

Kinetics of thermal degradation of poly(aryl ether)s containing phthalazinone and life estimation

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Abstract New special engineering thermoplastics, poly(phthalazinone ether sulfone) (PPES) and poly(phthalazinone ether sulfone ketone) (PPESK), containing phthalazinone are synthesized through step-polymerization. The kinetics of thermal degradation of PPES and PPESK (1/1) in nitrogen is investigated at several heating rates by thermogravimetry (TG). It is concluded that, based on using Sata-ava's theory, the thermal degradation mechanism of PPESK (1/1) is nucleation and growth, the order of reaction of the degradation process is one ($n = 1$). In contrast, the thermal degradation mechanism of PPES is a phase boundary controlled reaction and the order of the reaction is two ($n = 2$). The kinetic parameters, including reaction energy and frequency factor of thermal degradation reaction for PPES and PPESK (1/1) are analyzed using isoconversional Friedman, Kissinger–Akahira–Sunose (K–A–S) and Ozawa method. In addition, the study focus on the influence of heating rate and ratio of ketone/sulfone on thermal stability and the life estimation are described.

Keywords Poly(aryl ether) · Thermal degradation · Kinetics · Life estimation

List of symbols

A	Frequency factor (min^{-1})
E	Apparent activation energy (kJ mol^{-1})
K	Rate constant (min^{-1})
R	Gas constant = 8.314×10^{-3} ($\text{kJ mol}^{-1} \text{K}^{-1}$)
t	Reaction time (min)
T	Sample temperature (K)
α	$(W_0 - W)/(W_0 - W_\infty)$
dz/dt	Normalized mass-loss rate (min^{-1})
β	Heating rate = dT/dt
W_0	Sample mass at start time (mg)
W	Sample mass at time t (mg)
W_∞	Sample mass at end time (mg)

Introduction

In the last few decades, the demand of advanced industries, in particular, of aerospace, has been a driving force for the development of new low density high performance materials to be employed in structural applications [1, 2]. Aromatic thermoplastic polymers and polyetherketones and polyethersulfones in particular, potentially offer favorable properties that make them very suitable for such applications [3–6]. Poly(aryl ether)s containing phthalazinone, developed by our team, is a kind of material with outstanding thermal stability, mechanical properties, radiation stability, and low flammability. It is well known and is an outstanding candidate in advanced industries such as aerospace. Furthermore, poly(aryl ether)s containing phthalazinone have great potential for general use such as films, structural applications, and coatings [7–11]. For this purpose, the material can be subjected to high temperature not only in the manufacturing, compounding, and processing stage, but also

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in service or during repair [5, 12]. Since thermal stability is related to both the initial temperature and the rate of degradation of polymers, determination of kinetic parameters associated with the degradation processes is an interesting topic of research. Another aspect of thermal analysis is on the durability assessment and lifetime prediction of the product. The study is very important for the improvement of the service performance of the product, especially for critical applications in defense and aerospace, which would help build up user confidence in other potential applications.

As far as the authors are concerned, no reports on the kinetics of the thermal degradation of PPES or PPESK (1/1, the molar ratio of sulfone/ketone) has been found in the published literature. Therefore, this work is intended to evaluate kinetic parameters of thermal degradation of PPES and PPESK (1/1). For this purpose, the data obtained by dynamic thermogravimetry (TG) are employed in three kinetic models: isoconversional Friedman, Kissinger–Akahira–Sunose (K–A–S), and Ozawa method. The methods use different data for calculating kinetic parameters. These three methods present the advantage that they do not require previous knowledge of reaction mechanism for determining the activation energy [13].

Experimental

Materials

The amorphous matrix, poly(phthalazinone ether sulfone ketone) (PPESK) used in this work, was synthesized from bis(4-chlorophenyl) sulfone and 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one according to the procedure reported by Jian et al. [14, 15]. The copolymer PPESK used in this work had a composition of sulfone/ketone molar ratio of 1/1 and the purified polymer was then dried in a vacuum oven at 150 °C for 48 h. The inherent viscosity of the synthesized PPESK (1/1) (the molar ratio of sulfone/ketone) was measured in chloride at 25 °C. The polymers have the following general structures,

DTG measurements

Dynamic programmed thermogravimetric analysis of PPES and PPESK (1/1) was carried out using Netzsch TG 209. The temperature of equipment was calibrated according to the procedure by Netzsch. The temperature calibration was repeated every month. The flow rate of nitrogen was kept constant at 40 mL min⁻¹. Several heating rates of 5, 10, 15, 20, and 30 °C min⁻¹ were carried out and samples of 5.0 ± 0.5 mg held in open alumina crucibles were used, and their mass were measured as a function of temperature.

