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The thermal decomposition kinetics of poly(ether–ether–ketone) (PEEK) and its carbon fiber composite [α]

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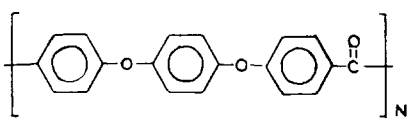
Abstract

The thermal decomposition behavior of poly(ether–ether–ketone) (PEEK) and its carbon fiber composite, APC-2, in nitrogen and oxygen has been investigated by thermogravimetry. The parameters of the decomposition kinetics obtained are as follows. In nitrogen, the apparent activation energies of PEEK and APC-2 are 198.2 kJ mol^{-1} and 210.3 kJ mol^{-1} respectively, while in oxygen they are 145.2 kJ mol^{-1} and 151.0 kJ mol^{-1} correspondingly. The results show that the thermal stability of either PEEK or APC-2 in nitrogen is better than that in oxygen, and the thermal stability of APC-2 is better than that of PEEK under the same experimental conditions.

INTRODUCTION

Poly(ether–ether–ketone) (PEEK) is a new high performance engineering thermoplastic. The chain structure of PEEK is



The main chain of PEEK consists of benzene rings, which enable PEEK to have excellent heat resistance and a long service life below 200 °C [1]. Moreover, PEEK also has good processability, mechanical properties, solvent resistance and high energy radiation resistance [1,2]. Because of these excellent properties, PEEK can take the place of thermosetting resins as a matrix for high performance composites. For example, an aromatic polymer composite, APC, developed by Imperial Chemical Industries (ICI), UK, is

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based on continuous unidirectional carbon fibers embedded in a PEEK matrix.

Thermal stability is one of the most important factors for a high performance engineering plastic's service life. The study of its thermal decomposition kinetic process will be important for predicting its thermal stability. This paper deals with thermal decomposition processes of PEEK and its carbon fiber composite by thermogravimetry (TG) in different atmospheres. Our results of the kinetic analysis of the thermal decomposition processes provide some basic data for establishing the conditions of processing and service of PEEK and its carbon fiber composite.

EXPERIMENTAL

The samples used in this study are PEEK and the PEEK–carbon fiber composite (APC-2) produced by ICI. The PEEK sample is a light yellow transparent amorphous film with thickness of 0.1 mm. The APC-2 sample consists of continuous unidirectional carbon fibers embedded in a PEEK matrix with a thickness of 0.18 mm. The carbon fiber content determined by TG was 66 wt.%, close to the value of 68 wt.% reported in the literature [3]. All the samples as received were dehydrated in a vacuum oven at 50 °C for 10 h and were cut into small pieces for TG measurements.

The decomposition behaviors of PEEK and APC-2 under different heating conditions were investigated separately in nitrogen and in oxygen by using a Perkin–Elmer Thermogravimetric Analyzer TGS-2, which is on-line with a computer for data acquisition and analysis. The temperature range was specified in the range 60–1000 °C and the heating rates were 5, 10, 20 and 40 °C min^{-1}. A mathematical calculation method for non-isothermal kinetic analysis, proposed by Flynn and Wall [4], was used to carry out the kinetic analysis from the experimental TG results. The thermal decomposition activation energy is calculated from the equation

$$\Delta E = -\frac{R}{b}\left[\frac{\mathrm{d}\log\beta}{\mathrm{d}(1/T_\mathrm{p})}\right] \tag{1}$$

where ΔE is the activation energy of decomposition, R is the gas constant, 8.314 J mol^{-1} K^{-1}, T_p is the corresponding temperature at a constant weight loss, β is the heating rate and b is a constant (0.457).

