

Kinetic Study of the Thermal Degradation of Poly(aryl ether ketone)s Containing 2,7-Naphthalene Moieties

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Received 16 September 2006; accepted 14 March 2007

DOI 10.1002/app.26548

Published online 10 October 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The degradation of poly(aryl ether ketone) containing 2,7-naphthalene moieties was subjected to dynamic and isothermal thermogravimetry in nitrogen and air. The dynamic experiments showed that the initial degradation temperature, temperature for 5% weight loss, and temperature corresponding to the maximum degradation rate of poly(aryl ether ketone) containing 2,7-naphthalene moieties were a little higher than those of poly(ether ether ketone) and almost independent of the 2,7-naphthalene moiety content. The thermal stability of poly(aryl ether ketone) containing 2,7-naphthalene moieties in air was substantially less than that in nitrogen, and the degradation mechanism was more complex. The results obtained under

the isothermal conditions were in agreement with the corresponding results obtained in nitrogen and air under the dynamic conditions. In the dynamic experiments, the apparent activation energies for the degradation processes were 240 and 218 kJ/mol in nitrogen and air for the second reaction stage as the heating rate was higher than 5°C/min. In the isothermal experiments, the apparent activation energies for the degradation processes were 222 and 190 kJ/mol in nitrogen and air, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1310–1315, 2008

Key words: kinetics (polym.); poly(ether ketones); thermal properties; thermogravimetric analysis (TGA)

INTRODUCTION

In recent years, aromatic poly(ether ketone)s have achieved a remarkable position among other thermoplastic polymers because of their unique combination of toughness, stiffness, thermooxidative stability, electrical performance, flame retardancy, and retention of physical properties at high temperatures. They have been successfully applied in many fields such as aviation, space flight, nuclear energy, communications, telecommunications, petroleum, machine manufacturing, and traffic to renew old products. However, because of the booming development of new science and technology in the world, high-performance materials have been required extensively and urgently. To improve the performance of poly(aryl ether ketone)s further and fulfill the requirements of some extreme conditions such as high temperatures, naphthalene rings have been introduced into polymer structures.^{1–4}

The thermal stability of a polymeric material is one of the most important properties for both processing and applications. Thermogravimetry (TG) is a technique widely used to characterize the thermal

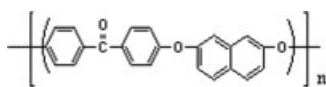
degradation of polymer materials. In this study, TG and differential thermogravimetry (DTG) measurements of poly(aryl ether ketone) (PAEK) containing 2,7-naphthalene moieties were reported. The thermal degradation temperature and kinetics of the polymer were studied under nonisothermal and isothermal conditions. The weight-loss curves were obtained in both nitrogen and air atmospheres, and its degradation behavior with respect to poly(ether ether ketone) (PEEK) was examined.

EXPERIMENTAL

PAEK copolymers with various compositions of 2,7-dihydroxy naphthalene (2,7-DHN) and hydroquinone (HQ) were synthesized by the nucleophilic substitution reaction of 4,4'-difluorobenzophenone with HQ in the presence of sodium carbonate and potassium carbonate.¹ The structural formula of PAEK containing 2,7-naphthalene moieties (PANЕК; the molar ratio of HQ to 2,7-DHN was 0 : 100) is shown in Scheme 1.

The glass-transition temperature (T_g), melting temperature (T_{melt}), and cold-crystallization temperature (T_c) were determined with a Mettler–Toledo 821e differential scanning calorimeter. Both the heat flow and temperature calibrations were performed with the procedures suggested by the supplier and

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Scheme 1 Structural formula of PAEK containing 2,7-naphthalene moieties.

reported in the operating instructions for the equipment. Samples of about 4–6 mg, held in sealed aluminum crucibles, and a heating rate of 20°C/min under a dynamic nitrogen flow were used for the measurements.