Kinetic methods

The application of dynamic TG methods holds great promise as a tool for unraveling the mechanisms of physical and chemical processes that occur during polymer degradation [16]. In this paper, three methods have been used to analyze the non-isothermal kinetics of PPES or PPESK(1/1).

Friedman method [17]

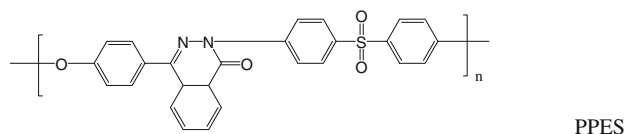
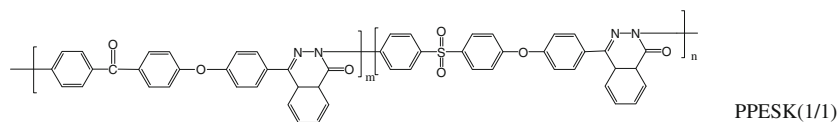
$$\ln\left(\frac{da}{dt}\right) = n \cdot \ln(1 - a) + \ln Z - \frac{E}{RT} \quad (1)$$

where α is the mass loss of the polymer undergoing degradation at time t ; n , Z , E , and R are the decomposition order, pre-exponential factor, activation energy, and universal gas constant (8.3136 J mol⁻¹ K⁻¹), respectively. For $\alpha = \text{const.}$, a plot of $\ln\left(\frac{da}{dt}\right)$ vs. $\frac{1}{T}$ should be a straight line whose slope allows an evaluation of the activation energy.

Kissinger–Akahira–Sunose(K–A–S) method [18]

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{ZR}{Eg(\alpha)}\right) - \frac{E}{RT} \quad (2)$$

From TG curves recorded at different heating rates β_i , temperatures T_i were read off from the conversions



$\alpha_i = 2.5\text{--}20\%$. The activation energies were calculated from the slope of the straight lines $\ln\left(\frac{\beta_i}{T^2}\right)$ vs. $1/T$.

Flynn–Wall–Ozawa method [19]

This is a conversional linear method based on the equation:

$$\log \beta = \log \left[\frac{ZE}{g(\alpha) \cdot R} \right] - 2.315 - \frac{0.457E}{RT} \tag{3}$$

where β , Z , E , and T have the known meanings. For $\alpha = \text{constant}$, the plot $\log \beta$ vs. $1/T$, obtained from thermograms recorded at several heating rates, should be a straight line from the slope of which the activation energy can be evaluated.

Determination of the most probable mechanism function

According to Satava method [20]:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = G(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{-E/RT} dT \tag{4}$$

the low temperature results in a negligible rate of the reaction. Integrating Eq. 4 for a curing time from $t = 0$ to time t with a degree of curing a yields:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = G(\alpha) = \frac{A}{\beta} \int_0^T e^{-E/RT} dT \tag{5}$$

To gain the approximate value of the temperature integration, given $u = \frac{E}{RT}$, $dT = -\frac{E}{R \times u^2} du$, Eq. 5 can be expressed as:

$$\begin{aligned} \int_0^\alpha \frac{d\alpha}{f(\alpha)} = G(\alpha) &= \frac{A}{\beta} \int_0^T e^{-E/RT} dT = \frac{AE}{\beta R} \int_\infty^u \frac{-e^{-u}}{u^2} d(u) \\ &= \frac{AE}{\beta R} P(u) \end{aligned} \tag{6}$$

