Thermal Degradation of Kevlar Fiber by High-Resolution Thermogravimetry

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ABSTRACT: A novel high-resolution thermogravimetry (TG) technique in a variable heating rate mode that maximizes resolution and minimizes the time required for TG experiments has been performed for evaluating the thermal degradation and its kinetics of Kevlar fiber in the temperature range ~ 25–900°C. The degradation of Kevlar in nitrogen or air occurs in one step. The decomposition rate and char yield at 900°C are higher in air than in nitrogen, but the degradation temperature is higher in nitrogen than in air. The initial degradation temperature and maximal degradation rate for Kevlar are 520°C and 8.2%/min in air and 530°C and 3.5%/min in nitrogen. The different techniques for calculating the kinetic parameters are compared. The respective activation energy, order, and natural logarithm of preexponential factor of the degradation of Kevlar are achieved at average values of 133 kJ/mol (or 154 kJ/mol), 0.7 (or 1.1), and 16 min^{-1} (or 20 min^{-1}) in air (or nitrogen). The technique based on the principle that the maximum weight loss rate is observed at the minimum heating rate gives thermal degradation results that were in excellent agreement with values determined by traditional TG experiments. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 565–571, 1999

Key words: Kevlar fiber; heating-resistance fiber; high-resolution thermogravimetry; variable heating rate thermal degradation; degradation kinetics

INTRODUCTION

Kevlar fiber is a high-strength, high-modulus, and high–heat-resistant organic material that is useful in a wide range of applications, including cable, rope, conveyor belt, tire cord, sporting goods, circuit board, fan blades, low-weight panels for aircraft interiors, fire-fighting clothing, body armor, and reinforcement in rigid composites and laminates for inflatable missiles, satellites, and aerospace structures. As such, it has received great attention from both industry and academia. The Kevlar fiber is one of the best materials for high-temperature application. The wholly aromatic rigid rod-like structure in the Kevlar fiber polymer main chain imparts high thermostability. Generally, Kevlar fiber can resist 450°C for a few minutes and 250°C for at least 1 month.

The thermal degradation can be studied by means of constant heating rate or isothermal thermogravimetry (TG) techniques. The constant heating rate technique is often faster to run than isothermal experiments. However, obtaining high-resolution data usually requires a low heating rate, thus increasing the time required for experiments.[1] High resolution is necessary to quickly achieve reliable degradation temperature and kinetic parameters that can be used to compare thermostability and assess lifetime. The thermal stability of Kevlar

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fiber by traditional constant heating rate TG has been investigated,[2–8] but there are few studies on thermal stability and degradation kinetics of Kevlar fiber by high-resolution TG.

A novel high-resolution TG provides a means to remarkably enhance the resolution while often reducing the time scale of the experiments. In the variable heating rate mode of the high-resolution TG, the heating rate is dynamically, continuously, and inversely varied with decomposition rate to maximize resolution, the capacity to separate closely occurring events. For example, the heating rate decreases automatically when the decomposition rate increases and increases when the decomposition rate decreases. Thus the heating rate will reach the maximum value at the maximum decomposition rate. The variable heating rate mode offers a choice of resolution ranging from zero to eight. If the resolution is zero, then the heating rate is constant; that is, a constant heating rate like in the traditional TG mode. If the resolution is larger than 0, then the instrument will react to smaller changes in the weight loss rate.[1] Sensitivity controls the magnitude of response relative to changes in the decomposition rate. In principle, the heating rate and temperature at the maximum degradation rate could be regulated by varying the initial heating rate, resolution, or sensitivity.

To study the thermostability of Kevlar fiber and the influence of testing atmosphere and mode on its stability, a high-resolution TG analysis was applied. From the TG data, conclusions were made on the thermal degradation temperature and kinetics by means of various calculating techniques.