RESULTS AND DISCUSSION

Thermal decomposition features of PEEK and APC-2

The thermogravimetric cuves of PEEK and APC-2 at a heating rate of 20 °C min^{-1} in nitrogen are shown in Fig. 1. It can be seen that no obvious

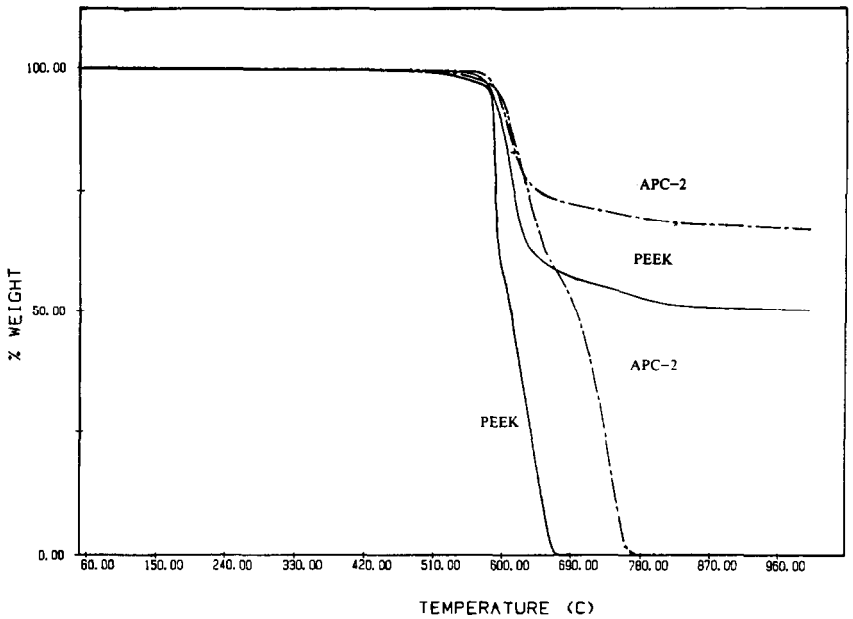

Fig. 1. TG curves of PEEK and APC-2 decomposing in different atmospheres at a heating rate of 20 °C min^{-1}: ———, data for PEEK; ·–·–·, data for APC-2.

weight loss from PEEK or APC-2 occurs at temperatures up to 550 °C, whereas a distinct weight loss takes place from both PEEK and APC-2 at temperatures above 550 °C. The extrapolated onset temperatures of the TG curves in Fig. 1 are listed in Table 1. Also listed in Table 1 are the maximum weight losses, the temperatures at which the weight losses approach the maxima and the values of ΔE in nitrogen and in oxygen for both samples.

In a nitrogen atmosphere, even when the temperature was as high as 1000 °C, none of the samples showed complete loss of weight. In an oxygen atmosphere, however, the weight losses of both PEEK and APC-2 terminated at 1000 °C. The TG curves of PEEK and APC-2 at the same heating rate in oxygen are also shown in Fig. 1. It can be seen that weight losses of both

TABLE 1

Comparison of thermal stability parameters of PEEK and APC-2 by TG

Sample	Atmosphere	Extrapolated onset temp. [a] (°C)	Temp. at max. wt. loss [a] (°C)	Max. wt. loss [a] (%)	ΔE (kJ mol^{-1})
PEEK	N_2	584	1000	49	198.2
APC-2	N_2	585	1000	17	210.3
PEEK	O_2	582	680	100	145.2
APC-2	O_2	589	780	100	151.0

[a] Heating rate, 20 °C min^{-1}.

PEEK and APC-2 begin near 500 °C and they become pronounced when the temperature reaches 600 °C. It is clear that in either N_2 or O_2 the APC-2 begins to decompose at a higher temperature compared with PEEK under the same conditions. In oxygen, the temperature for 100% weight loss for PEEK is 680 °C, while it is 780 °C for APC-2. In Fig. 1, the TG curves of PEEK and APC-2 appear both as basically simple processes in a nitrogen atmosphere. In contrast, in oxygen the TG curves become complicated. In the first stage, in the range 500–580 °C, there occurred only slight losses in weight from both samples, and the percentage weight losses were less than 5%. The rates of weight loss increased beyond 600 °C. With a rise in temperature a turning point appeared in each curve from which the rate of weight loss slowed down, and then the second stage of weight loss appeared until the weight loss reached 100%. The above experimental results indicate that the thermal stabilities of both PEEK and APC-2 in nitrogen are better than those in oxygen, and the thermal stability of APC-2 is better than that of PEEK under the same experimental conditions.