According to Doyle’s approximation function [21],

$$\lg[G(\alpha)] - \log[P(u)] = \log\left(\frac{AE}{\beta R}\right) \tag{7}$$

$$\lg[P(u)] = -2.315 - 0.4567 \frac{E}{RT} = a + \frac{b}{T} \tag{8}$$

where $G(\alpha)$ is the integral function of conversion, a and b are constant. It is obvious that the right hand side of Eq. 7 is not related with T , if β is given, while $P(u)$ in Eq. 8 is linearly related with $1/T$. $\lg P(u)$ vs. $1/T$ should form a straight line, and $\lg[G(\alpha)]$ vs. $1/T$ must have a linear relationship. If there is only one $G(\alpha)$ that shows linear relationship with $1/T$, the $G(\alpha)$ can be determined as the probable mechanism function. If there are several $G(\alpha)$, the

Table 1 Partial functions of 31 expressions for the most frequently used mechanisms of solid-state processes [23]

No.	Mechanism $G(\alpha)$
8	$\left[\left(\frac{1}{(1+\alpha)^{\frac{1}{3}}} \right) - 1 \right]^2$
9	$-\ln(1-\alpha)$
10~16	$[-\ln(1-\alpha)]^n$ ($n = \frac{2}{3}, \frac{1}{2}, \frac{1}{3}, 4, \frac{1}{4}, 2, 3$)
17~22	$1 - (1-\alpha)^n$ ($n = \frac{1}{2}, 3, 2, 4, \frac{1}{3}, \frac{1}{4}$)

one with an E approximating to E_{Ozawa} , is the probable mechanism function.

Coats–Redfern equation [22]:

$$\ln \left[\frac{G(\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \tag{9}$$

First, the basic data T , α , $\frac{d\alpha}{dT}$ of TG are put into Eq. 9, the plot of $\ln \left[\frac{G(\alpha)}{T^2} \right]$ vs. $1/T$ gives a straight line, combined with 31 mechanism functions [23], E_a can be calculated from the slope $\frac{-E_a}{R}$, then if the E_a is closed to the value calculation by Ozawa method and correlation coefficient r is better, we can determine the probable mechanism function.

In the case of polymers, this integral function, $G(\alpha)$, is shown either as a sigmoidal function or a deceleration function. Table 1 shows different expressions for $G(\alpha)$ for the different solid state mechanisms. These functions have been used well for the estimation of the reaction solid-state mechanism from non-isothermal TG experiments.

Results and discussion

Thermal degradation of PPES and PPESK (1/1)

Figure 1 shows the thermogravimetric (TG) and differential thermogravimetric (DTG) curves for PPESK (1/1) at various heating rates 5, 10, 15, 20, and 30 °C min⁻¹. It can be seen that the polymer is stable up to approximately 450 °C and close roughly about 40% of its mass, which illustrates that the polymer has excellent stability. Additionally, the unresolved DTG peaks observed in the experiments under N₂ flow indicate that PPESK (1/1) degraded through two stages for all five heating rates in an inert environment. The DTG curves show in all cases two incompletely resolved DTG peaks, thus verifying the occurrence of partially overlapped degradation processes. We attribute this degradation to random chain scission (first stage) to which branching and crosslinking become superimposed at higher temperatures (second stage). This was supported by the large mass loss associated with the