EXPERIMENTAL

Kevlar fiber is a commercially available golden fiber prepared by dry-jet wet-spinning from a liquid crystalline solution of poly(*p*-phenylene terephthalamide) (PPTA) in concentrated sulfuric acid with subsequent heat drawing and treatment. Kevlar fiber was chosen because it is a typical highly heat-resistant material whose kinetic parameters of thermal degradation have been reported based on the traditional constant heating rate TG.[2–5]

TG analyses (TGA) were run under both nitrogen and air flow of 30 mL/min on a high-resolution TG 2950 thermal analyzer (Hi-Res™ TGA) induced by TA Instruments, Inc. (New Castle, DE) using the high-resolution mode interfaced to a TA Instruments 2000 controller with a General V.4.1C microprocessor. Sample size in all experiments was ~ 0.47–0.53 mg in air and nitrogen. The initial heating rate and resolution were fixed at 50°C/min and 4.0, respectively. The sensitivity was fixed at its default value of 1 in the temperature range of ~ 25–900°C. The thermal degradation temperatures and kinetic parameters were determined using the techniques described previously.[6] These data were compared to values in the literature.

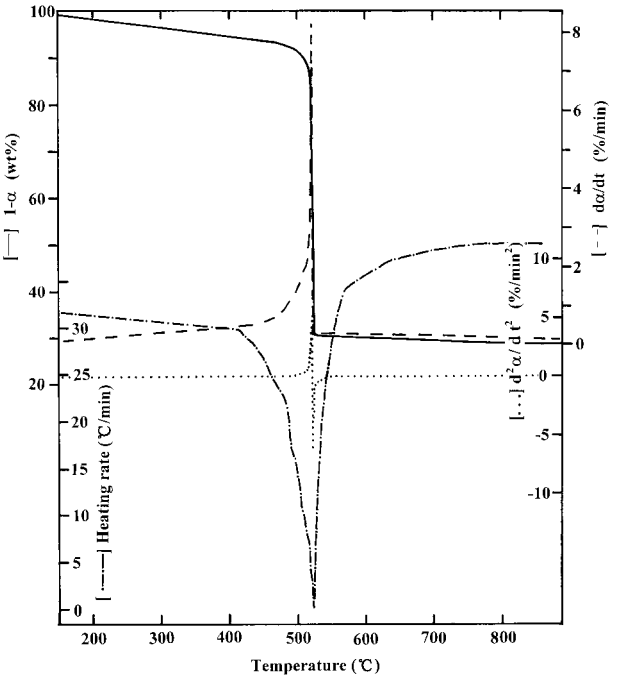

Figure 1 High-resolution TG (——), DTG (– – –), 2DTG (· · ·), and heating rate (– · – ·) curves of the Kevlar fiber in air flow at an initial heating rate 50°C/min and resolution 4.

RESULTS AND DISCUSSION

Thermostability

High-resolution TG, derivative thermogravimetry (DTG), second derivative thermogravimetry (2DTG), and heating rate curves in air and nitrogen for Kevlar fiber are shown in Figures 1 and 2. The maximum decomposition rate coincided exactly with the minimum heating rate. The thermal degradation of Kevlar occurs through one rapid degradation step. Before the major rapid degradation process, a slow weight loss of ~ 3.5%

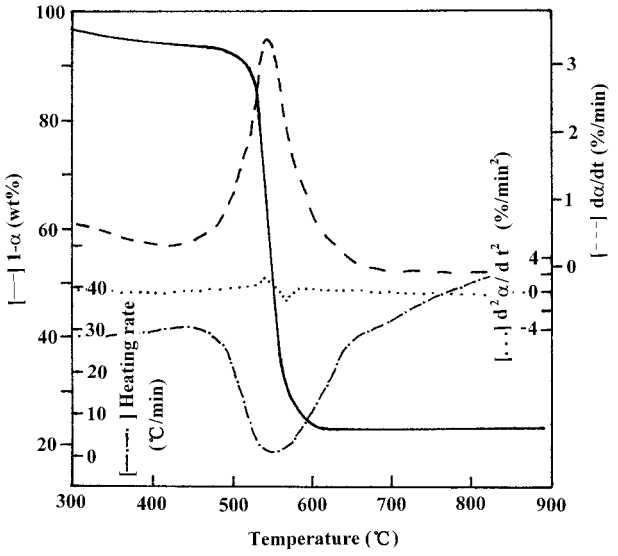

Figure 2 High-resolution TG (——), DTG (– – –), 2DTG (· · ·), and heating rate (– · – ·) curves of the Kevlar fiber in nitrogen flow at an initial heating rate 50°C/min and resolution 4.