Thermogravimetric analysis was performed on a PerkinElmer TGA 7 instrument. The temperature calibration of the thermobalance was made according to the procedure suggested by the user manual for the equipment. This procedure is based on the changes in the magnetic properties of three metal samples (aluminum, nickel, and iron) at their Curie points (154.2, 355.3, and 780.0°C, respectively). Degradation experiments were performed under both isothermal and dynamic heating conditions with samples of 4–8 mg placed in alumina open crucibles under either nitrogen or air at a flow rate of 20 mL/min, and the weight losses of the samples as a function of the temperature or time were measured. The degradation experiments under dynamic conditions were carried out through the heating of samples from 200 to 800°C at the chosen heating rates, and the following characteristic degradation temperatures were selected: the initial degradation temperature (T_i ; i.e., the temperature for 1% weight loss), the temperature for 5% weight loss (T_5), and the temperature corresponding to the maximum degradation rate (T'). In the experiments under isothermal conditions, the samples were quickly heated from 35°C to the selected temperature and then maintained at that temperature for 90 min.

RESULTS AND DISCUSSION

Figure 1 shows the differential scanning calorimetry (DSC) thermograms of quenched samples of the copolymers. The composition dependences of T_g , T_{melt} , and T_c for the copolymers are shown in Figure 2. With an increasing content of the naphthalene moieties, T_g and T_c increase, whereas T_{melt} decreases. As the molar fraction of 2,7-DHN is higher than 0.3, no T_c and T_{melt} can be detected. As everyone knows, the important factor influencing T_g is the chain flexibility, which is governed by the nature of the chemical groups that constitute the main chain. Because the volume of naphthalene is larger than that of phenylene, the incorporation of 2,7-naphthalene moieties into PEEK will impede the rotation and stiffen the main chain, thereby causing an increase in T_g . Moreover, the presence of naphthalene moieties in PEEK will destroy the regularity of the chain, reduce

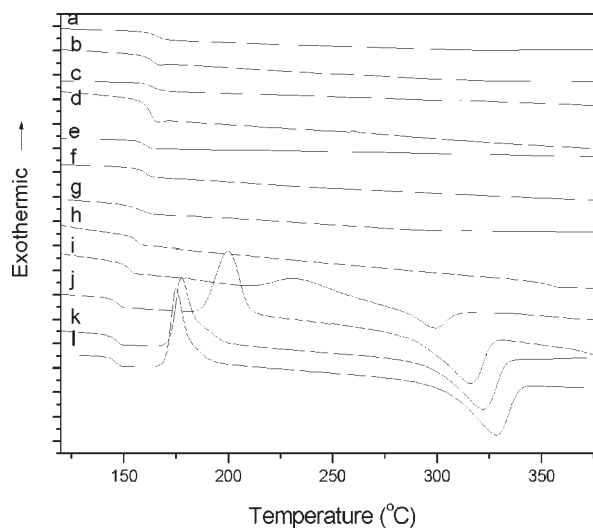


Figure 1 DSC thermograms recorded during the first runs at 20°C/min for quenched samples of PAEK copolymers with the following molar fractions of 2,7-DHN: (a) 1.00, (b) 0.90, (c) 0.80, (d) 0.70, (e) 0.60, (f) 0.50, (g) 0.40, (h) 0.30, (i) 0.20, (j) 0.15, (k) 0.10, and (l) 0.05.

the ability of crystallization, and hence cause the increase in T_c and decrease in T_{melt} with increasing 2,7-naphthalene moiety content. As the molar fraction of 2,7-naphthalene moieties is high enough, no crystallization takes place at all.