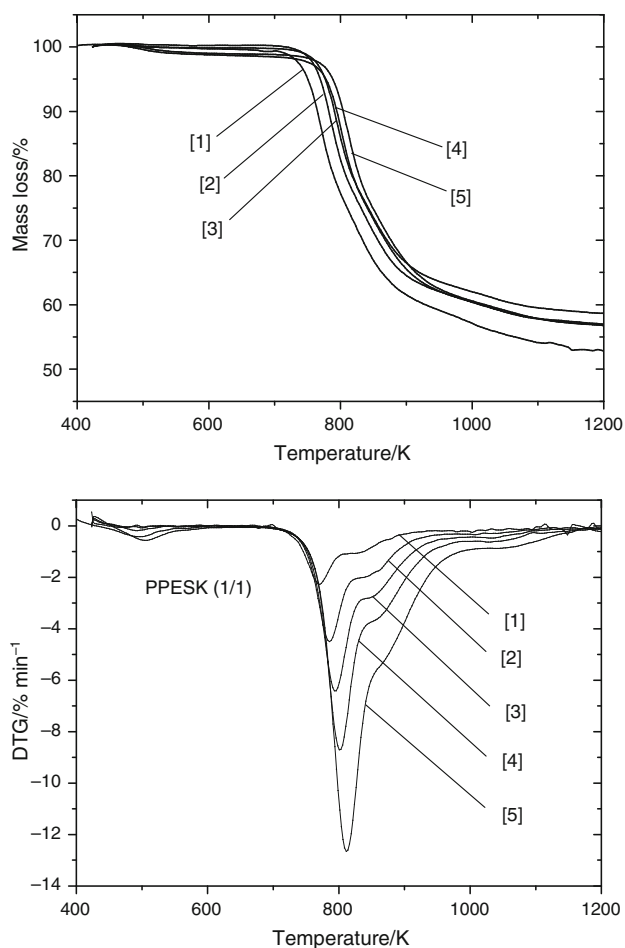


Fig. 1 Dynamic TG and DTG curves for PPESK(1/1) at five heating rates in nitrogen. [1] 5 °C min⁻¹, [2] 10 °C min⁻¹, [3] 15 °C min⁻¹, [4] 20 °C min⁻¹, [5] 30 °C min⁻¹

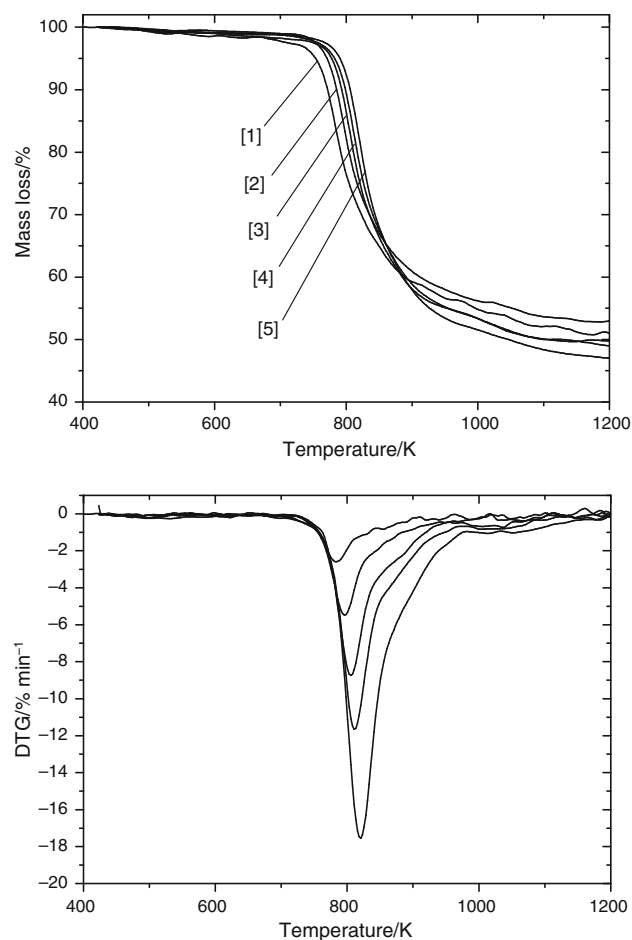


Fig. 2 Dynamic TG and DTG curves for PPES at five heating rates in nitrogen. [1] 5 °C min⁻¹, [2] 10 °C min⁻¹, [3] 15 °C min⁻¹, [4] 20 °C min⁻¹, [5] 30 °C min⁻¹

first sharp DTG peak, which only a small mass loss was associated with the irregular broad second one, with the formation of a residue stable up to 900 °C. These results are in agreement with some literature data in which the occurrence of the processes of random chain scission, branching and crosslinking, has been observed during the thermal degradation of polymers (PEK, PEEK, PES) having similar structures to those of our polymers [24–26]. Additionally, higher heating rates of degradation occur at different temperatures for various heating rates, a higher heating rate shifts the rate curve to a higher temperature range, and also results in a higher peak rate. Similar results also were found for PPES in Fig. 2.