of initial weight centered at 300°C occurred in nitrogen but hardly ever occurred in air, possibly because of concurrent oxidation. A similar result has been observed by Brown and Ennis.[3] Between 300 and 500°C, no significant weight loss occurred, and above 530°C a rapid weight loss of 55% occurred up to 575°C, passing the maximum decomposition rate, which is coincident with the minimum heating rate of ~ 2°C/min. Above 575°C, the subsequent weight loss is very slow. The total weight loss at 900°C is 78%.

Applying the DuPont 2000 standard program, the characteristics of TG and DTG traces were obtained: the onset temperature of the main degradation step (T_d), determined as the intersection of the extrapolated baseline with tangent drawn in the inflection point of the TG trace; the temperature at the maximum degradation rate in the main degradation (T_{dm}); the maximum degradation rate $(d\alpha/dt)_m$; and the char yield. The results, along with the reported values in the literature, are listed in Table I.

The different characteristics of thermal degradation of Kevlar fiber in air are evident from Figure 1 and Table I. An initial weight loss of 2% at 100°C was attributed to the release of absorbed water. After this period, a very slow weight loss of 7% occurs up to 480°C, and above 519°C the rate of weight loss increased dramatically to a maximum at 521°C, corresponding to the minimum heating rate of ~ 2°C/min. Above 521°C, subsequent weight loss is very slow to a residual weight of 27% at 900°C. The T_d and T_{dm} are lower and the DTG peak is much sharper in air than in nitrogen, and the decomposition rate of the main degradation process is higher in air. The interval between T_d and T_{dm} is much smaller in air than in nitrogen. These all imply lower thermostability and rapider degradation in air than in nitrogen.

Table I Characteristics of Thermal Degradation of Kevlar Fibers by High-Resolution (Variable Heating Rate) TG and Traditional (Constant Heating Rate) TG

Fiber	Atmosphere	Heating Rate (°C/min)	T_d/T_{dm} (°C)	$(d\alpha/dt)_m$ (%/min)	Char yield (wt %/°C)	Reference
Kevlar	Air	Variable	520/521	8.2	28/650	This study
Kevlar 29	Air	—	520/529	—	50/538	2
Kevlar 49	Air	—	500/534	—	5/590	3
PPTA[a]	Air	10	498/539	9	10/650	7
PPTA	Air	10	515/535,560	—	32/600	9
Kevlar	Nitrogen	Variable	530/546	3.5	22/650	This study
Kevlar 29	Nitrogen	—	540/565	—	62/650	2
Kevlar 49	Nitrogen	—	539/564	—	64/650	3
Kevlar 49	Nitrogen	2	531/553	3.0	61/650	4
PPTA[a]	Nitrogen	10	513/548	8.5	45/650	7
PPTA	Nitrogen	20	555/595	—	—	8
PPTA	Argon	10	555/585	—	65/650	9

[a] A low-crystalline and low-orientational fiber prepared by the usual dry–wet spinning method from an isotropic solution containing 1.5% Kevlar fiber, as opposed to the Kevlar fiber spun from an anisotropic solution.