Dynamic experiments

The TG curves of PANEK, PEEK, and some copolymers measured under a nitrogen atmosphere at a heating rate of 20°C/min are shown in Figure 3, and the influence of the 2,7-naphthalene moiety content on T_i , T_5 , and T' is shown in Figure 4. To compare

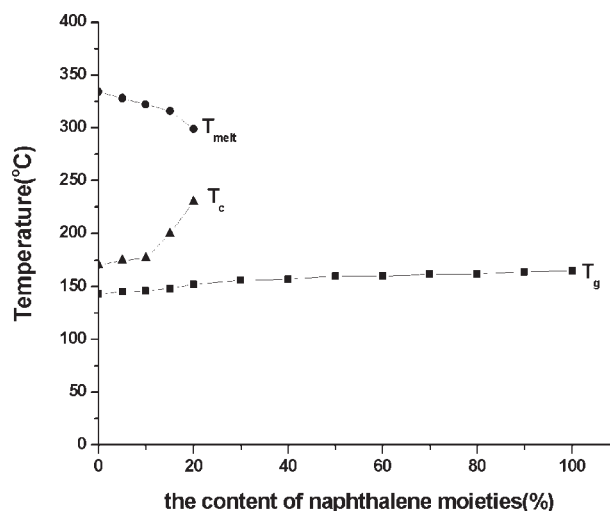


Figure 2 T_g , T_{melt} , and T_c of copolymers with different molar fractions of 2,7-DHN.

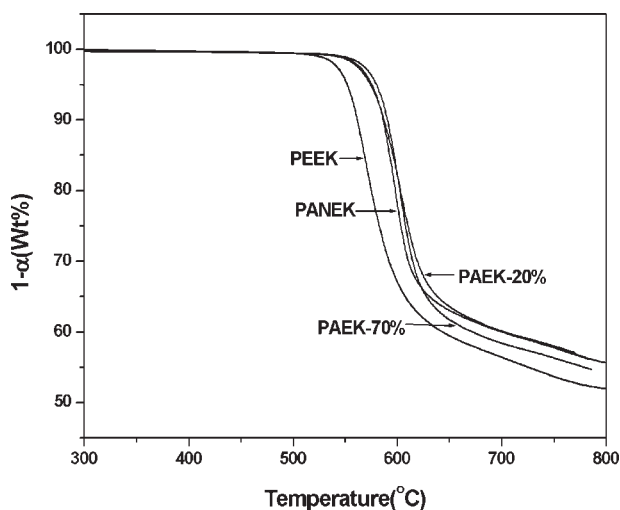


Figure 3 TG curves of PANEK, PEEK, PAEK-20%, and PAEK-70% in nitrogen at a heating rate of 20°C/min.

the experimental results and the theoretical values,^{5,6} the linearly additive values of PANEK and PEEK, taken as the theoretical values, are marked by dotted lines. T_i , T_5 , and T' of PANEK are a little higher than the corresponding values of PEEK. The characteristic temperatures of the copolymers are higher than the linearly additive values of the homopolymers and almost independent of the molar ratio of 2,7-naphthalene moieties.

For clarifying the kinetics of degradation, experiments with PANEK, PEEK, and some copolymers were performed at heating rates of 1, 2, 5, 10, 20, and 30°C/min from 200 to 800°C in nitrogen and air. To make the picture clearer, only some DTG curves at a heating rate of 20°C/min, taken in nitrogen and air, are presented in Figures 5. The DTG curves obtained under the nitrogen condition show one

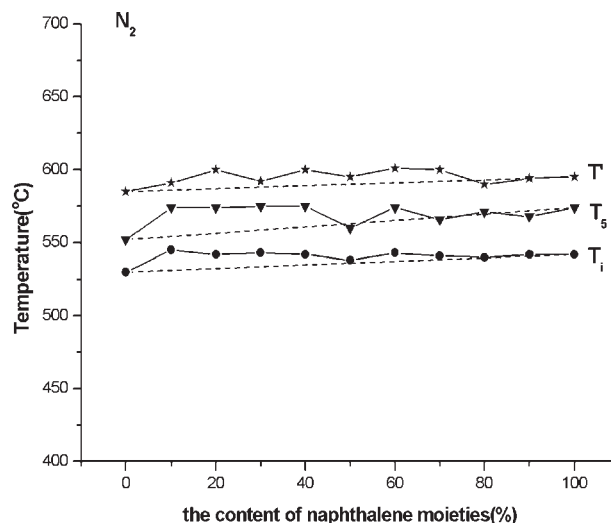


Figure 4 T_i , T_5 , and T' of copolymers with different molar fractions of 2,7-DHN. The continuous lines show the experimental values, and the dashed lines show the values calculated according to theory.