Characteristic degradation temperature obtained from these thermograms is shown in Table 2. It can be concluded that the kinetic parameters of PPES and PPESK (1/1) change with the heating rate. The results show that the onset temperature of TG, peak temperature of DTG, decomposition temperature of T_d , $T_{5\%}$, and T_m mass loss all followed the order PPES > PPESK (1/1). Most of T_d , $T_{5\%}$, T_m , H_m and α_m

values increasing significantly with as the heating rate changes from 5 to 30 °C min⁻¹. The average sensitivities of H_m , α_m , and T_m to heating rate for PPES, respectively, are $6.9 \times 10^{-3} \text{K}^{-1} \text{min}$ ($\partial H_m / \partial \beta$), $1.37 \times 10^{-3} \text{K}^{-1} \text{min}$ ($\partial \alpha_m / \partial \beta$) and 1.7min ($\partial T_m / \partial \beta$), indicating that the T_m varies sensitively with heating rate, whereas H_m and α_m do insensitively. The polymer, PPESK (1/1), has similar results.

The Friedman method has been primarily employed to analyze the TG data of PPES or PPESK (1/1), which is probably the most general of the derivative techniques. This method is based on the intercomparison of the rates of mass loss dx/dt with different linear heating rates β for a given fractional mass loss. The activation energy was determined by using the Friedman method from a liner fitting of $\ln(dx/dt)$ versus $1000/T$ over a wide range of conversions. The results of the Friedman analysis are given in Fig. 3, which shows that the best fitting straight lines are nearly parallel, indicating that the activation energies at different degrees of conversion are almost similar and confirm the validity of the approach used. Similarly,

Table 2 Kinetic parameters of thermal degradation of PPES and PPESK(1/1)

Heating rate/ °C min ⁻¹	PPES				PPESK(1/1)			
	$T_d/T_{5\%}/K$	T_m/K	$H_m/\%$	$\alpha_m/\%$	$T_d/T_{5\%}/K$	T_m/K	$H_m/\%$	$\alpha_m/\%$
5	709/761	780	2.79	12.48	716/751	770	2.38	12.22
10	745/775	794	5.73	13.32	744/769	787	4.68	12.23
15	746/783	806	9.20	15.85	745/777	794	6.83	11.29
20	763/791	812	12.53	15.95	545/779	801	9.37	13.10
30	778/800	820	19.97	15.71	605/790	812	15.44	13.32

Note: T_d temperature for 1% mass loss, $T_{5\%}$ temperature for 5% mass loss, T_m peak temperature, H_m peak height, α_m conversion at peak temperature

according to the above-mentioned equations, the plots of $\ln(\beta/T^2)$ vs. $1000/T$ (K–A–S) and $\log \beta$ vs. $1000/T$ (Ozawa) corresponding to different conversions α can be obtained by a linear regression of least-square method, respectively. The K–A–S and Ozawa analysis results are presented in Figs. 4 and 5. Activation energies calculated from the slopes corresponding to the different conversions for PPES or PPESK (1/1) have been summarized in Tables 3 and 4, respectively. If E_a values are independent of α , the decomposition may be a simple reaction [27, 28]. However, if E_a values are dependent on α should, the decomposition should be interpreted in terms of multi-step reaction mechanisms [29–36]. The activation energy values of PPES, found to be between 279.97 and 359.77 kJ mol⁻¹ by using Friedman method, are higher than those produced by the K–A–S and Ozawa methods. The activation energy values increase largely in the increasing α (2.5–20%) (Table 3), so we draw a conclusion that PPES may be a multi-step reaction. The activation energy values of the reduction step were calculated to be between 179.65 and 291.45 kJ mol⁻¹ by using the K–A–S method, and are close to the values calculated by the Ozawa method. It is clear in Table 3 that the activation energy assumes a value of 179.65 kJ mol⁻¹ at the beginning of the decomposition reaction and, with increasing mass loss, up to a value of 5291.45 kJ mol⁻¹ (K–A–S method). This increasing dependence of E_a on α causes us to draw the conclusion that the decomposition reaction process PPES is indeed a complex kinetic mechanism (successive or parallel reactions, competitive reactions, etc.). This result shows that the importance of the isoconversional methods consists just in their capacity to evaluate the E_a versus α without the knowledge of the kinetic model. The average activation energies of PPESK (1/1) calculated by the Friedman, K–A–S, and Ozawa methods are obtained to be 231.90, 222.93, and 224.22 kJ mol⁻¹, respectively. It is seen that the activation energy values calculated by the K–A–S method are close to those obtained by the Ozawa method (Table 4). The decomposition reaction mechanism of PPESK (1/1) is similar to that of PPES.