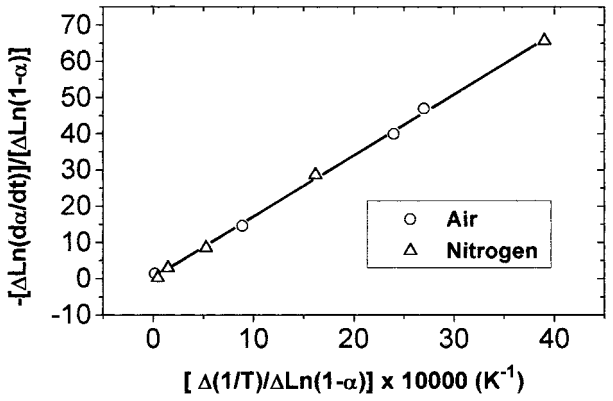

Figure 3 Application of the Freeman–Carroll method to the high-resolution TG data obtained in air (○) and nitrogen (△).

It is seen from Table I that especially in nitrogen, the T_d, T_{dm}, and char yield examined, by the high-resolution TG are usually lower than the corresponding values in the literature by the conventional constant heating rate TG. This is clearly because of its lower heating rate, down to 2°C/min during the obvious degradation, as shown by the heating rate curves in Figures 1 and 2 in the variable heating mode used in this study regardless of its high initial heating rate of 50°C/min. Table I shows that the PPTA fiber with low crystallinity and poor orientation appears to exhibit a little lower T_d at 10°C/min than all of the highly crystalline and well-orientated Kevlar fibers, even at a lower heating rate of 2°C/min, despite the fact that they have same macromolecular structure. This indicates that the morphology of Kevlar fiber has a certain influence on its thermal stability.

Degradation Kinetics

The kinetic parameters were calculated on the basis of five methods for only the major degradation process ranging from 470 to 540°C.[6]

Freeman-Carroll Method

$$\Delta[\ln(d\alpha/dt)]/\Delta[\ln(1-\alpha)] = n - (E/R)\cdot\Delta(1/T)/\Delta[\ln(1-\alpha)] \quad (1)$$

where Δ is the very small difference value for constant $\Delta(1/T)$ equal to 0.00002. The dependence of $\Delta[\ln(d\alpha/dt)]/\Delta[\ln(1-\alpha)]$ versus $\Delta(1/T)/\Delta[\ln(1-\alpha)]$ represents a straight line with slope $-E/R$ and segment n on the ordinate. The parameters of the most probable straight lines were obtained by regression analysis. The fitting of experimental data with kinetic eq. (1) is statistical, because the correlation coefficient exceeds 0.998 for all the samples. Note that the kinetic data might be seriously affected by even minor errors in determining the $\Delta[\ln(1-\alpha)]$ value because of the very small $\ln(1-\alpha)$ value.

Friedman Method

$$\ln(d\alpha/dt) = n\cdot\ln(1-\alpha) + \ln Z - E/RT \quad (2)$$

where n, Z, E, and R are the decomposition order, preexponential factor, activation energy, and universal gas constant (8.3136 J/mol · K), respectively. The dependence of $\ln(d\alpha/dt)$ or $\ln(1-\alpha)$ versus $(1/T)$ represents a straight line with slope $-E/R$ or $-E/(R\cdot n)$.

Chang Method

$$\ln[(d\alpha/dt)/(1-\alpha)^n] = \ln Z - E/RT \quad (3)$$

The dependency of $\ln[(d\alpha/dt)/(1-\alpha)^n]$ versus $(1/T)$ should give a straight line with slope