peak, whereas two peaks can be observed for the samples degraded in air. This implies that the weight loss occurs in one stage in nitrogen but in two stages in air.

There are many methods for the kinetic evaluation of TG thermal degradation data.^{7–20} In this study, the Kissinger method²¹ has been used to determine the apparent activation energy (E_a) associated with the degradation process. The expression derived by Kissinger is as follows:

$$\ln(\Phi/T_m^2) = \ln(nRAW_m^{n-1}/E_a) - E_a/RT_m \quad (1)$$

where Φ is the heating rate, T_m is the temperature at the maximum rate of weight loss, n is the apparent

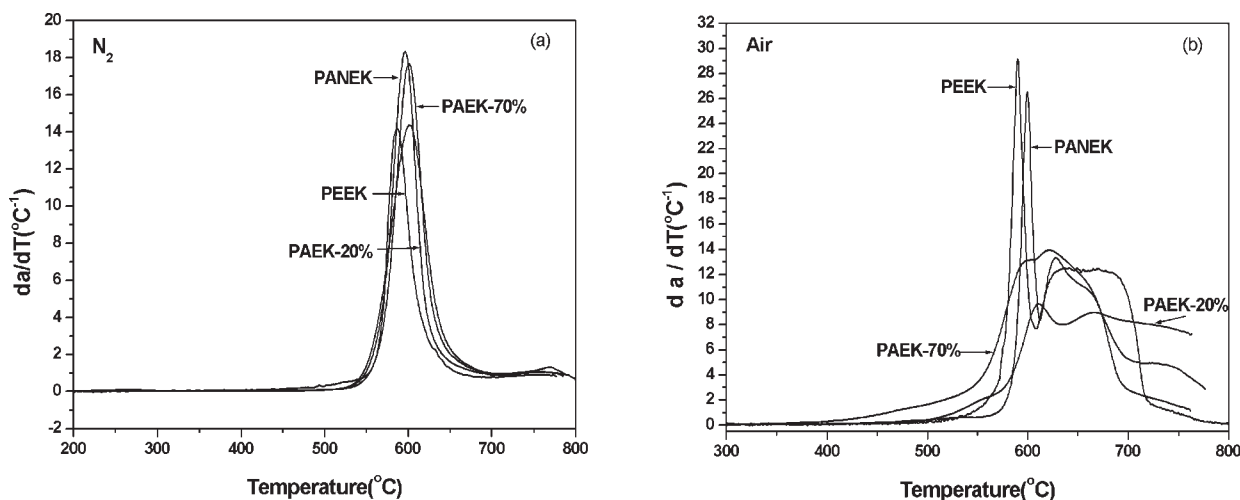


Figure 5 DTG curves of PANEK, PEEK, PAEK-20%, and PAEK-70% in (a) nitrogen and (b) air at a heating rate of 20°C/min.