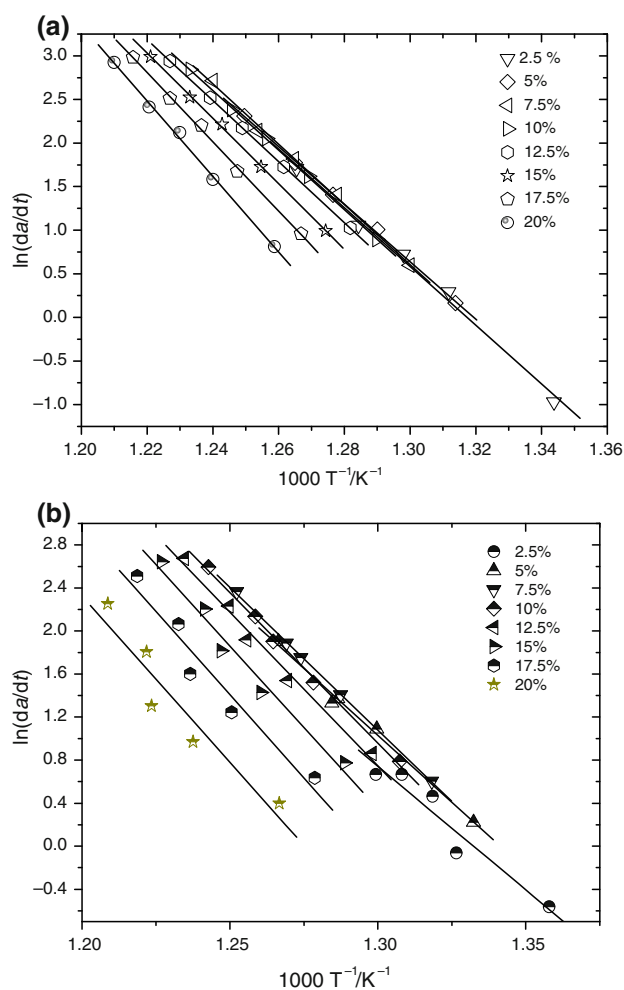


Fig. 3 The isoconversional straight lines calculated by Friedman equation. PPES (a) and PPESK (1/1) (b)

Through analyzing the activation energies obtained by these three methods, we could find that the E values for PPES are much higher than those for PPESK (1/1), no matter what method has been used. This analysis reveals that PPES has more thermal stability than PPESK (1/1). The sulfone group exhibits stronger electronegative characteristics that

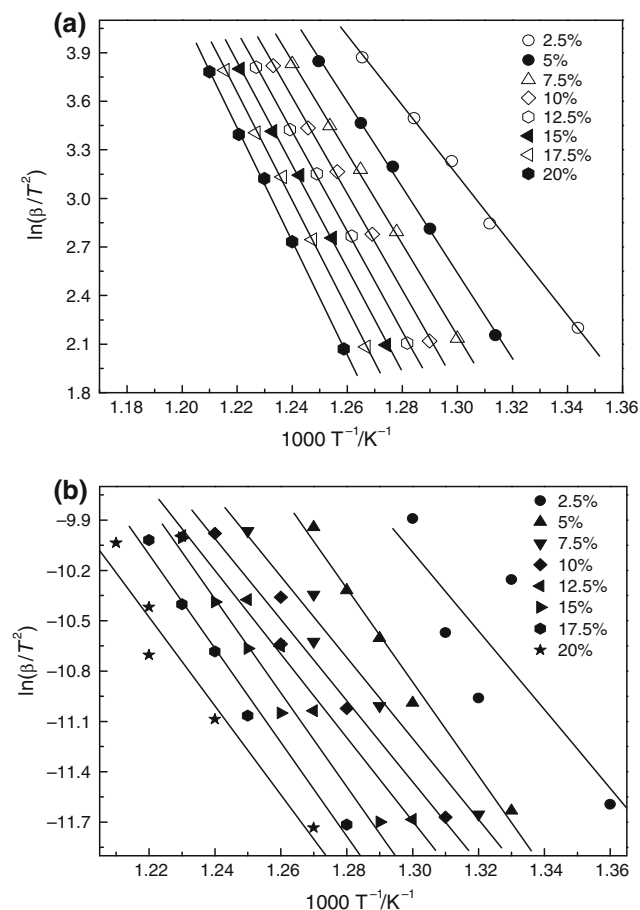


Fig. 4 The isoconversional straight lines calculated by K–A–S equation. PPES (a) and PPESK (1/1) (b)

lead to the delocalization of π -electrons from the aromatic rings than ketone group does, the main chain of PPES has more rigidity than that of PPESK (1/1).