Effect of heating rate

The TG measurements were conducted at four heating rates of 5, 10, 20 and 40 °C min^{-1} in N_2 and O_2 separately. The TG curves obtained at these

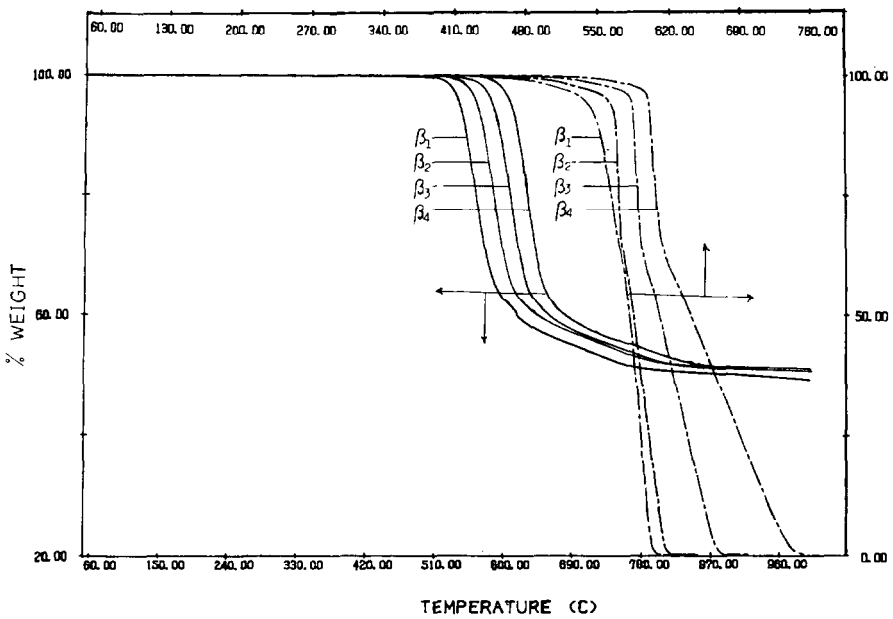

Fig. 2. TG curves of PEEK decomposing at different heating rates: ———, data obtained in N_2; ·–·–·, data obtained in O_2; β_1, β_2, β_3 and β_4 denote the heating rates of 5, 10, 20 and 40 °C min^{-1} respectively.

four heating rates for PEEK are shown in Fig. 2 and those for APC-2 in Fig. 3. In nitrogen, TG curves of both samples shift regularly toward higher temperature with increasing heating rate. However, in oxygen the TG curves become more complex with increasing heating rate. It can be seen from Figs. 2 and 3 that the dash–dot curves shift regularly with heating rate at smaller percentages of weight loss, but quite irregularly at higher percentages of weight loss. It is of interest to note the effect of heating rate on the decomposition rate, i.e. the slope of each curve in the section of weight loss of more than 40%, where the decomposition rate appears evidently to decrease with increasing heating rate. We consider this tendency to decrease to be related to the reaction rate between the sample and oxygen. As there is plenty of time for the sample to react with oxygen at a lower heating rate, which is favorable for further decomposition, the TG curves appear to be more regular. However, when the heating rate is increased to as high as 40 °C min^{-1}, there may not be enough time for the sample to react with oxygen because there is insufficient time for the evolved decomposition products to diffuse away from the sample–oxygen interface. In other words, the decomposition rate is not only related to the area of the interface between the sample and oxygen but also depends on the diffusion rate of the decomposition products.