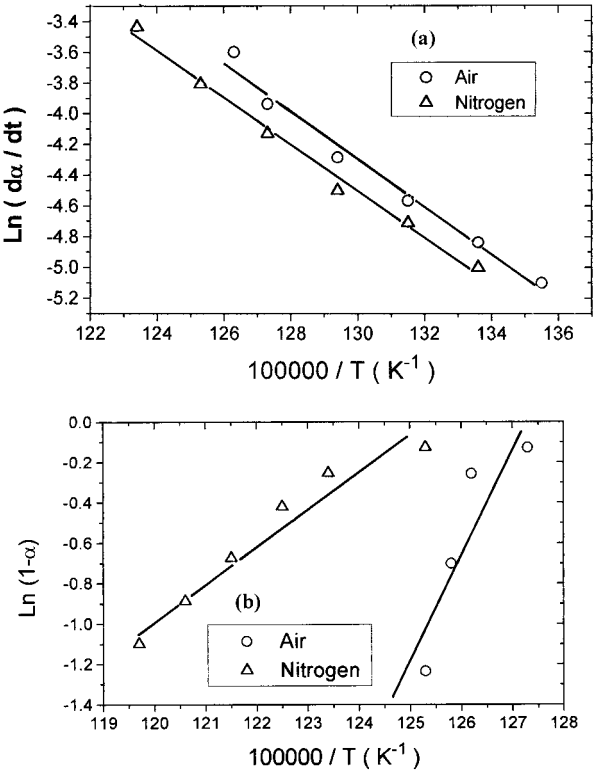

Figure 4 Application of the Friedman method to the high-resolution TG data obtained in air (○) and nitrogen (△).

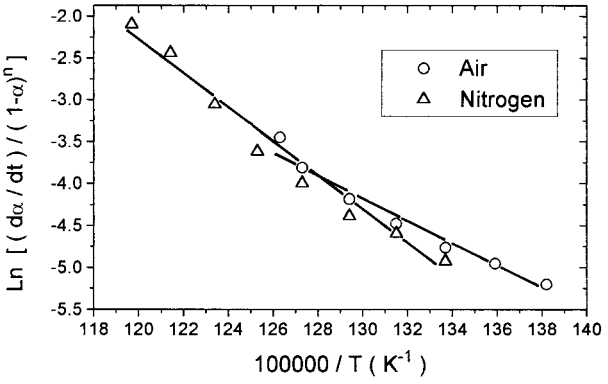

Figure 5 Application of the Chang method to the high-resolution TG data obtained in air at $n = 1.0$ (○) and in nitrogen at $n = 1.5$ (△).

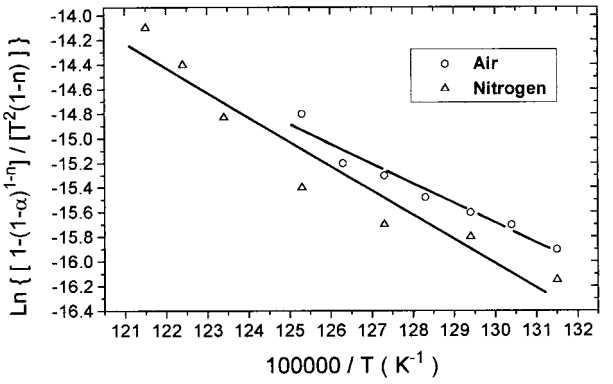

Figure 6 Application of the Coats–Redfern method to the high-resolution TG data obtained in air at $n = 1.0$ (○) and in nitrogen at $n = 1.5$ (△).

$-E/R$ and intercept ln Z on the y-axis if the correct n is assumed.

Coats–Redfern Method

$$\ln\{[1-(1-\alpha)^{1-n}]/[T^2(1-n)]\} = \ln\{(ZR/qE) \times [1-(2RT/E)]\} - E/RT \quad (n \neq 1) \quad (4)$$

where q represents the heating rate. Plotting the first member of eq. (4) against $1/T$ allows us to obtain the E value when n is correctly selected.

Kissinger Method

$$\ln(q/T^2) = \ln[ZRn(1-\alpha)^{n-1}/E] - E/RT \quad (5)$$

Plotting ln q/T^2 versus $1/T$ will form a straight line with the slope of $-E/R$ and the intercept of $\ln[ZRn(1-\alpha)^{n-1}/E]$. The decomposition order can be calculated from the second derivative thermogravimetry peak representing the shape index of the derivative thermogravimetry peak as follows:

$$n = 1.88|(d^2\alpha/dt^2)_L|/|(d^2\alpha/dt^2)_R| \quad (6)$$

Then the Z value can be obtained from eqs. (5) and (6).