Determination of kinetic mechanism [37]

Study on all 31 mechanism functions, from which the selected mechanism functions are listed in Table 1, deduces that function numbers 5, 9, 12, 14, and 30 have linear relationship with $1/T$. The activation energy can be calculated from the Coats and Redfern equation combined with conversion functions 5, 9, 12, 14, and 30. The most probable mechanism function was assumed to be the one with the high correlation coefficient and with activation energies from the Coats and Redfern method closed to the optimized values from the Ozawa and K–A–S methods. The results show that only function number 9, whose decomposed energy is 266 kJ mol^{-1} , is closed to E_{Ozawa} . This can adequately validate that the non-isothermal kinetic parameters of thermal degradation of PPESK or PPES can be reliably calculated with correctly chosen $G(\alpha)$ functions. Based on these results, we can draw a conclusion that the

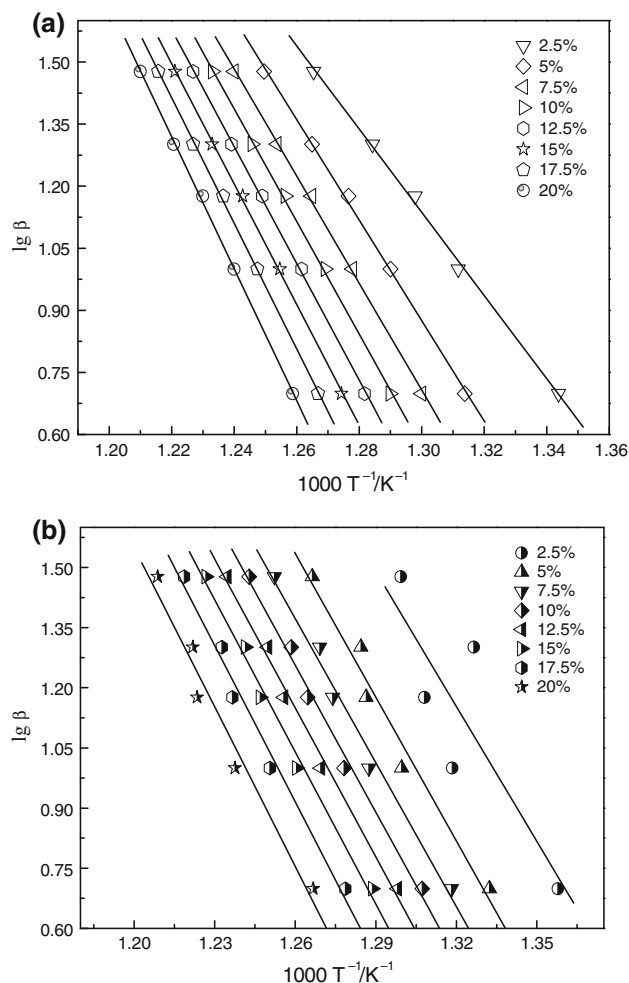


Fig. 5 The isoconversional straight lines calculated by Ozawa equation. PPES (a) and PPESK (1/1) (b)

thermal degradation mechanism of PPESK(1/1) involves formation of nucleation and growth of nucleation, and the order of reaction of the degradation process is one ($n = 1$). However, the thermal degradation mechanism of PPES is a phase boundary controlled reaction, and order of reaction $n = 2$ according to this method.