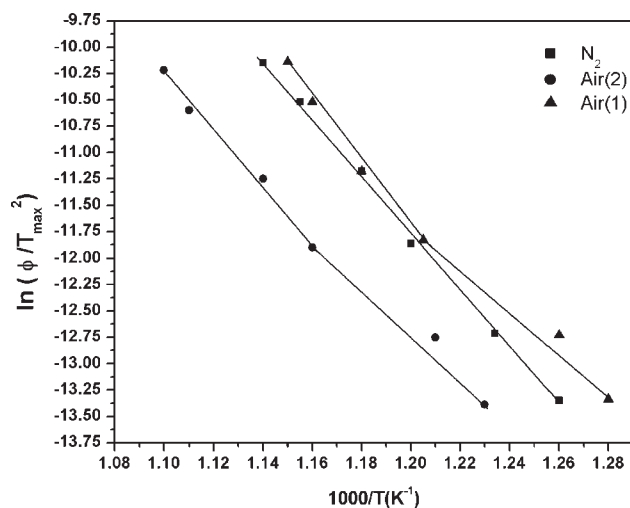


Figure 6 Kissinger plots of PANEK degraded in nitrogen and air (first- and second-stage data).

reaction order, R is the universal gas constant, A is the pre-exponential factor, and W_m is the weight of the sample at the maximum rate of weight loss. Thus, the value of E_a can be determined from a plot of $\ln(\Phi/T_m^2)$ versus $1/T_m$ for the various heating rates.

The plots obtained for PANEK degraded in nitrogen and the plots for the first and second reaction stages in air are shown in Figure 6. A single-approach straight line was obtained for the experiments performed in nitrogen, and an E_a value of 240 kJ/mol was calculated from the slope, confirming the apparently simple kinetics in nitrogen. Two curves corresponding to the two reaction stages in air were obtained, each of which consists of two segments corresponding to the two groups of heating rates. Consequently, the calculated E_a values at the fast heating rates ($\geq 5^\circ\text{C}/\text{min}$) of 254 and 218 kJ/mol for the first and second reaction

TABLE I
Apparent E_a Values of PANEK and PEEK

	Dynamic			Isothermal	
	N ₂	Air		N ₂	Air
		First degradation stage	Second degradation stage		
PANEK	240	254 ^a 181 ^b	218 ^a 166 ^b	222	190
PEEK	194	238 ^a 167 ^b	188 ^a 139 ^b	194	178

^a Heating rate $\geq 5^\circ\text{C}/\text{min}$.

^b Heating rate $\leq 5^\circ\text{C}/\text{min}$.

stages, respectively, are higher than those of 181 and 166 kJ/mol measured at the slow heating rates ($\leq 5^\circ\text{C}/\text{min}$; see Table I). This variation in E_a with the heating rate clearly indicates the complex nature of the degradation mechanism in air. A comparison of the data from the fast and slow heating rate experiments performed in both nitrogen and air suggests that in air the controlling mechanism is the transport of oxygen through the melt, which is then responsible for thermal oxidative degradation. At the fast heating rate in air, the oxygen diffusion probably matches the heating rate and temperature rise. Also in Table I, the E_a values found for PANEK are higher than the corresponding ones for PEEK.

Isothermal experiments

The degradation experiments for PANEK as well as PEEK were performed between 400 and 600°C, and some of these data in nitrogen and air are shown in Figures 7 and 8.