Five plots based on eqs. (1)–(5) for the determination of kinetic parameters are shown in Figures 3–7. For comparative purposes the kinetic results from the five analytical techniques of the experimental data are summarized in Table II. Obviously, there are a few variations in three kinetic parameters depending on the mathematical approach taken in the analyses, the temperature range used in these calculations, and the testing atmosphere. In particular, the variation range of the kinetic parameters is narrower in air than in nitrogen. It is interesting that the E value calculated by the Chang method is the lowest in air but the highest in nitrogen in the five methods used. The relationship between $\ln(1-\alpha)$ and the reciprocal temperature calculated by eq. (2) of the Friedman method deviate strongly from the straight line especially in air, as seen in Figure 4(b), suggesting that this method might not be suitable for calculating the decomposition order based on the high-resolution TG. Almost the same kinetic parameters and the correlation coefficient larger than 0.9989 in air and nitrogen were ob-

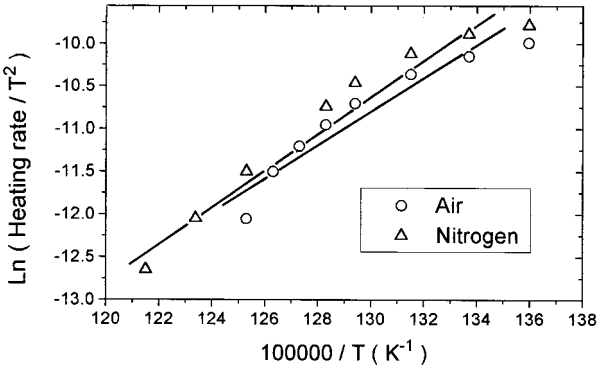

Figure 7 Application of the Kissinger method to the high-resolution TG data obtained in air (○) and in nitrogen (△). The slope of the plot of ln(heating rate/T^2) versus $1/T$ should equal E/R, because the heating rate decreases with the increase of decomposition rate or temperature in the major degradation stage below 521°C (in air) or 546°C (in nitrogen), as shown in Figures 1 and 2.

Table II Kinetic Parameters of Thermal Degradation of Kevlar Fiber by a High-Resolution TG Measurement in Both Air and Nitrogen

Calculating Method	Testing Atmosphere	E (kJ/mol)	n	ln Z (min^{-1})	Correlation Coefficient
Freeman–Carroll	Air	140	0.1	18	0.9989
Freeman–Carroll	Nitrogen	141	0.1	17	0.9996
Friedman	Air	129	0.3	10	0.9906(0.8885)[a]
Friedman	Nitrogen	127	0.9	15	0.9952(0.9714)[a]
Chang	Air	116	1.0	13	0.9839
Chang	Nitrogen	171	1.5	23	0.9864
Coats–Redfern	Air	132	1.0	16	0.9752
Coats–Redfern	Nitrogen	164	1.5	21	0.9620
Kissinger	Air	150	1.3	20	0.9505
Kissinger	Nitrogen	169	1.8	22	0.9729
Average	Air	133	0.7	16	
Average	Nitrogen	154	1.1	20	

[a] The data in the parentheses correspond to the correlation coefficient for calculating decomposition order

tained only through the Freeman–Carroll method. The high-resolution TG curves of Kevlar fiber appear to be the best fit for the Freeman–Carroll equation and the worst fit for the Kissinger equation for calculating kinetic parameters. It was felt that the Freeman–Carroll and Friedman methods are the best methods for calculating the activation energy. These results clearly suggest the problems entailed in applying different analytical methods to solve complex thermal degradation.