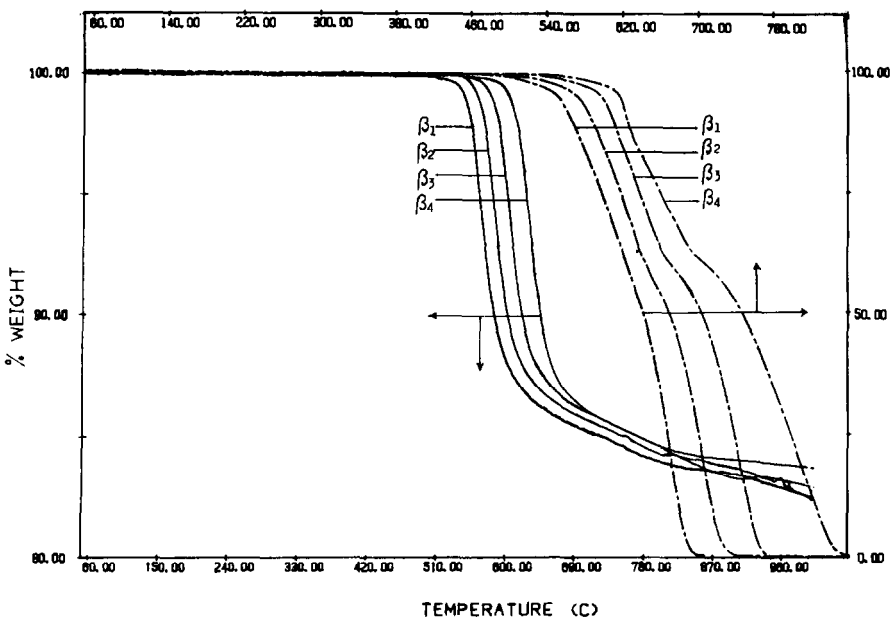

Fig. 3. TG curves of APC-2 decomposing at different heating rates: ———, data obtained in N_2; ·–·–·, data obtained in O_2; β_1, β_2, β_3 and β_4 denote the heating rates of 5, 10, 20 and 40 °C min^{-1} respectively.

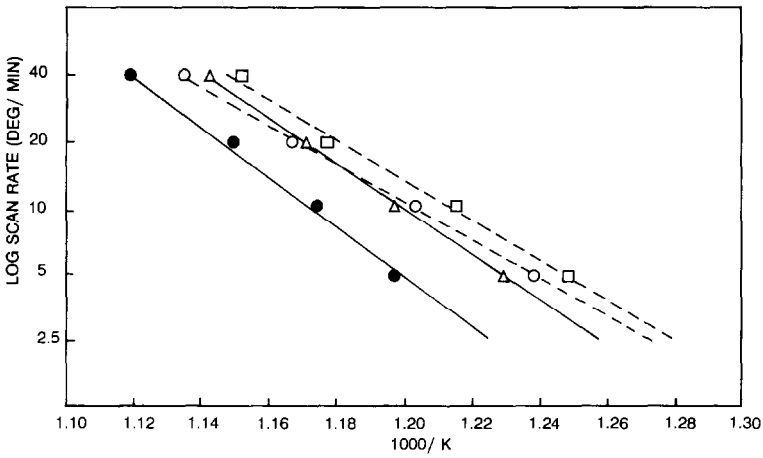

Fig. 4. Plots of log β vs. $1/T_p$ for PEEK and APC-2 in N_2 and O_2: ———, data obtained in N_2; — — —, data obtained in O_2; △ and □, data for PEEK; ● and ○, data for APC-2.

Kinetics of thermal decomposition

For the kinetic analysis we took the readings of temperature, T_p, at a constant weight loss from TG curves at different heating rates, β_1, β_2, β_3 and β_4. According to eqn. (1), it was therefore possible to plot log β against $1/T_p$ at several weight losses, viz. 2.5, 5 and 10%. From the slope of the plot of log β vs. $1/T_p$, the activation energy ΔE can be obtained. Figure 4 shows the plots of log β vs. $1/T_p$. Each was evaluated by taking an average over three original plots at weight losses of 2.5%, 5% and 10% respectively. The values of ΔE obtained from the slopes of the plots in Fig. 4 are given in Table 1. In nitrogen, the apparent activation energies of PEEK and APC-2 are 198.2 kJ mol^{-1} and 210.3 kJ mol^{-1}, respectively, while the corresponding values are 145.2 kJ mol^{-1} and 151.0 kJ mol^{-1} in oxygen. The results obtained from kinetic analysis once again indicate that the thermal stabilities of either PEEK or APC-2 in nitrogen are better than those in oxygen, and, additionally, that the thermal stability of APC-2 is better than that of PEEK under the same experimental conditions.

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