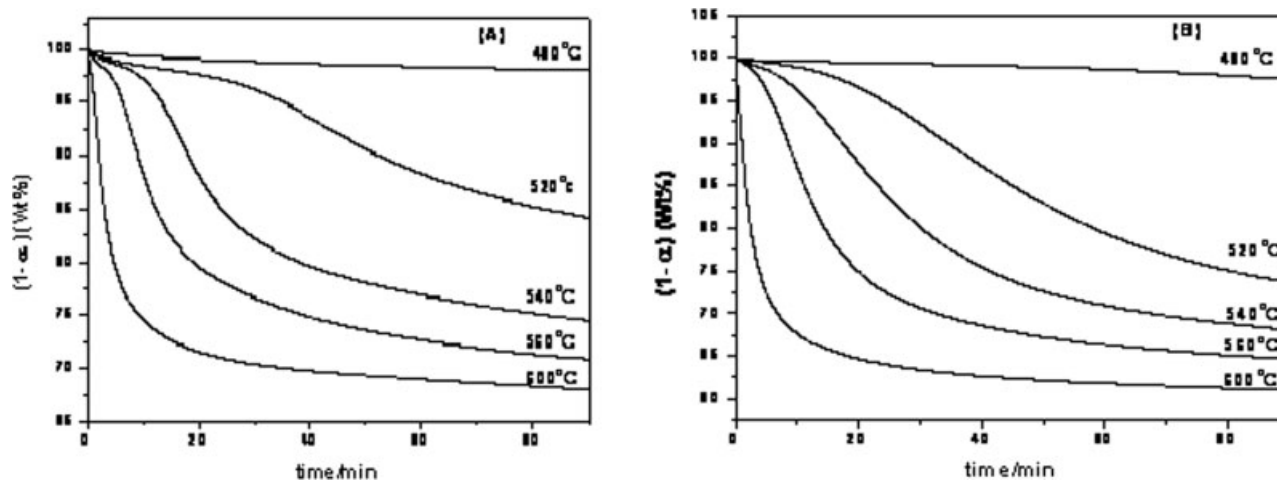


Figure 7 Isothermal degradation curves of (A) PANEK and (B) PEEK in nitrogen at 480, 520, 540, 560, and 600°C.

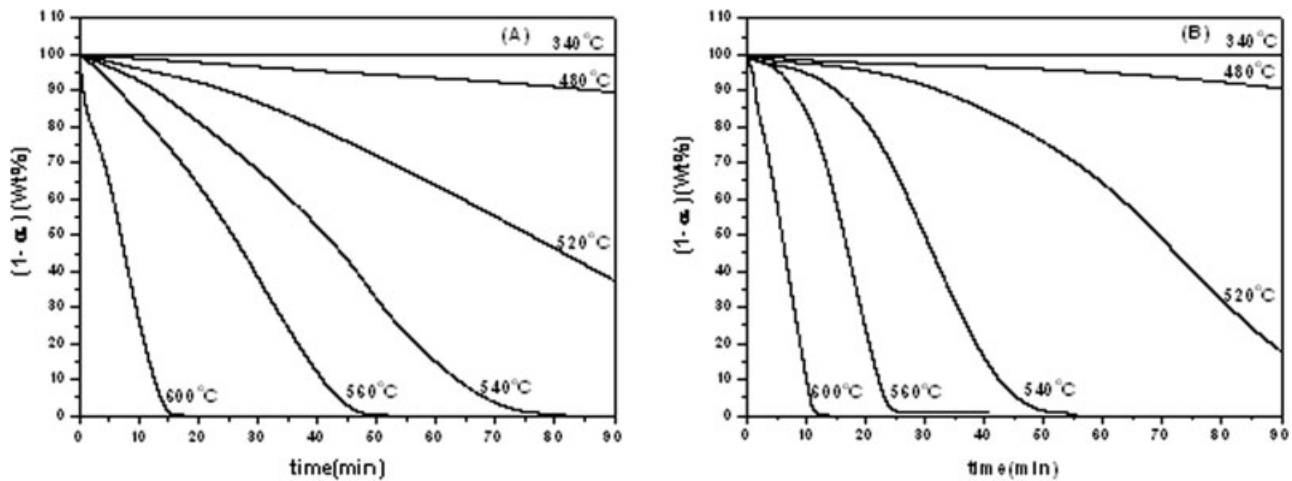


Figure 8 Isothermal degradation curves of (A) PANEK and (B) PEEK in air at 340, 480, 520, 540, 560, and 600°C.