Table II shows that the E and n values are lower in air than in nitrogen. From this one can infer that the degradation rate is more rapid in air because the thermooxidative degradation reaction of Kevlar fiber in air leads to the formation of more volatile products such as carbon dioxide, carbon monoxide, and water at 300–500°C and benzene, benzoic acid, *p*-phenylene diamine, benzonitrile, aniline, benzanilide, and other carboxyl aromatics at 500–540°C, resulting in a faster degradation.[5] The thermal degradation between 500 and 540°C was initiated by the homolytic cheavages of the amide and aromatic amine bonds accompanied by decarboxylation of carbonyl groups.[5]

Lifetime Prediction

There is an increased interest in the long-term property of Kevlar fiber. The *isothermal lifetime* can be predicted by the following equation:

$$\text{Lifetime} = \{[1 - (1 - \alpha)^{1-n}]/[Z(1 - n)]\} \exp(E/RT) \quad (7)$$

Figure 8 shows the estimated isothermal lifetime of Kevlar fiber. On the basis of the data at 0.8% weight loss in air in Figure 8, it might be predicted that Kevlar fiber could withstand exposure at a temperature up to 400°C for 19 min, at 240°C for 526 h, or at 200°C for at least 10 months without any serious degradation. The time required for degradation in nitrogen to reach 0.8% weight loss varied from 2 min at 450°C to 93 centuries at 120°C, which is much longer than the lifetime (ca. 6 days) determined experimentally in the literature.[4] This suggests that the lifetime prediction at a lower temperature (<230°C) obtained using the kinetic parameters at an elevated temperature (above 450°C) is unreliable. However, the isothermal lifetime predicted at >

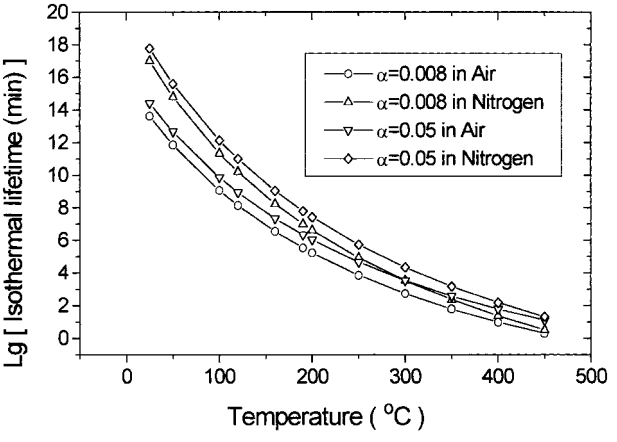

Figure 8 Estimated isothermal lifetime of Kevlar fiber in air (○ and ▽) and nitrogen (△ and ◇) at two weight losses α of 0.008 (○ and △) and 0.05 (▽ and ◇).

240°C appears to be believable. For example, according to eq. (7) and the average kinetic parameters listed in Table II, the isothermal lifetime of 0.7% weight loss at 240°C in air is 459 h. It is claimed that the long-term heat resistance limit is about 240°C, at which a 30% loss in tensile strength occurs after 450 h in air.[10] Possibly, a 0.7% weight loss after 459 h at 240°C corresponds to a 30% loss in tensile strength after 450 h at the temperature.

CONCLUSIONS

The thermal degradation of Kevlar fiber was thermogravimetrically studied using a high-resolution thermogravimetry in the temperature range 25–900°C. This is mainly a single-step process. The weight-loss rate depends on the testing atmosphere and is more rapid in air than in nitrogen. Kevlar fiber has excellent thermostability and small weight loss below 300°C, but above 520°C the thermal decomposition progressed very rapidly. The Freeman–Carroll and Friedman calculating methods seem to be applicable to more points on the high-resolution TG curves and provide more satisfactory mathematical approaches in the calculation of activation energy of thermal degradation of Kevlar fiber. The initial thermal decomposition temperature, activation energy, decomposition order, and frequency factor for the major step of degradation in nitrogen are 530°C, 154 kJ/mol, 1.1 and 4.85×10^8 min^{-1}, respectively. These values in air reduced to 520°C, 133 kJ/mol, 0.7 and 8.89×10^6 min^{-1}, respectively.

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