Lifetime estimation

The lifetime t_f of polymer to failure can be determined when the mass loss reaches 5%. On the basis of the kinetic data derived from dynamic nonisothermal TG, value E , n , and $\ln Z$ listed in Table 3, the lifetime estimation for PPES generated from the mass loss of 5% is predicted by using the following equation [38]:

$$t_f = \frac{(1 - 0.95^{1-n}) \cdot \exp\left(\frac{E}{RT}\right)}{Z(1-n)} \quad (n \neq 1) \quad (10)$$

According to Eq. 10, the lifetime estimation of pure components at 100, 200, 300, 350, 400, 450, and 500 °C

Table 3 Kinetic parameters of thermal degradation of PPES calculated by three equations

PPES $\alpha/\%$	Friedman method		K–A–S method		Ozawa method	
	$E_a/\text{kJ mol}^{-1}$	$\ln Z/\text{min}^{-1}$	$E_a/\text{kJ mol}^{-1}$	$\ln Z/\text{min}^{-1}$	$E_a/\text{kJ mol}^{-1}$	$\ln Z/\text{min}^{-1}$
2.5	279.97	45.03	179.65	25.15	182.83	31.26
5	274.39	44.19	219.51	31.26	220.93	37.45
7.5	287.15	46.12	234.59	33.56	235.38	39.79
10	283.68	45.50	247.47	35.48	247.70	41.76
12.5	290.57	46.38	256.77	36.83	256.61	43.14
15	311.60	49.29	265.28	38.03	264.77	44.38
17.5	330.21	51.76	276.92	39.64	275.89	46.04
20	359.77	55.75	291.45	41.62	289.76	48.06
Average	302.17	48.00	246.46	35.20	246.73	41.49

Table 4 Kinetic parameters of thermal degradation of PPESK (1/1) calculated by three equations

PPESK (1/1) $\alpha/\%$	Friedman method		K–A–S method		Ozawa method	
	$E_a/\text{kJ mol}^{-1}$	$\ln Z/\text{min}^{-1}$	$E_a/\text{kJ mol}^{-1}$	$\ln Z/\text{min}^{-1}$	$E_a/\text{kJ mol}^{-1}$	$\ln Z/\text{min}^{-1}$
2.5	190.99	30.63	202.33	14.65	204.12	35.23
5	206.85	33.42	215.86	16.67	217.22	37.27
7.5	220.74	35.67	215.94	16.72	217.76	37.39
10	232.59	37.43	220.78	17.47	222.13	38.11
12.5	237.76	38.06	223.78	17.90	225.04	38.56
15	251.60	39.85	229.04	18.62	230.14	39.29
17.5	257.60	40.33	235.39	19.44	236.32	40.12
20	257.23	39.68	240.29	19.94	241.05	40.64
Average	231.90	36.88	222.93	17.68	224.22	38.33

Table 5 Estimated lifetime t_f of PPES based on the mass loss $\alpha = 5\%$

	t_f/min						
	100°C	200°C	300°C	350°C	400°C	450°C	500°C
PPES	8.62×10^{17}	4.4×10^{10}	7.88×10^5	1.24×10^4	362.6	17.3	1.22

are reported in Table 5. The lifetime estimation of pure PPES at 100 °C is 8.62×10^{17} min. The lifetime estimation of the PPES is 7.88×10^5 min as the temperature increases to 300 °C, which demonstrates that the polymer possesses excellent thermal resistance. The thermal degradation mechanism of PPESK (1/1) is randomly nucleating and nucleus growth, with order of reaction $n = 1$, so it does not fit for the equation.

Conclusions

The kinetics of thermal degradation of poly (phthalazine ether sulfone) (PPES) and poly (phthalazine ether sulfone ketone) PPESK (1/1) in nitrogen have been

studied at several heating rates by thermogravimetry analysis (TG). The kinetic parameters, including the reaction active energy and the frequency factor of degradation reaction for PPES and PPESK (1/1), have been analyzed by isoconversional Friedman, Kissinger–Akahira–Sunose (K–A–S), and Ozawa methods. The results have shown that PPES is more stable than PPESK (1/1). For both PPES and PPESK (1/1), T_m is more sensitive to the variation of the heating rate, whereas H_m and α_m is less sensitive. According to the Satava method, the thermal degradation mechanism of PPESK (1/1) is randomly nucleating and nucleus growing, and order of reaction $n = 1$. The thermal degradation mechanism of PPES, however, is a phase boundary controlled reaction and has order of reaction $n = 2$.

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