The results were analyzed by the method initially proposed by Flynn,²² which has been successfully used by others.^{23–25} This method involves the integral form of the general kinetic equation for the thermal decomposition of solids under isothermal conditions²⁶

$$g(\alpha) = kt \quad (2)$$

and the well-known Arrhenius expression

$$k = A \exp(-E/RT) \quad (3)$$

By combining these two equations, taking logarithms, and transposing, we can obtain the following expression:

$$\ln t = a + b \times 1/T \quad (4)$$

where $a = \ln[F(1 - D)] - \ln A$, $b = E_a/R$, and $F(1 - D)$ is a function of the degree of degradation (D). According to this equation, the logarithm of the time taken to reach a fixed value of D linearly depends on the reciprocal of the temperature. The apparent E_a value can thus be calculated from the value of the slope. Using the data in Figures 7 and 8, we determined the linear relationship $\ln t = f(1/T)$ (see Figs. 9 and 10). As shown in Table I, in the isothermal case, the apparent E_a value of PEEK is always lower than that of PANEK.

In other words, the thermal stability of PANEK, assessed in both nitrogen and air atmospheres, appears to be substantially higher than that of PEEK. In fact, the TG curves of PANEK obtained under isothermal heating conditions show lower weight losses than those for PEEK heated under the same conditions (see Table II). For example, the weight percentage loss observed for PANEK in nitrogen under

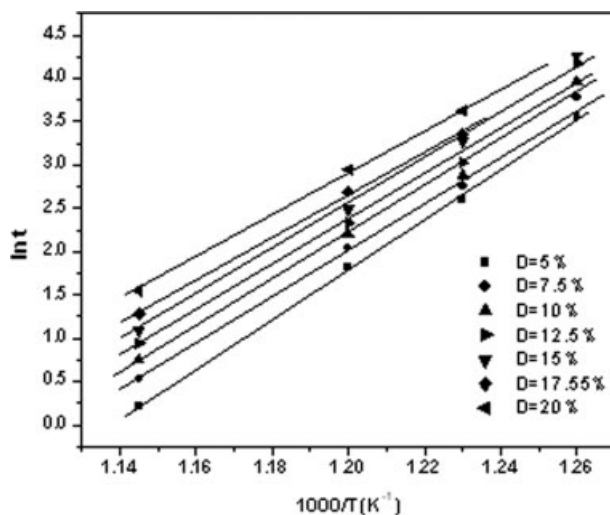


Figure 9 Flynn plots of PANEK degraded in nitrogen.

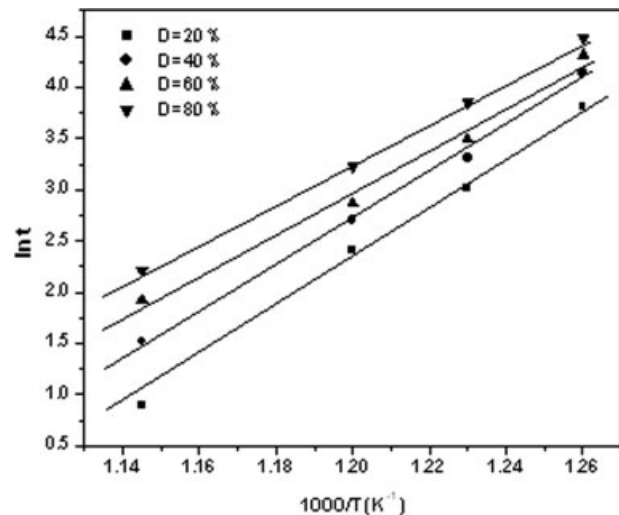


Figure 10 Flynn plots of PANEK degraded in air.

TABLE II
Weight Losses of PANEK and PEEK Under Isothermal
Conditions in Nitrogen and Air After 90 min

Temperature (°C)	PANEK		PEEK	
	N ₂	Air	N ₂	Air
300	0.1	0.3	0.2	0.3
340	0.1	0.3	0.2	0.3
400	0.3	1.6	0.5	2.8
480	1.9	9.5	2.6	10.5
520	15.8	62.6	26.3	82.3
540	25.5	100 (81 min)	31.9	100 (55 min)
560	29.2	100 (50 min)	35.4	100 (35 min)
600	32.1	100 (16 min)	39.0	100 (13 min)

isothermal conditions (560°C) is 29.2% after 90 min, whereas for PEEK, it is 35.4%.

