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