CONCLUSIONS

The experimental results indicate that the T_g values of PAEK containing 2,7-naphthalene moieties are higher than those of PEEK and the T_g increases with increasing naphthalene content. T_i , T_5 , and T' of PAEK containing 2,7-naphthalene moieties are a little higher than those of PEEK and are almost independent of the naphthalene content. The thermal degradation of PANEK occurs through one stage in nitrogen but through two stages in air. The thermal stability of PANEK, however, greatly decreases in an oxidative environment. In both dynamic and isothermal cases, the apparent E_a values of PANEK are always higher than those of PEEK.

References

- Liu, S. J.; Niu, Y. M.; Zhu, X. L.; Wang, G. B.; Jiang, Z. H. *Chem J Chin Univ* 2006, 22, 114.
- Niu, Y. M.; Wang, G. B.; Zhang, S. X.; Na, Y.; Jiang, Z. H. *Polym Int* 2005, 54, 180.
- Niu, Y. M.; Chen, X. B.; Zhang, Y. H.; Zhu, X. L.; Jiang, Z. H. *J Macromol Sci Pure* 2004, 41, 1095.
- Niu, Y. M.; Zhang, S. X.; Zhu, X. L.; Liu, L. Z.; Wang, G. B.; Jiang, Z. H. *J Macromol Sci Pure* 2005, 42, 640.
- Naffakh, M.; Ellis, G.; Gómez, A.; Marco, C. *Polym Degrad Stab* 1999, 66, 405.
- Naffakh, M.; Gómez, A.; Marco, C.; Ellis, G. *Polym Eng Sci* 2006, 46, 129.
- Flynn, J. H. *Polym Eng Sci* 1980, 20, 675.
- Brauman, S. K.; Pronko, J. G. *J Polym Sci Part B: Polym Phys* 1988, 26, 1205.
- Day, M.; Suprunchuk, T.; Cooney, J. D.; Wiles, D. M. *J Appl Polym Sci* 1988, 36, 1097.
- Day, M.; Cooney, J. D.; Wiles, D. M. *J Appl Polym Sci* 1989, 38, 323.
- Day, M.; Sally, D.; Wiles, D. M. *J Appl Polym Sci* 1990, 40, 1615.
- Arzak, A.; Eguiazabal, J. I.; Nazabal, J. *Polym Eng Sci* 1991, 31, 586.
- Jonas, A.; Legras, R. *Polymer* 1991, 32, 2691.
- Cole, K. C.; Casella, I. G. *Thermochim Acta* 1992, 211, 209.
- Nam, J.; Seferis, J. *J Polym Sci Part B: Polym Phys* 1992, 30, 455.
- Bas, C.; Battesti, P.; Alberola, N. D. *J Appl Polym Sci* 1994, 53, 1745.
- Montaudo, G. *Macromol Chem Phys* 1994, 195, 1241.
- Chen, J.; Chen, M.; Chao, S. *Macromol Chem Phys* 1998, 199, 1623.
- Perng, L. H.; Tsai, C. J.; Ling, Y. C. *Polymer* 1999, 40, 7321.
- Giancaterina, S.; Rossi, A.; Rivaton, A.; Gardette, J. L. *Polym Degrad Stab* 2000, 68, 133.
- Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
- Flynn, J. H. In *Laboratory for Macromolecular Chemistry*; McCuffrey, E., Ed.; McGraw-Hill: New York, 1970; p 255.
- Krishman, K.; Ninan, K. N.; Madhusudanan, P. M. *Thermochim Acta* 1984, 79, 279.
- Krishman, K.; Ninan, K. N.; Madhusudanan, P. M. *Thermochim Acta* 1985, 90, 229.
- Basan, S.; Guven, O. *Thermochim Acta* 1986, 106, 169.
- Sestak, J. *Thermochim Acta* 1971, 3, 1.